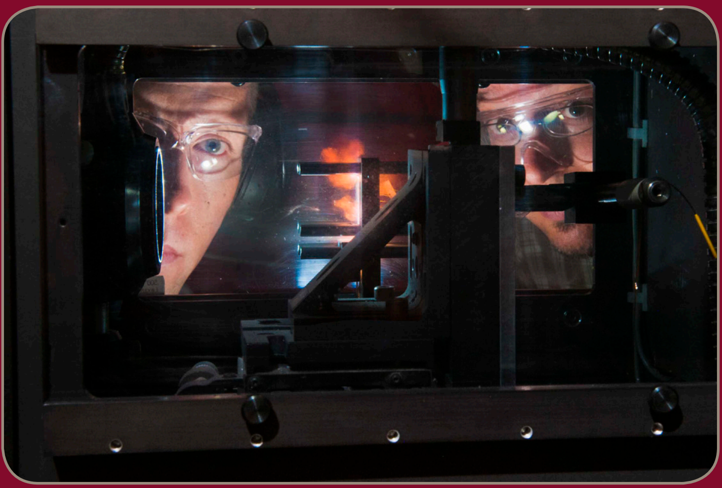
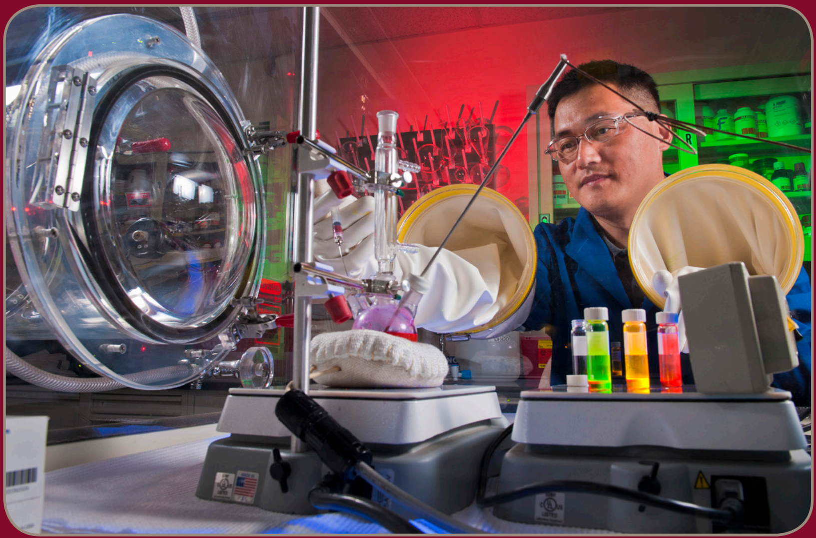
LDRD

Laboratory Directed Research and Development

2013 ANNUAL REPORT







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Sandia National Laboratories

NNSA
National Nuclear Security Administration

Cover photos (clockwise):

A special chamber for safely studying the details of explosive reactions is used in Project 156704 by Alexander Tappan and Robert Knepper.

Ring: The fundamental processes whereby pathogens infect living cells are being studied using supported lipid bilayers that mimic the chemistry, physical structure, and mechanics of cell membranes developed in project 151349.

Blue/Red/Green bottles: Luminescent dyes using different lanthanide ions to provide different colors are being developed in project 157690 as replacements for fluorescent organic dyes as reporters for biological imaging and assays.

The Biomimetic Lung Toxicity Screening Platform (bioMIMIC) is a practical in-vitro tissue-on-a-chip screening platform that models the air sac/blood vessel interface and is suitable for use in BSL3/4 labs developed in Project 151350.

Quantum-dot solids with precisely controllable interparticle spacing that allows tuning of optical and electronic properties are prepared by Hongyou Fan in an inert-atmosphere glove box developed in project 165700.

Anne Ruffing examines a flask of genetically engineered cyanobacteria that can serve as bio-diesel feedstock developed in project 142441.

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Abstract

This report summarizes progress from the Laboratory Directed Research and Development (LDRD) program during fiscal year 2013. In addition to a programmatic and financial overview, the report includes progress reports from 447 individual R&D projects in 16 categories. Information for 270 projects in their final year is presented in a more comprehensive format, while those 177 in their pre-final years, only an abstract is presented herein.

National Nuclear Security Administration

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

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Message from Julia Phillips, Vice President and Chief Technology Officer

Laboratory Directed Research and Development (LDRD) is essential for maintaining the critical science, technology, and engineering (ST&E) capabilities required to carry out our national security mission, including the safety and security of the nuclear deterrent. Through the LDRD program, Sandia National Laboratories and other Department of Energy (DOE) laboratories pursue high-risk, mission-driven research that pushes the frontiers of science and engineering and ensures the United States maintains science and engineering superiority in a world replete with threats to our national security. It also helps Sandia and other labs attract and retain many of the nation's best and brightest scientists and engineers to carry out that vital work. Through its support of this indispensable sole discretionary R&D program, the US Congress has recognized the value of LDRD on fulfilling our mission to protect Americans at home and abroad.

The research investments provided by the LDRD program are essential to implementing Sandia's research strategy, whose goals are to: 1) provide critical differentiation in the delivery of mission through a multidisciplinary research portfolio; 2) tackle groundbreaking challenges that create transformational opportunities in national security; and 3) steward and nurture a vibrant, problem-rich research environment.

The FY 2013 LDRD Annual Report highlights the diverse research that Sandia conducts to support our national security missions, often in collaboration with scientists and engineers in academia, industry, and other government labs. The LDRD program provides direct and indirect benefit to current and emerging DOE and National Nuclear Security Administration (NNSA) missions and research priorities. Our history of executing this program has also shown a remarkable ability to anticipate the research needs of future missions and priorities.

The FY 2013 LDRD program supported 447 projects at a cost of $168M. LDRD proposals undergo a robust peer review, resulting in the selection of projects that are of the highest technical quality and which are well aligned with Sandia's vital national security missions.

SANDIA FY 2013 PROGRAM OVERVIEW

Introduction

How vital is the LDRD program to fulfilling our mission? The benefits of LDRD research pervade almost every mission area of the Laboratories, making it possible to accomplish our critical national security role. Breakthroughs have occurred in areas as diverse as new sensor technologies, quantum science and technology, nanotechnology, metamaterials, computational modeling and simulation, molecular biology, and alternative fuels.

For example, research funded by Sandia's LDRD program enabled the only strategically radiation-hardened microelectronics capability in the United States. This capability is vital to the effective performance of the nuclear stockpile and our nonproliferation missions, and to the success of the nation's satellite and space programs. LDRD also advanced the capability to measure materials properties in extreme environments important to nuclear weapons performance. This capability helps make it possible to certify the performance of nuclear weapons without underground testing.

LDRD also miniaturized high-resolution radar technology so that it could be mounted on small planes to gather intelligence in support of our national security and to help save the lives of American soldiers on the battlefield. And, LDRD can have unexpected payoffs as seen by the project to alleviate the problematic heat build-up on fiber optics laser systems. The technology that resulted from this project is a small — approximately 10 cm in diameter — device that provides a 30-fold improvement in heat transfer. Termed the "Sandia Cooler," it has potential cooling applications in laptop computers, automobiles, LED lighting, both large and small appliances and electronics, and even building air conditioning systems.

Sandia's LDRD program is operated in compliance with DOE Order 413.2B. The program supports the missions of the DOE/NNSA, Department of Homeland Security, Department of Defense, and other federal agencies. It underpins DOE missions in nuclear security, energy security, scientific discovery and innovation, and the broader national security missions of our partners in the Work for Others (WFO) program.

LDRD projects are chosen for their technical quality, their differentiating and programmatic value to Sandia, and their relevance to the missions of DOE/NNSA and other federal agencies. LDRD scientific advances and technology innovations provide multiple benefits to all Sandia stakeholders, consistent with congressional intent and the Laboratories' strategic goals.

Program Strategy

Sandia's LDRD program is an essential part of the Laboratories' research strategy. It touches other key elements of that strategy, which consist of research challenges designed to develop solutions that can surmount critical technical obstacles, and the translation of technologies into intellectual property that can be licensed to companies for commercialization. Sandia integrates LDRD into the overall strategy to fulfill the following goals: enable our national security missions now and in the future; advance the frontiers of science and technology; and, attract and retain a world-class research community.

The FY 2013 LDRD program structure supported these goals through strategic investments in five primary Program Areas each consisting of smaller focused investment areas (IAs).

Research Foundations (RF) Program Area

The RF Program Area seeks to anticipate and provide for the future science, technology, and engineering (ST&E) needs of the Laboratories, fostering our science base as a means to further develop the critical existing and future ST&E capabilities needed to support our national security missions. In FY 2013, there were eight RF investment areas, seven of which align to Sandia's RF areas: Bioscience, Computing and Information Sciences, Engineering Science, Nanodevices and Microsystems, Materials Science, Radiation Effects and High Energy Density Science (REHEDS), and Geoscience. An eighth RF investment area, called "New Ideas," supports leading-edge research that lies outside Sandia's current research foundation focus areas, but that may lead to breakthroughs in science and technology that could profoundly impact our national security mission.

Mission Technologies Program Area

The Mission Technologies Program Area seeks to create and nurture the ability to provide innovative solutions for NNSA, DOE, and Work for Others (WFO) sponsors of Sandia’s mission areas, creating and accelerating the development of technologies needed to address national security issues. The four Mission Technologies investment areas align with the Sandia’s Strategic Management Unit (SMU) structure: Nuclear Weapons; Defense Systems and Assessments; Energy, Climate, and Infrastructure Security; and International, Homeland, and Nuclear Security.

Mission Challenges Program Area

The Mission Challenges Program Area targets the most complex and difficult ST&E problems facing our nation that no one agency or industry can solve on its own, pursues key ST&E challenges spanning many years of R&D effort across multiple portfolios and disciplines, and seeks to create breakthroughs in science or engineering in support of these challenges. In FY 2013, there is one Mission Challenge IA: Cybersecurity.

Grand Challenge Program Area

Grand Challenges address some of the most difficult problems facing our nation, using large multidisciplinary teams to create significant ST&E advances that lead to unique or differentiated capabilities not likely to be established elsewhere.

Corporate Investments Program Area

The Corporate Investments Program Area has a broad Labs-wide focus, promoting strategic collaborations with academia or addressing initiatives directed by the Chief Technology Officer (CTO) or Sandia management. Early Career R&D projects provide an opportunity for new research staff members to build new research capabilities through LDRD as they become integrated into the Sandia workforce and contribute to mission-driven projects. Exploratory Express LDRD projects are smaller, short-term projects that provide an opportunity for staff to quickly test or mature a novel idea that has potential to become very important for one of Sandia's strategic missions. This new investment area was created in FY 2013 to support one of the three goals of Sandia’s Research Strategy – “Steward and nurture a vibrant problem-rich research environment that is a fundamental element of the Laboratories’ mission success” – by providing a vehicle to explore ideas that are generated by researchers spontaneously throughout the year rather than in response to a specific Investment Area during the annual call. Another new investment area initiated in FY 2013, “Research Challenges,” addresses the Research Strategy goal to: “Pursue a small number of transformational interdisciplinary research challenges that enable the Laboratories to solve strategic mission challenges by building on our research foundations.”

Selection Process

The process for selecting LDRD projects begins each year with an annual Labs-wide call for ideas. The ideas are requested from and directed to particular investment areas that cover the gamut of research within the laboratory. As described above, the investment areas align with the Laboratories' research strategy and the strategic management programs, which carry out the mission work.

Interested researchers submit proposals that are directed to the appropriate investment areas for evaluation. Each investment area has a team that reviews the proposals for leading-edge R&D that may have potential impact on Sandia's future national security mission needs. Independent technical and programmatic appraisals are conducted for each new proposal before a final set of projects is selected within each investment area based on available funds.

All LDRD principal investigators must submit annual status reports, pursue publication in professional journals as applicable, and submit detailed final reports on their findings.

Of the 902 ideas submitted in response to the annual FY 2013 LDRD program call for ideas, 200 were invited to submit full (initial-funding) proposals, and 89 of these were approved for funding. In addition, there were 32 new Early Career R&D projects, 11 Exploratory Express projects, and 56 other new projects for a total of 177 new projects. The new projects were added to the 270 continuing projects for a total of 447 projects in FY 2013, with a total cost of $168M.

FY 2013 Budget

Figure 1 illustrates a breakdown of the FY 2013 LDRD portfolio by Program Area cost.

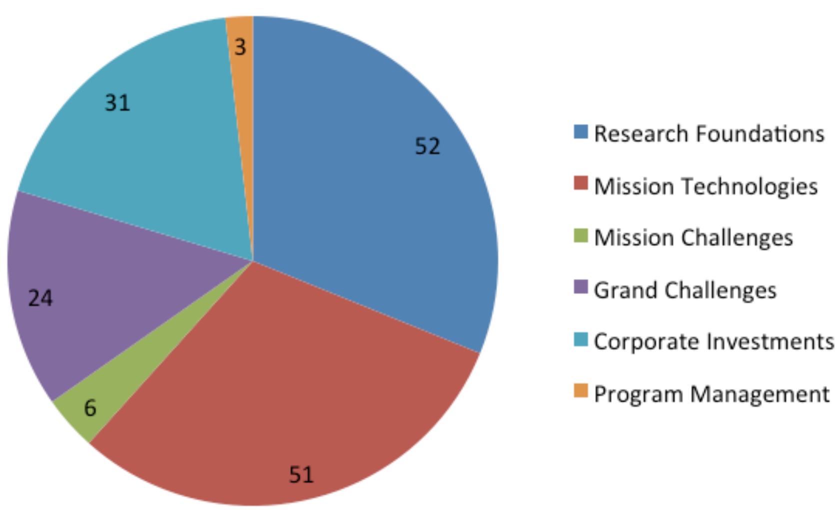


Figure 1: FY 2013 LDRD Portfolio by Program Area Cost ($M)

Program Performance

Enabling our National Security Missions

LDRD projects are selected following rigorous review of technical quality, differentiating and programmatic value to Sandia, and relevance to DOE/NNSA missions (nuclear security, energy security, environmental remediation, and scientific discovery and innovation), as well as the national security missions of the Department of Homeland Security, the Department of Defense, and Other Federal Agencies. As a result, the scientific advances and technology innovations from LDRD provide multiple benefits to all stakeholders, consistent with Congressional intent and our Laboratories' strategic goals. Figure 2 shows the mission relevance of the FY 2013 LDRD portfolio and illustrates the broad support for current and planned national security. The dollar amounts total more than 100 percent of the total FY 2013 costs since most projects have relevance to more than one mission area.

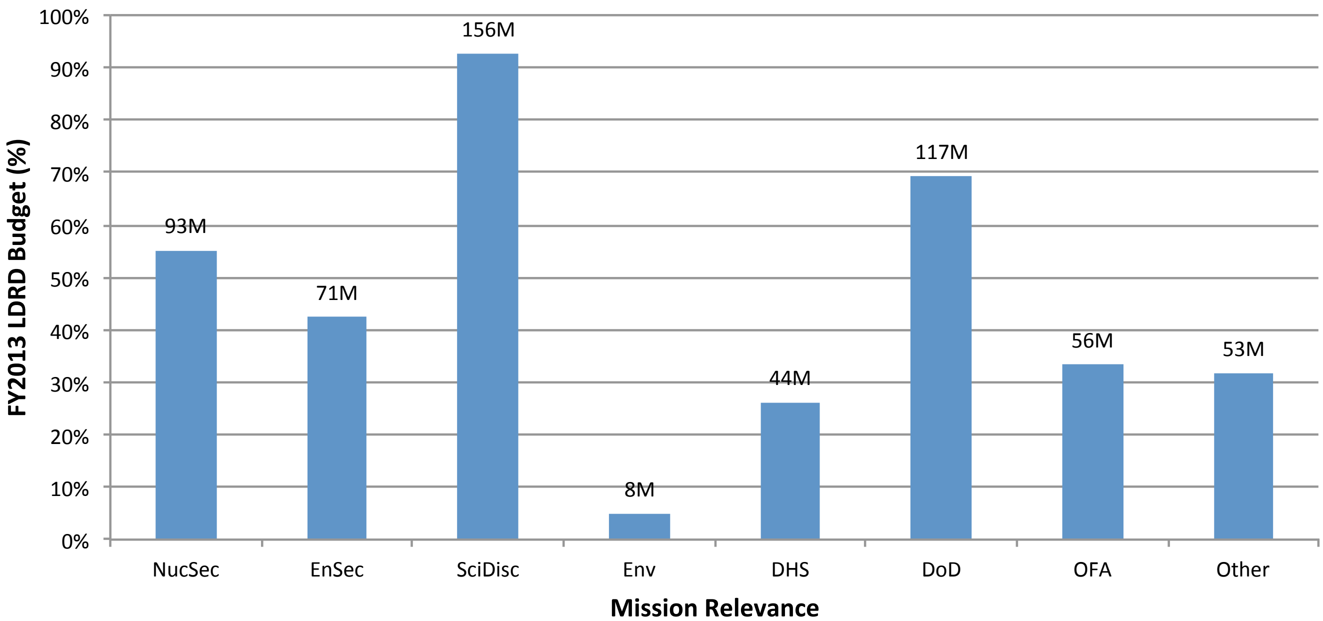
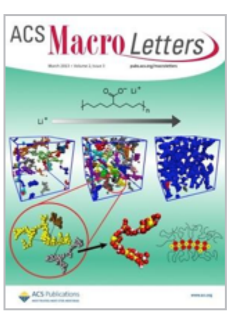


Figure 2. The FY 2013 LDRD portfolio supports multiple missions. DOE/NNSA missions: nuclear security (NucSec), energy security (EnSec), scientific discovery (SciDisc), environmental responsibility (Env); and Department of Homeland Security (DHS), Department of Defense (DoD), Other Federal Agencies (OFA), and other organizations, e.g., industry (Other).

Advancing the Frontiers of Science and Engineering

LDRD creates and builds new knowledge and novel technologies that develop new capabilities and produce major scientific advancements through leading edge R&D. Supporting evidence includes success stories, awards and recognition, as well as statistical measures of outputs such as publications and intellectual property.

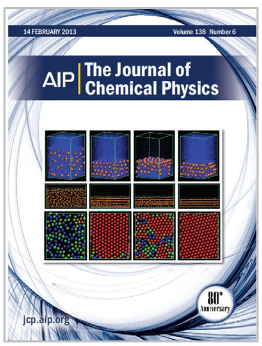
Technical success in Sandia's LDRD program is illustrated in part by the documentation of LDRD research in peer-reviewed journals and publications during FY 2013, including these examples featured on journal covers:



"Atomistic Simulations Predict a Surprising Variety of Morphologies" in the March 2013 issue of *American Chemical Society Macro Letters* described the work of several Sandians to carry out fully atomistic molecular dynamics simulations of melts of lithium-neutralized precise ionomers, which revealed the structural features of ionic aggregates in unprecedented detail. They found that traditional assumptions of spherical ionic aggregates with liquid-like ordering, which is typically used to interpret experimental scattering data, is too simplistic, and that a more rich and complex set of structures exist that also fit the scattering data.

"Self-Assembly in a Mixed Polymer Brush with Inhomogeneous Grafting Density Composition" in the June 14, 2013, issue of *Soft Matter* described the work of two Sandians and other researchers to analyze the possibility of obtaining long-range ordering from the self-assembly of A-B binary mixed brushes similar to diblock copolymer thin films. Their work focused on the correlation between the spatial distribution of the grafting points and the self-assembly.

Two Sandians joined several other scientists in writing "The Mechanical Behavior and Deformation of Bicrystalline Nanowires" in the January 2013, issue of *Modelling and Simulation in Materials Science and Engineering.* The paper investigated the competition between free surfaces and internal grain boundaries as preferential sites for dislocation nucleation during plastic deformation in aluminum bicrystalline nanowires. The work suggested that the cooperation of numerous mechanisms and the structure of internal grain boundaries are crucial in understanding the deformation of bicrystalline nanowires.



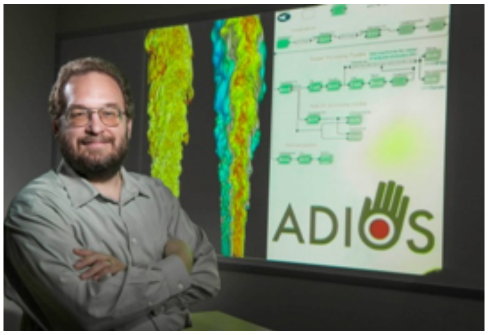
"Molecular Dynamics Simulations of Evaporation-Induced Nanoparticle Assembly" in the February 14, 2013, issue of *AIP: The Journal of Chemical Physics*, presented large-scale molecular dynamics simulations of the evaporation-induced assembly of nanoparticles suspended in a liquid that evaporates in a controlled fashion. The results have important implications in understanding assembly of nanoparticles and colloids in nonequilibrium liquid environments.

FY 2013 Awards and Recognition

R&D 100 Awards: In FY 2013, Sandia received three R&D 100 Awards and contributed to a fourth R&D 100 Award, three of which had their roots in LDRD projects.

Mantevo Suite 1.0, submitted by Mike Heroux and his team, an integrated collection of small software programs (miniapps) that model the performance of full-scale applications, yet require code only a fraction of the size of the full application.

Membrane Projection Lithography, submitted by Bruce Burckel and his team, a fabrication technique that enables the creation of a diverse array of microscopic 3-D structures with macroscopic impact.



ADIOS: Adaptable I/O System for Big Data, submitted by Oak Ridge National Laboratory with key contributions from Jay Lofstead, a Sandia LDRD-funded researcher at the Georgia Institute of Technology (now a Sandia employee). ADIOS provides adaptable, easy-to-use, and scalable I/O plugins across a variety of platforms. It can scale data-intensive applications that were previously daunting.

Professional Society Fellows: In FY 2013**,** Sandia LDRD participants who were selected as fellows in their professional societies include:

- American Ceramic Society: Bill Hammetter and Paul Clem
- American Chemical Society: Nancy Jackson
- American Physical Society: Mark Herrmann
- IEEE: Subhash Shinde

Additional awards and recognition to LDRD projects and participants are listed in Appendix A.

LDRD Performance Measures

Table 1 shows the relative contribution of LDRD-related outputs to total Sandia outputs for publications, intellectual property and other measures used to assess program performance.

Refereed Publications (CY 2008-2012) LDRD -supported Publications % due to LDRD	**3856** **1018** **26%**
Technical Advance/Records of Invention (FY2009-2013) LDRD-supported Technical Advances % due to LDRD	**1548** **819** **53%**
Patents Issued (FY 2009-2013) LDRD-supported Patents % due to LDRD	**414** **189** **46%**
Software Copyrights (2009-2013) LDRD-supported software copyrights % due to LDRD	**426** **103** **24%**
Postdocs (FY 2009-2013) LDRD-supported Postdocs % due to LDRD	**908** **512** **56%**
Postdoc Conversions (FY 2009-2013) LDRD-supported Postdoc Conversions % due to LDRD	**128** **93** **73%**
R&D 100 Awards (CY2009-2013) LDRD Supported R&D 100 Awards % due to LDRD	**22** **15** **68%**

BIOSCIENCE

The Bioscience Investment Area focuses on developing tools to lessen two national security risks: biodefense and emerging infectious diseases, and the United States' reliance on fossil fuels.

The research in biodefense includes developing better ways to detect, characterize, and contain harmful pathogens. The strategy integrates advanced technologies with an understanding of human health and immune response. The goal is to improve the response to disease outbreaks and to limit their spread.

The research regarding the nation's reliance on fossil fuels focuses on developing efficient, economical biofuels that can replace or reduce current gasoline, diesel, and aviation fuel consumption. The research includes two sources of energy: lignocellulose, or dry plant matter, and algae. The aim is to find efficient and economical methods to convert lignocellulose into fuels and to understand the factors that govern algal pond stability and identify molecular mechanisms that can be used for lipid/fuel production.

The Biomimetic Lung Toxicity Screening Platform (bioMIMIC) is a practical in-vitro tissue-on-a-chip screening platform that models the air sac/blood vessel interface and is suitable for use in BSL3/4 labs (Project 151350).

BIOSCIENCE

Genetic Engineering of Cyanobacteria as Biodiesel Feedstock

142441

Year 4 of 4
Principal Investigator: A. Ruffing

Project Purpose

The current dependence on fossil fuels for energy is an imminent threat to our national security.Energy independence through alternative energy development is necessary to address this political and economic threat. Biofuels are prime candidates for the supplementation and eventual replacement of fossil-fuel-derived energy. Major challenges in biodiesel production include: 1) maximizing the production rate to meet the high demand of current energy consumption and 2) developing low-energy and cost-effective methods for isolation and purification of the biodiesel. Photosynthetic microorganisms offer a promising solution to these challenges while at the same time addressing growing environmental concerns through CO2 mitigation. Algae, natural photosynthetic oil producers, are the focus of most biodiesel research efforts, and little attention has been given to other photosynthetic microorganisms, particularly cyanobacteria. Cyanobacteria do not naturally produce oil like algae; however, there are other advantages to using cyanobacteria for biodiesel feedstock production. Unlike algae, cyanobacteria have well-established methods for genetic engineering, as evidenced by the genetic engineering of cyanobacteria for the production of first-generation biofuels including ethanol and butanol. Furthermore, cyanobacteria will naturally secrete fatty acids, a biodiesel precursor, into the extracellular media, simplifying downstream product isolation. This project investigates the feasibility of engineering cyanobacteria for the production of fatty acids as biodiesel feedstock. The engineered cyanobacteria are subjected to additional investigation to determine the physiological effects of the genetic manipulation. If successful, this project will develop a new method for the production of biodiesel feedstock with reduced downstream processing requirements compared to conventional algal biodiesel production. The PI is a Sandia Truman Fellow.

Summary of Accomplishments:

Noteworthy accomplishments:

- Tested the toxicity of potential biofuel products for three genetically tractable strains of cyanobacteria. Synechococcus sp. PCC 7002 was shown to have high tolerance to short-chain alcohols such as ethanol and butanol.
- Successfully engineered two cyanobacterial hosts for the production and excretion of free fatty acids. The concentration of free fatty acids produced by the engineered cyanobacteria was high enough to lead to free-fatty-acid precipitation and visible accumulation at the surface of the culture.
- Identified major limitations in free-fatty-acid accumulation, most notably the negative physiological effects on the cyanobacteria host. Using RNA-seq technology, potential gene targets were identified for helping the cyanobacterium to cope with the physiological stresses of free-fatty-acid production. Several of these genes were targeted for genetic manipulation, and nine genes were found to improve the host physiology during free-fatty-acid production.
- Determined that selection of the cyanobacterial host significantly influenced the rate of free-fatty-acid production. Synechococcus sp. PCC 7002, a marine cyanobacterium, was engineered to produce higher levels of free fatty acid compared to Synechococcus elongatus PCC 7942, a freshwater cyanobacterium, with minimal physiological effects. The apparent free-fatty-acid resistance of Synechococcus sp. PCC

7002 was found to be dependent on temperature and free-fatty-acid concentration.
- Determined that gene expression levels were important for high free-fatty-acid production in the cyanobacterial host. In particular, overexpression of the carbon-dioxide-fixing enzyme, RuBisCO, led to a three-fold increase in free-fatty-acid production.

Significance:
This project conducted fundamental research to increase biofuel production from cyanobacteria, a form of microalgae. Microalgal biofuels have the potential to play a key role in energy security and in enabling US energy independence but will require scientific and engineering advancements to achieve economic sustainability. This work has demonstrated the ability of genetically engineered cyanobacteria to produce hydrocarbon-based fuels for renewable energy production. Furthermore, scientific advancements in the understanding of cyanobacterial physiology and genetic responses have been achieved. These accomplishments advance two DOE mission areas: Energy and Science and Innovation.

Refereed Communications:
A.M. Ruffing, "Metabolic Engineering of Hydrocarbon Biosynthesis for Biofuel Production," Book Chapter: Liquid, Gaseous and Solid Biofuels – Conversion Techniques, *Intech*, 2013, pp. 263-298.

A.M. Ruffing, "RNA-Seq Analysis and Targeted Mutagenesis for Improved Free Fatty Acid Production in an Engineered Cyanobacterium," *Biotechnology for Biofuels*, vol. 6, August 2013.

A.M. Ruffing, "Borrowing Genes from Chlamydomonas Reinhardtii for Free Fatty Acid Production in Engineered Cyanobacteria," *Journal of Applied Phycology*, vol. 25, pp. 1495-1507, January 2013.

Tailoring Next-Generation Biofuels and their Combustion in Next-Generation Engines

151308

Year 3 of 3
Principal Investigator: C. A. Taatjes

Project Purpose:

Increasing energy costs, the dependence on foreign oil supplies, and environmental concerns have emphasized the need to produce sustainable renewable fuels and chemicals. Domestically produced biofuels for the transportation sector will be key to meeting national goals for energy security and climate-change mitigation. The strategy for producing next-generation biofuels must include efficient processes for biomass conversion to liquid fuels, and the fuels must be compatible with current and future engines. New clean and efficient combustion strategies that rely on compression ignition are extremely sensitive to changes in fuel chemistry. Nevertheless, biofuel development generally takes place without any consideration of combustion characteristics, and combustion scientists typically measure biofuel properties without any feedback to the production design. We seek to optimize the fuel/engine system by bringing combustion performance, specifically for advanced next-generation engines, into the development of novel biosynthetic fuel pathways. We have developed an innovative coupling of combustion chemistry — from fundamental reaction kinetics to engine measurement — and the optimization of fuel production using metabolic engineering. We have engineered new means for biofuel production from lignocellulosic biomass using metabolic pathways discovered in endophytic fungi and concurrently have generated the combustion-chemistry knowledge base to model utilization of the biofuel. Current biofuel production from lignocellulosic material starts with pretreatment and enzymatic hydrolysis to obtain monomeric sugars, which are then fermented. The fungus-based biosynthetic approach may avoid these two costly steps by using a consolidated process that directly breaks down lignocellulosic biomass by extracellular hydrolytic enzymes and produces an infrastructure-compatible biofuel by fermenting the liberated monomeric sugars. This project has established a framework linking fundamental chemistry, engine science, and synthetic biology for fuel production for co-development of engines and biofuels.

Summary of Accomplishments:

We created a robust and flexible framework for coordination of biofuel production and utilization research that can enable co-development of fuels and engines. This framework can be applied for a range of biofuel production and combustion strategies.

We analyzed the combustion chemistry of ketone fuels, one class of fuel molecules produced by endophytic fungi from lignocellulosic biomass. We characterized an important radical rearrangement pathway in ketone ignition chemistry. We demonstrated that some ketones, for example 2,4-dimethylpentan-3-one, can be advantageous fuels for advanced engines, showing higher thermal efficiencies than gasoline in homogeneous-charge compression-ignition (HCCI) engines. We developed a working model for ketone ignition chemistry and validated it against a range of experimental targets.

We showed that several endophytes produce a wide spectrum of bioactive volatile organic compounds (VOCs) that contain a high energy density, making them promising potential replacements for fossil fuels. Genomic data mining identified that these endophytes possess an extensive complement of cellulolytic enzyme machinery, which indicates they have a robust capacity for degrading cellulosic biomass. We determined the dynamics of the cellulolytic machinery of these four strains in the presence of different feedstocks. Moreover, the putative terpene synthase (TS) genes annotated in the genomes were informatically and functionally characterized, expressed, and optimized in E coli. We tested the fundamental ignition chemistry of cineole, one of the principal fuel molecules produced by the action of these TS, and developed a preliminary model for cineole autoignition.

Significance:

The framework put into place under this project can enable co-development of biofuels and engines, allowing efficient exploration of new production platforms and facilitating their utilization. Such a framework can enhance national goals towards secure and sustainable transportation fuels.

The characterization and engineering of new metabolic pathways for breakdown of lignocellulosic biomass and production of useful organic molecules may enable more effective biomass conversion processes with less need for expensive pretreatment.

The ignition chemistry investigations will facilitate the development of clean, efficient combustion strategies that exploit emerging fuel stocks.

Refereed Communications:

A.M. Scheer, O. Welz, D.Y. Sasaki, D.L. Osborn, and C.A. Taatjes, "Facile Rearrangement of 3-Oxoalkyl Radicals is Evident in Low-Temperature Gas-Phase Oxidation of Ketones," *Journal of the American Chemical Society*, vol. 135 pp. 14256-14265, August 2013.

Y. Yang and J.E. Dec, "Bio-Ketones: Autoignition Characteristics and their Potential as Fuels for HCCI Engines," *SAE International, Journal of Fuels and Lubricant*, vol. 6, pp. 713-728, October 2013.

Systems Biology in 3D: Monitoring and Modeling the Dynamics of Francisella tularensis-associated Granuloma Formation

151348

Year 3 of 3
Principal Investigator: S. M. Brozik

Project Purpose:

Formation of granulomatous-necrotic lesions in mice infected with *Francisella tularensis* (Ft), a category A bioterrorism agent, may serve to control and regulate early stages of infection. Traditional sample-sacrifice experimental protocols have enabled significant insight into the cellular composition of these granulomas; however, an understanding of multiscale mechanisms and host-pathogen interactions that mediate Ft-related granuloma formation is lacking. Specifically, we propose to explore: 1) the functional role of macrophages and effector molecules (e.g., nitric oxide (NO) and reactive species) in formation and establishment of an unfavorable granulomatous microenvironment and 2) the intracellular response of Ft within the granuloma-associated microenvironment.

Existing experimental methods do not capture the dynamics of host-pathogen intra/intercellular events that lead to 3D granulomatous structures, thereby preventing full exploration of the role of these structures on immunopathogenic outcomes of Ft. Using a multidimensional systems-biology approach, we will investigate the correlation between intracellular-scale events (e.g., chemokine-mediated cell recruitment, NO biosynthesis) and granuloma formation. Further, we will explore the impact of granulomatous structures on Ft viability and dissemination during infection. We will develop an experimental platform to enable real-time dynamic profiling of Ft infection of host mononuclear cells in a 3D environment. The platform will consist of a 3D microfluidic porous collagen-based scaffold that will serve as a synthetic extracellular matrix (ECM) for interrogating host-cell responses to pathogen exposure in an ex-vivo microenvironment. This platform will enable real-time optical and electrochemical monitoring of Ft-infection and granuloma-formation events. Quantitative and semi-quantitative spatio-temporal observations will be used to develop a theoretical model of this important host-response mechanism, which will enable us to explore and develop new hypotheses regarding the relative kinetics of host-response and effective protection during Ft infection.

Summary of Accomplishments:

We have developed a multidimensional empirical and theoretical model of host immune response to Ft infections and subsequent formation of granulomatous lesions. We tested these models through experimentation by determining the effects of hydrogen peroxide (oxidative stress) on Ft metabolic and transcriptomic changes. Metabolic analysis revealed significant differences between the control and the high hydrogen peroxide (H_2O_2) group, and our data also suggest that the low H_2O_2 group may exhibit an adaptive response during the first exposure to H_2O_2. We have also extended our agent-based modeling (ABM) platform to explicitly include O_2-mediated cellular/intracellular response and began integrating intracellular mechanistic models, which will enable 3D model development.

We investigated the ability of Ft-infected macrophages to induce migration of non-infected macrophages due to cytokines and chemokines released by the infected cells using standard transwell migration assays and showed that Ft-infected bone-marrow-derived macrophages (BMDMs) induced migration 15% and 5% more than controls three and six hours, respectively, post-infection. We have fabricated two microfluidic devices for 3D in-vitro studies. Our second-generation device is capable of maintaining a constant flow of cells and medium through the upper and lower wells. Using RAW264.7, we have demonstrated the ability to introduce cells, both infected and noninfected, into all three channels and maintain cell viability. We carried out initial 3D migration studies using our first-generation device with both bone-marrow-derived macrophages and RAW264.7 cells pre-stimulated with interferon gamma (IFN-gamma). We observed cellular uptake of Ft, initial indications of cellular aggregation due to infection, and evidence of infection-mediated cell death/bursting. Using a MATLAB-based image analysis tool, we quantified cellular velocity, displacement, and directedness to characterize how host and bacterial cells move and interact in 3D.

Significance:

The goal of this work was to understand the role of the granulomatous structures in infection by *F. tularensis*, a category A bioterrorism agent. Results will contribute to efforts to understand whether Ft-granuloma formation is simply an effective host defense mechanism or, as in Mtb-granulomas, Ft can potentially adapt to the changing microenvironment, enabling the pathogen to hide out within these structures and thereby to evade complete elimination by the host. This can provide insight of significant relevance to DOE and national security missions with regard to biodefense.

Refereed Communications:

E.E. May, A. Leitao, A. Tropsha, and T.I. Oprea, "A Systems Chemical Biology Study of Malate Synthase and Isocitrate Lyase Inhibition in Mycobacterium Tuberculosis during Active and NRP Growth," *Computational Biology and Chemistry,* vol. 47, pp. 167-180, December 2013.

Host-Virus Interaction Using an Artificial Host Cell System

151349

Year 3 of 3
Principal Investigator: D. Y. Sasaki

Project Purpose:

The goal of this project is the development of a model system for understanding the entry pathway of pathogenic (Henipah) viruses. As a response to a primary threat to national security, understanding the entry pathways of pathogenic viruses is vital in developing strategies for their sensitive detection and mitigation of infection. While much has been learned about the biochemistry of pathogen invasion from studying interactions with host cells, the complexity of cellular processes makes it difficult to isolate the fundamental requirements for infection. The role of receptor clustering, lipid composition, and membrane phase in viral entry remain ambiguous using a live cell approach. As a complement to such studies, we propose to develop model systems to understand the mechanism of pathogen infection by recreating the essential early events by enveloped viruses. Our artificial host will consist of a supported lipid bilayer (SLB) that will mimic the chemistry, physical structure, and mechanics of cellular membranes. The structure and mechanics of the membrane will be tailored by the use of incorporated lipid components to create specific phases, polymer cushions to minimize substrate interactions, and lipid domain architectures to mimic raft-like assemblies in cells, which are known sites of viral entry. Chemistry will be tuned to enhance affinity (electrostatics, sterol content) and specific coupling (receptor proteins) of the viral particles. Scanning point-mutation libraries will allow us to probe specific amino-acid sites on the Nipah G stalk region to gain insight on structure and chemistry of the viral ligands on fusion. Fusion events will be followed using total-internal-reflectance-fluorescence (TIRF) microscopy to capture hemi-fusion and full-fusion processes. Using this minimalistic approach, we hope to provide a detailed understanding of the mechanisms of enveloped virus fusion and facilitate new methods for potential rapid screening of pathogenic agents.

Summary of Accomplishments:

The research conducted provides new understanding of the role of membrane proteins in viral-particle affinity and entry into cellular membranes. With the G attachment protein of the Nipah virus, we found that cysteines in the stalk domain of NiV-G are not only important for maintaining the oligomeric stability of G, but also for proper folding of a unique subdomain located in the membrane distal region of the stalk that is necessary for F-triggering. These studies supplemented our knowledge of the function of the stalk domain of paramyxovirus attachment proteins in F triggering and identified a critical microdomain that can be targeted for therapeutic or vaccine development. Precisely how membrane fusion between the viral particle and cell membrane occurs is poorly understood. Through model studies, we found that steric pressure of membrane-bound proteins confined to a lipid domain can drive curvature, a defining property of a membrane undergoing fusion or fission. This work not only provides an understanding of protein-induced curvature in lipid membranes but also calls into question some of the long-held theories of how membrane curvature is induced in endocytosis. We also showed that protein-membrane interactions not only drive membrane curvature but can also be defined by the curvature of the membrane itself. We have found that, by using a nanoscale bump surface, it is possible to selectively partition receptor molecules for protein affinity to specific sites in a membrane. Our efforts in understanding the relationship between protein assembly and membrane structure will further aid in the development of pathways to mitigate pathogen invasion and disease.

Significance:

Results of our research into viral-particle recognition and fusion to cell membranes provided valuable insights into the roles that protein affinity and confinement within lipid domains play in membrane curvature in cellular fusion/fission events. Our results include understanding of: 1) assembly of the G attachment protein of Nipah virus, using point mutation studies, for viral-particle affinity and fusion to the cell membrane, 2) lateral pressure of surface-bound proteins to induce curvature in lipid membranes, and 3) the role of membrane curvature in the selective partitioning of molecular receptors and specific affinity of associated proteins.

Refereed Communications:

S.M. Hoppe, D.Y. Sasaki, A.N. Kinghorn, and K. Hattar, "In-Situ Transmission Electron Microscopy of Liposomes in an Aqueous Environment," *Langmuir*, vol. 29, pp. 9958- 9961, July 2013.

M.O. Ogunyankin, D.L. Huber, D.Y. Sasaki, and M.L. Longo, "Nanoscale Patterning of Membrane-Bound Proteins Formed through Curvature-Induced Partitioning of Phase-Specific Receptor Lipids," *Langmuir,* vol. 29, pp. 6109-6115, May 2013.

J.C. Stachowiak, E.M. Schmid, C.J. Ryan, H.S. Ann, D.Y. Sasaki, P.L. Geissler, M.B. Sherman, D.A. Fletcher, and C.C. Hayden, "Membrane Bending by Protein-Protein Crowding," *Nature Cell Biology*, vol. 14, pp. 944-949, August 2012.

Biomimetic Lung Toxicity Screening Platform (bioMIMIC)

151350

Year 3 of 3
Principal Investigator: A. Hatch

Project Purpose:

While the use of engineered nanomaterials continues to burgeon, questions relating to potentially harmful human health effects linked to nanomaterial exposure have not been convincingly addressed. Animal models are considered the gold standard for physiological insight into nanomaterial toxicity, but they are not feasible as first-line screening tools due to high study costs and potential interspecies variability. Conversely, single-phenotype Petri dish studies can provide cellular-level toxicity readouts in a scalable manner but seldom represent integrated tissue-level physiological responses. To overcome these deficiencies, the National Research Council's report entitled, "Toxicity Testing in the 21st Century: a Vision and a Strategy," has identified a critical need for scalable, physiologically relevant in-vitro tissue mimics that can minimize or replace animal toxicity studies while providing insight into the human effects of nanomaterial exposure. The goal of this project is to develop a microfluidic, cell-based platform that will enable the detailed study of integrated toxicity responses induced by exposure to engineered nanomaterials. We will generate the tissue mimic by creating an ordered multi-phenotypic construct that will provide an accurate representation of the alveolar-capillary interface found in the lung. Toxicity responses to well-characterized nanomaterial exposure will be quantified using commercial and Sandia techniques.

Summary of Accomplishments:

We developed advanced means for suspending multiple cell layers in a microfluidic tissue construct. A technical advance disclosure was filed describing our approach to creating suspended membranes that can be as thin as 0.001 mm. Additionally, different types of primary alveolar/capillary cells were cultured on both sides of the ultrathin membrane forming apical and basal tissue layers with vascular compartments for perfusion. This membrane is 10-fold thinner than existing approaches and is thus the only reported means for accurately representing the spacing between suspended alveolar/capillary tissue layers in vitro.

We advanced technologies for making a practical in-vitro tissue-on-a-chip screening platform. The approach is affordable and scalable, which is made possible by using low-cost laminate fabrication techniques similar to commercialized low-cost manufactured products. This offers advantages over more conventional fabrication strategies utilized in academic labs such as polydimethylsiloxane (PDMS), etched silicon, and glass. Furthermore, the approach is: 1) highly scalable for conventional microarray spacing of tissue constructs and for 96-well spacing of fluidic access ports, 2) highly reconfigurable including variations for interconnecting tissue compartments, 3) compatible with extraction of transcriptomics and proteomics samples for high quality data from each tissue compartment, 4) compatible with imaging with typical cell stains at different stages of an experiment, 5) compatible with typical hazard controls and operational restrictions in BSL3/4 environment, and 6) suited for affordable research studies with small numbers of primary cells in each tissue compartment.

Significance:

The developed technologies advanced the frontiers of in-vitro tissue imaging in the spatial organization of vascularized suspended tissues, including alveolar-capillary interfaces, and also dramatically enhanced the affordability and accuracy of information gleaned in infectious-disease and toxicity-screening studies. This is, in part, because the design can be manufactured at low cost and also because primary cells, more relevant than typical cell lines, can be used in affordable numbers and constructed in a meaningful way.

More accurate in-vitro models are critical to national security missions for infectious-disease research and for rapid discovery of effective countermeasures.

CVD Encapsulation of Mammalian Cells for Hazardous Agent Detection

151375

Year 3 of 3
Principal Investigator: J. C. Harper

Project Purpose:

Despite significant progress made in the last few decades towards portable and robust detection systems, biological detection devices still face major limitations. Living-cell-based sensors have proven effective in addressing real-time and near-neighbor detection issues; however, relevant mammalian cell-line-based sensors require frequent replenishment with new cells and function in limited environments (stable, developed regions). To be practical for the warfighter and for defense of structures in less developed regions, cell-based sensors require a functional biocompatible interface between the immobilized/encapsulated cells and the macro world. This interface would expand the range of environments for which the sensor would be practical and would limit required technical expertise for operation. To meet the need for robust, easy-to-use threat-detection systems, we are developing a chemical-vapor-deposition (CVD) technique designed to coat cells in silica. Preliminary results have shown this method to be effective in encapsulating Jurkat cells (immortalized T lymphocytes) in a conformal thin silica shell. Unlike methodologies based on sol-gel technology, CVD encapsulates single cells, is easily tunable, and reduces the stresses exerted on cells due to exposure to toxic by-products. These benefits of the CVD system may allow for the production of cell-based systems with viabilities and activities of several weeks, as opposed to the two-day viability for the most relevant cell-based sensing line, CANARY. This advance would be a significant breakthrough by making cell-based biosensors practical in a wide range of environments, including less stable regions with limited infrastructure. If successful, we expect the CVD method could be adapted to yeast or mammalian cell lines, further expanding the utility of cell-based sensors. The work is in collaboration with New Mexico Tech.

Summary of Accomplishments:

Using the novel Chemical Vapor into Liquid (CViL) deposition process, the high vapor pressure of silica alkoxides was utilized to precisely deliver silica into an aqueous medium, facilitating cellular silica encapsulation as hydrolyzed silica was formed (in situ), or by mixing cells with condensed polymeric silica post CViL reaction. Silica particle formation and association with cells was measured using scanning electron microscopy with energy-dispersive x-ray spectroscopy (SEM-EDS), with higher resolution characterization of cell-silica interactions elucidated via fluorescence microscopy. The ability of encapsulated cells to act as biosensors was also shown using fluorescence-plate-reader analysis to measure beta-galactosidase reporter enzyme turnover. The results demonstrate that the silica CViL technique holds great promise for cellular encapsulation for biosensor design, showing that living cells are encapsulated in amorphous silica, maintain long term viability, and are responsive. One impactful result of this study is data showing that Jurkat cells, a lymphocyte-derived cancer cell line, can be encapsulated in silica while maintaining overall cell integrity. This initial success provides evidence that the silica CViL approach could be used to encapsulate other lymphocyte-based cell lines, such as CANARY and RBL. These two cell lines have been shown to be capable of rapid, real time detection of hazardous agents with very low detection limits. However, these cell lines are fragile in ex-vivo environments, needing to be replaced nearly daily. Future efforts will be made to utilize silica CViL to engineer silica encapsulation of CANARY and RBL cells that maintain sensing function and can be incorporated into sensing devices. Additionally, the ability to control silica structure through tuning CViL reaction parameters (i.e., reaction time, silica sol-cell association time, introduction of functional component additives, addition of ameliorants, differing silica alkoxides) allows for the development of cell-silica architectures with diverse applications such as water filtration and environmental remediation, bioelectronics, catalysis, and medical diagnostics.

Significance:

This study has yielded fundamental understanding of the requirements for interfacing biological materials with nanomaterials and has demonstrated the first successful encapsulation of living cells in a silica nanostructured composite for cell-based sensing using the CViL process. The resulting technology will allow for development of robust chem/biosensors that will directly impact the early warning needs of DoD (DTRA/DARPA) and DHS, prove useful in remote sensing for treaty verification (DOE), and find application in medical diagnostic technologies (National Institutes of Health/Biomedical Advanced Research and Development Authority).

Refereed Communications:

J.C. Harper, T.L. Edwards, T. Savage, S. Harbaugh, N. Kelley-Loughnane, O.M. Stone, C.J. Brinker, and S.M. Brozik, “Orthogonal Cell-Based Biosensing: Fluorescent, Electrochemical, and Colorimetric Detection with Silica-Immobilized Cellular Communities Integrated with an ITO/Plastic Laminate Cartridge,” *Small*, vol. 8, pp. 2743-2751, September 2012.

Biodefense and Emerging Infectious Disease (BEID) Applications of Engineered Nanoparticles

151379

Year 3 of 3
Principal Investigator: C. E. Ashley

Project Purpose:

Virus-like particles (VLPs) of MS2 bacteriophage self-assemble from 180 copies of a single coat protein into a monodisperse, 28-nm icosahedron that is highly tolerant of multivalent peptide display. MS2 VLPS are, therefore, well suited for use as potently immunogenic vaccines against viral or bacterial pathogens. The utility of MS2 VLPs in vaccine development applications can be greatly enhanced though their development as a platform for random peptide display, which, upon synthesis of a complex library, will enable identification of peptide sequences with an affinity for any material. The goal of our proposed research is to develop a complex random peptide library entirely in vitro using MS2 VLPs as a display platform. In-vitro VLP display is entirely novel and will enable the convenient production of high-complexity libraries (> 10^{11} members) and will make library construction and affinity selection amenable to automation. We will then utilize monoclonal antibodies (mAb500, mAb525, and mAb551, which were raised by immunizing mice with linear peptides, specifically PEVCWEGVYNDA for mAb500, FLDSNQTAENPVFTV for mAb525, and LAEDDTNAQKTI for mAb551, conjugated to the carrier protein, KLH) against Nipah virus (NiV), a BSL-4 select agent, to affinity-select VLPs that display peptide mimotopes. We will test the ability of selectants to elicit a neutralizing, protective antibody response using in-vitro neutralization assays and in-vivo challenge assays. VLP display promises to be a remarkably powerful, universal technology that will enable rapid, cost-effective identification of vaccine candidates in order to effectively combat biodefense and emerging infectious disease (BEID) agents. The PI is a Sandia Truman Fellow.

Summary of Accomplishments:

We have shown that subjecting random peptide libraries displayed on MS2 VLPs to affinity selection against neutralizing antibodies enables rapid identification of vaccine candidates without requiring that the target pathogen be isolated, cultured, and characterized. For example, mAb525 neutralizes NiV and HeV pseudoviruses at concentrations of 0.2 nM and 8 nM, respectively and competes with ephrin B2 and ephrin B3 for binding to NiV-G. Four rounds of affinity selection against mAb525 yield VLPs that display the peptide, GTNQTAENPI. Immunization of mice with VLPs that display 90 copies of this peptide results in high-titer, peptide-specific antibody responses, which is consistent with previous results that demonstrate MS2 VLPs trigger potent antibody responses against small molecules displayed on their surfaces in dense, repetitive arrays. Importantly, however, antisera against the affinity-selected VLP neutralizes NiV and HeV pseudoviruses in vitro at dilutions as high as 1:2056 and protect ex-ovo avian embryos from lethal challenge with the NiV pseudovirus at dilutions as high as 1:10,240. Our results demonstrate that affinity selection against neutralizing antibodies yields VLP vaccines that, in turn, raise neutralizing, protective antibody responses upon immunization. Thus, the MS2 VLP technology promises to enable rapid development of vaccines against emerging, re-emerging, or engineered pathogens since, in theory, the only input information that we require is convalescent antisera.

Significance:

We demonstrate that our MS2 VLP technology is the first platform that enables identification of vaccine candidates using only neutralizing antibodies against the target pathogen. Specifically, we show that panning complex, random peptide libraries displayed on MS2 VLPs against antibodies that recognize Nipah or Hendra virus results in VLP-based vaccine candidates that trigger neutralizing, protective antibody responses in mice. These results significantly advance the biological defense mission of Sandia by demonstrating that the MS2 VLP technology might be used to rapidly identify vaccines against emerging, re-emerging, or engineered pathogens using only convalescent anti-sera from infected individuals.

Refereed Communications:

D. Tarn, C.E. Ashley, M. Xue, E.C. Carnes, J.I. Zink, and C.J. Brinker, "Mesoporous Silica Nanoparticle Nanocarriers: Biofunctionality and Biocompatibility," *Accounts of Chemical Research*, vol. 46, pp. 792-801, February 2013.

Luminescent Lanthanide Reporters for High-Sensitivity Novel Bioassays

157690

Year 3 of 3
Principal Investigator: M. Anstey

Project Purpose:

Biological imaging and assay technologies rely on fluorescent organic dyes as reporters for a number of interesting targets and processes. However, limitations of organic dyes such as small Stokes shifts, spectral overlap of emission signals with native biological fluorescence background, and photobleaching have all inhibited the development of highly sensitive assays. The polymerase chain reaction (PCR) is a current work-around for increasing sensitivity, but PCR can introduce bias into the sample and complicate data interpretation. In addition, a need is arising for identifying multiple targets for biomarker discovery or pathogen detection from a bioterrorist attack. These multiplex assays are currently expensive and complex, utilizing microarray plates or multi-wavelength excitation/emission detection systems, which limit their application. What is needed is a new type of fluorescent moiety that offers improved properties over organic dyes, enables cost-effective multiplexed analysis, and provides opportunities for new and novel high-sensitivity bioassays.

To overcome the limitations of organic dyes for bioassays, we propose to develop lanthanide-based luminescent dyes and demonstrate them for molecular reporting applications. This relatively new family of dyes was selected for their attractive spectral and chemical properties. Luminescence is imparted by the lanthanide atom and allows for relatively simple chemical structures that can be tailored to the application. The photophysical properties offer unique features such as narrow and non-overlapping emission bands, long luminescent lifetimes, and long wavelength emission, which enable significant sensitivity improvements over organic dyes through spectral and temporal gating of the luminescent signal.

Growth in this field has been hindered by the advanced synthetic chemistry techniques that are required and by access to experts in biological assay development. At Sandia, a multidisciplinary partnership between chemistry, biology, and engineering is easily formed that will allow this project to advance the state of the art.

Summary of Accomplishments:

We developed lanthanide-based dyes that are amenable to various types of biological assays of interest at Sandia. Specifically, we invented 18 new organic molecules using "Click" methodology that bind lanthanide atoms strongly. We obtained monometallic complexes, a double-ligand bimetallic complex, and four polymeric, multimetallic complexes. The double-ligand bimetallic was of particular interest because of its spiral binding motif.

Luminescent studies of these compounds showed enhanced photoemission of the lanthanide atom compared to the free salt. This is due to absorption by the ligand pi-system with energy transfer to the lanthanide excited states. Excitation was performed at 254 nm regardless of ligand structure and identity of the lanthanide atom. Each lanthanide gave the expected emission pattern in the visible and infrared regions of the electromagnetic spectrum. Quantum efficiencies of these energy transfers have not yet been measured, but the Tb and Eu luminescences are sufficient for visual identification in a fully lit environment. Additionally, these complexes are capable of multiphoton upconversion when exposed to a 632-nm laser source, giving the emission patterns of the respective lanthanide element.

A collaboration with Prof. John Arnold (UC Berkeley) was begun to explore a new ligand motif: corrole. This structure is similar to a porphyrin but lacks a methyne unit between adjacent pyrrole rings. This allows the structure to adopt overall a -3 charge state upon deprotonation, matching the lanthanide's +3 charge. The lanthanide is chelated by the four pyrrole moieties and sits above the plane of the corrole ring. A capping ligand binds to the exposed face of the metal atom. However, due to the extended conjugation in the structure, these ligands absorb at fairly long wavelengths (~450 nm). Energy transfer to terbium and europium was not possible in these complexes.

Significance:

A robust, cost-effective, and multiplexed fluorescent reporter system would be an invaluable tool for the detection of biological molecules in clinical and environmental samples. This project provides the DHS, DoD, and DOE with an alternative to current organic dyes in assays specifically geared towards bioterrorism. The Center for Disease Control also demands similar advances in diagnostic medicine, and a successful lanthanide reporter system can provide that advancement in the form of improved fluorescence imaging, MRI, and bioagent detection.

Refereed Communications:

H.L. Buckley, M.R. Anstey, D.T. Gryko, and J. Arnold, "Lanthanide Corroles: A New Class of Macrocyclic Lanthanide Complexes," *Chemical Communications*, vol. 49, pp. 3104-3106, February 2013.

Pathogenicity Island Mobility and Gene Content

158185

Year 3 of 3
Principal Investigator: K. P. Williams

Project Purpose:

Key goals towards national biosecurity include improved methods for diagnosing pathogens (natural or engineered), predicting their emergence, and developing vaccines and therapeutics. These goals could be achieved, in part, through a comprehensive analysis of bacterial genes that promote pathogenicity and of the mobile DNA elements (pathogenicity islands) where such genes typically reside. Our current knowledge of bacterial pathogenicity genes is extremely limited and typically based on painstaking laboratory study. We will develop an automated system to identify islands as soon as genomes are posted at GenBank and to analyze island gene content and mobility. The resulting island database will address a cyber infrastructure need and provide a short list of potential pathogenicity genes in a new pathogen, enabling deeper bioinformatic island analysis that may allow positive identification of novel pathogenicity genes.

Multiple islands can accrue throughout a genome to combinatorially enhance or modulate pathogenicity. Diverse islands can even appear in tandem arrays at genomic integration hotspots, a configuration promoting inter-island recombination events that may produce new islands with novel gene combinations. The proposed database will enable an in-depth analysis of island genomic sites and arrangements and their phylogenetic distributions to shed light on how island mobility, evolution, and functional cooperation promote pathogenicity.

Pathogenicity islands are poorly understood and present unique challenges for study, but meeting these challenges to better understand island nature, especially learning how to identify the cryptic pathogenicity genes they may carry, will bear tremendous payoffs for human health, microbial ecology, and biosecurity.

Summary of Accomplishments:

We developed a program for finding mobile DNA elements that target tRNA genes in bacterial genomes, finding over 4000 genomic islands. These data were combined with a downloaded list of mobile elements that are bacteriophage-like. This set will be further expanded by our new method that uses the islands as a training set to find new genomic islands. We have already tested this new method in one genome where 10 training islands helped identify two previously undetected islands. This is one step in developing a naturalness score for suspect genomes.

We have processed the Slezak database of vector sequences and evaluated them for their occurrence in natural genomes as a preliminary step in a toolmark detection tool.

We have sequenced, assembled and annotated the complete genome, including four plasmids, of Klebsiella pneumoniae BAA-2146, the first US isolate encoding the beta-lactamase NDM-1. We found 22 antibiotic-inactivating enzyme genes, eight of which are for beta-lactamases. We have analyzed the evolution of the plasmids and genomic islands in the chromosome.

Significance:

We are developing tools for assessing antibiotic-resistance and virulence potential of bacterial biothreats and are on track to develop a tool for assessing the potential that a bacterial biothreat was purposely engineered. Our bioinformatics tools are already contributing to other biothreat research efforts at Sandia.

Production of Extremophilic Bacterial Cellulase Enzymes in *Aspergillus Niger*

158186

Year 3 of 3
Principal Investigator: J. M. Gladden

Project Purpose:

Lignocellulosic biofuels hold great promise for dramatically reducing the US dependence on foreign oil. These technologies aim to convert sugars derived from plant biomass feedstocks into biofuels. Current biofuel processing configurations operate under mesophilic conditions, but there is a push toward thermophilic conditions for a variety of reasons, including reduced contamination, more efficient fuel recovery, better enzyme kinetics, and higher metabolic rates — all of which would significantly reduce costs for biofuel production.

A few companies have already begun developing thermophilic biofuel production hosts but have yet to complete the thermophilic bioprocessing configuration by developing a cellulase cocktail. The thermophilic biofuel system offers several advantages over current mesophilic approaches, most importantly the significant reduction of opportunistic microbial infection. Commercial cellulase cocktails are derived from filamentous fungi that produce very high enzyme titers, essential for commercialization. Unfortunately, these enzymes are inactive at high temperatures. Thermophilic bacteria produce highly stable thermophilic cellulases and are an excellent alternative. However, bacteria generally produce low titers of these enzymes, an order of magnitude too low. To overcome this barrier, we propose to develop a high titer thermophilic bacterial cellulase cocktail by expressing these bacterial enzymes in a commercial filamentous fungal host, *Aspergillus niger*.

Our proposed approach would represent the first time an entire bacterial pathway was reassembled in filamentous fungi. We aim to produce the first high-titer thermophilic cellulase cocktail with the potential for significantly reducing the costs of commercial cellulosic biofuels. Expression of bacterial enzymes in filamentous fungi has historically proven difficult because these enzymes are quite foreign to fungi, which leads to poor expression and inhibitory modifications. We have devised a multipronged approach to overcome these barriers, including fusion to fungal enzymes and extensive engineering of the bacteria genes to make them more compatible with fungi.

Summary of Accomplishments:

This project developed *A. niger* as a heterologous expression system capable of producing secreted enzymes. This system could be applied to targets relevant to bioenergy and biodefense. It was then demonstrated that this expression system could be used to produce a variety of thermophilic bacterial cellulases enzymes, enabling the development of advanced cellulase cocktails for biofuel production from lignocellulosic biomass.

Significance:

The US Renewable Fuel Standard 2 (RFS2) legislatively mandates 16 billion gallons of cellulosic biofuels by 2022 as one step toward reducing our dependence on foreign oil. The DOE has the mission to ensure energy security through reliable, clean, and affordable energy. Our project targets the reduction of the costs associated with cellulosic biofuel production through the production of cost-competitive enzyme cocktails by recombinant fungi.

Intra-Membrane Molecular Interactions of K^+ Channel Proteins: Application to Problems in Biodefense and Bioenergy

158410

Year 3 of 3
Principal Investigator: E. Moczydlowski

Project Purpose:

The goal of this project is to develop new methods to measure and analyze the structural basis of K^+-channel tetramer stability for applications in biodefense and bioenergy. Ion-selective channel proteins are key effectors of electrophysiological processes linked to cell-membrane signal transduction, mechanisms relevant to microbial pathogenesis and bioenergy production. The aqueous pore of most channel proteins is formed at the central interface of identical or homologous subunits of a torus-like complex embedded within a lipid membrane. All known highly K^+-selective channels from viruses to humans share a structurally homologous pore domain, which is a complex of four subunits (homo- or hetero-tetramers). Since integrity and stability of such multi-subunit protein complexes is required for assembly and function of most channels, molecular mechanisms underlying intra-membrane protein-protein interactions are of fundamental interest.

The scientific problem addressed by this project may be is described as follows:

What is the molecular basis of tetramer stability of K^+ channel proteins?

How does tetramer stability correlate with ion discrimination, binding affinity, and conductance?

How do channel functions of ion selectivity, open-closed gating dynamics, signaling, and pharmacology depend on inter-subunit interactions?

Despite intensive research on K^+ channels, the relationship between tetramer stability and channel function remains virtually unexplored. It is known that lowering extracellular K^+ results in loss of function of many K^+ channels; however, the molecular basis of this phenomenon is poorly understood. The scientific challenge is to develop new approaches to measure, analyze, and engineer the molecular specificity and energetic basis of intra-membrane subunit-subunit interactions of K^+ channels. This knowledge can be applied to discovery of new classes of small molecules that disrupt channel function for treatment of human diseases and suppression of pathogenic microbes. It can also be used to design highly stable K^+ channels for engineering of hybrid material nanodevices in the emerging field of bionanoelectronics.

Summary of Accomplishments:

We used KcsA, a membrane protein of Streptomyces lividans as a model K^+ channel of known structure, to investigate the molecular basis of tetramer stability as follows:

- The intra-membrane structure of the tetramer was subjected to bioinformatic analysis of inter-monomer contacts at the subunit interface. In the region from the pore helix to the inner helix, the monomer/monomer subunit interface contains 23/26 residues and ~1,249 Å^2 of surface area for the closed conformation in comparison to 17/17 residues and ~588 Å^2 for the open conformation of the channel. Such large structural changes at the subunit interface suggest that tetramer stability may be significantly less for open vs. closed states of the channel. This finding implies that structural stability of K^+ channels may be highly dependent on gating and functional activity.

- The effect of two local anesthetics (LAs), lidocaine and tetracaine, on tetramer stability of KcsA was analyzed to determine whether drug binding might have long term effects on quaternary structure as previously suggested for the mammalian cardiac Kv1.5 channel. Thermal dissociation experiments demonstrated a mutually antagonistic ligand interaction between LAs and K^+. Higher concentrations of tetracaine are required to induce thermal dissociation of KcsA tetramer in the presence of 5 mM K^+ (IC_{50} = 4.2 mM) vs. the absence of K^+ (IC_{50} = 1.2 mM). Similarly, a higher range of [K^+] is required to stabilize tetramer in the presence vs. absence of LAs.
- Molecular simulation of LA docking to the central cavity of the ion-conduction pore demonstrated that lidocaine and tetracaine can bind to KcsA in a variety of conformations with similar binding energies. Significant repulsive interactions observed between the protonated-amine drug cation and K^+ bound to the selectivity filter are consistent with the antagonistic interaction between K^+ and LA drugs observed in our experiments.

Significance:

This project produced new evidence that organic cation drugs may affect tetrameric quaternary structure of K^+ channel proteins. This finding may have applications in development of high-throughput assays to screen for molecules that specifically inhibit or enhance the tetramer stability of certain ion-channel drug targets. Since K^+ channels exhibit considerable structural and sequence diversity, such assays may identify channels that are especially sensitive to this form of pharmacological manipulation. This approach could have considerable utility in treatment of numerous diseases known as channelopathies that involve genetic defects of particular ion channels. Biodefense applications could also favorably impact national security.

Refereed Communications:

C.J. Huang, L. Schild, and E.G. Moczydlowski, "Use-Dependent Block of the Voltage-Gated Na^+ Channel by Tetrodotoxin and Saxitoxin: Effect of Pore Mutations that Change Ionic Selectivity," *Journal of General Physiology*, vol. 140, pp. 435-454, October 2012.

N.W. Gray, B.S. Zhorov, and E.G. Moczydlowski, "Interaction of Local Anesthetics with the K^+ Channel Pore Domain: KcsA as a Model for Drug-Dependent Tetramer Stability," *Channels*, vol. 7, pp. 182-193, May 2013.

E.G. Moczydlowski, "The Molecular Mystique of Tetrodotoxin," *Toxicon,* vol. 63, pp. 165-183, December 2012.

Functional and Robust Asymmetric Polymer Vesicles

158478

Year 3 of 3
Principal Investigator: W. F. Paxton

Project Purpose:

In a living cell, the directional exchange of matter, energy, and information across the membrane is facilitated primarily by transmembrane proteins (TMPs) that are asymmetrically distributed and oriented. Mimicking this asymmetry and function in synthetic hybrid systems is a longstanding challenge in biomolecular and materials science. We seek to understand the principles that govern the reconstitution of TMPs into robust matrices in order to create vesicles that are both radially and axially asymmetric. We intend to: 1) explore systematically the parameters that govern vectorial insertion of TMPs in robust biomimetic environments and 2) use what we learn to create radially and axially asymmetric hybrid constructs that could be used to regulate the transport of charge in energy production and storage systems and to understand signal transduction at immunological synapses between cells and model biomimetic membranes.

Many reports demonstrate that TMPs can be reconstituted into synthetic vesicles and that they retain their activity after reconstitution, yet none have provided a general strategy for controlling the orientation of protein insertion. Furthermore, lipid-based vesicles (liposomes) typically used in reconstitution experiments lack the chemical and mechanical stability required for materials science applications. Polymer-based vesicles (polymersomes) developed over the past decade possess many of the desirable properties of liposomes while at the same time exhibit remarkable stability relative to their lipid-based counterparts. Our approach to integrating TMPs in biomimetic environments capitalizes on recent developments in: 1) preparing polymersomes, 2) reconstituting TMPs in vesicle assemblies, and 3) fusing synthetic vesicles to prepare robust hybrid structures that are both radially and axially asymmetric. The successful execution of the proposed work will bring new fundamental understanding to the role that intermolecular interactions play in protein insertion mechanisms. We anticipate that our approach will afford a versatile platform for integrating TMPs into robust scaffolds that will allow the rational design of an entirely new class of asymmetric biomimetic materials.

Summary of Accomplishments:

This work required an understanding of the flux of ions across bilayer membranes composed of lipids or polymer amphiphiles. We measured the hydroxide ion flux across lipid and polymer vesicle membranes and found that polymer vesicles are substantially less permeable than lipid vesicles and that their permeability could be tuned by increasing the molecular weight of the polymer amphiphiles.

More importantly, we found that polymer vesicles could sustain very high pH gradients that persisted for several weeks, and we used this feature to show that polymer vesicles could function as artificial lysosomes, facilitating the collection and digestion of hydrolyzable chemical species. This behavior demonstrates the utility of polymer vesicles as nanoreactors.

We also found that transmembrane proteins could be reconstituted into polymer vesicle membranes to create hybrid biotic/abiotic structures that can pump ions against a concentration gradient. These types of structures have potential to rival the function and stability of purely biological structures.

Significance:

Preliminary results demonstrate some control over the reconstitution of TMPs using charged polymers, addressing an open and important question in biochemistry and biophysics of particular importance to DOE-BES for development of hierarchically self-assembling materials and bio-hybrid materials with novel structures, functions, and properties. The preliminary data is also highly relevant to other agencies including DTRA, the Office of Naval Research, DARPA, and DHS that are interested in understanding and developing new platforms for delivery of therapeutics and prophylactics in humans, including those that would mitigate against biological and chemical weapons.

Mechanism of Fusion of Pathogenic Enveloped Viruses with the Endosomal Membrane

158832

Year 2 of 3
Principal Investigator: M. S. Kent

Project Purpose:

Pathogenic membrane-enveloped viruses including flaviviruses, arenaviruses, and paramyxoviruses cause devastating infectious diseases (e.g., hemorrhagic fever, encephalitis) and pose major biodefense threats. For these viruses, fusion of the viral membrane with the cellular endosomal membrane is essential for viral replication and infectivity. Fusion of the two membranes is driven by pH-dependent conformational changes of a dedicated protein, called E in flaviviruses. Crystal structures have been determined for the pre-fusion and post-fusion states of E, but only for truncated mutants lacking important flexible and membrane-spanning portions. Thus, a huge gap in knowledge exists regarding conformational changes of E upon binding to the endosomal membrane and during the intermediate stages of fusion and also regarding the mechanism by which E anchors into the endosomal membrane. The goal of the proposed work is to address: 1) E protein membrane-bound structure and 2) E protein anchoring to endosomal membranes.

It is very difficult to resolve conformational changes of membrane-bound proteins because crystallization of proteins in the membrane-associated state is extremely challenging and cannot capture structural transitions that occur as a function of solution conditions. However, at Sandia, we have developed a capability to do that based on neutron reflectivity (NR) and fluorescence energy transfer (FRET). We will perform NR analysis of membrane-bound E as a function of pH, which will provide global structural information. Specific local information (i.e., distances between specific residues or between particular residues and the membrane) will be supplied by FRET. Site-specific mutation of E protein will be performed to introduce labels for FRET, whose effects on function will be screened in-vitro and in live-cell fusion assays. We will resolve the lateral organization of E using several methods and also the interactions that anchor the tip of E into the endosomal membrane using molecular simulations and atomic force microscopy (AFM) measurements.

Utilizing Biocomplexity to Propagate Stable Algal Blooms in Open Systems – Keeping the Bloom Going

158835

Year 2 of 3
Principal Investigator: E. T. Yu

Project Purpose:

Open-pond cultivation of algae holds great promise as an economically viable option for producing the quantities of biomass required to replace a significant fraction of the nation's petroleum-based transportation fuels. Although higher algae productivities are regularly touted, established algae facilities have lower yields because they are unable to sustain high production rates due to culture instability. Maintaining pond stability is thus one of the most significant barriers facing commercialization of algal biofuels, and understanding the factors that promote biological stability and the means by which stable communities naturally limit invasion of undesirable species is a critical first step to mass algae production. Algae naturally grow in complex ecosystems; it has been demonstrated that these diverse microbial populations coexist through niche partitioning and are robust to environmental fluctuations, able to weather periods of nutrient limitation, and capable of resisting various insults (invading species, predators, pathogens). Utilizing mixed communities necessitates an understanding of how interactions among individual system components contribute to global population dynamics and, ultimately, to stability. We will investigate the microbial community dynamics in natural and manipulated algal ecosystems to understand the niche roles (symbiotic relationships) necessary to achieve and maintain a stable algal consortium. Specifically, we will: 1) investigate the community structure (metagenomics) of natural algal consortia as function of system perturbations (e.g., addition of predator, pH/temperature changes), 2) identify critical functions that stabilize the community by constructing and interrogating representative mixed cultures in vitro for functional validation, 3) develop quantitative measures of functional diversity that differentiate stable from unstable communities, and 4) use agent-based models (ABM) to understand the relationship between biocomplexity/biodiversity and stability. We will initially focus on predation as a stressor and move on to other stressors (e.g., nutrient, pH, or temperature excursions). This knowledge will be applied to develop stable, high-biomass-producing, artificial, consortia that are better suited for outdoor algal biofuels production.

Genomic Functionalization: The Next Revolution in Biology

162034

Year 2 of 3
Principal Investigator: P. Imbro

Project Purpose:

Next-generation sequencing, "omics" technologies, and computational methodologies have provided an exponential growth in biological data relevant to national priorities in biodefense and bioenergy. The potential of the sequence data has yet to be fully realized, however, as we do not understand the function or significance of most genome subsequences. This project will develop a prototype genomic functionalization capability and test this capability for clinical metagenomics applications to national defense and health care. This project will define an architecture for gathering and intersecting genomic and other "omic" data with operational and functional metadata and use advanced data integration tools and knowledge extraction tools to establish useful correlates of genome sequence patterns.

One of the challenges to this effort is the integration of a range of genomic functionalization data and information to produce useful/actionable associations of genomic data with predictive outcomes. The Internet has revolutionized communication and data accessibility, and it has also catalyzed dramatic advances in knowledge-extraction methods and their application to massive data. In particular, advances in recommender systems, machine learning, and network analysis allow association of diverse input data types (e.g., "omic" data) with metadata (e.g., hospital/public health records). These knowledge extraction methods have not heretofore been widely applied to genomic functionalization. We propose to define data architecture and apply modern knowledge-extraction methods (i.e., hypothesis-generation engines) to the problem of identifying genomic sequence "keys" for associative structures between diverse input data types and functional/outcome patterns captured in metadata. However well such methods process the input data, the outputs we can expect are only as good as the definitions of impact or functionality captured in the metadata. A second innovation will be to develop methods to establish metadata categories for different application spaces such as biological threat detection, biosurveillance, and bioenergy production that increase the utility of the associations discovered.

Self-Deconstructing Algal Biomass as Feedstock for Transportation Fuels

164662

Year 2 of 3
Principal Investigator: R. W. Davis

Project Purpose:

The potential for producing biofuels from algae has generated much excitement based on projections of large oil yields with relatively little land use. However, numerous technical challenges remain for achieving market parity with conventional non-renewable liquid fuel sources. Among these challenges, the energy intensive requirements of traditional cell rupture, lipid extraction, and residuals fractioning of microalgae pose great opportunities for translational research in the nascent field of algal biotechnology. To date, solutions to the aforementioned problems have been sought using technology developed primarily for petrochemical applications. A targeted biological approach to these issues could dramatically reduce both the capital and operating costs of producing fuels from algae. Our novel solution to address these problems is to employ methods of biological engineering to eliminate the need for hardware- and energy-intensive methods for cell rupture, lipid extraction, and residuals fractioning by introducing a triggered cell lysis and enzymatic conversion functionality in a halophilic microalgae suited for mass culture. The output of the proposed enzymatic deconstruction process will consist of a slurry of phase-segregated lipidic and aqueous algal metabolites for subsequent transformation to transportation fuels by transesterification, fermentation, and anaerobic digestion.

Until recently, very little progress has been made employing biological engineering for microalgal biofuels applications. However, achievements in genetic analysis and minimally perturbative methods of algal transformation have opened the gates for new research in this area. A prime target for employing biological engineering is the development of biochemically triggered expression of “deconstruction genes” for decomposing the algal extracellular matrix (ECM). Not only would this process lead to a low-cost lipid extraction process, but the polysaccharides that compose the ECM will be converted to sugars for fermentation. Our strategy will focus on coupling expression of exogenous mesophilic cellulase and protease enzymes to genes involved in responding to nutrient limitation. This approach will facilitate maximal biomass accumulation prior to deconstruction.

Unknown Pathogen Detection in Clinical Samples: A Novel Hyperspectral Imaging and Single-Cell Sequencing Approach

165607

Year 1 of 3
Principal Investigator: B. Carson

Project Purpose:

Detection of pathogens in pre-symptomatic stages of infection is challenging. Most diagnostic techniques are insufficiently sensitive to detect infection and identify viruses, in particular, at these early stages. Recently, second-generation sequencing has been applied to this problem. However, despite substantial progress, the signal-to-noise ratio inherent in this technique makes pathogen identification in clinical samples prohibitive, thus leaving treatment decisions dubious. We will address this critical problem by identifying spatial and spectral signatures of host response that differentiate uninfected human blood cells from those infected with a pathogenic virus without requiring a priori knowledge of its identity. We will integrate hyperspectral imaging with microfluidic cell sorting to: 1) separate individual infected and uninfected cells and 2) use high-throughput sequencing to analyze individual cells. We envision that this will greatly improve the ability to identify pathogens in clinical samples since pathogen-negative cells from the same sample will serve as control. Only single-cell analysis can accomplish this, and our success will greatly improve Sandia's ability to address important problems for the National Institutes of Health and the nation's biodefense. Moreover, this new capability would transform not only our ability to diagnose infection with unknown pathogens early in disease but also enable the identification, characterization, and countermeasure development for emerging and engineered viruses.

No current technology can isolate infected cells without knowing pathogen identity; thus, there is presently no way to identify unknown viral pathogens in individual infected blood cells. State-of-the art cell sorters lack the ability to sort on spatial characteristics so they cannot utilize the majority of the information contained in a stained cell. This project presents a novel solution to these problems, integrating key Sandia capabilities in hyperspectral imaging and single-cell microfluidics. This is high risk because it requires developing new integrated technology to identify cell-state-specific but pathogen-independent markers, data processing with extreme speed, and efficiency of optics, analysis algorithms, and system control.

Understanding and Regulation of Microbial Lignolysis for Renewable Platform Chemicals

165608

Year 1 of 1
Principal Investigator: S. Singh

Project Purpose:

DOE's vision of "a viable sustainable domestic biomass industry that produces renewable biofuels, enhances US energy security, reduces US oil dependence and provides environmental benefits" is contingent upon successful implementation of lignocellulosic biorefineries with renewable chemicals as part of the product chain. As lignin is the only source of renewable aromatics, utilization of lignin for high-value co-products will enable biofuel industries to become cost competitive with petrochemicals. The potential US market for a lignin-derived octane enhancer alone is estimated to be 2.2 billion gallons per year. The prospects of macromolecular lignin being utilized as raw materials for fuels and chemicals have been highly touted, but no conversion technologies have been realized at any significant scale. Novel approaches and disruptive technologies are needed for efficiently converting lignin to platform chemicals. This necessitates bridging the gap in our current understanding of the molecular basis of microbial lignolysis and the discovery of efficient pathways.

Depolymerization of lignin is a very complex process, and the roles of only a relatively few enzymes and genes are known. Typical approaches utilizing low-molecular-weight lignin model compounds that ignore the synergism of fungi and bacteria have provided only limited information. Multiple enzymes and pathways are hypothesized to be relevant and demand a 'multidisciplinary approach' utilizing native lignin to decipher the mechanism of depolymerization. We will leverage our expertise in lignin analytics, high-throughput lignase assays, and microfluidic cell sorting combined with state-of-the-art omics, cell-free protein expression, genetic manipulation, and bioinformatics to develop solutions for the production of chemicals from lignin produced by the pulp and biofuel industries. Our innovative approach will involve selecting task-specific unique microbes from a variety of ecosystems, cloning for metabolic de-regulation of pathways, engineering strains for improved conversion rate, and identifying gene products and suitable hosts for hyper-productivity and future synthetic biology efforts.

Summary of Accomplishments:

Our research effort was focused on: 1) development of analytical tools for lignin and examination of actions of lignolytic microbes and enzymes on native lignocellulosic-derived polymeric lignin and 2) mining data acquired from community sequencing projects (Sandia-UNM-JGI collaboration) collected from Sevilleta Long-Term Ecological Research in NM. We analyzed six microorganisms and eight enzymes for potential lignolytic activity with ten lignin substrates (140 reactions) in order to determine the depolymerization of polymeric lignin. Toward this end, we developed a workflow consisting of fluorescence, mass spectrometry, size exclusion chromatography, and nuclear magnetic resonance (NMR) to monitor depolymerization over a four-week time frame. We developed novel mass-spectrometry-based methods to analyze polymeric lignin, which has proven to be a difficult substrate to analyze due to its polymeric nature. For the first time, we demonstrated that polymeric lignin could be broken down in the absence of any cofactors and mediators. In parallel with these experimental approaches, we sought to discover novel lignolytic genes from an aridland ecosystem, which is much less studied for its lignolytic potential. We developed a standardized pipeline for integrating metagenomic data with field experiments. Using ~600 million metagenomic sequence reads from the Sevilleta Long-Term Ecological Research Arid-land Ecosystem, we identified 127 enzyme gene targets that can be assigned to peroxidase, laccase, or generally as carbohydrate-active gene families. Using various bioinformatics techniques to select the highest quality genes, we filtered the number of potential gene targets down to 35 distinct gene clusters, which can further be inserted and transplanted in suitable host organisms. This standardized bioinformatics pipeline will provide a first-of-its-kind toolkit for integrating metagenomic data with experimental enzymology and will be generally useful for generating potential lignolytic gene targets. The list of candidate genes will provide a basis for transforming organisms to increase lignolytic production.

Significance:

Our project was directed at understanding microbial lignolysis for renewable platform chemicals using microbial and enzymatic lignolysis processes to break down lignin for conversion into commercially viable drop-in fuels. We successfully demonstrated, for the first time, that polymeric lignin could be broken down in the absence of any cofactors/mediators and is an industrially relevant route to conversion of waste polymeric lignin from the pulp industry to renewable aromatics. Our effort is in line with the mission of the DOE is "to ensure America's security and prosperity by addressing its energy, environmental and nuclear challenges through transformative science and technology solutions."

The Engineering and Understanding of Nanoparticle/Cellular Interactions

165609

Year 1 of 3
Principal Investigator: C. J. Brinker

Project Purpose:

Engineered nanoparticle/cellular interactions encompass a broad spectrum of emerging topics in national security and the health and well being of the nation. Engineered nanoparticles could detect the onset of cancer or infectious disease as well as selectively deliver customized therapeutic "cocktails" and imaging agents to treat the disease and to provide in-vivo diagnostics of the progress of therapy. Understanding and engineering nanoparticle (NP)/cellular interactions on scales ranging from the sub-cellular to the organism level are crucial to targeted drug delivery as well as assessing potential ES&H hazards of NPs and engineering new safer-by-design nanoparticles. Although hundreds of engineered nanocarriers are under development, they all fall short of addressing the multiple challenges of targeted delivery, and they cannot be systematically varied/engineered to establish structure-activity relationships or address personalized medicine.

We recently invented a new composite nanocarrier termed a "protocell." Targeted protocells are formed by fusion of a lipid bilayer on a nanoporous, cargo-loaded nanoparticle core followed by modification with targeting and trafficking ligands. They combine the advantages of FDA-approved liposomes (low inherent toxicity, immunogenicity, long circulation times) and porous particle nanocarriers (stability and an enormous capacity for multiple cargos). However, the protocell's supported lipid bilayer (SLB) uniquely represents a reconfigurable surface that can engage in complex biomolecular interactions with a cell surface, directing internalization and intracellular trafficking. Exploiting the modular nature and synergistic characteristics of the protocell, the goal of this project is to design and fabricate next-generation protocells that overcome multiple grand challenges of current nanocarrier platforms with respect to in-vivo cargo capacity and diversity, circulation time, controlled release, targeting, and cell-specific toxicity and safety.

Identification of Nucleic Acid Biomarkers of Infection in Blood

165767

Year 1 of 3
Principal Investigator: S. Branda

Project Purpose:

Infectious-disease surveillance and outbreak mitigation require rapid, accurate, and reliable means of distinguishing infected vs. healthy individuals to enable rational use of countermeasures (diagnostics, therapies, quarantine). Screening populations based on direct detection of the causative pathogen can be problematic because readily accessible specimens such as blood often contain little or no pathogen, particularly at pre-symptomatic stages of disease. However, host response to the pathogen is rapid, robust, and evident in blood throughout the course of infection. Thus, screening populations based on host-response biomarkers in blood is an attractive approach, especially if the biomarkers are nucleic acids (NAs), as these can be efficiently recovered from tiny specimens (e.g., finger stick draws) and detected with tremendous sensitivity and specificity via polymerase chain reaction (PCR). Proof-of-concept studies have not been definitive, however, largely because use of sub-optimal sample preparation and detection technologies has precluded comparative analysis of clinical specimens with sufficient sensitivity, specificity, and throughput.

Sandia has developed new methods and technologies for: 1) selective isolation of NAs that are unique to, or shared between, clinical specimens and 2) highly efficient preparation of NAs for second-generation sequencing (SGS). We will use this sample preparation pipeline to carry out high-throughput, high-quality screens for both universal and pathogen-specific NA biomarkers of infection. Blood specimens from three study sets [non-human primates (NHP) infected with biodefense-related pathogens; human vaccine recipients; human burn patients who become septic] will be fractionated (e.g., DNA vs. RNA), and each NA pool converted into an SGS-compatible library. Molecular suppression of libraries preceding SGS will enable identification of rare NAs that segregate with infection state. Biological and statistical interactions between candidate biomarkers will be identified through pattern recognition and network/pathway analyses. A predictive framework based on pathway activation signatures will be generated via supervised classification methods. Through this systematic and comprehensive approach, we will identify and verify robust, predictive panels of NA biomarkers of infection.

Consolidated Bioprocessing and Biofuels Production Platform

165822

Year 1 of 3
Principal Investigator: R. W. Davis

Project Purpose:

Depleting fossil reserves and environmental concerns are the major catalysts for research into alternatives for transportation energy that are renewable and carbon neutral. Particularly, lignocellulosic biomass has emerged as a promising feedstock. Biochemical conversion of this feedstock into fermentable sugars and subsequent transformation into infrastructure-compatible advanced biofuels is a national grand challenge. This research aims to reduce biofuel production costs by building a consolidated bioprocessing (CBP) platform, reducing processing steps. We propose to develop the thermophilic, cellulolytic bacterium Clostridium thermocellum as a chassis to engineer a microbial bioreactor that both degrades cellulosic feedstock and produces advanced infrastructure compatible biofuels. We will consolidate biomass pre-treatment and advanced biofuel production to a single bioreactor platform. CBP will reduce unit operations and increase process efficiency by reducing mass transport phenomena and processing steps and costs.

Our proposed CBP chassis C. thermocellum is a rapid cellulose-degrader. Although there are published reports of recombinant DNA transfer into C. thermocellum, genetic techniques are not well established to manipulate the organism routinely and no heterologous gene expression has been reported in the literature. The goal of the research with UCLA is to: 1) establish a thermostable variant of the keto-acid pathway for isobutanol production and 2) introduce this pathway into C. thermocellum for CBP of cellulosic biomass to produce advanced biofuels. Our previous results demonstrated that the current rate-limiting enzyme in the keto-acid to isobutanol pathway is ketoisovalerate decarboxylase (Kivd). Therefore, we propose to engineer and express a thermostable and high activity analog of Kivd based on recent computational models. We will then develop a heterologous expression system driven by a single subunit RNA polymerase (ssRNAP) such as phage T7RNAP instead of attempting to understand native transcriptional regulation of C. thermocellum. Anticipated challenges during this research are: retaining thermostability in a mesophilic host system and optimization of the expression systems.

Removal of Abundant Nucleic Acid Sequences from Complex Mixtures via Isotachophoresis

166536

Year 1 of 1
Principal Investigator: R. Meagher

Project Purpose:

Detecting pathogens directly in clinical samples is very challenging due to the low abundance of pathogen genetic material, relative to normal host background. This is particularly problematic when using an “unbiased” technique such as DNA sequencing to search for new or unusual pathogens, as in the case of an emerging infectious disease or a novel engineered biothreat. To aid in the detection of rare sequences, we propose to use isotachophoresis (ITP) functionalized DNA capture gels as a sample preparation tool for pathogen discovery by sequencing. The goal of our sample preparation technique is to selectively remove the highly abundant but non-informative host sequences, allowing sequencing and computational effort to focus primarily on the informative but low-abundance pathogen sequences.

The project will build upon the existing collaboration between Stanford University and the RapTOR research team at Sandia on novel sample preparation techniques for sequencing. Host subtraction by hybridization has been implemented at the bench scale, but the process is slow (~6 hours) and requires a large excess of costly capture probes. We aim to substantially improve both the speed and efficiency of this process, achieving equal or better removal of host sequences in much less time (~10 minutes) with more economical use of reagents, using a scalable workflow.

Our work will integrate ITP-aided hybridization assay with a capture gel to immobilize the full spectrum of human cDNA scripts. Previous work shows that the combination of techniques has substantial promise for accelerating hybridization and achieving specific and efficient removal of undesired sequences. However, integrating ITP and capture gels for a complex cDNA library at a scale relevant for processing clinical samples requires significant theoretical as well as experimental effort, including designing a high-throughput microfluidic device capable of processing a 1-10ul input sample and developing protocols to simultaneously maximize removal of host sequences and minimize loss of pathogen sequences.

Summary of Accomplishments:

The project resulted in development of a new, comprehensive model for the effects of temperature on ion mobility in electrophoresis. This model is a necessary precondition for predicting and understanding the process of nucleic-acid hybridization during the proposed isotachophoretic capture process. The model takes into account temperature dependent effects on viscosity, ionic strength, acid-base equilibrium, and solvation.

On the experimental side, research focused initially on developing strategies to accomplish on-chip capture of nucleic acids using immobilized capture gels. The strategy showed promise when using relatively short model nucleic acids (~100 bases) but ran into unexpected problems when using larger nucleic acids. It was hypothesized that the difficulties were related to overloading of the pores of the capture gel. Subsequent efforts focused on either creating macroporous gel or using non-crosslinked polymer capture matrices, but neither of these approaches were able to achieve the necessary reproducibility of capture performance.

During the course of the project, a novel bead-based assay for detecting DNA or RNA targets by hybridization was conceived and tested. The assay relies on a target sequence forming a “bridge” between two beads (“A” and “B”), each labeled with a capture probe complementary to a different part of the target and with spectrally distinct fluorophores. The presence of target is identified by detecting colocalization of “A” and “B” using a novel image-based algorithm for detecting particle colocalization. The novel assay provides key advantages over bead-based assays requiring a flow-cytometry readout; most notably the assay is simple to implement, requiring a fairly straightforward imaging setup without expensive lasers, high speed electronics, or precision fluidics as required for flow cytometry.

Significance:

The comprehensive model of temperature effects on electrophoretic mobility is an important contribution to the basic science of electrokinetics and will impact the ability of researchers in many fields who rely upon electrophoresis and isotachophoresis for analysis of proteins, nucleic acids, and small molecules. The electronkinetic capture-based approach for sequencing-library preparation was ultimately not realized in this research, but the fundamental technique of capture combined with electrokinetics led to a bead-based assay for detecting nucleic acid signatures, which could lead to new tests for detecting pathogens in clinical samples suitable for use in point-of-care or low-resource settings.

A Modular Nanoparticle Platform for Treatment of Emerging Viral Pathogens

166539

Year 1 of 2
Principal Investigator: E. C. Carnes

Project Purpose:

Antiviral drugs must typically be administered in large, frequent doses to effectively treat viral infections, including those caused by emerging and engineered viruses. High doses can, however, cause toxic side effects to the host and, if taken improperly, can accelerate the evolution of drug-resistant pathogens. There is, therefore, a need to develop biocompatible nanoparticle delivery vehicles to reduce the number, frequency, duration, and dosage of treatments, delay treatment beyond the current limit, and prevent recurrent disease. Most state-of-the-art nanocarriers, including liposomes and polymeric nanoparticles, suffer from low capacity, poor stability, and minimal uptake by target cells. This project seeks to address these limitations by designing a modular, highly adaptable nanocarrier, termed a protocell, which synergistically combines advantages of liposomes and mesoporous silica nanoparticles.

Protocells comprise a mesoporous silica nanoparticle (MSNP) core encased within a supported lipid bilayer. They simultaneously exhibit extremely high loading capacities (>1000-fold higher than comparable liposomes) for chemically disparate therapeutic and diagnostic agents, long-term stability in complex biological fluids, and subnanomolar affinities for target cells at low ligand densities. Our ability to precisely control loading, release, stability, and targeting specificity as well as our ability to engineer the particle size, shape, charge, and surface modification(s) allows us to dramatically reduce dosage and off-target effects, mitigate immunogenicity, maximize biocompatibility and biodegradability, and control biodistribution and persistence. Protocells, due to their unique biophysical properties, are one million times more effective at treating human liver cancer than state-of-the-art liposomes. In this project, we seek to extend the utility of protocells to emerging viruses that have relevance as potential biothreats and will assess the prophylactic and therapeutic potential of protocells that are loaded with traditional and novel anti-viral agents (such as siRNAs) and targeted to both potential host cells and already infected cells.

Recombinant Vesicular Stomatitis Virus for Therapeutic Antibody Epitope Mapping and Vaccine Development

170801

Year 1 of 3
Principal Investigator: O. Negrete

Project Purpose:

Identification and characterization of antibody binding sites (epitopes) are important for the development of novel vaccines, therapeutics, diagnostics, and affinity reagents. Several methods have been established to map epitopes on target antigens, including x-ray co-crystallography of antibody-antigen complexes, array-based peptide scanning, and "shotgun" mutagenesis mapping. Combinatorial techniques, such as phage display, are less labor- and cost-intensive but are unable to reliably map complex 3D conformational epitopes. Rapid and cost-effective methods for mapping neutralizing-antibody binding sites at high resolution are currently lacking. This proposal seeks to develop a novel technology based on recombinant vesicular stomatitis viruses (rVSV) that provides rapid information about the amino acid sequences of therapeutic neutralizing-antibody epitopes to aid in vaccine development for priority pathogens of national security concern.

Many priority pathogens classified as potential agents of bioterrorism by the NIAID require handling in high-level biocontainment facilities and a complex biosafety infrastructure (e.g., high containment labs, select agent registration/permits). This project seeks to create a rapid capability for the high-resolution mapping of antibody epitopes for BSL-3 and BSL-4 biothreat pathogens under BSL-2 containment. We will accomplish this goal by creating libraries of pseudotyped rVSV variants displaying high-complexity randomly mutagenized biothreat antigens. Once the rVSV libraries are developed, we will recover detailed information about the amino-acid sequences of conformational epitopes recognized by multiple monoclonal antibodies or polyclonal antisera in less than one week using minimal amounts of each antibody.

Systems-Level Synthetic Biology for Advanced Biofuel Production

170804

Year 1 of 3
Principal Investigator: A. Ruffing

Project Purpose:

The US is currently reliant upon foreign fossil-fuel resources, representing a significant threat to national security. The limited supply of fossil fuels presents a significant challenge for future energy provision, and the accumulation of carbon dioxide from fossil-fuel combustion may lead to significant changes in the global climate. The development of a renewable energy source, such as biofuels derived from microalgae, will help lead to energy independence for the US while also addressing concerns of fossil-fuel supply and climate change. However, microalgal fuel production is currently limited by the low natural productivities of microalgae. Synthetic biology techniques may be applied to improve the fuel-producing capacity of these microorganisms, yet the impact of this strategy is limited by the "one part (or circuit) at a time" approach of traditional synthetic biology. To reach the fuel-production rates necessary to make this process economically viable, microalgae must be genetically modified at a systems level to optimize the entire genome for fuel production. Hence, new methods and synthetic biology tools must be developed for these microalgal hosts.

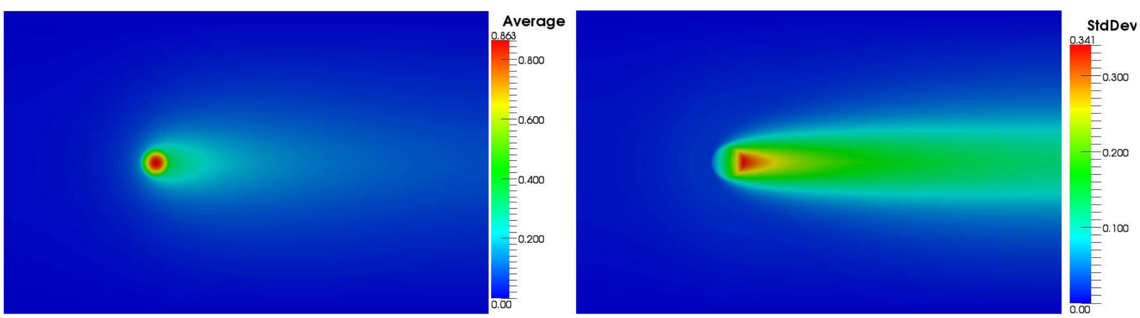
This proposal seeks to develop a systems-level synthetic-biology approach for targeted genetic manipulation of microalgae. With this technique, multiple genetic targets will be modified in a single transformation step, leading to a significant reduction in the time required for strain development. As an example, consider a strain requiring ten genetic modifications for improved fuel production. The traditional approach would typically require ten months for strain development, assuming a conservative four weeks per genetic modification. The proposed systems-level approach would construct the same strain in only one month. Additionally, the systems-level synthetic-biology technique would generate variants with different combinations of the ten targeted modifications. Given the inherent nonlinearity of biological systems, these combination variants may have unknown synergistic effects, resulting in increased fuel production and informing our basic understanding of fundamental microalgal biology.

COMPUTING AND INFORMATION SCIENCES

The Computing and Information Sciences Investment Area sponsors research that builds more accurate predictive models and delivers reliable science and engineering results by advancing the state of the art in mathematics, computing, and cybersecurity.

A goal is to reduce space and power requirements for future supercomputing systems. Strategies include changing the nature of computing devices and their impact on computer architecture, software, and algorithms, and exploring low-power architecture and resilient hardware. Computing is ubiquitous at Sandia and is essential to carrying out our missions. Every one of our national security areas — from nuclear weapons to homeland security and defense to energy and climate — relies on advanced computing to deliver forefront solutions to our customers.

Researchers in computational engineering are advancing the math and science needed for predictive simulation, design optimization, and quantifying margins and uncertainties. Cybersecurity researchers are developing graphs and streaming algorithms and data analysis tools, taking into account human capabilities. A deeper understanding of the cybersecurity environment will guide US decisions on how best to protect critical cyber assets.



Color map of the average (left) and standard deviation (right) for the cylinder in cross flow convection diffusion problem (Project 155551).

COMPUTING AND INFORMATION SCIENCES

Network and Ensemble Enabled Entity Extraction in Informal Text (NEEEEIT)

151292

Year 3 of 3
Principal Investigator: W. P. Kegelmeyer

Project Purpose:

Much of the world's actionable information is locked up in increasingly unmanageable volumes of text. This has inspired work in "entity extraction" (EE), which is the detection of meaningful terms in text: persons, places, dates, etc. Robust, accurate entity extraction is the crucial first step for all information extraction from text; you can't "connect the dots" unless you identify the dots in the first place.

Entity extraction research has so far focused on clean, edited, "formal" text. Unfortunately, much of the information of interest is in personal, informal text, such as email or blogs. These differ from the Medline abstracts and Reuters news stories commonly studied in that they tend to be riddled with errors of spelling and grammar, abbreviations, and a terseness and obliquity of reference borne of the context shared by sender and receiver. The informal text domain has received scant study; just enough to show that it causes the performance of existing methods to drop precipitously.

We plan to vastly improve the accuracy of entity extraction in informal text, via application of Sandia-specific expertise in "ensemble" machine learning methods. Further, we will exploit new high performance computing network capabilities to permit the integrated analysis of a full conversational thread. The potential of this approach is recognized, but scaling issues have, prior to recent Sandia work, prevented their exploration.

By creating methods to make accurate entity extraction in informal text possible, and by leveraging Sandia's investments in informatics frameworks, we will deliver a system that starts with raw email or blogs and produces high quality entity identification, suitable for search, linking, visualization, and analysis.

Summary of Accomplishments:

We have deeply analyzed the properties of conditional random field (CRF) machine learning models in the context of ensemble methods, all in service of named entity recognition (NER). NER is the detection of meaningful terms in text: persons, places, dates, etc. Robust, accurate entity extraction is the crucial first step for all information extraction from text.

To enable this analysis, we created a CRF implementation, PyCrust, which permits an unprecedented degree of internal manipulation and instrumentation. We further wrote a computational harness, NEEEEIT, to permit flexible experimentation and visualization of ensembles of PyCrust CRFs.

From detailed experimental investigation and testing we have learned that:

- It is possible to increase the accuracy of CRFs through ensemble methods, such as "bagging," if the CRF model is engineered to generate more variance error.
- Unlike some other ensemble domains, ensembles of CRFs are sensitive to "toxic" attributes in the data, and so reward preprocessing methods such as "forward feature selection" to find and remove those attributes. This has further speed benefits, as CRFs speed up faster than linearly with the reduction of feature classes.
- We discovered an entirely novel ensemble method, "clone editing," that is not only unique to CRFs but which is currently supported only by PyCrust's conception of CRFs. Ensembles of edited clone CRFs are demonstrably no less accurate than standard bagging with standard PyCrust CRFs, but are computationally much more tractable, as the complex extraction of a single CRF may then quickly generate many variants with only minimal additional computation.

Significance:

We advanced the frontiers of science and engineering through deepening our technical understanding of ensemble machine learning methods, and thereby broadened the scope of their applicability as well. We have worked out how to generalize ensemble methods to CRFs, demonstrated that their ensemble accuracy can indeed be increased by proper use of ensemble techniques and methods to increase individual variance, and generated a new CRF code, "PyCrust," and a surrounding application environment, network and ensemble enabled entity extraction in informal text (NEEEEIT) that implements those advances.

Statistically Significant Relational Data Mining

151295

Year 3 of 3
Principal Investigator: C. A. Phillips

Project Purpose:

In many data mining applications, especially the search for "unexpected" or "significant" structure in graph-based social information, it is difficult to specify exactly what is being searched. For example, given a graph where nodes represent people and edges represent relationships between people, there is general agreement that a community is a set of nodes more connected internally than to the rest of the graph. But no formal graph theoretic definition of connectedness seems to capture what a human perceives to be the correct communities in all cases. Most community detection algorithms combine approximate optimization of a metric with ad hoc statistical methods. To date, there are no rigorous ways to determine whether an algorithm has succeeded in finding the "correct" answer in a real data set, or even in specially constructed benchmarks. Similar questions arise in other graph-data-mining problems that search for specific patterns, or attempt to explain (dynamic) relationships.

We will develop statistically rigorous methods for finding, understanding and testing the significance of graph properties and structures. These methods can be incorporated into data mining algorithms either integrally, or as a post-processing "acceptance" test. We will develop methods to evaluate the "correctness" of an algorithm.

Bayesian methods offer one plausible approach. Each graph problem provides unique challenges. We must formally describe a priori domain knowledge and constraints ("prior distributions"). We must create plausible random graph models, describing ways a community, pattern, etc., might evolve from these distributions. Then we must compute conditional probabilities that characterize the most likely solutions given the structure of the input instance. Although the general methods are well known to statisticians, they require customization to the structure of each problem. These methods have not been applied to evaluating the correctness of efficient graph algorithms.

Summary of Accomplishments:

We developed a new Bayesian community detection method. It has a simple prior distribution and provably convergences to the posterior distribution. On a college football data set, it performed well, illustrating improved ability to detect communities when the prior was adjusted to have a notion of conference independence. This method gives a distribution of assignments rather than a point solution. It infers the number of communities. We discovered a significant "scaling" problem with information-theoretic community comparison methods. We have characterized the problem mathematically and experimentally. We have developed two new methods for determining when to sample from a Markov chain to find independent draws from a random graph distribution. We have developed new methods for graph comparison, graph clustering, and finding anomalous communities. The graph comparison method involves creating signatures for a graph based on topology and edge/node attributes. Earthmover's distance between the signatures gives an approximate distance measure between the graphs. We can then create a dendrogram on a set of graphs, where distance in the dendrogram models distance between graphs. We have developed new multithreaded methods for exact subgraph isomorphism and approximate versions based on the number of edits from the base pattern. We have developed a new statistically motivated probabilistic graph model: the local structure graph model (LSGM). Similar to a latent variable approach, the model is specified through full conditional binary distributions;

however, random edge variables are not conditionally independent. Rather, they exhibit Markov dependence where edges are conditionally dependent on edges that belong to the same neighborhood. Thus, the definition of neighborhoods defines the dependence structure. LSGM allows the user to better explain and control local dependencies. There is a more straightforward interpretation of parameters (compared to other models) though it does still have model degeneracy.

Significance:

The methods developed under this project have been impactful, both internally within Sandia and to external sponsors. The project team has suggested methods, or influenced research directions for two internally funded LDRD projects, an NA22 application, DOE ASCR, and DARPA projects.

Refereed Communications:

J. Guo, A.G. Wilson, and D.J. Nordman, “Nonparametric Methods for Community Detection,” to be published in *Technometrics*.

Control and Optimization of Open Quantum Systems for Information Processing and Computer Security

151299

Year 3 of 3
Principal Investigator: M. Grace

The purpose of this project is to explore the fundamental limits of controlling quantum systems and to analyze the implications of these limits, especially in the context of quantum information processing (QIP). Achieving the error threshold for fault-tolerant QIP is extremely difficult given device/control fluctuations, experimental constraints, and the unavoidable coupling of a quantum computer to its surrounding environment. We will be developing a crucial enabling technology; namely, the ability to control and explore processes at the atomic level, computationally, especially in the presence of uncertainty and time-dependent noise. This work will provide a tool to guide experimentalists and theoreticians in creating practical QIP controls and devices. Another goal of our project is to mathematically analyze the critical structure of the quantum-control landscape for stochastic quantum systems (SQS) (i.e., identifying the fraction of critical points corresponding to global extrema, local extrema, and saddles). While numerical simulations produce optimal control (OC) solutions for SQS, a mathematical analysis of the landscape will reveal the general underlying structure of this control problem. Knowledge of this structure can influence profoundly the choice of algorithms used to locate OCs and the design of quantum technologies.

Summary of Accomplishments:

We explored quantum control landscape (QCL) for ideal, closed qubit systems, calculating the energy-time Pareto fronts for multiqubit entangling operations. We developed two distinct efficient propagation schemes for simulating stochastic quantum systems. These methods will be used in OC calculations, which require multiple sequential simulations to achieve convergence. Monte Carlo methods for these calculations are expensive and scale unfavorably with the dimension of SQS; hence, the need for an alternative. Combining our numerical methods and OC simulations will allow us to quantify the limits of control for realistic SQS. We also developed two robust control protocols for uncertain and stochastic quantum systems. Working with the University of New Mexico, we unified the complete QCL critical structure for closed quantum systems, from state-transition to unitary objectives via partial isometries. Working with Princeton University, we formulated an objective functional to quantify the effects of control noise and a hybrid optimization heuristic to find controls that are robust to stochastic control noise. Working with the University of Southern California, we began the analysis of the QCL critical structure for open quantum systems. Additionally, we have developed a mathematical functional to quantify the “entanglement” capacity of quantum operations through iterated optimization. Entanglement is a crucial property for QIP; consistently measuring the entangling power of operations is necessary to generate controls that produce this resource. Rather than previous state-based approaches, our functional uses quantum operations directly as inputs to compute entanglement capacity; this work is still in progress and properties of the entanglement measure are being fully characterized.

Significance:

The resulting analysis and computational tools will be extremely useful to Sandia’s entire quantum device engineering efforts. This research will establish Sandia as a pioneer in quantum control and decoherence management.

Refereed Communications:

K.C. Young and M.D. Grace, "Simulation of Stochastic Quantum Systems Using Polynomial Chaos Expansions," *Physical Review Letters*, vol. 110, p. 110402, March 2013.

M. Sarovar and M.D. Grace, "Reduced Equations of Motion for Quantum Systems Driven by Diffusive Markov Processes," *Physical Review Letters*, vol. 109, p. 130401, September 2012.

From Neurons to Algorithms

151345

Year 3 of 3
Principal Investigator: F. Rothganger

Project Purpose:

How does the human mind work? This is an ageless scientific question, a challenge of truly epic proportions. It is such a large problem that we are tempted to pretend that we are not interested, and rather focus on more mundane issues.

Yet there are many beneficial applications to be had along the way. A machine with human-like pattern classification ability can be scaled up to search large amounts of data or detect anomalies and attacks on computer systems. A model that accurately reflects the sentiments of our adversaries can help us predict their actions, or perhaps to avoid creating enemies altogether.

The human brain is the most complex object in the known universe. Hordes of scientists are actively engaged in studying its various parts. For example, the annual conference of the Society for Neuroscience draws over 30,000 people presenting on over 1,000 topic areas. There are experts in many different domains at many different scale levels.

All this knowledge must be integrated into a unified model. It is beyond the capacity of any individual to comprehend. Ultimately, the complete model of human cognition cannot exist as an idea in one person's mind. Rather, it will be an information structure held in a large computer system.

The goal of this project is to build the scaffolding for that system. Around us wait powerful tools for this task: large parallel computing, big data processing, model reduction techniques, uncertainty-quantification, and visualization. If we wield them well, we can foster a scientific breakthrough.

Our approach is to take the vast amount of data from various sources in various formats, convert it to computable form, and analyze the resulting structures. This will ultimately require input from the entire community, so we encourage participation by providing tools that are easy to use and which add value for the contributor.

Summary of Accomplishments:

The primary outcome of this project is a modeling language that captures the essential structure and relationships of neural systems along with their dynamics. We have also created a software tool, which enables users to develop and test models using this language. The tool has been approved for open source release, and now resides on a public web-site at http://code.google.com/p/n2a

We have implemented the following neural models as test cases:

- The Hodgkin-Huxley cable equations
- A previously published biologically realistic model of the dentate gyrus (Aimone et al., 2009)
- 80-20 networks (80% excitatory, 20% inhibitory) based on Izhikevich units
- Internal cell signals involved in dynamics of learning

The N2A tool supports two simulation environments:

- Xyce, the parallel circuit simulator developed by Sandia
- C++, a direct code generator that creates stand-alone simulation programs

We have developed deepening ties with the neuroinformatics community, and continue to strive for deeper integration with other databases and tools. In particular, we have opened a conversation with the Neuroscience Information Framework (NIF) (http://neuinfo.org) about curating some of our models and integrating them with the NIF ontology.

Significance:

A key challenge in neuroinformatics is how to assemble models into larger systems and how to combine various kinds of representations (mathematical, qualitative, experimental). N2A helps advance the field by providing a coherent framework that combines ontological and numeric representations.

Such a representation is clearly necessary if we ever hope to model the entire brain and perhaps discover how our minds work. This will support national security missions by enabling computers to provide better (that is, more human-like) anomaly and threat detection.

Refereed Communications:

L.M. Rangel, L.K. Quinn, A.A. Chiba, F.H. Gage, and J.B. Aimone, "A Hypothesis for Temporal Coding of Young and Mature Granule Cells," *Frontiers in Neuroscience*, vol. 7, May 2013.

Incremental Learning for Automated Knowledge Capture

151346

Year 3 of 3
Principal Investigator: Z. O. Benz

Project Purpose:

People responding to high-consequence, national-security situations need tools to help them make the right decision quickly. The dynamic, time-critical, and ever-changing nature of these situations, especially those involving an adversary, requires models of decision support that can dynamically react as a situation unfolds and changes. Automated knowledge capture is a key part of creating individualized models of decision making in many situations because it has been demonstrated as a very robust way to populate computational models of cognition. However, existing automated knowledge capture techniques only populate a knowledge model with data prior to its use, after which the knowledge model is static and unchanging. In contrast, humans, including our national security adversaries, continually learn, adapt, and create new knowledge as they make decisions and witness their effect. This artificial dichotomy between creation and use exists because the majority of automated knowledge capture techniques are based on traditional batch machine-learning and statistical algorithms. These algorithms are primarily designed to optimize the accuracy of their predictions and only secondarily, if at all, concerned with issues such as speed, memory use, or ability to be incrementally updated. Thus, when new data arrives, batch algorithms used for automated knowledge capture currently require significant recomputation, frequently from scratch, which makes them ill-suited for use in dynamic, time-critical, high-consequence decision making environments.

Summary of Accomplishments:

In the first year of this project, we accomplished the primary goal of establishing a benchmark for existing incremental learning algorithms. To do this, we developed novel ways of measuring and comparing batch and incremental algorithms by developing experimental procedures that mimic typical contexts in which incremental algorithms are used for automated knowledge capture.

In the second year of this project, we investigated novel ways of combining incremental and batch algorithms, such as updating a knowledge model incrementally after batch learning has occurred on it with an iterative approach. Work has focused on leveraging streaming random forest algorithms to prepare experiments that seek to find balance between batch and incremental approaches.

In the final year of the project, we focused specifically on streaming random forests as a learning construct in which to perform experiments. Additionally, we explored the space of unsupervised machine learning algorithms, focusing on variants of the K-Means algorithm.

All work is developed and deployed in Sandia's open source Cognitive Foundry software package, providing direct utility of the research to current and future users. A streaming data pipeline has been created within the Foundry, and is quickly reaching maturity as a platform for working with incremental data from a variety of sources.

Significance:

This project supports the national security missions of DOE, DoD and DHS by providing science and technology in support of the human element that is critical to many mission areas. It addresses a fundamental barrier to using computational models of cognition by updating models with relevant knowledge in a timely manner to support a human's ability to understand and act in urgent and uncertain situations with nationally significant consequences. This will also increase their applicability to environments such as physical and cyber security that involve adversaries who constantly adapt tactics and strategies by also enabling the models to adapt.

A Comprehensive Approach to Decipher Biological Computation to Achieve Next Generation High-Performance Exascale Computing

151347

Year 3 of 3
Principal Investigator: C. D. James

Project Purpose:

The human brain (volume=1200cm^3) consumes 20W and is capable of performing > 10^{16} operations/s. Current supercomputer technology has reached 10^{15} operations/s, yet requires 1500m^3 and 3MW, giving the brain a 10^{12} advantage in operations/s/W/cm^3. Thus, to achieve next generation exascale (10^{18}) computational capabilities, two objectives need to be accomplished: 1) improved understanding of computation in living biological tissue and 2) a paradigm shift towards neuromorphic computing where hardware circuits mimic properties of neural tissue. To address 1), we will interrogate corticostriatal networks in mouse brain tissue slices, specifically with regard to their frequency filtering capabilities as a function of input stimulus. This investigation is crucial to deciphering the information processing (filtering and thresholding) that occurs in these networks during decision-making processes. To address 2), we will instantiate biological computing characteristics into hardware devices with future computational and memory applications. Biological computing characteristics that will be explored include multi-bit storage/processing, metastable states, dynamic state changes that evolve with time, and frequency selectivity. Multiferroic materials and resistive memory devices will be examined with regard to their application to neuromorphic computing strategies. Devices will be modeled, designed, and fabricated in the MESA facility in consultation with our internal and external collaborators. We will also investigate the potential for importing neuromorphic device models into Xyce, Sandia's parallel computing circuit simulator software. Finally, we will assemble a breadboard circuit demonstration with an incorporated neuromorphic device to demonstrate the utility of such technology.

Summary of Accomplishments:

We characterized meta-plasticity in living corticostriatal networks, a term we use to describe when a network's frequency filtering properties are changed by a stimulus, and then future stimuli are processed differently due to the change in filtering characteristics. We also analyzed laser-based stimulation of living neurons (documented in the field for many years, phenomenologically), shedding light on potential cell-signaling mechanisms by which neurons respond to such stimulation. We developed a model for designing multi-layered resistive memory devices with predictions of improved switching characteristics such as a wider range of tunable resistance states and less catastrophic switching. Using this model, we designed and fabricated multi-layered resistive memory devices using tantalum oxide and silicon dioxide in order to test the model experimentally. We fabricated an embedded microelectrode multiferroic memory device and assessed in plane electrical polarization with this novel structure. We developed a model to explain the dynamics of switching in tantalum oxide based memristor devices. We have designed and built a printed circuit board for a voltage to frequency converter into which electrical components (including memristors) can be incorporated to highlight the tuning advantages of using memristive devices in such systems.

Significance:

The wet biology work in this project advanced two frontiers in science: 1) we helped clarify the molecular mechanisms by which neurons are stimulated with light and 2) we characterized the dynamic changes in frequency filtering in corticostriatal neural networks. For the hardware component of this effort, we advanced science and engineering in 3 areas: 1) physics-based modeling of resistive memory devices, 2) multi-axis characterization of multiferroic films, and 3) fabrication of memristor devices of different materials systems including tantalum oxide, silicon dioxide, and germanium selenide (with silver filaments).

Refereed Communications:

P.R. Mickel, A.J. Lohn, B.J. Choi, J.J. Yang, M.-X. Zhang, M.J. Marinella, C.D. James, and R.S. Williams, "A Physical Model of Switching Dynamics in Tantalum Oxide Memristive Devices," *Applied Physics Letters*, vol. 102, p. 223502, 2013.

P.R. Mickel, S. Buvaev, A. Kamalov, H. Jeen, P. Finnegan, A. Biswas, A.F. Hebard, and C.D. James, "Measurement of the Polarization Vector in BiMnO3 Multiferroic Thin Films using Surface and Embedded Microelectrodes," *Journal of Applied Physics*, vol. 114, p. 094104, 2013.

P.R. Mickel and C.D. James, "Multilayer Memristive/Memcapacitive Devices with Engineered Conduction Fronts," *The European Physical Journal Applied Physics*, vol. 62, p. 30102, 2013.

Automated Generation of Spatially Varying Stochastic Expansions for Embedded Uncertainty Quantification

155551

Year 3 of 3
Principal Investigator: E. C. Cyr

Project Purpose:

Uncertainty quantification (UQ) is increasingly recognized as necessary to assess the effect of variability of input parameters on a physical model. For phenomena described by systems of partial differential equations (PDEs), the variability is derived from coefficients, boundary conditions, or forcing terms, which are all modeled by a random variable with a particular distribution or a range of possible values. The result is a PDE that has a stochastic solution that reflects the variation in the input.

Current UQ methods, like stochastic collocation or Monte-Carlo sampling, approximate the stochastic solution by treating the required resolution of the uncertainty as uniform across the physical domain. To understand the consequence of this, consider a convection-dominated flow where uncertainty is injected at a point in the domain. Only the solution downstream of the injection point will be affected by the uncertainty. The upstream solution will be fully defined by the deterministic PDE. Modern UQ methods would approximate both the upstream and downstream solutions with the same resolution. But this wastes computational resources on the upstream solution and may under resolve the solution downstream. For more realistic multi-physics applications that are characterized by a range of time and spatial scales, the required degree of resolution of the stochastic solution across the physical domain is an open question.

This research hypothesizes that the solution is more efficiently and accurately approximated by varying the resolution of the stochastic expansion across the spatial domain. Furthermore, using embedded UQ technology, the expansion can be constructed using adjoint-based error estimation and refinement. The potential benefit is two-fold: 1) any investigation into the spatially varying resolution requirements of the stochastic solution represents novel research that will shed light on the nature of uncertainty in PDE systems and 2) an adaptive refinement algorithm would better utilize computational resources enabling simulation of larger, more complex physical systems, revealing greater insights into more challenging physics.

Summary of Accomplishments:

The primary accomplishment of this project was to demonstrate that by varying the resolution of stochastic expansions across the spatial domain, the solution to a stochastic PDE can be computed with fewer unknowns leading to greater efficiency. A caveat to this result is that it is most relevant to PDEs with strong spatial locality due to convection or nonlinearities. Highly diffusive PDEs tend to smear the uncertainty uniformly across the domain.

As part of this demonstration, we developed several new technologies. First, we implemented a spatially varying discretization library and embedded it within the Stokhos package. This technology is freely distributed with the open source Trilinos framework that includes Stokhos. Currently, this is a one-of-a-kind technology that is unique to Sandia. A second accomplishment was the mathematical development of an adaptive algorithm for construction of the spatially varying discretization. To this end, we developed several error indicators that attempt to separate the spatial error from the stochastic error. We also developed element-based and unknown-based marking strategies which, based on the error indicators, select deterministic degrees of freedom to refine.

We demonstrated this combined spatially varying and adaptive technology on several scalar PDEs of interest. In particular a 1D prototypical convection-diffusion problem, a 2D high Peclet number convection diffusion problem with an internal layer. And a more practical heat transfer problem between a cylinder and a fluid.

Significance:

Development of embedded enhanced uncertainty quantification (UQ) capability enables simulation of more complex physics with greater confidence in results. This high-risk project provides an alternate approach to tackling the exponential growth problem in UQ. UQ in computational modeling for the Nuclear Weapons community is a preeminent issue when the analysis is used for weapons system qualification for life extension programs as well as the annual assessment. Additionally, engineering analysis problems, like those defining energy and climate models, benefit from UQ approaches.

New Methods of Uncertainty Quantification for Mixed Discrete-Continuous Variable Models

156158

Year 3 of 3
Principal Investigator: L. E. Bauman

Project Purpose:

The scale and complexity of problems such as designing power grids or planning for climate change are growing rapidly, driving the development of complicated computer models that incorporate both continuous and discrete data. Both the models and the data are uncertain. Uncertainty quantification (UQ) provides the underpinnings necessary to establish confidence in these models and their use to support risk-informed decision making. However, there are only a few approaches for mixed discrete-continuous variable models, and these become obsolete when there are multiple discrete variables or when the discrete variables are completely non-numeric. Therefore, researchers focus on the uncertainty in their particular problem taking advantage of symmetries, simplifications or structures. For example, uncertainty propagation in certain dynamical systems can be efficiently carried out after various decomposition steps.

By combining some ideas from statistical genetics and computer experiments, we plan to develop a new method for performing UQ for mixed discrete-continuous models. The focus will be on two general classes of problems: moderate scale problems (model choices) with a modest number of discrete variables and large scale problems where the discrete parameter space may be larger than the continuous one (repeated units).

In classical biometrics when heritabilities are estimated, the aggregate effects of unobserved discrete genotypes are modeled as additive, continuous random variables. In computer experiments, one approach is to treat the deterministic output of a simulator as the sum of a fixed function and a random process. These approaches will be combined to create a new way to treat discrete variables in mixed variable problems. The key concept is to aggregate and transform the discrete variables into a continuous probabilistic variable, also leading to potential new capabilities for handling high dimensions.

This method will provide a new tool for UQ focused on efficient estimation of the cumulative distribution function (CDF) of possible output function values given the uncertain input values.

Summary of Accomplishments:

Uncertainty quantification has seen intense research focus for models designed for continuous inputs only. A new approach to uncertainty quantification for mixed discrete-continuous variable models was developed that entails transforming the discrete variables into associated continuous quantities, so that methods designed for continuous inputs can be used.

The goal for this project was to find appropriate problems and ways to transform the discrete variables into a continuous one in order to take advantage of all the efficiency improvements in UQ methods designed for continuous inputs only. We have defined a set of problems denoted “model choice problems” and created algorithms to quantify the uncertainty in a way that produces comparable results to benchmark results in less time.

The work has created the foundations for a new approach to efficient uncertainty quantification for mixed discrete-continuous models based on ANOVA functional decompositions and the foundations for new types of surrogates created by mixing and matching other surrogate models such as Gaussian process models or spline models.

Significance:

These methods are motivated by specific examples of interest to Sandia such as life extension programs (LEPs), where modeling is key to surety assessments or resource allocation problems, where uncertainties abound focusing on optimal solutions robust to uncertainties rather than absolute optimality. The UQ techniques can be integrated into many domain-specific model-based analyses to assess confidence in model predictions, the effects of uncertainties on long-term planning, and risk-informed decision making. Such themes are pervasive throughout Sandia's thrust areas of nuclear, energy, and cyber-security; thus, uniquely positioning Sandia to contribute solutions to a wide range of problems posed by DOE, DoD, and DHS.

Multilevel Summation Methods for Efficient Evaluation of Long-Range Pairwise Interactions in Atomistic and Coarse-Grained Molecular Simulation

157688

Year 3 of 3
Principal Investigator: S. D. Bond

Project Purpose:

The availability of efficient algorithms for long-range pairwise interactions is central to the success of numerous applications, ranging in scale from atomic-level modeling of materials to astrophysics. Molecular dynamics (MD), in particular, can require months of supercomputer time, due to the expense of the large number of force evaluations required. The challenge is to design reliable, efficient, portable, scalable algorithms for calculating long-range interactions in large systems. Scalability and portability are of particular concern for modern exascale supercomputers with hybrid architectures and massive numbers of processors.

A diverse set of methods has evolved for rapid approximation of long-range interactions, including fast-multipole methods and Fourier-based particle-mesh Ewald methods. Multipole methods excel when applied to systems with large variations in density (e.g., astrophysics), but have generally been considered less competitive for more uniform systems (e.g., molecular dynamics). As a result, state-of-the-art MD codes like NAMD and LAMMPS, use particle-mesh Ewald.

Due to the use of the Fast Fourier Transform (FFT), particle-mesh Ewald methods do not scale well as the system size is increased, with a computational cost proportional to N log N, where N is the number of atoms. The FFT also has a large communication overhead, due to the parallel scalability problems associated with the matrix transpose.

This project will focus on the development and analysis of the multilevel summation method (MSM), which is a relatively new algorithm for computing pairwise interactions. Compared to particle-mesh Ewald methods, the MSM is lesser known, with the first MD studies appearing within the last five years. Preliminary studies have found that it has a computation cost proportional to N, rather than N log N, and relatively low communication overhead (uses nested grids instead of the FFT). Development of this method has the potential to dramatically improve the efficiency of MD software used for predictive simulation of materials.

Summary of Accomplishments:

We implemented a parallel version of the multilevel summation method in the LAMMPS software package. We analyzed its performance and found that it scales linearly with the number of input charges, as predicted by theory. We applied the multilevel summation method to a Laplacian-centered integral equation formulation of the Generalized Poisson Equation. The method represents the solution by an effective charge layer at the boundary of dielectric discontinuities. We analyzed the resulting method and found that it scales linearly with the number of cells in the meshed boundary layer, as predicted by theory. We demonstrated that the new method can be used as a preconditioner for the Poisson Boltzmann Equation, facilitating the efficient approximation of the electrostatic potential used in implicit solvent calculations.

Significance:

Our development of more efficient algorithms for the evaluation of long-range pairwise interactions will enable molecular dynamics simulation of larger systems with more accurate material models. This research has significantly improved the asymptotic scalability of simulation software, allowing for more efficient use of the massive numbers of processors in modern supercomputers. Ultimately, enabling larger simulations will enhance the predictive capability of software used for modeling materials of interest.

High Performance Graphics Processor-Based Computed Tomography Reconstruction Algorithms for Nuclear and Other Large-Scale Applications

158182

Year 3 of 3
Principal Investigator: E. S. Jimenez, Jr.

Project Purpose:

The goal of this work is to develop a fast computed tomography (CT) reconstruction algorithm based on graphics processing units (GPU) that achieves significant improvement over traditional central processing unit (CPU) based implementations. The main challenge in developing a CT algorithm that is capable of handling very large datasets is parallelizing the algorithm in such a way that data transfer does not hinder performance of the reconstruction algorithm. General purpose graphics processing unit (GPGPU) is a new technology that the S&T community is starting to adopt in many fields where CPU-based computing is the norm. GPGPU programming requires a new approach to algorithm development that utilizes massively multi-threaded environments. Multi-threaded algorithms, in general, are difficult to optimize since performance bottlenecks occur that are non-existent in single-threaded algorithms such as memory latencies. If an efficient GPU-based CT reconstruction algorithm can be developed, computational times could be improved by a factor of 20. Additionally, cost benefits will be realized as commodity graphics hardware could potentially replace expensive supercomputers and high-end workstations.

Development of a fully optimized reconstruction algorithm may require a dramatic restructuring of the entire algorithm in order to achieve optimal performance. This project will take advantage of the CUDA programming environment and attempt to parallelize the task in such a way that multiple slices of the reconstruction volume are computed simultaneously. This work will also take advantage of the GPU memory by utilizing asynchronous memory transfers, GPU texture memory, and (when possible) pinned host memory so that the memory transfer bottleneck inherent to GPGPU is amortized. Additionally, this work will take advantage of GPU-specific hardware (i.e., fast texture memory, pixel-pipelines, hardware interpolators, and varying memory hierarchy) that will allow for additional performance improvements.

Summary of Accomplishments:

We discovered three approaches to large-scale computed tomography reconstruction. All three have significantly furthered the state-of-the-art for computed-tomography reconstruction algorithms. We also discovered that our newly developed approaches have significantly boosted energy efficiency metrics by up to 35-fold. We have demonstrated that these approaches can reconstruct up to one trillion 3D pixels (a feat never done as far as the authors are aware) in less than 24 hours; traditional approaches would require up to five years to perform the same calculation. We have learned new irregular properties of reconstruction algorithms when applied to GPU technology and will further explore this discovery in future projects.

This work resulted in four invention disclosures:

1) A High-Performance Multi-GPU based Large Scale Radiography and Computed Tomography Dataset Simulator
2) Cluster-Based Modularized Approach to GPU-Based Computed Tomography with Non-Linear Load Balancing and Node-Interconnect Optimizations

3) Modularized Approach to GPU-Based Computed Tomography Improves Global Performance in High-Performance Systems
4) Irregular Approach to Large-Scale Computed Tomography on GPUs

Significance:

We have communicated our results through multiple scientific publications stating the discovery of irregular properties of computed tomography algorithms on GPUs. The results of this work are already being utilized at Sandia. This technology has greatly improved inspection and evaluation capabilities at Sandia and can now be used to improve detection applications in all national security missions.

Refereed Communications:

L.J. Orr and E.S. Jimenez, "Preparing for the 100-Megapixel Detector: Reconstructing a Multi-Terabyte Computed Tomography Dataset," in *Proceedings for the Penetrating Radiation Systems and Applications XIV workshop at the SPIE International Symposium on SPIE Optical Engineering+Applications*, 2013.

E.S. Jimenez and L.J. Orr, "Rethinking the Union of Computed Tomography Reconstruction and GPGPU Computing for Industrial Applications," in *Proceedings for the Penetrating Radiation Systems and Applications XIV workshop at the SPIE International Symposium on SPIE Optical Engineering+Applications*, 2013.

E.S. Jimenez, L.J. Orr, and K.R. Thompson, "An Irregular Approach to Large-Scale Computed Tomography on Multiple Graphics Processors Improves Voxel Processing Throughput," in *Proceedings for the Conference on High Performance Computing Networking, Storage and Analysis, SC 2012, Workshop on Irregular Applications: Architectures and Algorithms (IA^3)*, 2012.

L.J. Orr, E.S. Jimenez, and K.R. Thompson, "High Performance Cluster-Based Approach to GPU-Based Computed Tomography," in *Proceedings on High Performance Computing Networking, Storage and Analysis*, 2013.

E.S. Jimenez, L.J. Orr, and K.R. Thompson, "A High-Performance and Energy-Efficient CT Reconstruction Algorithm to Reconstruct Multi-Terabyte Datasets," in *Proceedings for the IEEE Nuclear Science Symposium and Medical Imaging Conference*, 2013.

E.S. Jimenez, L.J. Orr, and K.R. Thompson, "Irregular Large-Scale Computed Tomography on Multiple Graphics Processors Improves Multiple Energy-Efficiency Metrics for Industrial Applications," in *Proceedings for the Conference on High Performance Computing Networking, Storage and Analysis*, 2013.

Sublinear Algorithms for Massive Data Sets

158477

Year 3 of 3
Principal Investigator: S. Comandur

Project Purpose:

Our ability to accumulate and store data is increasing rapidly. More and more, we are faced with massive data sets. These could be Internet graphs, network traffic data, or genetic sequences of various organisms. Having gathered this data, we face the problem of processing it to learn something meaningful. In many cases, the data is extremely large, and most standard procedures are just inefficient. We need to develop sublinear algorithms (i.e., procedures that look at a tiny fraction of the data). The goal is to determine non-trivial properties of the data, such as recurring patterns in a string, sparse cuts in graphs, or communities in a cyber network.

These kinds of varied combinatorial and graph problems require very different kinds of sampling and algorithmic strategies. Over the past decade, the theoretical computer science and discrete mathematics community have developed some algorithmic sampling tools for sublinear algorithms. This has yielded sampling procedures that are believed to be applicable for a large variety of problems.

This is an exciting and deep area of mathematical study, but most of the work has a very narrow, theoretical focus. The theoretical models are very rudimentary and many new ideas are needed to apply these sampling tools to specific problems. At a high level, our aim is to develop new theoretical sampling techniques and connect them to real-world issues at Sandia. This project promises to work both at the mathematical and practical levels. Any theoretical insights gained would be considered novel mathematical results in their own right. But understanding how these relate to real-world problems is unchartered territory in itself. This project would be one of the first comprehensive investigations in the study of sublinear algorithms for massive dataset problems.

Summary of Accomplishments:

We initiated the practical use of sublinear algorithms for massive data analysis problems at Sandia. This research branched out into various areas of data mining, such as graph modeling and graph analysis. Most of the research has been published in peer-reviewed conferences and journals.

We performed a theoretical analysis of SKG graph generator, used for the Graph 500 benchmark. We found numerous problems and a theoretical fix for the degree distribution. This influenced the current SKG Graph 500 benchmark. We showed that the SKG model was very similar to the Chung-Lu model. The Chung-Lu model is considered a poor model for real graphs, so this suggests that SKG is also not good for real-world modeling. We designed a new graph model that had provably good degree distributions and clustering guarantees. We are working on large-scale implementations for a graph benchmark.

Counting triangles in graphs is a fundamental problem for social network analysis. We designed and described a method for counting triadic measure in graphs. This paper was submitted and awarded the best research paper at the SIAM Conference on Data Mining. We designed and described a new streaming algorithm for triangle counting. This paper was submitted and awarded the best student paper at the SIGKDD conference on Knowledge Discovery and Data Mining. We scaled our algorithms to MapReduce. We have the largest triangle counting results ever published in this paper.

Significance:

Our work has influenced the modeling of large data benchmarks, an important mission area for Sandia. This has also pushed the boundaries of the mathematics and algorithms in the area of massive graph analysis. Our triangle-counting algorithms are probably the state-of-the-art, in terms of scalability and accuracy. This work is at the cutting edge of practical algorithms research. Many national security missions involve data analysis and our methods will impact the efficiency of such analysis.

Refereed Communications:

C. Seshadhri, A. Pinar, and T.G. Kolda, "An In-Depth Analysis of Stochastic Kronecker Graphs," *Journal of the ACM*, vol. 60, April 2013.

C. Seshadhri, A. Pinar, and T.G. Kolda, "Triadic Measures on Graphs: The Power of Wedge Sampling," in *Proceedings of the SIAM Conference on Data Mining (SDM)*, 2013.

J. Ray, A. Pinar, and C. Seshadhri, "Are We There Yet? When to Stop a Markov Chain while Generating Random Graphs," Workshop on Algorithms and Models for the Web Graph (WAW), 2012.

M. Jha, C. Seshadhri, and A. Pinar, "A Space Efficient Streaming Algorithm for Triangle Counting Using the Birthday Paradox," in *Proceedings of SIGKDD Knowledge Discovery and Data Mining (KDD)*, 2013.

A. Pinar, C. Seshadhri, and T.G. Kolda, "The Similarity between Stochastic Kronecker and Chung-Lu Graph Models," in *Proceedings of the Twelfth SIAM International Conference on Data Mining*, 2012.

C. Seshadhri, T.G. Kolda, and Ali Pinar, "Community Structure and Scale-Free Collections of Erdos-Renyi Graphs," *Physical Review E*, vol. 85, p. 056109, 2012.

D. Chakrabarty and C. Seshadhri, "Optimal Bounds for Monotonicity and Lipschitz Testing over Hypercubes and Hypergrids," in *Proceedings of Symposium on Theory of Computing (STOC)*, 2013.

D. Chakrabarty and C. Seshadhri, "An o(n) Monotonicity Tester for Boolean Functions over the Hypercube," in *Proceedings of Symposium on Theory of Computing (STOC)*, 2013.

Scheduling Irregular Algorithms

158787

Year 2 of 3
Principal Investigator: E. G. Boman

Project Purpose:

Scheduling is the assignment of tasks to processors for execution and it is an important concern in parallel programming. Most prior work on scheduling has focused either on static scheduling of applications where the dependence graph is known at compile time or on dynamic scheduling of independent loop iterations. However, many algorithms are irregular, which generally means that loop iterations are not independent and the dependence graph is not known at compile time. In addition, scheduling traditionally focuses on improving locality or maintaining good load balance, but for irregular algorithms, even the amount of work may vary with the scheduling policy. The purpose of this project is to investigate novel strategies for partitioning the computations of a simulation into tasks that can be assigned dynamically to processors or processes or threads so that irregular applications can run efficiently and at increased scales of thousands to millions of processors.

Irregular applications include traditional scientific applications (partial differential equations, grids, particles) that are dynamic, either in their geometry or their time dependence. It also includes data-centric applications, such as those in informatics or graph analysis, where huge volumes of data are processed and the computation is often more memory-bound than compute-bound. Achieving high parallel performance for these kinds of applications is difficult for programmers to achieve due to load imbalances and the dynamic nature of the problems. As supercomputer architectures move to more processors and accelerated hardware such as many-core CPUs and GPUs, the challenge is exacerbated. One possible solution is to automate more of the parallelization process by appealing to the compiler or a run-time system to partition the simulation's workload effectively and schedule the large number of small tasks on available resources (processes, threads, etc.). This project aims to extend the state of the art for that model, and apply it to interesting large-scale scientific applications. The work is in collaboration with UT-Austin.

Breaking Computational Barriers: Real-Time Analysis and Optimization with Large-Scale Nonlinear Models via Model Reduction

158789

Year 2 of 3
Principal Investigator: K. T. Carlberg

Project Purpose:

Despite developments in high-performance computing, physics-based simulations can take weeks to complete. This constitutes a barrier for many engineering applications. For example, uncertainty quantification (UQ) requires simulations to be completed in minutes; control requires real-time analysis. For nonlinear models, existing surrogate models often fail to meet these time constraints without introducing unacceptable errors.

This project's purpose is to enable accurate, near-real-time analysis using physics-based nonlinear models via reduced-order models (ROMs). The resulting framework will be generalizable to a wide range of problems including real-time control of power grids and UQ of thermo mechanical systems. The work builds upon the GNAT nonlinear model reduction method [Carlberg, et al., 2011]. The PI is a Sandia Truman Fellow.

The project consists of three major parts:

1) Devise a data-driven model-reduction framework. First, leverage temporal simulation data. Second, leverage (physical) experimental data. Third, through collaboration with the University of Washington, devise error estimates for the Lagrangian dynamical system ROM solution. Fourth, refine the ROM solution.
2) Integrate within target tasks (UQ and optimization). First, cast ROM error as statistical uncertainty. Second, in collaboration with George Mason University, integrate ROMs within an optimization framework.
3) Deploy on Sandia's applications. First, preserve problem structure (e.g., energy conservation) in the ROM. Second, develop a model-reduction software package, resulting in Razor, a Trilinos-based model reduction software package. Third, deploy on cavity flow, thermomechanical, and quantum-mechanical application problems at Sandia.

Exploring Heterogeneous Multicore Architectures for Advanced Embedded Uncertainty Quantification

158792

Year 2 of 3
Principal Investigator: E. T. Phipps

Project Purpose:

In the near future, high-performance computing will undergo dramatic changes as heterogeneous multicore nodes are incorporated into distributed memory architectures. Significant work is under way to exploit these new architectures for single-point forward simulations. However, the propagation of uncertainties from simulation input data to simulation output quantities is critical to the quantification of uncertainties in predictive simulation. Since one avenue of forward uncertainty propagation relies solely on sampling a simulation code over the uncertain input space (so-called non-intrusive approaches), any improvement in the forward simulation enabled by multicore architectures will result in commensurate improvement in the forward uncertainty calculation. However, even with these improvements, there will be many problems of strategic interest where the computational requirements for accurate uncertainty propagation will still be too great. To address these challenges, it is critical to develop new architecture-aware uncertainty propagation algorithms that fully exploit the performance benefits of heterogeneous multicore architectures.

The purpose of this project is to create new embedded uncertainty quantification methods that fundamentally alter the structure of a simulation code to implement forward uncertainty propagation directly, leveraging high on-node core and thread counts, with the aim of achieving significant reductions in overall computational run times and increased scalability over non-intrusive methods. This requires fundamental algorithmic, computer science, and software research to develop algorithms and approaches that can leverage to the greatest extent possible the capabilities provided by these emerging architectures. Significant challenges are developing effective uncertainty-adapted solution strategies that scale to very high thread counts and software tools that allow these approaches to be incorporated in a diverse set of scientific simulation codes. The project is foundational across all Sandia scientific computing missions and is illuminating a path to exascale computing where uncertainty quantification, not single-point forward simulation, is the driving technology.

Architecture- and Resource-Aware Partitioning and Mapping for Dynamic Applications

158793

Year 2 of 3
Principal Investigator: K. D. Devine

Project Purpose:

Our goal is to increase application performance and computer system efficiency by incorporating static and real-time architecture and system-performance information into decisions about applications' resource use. In FY 2013, we focused on data collection and delivery, power management, and task mapping, as outlined below. In FY 2014, we will emphasize integration and evaluation of new capabilities in unstructured applications.

Data collection for performance characterization:

- We developed new tools for understanding and accessing Cray's network performance counters.
- We used Gemini router performance counters to measure network congestion and quantify the benefits of task mapping in the MiniGhost finite-difference miniapp.
- We enriched our node-subsystem representation with network topology information and interfaces for extracting system information and building models of inter- and intra-node topologies.

Power management in multicore systems:

- We demonstrated adaptive on-node concurrency management for reducing power consumption; our strategies measure memory bandwidth and power consumption, and dynamically reduce concurrency when memory bandwidth is saturated.
- On a single multicore node, dynamic throttling achieved 8% power reduction (10 watts) without increasing application execution time for the LULESH Lagrangian hydrodynamics miniapp.
- On a hybrid 27-node (432-core) system, dynamic throttling reduced total power draw by 7.4% (270W). Execution time actually decreased compared to using all threads due to decreased memory bandwidth contention.

Effective mapping of tasks to cores in parallel systems:

- We developed coordinate-based task mapping that decreases runtime of MiniGhost by up to 35% on Cielo; average improvement increases with machine size (4% on 4K cores; 28% on 64K).
- We implemented coordinate-based task mapping using multijagged partitioning in Zoltan2, including new strategies for selecting optimal subsets of nodes (via k-clustering), shifting node orientations based on machine coordinats, and computing mappings with rotations of allocations.
- We integrated Gemini performance counters and Cielo's 3D torus model into the libtopomap graph-based task-mapping library and made libtopomap operational for Cielo up to 64K cores.

Automated Algorithms for Achieving Quantum-Level Accuracy in Atomistic Simulations

158794

Year 2 of 3
Principal Investigator: A. P. Thompson

Project Purpose:

Molecular dynamics (MD) is a powerful materials science simulation tool for bridging between quantum mechanical (QM) systems with a few hundred atoms and the length/time scales required to model entire microscale devices. However, the impact of MD is severely limited by the lack of suitably accurate interatomic potentials for many important materials. Examples include III-V semiconductor compounds for Qualification Alternatives to the Sandia Pulsed Reactor (QASPR) and refractory metal alloys for the Predicting Performance Margins (PPM) program. Building traditional physics-based potentials is a time-consuming, high-risk endeavor, incompatible with time-sensitive, mission-critical projects. A recent breakthrough enables automated development of quantum-accurate potentials for metals and semiconductor compounds with systematically controllable accuracy. This game-changing capability for predictive materials modeling may enable timely MD simulation of materials of arbitrary chemical composition with unprecedented fidelity, limited only by the availability of relevant QM training data.

The Gaussian-approximation potential (GAP) approach of Bartok, et al., demonstrated that the bispectrum of the neighbor atom density can produce accurate surrogates for QM models. Assuming linear dependence of energy on bispectrum components, we have developed a general form for potentials called Spectral Neighbor Analysis Potential (SNAP). We have built an in-house capability for automated generation of SNAP potentials for arbitrary materials using DAKOTA optimization coupled to the Large-scale Atomic/Molecular Massively Parallel Simulator molecular dynamics (LAMMPS MD) code. With this capability, we have generated a SNAP potential of unprecedented accuracy for tantalum metal that can model the motion of screw dislocations. We have also generated candidate SNAP potentials for indium phosphide, an important III-V semiconductor compound. We created a scalable parallel implementation of the SNAP potential in LAMMPS and demonstrated unprecedented strong scaling on petascale computers (Sequoia, Titan). Going forward, we will improve the indium phosphide potential, develop a new potential for silicon dioxide, improve the SNAP software framework, and demonstrate the computational efficiency of the LAMMPs implementation.

Fault Survivability of Lightweight Operating Systems for Exascale

158802

Year 2 of 3
Principal Investigator: K. B. Ferreira

Project Purpose:

Concern is growing in the High Performance Computing (HPC) community regarding the reliability of proposed exascale systems. Research at Sandia has shown that the reliability requirements of these machines will greatly reduce their scalability. Current fault-tolerance techniques have focused on application faults and ignored the most critical software running on a node, the operating and runtime system.

We can think of the operating system (OS) on these machines as a single, scalable application that manages the available resources on a node. Today's OSs and runtime systems make many of the same assumptions about reliability that applications do. Many of these basic assumptions will need to be addressed to enable more reliable system software.

HPC system software needs to be able to continue running through faults if emergent application-level fault tolerance is to succeed. This is in contrast to current OSs, which are unable to recover from the vast majority of failures. We will examine the structure of modern HPC OSs with the goal of characterizing important reliability assumptions and determining alternative strategies for exascale systems. For example, errors in memory and logic can have different impacts on the OS and a cost/benefit model for different approaches to handling such errors will need to be developed and analyzed.

In contrast to current fault-tolerance methods that are focused on application faults, this work is focused on ensuring the operating and runtime systems can continue in the presence of faults. This is a much finer-grained and dynamic method of fault-tolerance than the current, coarse-grained, application-centric methods. Handling faults at this level has the potential to greatly reduce overheads. Additionally, in contrast to much of the current work, this work focuses on more realistic fault models, for example, silent data corruption. Lastly, in this project, we investigate forward recovery methods rather than the expensive rollback methods (for example checkpoint/restart) of current work.

Next-Generation Algorithms for Assessing Infrastructure Vulnerability and Optimizing System Resilience

158804

Year 2 of 3
Principal Investigator: C. A. Phillips

Project Purpose:

The US economy and way of life are increasingly dependent on complex, adaptive, networked systems. These systems arise in critical infrastructure (e.g., electricity and water systems, transportation, banking, and finance), global trade, and supply chains, etc. Thus, understanding their behaviors under attack or disruption and increasing their resilience is an important national security challenge. A key component of these systems, which must be accounted for in vulnerability analysis, is their intelligent management by human system operators. Under attack, these actions ideally mitigate (though sometimes exacerbate) the system's response and also influence the subsequent behavior of the attacker.

The theme of this project, in collaboration with the University of Florida, involves bi-level discrete optimization problems for network design and security. Bi-level optimization problems involve two entities that make decisions in a non-cooperative fashion, often involving one primary entity whose actions are opposed by an adversarial entity. While contemporary mathematical programming techniques have been studied for simple cases, the methods cannot yet be extended to complex adversary actions or arbitrarily deep chains of operator/adversary interactions. This research seeks to develop new mathematical theory and algorithms in these areas.

If the research is successful, it will greatly expand the class of bi-level optimization problems that can be addressed with modern computational tools, and can be applied to varied national security mission areas including enhancing understanding of US critical infrastructure systems. As both foundational mathematical theories and practical implementations applicable to real-world problems do not yet exist, this project will create the scientific basis and demonstrate feasibility of an approach which could be differentiating to Sandia's national security missions and customers.

Using High Performance Computing to Examine the Processes of Neurogenesis Underlying Pattern Separation/Completion of Episodic Information

158836

Year 2 of 3
Principal Investigator: J. B. Aimone

Project Purpose:

One of the most perplexing questions pertaining to our understanding of memory concerns how the brain distinguishes between patterns of related events that are separated in time. Understanding this question could have far-ranging impacts with regard to Sandia's ambition to establish next-generation memory processing and pattern classification systems. Studies have provided evidence that the dentate gyrus (DG) processes highly convergent information from cortical regions of the brain. This information is further processed and associated within the CA3 subarea of the hippocampus to help distinguish patterns of events. Studies suggest this process is aided in the DG through neurogenesis. Neurogenesis may serve to support the process of discriminating (separating) patterns by reducing similarity between new and older event information. It may also support pattern completion by increasing associations between temporally similar events, which are then transmitted to the CA3 area of the hippocampus as sparse inputs. Unfortunately, little is known about how the underlying processes of these subareas work as a system. Also, the computational models that have been developed tend to have very reduced representations of the actual neural processes, greatly diminishing their generalizability to actual brain functioning. Accordingly, we plan to neurocognitively model the population dynamics of a fully representative, neurogenesis association system in order to examine how these subareas enable pattern separation and completion of information in memory across time as associated experiences. Only 15 years ago, most neuroscientists believed that the brain did not add new cells over the course of its lifetime. While initially controversial, it has been increasingly appreciated that neurogenesis occurs in certain regions of the brain, with debate having now turned to the functional role of neurogenesis. Successful completion of this research would place Sandia at the forefront of one of the most significant paradigm shifts in the history of neuroscience, which could have major ramifications for efforts to emulate neural processes in computer code.

Interaction-Driven Learning Approaches to Complex Systems Modeling

159005

Year 3 of 3
Principal Investigator: A. V. Outkin

Project Purpose:

Combining interaction-driven and machine learning models into one cohesive framework will allow Sandia to develop complex systems models that will adapt the model parameters and structure in real time, while harnessing the predictive power inherent to interaction-driven models. It will place Sandia in a leading role to provide decision support in areas such as response to natural or man-made disasters, sensor data processing, and cyber security.

While interaction-driven models provide significant predictive and explanatory power, they often require lengthy validation and calibration and generally cannot be used for real time decision making. Additionally, once great effort is expended to carefully calibrate and validate these models, the real-world structure that the model was built to represent may have already changed or evolved, making the model obsolete.

Machine learning can process large datasets and learn complex rules from observable system inputs. However, machine learning does not provide a fundamental understanding of how results were generated or when they became invalid, nor does it provide predictions regarding interventions. This is where the interaction-driven models will constrain the adaptation of learning models to the fundamental truths that lie within the system. A review of the literature has shown that this idea is novel and unique. We will prove and cross-validate this approach on information-rich domains such as sensor networks data processing.

Developing this framework will enable analysts to use partially calibrated interaction-driven models for prediction in real-time. It will reduce demands on model validation and allow the modelers to focus on the logic driving the system and generating its dynamics. It will place Sandia in a leading role to provide decision support when information is incomplete and quick or real-time actions are necessary, including response to natural or man-made disasters, sensor data processing, and cyber security.

Summary of Accomplishments:

- We developed a theoretical Interaction-Learning framework for prediction, model selection and recalibration using a combination of interaction-driven models, machine learning (statistical learning theory and empirical risk minimization) and information theory (Aikake Information Criterion).
- We developed software implementation for the framework using python, scikit-learn, R, and Tcl/Tk. We demonstrated the framework using existing interaction-driven models and data sets.
- Internally, we collaborated with Sandia's Dante team. We demonstrated the framework applicability to combat and battlefield simulations, using Dante data and model.
- We demonstrated the framework applicability to network dynamics prediction.
- We demonstrated the framework's ability to exceed the predictive power of learning models when the underlying system experiences structural change or novel or previously unobserved novel conditions.

- We tested the ability to run the interaction-driven models on a high performance computer cluster to allow a more thorough investigation of the model parameter space and of applicable learning algorithms and demonstrated the feasibility of imitating the performance of a real-world complex systems using only partially calibrated interaction-driven models.
- We established collaborations, or are in the process of establishing collaborations, with Rutgers University, REMI, the University of Vermont, and University of Washington.

Significance:

The framework advances the state of the art in the following ways: 1) improves the accuracy and completeness in analysis of complex systems, 2) utilizes causal and partial understanding of the system operations for prediction, and 3) utilizes incomplete interaction-driven models for prediction, control, and strategy development in real-world complex systems.

The framework can be applied to the following problems: 1) natural and man-made disruptions, such as floods or hurricanes, to provide real-time analysis and better coordination of disaster response and 2) analysis of adversarial strategic domains with limited information (i.e., battlefields and physical security, cyber security, or sensor networks by translating signals into models, strategies, and actions).

Refereed Communications:

A.V. Outkin, "An Agent-Based Model of the NASDAQ Stock Market Historic Validation and Future Directions," *Computational Social Sciences Society of Americas*, 2012.

Transactions for Resilience and Consistency in Integrated Application Workflows for High Performance Computing

159006

Year 3 of 3
Principal Investigator: G. F. Lofstead

Project Purpose:

The scientific discovery process often involves a series of steps that may include simulation, analysis, and visualization with intermediate results staged on the storage system. For large-scale applications, the time, space, and power overhead of storing transient data is already overwhelming and will increase as machines and applications continue to increase in scale. This imbalance will reduce the usefulness of the machines if the current compute and analysis approach of using the storage array to store intermediate data continues. The amount of time spent moving data to and from storage will dominate the computation time, forcing a reduction in the amount of data written. This will make it difficult to generate the scientific insights that are the primary mission of these future platforms. Given these challenges, there is tremendous benefit in coupling these steps as an "integrated application workflow" (IAW). This approach eliminates storing transient data on the storage system but introduces new challenges with respect to resilience and data consistency.

For Sandia's CTH shock physics code, understanding the dynamics of material fragments and fragment tracking is key for scientific insights. Generating fragment information requires separate analysis on the raw CTH data at every time step. An IAW for fragment detection eliminates the need to persistently store intermediate results making tracking fragments practical. Resilience is imperative because a failure or data corruption anywhere in the IAW invalidates the result.

Dramatic changes in data management must be made to achieve exascale computations. IAWs represent a fundamental change in the way computational science leads to insight; however, without resilience, IAWs are not practical at scale. A transaction-based technique provides a robust and scalable solution to resilience for IAWs.

Traditional distribution transaction management systems focus on a single client with multiple servers (1-N). For the High Performance Computing (HPC) environment, however, there are potentially millions of clients interacting with thousands of servers (M-N). Collective input/output (IO) is an existing M-N style operation for HPC. To reduce the number of small IO operations, an initial phase rearranges data across the M processes before writing to N storage targets. The extreme overhead at scale shows what not to do while giving hints on how to manage some of the tasks, such as identifying the group of processes as a whole and the total amount and distribution of data.

Summary of Accomplishments:

An alternative approach that supports the data volumes necessary for making effective use of HPC computational capability is to keep the data within the compute area between the simulation and analysis steps, until it has been reduced to a volume that can be effectively stored on the storage array. By moving these transient intermediate results off the storage array, the scientific workflow process can continue to function at the same or even greater detail level as today. Key to making this a viable model for application scientists is to provide the level of trust they have with the storage array for these more volatile storage locations.

In achieving this approach, we first developed a complete, logical protocol that demonstrated a potential way to manage the messaging. The limits in the messaging volume and size and the requirements on the server processes to full participate informed the second-generation protocol. The second generation is scalable and capable of incorporating all operations required for a transaction for 64K processes in less than 0.45 seconds. The fault detection and recovery mechanism is proven as well for all system components. The time overhead is limited to the timeout plus normal operation time of approximately 0.03 seconds. Message volume and load is managed through the hierarchical structure and local calculation of process roles rather than global assignment. The requirement on managed server processes is limited to marking an operation with limited visibility and having a way to make the visibility general.

Second, we developed simple datastore and metadata components that represent the functionality required for staging data between components of an IAW using the transactions mechanism to manage visibility, correctness, and completeness. By incorporating functionality like transactions, we can offer much of the semantics exhibited by storage arrays within the compute area. In particular, it can mimic the kinds of data set blocking and reliability features application scientists depend on for trustworthy storage of intermediate results.

Third, the system was proven for system reconfiguration operations as well. A LAMMPS configuration with feature detection processes operating on live data was demonstrated. As part of the example, the number of feature detection processes is adjusted without shutting down the system, but only making the number of replicas available once they have been successfully deployed, configured, and started. The transactions protocol offers a systematic way to manage the operations.

Significance:

The transactions project successfully demonstrated a technique for offering very low overhead, scalable, messaging and fault detection for data movement and other operations. With this key feature, we can earnestly develop more complex compositions of simulation and analysis within the compute area with trust that as data flows through the composition, it is both accurate and complete making the final output trustworthy. With this kind of functionality, will we be able to confidently take advantage of future computation platforms for our mission needs.

Solution Methods for Network-Based Scheduling Problems

159054

Year 2 of 2
Principal Investigator: J. J. Carlson

Project Purpose:

The purpose of this research is to develop solution techniques for a new class of network-based scheduling problems. Motivating applications for this problem class include infrastructure restoration after an extreme event and plug-in hybrid electric vehicle (PHEV) battery charging and discharging within a smart grid. Infrastructures, such as power grids and transportation systems, can be modeled as networks. Network managers must coordinate repairs or operational decisions using limited resources in order to maximize performance. Selecting which components to repair or utilize (downed power lines, batteries to charge/discharge) can be viewed as network design decisions. Traditional network design decisions only focus on the end performance of the design (i.e., the network operation after all components are repaired). Clearly, in infrastructure restoration the success of the efforts depend on how well the services come back online. Therefore, it is important to allocate resources, such as work groups, to implement network design decisions. This resource allocation can be viewed as scheduling decisions. This novel model incorporating the combination of decisions occurring simultaneously increases the problem difficulty, which motivates the need for both exact and approximate solution methods. In collaboration with Rensselaer Polytechnic Institute, we will adapt these methods when not all information (components that need repair, battery demand) is available at the start.

Summary of Accomplishments:

Over the course of the research, solution techniques were developed for a new class of network-based scheduling problems. These techniques were successfully applied to several problem classes including infrastructure restoration after an extreme event and PHEV battery charging and discharging within a smart grid. The techniques were also applied to optimization problems related to power grids and transportation systems.

Significance:

Extensive research has been conducted in network design and scheduling separately. However, limited research has been conducted for the combination of these problems, denoted here as network-based scheduling. This problem integration captures the resource allocation aspects of network design, such as the time required to construct or repair networks and how the design influences network function over time. This new and novel way of modeling allows for many areas of exploration, but due to the increased problem difficulty, it calls for creative solution techniques that ensure an appropriate solution is attained within a reasonable amount of time to aid system managers.

Refereed Communications:

S.G. Nurre, B. Cavdaroglu, J.E. Mitchell, T.C. Sharkey, and W.A. Wallace, “Restoring Infrastructure Systems: An Integrated Network Design and Scheduling Problem,” *European Journal of Operational Research*, vol. 223, pp. 794-806, December 2012.

S.G. Nurre and T.C. Sharkey, “On Student Use and Perception of Video Tutorials in an Undergraduate Operations Research Course within an Engineering Curriculum,” in *Proceedings of the Industrial and Systems Engineering Research Conference*, 2013.

Processor Modeling for use in Large-Scale Systems Models

161139

Year 2 of 2
Principal Investigator: E. Debenedictis

Project Purpose:

Through Sandia's Presidential Early Career Awards for Scientists and Engineers (PECASE) partnership with New Mexico State University, a Monte Carlo-based processor modeling (MCPM) technique is being developed that can be used for performance analysis and prediction of contemporary and future processor architectures. These models abstract the execution pipeline into a stochastic model using both processor and application characteristics. Currently, both in-order and out-of-order execution and multi-core architecture can be modeled. In this LDRD project, we will perform new and continued work in three areas: 1) development of the MCPM technique to enable out-of-order, multi-core processor modeling, 2) MCPM integration within SST (Sandia Structural Toolkit), and 3) Mantevo benchmark performance analysis and validation.

SST is a system-level, parallel simulator that supports component models at varying levels of abstraction. We seek to fully integrate the stochastic processor models into the new stable core of SST. In some cases, this includes developing front-ends to support various Industry Standard Architectures, including instruction decode and functional execution.

The Mantevo benchmarks were originally developed from key applications at Sandia and are intended to be short-running kernels representative of these applications. We will perform a performance analysis at the architecture and microarchitecture levels that will provide a detailed picture of benchmark behavior. We will validate this data against each of the original applications from which these benchmarks were derived.

The complexity of contemporary and future computer processors has changed the methodology and tools that have been traditionally used for performance and design space analysis. Cycle-by-cycle simulation is very accurate and robust, but prohibitively slow, with slowdowns on the order of 10,000. Therefore, new techniques and tools must be developed for the design and analysis of processors and processor systems. Further, the planned integration work will contribute processor models of an abstraction level that are currently not available in SST. Finally, the work on the Mantevo benchmarks will provide a much-needed validation at the microarchitecture level.

Summary of Accomplishments:

Over the life of the project, we went through several simulation methods before developing one that demonstrated superior performance. We started by simulating in-order execution of processors (like the UT simulator called SimpleScalar). However, this method proved infeasible for applications at the scale required by Sandia. This led to a shift to abstract modeling, which projects running time without simulating each instruction and is, therefore, much faster for the simulator to execute. This resulted in processor models for cell, Itanium, Opteron, Niagara I and II, and others. The overall result is that we discovered and demonstrated a simulation method that is much more efficient to the extent necessary to practically model current and future architectures that may have billion-transistor chips. Even more importantly, this is evolving to be the only feasible method for simulating exascale systems to date.

Significance:

This work will help enable exascale supercomputers, which are tied to national security missions and science simulation. This work may be the only feasible method of assessing architecture for exascale and thus enabling the co-design cycle.

Refereed Communications:

W. Alkohlani and J. Cook, "Towards Performance Predictive Application-Dependent Workload Characterization," in *Proceedings of the High Performance Computing, Networking, Storage and Analysis (SCC), 2012 SC Companion*, pp. 426-436, 2012.

W. Alkohlani and J. Cook, "Towards Performance Predictive Application-Dependent Workload Characterization," to be published in *ACM SIGMETRICS Performance Evaluation Review*.

A Cognitive and Economic Decision Theory for Examining Cyber Defense Strategies

161871

Year 2 of 3
Principal Investigator: A. Bier

Project Purpose:

The purpose of this project is to discover how psychological, social, and economic factors drive decision making about intra- and inter-group interactions in cyber defense. Cyber attacks pose a major threat to modern organizations, but little is known about the social aspects of decision making among organizations that face cyber threats. Additionally, we do not have empirically grounded models of the dynamics of cooperative behavior among vulnerable organizations. The effectiveness of cyber defense can likely be enhanced if information and resources are shared among organizations that face similar threats. Cyber defense teams must balance potential benefits from cooperation against motivations not to cooperate, such as potential for embarrassment, group inertia, or competitive strategy. Despite these risks, cooperation could mitigate a range of cyber-related vulnerabilities, including espionage, identity theft, and attacks on critical infrastructure.

This research will develop a computational model for researching the psychological, social, and economic factors that drive decision making about intra- and inter-group interactions in cyber defense. The model will incorporate cultural, cognitive, and institutional constraints and conditions to simulate how cognition and environmental circumstances determine cyber defense strategies and behaviors. The model will serve as a test bed for studying theories of cognition in cyber environments, potentially enhancing scientific knowledge of cognitive processes and improving our ability to model decision making in any context.

If successful, this project will result in the first psychological-socio-economic dynamic model designed for this type of analysis. Validation and uncertainty quantification will bolster confidence and enhance the utility of results. The model will enable better understanding and anticipation of cyber defenders' reactions to organizational strategies and priorities, giving insight into strategic policy design. It will be applicable to any set of organizations, create flexibility in application and provide useful insight into cognitive processes in cyber defense and cooperation.

Operationally Relevant Cyber Situational Awareness Tool Development

165611

Year 1 of 3
Principal Investigator: R. G. Abbott

Project Purpose:

The effectiveness of cyber security incident response team (CSIRT) members is a key component in the cyber security of organizations. When investigating an incident, CSIRT personnel must cope with large volumes of data that can be terabytes in size. From this mountain of network, system and log data, analysts must extract the subtle, and often complex, patterns of adversary activity. The difficulty of extracting information from these large data sets has resulted in the development of sophisticated software tools to aid in this analysis. In turn, this has created an industry that aggressively markets these products to DOE, DoD, and other government agencies.

While enumerating the features of these software tools is easy, assessing the overall benefit to an analyst or an organization (i.e., the actual utility of the tool) is much harder. The result is that decisions regarding acquisition and use of these tools rely on subjective judgments. The goal of this research is to develop methods that accurately and objectively predict the utility of a tool to CSIRT members and an organization. Today, we do not even know what the appropriate measures of human performance might be. Furthermore, given that in the cyber domain, the defender often never knows ground truth, the cyber domain presents challenges that are unique to this domain, posing research questions regarding human situation awareness and decision making that has not been addressed within other domains.

Measuring performance is generally simple such as determining false-positive rates or precision recall. However, measuring utility is more complex, often involving a trade-off between desirable features such as time savings and depth of coverage. The risks associated with this project arise from the lack of foundational research concerning the human-in-the-loop component of cyber, and the need to develop innovative experimental protocols for conducting valid studies of human performance within a simulated cyber operations environment.

Does Solution Adaptivity Help or Hinder Solution Verification?

165612

Year 1 of 1
Principal Investigator: W. J. Rider

Project Purpose:

The question in the project title arises due to lack of integration between two important topics in the numerical solution of partial differential equations (PDEs). The first topic, solution-adaptive methods (SA), offers the potential to achieve a fixed level of discretization error using fewer mesh points than non-adaptive methods. The second topic, solution-verification (SV), offers the potential of more credible modeling and simulation. A disconnect exists between the SA and SV perspectives. On the one hand, SA requires non-uniform, locally refined meshes that reduce discretization error. On the other hand, SV requires the use of systematic, globally refined meshes to ascertain the asymptotic regime. So, what is a practitioner to do? Do only solution-adaptivity and claim solution-verification is not necessary? Only do SV? Try to obtain the best of both approaches? Current S&T has not paid sufficient attention to this issue because the two topics were developed in somewhat separate and uncoordinated sub-communities, those being (primarily) finite elements for solution-adaptivity and verification, validation, and uncertainty quantification (VVUQ) for solution-verification. Technical challenges involved in this research are: 1) to determine if one can meaningfully define what it means for a solution-adaptive mesh to be in the asymptotic regime, 2) investigate solution-adaptive methods that both adapt the mesh and ascertain whether a given solution-adapted mesh is in the asymptotic regime, and 3) determine if SA and SV can be done separately, but synergistically.

Literature on the integration of solution-verification and solution-adaptivity is sparse, which indicates that the opportunity for integration remains open. Whether or not such integration can be achieved is unclear, but it is important for the community to attempt. The potential reward of achieving integration would be a clearer message and course of action available to practitioners in terms of fast, accurate, and credible numerical solutions to PDEs.

Summary of Accomplishments:

Solution adaptivity is one of the prime candidates for improving the efficiency of computations. Here we examined both mesh (i.e., h-refinement) refinement as well as order refinement (p-refinement), as well as their combination h-p refinement. Verification is an important activity for both demonstrating the correctness of code implementations in the case of code verification and estimating numerical error in the case of solution verification. Can the two combine to assist the creation of quality computations?

We discovered that the answer is a partial yes, but only if the adaptation is done properly. This requires the solution, or more precisely an error indicator defined by the solution, to guide the mesh refinement rather than preconceived notions of where the solution will be interesting. In the case with proper adaptivity, the solution is reliable and efficient. For example, using an adaptive solution in a pre-defined region of interest can result in an unreliable solution that could be improperly viewed as converged. Indeed, this approach will appear to be insensitive to further refinement, but in reality is not converged at all. On the basis of our findings, our guidance is to use the solution to guide the refinement *even if the region of practical interest is not refined*. The key is to keep the highest effective resolution where the solution has the greatest variability and therefore the largest error.

In order to put the work into proper perspective for Sandia we have examined recent applications of verification to applied mission focused thermal analysis. In both cases, several mesh refinements were available including the limited use of higher polynomial bases for approximation. Generally speaking, the applied analysis of thermal problems does not use the sort of metrics for which theoretical results exist such as normed error. Instead the analysis relies upon point values measured through embedded tracers in the simulated domain.

Significance:

Our examination of these cases yielded an important understanding of how these analyses should be conducted. We found that the measures used by analysts can be expected to converge properly if the adaptive mesh or basis is utilized properly and, just as importantly, we found characteristic behavior of non-convergence if improper refinements are used. This will impact analysts' ability to provide confident simulation-based results to a number of mission-related thermal analysis calculations, such as those relevant to heat transfer in power generation devices.

Cognitive Computing for Security

165613

Year 1 of 3
Principal Investigator: E. Debenedictis

Project Purpose:

We plan to implement a brain-inspired computing method with memristors for the purpose of computing securely. Cognitive computing and artificial neural networks have been studied as ways for a computer to duplicate the brain's "smart thinking", but timely issues in cyber security suggest a different goal may be important as well. This other goal may be to think (process information) without revealing information (secrets) upon which that thinking is based — such as an encryptor not revealing the key upon which the encryption is based. Artificial neural circuits duplicate to some extent the thinking in the brain, yet interrogation of prisoners to learn their secrets is not done by taking apart brains. So the security method for brains has a different basis than that basis in electronics.

The project will develop an artificial neural network based on a new nanoelectronic device called a memristor, creating a new type of computing with a different basis for security. This project is combining and reapplying activities from the fields of artificial intelligence and nanotechnology. Artificial neural networks have been studied mainly for the purpose of emulating the "smart thinking" of human brains. Most of this research has been done in simulation because neural networks are difficult to understand due to heavy intermixing of information. This project will target moderate complexity neural networks and will use the intermixing of information as a security advantage. Security advantages will be conferred both by the physical advantages of the memristor technology and the complexity of the neural circuits. A demonstration of physical security is essential in this project to both understand how practical implementations may be, and to understand the difficulty an adversary would face if they tried to extract information.

Situational Awareness of Topic Drift and Birth-Death in Cybersecurity

165614

Year 1 of 3
Principal Investigator: J. B. Ingram

Project Purpose:

Traditionally, most research in intrusion detection has been focused solely on network traffic data, presumably because mature software tools exist that make it easy to collect. Recently, however, software tools that collect host state data have matured to the point that allows large-scale collection. However, cyber analysts would currently have to analyze this voluminous data in a manual, time-consuming process through in-depth investigation of user-defined searches.

This project plans to increase situational awareness of cyberspace by using machine learning to automatically detect compromised hosts via analysis of host state. Our work will correlate low-level state (programs in memory, disk, registry keys, etc.) and behavior (e.g., network access patterns) to provide a holistic picture of a host's health. To allow analysts to comprehend and manage thousands of evolving host profiles, we combine analyst intuition with clustering and classification techniques (from Sandia and academia) that can recognize emerging concepts, track concept evolution, and retire defunct concepts. Awareness of changing concepts is important because machines evolve during normal operations (e.g., Microsoft software updates). Humans would perceive no semantic difference, but static classifiers would produce noisy alerts. Similarly, a novel concept may signal a zero-day cyber event.

The first stage in our pipeline is to extract host-level features and train per-host anomaly detection models that are sensitive to the normal behavior of the corresponding computer. Offline, alerts from anomalous machines are clustered for both analyst visualization and discovery of common anomaly categories. Classifier models are trained to triage new alerts into common categories or a default "unknown" category. Analysts provide meaning to "unknown" items, and this feedback improves both the anomaly detectors and classifiers.

Pipelines similar to ours have been built, but our distinguishing features include: host-specific data rather than network data, models contextualized to each host, and explicitly modeling the emergence, evolution, and cessation of concepts.

Sublinear Algorithms for In Situ and In-Transit Data Analysis at Exascale

165615

Year 1 of 3
Principal Investigator: J. C. Bennett

Project Purpose:

Post-Moore's law scaling is creating a disruptive shift in simulation workflows as saving the entirety of raw data to persistent storage becomes increasingly expensive. Consequently, we are shifting away from a post-process centric data analysis paradigm towards a concurrent analysis framework in which raw simulation data is processed as it is computed. This shift is introducing enormous research challenges for data analysis. Algorithms must adapt to machines with extreme concurrency, low communication bandwidth, and high memory latency, while operating within the time constraints prescribed by the simulation. Furthermore, input parameters are often data dependent and cannot always be prescribed. The study of sublinear algorithms is a recent development in theoretical computer science and discrete mathematics that shows significant promise in its potential to provide solutions to some of these fundamental issues. These algorithms find small portions of the input that reveal information about global properties of the input. We intend to design sublinear algorithms that efficiently perform in situ and in-transit analysis at extreme-scale. A concrete problem of focus is the sublinear computation of feature-based statistical summaries, a commonly used tool for applications like energy and climate. Extreme-scale scientific simulations are facing major roadblocks as compute capabilities are outpacing input/output (I/O) capabilities. The approaches of sublinear algorithms address the fundamental mathematical problem of understanding global features of a data set using limited resources. These theoretical ideas are directly aligned with practical challenges of in situ and in-transit computation in which vast amounts of data must be processed under severe communication and memory constraints. The study of sublinear algorithms is a recent development and there is no precedent in applying these techniques to large-scale, physics-based simulations. Any success in applying sublinear approaches for a tool like feature-based statistical summaries would likely lead to algorithmic improvements for many scientific High Performance Computing problems.

Strong Local-Nonlocal Coupling for Integrated Fracture Modeling

165616

Year 1 of 3
Principal Investigator: D. J. Littlewood

Project Purpose:

The purpose of this project is to formulate a mathematically consistent coupling approach for local and nonlocal models, to develop the corresponding numerical algorithms, and to deploy those algorithms in Sandia's Sierra/SolidMechanics simulation code. A key result of this work will be a fully integrated computational simulation tool for coupling peridynamics and classical finite element analysis. Combined analyses in which peridynamics is employed only in regions susceptible to material failure will enable analysts to utilize the unique failure-modeling capabilities of peridynamics while leveraging the broad set of classical finite-element modeling tools. Recent work in the literature on local-nonlocal coupling has failed to address key issues, including determination of mathematical bounds on numerical artifacts at the local-nonlocal boundary and algorithm design compatible with production analysis codes. Resolution of these issues, and the subsequent deployment of a local-nonlocal coupling scheme, will provide direct impact to Sandia in the form of an integrated fracture modeling capability.

We seek to develop a mathematically consistent formulation for local-nonlocal coupling that allows for full integration of peridynamics with classical finite element analysis. We will focus on two classes of coupling approaches. The first is comprised of blending methods. These are interface models that extend approaches currently employed for domain decomposition. The second class achieves local-nonlocal coupling in the context of a unified model by selective reduction of the peridynamic horizon. Coupling algorithms will be vetted in an open-source, collaborative software framework. A primary risk is that formulations will not be amenable to implementation in a production code. Prototype construction via Trilinos agile components will mitigate this risk by providing a proving ground for algorithm development. Coupling schemes will be validated through comparison against the perforation experiments of Borvik, et al., and the spallation experiments of Dandekar. A single coupling scheme, selected through analysis of the prototype software, will be implemented in Sierra/SolidMechanics.

Efficient Probability of Failure Calculations for QMU Using Computational Geometry

165617

Year 1 of 3
Principal Investigator: S. A. Mitchell

Project Purpose:

We consider the quantification of margins and uncertainties (QMU) problem of estimating probability-of-failure. These are ubiquitous safety and reliability calculations, but we focus on analyzing electrical device and circuit failures induced by hostile radiation environments for the Qualification for the Sandia Pulsed Reactor (QASPR). Xyce and Charon model complex electrical failure scenarios where "failure" arises from local voltage levels outside thresholds, shutoff times being too long, etc.

Calculating failure probabilities is much harder than computing means and variances over simulations. Challenges include large input uncertain parameter spaces (dimension > 10), small probabilities (<10-6), high cost per model run (hours on hundreds of CPUs), nonlinearity, and discontinuities. QASPR QMU milestones will likely be hampered by non-smooth and multimodal responses over 10-20 model parameters. Effective reliability methods must identify and characterize tiny critical subspaces in a vast parametric space, given highly restrictive simulation budgets.

We will develop new methods for exploring high-dimensional parameter spaces, based on our prototype concrete algorithm that solves simple problems, including some QASPR single-mode failures. We enumerate research directions that have been vetted and have promise to generalize this to harder problems.

Our new approach uses computational geometry to cut off wide swaths of space requiring no further exploration, and geometry-guided exploration of the remainder. These swaths are spheres and slabs around sample darts, where the function estimate is either entirely above or below some threshold. Our second geometric innovation replaces single point samples (0d-darts), with a hierarchy of flat subspaces called kd-darts (e.g., lines for k=1). Flat exploration can be made more efficient by exploiting a surrogate function's analytic form, our third major innovation. Flats are very good at intersecting (detecting) long and thin failure regions. This shape is typical of reliability calculations because parameters differ in significance. But even for cubical failure regions, initial mathematical analysis indicates that failure probabilities converge faster for kd-darts than point-based Monte Carlo sampling.

A Universal Quantum Transport Computational Capability for Cross-Technology Comparisons of Beyond-CMOS Nanoelectronic Devices

165618

Year 1 of 2
Principal Investigator: D. Mamaluy

Project Purpose:

As industry and academicians work to increase the speed of transistors by shrinking their size to nanometer dimensions with the gate lengths of 10 nm or less, conventional theories used to predict device behavior are becoming obsolete because they fail to account for quantum effects. Existing semi-classical Technology Computer Aided Design (TCAD) tools work only with conventional complementary metal-oxide-semiconductor (CMOS) devices, and while there is a significant effort in the computational nanoelectronics community to simulate a particular promising novel beyond-CMOS device, there is no common tool that would allow comparing the performance of different types of beyond-CMOS devices, such as ultra-scaled Si and III-V FinFETs, carbon nanotube field-effect transistors (FETs), graphene-based and other 2D material-based transistors, single-electron transistors or tunneling FETs. We plan to create a universal quantum transport simulator that will allow assessment and comparison, within a reasonable simulation time, of the performance of these different types of beyond-CMOS transistor technologies. The simulation tool will be based on a novel numerical method called contact block reduction (CBR) that was developed. The CBR method provides an efficient and accurate implementation of the Non-Equilibrium Green's Function (NEGF) formalism for quantum transport simulation that turns out to be significantly faster than other existing methods, as identified by independent reviews. The planned universal, state-of-the-art computational tool will allow predicting performances of both already existing and not yet experimentally studied nanodevices, performing their geometry and material/doping optimization and process variation analysis, thus helping to select the best design options for each beyond-CMOS technology type. Furthermore, the simulator will greatly aid in identifying, characterizing and comparing different novel nanodevice paradigms that can serve as the foundation for post-Moore's law computing. It will, thus, directly contribute to Sandia's mission to design and influence DOE exascale systems for scientific computing by helping to select the most suitable nanodevice paradigms for extreme scale computing systems.

Adaptive Multimodel Simulation Infrastructure (AMSI)

166140

Year 1 of 3
Principal Investigator: M. W. Glass

Project Purpose:

The purpose of this research is to create a simulation infrastructure to facilitate both the incorporation of proven legacy components to build single simulation scale-tasks and implementation of multimodel adaptive simulations. This infrastructure will leverage high-level programming techniques and variations on component-based techniques to facilitate the easy integration of legacy software components for use in the infrastructure. It will also provide support for dynamic management of multiscale simulation execution on high performance computing (HPC) machines, both managing the execution of individual scales and scale-tasks and easing the transfer/communication of scale-coupling data between simulation scales.

Runtime adaptation of the parallel execution space discretization/scale-task assignment will be accomplished through control functions and user-defined control algorithms operating on user-defined simulation/scale metadata. The control functions will be decentralized – local/hierarchical – in nature in order to avoid collective blocking/synchronization of processes executing separate scale-tasks. Removing the requirement of low-level programming expertise in order to construct simulations, domain-specific experts, and industry-level users will be able to re-use proven legacy software components in order to simulate the physical phenomena of importance to them. Further, the infrastructure aims to allow improved multiscale simulation performance through providing dynamic simulation-adaptation control functionalities.

The implementation of a massively parallel multiscale/multiphysics simulation requires expertise not only in the physical domain of interest, but also in parallel programming and software engineering. Incorporation of software components used in these simulations can require a great deal of expertise and effort. The successful development of this infrastructure will greatly reduce the efforts to implement massively parallel multiscale/multiphysics simulations and allow the reuse of legacy components.

This work is in collaboration with Rensselaer Polytechnic Institute (RPI).

Kernel and Meshless Methods for Partial Differential Equations

166141

Year 1 of 3
Principal Investigator: R. B. Lehoucq

Project Purpose:

The purpose of the project is to understand the use of kernel and meshless methods for partial differential equations (PDEs).

Efficient methods for solving partial differential equations and methods in image processing are at the core of a multitude of engineering and science problems, which are critical to a myriad of national security missions. For example, simulations of physical systems are often modeled by partial differential equations. Improved methods for solving partial differential equations will allow for more timely and rapid simulations, which are critical to many projects.

We anticipate that our results will offer new methods to improve the computation of solutions to numerical PDEs. We further anticipate that our techniques can be applied to the integral equations defining nonlocal peridynamic mechanics.

This work is in collaboration with Texas A&M University.

Enabling Bidirectional Modality Transitions in Collaborative Virtual Environments

166537

Year 1 of 3
Principal Investigator: K. M. Mahrous

Project Purpose:

Due to the time and cost of manufacturing, nearly all items, from metal casings to weapons to buildings are first designed virtually. Most collaborative engineering environments allow for the manipulation and visualization of these virtual designs through a 2D interface (e.g. computer monitor), which is an insufficient substitute for interacting with the model in 3D (regardless of scale). In a collaborative design process, this often makes it difficult to thoroughly review and discuss designs. This is exacerbated by geographically distributed teams.

This project aims to address this problem by enhancing the work done in Collaborative Virtual Environments (CVEs). Current CVEs focus on visual (2D or 3D) interactions with the design — enhanced CVEs incorporate haptic feedback via devices such as force-feedback gloves. We will explore this research direction further but also to take an entirely novel approach by introducing 3D materializers into the environment so that we can interact with cheap, quickly made, but still geometrically identical copies of objects. Furthermore, the ability of current CVEs to transform physical objects into virtual ones via 3D scanning algorithms will be extended to form a bidirectional pipeline that allows for a physical to virtual to physical sequence where the object can be modified in both forms — we deem this novel procedure the Multimodal Collaboration Pipeline (MCP).

This work is in collaboration with the University of California at Davis.

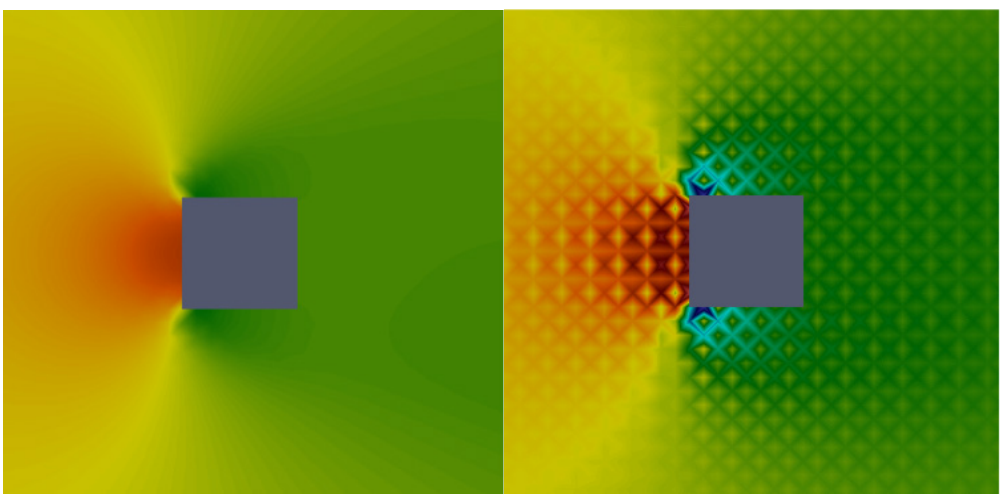
Current CVEs only allow for 3D scanning to convert physical objects into virtual ones, which necessitates that the engineer do most of the work in one of the two domains. By closing the gap and allowing for bidirectional modality transitions between the physical and virtual domains, we are creating a cutting-edge CVE with the potential to reduce manufacturing costs and design time. We aim to apply our findings to a novel engineering environment for designers, and the multitude of domains that require object scanning, reconstruction, or analysis via indirect means.

ENGINEERING SCIENCES

The Engineering Sciences Investment Area is revolutionizing and refining our understanding of complex engineered systems. The work involves theory development, experimental diagnostics, and computation and modeling to improve systems and bolster national security.

Engineering Sciences has a three-pronged approach to research. It works to increase the use and impact of computer simulation throughout Sandia. It delivers critical engineering analysis to meet design requirements. And, it takes a national leadership role in advancing engineering sciences. The work employs many strategies, such as addressing high-impact, coupled-physics simulations; integrating physical and computational simulation; and building partnerships with leaders in engineering sciences.

Engineering Sciences fosters knowledge across multiple topic areas including solid mechanics, fluid mechanics, structural dynamics, thermal and combustion sciences, aerodynamics, shock physics and energetics and electromagnetic sciences. It takes advantage of Sandia's large-scale test facilities, high-performance computing resources and sophisticated modeling, and simulation and visualization capabilities. It leverages corporate expertise in material sciences, nanosciences, and microsciences.



Pressure field created by flow over a blunt object demonstrating (left) pressure locking phenomena along the leading edge where solution gradients are under-resolved, and (right) amelioration of pressure oscillations with suitable pressure stabilization (Project 156251).

ENGINEERING SCIENCES

Quantifiably Secure Power Grid Operation, Management, and Evolution

151288

Year 3 of 3
Principal Investigator: J. Watson

Project Purpose:

This project will develop decision-support technologies to enable rational and quantifiable risk management for the key grid operational timescales.

Risk or resiliency metrics are foundational in this effort. The 2003 Northeast Blackout investigative report stressed the criticality of enforceable metrics for system resiliency—the grid's ability to satisfy demands subject to perturbation. However, we lack well-defined risk metrics and decision-support tools to address the pervasive uncertainties associated with renewables generation, which severely impacts efforts to rationally improve grid security.

For second-to-minute time scales, robust control systems must mitigate the impact of failure cascades, forming self-sustaining island network topologies to facilitate rapid service restoration. For day-ahead unit commitment, decision-support tools must account for topological security constraints, economic costs, and supply and demand variability, especially given high renewables penetration. For long-term planning, transmission and generation, expansion must ensure realized demand is satisfied for projected technological, climate, and growth scenarios. The time scales are tightly coupled and, consequently, must be studied in concert.

Our decision-support tools will analyze and enforce tail-oriented risk metrics for explicitly addressing high-consequence events. Historically, decision-support tools for the grid consider expected cost minimization, largely ignoring risk and instead penalizing loss-of-load through artificial parameters.

Our technical focus is the development of scalable solvers for enforcing risk metrics. We will develop advanced stochastic programming solvers to address generation and transmission expansion and unit commitment, minimizing cost subject to pre-specified risk thresholds. Despite significant promise, major algorithmic challenges remain to address regional and national grid scales. With renewables, security critically depends on production and demand prediction accuracy. We will use powerful filtering techniques for spatio-temporal measurement assimilation to develop short-term predictive stochastic models. Novel robust control algorithms will be developed to enforce risk thresholds for unit commitment and failure cascade mitigation. These algorithms currently and unrealistically (given renewables) assume tightly bounded uncertainties.

Summary of Accomplishments:

We developed and demonstrated the first algorithm capable of solving a key operations problem in the electricity industry (unit commitment) given explicit representations of uncertainty, in the required time scales (under 30 minutes). By considering uncertainty explicitly, we are able to significantly reduce the amount of generating reserves held by utilities, thus reducing cost and associated emissions. We were able to counter the uncertain nature of renewable wind and solar farm generation sources, and load as determined by the aggregate utility demand for power.

We initiated independent interactions with the DOE Federal Energy Regulatory Commission (FERC) and Texas A&M researchers to assess existing algorithms for solving the AC (alternating current) optimal power flow optimization model, or ACOPF. In contrast to the unit commitment problem, which is solved daily, optimal power flow is solved by electricity grid operators at least every five minutes of operation. Further, the ACOPF is a subproblem that is often found in other grid operations problems. Current algorithms for solving the ACOPF are inefficient, yield suboptimal solutions, or both. Our research to date has yielded improved algorithms for solving the ACOPF, both for the standard formulation of the problem and a more realistic variant that considers dynamical system behavior.

We developed a novel technique for characterizing the risk-versus-cost tradeoff in general optimization problems, using electrical grid generation expansion as an illustrative study. This technique enables decision makers to analyze and quantify the cost associated with a particular risk preference.

Significance:

Optimization problems are foundational in electricity grid operations and planning problems. In turn, the electricity grid is a foundational national security infrastructure. Improving electricity grid function through novel, advanced optimization algorithms impacts grid operators (utilities and independent system operators) by reducing production costs and emissions, providing more accurate and reliable expansion plans, and improving delivery reliability. The resulting algorithms advance the frontier of our ability to rigorously solve general optimization problems with significant non-linearity and uncertainty, impacting fields ranging from engineering science to logistics management. Results from this project formed the basis for a funded (FY 2013 and FY 2014) project from DOE's Advanced Research Projects Agency's Green Energy Network Integration (GENI) initiative, with the goal of maturing the developed algorithm and transitioning the technology to commercial vendors of electrical grid management software.

Refereed Communications:

Q. Wang, J.P. Watson, and Y. Guan, "Two-Stage Robust Optimization for N-k Contingency-Constrained Unit Commitment," *IEEE Transactions on Power Systems*, vol. 28, pp. 2366-2375, August 2013.

Z. Friedman, J. Ingalls, J.D. Siirola, and J.P. Watson, "Block-Oriented Modeling of Superstructure Optimization Problems," *Computers and Chemical Engineering*, vol. 57, pp. 10-23, October 2013.

C. Zhao, J. Wang, J.P. Watson, and Y. Guan, "Multi-Stage Robust Unit Commitment Considering Wind and Demand Response Uncertainties," *IEEE Transactions on Power Systems*, vol. 28, pp. 2708-2717, August 2013.

Predicting Structure-Property Relationships for Interfacial Thermal Transport

151289

Year 3 of 3
Principal Investigator: E. S. Piekos

Project Purpose:

Microsystems are a key component in a vast array of applications and impact most Sandia mission thrusts. Over time, microsystems designers have increased the number of material regions in a typical device while decreasing their spatial extent. From a thermal perspective, this trend increases the relative importance of interfacial transport compared to traditional bulk transport. Consequently, interfacial thermal transport is an increasingly important factor in numerous Sandia-developed microsystems, including high-power electronics, coolers for space-based sensors, microelectromechanical systems (MEMS), LED lighting, and thermoelectric power modules. Predictive tools are essential for characterizing existing designs during manufacture and operation, as well as for leveraging interfacial transport to enhance functionality in future designs.

Current models for interfacial thermal transport are inherently limited due to the nearly ubiquitous assumption of a perfect boundary. As a result, the transport is treated as an intrinsic material property, independent of interface structure, despite ample experimental evidence to the contrary.

We have worked to develop predictive tools for thermal transport through realistic interfaces. These tools provide experimentally validated structure-property relationships for nanostructural features, including boundary scattering and compositional intermixing. The tools were developed through a "bottom-up" computational approach, combined with systematic fabrication, disruption, and characterization of interfaces.

Interfacial thermal transport at imperfect boundaries is an inherently multiscale problem, with many interacting effects arising from the fact that lattice perturbations can extend over many unit cells and many types of defects can exist simultaneously. An organized inquiry places great demands on simulation, sample fabrication, microstructural characterization, and thermal transport measurement, all of which must be performed in close communication with one another to disentangle competing effects. Sandia's strength in these areas provided a unique opportunity to perform such an inquiry and to replace decades-old simplifications with validated physics-based models.

Summary of Accomplishments:

Over the life of this project, we have appreciably advanced the state of understanding in the mechanisms of thermal transport at material interfaces. We have provided a wealth of thermal conductance data, both measured and simulated via molecular dynamics, for a wide range of interfaces under varying conditions that will be used in developing new microsystem models by researchers and designers faced with representing interfacial transport effects.

Significance:

Thermal transport at interfaces is an increasingly important factor in microsystems designed for various national security missions, including high-power electronics, coolers for space-based sensors MEMS, sensors, LED lighting, and thermoelectric power modules. This project has provided models that can be used to improve the predictive power of design tools, thus increasing the likelihood of a successful design. Several publications have appeared in high-impact factor journals and garnered attention by notable members of the worldwide research community.

Refereed Communications:

J.C. Duda, T.S. English, E.S. Piekos, T.E. Beechem, T.W. Kenny, and P.E. Hopkins, "Bidirectionally Tuning Kapitza Conductance through the Inclusion of Substitutional Impurities," *Journal of Applied Physics*, vol. 112, p. 073519, October 2012.

R. Cheaito, J.C. Duda, T.E. Beechem, K. Hattar, J.F. Ihlefeld, D.L. Medlin, M.A. Rodriguez, M.J. Campion, E.S. Piekos, and P.E. Hopkins, "Experimental Investigation of Size Effects on the Thermal Conductivity of Silicon-Germanium Alloy Thin Films," *Physical Review Letters*, vol. 109, p. 195901, November 2012.

R. Cheaito, J.C. Duda, T.E. Beechem, K. Hattar, J.F. Ihlefeld, E. Piekos, A. Misra, J.K. Baldwin, and P.E. Hopkins, "The Effect of Ballistic Electron Transport on Copper-Niobium Thermal Interface Conductance," in *Proceedings of the ASME 2013 Summer Heat Transfer Conference*, HT2013-17541, 2013.

Physics-Based Multiscale Stochastic Methods for Computational Mechanics of Heterogeneous Materials

151291

Year 3 of 3
Principal Investigator: J. B. Lechman

Project Purpose:

Classical continuum models of transport in complex, heterogeneous systems (groundwater contaminant transport, charge carrier transport/storage in composite electrodes) frequently struggle to give reliable results, while detailed microscopic methods (molecular dynamics) are computationally prohibitive at large scales. However, it is often unrecognized that these systems exhibit related phenomena, which can serve as a unifying basis for a generalization of continuum mechanics beyond classical assumptions. Common features include long-range correlations and multiple overlapping/competing length and time scales that render the classical assumptions of scale separation and 'slowly' varying mass, momentum, and energy densities suspect. Recent developments in nonlocal models make it possible to relax classical continuity assumptions without sacrificing mathematical verification, computational feasibility or model validation. Hence, we seek nonlocal models that are thermodynamically and physically consistent at scales intermediate to the atomistic (micro) and component/process (macro) scales. As an archetypal heterogeneous material, we will develop a physically based, mesoscale, stochastic continuum model of colloidal suspensions (diffusive transport in random media).

Although recent effort has focused on spatial nonlocality in various systems, we will develop temporally nonlocal models in the framework of nonequilibrium statistical mechanics to connect meso- and macroscale continuum models to underlying microscopic dynamics and stochastic processes. This will capture inherently nonlocal phenomena (e.g., cooperative/correlated dynamics, or non-Fickian behavior). This is a novel approach that distinguishes Sandia's capabilities. Many researchers seek to capture these features through higher-order gradient expansions of relevant fields or through homogenization. We seek to capture nonlocal effects through integral equation formulations as opposed to partial differential equation-based models. A high-risk focus of this effort will be establishing the physical basis of the approach in terms of developing experimental techniques to access relevant length and time scales for validation of the model system results.

Summary of Accomplishments:

In this project, we have learned that self-diffusion of colloids in fluid dispersions, considered as an archetypal heterogeneous material, is well modeled by a generalization of the diffusion equation to a nonlinear Fokker-Plack equation. This equation is capable of capturing the non-Fickian transport (i.e., mean squared displacement of colloids not proportional to time) and the non-Gaussian nature of the particle displacement distributions. Both of these aspects are crucial to accurately resolve the stochastic aspects of the physical processes involved in the transport. We have demonstrated that the same type of model can be applied to thermal conduction through particle dispersions. This is a seemingly disparate application, but nonetheless one that is analogous in terms of the stochastic processes involved in the transport of energy. We have also learned that self-diffusion hard-spheres in inhomogeneous systems are similarly nonlinear, in that the diffusion constant appears to be dependent on the density of the particles. We have drawn the connection of these nonlinear models to so-called Superstatistics and Tsallis statistics in particular. These describe diffusion in a fluctuating or noisy environment. However, further work is required to make this connection more rigorous. Additionally, we have implemented a Generalized Langevin capability in the molecular dynamics code Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS). We have learned how these types of models can be obtained from velocity autocorrelation of interacting random walkers. Generalized Langevin equations are of interest, as they appear to be a potentially easier route to experimentally determine models for stochastic particle dynamics. To this end, we have built and demonstrated a Diffusing Wave Spectroscopy apparatus for measuring the mean squared displacement of dense colloidal dispersions.

Significance:

This project forms the basis of a generalization of traditional applied mechanics by bridging generalized stochastic process models to generalized continuum transport models. Specifically, we demonstrated a methodology for multiscale effects embedded in one continuum approach leveraging existing strengths in atomistic and coarse-grained materials modeling and high-performance computing for applications such as initiation of energetic materials, reliability of composite electrode energy storage devices, porous flow and others. Customers demanding high reliability and well-defined performance margins will potentially benefit from an increase in business capture success provided by these new methodologies.

Multiscale Modeling for Fluid Transport in Nanosystems

151294

Year 3 of 3
Principal Investigator: J. A. Templeton

Project Purpose:

Fluid transport processes at the nanoscale play an important part in the performance of many nanosystems, such as Li-ion batteries, supercapacitors, and gas-phase detectors. A commonality in these devices is that they often consist of nanoscale components (interfaces, pores, etc.) connected to a much larger bulk reservoir system. Interaction with the bulk critically affects the performance of the nanosystem since the same fluid exhibits different behavior at different scales via high concentration gradients and chemical reactions. Two-way feedback between these scales is required to accurately predict system response. For example, the high voltage double layers that form in electrical energy storage devices deplete the electrolytic ion concentration, thereby modifying the transport to the double layer. Capturing this feedback is complicated because different simulation approaches are required for the nanoscale features and the bulk flow. Atomistic simulation can model the complexity of nanodevices, but is intractable for the bulk. Therefore, the bulk must be resolved using macroscale simulation approaches (e.g., finite elements). New algorithms are needed to accurately account for time dependent mass, momentum, and thermal transport between these two regions while capturing all the physics needed for accurate device simulation, including electric fields and chemistry.

Summary of Accomplishments:

This project created novel theories and numerical methods for coupling atomistic descriptions of fluids with finite element models of transport processes. Our first discovery was that existing time integration methods were not sufficiently stable for this task. We, therefore, designed a new integrator based on the fractional step method, which greatly increased the robustness of simulations. We also developed the first, to the best of our knowledge, computational coarse-graining theory from molecules to continua as well as an efficient parallel algorithm for computing it in the molecular dynamics code Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS). The theory was applied to electric double layers in which we were able to quantitatively decompose the system in the Stern and diffuse layers. A new spatial control algorithm for molecular dynamics was designed, which can simultaneously maintain multiple species concentrations, velocities, and temperatures at desired levels. The method was used to enable uncertainty quantification studies of salt water flow through a silica nanopore. We then generalized the velocity and temperature coupling to function within the finite element (FE) coupling framework to model electrokinetic flows. In doing so, we learned that the standard Navier-Stokes momentum equations are inappropriate at this scale and for this coupling method. Therefore, we derived an FE model for fluctuating hydrodynamics to use within our framework. To allow for more accurate coupling between atoms and electric fields, we derived several new types of boundary conditions, including free-space boundary conditions and material-specific electrode boundary conditions, both of which couple to the atoms through an FE electric potential solver.

Significance:

Our results enabled new types of simulations to be performed that can advance current scientific understanding and engineering practice. They are directly appropriate to improve modeling of batteries and super-capacitors because the atomic motions, which are critical at electrolyte/electrode interfaces, can be captured with high fidelity and less expensive FE models can describe the bulk transport processes. Addition of the electric field with boundary conditions coupled to the atoms is a distinguishing capability that has been implemented into the

AtC package associated with the LAMMPS molecular dynamics simulator and released as open-source code to impact a broad community. The methods can also enable more accurate simulation of micro- and nanofluidic devices, which are an important component of many chemical detectors.

Refereed Communications:

F. Rizzi, R.E. Jones, B.J. Debusschere, and O.M. Knio, "Uncertainty Quantification in MD Simulations of Concentration Driven Ionic Flow through a Silica Nanopore. II. Uncertain Potential Parameters," *The Journal of Chemical Physics*, vol.138, p. 194105, May 2013.

F. Rizzi, R.E. Jones, B.J. Debusschere, and O.M. Knio, "Uncertainty Quantification in MD Simulations of Concentration Driven Ionic Flow through a Silica Nanopore. I. Sensitivity to Physical Parameters of the Pore," *The Journal of Chemical Physics*, vol. 138, p. 194104, May 2013.

K.K. Mandadapu, J.A. Templeton, and J.W. Lee, "Polarization as a Field Variable from Molecular Dynamics Simulations," *The Journal of Chemical Physics*, vol. 139, p. 054115, August 2013.

Integrated Nano- and Quantum Electronic Device Simulation Toolkit

151297

Year 3 of 3
Principal Investigator: E. Nielsen

Project Purpose:

The next generation of semiconductor devices will have to confront quantum mechanical effects, including phenomena to be avoided, such as gate leakage, as well as new behavior that can be harnessed, such as entanglement. Few electron nanodevices have been developed to use entanglement in quantum computing and sensing beyond the traditional quantum limits, but the resulting entangled device states are extremely sensitive to atomic scale effects that are not traditionally considered in nanoelectronics modeling. The community is presently without a multiscale simulation capability that appropriately captures how atomic scale phenomena propagate through to the mesoscale device physics.

To describe these devices, we need to enhance existing device simulators in several ways. Quantum mechanical effects must be accounted for by solving the coupled system of the Schrodinger and Poisson equations. Where atomic-scale effects, such as the multiple valleys in silicon, are important, tight binding solutions for electronic wave functions are necessary for predictive simulations. Furthermore, in systems with many electron-excited states, configuration interaction techniques are needed to properly capture multielectron wave functions.

We propose developing a suite of simulation tools that includes Schrodinger-Poisson, tight binding, and configuration interaction capabilities, and thereby addresses current and future issues critical to simulating quantum-scale electronic devices.

Summary of Accomplishments:

We developed a simulation tool capable of performing semiclassical and quantum mechanical calculations on realistic 3D devices. We demonstrated the correctness of the tool by comparison with existing numerical tools and with analytically solvable problems. This Quantum device Computer Aided Design (QCAD) tool has been proven useful for the design and analysis of double quantum dot devices intended to form quantum bits.

Significance:

We developed a simulation toolkit with increased speed and capability over existing tools, which have enabled an unprecedented amount of theoretical analysis of solid-state quantum devices. This project has accelerated the design of solid-state quantum devices and the analysis of results from such devices. This has led to an understanding of the fundamental physics and engineering governing solid-state quantum devices. This project was relevant to the DOE's mission of scientific discovery and innovation.

Interface-Tracking Hydrodynamic Model for Droplet Electro-Coalescence

155327

Year 3 of 3
Principal Investigator: L. C. Erickson

Project Purpose:

Many fluid-based technologies rely on electrical fields to control the motion of droplets (e.g., microfluidic devices for high-speed sorting of water droplets in oil or for purifying biodiesel fuel). Precise control over droplets is crucial for these applications. However, electric fields can induce complex and unpredictable fluid dynamics. For example, oppositely charged water drops immersed in silicon oil experience attractive forces that favor their coalescence. Recent experiments with high-speed cameras (Ristenpart, et al., 2009) demonstrate the counter-intuitive behavior that these oppositely charged droplets bounce rather than coalesce in the presence of strong electric fields. A transient aqueous bridge forms between approaching drops prior to pinch-off. This observation applies to many types of fluids, but neither theory nor experiments have been able to offer a satisfactory explanation. Analytic hydrodynamic approximations for interfaces become invalid near coalescence; therefore, detailed numerical simulations are necessary. This is a computationally challenging problem that involves tracking a moving interface and solving complex multiphysics and multiscale dynamics, which are beyond the capabilities of present simulations. An interface-tracking model for electro-coalescence can provide a new perspective to a variety of applications in which interfacial physics are coupled with electrodynamics, including electro-osmosis, fabrication of microelectronics, fuel atomization, oil dehydration, nuclear waste reprocessing and solution separation for chemical detectors.

Accurate and stable interface-tracking methods capable of capturing and predicting coalescence and break-up of interfaces are currently a major challenge in the computational science community. The inclusion of electric forces poses a further challenge due to the complexity of electrostatic and hydrodynamic interactions involved in coalescence, requiring a novel modeling approach to understand this phenomenon. This project entails the creation of an interface-tracking model using the advantages of the Conformal Decomposition Finite Element Method (CDFEM) with the capability to reproduce experiments and make predictions for future experiments.

Summary of Accomplishments:

The final report from this project has been completed and a journal article is in preparation for submission to *Journal of Computational Physics*. This work has been presented externally at the American Physical Society Division of Fluid Dynamics (November 2012) and at US National Congress on Computational Mechanics (July 2013). In addition, we have implemented code changes to support electrohydrodynamic flow problems in Sierra/Aria with applications for lab on a chip technology, purifying biodiesel fuel, and high throughput droplet sorting devices. These code changes have been documented and are available in the Aria User's manual. We have also created and documented verification problems with analytical solutions for the new models created to the code as part of this project. We validated our method with experimental results in the literature and made suggestions for improvements to the model. One of these ideas was the use of shell elements along the interface on which charge density could be tracked in order to more accurately capture the charge transfer dynamics between an insulating fluid and a conducting fluid. We analyzed the advantages and disadvantages of Arbitrary Lagrangian-Eulerian (ALE) methods versus traditional diffuse level set methods compared to the CDFEM. We derived the set of equations required to solve multi-phase electrohydrodynamic problems involving droplet coalescence and analyzed the parameter regimes to distinguish which assumptions are appropriate for our modeling purposes. We also investigated the possibility of combining LAMMPS with SIERRA to create a dissipative particle dynamics (DPD) mesoscopic coupled version of the code in order to treat the aqueous bridge at contact more closely (FY 2012).

Significance:

This project has advanced Sandia's internal simulation capability for modeling multiphase electrohydrodynamic fluid problems. This interface-tracking method is a useful tool for predictive simulations with applications in electro-osmosis, lab on a chip sensor technology, fuel atomization, and biodiesel fuel purification. It is applicable to Sandia's core nuclear weapon, defense, homeland security and energy security missions, impacting technologies such as sensors, fuel cells, batteries, and microsystems fabrication for NW. Our verification and validation studies demonstrate the capability of the model. This project has also helped improve the capability of CDFEM, which is a versatile method for a wide range of multiphase simulations.

Softening Behavior of Post-Damage Quasi-Brittle Porous Materials

155798

Year 3 of 3
Principal Investigator: T. J. Fuller

Project Purpose:

The state of the art in vulnerability assessment of shock and blast loaded components requires tracking material behavior through failure, to the point of fragmentation and beyond. Due to large pressures during initiating events, it is also necessary to have an accurate equation-of-state representation of the material's hydrostatic response. Coupling a material's damage response with the equation-of-state response is made particularly challenging for porous quasi-brittle materials such as concrete, ceramics, rock, etc., which exhibit dilatant inelastic flow in response to shear dominated deformation. Unlike metals, these materials develop large mean stresses during shear-dominated loadings. Coupling the large mean stresses predicted by the material model and the associated changes in density with the equation of state presents a number of challenges, in addition to known challenges associated with the loss of hyperbolicity of the governing equations, as a result of material softening.

The core of the proposed research is the development of a softening model that couples the constitutive response with the host finite element code's equation-of-state routines and void insertion and fracture models. Currently, when softening and damage develop in a material, shock hydro codes use iterative procedures to couple the constitutive response with that of the equation of state. The density and strain rate sent to the constitutive model are modified such that the mean stress from the constitutive model and the pressure from the equation of state are equivalent. Modified densities imply void insertion and fracture, independent of the constitutive response. Rather than employ an iterative procedure outside of the constitutive model, we seek to develop a scheme whereby the constitutive model informs the finite element code of fracture initiation and void insertion. The research will be performed in the ALEGRA finite element code due to its applicability to shock and blast loading.

Summary of Accomplishments:

A key focus of this project was the development of constitutive softening routines in the Kayenta material model and integration of those routines in the ALEGRA finite element code. As a result of this project, we developed several new technologies that have since been deployed at Sandia:

1) New algorithms were implemented in the Kayenta material model, incorporating a high-pressure equation of state in a thermodynamically consistent manner.
2) Kayenta has been deployed in the Sierra SM suite of tools including integration with the multi-level control failure algorithms.
3) Equation-of-state and damage routines in Kayenta were fully integrated in release versions of the ALEGRA finite element code.
4) Improved descriptions of material damage and softening were developed, including a novel spall failure criterion.

5) New forms of fitting functions for elastic moduli were implemented and orthotropic jointing capabilities enhanced.The new technologies implemented in ALEGRA, in particular, have been instrumental to scientists at the Army Research Lab in designing ceramic armor systems.

Significance:

Tracking material behavior beyond the point of failure and fragmentation is critical for reliable vulnerability assessments of shock and blast loaded components. The technologies developed and deployed as part of this project provide tools for making such assessments. Questions were answered concerning stability of solution methods in Eulerian shock-hydro codes and doors have been opened for further critical assessments of the interaction of material softening with host finite element codes.

Successful outcome of this research will enable simulation of a broad class of problems ranging from those dealing with vulnerability of infrastructure or the integrity of the underground.

Developing Highly Scalable Fluid Solvers for Enabling Multiphysics Simulation

156251

Year 3 of 3
Principal Investigator: J. Clausen

Project Purpose:

Computing hardware is trending towards distributed, massively parallel architectures in order to achieve high computational throughput. For example, Cielo will use 43,104 cores and Intrepid at Argonne uses 163,840 cores. Next-generation machines will continue this trend, with Sequoia at Lawrence Livermore using 1.6 million cores. This project will develop a fluid simulation algorithm based on artificial compressibility (AC) that is capable of scaling on massively parallel architectures.

Traditional incompressible-flow solvers are based on the incompressible Navier-Stokes (NS) equations, in which the continuity equation acts as a constraint imposing a divergence-free velocity field. In this case, no direct coupling of pressure to velocity exists requiring an implicit solution. The fully coupled finite-element (FE) schemes currently used at Sandia scale to only O(100) processor cores. As an alternative, fractional step (FS) methods such as the popular pressure correction method gain some scalability; however, they must still solve a Poisson equation for the pressure field, which creates a high communication load between processors resulting in poor scalability at O(10,000) processors. An explicit FE method based on AC will allow for a local update procedure resulting in excellent scalability on O(100,000) processors. However, as originally formulated, the AC method shows transient errors that must be addressed. The proposed solution uses a recently derived reformulation of the NS equations to eliminate these errors while retaining an explicit formulation.

Summary of Accomplishments:

We have developed an extension to the standard AC techniques called the Entropically Damped Artificial Compressibility (EDAC) method. This method uses a new thermodynamic constraint in order to form a modified pressure evolution equation to use in place of the continuity equation. The original AC formulation enforces isentropic behavior, which is undesirable since it minimizes dissipation of acoustic pressure waves. These pressure waves are entirely numerical and undesirable. The EDAC method, in contrast, is not isentropic and serves to damp out the pressure fluctuations created through the introduction of a small, but finite, amount of compressibility.

To demonstrate the massive scalability of EDAC methods, a scalability study was undertaken on the Sequoia supercomputer. Scalability is shown to over one million cores.

Despite their attractiveness, fully explicit methods have significant limitations, namely the time step limitations due to diffusion, acoustic wave propagation, and convection. As such, these methods excel in transient simulations where time accuracy requires time steps on the order of the stability limits. Examples include turbulent direct numerical simulation (DNS) and suspension and multiphase flows. Whether explicit methods can become competitive with traditional implicit-based methods remains an open research question.

Significance:

This project investigated a potential fluid solver capable of scaling with Sandia's increasingly parallel computational resources. Despite the uncertainties, the benefits of a scalable fluid solver will impact several areas at Sandia. This impact is most important in problems where high temporal resolution is required, for example suspension and emulsion flows, thermal convective flows, melt flows, and fluid–structure interaction. Advanced fluid simulation capabilities are integral to maintaining the viability and safety of the nuclear weapons stockpile. The highly scalable methods developed are required to leverage the increasingly parallel computational platforms used by Sandia and the NNSA in pursuit of this mission. Owing to the ability of the EDAC method to scale to such large core counts, the Scientific Applications and User Support group at Sandia plans to use the code in the future to evaluate performance and scalability of hardware and software stacks on various clusters around DOE including Sequoia and Cielo.

Refereed Communications:

J.R. Clausen, "Entropically Damped Form of Artificial Compressibility for Explicit Simulation of Incompressible Flow," *Physical Review E*, vol. 87, p. 013309, January 2013.

Simulation of Primary Fuel Atomization Processes at Subcritical Pressures

156703

Year 3 of 3
Principal Investigator: M. Arienti

Project Purpose:

New biofuel formulations and modifications in engine design toward high efficiency and low emissions require better predictive computational capabilities — a need Sandia has responded to with increasingly sophisticated combustion codes. However, the distribution of fuel spray near injection must provide the correct boundary conditions to these codes. Direct observation of fuel atomization is difficult: nozzles are typically about a millimeter long and a fraction of a millimeter in diameter, and the flow moves at speeds on the order of several hundred meters per second. The fact that the fuel can partially vaporize in the nozzle adds another level of complexity. Overall, the understanding of the physics that controls the fuel/air distribution of many combustion devices, particularly at high pressure, is quite limited. The proposed effort aims at a greater insight on aspects of this complex physics.

The project explores the fuel subcritical behavior (in temperature) in the liquid core and dense spray regions. It is numerical in nature and provides an improved understanding of the early stages of fuel atomization (primary atomization), as well as the capability to guide future experiments and diagnostics development. Currently, external (with respect to the injection nozzle) simulations of primary atomization can be carried out with simplified inlet conditions. Conversely, internal flow calculations with vapor bubbles formation and flow separation are stopped at the nozzle orifice. Neither of these two capabilities is currently available at Sandia, which justifies another project on this topic. The innovating element of the project is in allowing the coexistence of liquid, vapor and gas in the same multiscale calculation of high-pressure flow. The coupling between orifice and external flow is crucial in capturing the pressure feedback from the combustion chamber to the fuel nozzle and, because of the high non-linearity of combustion, it will substantially improve the predictive power of engine simulations.

Summary of Accomplishments:

We developed a first-principles capability (no sub-grid models) where the internal and external flows involved in primary atomization are seamlessly calculated across the injection hole. To this end, the combined level-set volume-of-fluid (CLSVOF) method for the free liquid surface was combined with a second level-set function for the solid wall boundary. Assuming no cavitation, validation was carried out with measurements of a scaled-up, transparent, six-hole Diesel nozzle. Flow field features of the internal flow were linked to the size distribution of the spray outside the injector. The capability of simulating the opening and closing motion of the needle — an essential element in understanding the transient dynamics of Diesel spray — was demonstrated using the “spray A” database from the Engine Combustion Network.

We also tested the extension of the incompressible multimaterial pressure solver to an all-velocity formulation: a momentum-conservative semi-Lagrangian advection algorithm enables the treatment of large density ratios, while the addition of a compressible term in the Poisson’s equation results in an efficient shock-capturing capability without recourse to the Godunov formulation. Density advection is carried out for each material separately, satisfying strict mass conservation requirements. A simulation can be set up based upon material compressibility (and in that case, what its equation of state is) or incompressibility. This arrangement is convenient in many liquid-gas simulations when only the gas phase needs to be treated as compressible, while signal transmission in the liquid can be ignored. A simulation of Diesel fuel injected at velocity larger than the sound speed of the gas phase — causing a leading oblique shock followed by several weaker acoustic waves — was successfully demonstrated. The time evolution of the transient fuel spray was compared with synchrotron x-radiography, showing good qualitative agreement in the strength of the leading shock.

Significance:

This study has contributed to advancing the state of the art in predictive simulation of fuel/air distribution in internal combustion engines. This aspect is critical in achieving fuel efficiency and is, therefore, relevant to DOE's energy security mission. Simulation results will be leveraged in current efforts to establish collaborations with the automotive industry. Besides engine applications, the introduction of compressibility in a code that can track multiple sharp interfaces is a unique asset that enables, for instance, the study of flow behavior in a disruptive environment or in two-phase heat transfer.

Refereed Communications:

M. Jemison, E. Loch, M. Sussman, M. Shashkov, M. Arienti, M. Ohta, and Y. Wang, "A Coupled Level Set-Moment of Fluid Method for Incompressible Two-Phase Flows," *Journal of Scientific Computing*, vol. 54, pp. 454-491, February 2013.

M. Arienti, X. Li, M.C. Soteriou, C.A. Eckett, M. Sussman, and R.J. Jensen, "Coupled Level-Set/Volume-of-Fluid Method for Simulation of Injector Atomization," *Journal of Propulsion and Power*, vol. 29, January 2013.

Accurate Model Development for Large Eddy Simulation of Turbulent Compressible Flow Problems

158482

Year 3 of 3
Principal Investigator: M. Howard

Project Purpose:

Accurate simulation of turbulence is vital for predicting complex physical flow behaviors. Turbulence spans a large range of time and length scales and capturing all of its effects is difficult. Direct Numerical Simulation is too computationally intensive for high Reynolds number problems. Reynolds averaged Navier-Stokes simulations are less accurate and often inapplicable to many problems. Large Eddy Simulation resolves the predominant flow features and models the smaller scale turbulence. Of these approaches, it is clear that Large Eddy Simulation (LES) offers the best promise, but several significant challenges exist for compressible problems. Appropriate subgrid scale modeling is an open area of research, especially for supersonic flows. Higher-order accurate numerical methods are essential for reducing discretization error. The interaction of the subgrid scale model and the discretization method is also an important factor that is not fully understood. The investigation of these areas requires an efficient and scalable algorithm and poses significant challenges for accurately predicting complex turbulent compressible flows.

This research effort is motivated by the assertion that a systematic investigation of hybrid structured-unstructured discretization methods and low-dissipation flux schemes, and the interactions between the two, combined with a focus on accuracy and scalability, enabling a LES capability that surpasses existing limitations for solving turbulent compressible flow problems of national interest. We proposed to rigorously identify the defining theoretical and numerical features of a successful LES scheme, and then develop a state-of-the-art capability for accurate LES of compressible flows. Several structured and unstructured spatial discretization methods as well as implicit, explicit, and hybrid time integration techniques were explored, enabling us to make broad assessments about discretization characteristics that few existing research efforts have addressed. Determining the merits of each discretization feeds directly into investigating appropriate filtering techniques, subgrid scale models, discretization errors and their interplay for this class of flows, all open and poorly understood topics.

Summary of Accomplishments:

This research began by designing, implementing and testing two different unstructured finite volume discretizations and several inviscid flux functions on canonical problems of interest that are relevant to unsteady turbulent compressible flows. This work was directed at investigating flux functions that obey secondary conservation, such as the preservation of kinetic energy or entropy. We learned that low-dissipation flux schemes are essential to accurately solving this class of flows, and that the grid quality and structure play a tremendous role in achieving this. Even low-dissipation flux schemes perform poorly on truly (but still high quality) unstructured grids. Based on this discovery, we investigated the use of structured grid methods and pursued a hybrid structured-unstructured finite volume method. The realization was made that a hybrid method allows for higher-order spatial accuracy with low-dissipation, secondary conservation flux schemes in regions that are amendable to structured grids while still allowing for unstructured grid methods to be used in geometrically complex regions. Several bottlenecks were encountered while developing a hybrid capability due to the fact that structured grid methods have not generally been accepted at Sandia, so common tools such as a mesh format that supports both structured and unstructured grids and structured grid partitioners are not available. Ultimately, we pursued a hybrid structured-unstructured finite volume method that allows for higher-order spatial accuracy and uses low-dissipation, secondary conservation flux schemes. This offers a "best of all worlds" capability that will enable accurate direct numerical simulation (DNS), LES, and hybrid Reynolds averaged Navier-Stokes (RANS)-LES simulation of complex turbulent compressible flow problems.

Significance:

The ability to accurately predict high-speed turbulent compressible flows greatly impacts DoD and DOE/NNSA national nuclear security missions. The current state of the art in predictive capabilities for problems in some flow regimes does not produce high enough fidelity to accurately capture the physics for qualification purposes. This research developed a capability that establishes Sandia as a leader in computational methods for accurate prediction of turbulent compressible flow phenomena and will directly impact ongoing and future stockpile Life Extension Programs (LEPs).

Electromagnetic Extended Finite Elements for High-Fidelity Multimaterial Problems

158795

Year 2 of 3
Principal Investigator: C. Siefert

Project Purpose:

Surface effects are critical to the accurate simulation of electromagnetics (EM), as current tends to concentrate near material surfaces. Sandia EM applications include exploding bridge wires for detonator design, electromagnetic launch of flyer plates for material testing and gun design, lightning blast-through for weapon safety, electromagnetic armor, and magnetic flux compression generators for various NNSA and DoD applications. These applications operate in a large deformation regime, where body-fitted meshes are impractical and multimaterial elements are the only feasible option. State-of-the-art methods use various mixture models to approximate the multiphysics of these elements. The empirical nature of these models can significantly compromise the accuracy of the simulation in this very important surface region. We propose to substantially improve the predictive capability of electromagnetic simulations by removing the need for empirical mixture models at material surfaces.

Highly accurate edge-based (compatible) discretizations form the basis for EM simulations at the NNSA labs, as they correctly respect the underlying physics. Unfortunately, there is no edge-based method that allows for resolution of subelement material interfaces. Our goal is to build a physically realistic EM scheme that resolves these critical subelement material surfaces. We propose to adapt ideas from the eXtended Finite Element Method (XFEM) to edge-based discretizations. The XFEM makes discontinuities at a subelement level possible, but has only been developed for nodal discretizations. Realizing our goal requires the development of: 1) a novel edge-based technique to enforce the appropriate continuity conditions across material boundaries within an element, 2) implementation of the technique, 3) a novel, fully implicit linear solver capability to solve the resulting equations, and 4) a novel way to preserve XFEM quantities through large deformations (remap). Sandia has the necessary expertise in XFEM, edge-based discretizations, and solvers.

Ultrafast Laser Diagnostics for Energetic Material Ignition Mechanisms: Tools for Physics-Based Model Development

158801

Year 2 of 3
Principal Investigator: S. P. Kearney

Project Purpose:

Despite its importance, a fundamental description of initiation in energetic materials has eluded researchers for decades, in large part because ignition results from mechanical and thermochemical mechanisms that are tightly coupled at extreme spatial and temporal scales of order microns and picoseconds. Access to these extreme time and length scales under dynamic loading conditions has, until recently, been restricted to simulations, and experiments to underpin the relevant physics are sorely needed to provide model developers with an appropriate physical foundation. The recent availability of femtosecond laser sources has opened the door to fundamental experiments with the required extreme resolution, and well-controlled measurements on the early time effects of shock drive have been reported. These experiments have largely been limited to homogeneous materials, while the majority of explosives of interest — both ideal and improvised — are heterogeneous in composition, with material microstructure effects that are absent in homogeneous samples, but which can dominate the response in many real explosives.

We propose two significant leaps forward: 1) development of new capabilities for controlled small-scale shock-drive experiments on heterogeneous samples and 2) development of state-of-the-art ultrafast laser-diagnostic approaches for spatially correlated imaging and spectroscopy on a single-laser-shot basis with extreme picosecond- and micron-scale resolutions. The new diagnostic capabilities will extend the time-duration of laser-shock-drive experiments into realms never before considered. We will advance the science of ultrafast imaging and spectroscopy for elucidation of the mechanical and thermochemical response of energetics to shock drive in well-controlled experiments on dynamically loaded heterogeneous materials. The measurements will provide new physical insight into the initiation process and provide fundamental data of interest to molecular-dynamics and mesoscale modelers. More significantly, these capabilities will yield the first resolved-scale measurements of mesoscale phenomena to enable breakthroughs in modeling of shock-induced ignition of abundant heterogeneous explosives.

Effect of Varying Convection on Dendrite Morphology and Macrosegregation

158803

Year 2 of 3
Principal Investigator: J. D. Madison

Project Purpose:

This work is in collaboration with the University of Arizona and Cleveland State University and is being established to 1) understand the effects of melt convection and shrinkage flow on dendritic microstructure, and 2) examine and model alloy macrosegregation during directional solidification. Microstructural morphology determines important macroscopic properties, therefore, enhanced control of microstructures are of economic importance in directionally solidified castings used in aerospace, power generation and other industries. Initially, research will examine microstructural changes caused by varying thermal gradients and differing solidification rates under both microgravity and normal gravitational conditions. It is anticipated that samples solidified under microgravity will produce microstructures practically free from the influences of convection, providing control cases in which the influence of convection can be reduced, if not eliminated, and be experimentally and subsequently modeled. Later research will focus on the effects of changing the cross-sectional sample area and the resulting changes in convection, shrinkage flows, and microstructural morphologies. These experiments will be carried out under normal gravitational conditions, and pending funding, under microgravity. The alloys used in these experiments will be Al-Si and Al-Cu, both of which are of commercial importance. The novel approach here is in the attempt to grow relatively large samples of dendritic alloy, free from the effects of convection with minimized shrinkage flows for comparison against gravitationally processed samples. In addition to characterization, experimental results will be compared to established solidification models with and without convective effects. This work is additionally innovative in that tools will be developed for furthering these types of investigations, such as techniques formation the automated extraction of composition and morphology from micrograph images, direct comparison of solidification models with experiment, and the extraction of convection and shrinkage induced melt velocities as well as the quantifying and isolating other convective effects which would be otherwise unattainable.

Next Generation Suspension Dynamics Algorithms

158805

Year 2 of 3
Principal Investigator: P. R. Schunk

Project Purpose:

The goal of this project is to refine and apply next-generation algorithms for the simulation of dense suspensions of colloidal particles from the nanoscale through micron size particles. The challenge is to conduct mesoscale simulations for tracking the motion and self-assembly of individual nanoparticles while accurately accounting for hydrodynamic interactions, stochastic Brownian forces, and interparticle forces. The algorithms must be scalable with O(Np) ops to facilitate simulations with several thousand particles, and fast enough to resolve long diffusive time scales for self-assembly and phase transitions. The long time scales require the efficiency of the mesoscale simulation algorithms. To resolve the relevant physics of self-assembly and phase transitions, suspensions of monodisperse spheres require particle counts O(1000), while suspensions of anisotropic particles or polydisperse spheres require significant larger systems. To meet these needs, we have developed the fast lubrication dynamics (FLD) algorithm, which provides excellent performance for prediction of physical phenomena while offering superior computational speed relative to competitive algorithms such as accelerated Stokesian Dynamics (ASD), dissipative particle dynamics (DPD) and stochastic rotation dynamics (SRD). Current extensions under way adapt these algorithms to nonperiodic systems and rigid system boundaries.

With a high performance FLD algorithm with proper verification and validation and scalability to large-scale computational clusters at Sandia, we will have a powerful tool for the analysis and development of novel nanostructured suspensions and materials. These algorithms are capable of tracking the dynamics of self-assembly and guided assembly of nanoparticle structures and provide an invaluable tool in developing synthesis strategies for novel nanomaterials. These materials are at the heart of numerous laboratory thrusts to address national needs in energy storage, energy conversion devices and energetic materials. This work is in collaboration with University of Illinois at Urbana-Champaign.

Multiscale Modeling of Brittle Heterogeneous Materials

158806

Year 2 of 3
Principal Investigator: T. Vogler

Project Purpose:

Heterogeneities and the mechanisms governing deformation in engineering materials often exist at length scales much finer than the engineering scale. Concrete is a good example. It possesses heterogeneities over many length scales while engineering structures are on the scale of meters. The scale of reinforcing phases such as aggregate and steel fibers is typically termed the mesoscale in concrete. Modeling at this scale is a methodology for understanding the role of microstructure during deformation, fracture, and failure. This scale is of particular interest due to the interfacial transition zone that exists between the cementitious matrix and the reinforcement, which typically acts as a crack nucleation point.

Peridynamics is used to capture plasticity, strain softening, and fracture of bulk phases. Peridynamics offers two distinct advantages over classical continuum models that rely on local balance laws: 1) peridynamics does not rely on derivatives of the displacement field and, therefore, the discontinuities inherent to cracks can be included in a mathematically consistent manner and 2) as a nonlocal theory, it is well suited to problems involving localization of plastic deformation and strain softening.

This project, in collaboration with Georgia Tech, studies the behavior and failure of ultra-high performance concrete (UHPC) under high-rate impact and penetration, using a multiscale approach capturing mesoscale deformation mechanisms to generate more accurate engineering-scale computations. Ordinary, pressure-dependent peridynamic plasticity has been formulated to more accurately model materials on both scales. Fine sand aggregate, steel fibers, and porosity are explicitly modeled at the mesoscale. We will determine the effect of reinforcement size and volume fraction and the optimal material configurations. The work will serve as a basis for the development of new modeling and future multiscale materials-design approaches. This problem has not been solved by current science and technology due to both the computational demand and lack of appropriate constitutive theories to accurately address the problem.

Heterogeneous Scalable Framework for Multiphase Flows

158997

Year 3 of 3
Principal Investigator: K. V. Morris

Project Purpose:

Computational modeling of turbulent combustion is vital for our energy infrastructure and offers the means to develop, test, and optimize fuels and engine configurations. In the case of internal combustion engines, fuel injection simulations provide insight into the required calibration for appropriate turbulent mixing and efficient combustion. In modeling the dilute spray regime away from the injection site and downstream of the atomization processes, considerable doubts persist regarding how to best parameterize and predict the various two-way couplings between the dispersed phase and the surrounding fluid turbulence. These couplings include mass, momentum, and energy exchanges.

Two categories of challenges confront the developer of computational spray models: 1) those related to the computation, and 2) those related to the physics. Regarding the computation, the trend towards heterogeneous, multi- and many-core platforms will require considerable re-engineering of codes written for a specific supercomputing platform. Regarding the physics, accurate methods for transferring mass, momentum and energy from the dispersed phase onto the carrier fluid grid have so far eluded modelers. Significant challenges also lie at the intersection between these two categories. To be competitive, any physics model must be expressible in a parallel algorithm that performs well on multiple computer platforms.

To exploit the countless computing hardware configurations available and confront the challenges regarding portability and performance optimization for current scientific applications, the proposed work will develop a novel software architecture that segregates the data computation and communication from the physical models.

This architecture will enable computational scientists to increase the versatility of present and future scientific codes. Current state-of the art spray model computations predict experimental results only for a narrow band of particle length and time scales. This work will simultaneously address a fundamental need to generalize these models to account for a wider range of particle scales, focusing on particles larger than the smallest turbulent eddies.

Summary of Accomplishments:

This project developed a novel approach to generic, object-oriented, mixed-language programming. The approach emulates generic programming in C, and exploits C interoperability support and actual generic programming features in Fortran 2003. The new concepts, and resulting flexibility, are illustrated by constructing an application where hardware architecture is encapsulated from the software implementation.

The application makes use of the object-oriented Fortran interface to the Trilinos project, which is comprised of two layers: CTrilinos and ForTrilinos. The project involved extensive refactoring and development of customized scripts that automate part of the generation of glue and explicit instantiation code.

Tpetra, Teuchos, and Kokkos encapsulate support for platform-independent algorithms in Trilinos. The refactored CTrilinos provides the infrastructure for emulating generic programing in C, which is required to support the Fortran interface, where the generic programing model is based on parameterized derived types

(PDTs). ForTrilinos publishes the generic, object-oriented and unified interfaces for all instances of a template class. The significant investment in infrastructure development resulted in a flexible, intuitive object-oriented Fortran interface with compile-time checking.

In conjunction with the two packages previously discussed, this project also developed a spray-tracking application programming interface (API) that abstracts away the platform-dependent parallelization concerns. The particle phase of this application is implemented in Fortran, and makes extensive use of coarrays and object-oriented programming features. Coarrays are a new feature introduced into the Fortran 2008 compiler standard to enable parallel processing using multiple copies of a single program. Each copy is called an image. According to the Partitioned Global Address Space (PGAS) model, each image can access its local data and the data from other images though the use of coindices. Scalability of over 85%, in 16,834 images, was obtained for the software design followed in the software development of the spray-tracking application.

Significance:

This project developed a novel multilanguage software infrastructure to provide object-oriented Fortran applications access to platform-independent communication/computation capabilities in the C++ Trilinos library. The project created customized-scripts to enable automatic generation of source code that emulates generic programming in C, and scripts that emulate template meta-programming in Fortran by exploiting generic and object-oriented programming features.

In addition to the open-source library contribution, the project developed a platform-agnostic spray-modeling application that provides the implementation of operators and object-oriented objects that are fully distributed, and illustrates the scalability that can be achieved by scientific applications using a functional programming paradigm.

Refereed Communications:

D. Rouson, K. Morris, M. Haveraaen, J. Xia, and S. Shende, "High-Performance Design Patterns for Modern Fortran," in *Proceedings of the International Conference for High Performance Computing*, *Networking, Storage and Analysis*, November 2013.

D. Rouson, H. Radhakrishnan, K. Morris, and S. Shende, "Test-Driven Parallelization of a Legacy Fortran Program," in *Proceedings of the International Conference for High Performance Computing, Networking, Storage and Analysis*, November 2013.

A. Nanthaamornphong. J. Carver, K. Morris, and S. Filippone, "Extracting UML Class Diagrams from Object-Oriented Fortran: ForUML," in *Proceedings of First International Workshop on Software Engineering for High Performance Computing in Computational Science and Engineering*, November 2013.

D. Rouson, H. Radhakrishnan, K. Morris, S. Shende, and S. Kassinos, "Parallelizing Legacy Fortran Software using Coarrays: A Case Study of Particle Representation Model (PRM)," in *Proceedings of the First International Workshop on Software Engineering for High Performance Computing in Computational Science and Engineering*, November 2013.

M. Haveraaen, K. Morris, and D. Rouson, "High-Performance Design Patterns for Modern Fortran," in *Proceedings of the First International Workshop on Software Engineering for High Performance Computing in Computational Science and Engineering*, November 2013.

A Micro to Macro Approach to Polymer Matrix Composites Damage Modeling

161865

Year 2 of 3
Principal Investigator: S. A. English

Project Purpose:

Traditionally, polymer matrix composites (PMC) damage is assessed on the lamina scale in which distributed loads among the constituents exceed some failure criteria and lead to a reduction in laminate stiffness. An array of methodologies has been proposed to simulate this phenomenon. No consensus yet exists on the correct method to model damage and failure in composites. A micromechanical approach uses fiber and matrix properties to define decomposed constituent-level damage evolution and failure and, thus, may be extended to more complex compositions. Similarly, mesoscale (yarn) models can be used to directly assess damage evolution and failure in woven PMCs. The main challenge is to develop and implement a composites damage-material model that uses a micro- and mesomechanical approach to determine homogenized macroscopic material response for varying levels of constituent complexity. Intermediate challenges include implementation and evaluation of multiple material models, development of methodologies and length scale estimations for micro- and mesomechanical modeling, comparison with existing models (analytical and empirical), and experimental validation for simplified cases with materials of interest. Sandia's high-performance computational capabilities allow for a detailed analysis of the microstructure, iterative optimization of material parameter selection, and other tasks not generally suited for industry.

Digital Holography for Quantification of Fragment Size and Velocity from High Weber Number Impacts

161867

Year 2 of 3
Principal Investigator: D. R. Guildenbecher

Project Purpose:

In transportation accidents, tanks containing flammable or hazardous liquids may impact rigid surfaces at high velocity. This can lead to liquid dispersion throughout large volumes. In these situations, knowledge of the initial fragment sizes and velocities is needed to elucidate the fundamental physics and provide boundary conditions for predictive models of dispersion. Previous attempts to acquire such data were unsuccessful due to the spatial limitations of phase Doppler anemometry, which records droplets at a point, and particle-tracking velocimetry, which records droplets in a 2D plane. To enable measurement of droplet statistics, innovative new methods are required to probe a large 3D domain in single-shot, short-duration experiments.

Significant advancement of the state of the art is proposed through the optimization of digital holography for quantification of the size, morphology, and velocity of liquid structures within a 3D measurement domain. The viability of digital holography has recently been established by a few proof-of-concept investigations. We propose three significant leaps forward for diagnostics for high-velocity droplet fields: 1) we will greatly improve temporal resolution through the use of nano- and pico-second laser pulses, 2) we will develop advanced algorithms to detect individual droplets and track them through multiple exposures, and 3) we will explore tomographic methods to improve the out-of-plane resolution of large-scale flow fields. Application of these techniques to high Weber number impacts will provide new physical insights into the governing mechanisms and fundamental data of interest to multiphase flow modelers. These data will enable significant breakthroughs in the development and validation of liquid dispersion simulations. Once perfected, this technique could be extended to many other systems where index of refraction variation leads to light scattering. Consequently, the future application of digital holography may prove game changing for diagnostics of complex, 3D phenomena.

Advanced Diagnostics for High Pressure Spray Combustion

164668

Year 2 of 3
Principal Investigator: S. A. Skeen

Project Purpose:

Predictive high-pressure spray combustion simulations under development at Sandia will enable more rapid and cost-effective engine design that leverages fundamental physical and chemical information to reduce pollutant emissions and maximize efficiency. Anticipated advancements are crucial to the transportation sector as more stringent emissions regulations are imposed and new synthetic and bio-derived fuels with varying properties find greater usage. Development of a predictive simulation capability requires experimental data to both inform and validate the models, but very limited information is currently available about the chemical structure of high-pressure spray flames under engine-relevant conditions. Probing such flames for chemical information using nonintrusive optical methods or intrusive sampling techniques is challenging because of the physical and optical harshness of the environment. For example, such flames are characterized by high velocities, temperatures, and pressures that make intrusive probing difficult. Further, beam-steering effects caused by refractive index gradients are exacerbated at high pressure, complicating optical diagnostics. And finally, engine-relevant injection times are only a few milliseconds, resulting in very small time-windows for measurements under quasi-steady conditions.

This experimental project will address the need for quantitative species information from high-pressure spray flames under engine relevant conditions by developing and applying a suite of diagnostics to the constant volume high-pressure spray flame chamber at the critical radiant flux (CRF). The cutting-edge nature of the work lies in the development of a multiwavelength soot extinction diagnostic setup capable of providing temporally resolved information about soot formation at very short time scales. In addition, we will apply optical diagnostics and develop novel sampling techniques to investigate the chemical structure of high-pressure spray flames under conditions previously unexplored by these methods.

Reduced Order Modeling for Prediction and Control of Large-Scale Systems

164678

Year 2 of 3
Principal Investigator: I. Kalashnikova

Project Purpose:

Numerous modern-day engineering problems require the simulation of complex systems possessing many unknowns. Despite improved computational tools, "high-fidelity" models are often too computationally expensive for use in a design setting. The continuing push to incorporate the quantification of uncertainties into modeling efforts critical to many Sandia applications can present an intractable computational burden due to the high-dimensional systems that arise.

The proposed research aims to enable real-time simulations of complex systems for on-the-spot decision making and control through the development of stable and efficient reduced order models (ROMs) that capture the essential physics of interest at a low computational cost. For many ROM approaches, general results regarding the models' fundamental mathematical properties are lacking, or the reduction is computationally intractable for large-scale problems. The proposed research will employ a provably stable and computationally tractable ROM technique co-developed by the researcher as a starting point to explore methods for developing stable and efficient ROMs for the control of large-scale systems. The work can be seen as the first step toward developing an effective model reduction technique to support decision making under uncertainty. Targeted applications include the quantification of the captive-carry environment for atmospheric transport/climate modeling.

For a ROM to serve as a useful predictive tool, the model should preserve the stability properties of the original system and be cost effective for large problems. As many ROM techniques are computationally intractable for large-scale systems or lack an a priori stability guarantee, there is motivation to explore new theoretically sound and computationally efficient techniques for building ROMs. Fundamental research regarding the ROM's robustness with respect to parameter changes and predictive capabilities will reduce the risk inherent in relying on a reduced model for predictive calculations.

Quantitative Imaging of Turbulent Mixing Dynamics in High-Pressure Fuel Injection to Enable Predictive Simulations of Engine Combustion

165646

Year 1 of 3
Principal Investigator: J. H. Frank

Project Purpose:

The purpose of this project is to develop a capability for quantitative-imaging measurements of high-pressure fuel-injection dynamics that will transform our understanding of turbulent mixing in transcritical flows, ignition, and flame stabilization mechanisms, and will provide essential validation data for developing predictive tools for engine-combustion simulations. Advanced, fuel-efficient engine technologies rely on fuel injection into a high-pressure, high-temperature environment for mixture preparation and combustion. However, the dynamics of fuel mixing and combustion are not well understood and cannot be accurately predicted. Quantitative measurements for model validation are lacking because spatially and temporally resolved measurements of turbulent mixing and combustion dynamics in multiphase, high-pressure, high-temperature flows pose significant diagnostic challenges. Advanced diagnostics development at engine pressures and temperatures are needed to enable quantitative high-resolution measurements of the temporal evolution of fuel injection. The proposed high-fidelity measurements will transform our understanding of fuel injection dynamics, which affect engine-combustion processes such as flame lift-off, soot formation, and cycle-to-cycle variations. These quantitative data will be used for testing turbulent mixing models that are central to Sandia's efforts to develop predictive fuel-injection simulations.

The development and application of high-fidelity imaging diagnostics for understanding fuel injection dynamics is ambitious considering the complexity of the experiments and the demanding temporal and spatial resolution requirements. Quantitative interpretation of high-speed imaging data at high pressure and high temperature are addressed by a detailed and innovative treatment of laser-based imaging measurements. To attain the extremely high data rates needed for tracking the motion of turbulent mixing (~100kHz), we are developing a pulse-burst laser system that will enable high-speed planar laser imaging of fuel vapor mixing, velocity, and ignition. This unique diagnostic capability will be compact, robust, and mobile, enabling broad applicability for high-repetition rate imaging of motion in many areas of interest to defense and energy security missions.

A Process and Environment Aware Sierra/SM Cohesive Zone Modeling Capability for Polymer/Solid Interfaces

165649

Year 1 of 3
Principal Investigator: E. D. Reedy, Jr.

Project Purpose:

The performance and reliability of many Sandia components depend on the integrity of interfaces between dissimilar materials. Unfortunately, our ability to predict the performance of critical polymer/solid interfaces is limited. We propose to address this by combining Sandia's cutting-edge nonlinear viscoelastic polymer modeling capability with recent advances in finite-element, cohesive-zone, fracture-modeling theory to create a significantly improved method for predicting interfacial failure. The anticipated outcome of this effort will be a unique capability that will enable Sandia's Sierra/SM finite-element code to predict how variations in processing, environment, geometry, and loading affect the performance and reliability of polymer/solid interfaces. The proposed effort must address several fundamental issues to succeed. For example, a physically based polymer constitutive model is essential since polymers undergo highly nonlinear relaxations during processing, aging, and mechanical loading. This is most strongly manifested in the highly stressed regions where failure usually initiates (e.g., sharp corners). However, it is unclear how to define and measure the primary parameters that define a cohesive zone interfacial fracture model (i.e., interfacial strength and the work of separation) when nonlinear energy dissipation in the bulk polymer dominates. The cohesive-zone model cannot be defined in terms of the molecular bonding between the joined materials since this would lead to the incongruity of modeling engineering components on the same nanometer-scale as the molecular interactions. Likewise, it is not clear how the well-known increase in apparent interfacial toughness would be incorporated with increasing crack-tip shear deformation. We will use molecular dynamics simulations, detailed finite element fracture analyses, and key interfacial fracture tests to resolve such issues. Tests of component-scale adhesively bonded joints will also allow us to validate our work and to further establish the sensitivity of interfacial fracture to variations in processing and environment.

Prediction of Spark Discharge Paths and Voltages

165652

Year 1 of 3
Principal Investigator: L. K. Warne

Project Purpose:

A fundamental problem we repeatedly encounter is how a spark discharge path selects among candidate conductors that are in proximity to an electrode (or plasma) at high voltage and the statistics associated with such spark attachments. This determines whether penetrant energy is diverted to chassis or leads to difficulties. This problem pertains to penetrations associated with metallic burnthrough by lightning continuing current, phenolic blast-through events driven by lightning return strokes, and to other penetrations.

A semiempirical static breakdown criterion we previously proposed will not answer fundamental questions (technical challenges) arising from the transient development of the spark, including:
1) discharge timing (lightning-driven voltages are time limited), 2) conductor impedance (floating electrodes and dielectrics), 3) probability of path and statistics of attachment, and 4) the presence of excited gas species, which may exist after penetrations.

There is a large body of work on sparkover, but the majority is empirical and not easily generalized to geometries and conditions (impedance, drive waveform, etc.) and of interest to Sandia.
Our objective is to develop rigorous tools for determining dynamical criteria for sparkover and discharge path in arbitrary gap geometries, with applications to components subjected to high voltage in gaseous environments.

Although there are models and experiments in the literature addressing sparkover development, there is no clear picture of how this event comes about. Our new insight is that the intermediate stage of spark development, bridging the initial gas ionization stage with the final heating stage and involving interactions of the discharge with the electrodes, sets the sparking condition. This has been largely ignored in the literature. If successful in understanding how this occurs, our first-principles model will be a major advance and essential for addressing the project's technical challenges.

Time-Resolved Optical Measurements of Shock-Induced Chemistry in Energetic Materials

165656

Year 1 of 3
Principal Investigator: D. L. Damm

Project Purpose:

The purpose of this project is to develop a fundamental understanding of the mechanisms for chemical energy release during mechanical shock loading of energetic materials. State-of-the-art models for shock initiation of explosives are not predictive and, thus, have limited utility for engineering design, analysis, and quantification of margins and uncertainty (QMU) for energetic components. The development of physically based predictive tools is severely limited by a lack of knowledge of the reaction chemistry and a poor understanding of the physics of chemical energy release at hotspots. The reactive processes occurring during shock initiation are poorly understood due to the inherent difficulty of making measurements on the very fast timescales, short length scales, and extreme conditions which are typically encountered.

Direct observation of thermodynamic states and shock-induced reactions in heterogeneous, condensed-phase solids is difficult due to the technical challenge of obtaining sufficient signal/noise-ratio while maintaining sufficiently high temporal and spatial resolution. Newly available optically thin, homogeneous samples may allow us to probe these reactions with unprecedented resolution. Vapor deposited films of certain explosives, including hexanitrostilbene (HNS), are relatively transparent, allowing measurement of optical emission from within the shocked material. The emission spectrum can be used to determine both temperature of the sample and the presence of chemical species, which evolve over time. The information will validate equation of state (EOS) predictions and provide insight into the reactive processes. The goal of this project is to develop a fundamental understanding of reaction mechanisms and kinetics and its relationship to the local thermodynamic state of the material. If successful, these experiments will revolutionize our understanding of initiation and will position us to fill a major knowledge gap that prevents the explosives community from developing predictive energetic material models.

Development of Non-Intrusive Methods to Measure Static and Dynamic Forces and Motions in Mechanical Joints

165659

Year 1 of 1
Principal Investigator: R. L. Mayes

Project Purpose:

Developing constitutive models of the physics in mechanical joints is currently stymied by the inability to measure forces and displacements within the joint. The current state of the art estimates whole joint stiffness and energy loss per cycle from external measured force input and one or two acceleration responses. To validate constitutive models beyond this state requires a measurement of the distributed forces and displacements at the joint interface. Unfortunately, introducing measurement devices at the interface completely disrupts the desired physics. A feasibility study is presented for a nonintrusive method of solving for the interface dynamic forces from an inverse problem using full field-measured responses. The responses come from the viewable surface of a beam. The noise levels associated with digital image correlation and continuous scanning laser Doppler velocimetry are evaluated from typical beam experiments. Two inverse problems are simulated — one that utilizes the extended sum of weighted accelerations technique (SWAT), and another, which is a new approach dubbed the method of assumed orthogonal forces. These methods are much more robust if the contact patch geometry is well identified. Various approaches to identifying the contact patch are investigated, including ion-marker tracking, Prussian blue and ultrasonic measurements. A typical experiment is conceived for a beam that has a lap joint at one end, with a single bolt connecting it to another identical beam. In a virtual test using the beam finite-element analysis, it appears that the SWAT inverse method requires evaluation of too many coefficients to adequately identify the force distribution to be viable. However, the method of assumed orthogonal forces appears viable with current digital image correlation (and probably other) imaging techniques.

Summary of Accomplishments:

We discovered a feasible nonintrusive method of reconstructing the dynamic force distribution at the lap joint interface. We utilized experimental full-field dynamic measurements of in-plane and out-of-plane displacements on the viewable surface of the beam comprising one side of the lap joint. Typical beam experiments were performed with digital image correlation and continuous scanning laser Doppler velocimetry to determine their capabilities and noise floor. The force reconstruction method takes into account the typical noise generated by the sensors in our experiments. We also confirmed the capability of two methods to determine the static contact area of the joint. More complex force distributions require more images to converge on the best estimate of the force.

Significance:

Large finite-element models are used to predict responses for generating component specifications in shock and vibration environments of nuclear weapon systems. Much uncertainty exists in these models due to unmodeled mechanical joints. Currently, stiffness and energy dissipation are calibrated from tests. No methods exist to predict the joint stiffness or energy dissipation, which can affect the amplitude of vibration by a factor of five for typical joints. To overcome this massive uncertainty, validated constitutive models of joints must be developed. This study demonstrated the feasibility of capturing experimental data to validate constitutive models.

Refereed Communications:

R.L. Mayes, M.S. Allen, and D.C. Kammer, "Correcting Indefinite Mass Matrices due to Substructure Uncoupling," *Journal of Sound and Vibration*, vol. 332, pp. 5856-5866, 2013.

3D Deformation Field throughout the Interior of Materials

165661

Year 1 of 1
Principal Investigator: H. Jin

Project Purpose:

With advances in numerical computation, finite-element analysis can calculate the 3D deformation field of a whole material body. Experimental measurements, however, have been limited to the surface of the material. The deformation field around internal features, such as particles, voids, and cracks, cannot be obtained. This is a major obstacle in developing and validating physically based models to predict material deformation and failure. With regard to ductile failure, experimentally determined deformation fields around voids are critically needed to understand void interaction mechanisms and establish quantitative void coalescence criteria. No such data exist today. Breakthrough in this area hinges on the ability to make 3D full-field local deformation measurements inside the material at the microscopic scale. The goal of this research is to develop a novel experimental technique to enable measuring 3D displacements and strain fields throughout the interior of a structural metal.

Our approach is to couple 3D imaging capabilities, such as x-ray computed tomography (XCT), with in situ loading and digital volume correlation (DVC) to achieve the deformation measurement inside a material body. XCT has been successfully applied in material science and mechanical engineering to achieve tomographic images that reveal internal features of the material. DVC, an emerging technique, relies on proper patterns to characterize 3D deformation fields. Unfortunately, the intensity patterns of tomograms of a metal alloy cannot be altered physically. In this research, we propose to study the feasibility of pre-existing tomographic images of structural metals for DVC analysis. We aim to improve 3D tomographic images via post-processing procedures and to identify critical XCT and reconstruction parameters that can improve the patterns in tomographic images. If successful, it will guide our future research in developing the novel experimental technique for 3D deformation measurement and will be a major advancement in experimental mechanics. It will enable fundamental understandings and subsequent modeling and engineering applications.

Summary of Accomplishments:

We analyzed the pre-existing tomography images from our previous in situ XCT experiments of aluminum alloy 7075-T7351 using currently available DVC algorithm and learned that these images have low-contrast and sparse features. The deformation measurements from these images, therefore, have large errors and deviations. However, we can successfully enhance the features in the tomography images via thresholding the intensity of these images. DVC can then be applied to the enhanced tomography images to obtain the displacement with high accuracy and precision. We also apply DVC to tomography images from the in situ XCT experiments that have real deformations. DVC is able to calculate reasonable displacement and strain results that are consistent with the global loading conditions applied to these specimens. Through this feasibility study, we proved that our original proposal that couples in situ XCT experiments with DVC to calculate the deformation field throughout the material body is feasible, though we face many challenges to improve on the results.

Significance:

This study demonstrated the feasibility of developing a unique experimental mechanics capability that enables scientific studies to gain a fundamental understanding of the deformation, damage and failure of metals. The study also will strengthen Sandia's leadership role in predictive simulations, which is important to the DOE

Science and Innovation mission. Ductile metals are widely used in nuclear weapons and the ability to precisely predict failure of these materials ultimately impacts DOE Nuclear Safety and Security mission. Transportation vehicles such as airplanes are made of aluminum alloys. The ability to predict the failure will benefit the Department of Transportation Safe Transportation mission and Homeland Security Global Aviation Security mission.

Refereed Communications:

H. Jin W.-Y. Lu, A. Mota, W.J. Foulk, G. Johnson, and J. Korellis, "A Study of Anisotropic Void Evolution in Aluminum Alloy Using X-Ray Tomography," *Experimental Mechanics*, vol. 53, pp. 1583-1596, July 2013.

Determining Constitutive Material Properties from Full-Field Experiments Using the Virtual Fields Method

165667

Year 1 of 2
Principal Investigator: S. L. Kramer

Project Purpose:

The purpose of this project is to create a framework for identifying plasticity material model parameters that uses an inverse problem methodology called the Virtual Fields Method (VFM) — which employs full-field experimental deformation measurements — in order to improve complex system predictive simulations by obtaining higher quality constitutive properties from the VFM material calibration process. The standard practice for determination of constitutive parameters for material models is to extrapolate material properties from simple tests with closed-form solutions. However, this practice cannot reliably characterize complex loading responses, failure, anisotropies, or heterogeneous behaviors, and requires several experimental test configurations that can be cost-prohibitive. With the maturation of full-field experimental methods that provide millions of data points from a single experiment, the constitutive parameter identification inverse problem need no longer rely on simple closed-form solution experiments. VFM requires as little as one experiment with heterogeneous deformation fields to populate a complex model. With constitutive models calibrated by deformations representative of real system behavior, predictive simulations should have reduced error and fewer uncertainties. The framework created through this project includes: 1) specimen geometry optimization, considering experimental noise and the user-defined parameters for VFM, via computational simulations of the entire VFM identification process, 2) experimental testing of the optimized specimen geometry using Digital Image Correlation to obtain full-field displacement measurements, and 3) identification of plasticity material properties from the experimental data. This research involves development of a VFM numerical code for material parameter identification, development of a tool for specimen geometry optimization, and demonstration of the VFM identification process for 304L stainless steel, which is considered well characterized even though it has been a challenge to computationally model in regions with necking and failure. Models using VFM-identified parameters and parameters from simple uniaxial tensile tests will be compared to validation experimental tests to evaluate the effectiveness of the VFM framework for plasticity model parameter identification.

High-Precision Testing and Structural Analysis of Li-ion Batteries

166152

Year 1 of 3
Principal Investigator: S. R. Ferreira

Project Purpose:

The purpose of this project is to use high-precision testing combined with materials characterization to improve the prognostic ability and performance evaluation of battery cells in a shorter time frame than is currently possible. We expect to advance capabilities in screening materials and in improving prognostics in lifecycle expectancy. Advances with current testing techniques and methodologies are becoming crucial, as the market for energy storage is moving into large-scale, long-term advanced technologies for electric vehicle and stationary storage applications. Current battery testing methods use low-precision testers. Long-term cycling is currently the only reliable way to determine life of energy storage devices. Long-term validation testing far exceeds the development cycle for battery technologies and is prohibitively expensive. A transformative way to quickly and reliably validate battery materials and battery life is critical to enabling advances in stationary-storage technology. Rapid, reliable battery evaluation, facilitated by high-precision testing, is being investigated. This will be used to understand and predict battery performance and life, and to better enable their adoption for stationary storage applications.

Extensive previous efforts to do rapid validation of battery life have been largely unsuccessful, especially using accelerated testing. An increase in the precision and accuracy of measurements may provide sufficient data for prognostication of battery life, thereby decreasing the duration of testing to weeks or months rather than years. University research has begun to test the concept of high-precision testing with positive preliminary results. We will expand on this work by evaluating battery cells before formation at beginning-of-life (BOL), and at intervals in state of health through the end-of-life (EOL). Early work has begun by developing the experimental setup, performing high-precision measurement capture and evaluating the results of early-cell cycling. This work is in collaboration with the University of New Mexico.

Upscaling Ab-Initio Quantum Chemistry Models for Nonequilibrium Reacting Flow Simulations

166153

Year 1 of 3
Principal Investigator: D. J. Rader

Project Purpose:

Many advanced engineering technologies that support national security involve nonequilibrium reacting flows. These flows are generated by re-entry vehicles, plasma environments, and detonations. During Earth re-entry, gas temperature in the shock region exceeds 10,000 Kelvin, which leads to air dissociation. The flow in the shock is in high nonequilibrium, making it difficult to characterize chemical kinetics by single-temperature Arrhenius rates. There is currently a lack of high-fidelity nonequilibrium chemistry models that would account for internal energy specific chemical processes. The ability to predict chemical reaction rates under conditions of thermodynamic nonequilibrium will greatly improve the ability to simulate flow fields and to predict thermal and structural loads for re-entry vehicles.

In collaboration with Purdue University, the proposed research focuses on the development of state-specific air chemistry model utilizing the compact polynomial expansion (PE) of quasi-classical trajectory (QCT) simulations on potential energy surfaces (PES) obtained from ab-initio quantum chemistry calculations. This methodology allows construction of nonequilibrium chemistry models for systems in which little or no experimental data exist.

A Compact Single-Camera System for High-Speed, Simultaneous 3-D Velocity and Temperature Measurements

166538

Year 1 of 2
Principal Investigator: J. H. Frank

Project Purpose:

The University of Michigan and Sandia collaborated on the initial development of a compact single-camera approach for simultaneously measuring 3D gas-phase velocity and temperature fields at high frame rates. A compact diagnostic tool will enable investigations of flows with limited optical access, such as near-wall flows in an internal combustion engine. These in-cylinder flows play a crucial role in improving engine performance. Thermographic phosphors were proposed as flow and temperature tracers to extend the capabilities of a novel, compact 3D velocimetry diagnostic to include high-speed thermometry. Spectral measurements on $BaMg_2Al_{10}O_{17}:Eu$ (BAM) phosphors were performed in a heated airflow to determine a preliminary optimal-optical configuration for accurate temperature measurements.

Modeling the Coupled Chemo-Thermo-Mechanical Behavior of Amorphous Polymer Networks

169249

Year 1 of 2
Principal Investigator: J. A. Zimmerman

Project Purpose:

Thermally activated shape-memory polymers (SMPs) have garnered significant attention in recent years for their potential broad range of applications and properties that can be tailored. Several different mechanisms can be employed to achieve the shape memory effect in polymers, but the two most common ones are the melt transition of semicrystalline polymers and the glass transition of amorphous polymers. For amorphous polymers, the temporary shape is obtained by deforming the material in its heated rubbery state. Cooling the material below the glass transition temperature (Tg) reduces the molecular mobility of the polymer chains, fixing the deformed shape in a nonequilibrium thermodynamic state. The temporary shape should be fixed indefinitely until the material is heated above the Tg. However, amorphous SMPs can experience a significant loss in shape fixity below Tg when stored for a prolonged period of time in water or in a humid environment. While the absorption of solvents, such as water, can be detrimental to the shape-memory effect of amorphous networks, the phenomena can also be harnessed to athermally activate shape recovery. This alternative to temperature-driven shape recovery can be attractive in applications where the controlled delivery of heat poses an intractable challenge (e.g., in a surgical environment).

The goal of this project is to investigate the effect of shape-memory programming, thermomechanical properties, and physical and environmental aging on the shape memory performance. This investigation includes physical and environmental aging factors that occur during storage and through exposure to solvents such as water. The project, performed in collaboration with Presidential Early Career Awards for Scientists and Engineers (PECASE) winner Professor Thao Nguyen at Johns Hopkins University, will develop a theoretical framework for chemo-thermo-mechanical behavior of amorphous polymers. The project will study the effects of physical aging and explore how solvent-induced environmental aging affects the thermoviscoelastic behavior of shape-memory polymers.

Determination of Surface-Mediated Degradation Products in Energetic Materials at Critical Interfaces

170974

Year 1 of 3
Principal Investigator: C. L. Beppler

Project Purpose:

The purpose of this project is to better understand the surface-mediated chemical degradation products that form in energetic materials (EM) through the use of state-of-the-art analysis methods. This project will apply state-of-the-art methods such as electrospray ionization-mass spectrometry (ESI-MS), secondary ion mass spectrometry (SIMS), attenuated total reflectance infrared spectroscopy (ATR-IR), and other suitable tools to probe the identities and formation pathways of surface-mediated EM degradation products.

This study is the first to apply more sensitive tools, which recently became available, to better understand how surface-mediated EM degradation occurs at material interfaces. These tools will probe the previously under examined nonvolatile degradation products in EM, a key deficiency in our knowledge of energetic material degradation. This knowledge will enable new and more accurate experimental and computational methods to predict critical aging parameters in energetic materials. The knowledge of these key aging parameters will enable more accurate predictions of how an energetic material will age, and provide better criteria for selecting materials that are chemically compatible with EMs.

Numerical Methods for Efficient Simulations and Analysis of Circuits with Separated Time Scales

171117

Year 1 of 3
Principal Investigator: M. N. Hsieh

Project Purpose:

The purpose of the project is to develop novel numerical methods for efficient modeling of complex fast/slow circuits (i.e., small circuits with strong, nonlinear oscillations, and separated fast/slow time scales). Circuit-level simulation and analysis can support electrical interface characterization and predict functional performance limits under untestable environments or scenarios. Complex fast/slow circuits can make the computation time of even a single simulation unmanageable. Parallel simulation cannot improve the computation efficiency because these circuits are typically small. Many numerical methods are proposed to speedup such simulations by utilizing multiple time variables to efficiently represent circuit signals with widely separated rates of variation (e.g., multi-time partial differential equation). However, existing methods become ineffective if the circuits have a small difference between the fast and slow rates of change, have multiple time scales, or have complex quasi-periodic behaviors in the fast time scale. These limitations make the utilization of existing methods inherently risky, and much of the risk lies in identifying a viable solution to overcome each of the limitations. Our circuits of interest may possess complex behaviors that are shown to be the outstanding challenges in this research field. If successful, this project will provide capabilities to simulate and analyze the entire operation cycles of complex fast/slow circuit with high fidelity in manageable time, which are not possible using existing technologies.

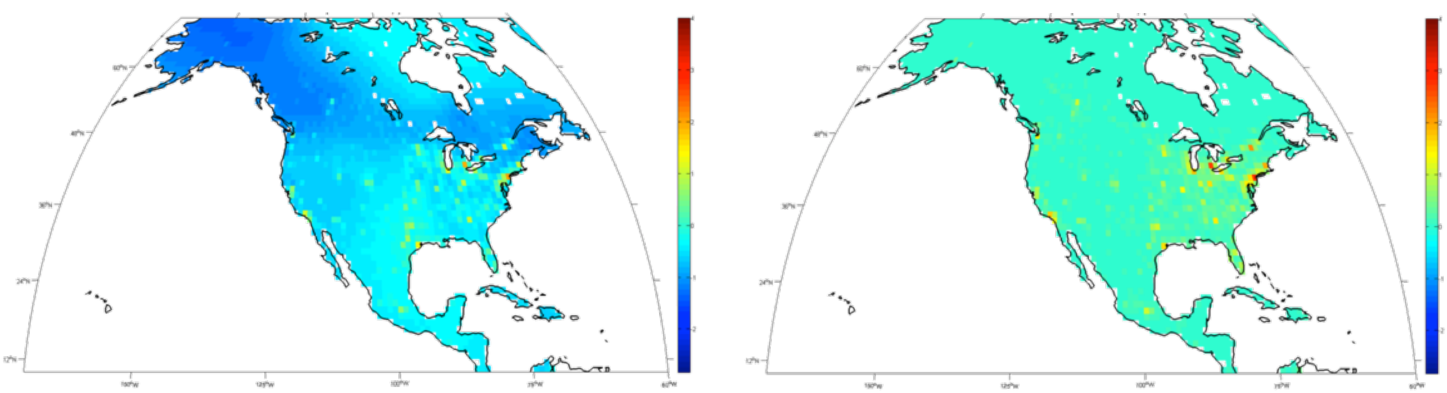
GEOSCIENCE

The Geoscience Investment Area focuses on developing a deep understanding of earth and atmospheric sciences as a means to solve problems in such areas as energy security, defense, intelligence, nuclear weapons, nonproliferation, disaster response, and climate security.

Researchers advance an understanding of the earth's subsurface by developing subsurface imaging at high resolution and reliability, detecting and characterizing underground formations, and addressing such challenges as high-noise environments, instrumentation sensitivity, and dynamic range.

A goal is to improve how manmade systems intersect with the subsurface. Strategies include studying subsurface fluid flow, biological effects on geo-processes in the deep subsurface, and rapid, silent, and environmentally friendly drilling systems.

Researchers also are working to reliably predict atmospheric and surface phenomena by developing exploratory tools such as climate models and geo-engineering instruments. They tackle cloud systems, sea and land ice models, and monitoring of greenhouse gases. And, they explore the effects of climate change on surface water and water chemistry.



Estimated June biospheric (left) and ffCO_2 fluxes (right) for June for the real-data study. Units: moles m^2s^{-1} (Project 151293).

GEOSCIENCE

Kalman-Filtered Compressive Sensing for High Resolution Estimation of Anthropogenic Greenhouse Gas Emissions from Sparse Measurements at Global Scale

151293

Year 3 of 3
Principal Investigator: J. Ray

Project Purpose:

This project seeks to develop techniques to infer the spatiotemporal distribution and dynamics of CO_2 emissions and uptake (i.e., anthropogenic and biospheric fluxes) from sparse observations of CO_2 concentrations. Such a characterization is critical to understanding the carbon cycle and predicting future climate variability and will play an important role in the verification of international CO_2 abatement treaties and management of mitigation programs. Accurate emissions characterization requires numerical simulations of atmospheric transport, conditioned on sparse data, with simultaneous quantification of uncertainties. An inverse problem can be formulated to reconstruct the location/character of CO_2 emissions and sequestration by minimizing the difference between observations and predicted values, subject to other known constraints. Many technical challenges arise, however: 1) large, ill-conditioned linear systems result from sparse measurements and complex diffusive dynamics, 2) extreme computational resources are required to address the high dimensionality of the uncertainty space, and, 3) a consistent and complete statistical framework is necessary for characterization of uncertainty. We address these issues through adaptation of novel image reconstruction techniques, efficient data assimilation methods, multiscale algorithms, and geostatistical Bayesian inverse methods.

Previously, we developed Bayesian techniques to reconstruct time-variant, spatial fields from limited measurements, by integrating concepts from compressive sensing (CS), Ensemble Kalman Filters (EnKF), and multiscale modeling. CS exploits sparse basis sets to achieve accurate multiscale field/image reconstruction from limited data. We will extend these approaches to dynamic fields such as CO_2 emissions and uptake, and integrate these techniques with efficient data assimilation methods. To this end, EnKF provides the necessary balance of computational efficiency and robust uncertainty characterization, as well as an avenue to explore assimilation of multiscale observations. Our algorithmic development will focus on supporting the CO_2 source flux estimation problem as a fundamental technical capability, but will be sufficiently general to be directly relevant to many problems in science and engineering.

Summary of Accomplishments:

We constructed three random field (RF) models for fossil-fuel CO_2 ($ffCO_2$) emissions and a method, based on sparse reconstruction, for estimating them from limited CO_2 concentration measurements. Currently, there are no competing models or methods for this work. We also discovered that $ffCO_2$ emission estimates could be obtained for the winter months without isotopic measurements, potentially allowing the use of copious satellite measurements in the estimation procedure.

We discovered that the strongly multiscale spatial distribution of ffCO_2 emissions necessitated the use of Haar wavelets to construct a RF model. Haars provided the sparsest representation when wavelet selection was performed using images of lights at night ("nightlights", a proxy for human activity and ffCO_2 emissions). The RF model was demonstrated in a synthetic-data atmospheric inversion, using a novel sparse reconstruction method, which embodied elements of compressive sensing to impose boundary conditions as well as algorithmic advancements to ensure the non-negativity of ffCO_2 fluxes.

We also devised an alternative RF model, based on Gaussian kernel representations of nightlights, which enables efficient estimation of highly localized ffCO_2 sources (e.g., in the Great Plains). This RF model was used to quantify the errors due to Gaussian assumptions in ensemble Kalman filters by comparing against estimates obtained using a Markov chain Monte Carlo method.

Finally, we addressed the problem of inferring biogenic and anthropogenic CO_2 fluxes jointly based on their (very different) spatial patterns. We augmented an existing geostatistical inversion method, with a model for ffCO_2 emissions derived from nightlights, thus creating the third RF model. Atmospheric inversions were predicated on CO_2 concentration measurements without isotopic information. We discovered that the inference of ffCO_2 emissions could be done without isotopic measurements only during the non-growing season when biogenic fluxes are comparable to ffCO_2 emissions.

Significance:

The methods we developed allow the inference of spatially resolved ffCO_2 emissions at the regional scale (e.g., US, etc). Competing methods are limited to estimating urban domes. These methods may contribute to a system that verifies ffCO_2 inventories or monitors a CO_2 abatement treaty.

Our finding that annual ffCO_2 estimates cannot be obtained without expensive isotopic measurements implies we will require measurements of chemically active products of combustion (e.g., CO, SO_2) which are amenable to remote sensing. It also necessitates an iterative extension of our sparse reconstruction scheme to address the nonlinearities introduced by reactive species.

Predicting the Future Trajectory of Arctic Sea Ice: Reducing Uncertainty in High-Resolution Sea Ice Models

157957

Year 3 of 3
Principal Investigator: K. J. Peterson

Project Purpose:

The purpose of this project is to improve the fidelity of sea-ice models and to develop methods to compare and propagate their uncertainties in order to provide new predictive capabilities for use in decision support.

Current generation Earth System Models (ESMs) vary greatly in their predictions for Arctic sea-ice evolution, but all have underestimated the rate of decline in minimum sea ice extent over the last thirty years. Sea-ice components of ESMs are multiphysics models with complex choices in the physical submodels and parameterizations used to define the governing equations and in the numerical methods used to discretize and solve the governing equations. They also contain many physical parameters with values that are inherently uncertain. A robust, predictive sea-ice modeling capability requires an understanding of how uncertainties are propagated by different numerical algorithms and a consistent approach for comparative evaluation of the physical fidelity of each model.

A novel framework for calibrating and validating sea-ice model output for ice motion and deformation using satellite and submarine data from the Arctic were used. The objective was to develop a systematic methodology to: 1) evaluate predictive capabilities of sea ice models, 2) discover the most important physical parameters contributing to uncertainties, and 3) assess the impact of numerical algorithms on sea ice simulations. Alternative numerical implementations and physical models were evaluated using the validation framework in order to determine the most relevant improvements. A distinguishing characteristic of the research is coordination of efforts in uncertainty/sensitivity analysis, physical modeling, and advances in numerical algorithms.

Summary of Accomplishments:

Satellite data obtained over the last few decades provided a wealth of information on sea-ice motion and deformation. The data clearly show that ice deformation is focused along narrow linear features and this type of deformation is not well represented in existing models. To improve sea-ice motion and deformation predictions, we incorporated an anisotropic rheology into the Los Alamos National Laboratory global sea ice model, CICE. The anisotropic elastic-decohesive rheology (EDC) explicitly models cracks in the sea ice, which provides a unique capability in a global sea-ice model and distinguishes it from the standard isotropic elastic-viscous plastic (EVP) model used in CICE. We implemented the EDC model with the capabilities to initiate multiple cracks per cell and to advect cracks with the motion.

After implementing the EDC model, we performed Monte Carlo sensitivity analyses using the Design Analysis Kit for Optimization and Terascale Applications (DAKOTA) to determine the impact of EDC and EVP material parameters on sea-ice response functions, such as total Arctic ice volume and root mean square velocity. We developed metrics for comparing model output with satellite-based ice motion and ice deformation data. Using these metrics as response functions in DAKOTA, we determined the most influential parameters from the EDC model for matching the satellite data. Two material strength parameters that exhibited the most significant impact on responses were further analyzed to evaluate their influence on a cost function incorporating error measures of model output compared with data. From the sensitivity analyses as well as from ten- year model runs, we learned that while the EDC model provides some benefit in velocity predictions over the EVP model, additional improvements are required to make this rheology a viable alternative for global sea-ice simulations.

Significance:

Climate change is a significant national security threat and the loss of Arctic sea ice is one of its most obvious manifestations. This research provides new insight into the impact of different sea-ice material models in comparisons with satellite data. Improved understanding of the important physical parameters will lead to a sea-ice modeling capability that more accurately reproduces ice motion and deformation and will better predict future Arctic sea-ice distribution and rate of sea-ice loss.

Aerosol Aging Processes and their Relevance to Human and Environmental Hazards

161873

Year 2 of 3
Principal Investigator: J. Santarpia

Project Purpose:

In this project, we characterized the atmospheric processes that affect the physical, chemical, and biological properties of airborne particulate matter to understand the fate of any aerosol in the atmosphere and assess the impacts or hazards it poses. For instance, the viability/toxicity and the fluorescence of chemical and biological warfare (CBW) agents and simulants released into the open atmosphere decay at vastly different rates than those enclosed in conventional laboratory apparatus due to atmospheric chemical interactions and compounds, termed open-air factors (OAF). Because CBW agents cannot be studied outside, there are very few open-air decay rates to inform operational hazard prediction models. Further, there is little understood about the effects of OAF on the biological detection signatures for agents. Current technologies are unable to detect the specifics of how long a biological attack may have occurred. Tracers used to simulate the transport of CBW agents, and validate models, often rely on ultraviolet (UV) light induced fluorescence (LIF) for detection. The fluorophores in the tracer material may also be subject to the same degradation processes that affect CBW agents and stimulants. Finally, the radiative and hygroscopic properties of both anthropogenic and naturally occurring super-micron aerosol particles (such as dusts and bacteria) are critically important to understanding Earth's climate processes. Laboratory measurements of these properties after known aging processes are relatively nonexistent.

This work develops new methods to study these complex problems and provide new information to inform a wide range of problems, including hazard prediction from Weapons of Mass Destruction (WMD) and climate. These results should help enable the predictive capabilities of these fields. These problems represent significant gaps in chemical and biological hazard assessment that have undergone limited, if any, study.

Methane Hydrate Formation on Clay Mineral Surfaces: Thermodynamic Stability and Heterogeneous Nucleation Mechanisms

165668

Year 1 of 3
Principal Investigator: R. T. Cygan

Project Purpose:

We will develop a comprehensive understanding of the heterogeneous nucleation of methane hydrates and their subsequent thermodynamic properties. This work will lead to more effective methods to extract subsurface methane (natural gas) from hydrates, and better control hydrate formation associated with oil extraction (pipeline flow assurance, Gulf oil disaster). Methane hydrates, which are ice-like water cages surrounding methane molecules, have the potential to play a significant role in our nation's energy security. Large untapped hydrate reserves exist in seafloor and Arctic sediments. A recent US Geological survey estimates 590 trillion cubic feet of methane hydrate — more than three times the amount of natural gas — is located on the North Slope of Alaska. The ability to utilize and control hydrate reserves is currently hindered by a lack of fundamental understanding of the natural environment's impact on the stability and formation of methane hydrates, which are often found in areas of clay-rich sediments. Most studies on hydrate nucleation and thermodynamic stability have focused on homogeneous systems, whereas heterogeneous systems are found in nature and in technical settings. The addition of nucleating mineral surfaces will impact the outcome and will advance this field toward an improved knowledge base furthering our ability to utilize natural-fuel sources.

Heterogeneous nucleation and thermodynamic stability of methane hydrates is an understudied phenomenon despite its critical importance. To address this challenge, cutting-edge simulation methods using Sandia's supercomputers will be required. Strategic experiments will both validate and inform the simulations. The primary scientific risk is that nucleation of a hydrate phase is a rare event. The successful outcome of this project is a comprehensive molecular-level picture of heterogeneous hydrates. Extension to a macroscopic laboratory bench scale enables the rational design of catalysts and inhibitors for hydrate formation and stabilization in energy and fuel applications.

Determination of Aerosol Scattering Characteristics for Atmospheric Measurements

165669

Year 1 of 3
Principal Investigator: M. Arienti

Project Purpose:

Sandia plays a major role in developing optical remote-sensing technology. Particularly, the systems developed for the Atmospheric Radiation Measurement (ARM) program can profile water vapor, temperature, and aerosol particles in a layer of atmosphere. This information is essential in establishing the effect of aerosols on albedo and cloud lifetime, which is increasingly recognized as an important element in precipitation modeling. While broadly successful, optical remote sensing relies on simplified assumptions on the dynamics of both individual particles and the airflow that can still impart large uncertainties in retrieved properties. These inaccuracies can be partially minimized via the next generation of optical instruments based, for example, on the nonlinear optical effects of small droplets, or microspheres. A microsphere can act as a lens and focus the incident radiation on a small region inside it, potentially increasing the particle signal-to-noise ratio. A broader approach to these topics requires the inclusion of deforming droplets and the assessment of the statistical optical response in a realistic atmospheric turbulent domain. The approach of combining fluid dynamics and optics is thus proposed.

The differentiating element in this project is the expertise in multiphase flow dynamics, which is expected to provide a better insight into the optical properties of microspheres and aerosol clusters suspended in the atmosphere. Available computational tools enable the assessment of realistic, non-ideal conditions, such as deformation in quasi-spherical droplets, multiple scattering from particle clusters, and the modifications of those effects inside a turbulent flow. The proposed approach treats the complexity of cloud diagnostics as a multiscale problem where the non-ideal effects are first assessed on the scale of an individual particle and then included as subgrid model into a much larger-scale simulation. Technology in the area of fast spray modeling can be leveraged to provide a novel treatment of natural occurring aerosols in the atmosphere that should greatly improve the environmental remote sensing products.

Appraisal of Hydraulic Fractures Using Natural Tracers

165670

Year 1 of 3
Principal Investigator: J. E. Heath

Project Purpose:

We will develop new methodologies using in situ natural tracers to evaluate local-to-reservoir-scale hydraulic fracturing efficiency, with a focus on application to shale gas. Maximizing fracturing efficiency improves producible reservoir volumes and can mitigate risk to groundwater resources. Current fracture characterization by pressure transient or production analysis and other methods poorly constrains fracture connectivity and hydraulic properties in terms of the integrated impact of fractures on fluid flow. Key reservoir characteristics govern natural tracer release during fracturing, including: 1) the number, connectivity, and geometry of fractures, 2) the distribution of fracture-surface-area to matrix-block-volume, and 3) the nature of multiple fluid phases (e.g., methane dissolved in groundwater or present as a free gas phase). We will estimate fracture characteristics from breakthrough of multiple natural tracers sampled at the wellhead using multirate-mass-transfer (MMT) theory. Favorable attributes include: 1) natural tracer concentrations that start with a well-defined initial condition, 2) a suite of tracers that covers a large range of diffusion coefficients, and 3) diffusive mass-transfer out of the matrix into fractures, causing elemental and isotopic fractionation and providing knowledge on the dominant mass transfer mechanism to the fracture system.

Natural tracers provide useful information in characterizing fracture surface area and transport velocities. However, existing techniques have never been applied in shale-gas systems, nor have natural tracer studies considered MMT theory. Previous MMT studies used injected tracers instead of the ubiquitous natural tracers. The existence of multiple phases and the heterogeneity of the matrix in shale gas formations complicate tracer interpretation in these environments, increasing the risk for non-uniqueness of underlying fracture-reservoir parameters generated through our improved breakthrough curve interpretation. By considering data from multiple naturally occurring tracers, our project promises techniques for much improved fracture network and fluid flow characterization through data that can be easily collected at wellheads.

Polyfunctional Desorption of Oil from Shales

171069

Year 1 of 3
Principal Investigator: P. V. Brady

Project Purpose:

We propose to build a science-based model of polyfunctional oil desorption from shales by: 1) combining experimental measurements and theoretical calculations to build first principles models of shale and oil surface chemistry, and 2) by linking them to predict wettability and oil recovery from shale. Understanding oil desorption from shales will require quantifying the relative contributions of electrostatic attraction, repulsion, and nonpolar binding to the separation of two complex polyfunctional materials — oil and shales. A science-based understanding of oil desorption should help better assess shale oil reserves and identify pathways for enhanced recovery of oil from shales.

Detecting Seasonal Changes in Permafrost Using in situ Seismic Velocities, Near-Field Soil Moisture Monitoring, and Remote Sensing

171381

Year 1 of 3
Principal Investigator: R. Abbott

Project Purpose:

The Arctic is important to Earth's climate system. In 2012, Arctic sea ice retreated the furthest in recorded history, opening the Arctic to commerce, resource exploration, and national security threats. The melting Arctic ice also increases sea-surface temperatures, which leads to increased storm severity around the globe. The melting of permafrost releases methane, which has been locked in the frozen ice layers, potentially causing further increases in Earth's temperature.

Current climate models do not have sufficient data to accurately predict the impact these factors will have on climate. The Arctic is not a homogeneous area in terms of precipitation, depth to permafrost, distance from the sea, etc. Therefore, data need to be collected from a variety of areas (coastal, inland, high and low precipitation, etc.). To effectively capture these data, remote-sensing methods that can collect accurate data over multiple scales are needed. These methods do not currently exist. Similarly, precipitation in the Arctic is difficult to measure. Differentiating between snow that is falling vs. snow that is being moved by the wind is essential for accurate water balances, but difficult to achieve in practice.

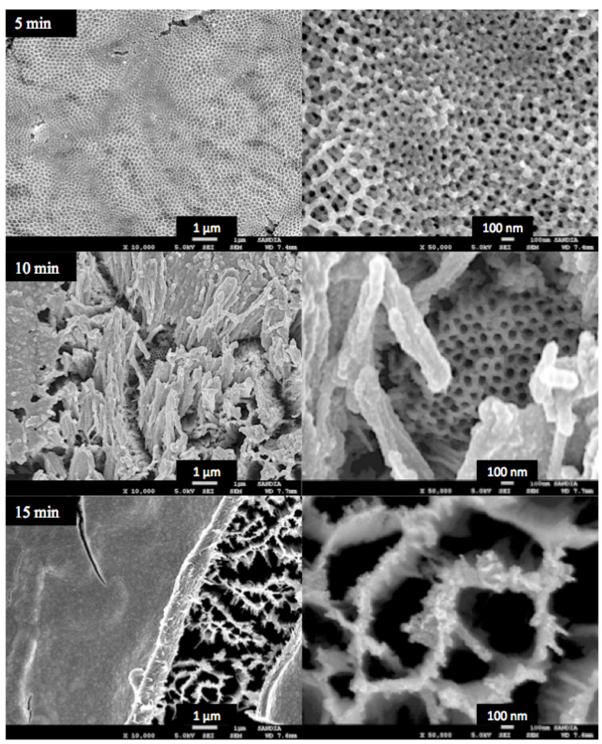
This project will apply recent advances in seismic research and soil moisture monitoring to the Arctic for the first time. The data from those efforts will be coupled with remote sensing data previously collected for national security purposes to determine if remote methods can be used to accurately collect data for use in climate models. Although Sandia has performed research in each of these areas, this will be the first time we will apply them to the climate arena. Since none of these techniques has been deployed in the Arctic, there is a high level of risk for the project. Results from this effort will contribute to a DOE Office of Science goal of improved understanding of Arctic water budgets.

MATERIALS SCIENCE

The Materials Science Investment Area focuses on materials analysis and creating new classes of materials. Materials that are critical to our missions span semiconductors to stainless steels, carbon composites to ceramics, polymers, and new materials development that provide specialized functionality and the understanding of interactions from the atomic through microscale.

Sandia's national security missions require fundamental materials understanding so that we may have confidence our products will perform safely, reliability and as intended in a variety of environments. A long, reliable lifetime in harsh environments, like those relevant to a nuclear weapon, a satellite or a nuclear power plant, places stringent requirements on our materials.

The research has major national significance since future security imperatives will depend on materials science breakthroughs. New materials will be vital to replacing obsolete technologies, meeting the latest system requirements and providing novel capabilities. As systems age, materials science will explain the chemical and physical mechanisms at work. Sandia's research strengthens understanding and predictability of the structure, properties and behavior of existing materials by exploring a variety of size scales under a wide range of environmental conditions. It improves the function of critical systems by creating new materials with dramatically enhanced properties, functions, and behaviors. And, it develops diagnostic tools and techniques to reveal fundamental mechanisms and enable materials science research.



SEM images of WO_3/TiO_2 materials as a function of electrodeposition time (Project 155797).

MATERIALS SCIENCE

Nanoscale Mechanisms in Advanced Aging of Materials during Storage of Spent "High Burnup" Nuclear Fuel

151328

Year 3 of 3
Principal Investigator: B. Clark

Project Purpose:

The decision to not pursue Yucca Mountain as a nuclear waste repository implies that spent nuclear fuel will have to be stored in a retrievable condition (with claddings maintaining necessary strength and ductility) for an indeterminate amount of time, conceivably on the order of centuries. Compounding this issue is the trend to discharge nuclear fuel after "high burnup" (i.e., greater than 45 GwD/MTU [gigawatt days per metric ton uranium]). Although the US has >25 years' experience in storage of low burnup fuel, there is no precedent for storage of high burnup fuel, where increased radiation dose, hydrogen uptake, and corrosive processes can significantly influence the mechanical properties of the cladding. Current efforts to model the degradation of claddings during interim storage rely heavily on empirical equations, limiting their capacity for long-time scale extrapolation. To provide fidelity in the ability to retrieve used fuel from storage either for transportation or further processing, extrapolative, physics-based models must be developed that can predict integrity of the cladding.

The goal of this work was to understand the degradation mechanisms in claddings during high burnup and in dry storage for development of high fidelity, predictive models. Experiments and modeling efforts have focused on the effects of hydride formation and accumulation of irradiation defects. Key results include: determination of the influence of composition and defect structures on hydride formation; measurement of the electrochemical property differences between hydride and parent material for understanding and predicting corrosion resistance; in situ environmental transmission electron microscope observation of hydride formation; development of a predictive simulation for mechanical property changes as a function of irradiation dose; novel test method development for microtensile testing of ion-irradiated material to simulate the effect of neutron irradiation on mechanical properties; and successful demonstration of an Idaho National Labs-based sample preparation and shipping method for subsequent Sandia-based analysis of post-reactor cladding.

Summary of Accomplishments:

Through the course of this project, we developed a new understanding of the variables influencing hydride formation and mechanical property degradation of used nuclear claddings. The data acquired, techniques developed, and interactions with the modeling community are critical for development of high fidelity, predictive simulations to determine the state of the cladding after long-term dry storage.

Using transmission electron microscopy and elastic recoil detection, we demonstrated that the rate of hydride formation in Zr-based alloys is determined in part by cladding composition, with Nb-containing alloys having the slowest rate of formation. Detailed electrochemical analysis confirmed that the result is composition dependent and we hypothesized that the Nb influences the surface energetics such that hydrogen is not as readily adsorbed. In addition, we showed that the size, type, and distribution of irradiated defects influence the rate of hydride formation: small interstitial loops closely spaced throughout the cladding substantially hindered the ingress of hydride whereas larger loops that were sparsely distributed had only a minimal effect.

Finally, to better understand the changes in mechanical properties, we developed a microtensile sample geometry for ion irradiation through the entire sample thickness to simulate in-reactor neutron damage. Samples were irradiated to increasing doses, up to 38 dpa, and results were compared with a mesoscale simulation developed as part of the project. Comparison of experiments to modeling was favorable, with both showing an increase in yield stress with increasing dose and a decrease in overall ductility.

Significance:

The technical contributions of this project will have a lasting impact on understanding degradation mechanisms in nuclear claddings for the prevention of radioactive material release. High fidelity characterization and analysis developed herein will enable development of high fidelity predictive simulations of the state of the cladding years from now. In addition, this capability could have broad impact on national security missions as well, where degradation of components over decades is of concern. The ability to characterize degradation and predict long-term performance would directly impact the stockpile stewardship mission.

Refereed Communications:

S. Rajasekhara, B.L. Doyle, D.G. Enos, and B.G. Clark, “Hydrogen Uptake in Zircaloy-2 Reactor Fuel Claddings Studied with Elastic Recoil Detection,” in *Proceedings of the AIP Conference on Application of Accelerators in Research and Industry*, pp. 270-275, 2012.

K. Hattar, S. Rajasekhara, and B.G. Clark, “In Situ TEM Ion Irradiation and Atmospheric Heating of Cladding Materials,” in *Proceedings of the Materials Research Society Symposium*, pp. 61-66, 2012.

Coherent Phonon Generation through Nanoscale Enhanced Light-Matter Interaction: Towards Novel Silicon Lasers, Broadband Phononic Signal Processing, and Optically Powered Micromechanics

151336

Year 3 of 3
Principal Investigator: P. Davids

Project Purpose:

The science of nanoscale light matter interactions, specifically the study of optical forces and photon-phonon coupling within nanoscale materials and geometries, provide fertile ground for tremendous scientific and technological advancement. Through deeper understanding of the physics of coherent phonon generation, new ultrafast methods for the study of thermal transport, phonon lifetimes and phonon dispersion within novel materials and nanoscale structures will be possible. Furthermore, improved understanding of optical force mediated photon-phonon coupling will enable efficient light-driven coherent phonon generation — such processes can be utilized to create significant improvements in radio frequency (RF), phononic, acousto-optic and optical signal processing performance via a new class of chip-scale hybrid photonic-phononic devices. However, these scientific and technological advances will require a new experimental and theoretical foundation for the study of light-matter interactions. Through this project, we will develop this scientific foundation by: 1) development of powerful new multiscale models for the treatment of optical force mediated photon-phonon coupling at all length scales, 2) development of rigorous models for the prediction of optical forces within nanoscale materials and geometries, and 3) by devising a flexible experimental platform for the study of optical forces and photon-phonon coupling at nanoscales. In achieving the aforementioned theoretical and experimental tasks, we will radically advance the science of nanoscale light-matter interactions. In the process, Sandia's unique Microsystems and Engineering Sciences and Applications (MESA) capabilities will be used to execute highly differentiated scientific studies and to develop highly differentiated chip-scale technologies of tremendous benefit to DOE's mission.

Summary of Accomplishments:

During the course of this project, we discovered new physics describing the transduction of optomechanical forces, fabricated novel integrated structures, developed novel measurement techniques and had numerous experimental findings.

In particular, we showed that simulated brillouin scattering is theoretically enhanced at the nanoscale through radiation pressure effects and published this work in *Physical Review X*. Moreover, we demonstrated this prediction by fabricating and testing suspended waveguide structures with enhanced optomechanical forces, publishing the work in *Nature Communications*. Recently, we were able to show very high performance optomechanical filtering and Machwave emit/receive (waveguide to waveguide transduction) in both photonic and phononic crystal guided suspended membrane devices.

The fabrication process developed for suspended waveguide structures has proven to be useful, not only for optomechanics, but also for mid-infrared silicon photonics. By suspending the silicon waveguides in a silicon nitride membrane, and removing the glass substrate below, we eliminated the barrier toward low-loss propagation of light from 2-6 µm in the complementary metal-oxide-semiconductor (CMOS) process. This capability has numerous national security related applications and work on this topic is ongoing. Finally, we developed a novel ultrafast asynchronous optical sampling (ASOPS) apparatus for observation of time-resolved dynamics of optomechanical nonlinear effects. To date, we have acquired groundbreaking data with >60 dB improved signal-to-noise ratio (SNR) and uncovered optomechanical modes which were previously unobservable. The key benefit of this technique is the ultra-high bandwidth and the ability to deconvolve multiple, interfering nonlinearities. Existing techniques are extremely limited since a nonlinearity, such as the Kerr effect, can completely obscure the optomechanical transduction. Moreover, this technique will allow us to directly observe phononic delayed transduction in the time domain.

Significance:

We made the following scientific and engineering advancements, which directly relate to mission and national security potential:

- First demonstration of stimulated Brillouin scattering (SBS) in nanoscale Si-photonic waveguides (2000x stronger than fiber)

- ASOPS Time-Domain Ultrafast Optomechanical Spectroscopy
  - First observation of nanoscale transient optomechanical nonlinear dynamics
  - First demonstration of optomechanical delayed transduction between waveguides (emit/receive)
  - First demonstration of broadband optomechanical transduction

- Developed 1D suspended membrane phononic crystal fab process at Sandia's Microsystems and Engineering Sciences and Applications (MESA)
  - Ideal for low-loss infrared Si-photonics (2-10 µm). Invention disclosure filed and devices fabricated (awaiting test)

Refereed Communications:

P.T. Rakich, Z. Wang, C. Reinke, P. Davids, and R. Camacho, "Traveling-Wave Phonon Emission at the Nanoscale," *Laser Science*, October 2012.

H. Shin, W. Qiu, R. Jarecki, J.A. Cox, R.H. Olson, III, A. Starbuck, Z. Wang, and P.T. Rakich, "Tailorable Stimulated Brillouin Scattering in Nanoscale Silicon Waveguides," *Nature Communications*, vol. 4, June 2013.

Theoretical and Experimental Studies of Electrified Interfaces Relevant to Energy Storage

151338

Year 3 of 3
Principal Investigator: C. C. Hayden

Project Purpose:

Major advances in electrochemical technologies for energy storage require improved understanding of electrolyte/electrode interfaces, including structure, interfacial species, and electrochemical processes, and the incorporation of this understanding into quantitative models. Such models will guide development of advanced designs and materials to increase efficiency and reduce aging and failure rates. Simplified models such as Helmholtz's electric double-layer (EDL) concept and even Gouy-Chapman-Stern's diffuse model fail to take into account the molecular nature of ion distributions, solvents, and electrode surfaces and, therefore, cannot be used in predictive, high-fidelity simulations for device design. The goal of this project is to develop detailed models of the structure and chemical properties of representative electrified interfaces, which we validate by multiparameter, minimally invasive experimental measurements. Such synergistic interaction between calculations and experiment is only now becoming possible with Sandia's rapid development of atomistic-to-continuum interfacial modeling and recent advances in spatially precise in situ optical probes enabled by emerging laser technology. Much of previous work in this field has focused on complex, integrated electrochemical energy-storage devices and/or materials that are not suitable for detailed modeling and in situ probing. Our approach attempts to gain a predictive understanding of complex interfaces present in such devices through coordinated experimental and theoretical studies of tractable (model) systems, which isolate important phenomena.

Summary of Accomplishments:

The theoretical component of this project has made important advancements in modeling electric double layer (EDL) structure. We developed a robust understanding of existing coarse-grained particle models in terms of packing structure and EDL capacitance and demonstrated that these models over-predict EDL capacitance by a factor of 20 versus more realistic models. Going beyond existing simple models, we have proven that molecular structure is important in the EDL to accurately predict capacitance based on the stability of intercalated molecules in condensed surface layers. In addition, we showed that the surface material can change EDL capacitance by over a factor of two. To the best of our knowledge, we obtained the first direct characterization of the electrical medium near the electrode, which has a dielectric varying an order of magnitude from the bulk. Using this metric to separate diffuse and compact parts of the EDL greatly improves coarse-grained circuit models. Finally, we developed a simulation framework to rapidly build models supporting future prototyping based on molecular dynamics of different material systems. The experimental portion of this project has developed a sensitive confocal Raman microscope with a custom transmission grating spectrometer for surface vibrational spectroscopy. Results of an initial study of voltage-dependent Raman spectra of graphene coated metallic electrodes in aqueous electrolytes suggest that charge doping of the graphene occurs in the field of the EDL. We have also implemented a polarization modulation reflection absorption infrared spectroscopy (PM-RAIRS) apparatus and used it to demonstrate vibrational spectroscopy of submonolayer components in model complex electrode surfaces. The PM-RAIRS apparatus provides the capability for species identification selective to interfaces. Finally, a new femtosecond laser enabled development of a surface-sensitive second harmonic generation spectrometer to study voltage-dependent interfacial optical properties. Calculations of these optical properties are just becoming available from our theoretical modeling studies.

Significance:

The systematic design of new electrochemical devices requires development of more detailed understanding and modeling of electrochemical interfaces. This project has supplied new modeling approaches and results that quantify the impact of using higher fidelity models and reveal important factors to include in this detailed modeling. Experimental results have provided new tools for testing and validating detailed predictions of new models, thus enabling feedback to improve the accuracy of the models.

Refereed Communications:

J.W. Lee, J.A. Templeton, K.K. Mandadapu, and J.A. Zimmerman, "Comparison of Molecular and Primitive Solvent Models for Electrical Double Layers in Nanochannels," *Journal of Chemical Theory and Computation*, vol. 9, pp. 3051-3061, May 2013.

Developing Thermoelectric Cryo-Cooling

151339

Year 3 of 3
Principal Investigator: D. L. Medlin

Project Purpose:

Many Sandia systems require low-temperature cooling near 77K, including space-based electronics for remote sensing/verification programs, and terrestrial devices such as photon detectors, mirrors, integrated circuits, and chem-bio sensors. However, conventional cryogenic coolers are large, expensive, high-powered, and difficult to integrate with electronics. On-chip, solid-state thermoelectric (TE) cryo-cooling can reduce cost and inefficiencies, enabling future systems.

TE performance requires a high figure-of-merit, zT, optimized by high electrical conductivity, high thermopower, and low thermal conductivity — properties found in Bi-based alloys. However, commercial state-of-the-art materials are limited to zT ~ 1, too low for real cooling applications that must constantly remove heat from a power source. Recent reports of nanostructured bulk materials have shown zT ~ 1.6, largely through reduced thermal conductivity. Further advances demand corresponding improvements in electric conductivity and thermopower.

Theory predicts 10-fold zT improvements in one-dimensional nanowires (diameters < 5 nm), due to quantum confinement, which creates peaks in the electronic density of states that enhance thermopower. Nevertheless, the present performance of nanowires is abysmal: the best reported zT = 0.12. A detailed literature review suggests this failure is due to inadequate attention to key materials factors (composition and crystallinity) affecting the electronic transport.

Our goal is to improve the compositional and structural control of Bi-based nanowires to enable enhanced thermoelectric performance.

We aim to develop nanowires optimized for structure, composition, and dimensionality through an integrated program of synthesis, characterization, and theory. We will use novel electrochemical deposition approaches to provide the necessary materials control, employ advanced microscopies to thoroughly evaluate material composition and structure, and measure the resulting transport properties on individual nanowires using novel probe platforms, guided by past theory and new modeling of nanoscale transport processes.

Summary of Accomplishments:

Over the course of this project, we made several key advances in the science and technology of thermoelectric nanowires. We established key growth processes required for electrodeposition of high-quality nanowires into porous anodic aluminum oxide (AAO) templates. A key aspect of our approach is the integration of the templates directly onto silicon. Important process challenges that we met include: optimization of Al film deposition and anodization to provide thicker templates (up to 7 micron) directly onto silicon, development of a W valve-layer approach for controlling termination of pore formation, and development of electrochemical chemistries and procedures for high quality growth of Bi_2Te_3 and BiSb-based nanowires. We also investigated approaches for post-deposition annealing to further improve the crystalline quality of the nanowires. Our work identified annealing regimes for optimizing both grain size as well as crystal texture, both of which are critical to controlling nanowire performance. Through detailed x-ray diffraction and electron microscopic studies, we advanced the mechanistic understanding of the microstructural evolution. In parallel, we advanced the theoretical underpinnings of nanowire thermoelectric transport. This work includes advances in understanding the dependence of thermal transport behavior on the thermal conductivity of the surrounding environment and the discovery of the potential for high thermoelectric efficient for nanowires operated in the space-charge-limited regime.

Significance:

Advanced TE materials performance will enable new technologies for cooling and power generation that are relevant to the national security missions of DOE and other agencies, including DoD and DHS. Potential applications include new solutions for cryo-cooling to improve the performance of critical electronic systems for various detectors (optical, microwave, RADAR, chem-bio, etc.), as well as enabling new technologies for long-lived power sources required for remote unattended operations.

Improving the Electrical and Thermal Resistance of Nanoscale Contacts

151340

Year 3 of 3
Principal Investigator: R. E. Jones

Project Purpose:

DOE's defense, nonproliferation, threat detection, and energy missions are looking increasingly toward nanoelectronics for solutions; however, these devices must be fabricated reliably and have high performance in order to fulfill this mission.

A fundamental factor limiting the performance of electronic and optoelectronic devices is the thermal and electrical resistance of the ubiquitous metal-semiconductor contact. This problem becomes more acute as devices move toward the nanoscale where these interfacial resistances tend to dominate. Also, the contact resistances are typically a source of device failure either during fabrication or later in service. While these effects have been studied extensively and are relatively well understood in bulk contacts, much of the physics must be reevaluated for metal-nanostructure contacts due to the low dimensionality affecting central parameters such as electrostatic interactions, strain, and interfacial energies. Pragmatically, this reconsideration is warranted as bulk techniques for improving contact properties (e.g., heavily doping the semiconductor) have been shown to be ineffective or inappropriate for contacts to low dimensional structures. Moreover, the techniques that do translate (e.g., high temperature annealing) are not always reliable or completely understood, leading to a cookbook approach to fabrication.

In response, we formed a research effort to discover the determining factors governing electron and phonon transport at contacts to nanotubes, nanofilms, and nanowires. The combined experimental, simulation, and theory thrusts established the fundamental physics of nanoscale contacts that will enable the realization of controllable contacts to nanostructures. This project took an integrated theoretical-experimental approach to investigate electronic, thermal, and electron-phonon processes at a nanoscale metal-semiconductor junction. It developed new models and discovered new phenomena specific to the physics of nanodevices. In particular, we have explored how structure and energetics at the interface affects transport and have translated these results to realizable fabrication techniques.

Summary of Accomplishments:

This project had a wide purview and the challenging task of connecting basic science to controllable fabrication parameters and realizable devices through the process of discovery.

Some of the highlights of the project are listed:

- Numerous demonstrated realizable means of improving contact resistance: manipulating finite size effects and utilizing nanopatterning, controlled annealing, contaminant reduction, particular adhesion layers, near device doping control, and nanowire-to-film geometries
- The efficacy of using the gate — instead of doping, which is ineffective — to modulate the contact barriers in one- and two-dimensional devices

- The development of a multiple-scale coupling method that uses molecular dynamics to model deposition, a density functional code to calculate the electronic states of the resulting atomic configuration, and a tight-binding code to predict electron transport performance in a manner that simulates the fabrication process and can lead to synthetic design of high performance electronic devices
- The discovery of fundamental differences in how a non-equilibrium population of electrons and phonons interact (i.e., in a powered state) in comparison to the often treated equilibrium state
- The development of a fundamental understanding of how an adhesion layer between the metal contact and the semiconducting device creates ideal thermal transmission
- Direct microscopy of an actual device configuration: a carbon nanotube (CNT) with an overlaid metal contact on a Si substrate
- A demonstrated factor of four improvement of the conductance of the common Au:Si contact by relatively straight-forward processing
- The discovery that the height of the Schottky barrier affects thermal conductance at the contact

These discoveries have been published in over 20 peer-reviewed articles and have changed our fabrication and design of nanoelectronics.

Significance:

DOE's defense, nonproliferation, threat detection, and energy missions are looking increasingly toward nanoelectronics for solutions; however, these devices must be fabricated reliably and have high performance in order to fulfill this mission. In particular, we have explored how structure and energetics at the interface affects transport and have translated these results to realizable fabrication techniques.

Refereed Communications:

X.W. Zhou, R.E. Jones, C.J. Kimmer, J.C. Duda, and P.E. Hopkins, "Relationship of Thermal Boundary Conductance to Structure from an Analytical Model Plus Molecular Dynamics Simulations," *Physical Review B*, vol. 87, p. 094303, March 2013.

R.E. Jones, J.C. Duda, X.W. Zhou, C.J. Kimmer, and P.E. Hopkins, "Investigation of Size and Electronic Effects on Kapitza Conductance with Non-Equilibrium Molecular Dynamics," *Applied Physics Letters*, vol. 102, p.183119, May 2013.

X.W. Zhou, R.E. Jones, J.C. Duda, and P.E. Hopkins, "Molecular Dynamics Studies of Material Property Effects on Thermal Boundary Conductance," *Physical Chemistry Chemical Physics*, vol. 15, pp. 11078–11087, May 2013.

C.B. Saltonstall, C.A. Polanco, J.C. Duda, A.W. Ghosh, P.M. Norris, and P.E Hopkins, "Effect of Interface Adhesion and Impurity Mass on Phonon Transport at Atomic Junctions," *Journal of Applied Physics*, vol. 113, p. 013516, 2013.

J.C. Duda, C-Y.P. Yang, B.M. Foley, R. Cheaito, D.L. Medlin, R.E. Jones, and P.E. Hopkins, "Influence of Interfacial Properties on Thermal Transport at Gold: Silicon Contacts," *Applied Physics Letters*, vol. 102, p. 081902, 2013.

N.Q. Le, J.C. Duda, T.S. English, P.E. Hopkins, T.E. Beechem, and P.M. Norris, "Strategies for Tuning Phonon Transport in Multilayered Structures Using a Mismatch-Based Particle Model," *Journal of Applied Physics*, vol. 111, p. 084310, 2012.

J.C. Duda and P.E. Hopkins, "Systematically Controlling Kapitza Conductance via Chemical Etching," *Applied Physics Letters*, vol. 100, p. 111602, 2012.

Advanced High Z NanoScintillators

151341

Year 3 of 3
Principal Investigator: B. A. Hernandez-Sanchez

Project Purpose:

Scintillators detect radiation by producing light upon exposure; unfortunately, the current detection quality suffers from low luminosity, volume restrictions, and chemical instability. Critical to overcoming these constraints are the elucidation of radiation interaction mechanisms for scintillating materials at multiple length scales (nano-micro-meso) and the discovery of novel high Z nanoscintillators for gamma-ray detection. The goal of this project is to determine the utility of size-selected high Z transition metal chalcogenides (MEx, E = S, Se, Te) as novel scintillating materials. Without these improved scintillator materials, the correct identification/detection of radiation sources continues to be a vulnerability to America. For the scintillation community to fully embrace nanomaterials and ultimately attract outside customers (DOE, DHS, Defense Threat Reduction Agency [DTRA]), it is critical that fundamental materials research be undertaken addressing the optimal crystallite size (nano, micro, meso) and the development of new materials. Once accomplished, direct sponsorship from a variety of sources that have already expressed interest is expected.

The development of novel scintillation materials and nanoscintillators is neither widespread nor established. Several key aspects prevent industry and academic pursuits: 1) single crystal growth techniques used to validate a materials performance for gamma-ray spectrometers — this restricts materials examined, 2) understanding of theoretical/fundamental radiation-detection physics occurring in materials are still under debate, which precludes research in nanomaterials, and most important 3) limited access to radiation characterization facilities. With its multidiscipline interactive researchers, Sandia is ideally suited to improve scintillators using in place expertise and capabilities to address critical materials, characterization, and production of scintillator devices. Existing scintillator issues will be overcome by: 1) systematically evaluating oxide scintillator size effects (nano, micro, meso), 2) developing novel size controlled scintillators based on unexplored high Z transition metal chalcogenides (MEx), 3) exploring activator concentration on properties, and 4) developing nanocomposite materials for device development. The expected results promise to revolutionize current scintillator detector capabilities.

Summary of Accomplishments:

The Advanced High Z Nanoscintillator project explored the development of novel nanoscale scintillators and the fundamental property changes resulting from particle size for radiation detection applications. Nanomaterials of doped (lanthanides) and undoped metal tungstates (MWO_4; M = Ca, Cd, Pb); yttrium aluminum garnet ($Y_5Al_5O_{12}$, YAG); lutetium aluminum garnet ($Lu_5Al_5O_{12}$, LuAG); bismuth germanium oxide ($Bi_4Ge_4O_{12}$, BGO), tungsten chalcogenides (WE_x; E= S, Se, Te); and alkaline earth chalcogenides (AEE; AE = Sr, Ba, Ca, E= S, Se, Te) were synthesized and compared to their bulk counterpart. Scintillation behavior was examined using photoluminescence, Uv-Vis, cathodoluminescence, radioluminescence, and ion beam luminescence, while structural stability was characterized by in situ ion irradiation transmission electron microscopy. Through these studies, we determined that nanoscintillators are promising detector materials because: 1) they can withstand ionizing radiation, 2) particle size or dopants can be used to tune emission wavelengths, 3) nanocyrstals are stable to radiation effects compared to larger particles that appear to suffer from radiation induced structural defects, and 4) nanoscintillators can be incorporated into various polymer matrices.

Significance:

By unraveling the fundamental synthesis and unknown nanoparticle-radiation mechanisms, developing novel scintillator materials, and establishing new capabilities to strengthen Sandia's Radiation Detection Programs, we are able to meet new technical requirements and eliminate security threats. The results of our project will enable Sandia to address the critical mission of monitoring activities associated with international nuclear safeguards and nuclear weapons treaty verification established by NNSA, DOE, DHS, and DTRA.

Refereed Communications:

B.A. Hernandez-Sanchez, T.J. Boyle, J. Villone, P. Yang, M. Kinnan, S. Hoppe, S. Thoma, K. Hattar, and F.P. Doty, "Size Effects on the Properties of High Z Scintillator Materials," in *Proceedings of the SPIE Conference on Penetrating Radiation Systems and Applications XIII*, 2012.

T.J. Boyle, A.T. Velazquez, D.T. Yonemoto, M.A. Rodriguez, and L.A. Steele, "Synthesis and Characterization of a Series of Rubidium Aryloxide Compounds," *Journal of Coordination Chemistry*, vol. 66, pp. 1189-1201, April 2013.

T.J. Boyle, L.A. Steele, and A. Saad, "Synthesis and Characterization of the Heavy Alkaline Earth Aryloxide Congeners," *Inorganica Chimica Acta*, vol. 394, pp. 259-268, January 2013.

S.M. Hoppe, K. Hattar, T.J. Boyle, J. Villone, P. Yang, F.P. Doty, and B.A. Hernandez-Sanchez, "Application of In Situ Ion Irradiation TEM and 4D Tomography to Advanced Scintillator Materials," in *Proceedings of the SPIE Conference on Penetrating Radiation Systems and Applications XIII*, 2012.

T.J. Boyle, D.T. Yonemoto, L.A. Steele, J. Farrell, P. Renehan, and T. Huhta, "Coordination Chemistry of N,N,N ',N '-Tetrakis(3,5-Substituted Benzyl-2-Oxide)-2,2 (Ethylenedioxy) Diethanamine Modified Group 4 Metal Alkoxides," *Inorganic Chemistry*, vol. 51, pp. 12023-12031, November 2012.

J. Villone, "Ion Beam Induced Luminescence of Advanced Materials and their Application in Radiation Detectors," doctoral dissertation, New Mexico Institute of Mining and Technology, 2013.

T.J. Boyle and L.A. Steele, "Lanthanide Halides and Lanthanide Alkoxides," Chapters in *The Rare Earth Elements: Fundamentals and Application. Alkoxides*, David Attwood, editor, Wiley, 2012.

Tailoring Thermal and Electric Transport Properties through Solid State Self Assembly

151343

Year 3 of 3
Principal Investigator: J. Ihlefeld

Project Purpose:

To be a viable high-impact energy scavenging method, thermoelectric devices must be composed of nontoxic and abundant elements and be stable in air to high temperatures. Currently, the best moderate temperature range (0 to ~800 °C) thermoelectrics are semiconductors comprised of relatively toxic and strategically limited p-block elements (i.e., tellurides, antimonides, and selenides). Many oxide materials would meet requirements for large-scale impact; however, their thermoelectric figures of merit ($ZT=TS^2s/k$, where T is the temperature, S is the thermopower, s is the conductivity, and k is the thermal conductivity) must be improved. The challenges for oxide thermoelectrics are low electronic conductivity and high thermal conductivities. While p-type oxides with ZT values approaching 0.8 have been identified, complementary n-type materials with equivalent ZTs have not been prepared. Virtually all groups researching oxide thermoelectrics focus on single-phase homogeneous ceramics, thin films, and single crystals.

There have been recent reports of improved thermopower in highly reduced oxide ceramics with increased carrier concentrations and phonon scattering in defective regions and separate reports of decreased thermal conductivity in oxide films with complex layered atomic arrangements. In this project, we are combining the benefits of these two studies through two approaches: 1) developing oxide ceramics with self-assembled nanostructured phases in the systems $SrNbO_3$ and $Zn(Ga,Mn)_2O_4$ where amphoteric dopants and processing atmospheres can be used to arbitrarily control carrier concentrations, while thermal treatments can control boundary geometries concentrations and 2) designing oxide materials where the mechanisms controlling electronic and thermal conductivity occur on separate crystal sublattices — a so-called phonon-glass electron-crystal in a perovskite crystal structure. These methodologies have yet to be investigated by other researchers for thermoelectric applications in oxide materials — those that are environmentally benign and abundant.

Summary of Accomplishments:

We made several new scientific observations over the course of this project. We measured and modeled the effect of grain size scaling on the thermal conductivity of $SrTiO_3$-based materials with nano-scale grain sizes. We developed an understanding of the phase stability of $Sr_2Nb_2O_7$ materials, including synthesis of a $SrNbO_3$ phase. We measured and modeled the effect of weakly bound crystallographic layers in $Sr_2Nb_2O_7$ on the cross-plane thermal conductivity. Bismuth and lanthanum-doped strontium titanate ceramics were prepared with thermoelectric figure of merits greater than 0.3 at 500K, demonstrating a ~90% increase over the current state of the art. We developed a room temperature Seebeck coefficient measurement instrument capable of rapid material screening. We developed an instrument capable of measuring Seebeck coefficient and electrical conductivity over broad temperature ranges (300-1300K) and varying atmospheres. Using this instrument, we measured a 1000X change in thermoelectric power factor in $SrTiO_3$ ceramics by altering the measurement atmosphere. This demonstrates that great care must be taken in discussing doping of oxide thermoelectric materials with a strong consideration of defect chemistry and also that the measurement atmosphere can affect the measured properties.

Significance:

We have advanced the frontier of oxide thermoelectric research by identifying critical missing variables in component performance: oxygen pressure and content. This result came about from the development of new instrumentation that measures properties of interest to national security programs and will have utility in this venue after the end of this project.

Refereed Communications:

B.M. Foley, H.J. Brown-Shaklee, J.C. Duda, R. Cheaito, B.J. Gibbons, D. Medlin, J.F. Ihlefeld, and P.E. Hopkins, "Thermal Conductivity of Nano-Grained $SrTiO_3$," *Applied Physics Letters*, vol. 101, p. 231908, 2012.

M.J. Campion, H. Brown-Shaklee, M.A. Rodriguez, J.J. Richardson, P.G. Clem, and J.F. Ihlefeld, "Crystallization Atmosphere and Substrate Effects on the Phase and Texture of Chemical Solution Deposited Strontium Niobate Thin Films," *Journal of the American Ceramic Society*, vol. 96, pp. 743-749, February 2013.

P.E. Hopkins, C. Adamo, L. Ye, B.D. Huey, S.R. Lee, D.G. Schlom, and J.F. Ihlefeld, "Effects of Coherent Ferroelastic Domain Walls on the Thermal Conductivity and Kapitza Conductance in Bismuth Ferrite," *Applied Physics Letters*, vol. 102, p. 121903, 2013.

Understanding and Controlling Low-Temperature Aging of Nanocrystalline Materials

151344

Year 3 of 3
Principal Investigator: C. C. Battaile

Project Purpose:

Nanocrystalline metals offer exceptional properties (e.g., high strength, fatigue resistance, radiation hardness, and low friction). The greatest hurdle to applying these materials is the fact that their grain structures evolve at ambient temperatures. Recent evidence indicates that nanocrystalline metals can even evolve at cryogenic temperatures faster than they do at room temperature. This can degrade properties and even accelerate failure. For example, large grains initiate fracture during fatigue of nanocrystalline nickel coatings and coarsening of nanocrystalline copper lines in integrated circuits degrades their electronic properties. Still, low temperature grain growth remains a mystery. Microstructures are usually thought to be stable below about 40% of the melting temperature. This is because the grain boundary velocity, v, is the product of the driving pressure, p, and the boundary mobility, M, which decreases exponentially with temperature. Using parameters measured in aluminum, for example, the velocity of nanoscale grain boundaries is about 40 micrometers per second at 70% of the melting temperature, but only about 1 femtometer per second at room temperature. According to these data, then, at cryogenic temperatures, the boundaries shouldn't move perceptibly within the lifetime of the universe! So how can we explain, and ultimately control, ambient-temperature grain growth in nanocrystalline metals in order to develop strategies for mitigating the inherent instability of these otherwise advantageous materials? The planned research will attempt to answer these questions by: 1) determining the conditions under which this anomalous behavior does and does not occur by performing micro-indentation experiments in air, liquid nitrogen, and liquid helium; 2) characterizing the nanoscale crystallography of the relevant microstructural features by conducting precession transmission electron microscopy (TEM) experiments; and 3) directly observing low-temperature grain growth via in situ indentation in the TEM.

Summary of Accomplishments:

Nanocrystalline copper films were created by both repetitive high-energy pulsed power to produce material without internal nanotwins, and pulsed laser deposition to produce nanotwins. Samples of these films were indented at ambient (298K) and cryogenic temperatures by immersion in liquid nitrogen (77K) and helium (4K). The indented samples were sectioned through the indented regions and imaged in a scanning electron microscope. Extensive grain growth was observed in the films that contained nanotwins and were indented cryogenically. The films that either lacked twins, or were indented under ambient conditions, were found to exhibit no substantial grain growth by visual inspection. Precession transmission electron microscopy was used to confirm these findings quantitatively and show that grain boundaries with a high degree of crystallographic symmetry proliferate during grain growth, implying that these interface types play a key role in governing the extensive grain growth observed here. Molecular dynamics simulations of the motion of individual grain boundaries demonstrate that specific classes of boundaries — notably those with high symmetry — exhibit anti- or a-thermal migration, meaning that their mobilities either increase or do not change significantly with decreasing temperature. An in situ cryogenic indentation capability was developed and implemented in a transmission electron microscope. Preliminary results do not show extensive cryogenic grain growth in indented copper films. This discrepancy could arise from the significant differences in configuration and loading of the specimen between the two approaches. Further research and development of this capability is needed.

Significance:

Nanocrystalline metals are in service, or under consideration, for a variety of weapons component applications, especially in miniature systems. However, many of their advantageous properties rely on their nanostructure and its inherent instability can dramatically limit reliability. The findings from this project provide key clues to the origins of this instability, the materials characteristics that promote it, and potential pathways for controlling it. A robust strategy for engineering nanoycrystalline metals will greatly increase their suitability and reliability for any number of applications in which their properties are advantageous.

Refereed Communications:

H.A. Padilla, II, B.L. Boyce, C.C. Battaile, and S.V. Prasad, "Frictional Performance and Near-Surface Evolution of Nanocrystalline Ni-Fe as Governed by Contact Stress and Sliding Velocity," *Wear*, vol. 297, pp. 860-871, January 2013.

G.J. Tucker and S.M. Foiles, "Molecular Dynamics Simulations of Rate-Dependent Grain Growth during the Surface Indentation of Nanocrystalline Nickel," *Materials Science and Engineering: A*, vol. 571, pp. 207-214, June 2013.

E.R. Homer, S.M. Foiles, E.A. Holm, and D.L. Olmsted, "Phenomenology of Shear-Coupled Grain Boundary Motion in Symmetric Tilt and General Grain Boundaries," *Acta Materialia*, vol. 61, pp. 1048-1060, February 2013.

J.G. Brons, H.A. Padilla, II, G.B. Thompson, and B.L. Boyce, "Cryogenic Indentation-Induced Grain Growth in Nanotwinned Copper," *Scripta Materialia*, vol. 68, pp. 781-784, May 2013.

Fundamental Investigation of CVD Graphene Synthesis

151377

Year 3 of 3
Principal Investigator: M. T. Brumbach

Project Purpose:

The purpose of this project is to discover new phenomena controlling the growth of graphene via Chemical Vapor Deposition (CVD). We intend to identify how residual adventitious carbon on the copper surface promotes graphene nucleation and leads to higher nucleation density and to discover a new method for reducing nucleation sites at the surface to grow large domain graphene. We find that copper oxide can act as a self-cleaning substrate for graphene growth by CVD. Using oxidized electropolished copper foil leads to a reduction in graphene nucleation density by over a factor 1000 when compared to using cleaned oxygen free copper foil.

Summary of Accomplishments:

We discovered that adventitious carbon or other carbonaceous compounds on the surface of Cu can increase graphene nucleation density. We also found that copper oxidation with subsequent reduction at temperatures above 900 °C is an effective way to clean the copper surface prior to graphene growth. Importantly, we demonstrated that the process could be used to grow large-area individual graphene domains of over a millimeter across.

Significance:

This work, in collaboration with the University of Texas-Austin, profoundly explains some of the mysteries of graphene growth. For many years, the impacts of the substrate have been a mystery among the community, and there has been an ethereal acceptance of a "magic" copper composition that has proved ideal. There has been a specific composition, and a specific supplier, of copper that has yielded repeatable and exceptional results, but with no clear explanation for the properties observed. This work clearly explains the role of surface species on the graphene nucleation and growth and provides guidance for researchers around the world attempting to grow large area graphene domains.

Refereed Communications:

Z.R. Robinson, P. Tyagi, T.M. Murray, C.A. Ventrice, S.S. Chen, A. Munson, C.W. Magnuson, and R.S. Ruoff, "Substrate Grain Size and Orientation of Cu and Cu–Ni Foils used for the Growth of Graphene Films," *Journal of Vacuum Science and Technology A*, vol. 30, p. 011401, 2012.

I.N. Kholmanov, C.W. Magnuson, A.E. Aliev, H. Li, B. Zhang, J.W. Suk, L.L. Zhang, E. Peng, S.H. Mousavi, A.B. Khanikaev, R. Piner, G. Shvets, and R.S. Ruoff, "Improved Electrical Conductivity of Graphene Films Integrated with Metal Nanowires," *Nano Letters,* vol. 12, pp. 5679-5683, October 2012.

Solar Fuel Cell for Photocatalysis of Organic Pollutants with Simultaneous H_2 Production

155797

Year 3 of 3
Principal Investigator: K. R. Reyes

Project Purpose:

The use of sunlight to split water is one promising possibility of storing solar energy in an energy carrier (hydrogen) to allow storage and distribution. For solar-to-hydrogen conversion, specialized semiconductors are needed to absorb sunlight and use this energy to produce clean hydrogen. Metal oxides are good candidates because of their good photocatalytic activity, but their efficiency is jeopardized by three important factors: 1) poor sunlight absorption, 2) poor charge-carrier mobility and 3) fast electron/hole recombination. This project will focus in the manipulation of semiconductors to correct each of those limiting factors using a comprehensive and synergistic approach. We plan to develop organized composite WO_3/TiO_2 nanostructures with a long absorption pathway to efficiently direct the flow of photogenerated charges and to optimize sunlight absorption. In addition, aqueous organic pollutants will be used as hole scavengers to reduce the electron/hole recombination in the photoanode and consequently increase the hydrogen production in the cathode.

Summary of Accomplishments:

Nanostructured WO_3/TiO_2 nanotubes with properties that enhance solar photoconversion reactions were developed, characterized and tested. The TiO_2 nanotubes were prepared by anodization of Ti foil, and WO_3 was electrodeposited on top of the nanotubes. Scanning electron microscopy (SEM) images show that these materials have the same ordered structure as TiO_2 nanotubes, with an external nanostructured WO_3 layer. Diffuse reflectance spectra showed an increase in the visible absorption relative to bare TiO_2 nanotubes and in the UV absorption relative to bare WO_3 films. Incident simulated solar photon-to-current efficiency (IPCE) increased from 30% (for bare WO_3) to 50% (for WO_3/TiO_2 composites). Comparing the absorption spectrum and IPCE plot, we can conclude that for all the wavelengths that the composite electrodes absorb photons, a photocurrent is generated. In addition, the electrode/electrolyte interfacial transfer was improved by incorporating the fast and irreversible oxidation of organic pollutants, resulting in higher photocurrents that can be used to drive reduction reactions. With the addition of diverse organic pollutants, the photocurrent densities exhibited more than a five-fold increase. Chemical oxygen demand measurements showed the simultaneous photodegradation of organic pollutants. Contrary to other bandgap reduction techniques, we showed that composite WO_3/TiO_2 nanostructures improved the solar spectrum absorption as well as the charge carrier transport. The results of this work indicate that the unique structure and composition of these composite materials enhance the charge carrier transport and optical properties compared with the parent materials.

Significance:

We demonstrated a low-cost synthetic approach to create WO_3/TiO_2 photoanodes for wastewater treatment with simultaneous hydrogen production. Each process in the operation of the photoelectrochemical cell was improved without jeopardizing the other processes, which resulted in an overall efficiency improvement. WO_3/TiO_2 electrodes were more active that TiO_2 or WO_3 alone for optical and photoelectrochemical measurements. These composite nanostructures showed an improvement in the photogenerated carrier transport and the absorption pathways, resulting in higher IPCE efficiencies. These materials are interesting candidates to drive simultaneous photochemical reactions, such as water reduction (H_2 production) and oxidation of pollutants in wastewater.

Refereed Communications:

K.R Reyes-Gil and D. Robinson, “WO_3/TiO_2 Nanotube Photoanodes for Solar Water Splitting with Simultaneous Wastewater Treatment,” to be published in *ACS Applied Materials & Interfaces*.

Beyond the Ideal Nanostructure: Local Environmental Effects on the Electronic and Optical Properties of Carbon Nanotubes

157694

Year 3 of 3
Principal Investigator: D. C. Spataru

Project Purpose:

Carbon nanotubes (CNTs) have attracted tremendous interest for a number of applications and also for the breadth of new scientific questions that they bring. The properties of isolated CNTs have been extensively studied. In most situations, however, these systems are subject to external perturbations, which make their behavior deviate from the ideal, isolated case. Examples include interaction with a substrate, other nanostructures, polymers or DNA encapsulation, metallic contacts, doping, applied electric or magnetic fields, applied strain, alignment in periodic arrays, and so on. Both electronic and optical properties of CNTs are expected to be altered by such environmental and dimensionality effects.

Predicting the changes in properties of CNTs due to a substrate is important not only for the potential integration of CNTs in functional devices, but also from a fundamental physics perspective. Consider a semiconducting CNT in a field-effect transistor configuration. The alignment of electronic states at the metal/CNT interface is critical to the device performance as it determines the activation energy necessary to inject an electron from the metal contact. How do the metal contacts or even the metallic gate affect the electronic states of the CNT?

The binding energy of excitons is another fundamental quantity important in optoelectronic and photonic applications, as it directly affects critical parameters such as exciton dissociation, electron-hole recombination or radiative decay rates. In isolated semiconducting, CNTs excitons bind with energies amounting to a large fraction of the quasiparticle (QP) bandgap.

In addition to addressing the above, we touched upon a fundamental issue in the physics of physisorbed molecules: can the optical gap of a small molecule get larger than the electronic gap as the molecule approaches a metallic surface?

Summary of Accomplishments:

We developed and applied a novel computational technique that can be applied to the study of electronic and optical properties of various nanostructures in complex environments. The technique is based on an embedding approach newly implemented in the context of the GW and Bethe-Salpeter methods. We applied this technique to the case of several nanostructures (such as carbon nanotubes and organic molecules) near a metallic surface.

We computed the renormalization of electronic and optical gaps in carbon nanotubes near a metal. The QP bandgap renormalization in semiconducting CNTs is found to scale as $1/(2h_a)$, with h_a the apparent nanotube height, and it can exceed half an eV. Also, the binding energy of excitons is reduced dramatically — by as much as 75% near the surface. Compensation between QP and excitonic effects results in small changes in the optical gap. The important role played by the nanotube screening response in establishing these effects is emphasized and a simple electrostatic model with no adjustable parameters explains the results of state-of-the-art calculations and generalizes them to a large variety of CNTs.

Within the embedding approach, it is apparent that the overall electron-hole interaction in a nanostructure cannot become repulsive in the presence of the metal surface. With an attractive overall electron-hole interaction, one can then envision a situation where the optical gap of a small organic molecule approaches the QP gap, but it does not exceed it. An interesting question is whether this situation can happen in the physisorption regime. Our state-of-the-art calculations performed on benzene near a metal surface indicated that the optical gap remains significantly larger than the electronic gap throughout the physisorption regime.

Significance:

We established a new computational capability for state-of-the-art calculations of electronic and optical properties of nanostructures in complex environments. This capability has been used to explain and predict important renormalization effects in carbon nanotubes and small organic molecules near a metal surface.

The work done supports the Enabling Capabilities program within the broader Energy Security program at Sandia, which works to reduce the risks of transformative energy solutions that will enhance the nation's security and economic prosperity. Our fundamental science study is also well aligned with the DOE's Basic Energy Science portfolio in materials science.

Refereed Communications:

C.D. Spataru, "Electronic and Optical Gap Renormalization in Carbon Nanotubes near a Metallic Surface," *Physical Review B*, vol. 88, p. 125412, September 2013.

Cubic Organic Scintillators as Improved Materials for Fast Neutron Detection

158481

Year 3 of 3
Principal Investigator: P. L. Feng

Project Purpose:

The purpose of the project is to develop improved fast neutron scintillator materials via systematic understanding of the effects of intermolecular interactions and crystal packing. The synthesized materials seek to fill a presently unmet need for low-cost, mechanically robust, and high-performance fast neutron discriminating scintillators. The employed strategy follows a rational design approach that is differentiated from the highly empirical nature of prior work. The design strategy was to exert synthetic control over the molecular point-group symmetry, which subsequently impacts the crystallographic packing arrangement and space group. Considering that crystallographic symmetry controls second-rank tensor properties such as strain, thermal expansion coefficient, light yield anisotropy, and transport mobility, our aim was to develop structure-property relationships as a means to design improved scintillator materials.

Summary of Accomplishments:

We designed, synthesized, and characterized seventeen new examples of organic molecular crystal (OMC) scintillators based upon the symmetry-dependent design principles described above. The synthesized compounds are distinguished by C_3 molecular point group symmetries and possess crystallographic structures that are higher in symmetry than all known OMC scintillators. Density-functional theory calculations were used in conjunction with detailed crystallographic analyses to understand the effects of symmetry upon the electronic structures and magnitude of intermolecular exchange interactions versus structures of the parent chromophores. The results show that high-symmetry crystalline packing allows for more efficient triplet-triplet interactions in the solid-state, which leads to longer diffusion lengths and excited-state lifetimes. Photophysical measurements reveal that these improved transport properties are correlated with faster scintillation decay kinetics and more efficient fast neutron discrimination capabilities. The combined results indicate that the synthesized materials are capable of replacing existing materials in current detector applications. Furthermore, this work provides an unprecedented route towards the rational design of new classes of scintillator materials via tailored synthesis and crystal engineering.

Significance:

The materials developed in this work will directly support homeland security efforts via improved detection of special nuclear materials (SNM). Current materials are limited by several factors, including one or a combination of high cost, fragility, or low neutron discrimination efficiency. We have demonstrated that the crystal design approach employed in this work is a viable route towards improving each of these quantities. We anticipate that this generalized strategy will result in revolutionary performance advances to enable the detection of smaller quantities of SNM in more challenging detection scenarios.

Refereed Communications:

P.L. Feng and M.E. Foster, “Pulse-Shape Discrimination in High-Symmetry Organic Scintillators,” *IEEE Transactions of Nuclear Science*, vol. 60, pp. 3142-3149, August 2013.

The Science of Battery Degradation

158810

Year 2 of 3
Principal Investigator: J. P. Sullivan

Project Purpose:

DOE has identified the transformation of our nation's energy systems towards clean energy technologies as its first mission statement goal. Electrical energy storage in the form of batteries is a key component of this vision. However, current large-scale battery technologies need substantial improvements in capacity and lifetime in order to meet performance and reliability goals. Although there has been considerable work to develop new battery materials, research to understand the limits of battery lifetime has lagged. The objective of this project is to identify, at the atomic level, the leading mechanism(s) that give rise to battery degradation. Detailed mechanistic understanding will be provided by a combination of newly developed and sophisticated characterization methods and atomistic to continuum-level modeling. Specifically, we will develop and apply in situ characterization methods that are based on transmission electron microscopy (TEM), scanning transmission x-ray microscopy (STXM), and highly surface sensitivity optical spectroscopies to realistic full-scale lithium-ion battery electrodes and isolated battery particles. We will also develop new electrochemical approaches, including quantitative nanoscale electrochemistry and electrochemical entropy measurements as a function of cycling. Modeling methods include ab initio modeling of electrolyte decomposition at electrode surfaces and continuum-level modeling of electrochemical battery degradation signatures, including electrochemical entropy measurements. These methods and models will be used to evaluate leading proposed mechanisms of degradation, including electrolyte decomposition, which leads to solid-electrolyte interphase formation and growth, and mechanical fracture, cracking, and delamination within the solid electrodes. Importantly, we will compare our identified features of degradation generated through lab and computational studies to the features found in state-of-the-art high lifetime commercial cells that have been cycled to the point of degradation. At the conclusion of this project, we expect to have a detailed understanding of the primary battery degradation mechanisms, and this will lead to new approaches to achieving high lifetime large-scale batteries.

In Situ Study of Dynamic Phenomena at Metal Nanosolder Interfaces Using Aberration-Corrected Scanning Transmission Electron Microscopy

158822

Year 2 of 3
Principal Investigator: P. Lu

Project Purpose:

Controlling metallic nanoparticle (NP) interactions plays a vital role in the development of new joining techniques (nanosolder) that bond at lower processing temperatures but remain viable at higher temperatures. The primary objective of this project is to develop a fundamental understanding of the actual reaction processes, associated atomic mechanisms, and the resulting microstructure that occur during thermally driven bond formation concerning metal-metal nano-scale (<50nm) interfaces. Current theory describes the formation of bonding at high temperatures based on micron-scale phenomena but nanoscale materials operate in a unique, unknown fashion. The reason for the change in metal-metal interactions is an open question but understanding this behavior is critical to the development of nanointeractions (i.e., nanosolders) and basic science. This question can only be answered with in situ, atomic-scale dynamic observation, enabled by state-of-the-art heating experiments in the newly acquired, unique, aberration-corrected scanning transmission electron microscope (AC-STEM), coupled with large-scale, high-fidelity molecular dynamic (MD) simulations. This research effort will provide an understanding of nanoscale interface interactions at elevated temperatures and provide science-based solutions that address several near-term, critical Sandia mission needs.

Recent in situ transmission electron microscopy (TEM) efforts have met with limited success due to lack of the specialized equipment necessary to address dissimilar metal interactions. By combining the state-of-the-art AC-STEM and TEM heating stage, NP synthesis expertise, atomic-scale characterization, in situ TEM, and atomic-scale MD modeling, we have a unique opportunity to understand/control complex nanoscale interface interactions. The AC-STEM offers sub-Angstrom imaging resolution uniquely coupled with near-real-time element mapping, revealing previously unobservable rapid atomic-scale compositional changes occurring at these nanoscale interfaces at elevated temperatures. Additionally, the in situ TEM heating holder possesses a fast thermal ramp (~1000 °C/s) enabling thermally quantized observation of these interactions. The experimental insight provided by in situ, dynamic observations will be coupled with atomic-scale MD modeling, further elucidating the mechanisms of bonding in metal-metal NPs and the influence of physical properties on the reaction mechanism.

Deciphering Adsorption Structure on Insulators at the Atomic Scale

158823

Year 2 of 3
Principal Investigator: K. Thuermer

Project Purpose:

Whether to understand ice-nucleation in clouds, lubricant degradation in micro-machines, or aqueous electrochemical kinetics, one wants a molecular-level knowledge of water-solid interactions. Water behavior at interfaces has, therefore, been the subject of hundreds of studies. Still, even the simplest issue — the structure of the first water layer on a solid surface — has been hard to resolve. For three decades, low-temperature, 2D wetting layers on close-packed precious metal surfaces were thought to be "ice-like" arrangements of water molecules, strained into registry. In the past year, via scanning tunneling microscopy (STM) and density functional theory (DFT)-supported interpretation, we overturned that idea, discovering the remarkably non-ice-like molecular arrangement adopted by water on Pt(111). That success offers the prospect of understanding how water binds to the more stable materials of which the world is largely comprised: oxides, sulfides, and salts. The obstacle is that these materials are generally insulators, for which high-resolution microscopic techniques have been unavailable. Molecular-scale images were indispensable to solving the Pt(111) wetting-layer structure. We can expect that high-resolution imaging will be equally important to understanding water on the more common materials.

By exploiting an atomic force microscopy (AFM) breakthrough, we aim to be the first to perform atomic-resolution studies of adsorbates on insulating surfaces relevant to environmental and technological processes bearing on national needs. Unprecedented resolution has been achieved with a novel tuning-fork type sensor known as "Q-plus." Proof-of-principle of the Q-plus technique — atomic resolution AFM of an adsorbed pentacene molecule — suggests breakthrough possibilities for molecules on oxides, assuming the technique proves robust enough. The risk will be to provide similarly high-resolution images of delicately bonded, adsorbed water. Our first goals are the wetting of muscovite and kaolinite, oxides ubiquitous in nature, implicated as cloud-seed materials, and subjects of many experimental and theoretical studies with no definitive conclusions. We will attempt to decipher adsorbed water-molecule arrangements by combining atomic-level imaging with DFT-based interpretation.

Crystalline Nanoporous Frameworks: A Nanolaboratory for Probing Excitonic Device Concepts

158825

Year 2 of 3
Principal Investigator: M. D. Allendorf

Project Purpose:

Electrooptical organic materials hold great promise for the development of high-efficiency devices based on exciton formation and dissociation, such as organic photovoltaics (OPV) and organic light-emitting devices (OLEDs). However, the external quantum efficiency (EQE) of both OPV and OLEDs must be improved to make these technologies economical. Efficiency rolloff in OLEDs and inability to control morphology at key OPV interfaces both reduce EQE. Only by creating materials that allow manipulation and control of the intimate assembly and communication between various nanoscale excitonic components can we hope to first understand and then engineer the system to allow these materials to reach their potential. The aims of this project are to: 1) develop a paradigm-changing platform for probing excitonic processes composed of crystalline nanoporous frameworks (CNFs) infiltrated with secondary materials (such as a complimentary semiconductor), 2) use them to probe fundamental aspects of excitonic processes, and 3) create prototype OPVs and OLEDs using infiltrated CNF as active device components. These functional platforms will allow detailed control of key interactions at the nanoscale, overcoming the disorder and limited synthetic control inherent in conventional organic materials. CNFs are revolutionary inorganic-organic hybrid materials boasting unmatched synthetic flexibility that allow tuning of chemical, geometric, electrical, and light absorption/generation properties. For example, bandgap engineering is feasible and polyaromatic linkers provide tunable photon antennae; rigid 1-5 nm pores provide an oriented, intimate host for triplet emitters (to improve light emission in OLEDs) or secondary semiconducting polymers (creating a charge-separation interface in OPV). These atomically engineered, ordered structures will enable critical fundamental questions to be answered concerning charge transport, nanoscale interfaces, and exciton behavior that are inaccessible in disordered systems. Implementing this concept also creates entirely new dimensions for device fabrication that could improve performance, increase durability, and reduce costs with unprecedented control of over properties.

Measuring the Microscopic Mechanics of Individual Intermolecular Systems

159167

Year 2 of 2
Principal Investigator: R. W. Friddle

Project Purpose:

The mechanical properties of materials, both within their bulk and at their interfaces, are ultimately decided by the inter-atomic potentials between neighboring molecules. In composites and smart materials, a degree of complexity is inherent due to the integration of typically organic fibers with inorganic metals or ceramics. Simplification of these systems is found through investigating key properties, such as bond breaking, configurational changes, and elastic deformations at the single molecule level. Understanding of the microscopic mechanics of individual molecules is critical to connect the properties of bulk materials with the molecules from which they are composed. However, techniques that can access these properties are scarce, leaving the accuracy of computational calculations to only be validated through indirect means. To bridge this gap, we will take an advanced approach to investigate intermolecular bondings, by mechanically probing single molecules with sub-nanometer spatial and piconewton force resolution.

Summary of Accomplishments:

Hardware modification of a commercial atomic force microscope (AFM) was completed for custom control and high-speed data acquisition (improving sampling rates from 65 kHz to 2 MHz). This allows for higher degree of finesse in manipulation of molecules and detailed programming of force protocols. Thermal fluctuations of the probe-bound system can now be tracked at sampling rates exceeding the resonance of the probe, which is necessary for the Umbrella Sampling approach to be used.

We found that the theoretical models used to describe the dynamics of forced bond rupture were inadequate over the broad range of experimental loading rates. We were able to show that, unlike the common belief that nanoscale contacts under force are far from equilibrium, they are actually close to equilibrium when driven at modest loading rates. This is because more often than not multiple connections exist at the contact, which establishes an equilibrium steady state between bound and unbound molecules. This theory has been shown to reconcile a number of inconsistencies in single- and multi-molecule bond rupture data.

We designed and tested an experiment to measure both rupture force and microscopic bond dynamics as a function of time. This involved building a conductive AFM capability to measure both forces in pico- to nano-Newton regime with tunneling current in the pico- to nano-amp regimes. We found that rupture is, in fact, correlated with tunneling current and, therefore, we were able to measure true intermolecular contact number in situ during tests. We also found that the dynamic role solvent plays in the formation of bonds at the nanoscale could be observed through following the time evolution of the tunneling current when the AFM probe is in contact with the surface.

Significance:

The aims of this project are to develop a technique that will support engineering of materials at macro- and nanoscales. The ability to fully characterize interfacial bonds requires not only knowledge of the force of failure, but also of the timescales of loading, and most importantly, the microscopic structure of the bonds under test. Interfacial rupture at the nanoscale is often variable due to surface roughness and inhomogeneous distributions of attaching molecules. The work developed here enables a built-in compatibility test by directly measuring the contact number and hence allowing a one-to-one comparison between nanoscale bond rupture tests.

Refereed Communications:

R.W. Friddle, A. Noy, and J.J. De Yoreo, "Interpreting the Widespread Nonlinear Force Spectra of Intermolecular Bonds," in *Proceedings of the National Academy of Sciences of the United States of America*, pp. 13573-13578, 2012.

J.J. De Yoreo, S. Chung, and R.W. Friddle, "Dynamic Force Spectroscopy: In Situ Atomic Force Microscopy as a Tool for Investigating Interactions and Assembly Dynamics in Biomolecular and Biomineral Systems," *Advanced Functional Materials*, vol. 23, p. 2462, May 2013.

A. Noy and R.W. Friddle, "Practical Single Molecule Force Spectroscopy: How to Determine Fundamental Thermodynamic Parameters of Intermolecular Bonds with an Atomic Force Microscope," *Methods*, vol. 60, pp. 142-150, April 2013.

Superconductive Silicon Nanowires Using Gallium Beam Lithography

159300

Year 2 of 2
Principal Investigator: M. D. Henry

Project Purpose:

The purpose of this project was to investigate two very interesting topics, individually and integrated, with the overriding theme of applicability to Microsystems and Engineering Sciences and Applications (MESA) fabrication facilities. First, superconductivity of gallium implanted silicon using a focused ion beam (FIB) was investigated. Specifically, the role of solid solubility of Ga in silicon, the dose dependence, and geometrical and dimensional aspects of this type of superconductivity were targeted for investigation. Second, fabrication of gallium-implanted silicon nanowires and cantilevers will be investigated along with the properties of those devices. It is expected that an understanding of the parameters necessary to generate superconductivity in silicon using a focused Ga beam will be developed for the direct writing of superconductive devices in silicon.

This work also investigated the potential of using other superconducting films, in conjunction with the created nanowires, to explore 1D superconductivity. In particular, this work investigated how to integrate these nanowires with sputtered niobium for creation of Josephson Junctions.

Summary of Accomplishments:

This work demonstrated the technique of using Ga lithography (implanting Ga with plasma etching, as opposed to milling) to create fully suspended silicon nanowires. The wire dimensions created were down to 20 x 30 nm and suspended over 10 µm. Research on this implantation and dry lithography method revealed excellent electrical properties such as effective resistivity below 0.001 ohm-cm and excellent Ohmic contacts for W-Si. This work detailed electrical properties of the devices spanning the phase space of dosing, annealing, size, and temperature. The method discovered here provided a method for fabrication of extremely small nano structures with good electrical contact to the macro world. This work also produced implanted films in silicon with good electrical resistivity below 10 K (creating wire runs down to 50 nm).

Testing of the suspended nanowires revealed a high sensitivity to surrounding pressure. This result drove the investigation into the use of these devices as Pirani pressure sensors, which could be geometrically modified for different pressure ranges. An in-depth theoretical investigation of the effect resulted in a mathematical description providing insight into the design of these structures. Results from this investigation also indicated that suspending nanowires for superconductive purposes would result in difficulties when attempting to make measurements on the devices at cryogenic temperatures.

A third result, and highly important, was a discovery made by attempting to create superconducting nanowires using sputtered Nb on the suspended Ga lithography nanowires. It was observed here that critical temperatures were significantly lower than that of bulk films. After an extensive investigation, it was discovered how sputtered niobium oxidizes, thus decreasing the superconductive properties. More importantly, it was discovered that tensile sputtered niobium films could resist bulk oxidation after two years in atmosphere. This result helped overcome a significant problem and is a potentially very valuable discovery for furthering superconducting electronics for supercomputers.

Significance:

The creation of the Pirani nanowire gauges directly fed into the efforts of Wafer Level Packaging of Aluminum Nitride micro resonator filters. The reduced size and high sensitivity of these devices make them ideal candidates for continuous monitoring of the hermetic conditions inside the packaging.

The results of the niobium oxidation investigation offer a significant understanding in the superconductive properties of this sputtered thin film. The results provide a path forward for the fabrication of niobium based superconducting electronics. This work should directly impact national security's objectives in making superconducting electronics supercomputers.

Refereed Communications:

M.D. Henry, E.A. Shaner, and R. Jarecki, "Silicon Nanowire Pirani Sensor Fabricated Using FIB Lithograhpy," in *Proceedings of the IEEE Device Research Conference*, 2013.

Alloys and Composites for Strong and Tough Freeform Nanomaterials

164677

Year 2 of 3
Principal Investigator: B. J. Kaehr

Project Purpose:

The pursuit of nanotechnologies has largely focused on the physics and chemistry of low dimensional materials and their potential impact on areas such as electronics, catalysis, and medicine. However, a crucial class of materials remains largely unexplored at the smallest scales, namely alloys and composites that dominate modern manufacturing for mechanically robust (macroscopic) structures and devices. Of critical importance is the ability to manufacture freeform, 3D designs and shapes using techniques such as casting.

The question arises: can engineered materials with freeform shapes be fabricated at nanoscales? Despite advances for developing nanomaterials with controlled composition, current synthetic practices generally limit forms to particles and wires. The development of nanoscale alloys with arbitrary form and controlled composition will require new material syntheses and manufacturing procedures.

The project will address this wholly unexplored area of materials science, by adapting recent breakthroughs in 3D nanofabrication toward the synthesis of mechanically robust freeform alloys and composites. Specifically, we will focus on 3D direct write methodologies for nanoscale materials comprised of alloys of iron (steels) and determine generalized strategies applicable to other alloy systems. The challenges that arise for maintaining strength and toughness as features sizes approach minimum grain size, crack length, etc., will be mitigated via concurrent development of hierarchical freeform composites.

Recent advances in 3D printing have begun to usher in a new era for rapid prototyping. Considering available methodologies such as robocasting, stereolithography and laser sintering, only multiphoton lithography has the capability to fabricate feature sizes <100 nm. However, the range of materials compatible with this technique is currently very limited. This project will aim to substantially broaden this material space by building upon recent breakthroughs for multiphoton lithography (MPL) of metals and composites. Beyond advancing fundamental nanoscience, realizing nanoscale freeform alloys will facilitate design and fabrication of next-generation 3D device architectures.

LEEM-PEEM Studies of Localization Mechanisms in InGaN-Based Heterostructures

165692

Year 1 of 3
Principal Investigator: T. Ohta

Project Purpose:

Scientific insight is crucial for improving the efficiency of optoelectronic devices that target energy mission needs. An example is InGaN light-emitting diodes (LEDs) for energy-efficient solid state lighting (SSL). A key fundamental question is: Why do blue-emitting InGaN alloys have high radiative efficiency despite having threading-dislocation (TD) densities that quench light emission in traditional semiconductors? It is hypothesized that structural and compositional inhomogeneities localize carriers away from crystalline defects, but the nature and degree of localization, its correlation with defects, and its dependence on composition are controversial. The nanoscale properties that influence carrier localization may also contribute to long-standing (~ 15 year) roadblocks to high-efficiency SSL, including the "green-yellow gap" in LED efficiency (where the efficiency of InGaN degrades at longer wavelengths) and the "efficiency droop" observed for InGaN LEDs operated at high currents. To circumvent these roadblocks, we will pursue the implementation of spectroscopic low energy electron microscopy — photoemission electron microscopy (LEEM-PEEM) — on test device structures as a new approach to revealing key structure-property relationships vital for understanding the carrier localization mechanisms impacting efficiencies.

We will use spectroscopic LEEM-PEEM to probe the surface potential, occupied electron density-of-states (DOS), and alloy composition of InGaN alloys with micro- to nanometer spatial resolution. Combined with controlled growth studies, time-resolved optical spectroscopy and detailed modeling of as-grown surface morphology/composition, these studies will enable unprecedented insight into the connection between microscopic/nanoscale materials properties and efficiency limitations of InGaN LEDs. The work leverages two world-class capabilities exclusively co-located at Sandia: our new spectroscopic LEEM-PEEM and state-of-the-art InGaN materials growth and characterization. The major thrust will be to explore the nanoscale materials properties that lead to carrier localization in InGaN, their correlation with materials defects, and the overall impact of these phenomena on InGaN LED efficiency.

Oxide-Based Proton-Conducting Membranes for Energy Conversion and Utilization

165694

Year 1 of 3
Principal Investigator: A. H. McDaniel

Project Purpose:

Next generation metal-ion conducting membranes are key to developing technologies like metal-air batteries or flow batteries that will enable grid-scale electrical energy storage, and thus facilitate the integration of intermittent renewable sources into the US energy infrastructure. NASICON-type materials, where the acronym stands for sodium super ionic conductor, are a broad class of compounds with $AM_1M_2(PO_4)^3$ stoichiometry and the choice of either "A" or "M" cation is widely variable. Other than stoichiometry, the defining feature of this material class is the formation of a 3D crystallographic framework that contains interconnected channels within which the mobile conducting ions are encapsulated by the "A" site(s). With these materials, it is possible to make devices such as batteries, fuel cells, gas sensors, catalyst supports, and even hosts for radioactive waste. The challenge is to design NASICON with optimal ion mobility and chemical stability. Current research involves a heuristic approach to probing the enormous array of possible material compositions that manifest ion conductivity in NASICON. A comprehensive molecular-level picture of the factors that influence ion conduction is missing.

The objective of this project is to analyze transport chemistry using a combination of in situ studies of structure, composition, and bonding, combined with first principles theory and modeling, to develop an atomistic understanding of mechanisms that give rise to ion conductivity. We will use a combination of novel, synchrotron-based soft x-ray diagnostics to probe the electronic states and defect structures in well-controlled, model NASICON systems. A unique research platform developed by Sandia will be used to resolve the oxidation state and valence band states in operating membranes. First principles theory and modeling will be used to interpret the experimental observations and enhance understanding of atomistic processes. This combination of novel experimental methodology and theory is truly innovative and represents a holistic approach to understanding ion conduction in NASICON.

Controlled Polarization Reversal for Ferroelectric Opening Switches (CPR for FEOS)

165695

Year 1 of 1
Principal Investigator: G. L. Brennecka

Project Purpose:

The ferroelectric opening switch (FEOS) concept was initially demonstrated in 2009 when Sandia researchers repeatedly delivered 10s of kA with sub-ns rise times. Subsequent application-focused endeavors failed because they were based upon extrapolations and assumptions of material response rather than on a fundamental understanding of ferroelectric domain reversal. In order to capitalize on this tremendously nonlinear phenomenon, we must determine the intrinsic limitations and critical parameters associated with ferroelectric domain nucleation and propagation.

High power opening switches would enable the use of inductive energy storage with ~100x greater energy density than capacitive energy storage, significantly faster rise times, and nearly a 10-fold increase in delivery efficiency to inductive loads. The FEOS is presently the only known approach with the potential for repeatable solid state operation at ambient temperatures. The breadth and level of potential impact of successful multi-scale FEOS technology is stunning, from feasible inertial confinement fusion (ICF) to efficient high power microwave generation and beyond. Successful development of any FEOS-based system requires a fundamental understanding of ferroelectric material response at a level that does not currently exist. This project will carry out a cutting-edge materials physics study to explore intrinsic material limitations to polarization reversal in terms of control of domain nucleation and propagation speed. One leg of this project will use an already-assembled custom pulsed power test bed to characterize material response under FEOS-relevant conditions in order to probe fundamental limitations using, among other tools, Preisach analysis of switching behavior. The other aspect will focus on laser effects on a single crystal ferroelectric ($LiTaO_3$) for potential laser triggering and/or creation of bulk nucleation sites within the single crystal. The intent is to explore the limitations of controlled polarization reversal in order to either illuminate a promising path forward or convincingly demonstrate impracticality of the FEOS concept.

Summary of Accomplishments:

We developed capabilities for performing high voltage and high power characterization of nonlinear dielectric materials and experimentally demonstrated the importance of nucleation for rapid polarization reversal in ferroelectrics. We fabricated highly textured bulk barium titanate ($BaTiO_3$) via templated grain growth (TGG) techniques and were able to quantitatively separate texture and composition effects from grain size effects in relation to polarization reversal. A huge amount of data on the high-power behavior of nonlinear dielectrics was collected and analyzed. Various iterations of a setup were constructed to characterize the effects of laser irradiance on ferroelectric polarization reversal and it was discovered that the voltage threshold for ferroelectric switching can be reduced when illuminated with appropriate wavelengths and powers of light. Most importantly, we explored polarization reversal in a wide variety of ferroelectric materials across a spectrum of relevant operating conditions, and failed to discover any physical limitations to the eventual development of a functional ferroelectric opening switch.

Significance:

This work is another step in the development of a fundamental scientific understanding of the dynamic response of nonlinear dielectric materials to high power drive conditions. Once developed, ferroelectric opening switches will enable significantly more efficient pulsed power systems which will, in turn, improve Sandia's capabilities for stockpile stewardship, high energy density physics experiments, and related national security needs.

Refereed Communications:

F.J. Zutavern, G.L. Brennecka, S.F. Glover, G.E. Pena, G.J. Denison, and J.M. Rudys, "A Testbed for High Voltage, High Bandwidth Characterization of Nonlinear Dielectrics," in *Proceedings of IEEE Pulsed Power Conference*, pp. 1-6, 2013.

Programmable Nanocomposite Membranes for Ion-Based Electrical Energy Storage

165696

Year 1 of 3
Principal Investigator: E. D. Spoerke

Project Purpose:

This project is focused on the study of bio-inspired ion transport materials and processes with the intention of manipulating ion concentration gradients to enable a novel electrical energy storage capability. The innovative approach pursued in this project takes inspiration from biological systems, such as the electric eel, to mate high energy density and high power density desired for next-generation electrical energy storage technologies. In the case of the electric eel, energy-dissipative ion pumps and gated ion-selective channels are used to manipulate large ion concentration gradients across membranes, enabling generation and discharge of 1A of current at over 600 Volts! We will strive to translate these concepts to a synthetic system, focusing on scientific questions about the integration of ion pumps and programmable ion channels in engineered materials and exploring behaviors impacting controlled transport, accumulation, and dissipation of ions for electrical energy storage (EES). Our effort combines expertise in nanomaterials, biomaterials integration, electrochemistry, and computation to explore this system, focused on development and characterization of molecular building blocks needed to systematically regulate ion transport. We will utilize light-powered ion pumps (bacteriorhodopsin), inserted into a “pump membrane” to control active establishment of ion concentration gradients, and rely on programmable surface chemistries applied to synthetic membrane channels in a “gate membrane” to provide critical ion gating capabilities. Materials and expertise established will facilitate valuable improvements in existing technologies (e.g., battery separators, water treatment technologies) and will provide a platform to develop a new scheme in electrical energy storage, and will position Sandia as a leader in an evolving field of bio-inspired energy storage.

Science-Based Design of Stable Quantum Dots for Energy-Efficient Lighting

165697

Year 1 of 3
Principal Investigator: J. E. Martin

Project Purpose:

Fluorescent and solid state lighting rely on rare earth elements (Y, Eu, Tb, and Ce) for which shortages are expected. We will pursue the replacement of these rare earths with photoluminescent quantum dots (QDs). To meet the extreme demands of lighting requires that QDs have greatly improved photo- and thermal stability. Increased stability can be achieved by coating the QDs with suitable shell materials, but these lead to stresses that generate defects both at the heterojunction and within the lattice. Such defects serve as non-radiative recombination centers that greatly reduce the quantum yield. To design QDs that have both high stability and quantum yield we will use alloying of both the cores and the shells. Continuum calculations show that alloying will greatly reduce the strains that lead to defect formation. We will use atomistic modeling to predict those graded compositions that have the highest stability to defect formation. Defect formation will be identified through photophysical characterization and with Sandia's unique Z-contrast aberration-corrected scanning electron transmission microscope (AC-STEM).

Predicting Growth of Graphene Nanostructures Using High-Fidelity Atomistic Simulations

165698

Year 1 of 3
Principal Investigator: K. F. Mccarty

Project Purpose:

Graphene continues to attract widespread attention due to its outstanding electronic and optical properties for next-generation electronics. In proposed applications, device functionality critically depends on producing graphene nanomaterials with high quality and uniformity (with few or no defects). Inserting these novel electronic materials into real-world devices requires discovering improved understanding to better control growth. Among the numerous methods for graphene synthesis, chemical vapor deposition (CVD) growth on transition metal substrates stands out for producing large-area films amenable to commercial applications. In particular, large-area graphene growth on Cu foils (the most commonly used substrate) shows the greatest promise because low solubility of carbon in Cu inherently favors single-layer graphene growth. However, despite its potential, the detailed mechanisms or conditions for controlled graphene growth are unknown or very poorly characterized, often leading to a wide variety of nanostructures. Specifically, how graphene grows on different Cu facets, what controls its in-plane orientation, and how intrinsic Cu defects affect nucleation and defect formation remain inadequately understood. Indeed, even how graphene is aligned, in terms of its crystallography, with Cu itself remains an open question. Consequently, it is extremely difficult to design experimental procedures that will lead to reproducible, controlled growth of optimal nanostructures. A theoretical understanding of the detailed mechanisms of graphene growth is needed to help tailor the experimental conditions to generate high-quality graphene nanostructures. The aims of this project are to: 1) develop a paradigm-changing computational capability for predicting the growth of graphene nanostructures on a metallic substrate, 2) validate the capability through comparison to experimental observations of graphene growth on Cu, 3) use this predictive tool to understand the fundamental mechanistic processes and conditions (temperature, pressure, deposition rate, substrate orientation) that govern high-quality growth, and 4) perform a proof-of-concept demonstration to down-select a subset of candidate growth experiments for graphene nanostructures to be carried out under specific conditions.

Spin-Based Field Effect Transistor Using Topological Insulators for "Beyond Moore" Information Technology

165699

Year 1 of 3
Principal Investigator: P. A. Sharma

Project Purpose:

In this project, we have focused on the application of topological insulator (TI) materials as a low temperature, low power, spin-based memory solution for high performance exascale computing. 3D TI possess a conducting surface state with spin polarization and a Dirac cone dispersion. The transport properties of these surface states are difficult to study due to the large conductivity in the bulk from native defects. In the present work, we investigate whether inhomogeneously doped structures can be created in the topological insulator Bi_2Se_3 using ion implantation, which would allow isolation of surface state transport at the space charge region of a p-n junction. As a first step, we focus on two questions. First, does ion implantation cause substantial disorder at the surface or bulk, which would destroy the surface state completely? Second, can ion implantation be used to dope Bi_2Se_3 from n to p-type? Isolation of topological surface states is the biggest problem in this field.

Tunable Quantum Dot Solids: Impact of Interparticle Interactions on Bulk Properties

165700

Year 1 of 3
Principal Investigator: M. B. Sinclair

Project Purpose:

This project will develop a fundamental understanding of the relationship between nanoparticle interactions and the different regimes of charge and energy transport in semiconductor quantum dot (QD) solids. QD-solids comprising self-assembled semiconductor nanocrystals such as PbSe are currently under investigation for use in a wide array of applications including light emitting diodes, solar cells, field effect transistors, photodetectors, biosensors, lasers, and thermoelectrics. These unique materials exist at the crossover between isolated particles and bulk materials. They retain many of the attractive features of the isolated particles such as size-tunable bandgaps, but interparticle interactions modify their behavior and cause charge and energy delocalization. At present, the relative contributions of charge and energy transport to device performance are not well understood. For example, a QD-solid solar cell with an efficiency of ~5% was recently demonstrated, but conflicting explanations of the underlying mechanism have been proposed: exciton migration and dissociation at the electrodes and direct photogeneration of electron-hole pairs. Device optimization requires a quantitative fundamental understanding of the means by which interparticle interactions lead to collective bulk behavior. The current state of the art in the study of interparticle effects relies on the utilization of different capping ligands to control the interparticle separation. However, the interpretation of experimental results is clouded by the large number of other variables that change as the ligand is varied. In this project, we will use a Sandia-developed mechanical compression method, in conjunction with nanoparticle self-assembly, to fabricate QD-solids with precisely controllable interparticle spacing. State-of-the-art optical probes, including ultrafast spectroscopy and non-contact photoconductivity will be used to characterize QD-solid behavior spanning the range from widely separated nanoparticles to sintered nanoparticle superlattices within a single, highly ordered QD-solid sample. This approach allows for an unambiguous unraveling of the behavior of this unique class of solids and will enable new directions in materials science for a variety of national security missions.

Nonlinear Response Materials for Radiation Detection

165701

Year 1 of 3
Principal Investigator: D. R. Wheeler

Project Purpose:

The goal of the project is to develop novel materials that can function as radiation sensitive materials. The goal is to further develop materials that function not as dosimeters but changes in specific properties in unique radiation environments. The materials ideally should respond in a nonlinear manner if possible.

Crossing the Membrane Barrier: Implications for Developing Medical Therapeutics

165824

Year 1 of 3
Principal Investigator: C. Ting

Project Purpose:

The interaction of nanoparticles with lipid membranes is a common theme underlying a number of important phenomena in bionanotechnology, ranging from cytotoxicity to the delivery of therapeutics. Importantly, membranes are soft matter systems comprised of lipids that self-assemble into fluid bilayers. As such, thermal fluctuations are important and many interesting membrane processes involve thermally nucleated (rare) events. We will address the difficult problem of nucleation in soft matter, with a particular focus on membranes.

Besides the long time scales associated with these rare events, a significant challenge arises because of the high dimensional free energy surface due to the complex molecules comprising the membranes. Hence, with any sizable nucleation barrier, direct computer simulation is unfeasible. The potential of mean constraint force method attempts to overcome this challenge by artificially choosing a reaction coordinate, which (in general) does not coincide with the true nucleation pathway. The transition path sampling method, while in principle applicable to any activated process, is impractical for systems involving large assemblies of complex molecules. Therefore, the current methods are insufficient for studying nucleation in these systems. This project will develop new theoretical methods to calculate rare nucleation pathways in soft condensed matter systems.

We will explore a wide range of challenging and previously intractable membrane nucleation problems. This is of interest for developing novel therapeutics, the nanoscale object often a pathogen or a therapeutic agent (e.g., gene/drug) that must be blocked from, or allowed entry into a cell. The research will be the first to provide a molecular description of the nucleation pathways involving nanoscale objects crossing the membrane barrier. The method developed and applied throughout this project lies at the forefront of current computational technologies. Beyond biosciences, it paves the way for studying a wide range of nucleation phenomena in, for example, polymer-nanoparticle composites, where applications range from optics to sensors to catalytic devices.

The PI is a Sandia Truman Fellow.

The Role of Grain Boundary Energy on Grain Boundary Complexion Transitions

165825

Year 1 of 2
Principal Investigator: S. M. Foiles

Project Purpose:

The thermodynamics of grain boundaries strongly influence the evolution of microstructure, which has a major influence on materials properties. Grain boundary complexions, a relatively new concept in materials science, are interfacial phases with distinct structures and compositions. Transformations between complexions can occur as a function of temperature, interfacial chemistry, stress, and grain boundary misorientations. Initial results indicate that complexion transitions change the relative interfacial energy of the grain boundaries and lead to a significant increase in the anisotropy of the grain boundary character distribution. These combined results suggest that the transitions may favor specific high-energy grain boundary planes. The goal of this work is to test this hypothesis.

If we can understand and control complexions, it will be possible to control microstructure development and predictably develop new materials. However, there is little basic knowledge about the thermodynamics and kinetics of the transformations between different complexions. In particular, it is not understood what controls the nucleation of complexion transitions. The current project addresses this gap.

It is hypothesized that grain boundary energy is influential in determining when or if a complexion transition will occur. Comparison of relative grain boundary energies and the population of abnormal grains at the interface of single crystal and doped-polycrystalline alumina link the nucleation of grain boundary complexion transitions to the reduction of grain boundary energy.

Doped alumina samples will be prepared, polished and thermally etched. Contact mode atomic force microscopy will measure the topographic images of the grain boundaries. Mullins' analysis allows the relative grain boundary energy to be calculated from the measurements. Measuring a large number of thermal grooves effectively samples over the anisotropy of the material and allows for the characterization of the distribution of interfacial energies of a given sample. The observed boundary energies will then be correlated with the observation of complexion transitions.

This work is in collaboration with Carnegie Mellon University.

Multiscale Modeling of Hybrid Composites

166636

Year 1 of 3
Principal Investigator: T. E. Buchheit

Project Purpose:

In collaboration with Texas A&M, this project will focus on two areas for investigation: constitutive modeling of nano- and microscale phenomena and multiscale modeling of hybrid composites for computationally enabled design and modeling. A hybrid shape memory alloy (SMA) + MAX phase ceramic (Ti_2AlC) composite currently being developed at Texas A&M will be used as an example material system. This project will develop a framework applicable to a broader range of high-performance material systems whose deformation behavior is governed by complex micromechanical mechanisms. Such a tool is needed to address both current and future engineering problems facing both institutions. Importantly, the new framework will explicitly account for microstructure and have the ability to simulate multiphase materials thus enabling the analysis and design of advanced material systems.

Creating a Novel Silicon Substrate for the MOCVD Growth of Low Defect GaN

168763

Year 1 of 3
Principal Investigator: A. A. Allerman

Project Purpose:

Current green light emitting diodes (LEDs) on gallium nitride (GaN) suffer from a host of problems including wavelength shift, power droop, high defect concentrations, and high manufacturing costs. GaN is traditionally grown on small (2-inch), expensive sapphire wafers. It is the lattice and thermal mismatch between the substrate and GaN itself that causes dislocations to form. GaN has been grown on Silicon (Si), traditionally in the uncommon (111) orientation, to alleviate the mismatch problem, but the quality is still not as good as GaN on sapphire. We intend to engineer a process to grow device quality GaN on traditional (100) Si substrates. Growth of GaN on Si would open up the market for GaN LED production. Processing time and costs would drop dramatically because the semiconductor industry already has the tools and raw materials. However, growth of GaN on Si presents challenges. We have recently shown that GaN can be grown on the {111} sidewalls of nano-grooved (001) Si, as well as that nanopatterning sapphire substrates can alleviate defect density. Combining these ideas, a nanopatterned but conventional electronic grade (001) oriented Si wafer could prove a cheap, scalable substrate for GaN growth. Our process would use standard (001) Si instead of the uncommon (111) type and a fast lithography and etching technique to form a nanopatterned substrate for epitaxial growth. Initial results suggest the achievement of very low dislocation density material. This shall form the basis for the goal of fully coalesced GaN templates and devices on standard Si substrates.

This work is in collaboration with Rensselaer Polytechnic Institute.

Modeling Tin Whisker Growth

170802

Year 1 of 1
Principal Investigator: C. R. Weinberger

Project Purpose:

The relatively recent move to lead free solders has reintroduced a common problem for electronic packaging: whiskering. Whiskering is a phenomenon wherein very high aspect ratio filaments, or whiskers, grow from the base metal. When these filaments grow long enough, they can create electric shorts. The potential for shorts creates a reliability issue for a wide range of products including satellites, airplanes, rockets, and missiles. The original mitigation strategy was to introduce lead into tin-based solders, which dramatically reduces whiskering. However, due to the elimination of lead in solder manufacturing processes, the whiskering problem has re-emerged.

In order to ensure electronic packaging reliability, a new solution to the whiskering problem must be found. However, a major impediment to a science-based solution is the lack of understanding of the mechanisms of whiskering. To help build our understanding of whiskering as well as tools to provide an engineering solution, it is imperative to build accurate models that reproduce the wide range of experimental observations. This project will use multiscale and multiphysics models to understand how and why whiskers form, and will ultimately suggest methods to mitigate whisker growth.

Summary of Accomplishments:

The goal of this project was to understand what role the tin microstructure plays in determining whisker growth. If we can determine how only one in thousands grows into whiskers, it may be possible to engineer the microstructure to limit growth. In the limited time invested in this project, we reviewed some basic models of whisker growth and ideas about elastic and plastic anisotropy in tin. We also evaluated candidates for interatomic potentials for tin, which may be useful in understanding diffusion and plastic anisotropy.

We tested two interatomic potentials for tin: modified embedded atom method (MEAM) and Tersoff. We tested MEAM potential on large-scale atomic/molecular massively parallel simulator (LAMMPS) for tin and found the parameters for elastic properties and structural energies have differences compared to published results. Tersoff potential does show more agreement compared to published results.

Significance:

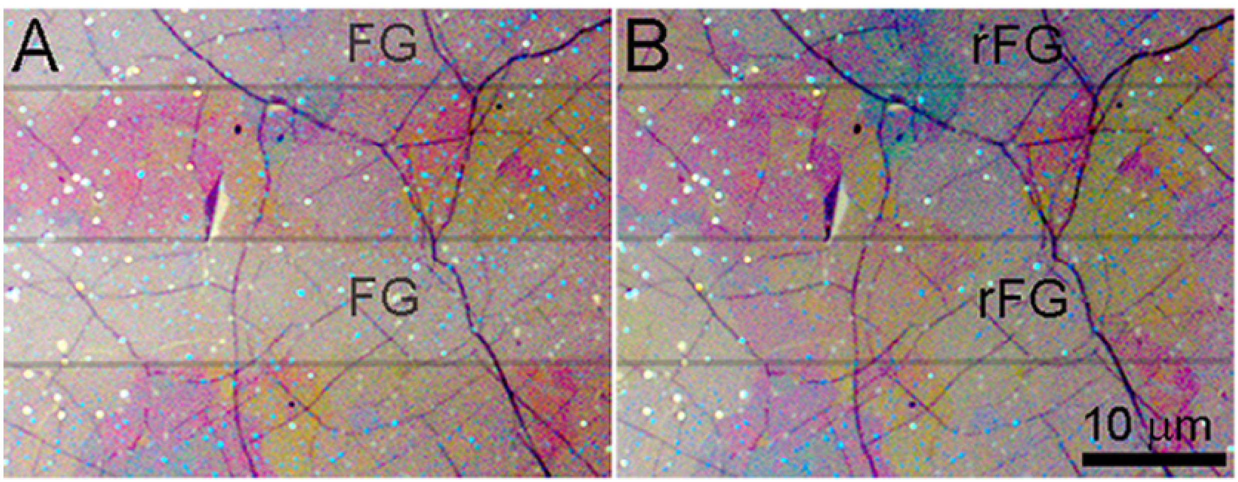
Tin whiskering is an important problem for the reliability of many microelectronic devices that are critical to applications in NW, satellites and Homeland Security. Our approach focused on the modeling of elastic and plastic anisotropy for initiation, which may help explain why only a certain population leads to sustained growth.

NANODEVICES AND MICROSYSTEMS

The Nanodevices and Microsystems Investment Area conducts creative, innovative R&D activities that increase our understanding of physical phenomena across the quantum-to-micro scales.

The foundation develops innovative nanoscale and microscale devices, achieves new methods of integration, and realizes novel microsystems-based complex systems. Adding microscale sensors, photonics, and microelectromechanical systems (MEMS) to our weapons platforms improves their performance and security.

By studying physical phenomena across the nano and microscales and by using new concepts, devices, and diagnostic tools, the Investment Area is creating more powerful microelectronics that are invulnerable to subversion. The work includes the development of advanced optoelectronics at the nano and microscale, and improved, ultraportable, multi-function sensor systems.



Local addition (A) and removal (B) of fluorineon the top surface of twisted bilayer graphene (TBG) films. Lines help guide the eye where TBG was fluorinated (labeled “FG”) and reduced (labeled “rFG”) (Project 158829).

NANODEVICES AND MICROSYSTEMS

Active Infrared Plasmonics

151329

Year 3 of 3
Principal Investigator: E. A. Shaner

Project Purpose:

The mid-infrared (mid-IR, 3-12microns) is a highly desirable spectral range for imaging, environmental sensing, and countermeasures. We will develop a new class of mid-IR devices based on plasmonic concepts that are dynamically controlled by tunable semiconductor plasma resonances or nanoscale mechanical movements. It is well known that any material resonance impacts dielectric properties; our primary challenge is to implement the tuning of a plasmon excitation with a voltage bias. We have demonstrated passive tuning of plasmonic structures in the mid-IR using semiconductors plasmas. In the mid-IR, semiconductor carrier densities on the order of 5E17cm^{-3} to 2E18cm^{-3} are desirable for tuning effects. Gate control of carrier densities at the high end of this range is near the limit of what has been demonstrated in literature for transistor-style devices. We will also investigate coupling between plasmonic resonances and intersubband transitions as another path for dynamic control. Combined with the fact that we are exploiting the optical properties of the device layers, rather than electrical, we are entering into interesting territory that has not been significantly explored to date.

External interests have identified the voltage control of resonances as being high risk. Even though we have demonstrated passive mid-IR control of both plasmonic and metamaterial structures using semiconductor plasmas (by varying the density in doped epi-layers of GaAs and InSb), dynamic tuning is the key effect needed for this research to progress. Once that capability has been demonstrated, electromagnetic simulations of plasmonic reflectance modulators, filters, and emission control structures should reliably guide development efforts based on the known behavior of semiconductor device layers. While all of these potential applications have mechanical alternatives, it is well known that achieving similar functionality in non-mechanical solutions is desirable in terms of reduced size, weight, power requirements, and response times.

Summary of Accomplishments:

We developed multiple approaches to controlling interactions between radiation and plasmonic excitations in order to demonstrate novel infrared optical responses. These efforts included exploring light-matter interaction from the THz to mid-infrared and included voltage controlled plasmonic devices, control of thermal radiation patterns from tailored surfaces, and the use of doped semiconductors as plasmonic materials in the mid-infrared.

Perhaps the most important development in our work was the use of doped silicon as a plasmonic material. That portion of our research is a key part of fabrication framework that allows silicon-based structures to operate in a plasmonic regime at long wavelengths (> 4 microns) and has continued to be used in Work for Others programs. In addition, we also made significant advances in polarization control structures for infrared wave plates (half and quarter wave). Finally, significant progress was made in plasmonic mechanically tuned structures to enable unprecedented control of thermal emission from surfaces. We expect further efforts along those lines will result in important advances for both temperature control (dynamic radiators) and for numerous defense applications requiring switchable infrared emission or reflection.

Significance:

We have obtained four DoD programs during the lifetime of this program, which speaks to the relevance of our efforts for national security. In general, the infrared spectrum is where thermal management and detection play a vital role. Our work directly impacts these areas by offering new ways to control this spectrum in both passive and dynamic ways. Additionally, we submitted three invention disclosures for these new concepts.

Refereed Communications:

T. Ribaudo, D.W. Peters, A.R. Ellis, P.S. Davids, and E.A. Shaner, "Highly Directional Thermal Emission from Two-Dimensional Silicon Structures," *Optics Express*, vol. 21, pp. 6837-6844, 2013.

J.R. Knab, A.J. Adam, E. Shaner, H.J. Starmans, and P.C. Planken, "Terahertz Near-Field Spectroscopy of Filled Subwavelength Sized Apertures in Thin Metal Films," *Optics Express*, vol. 21, p. 1101-1112, January 2013.

Monolithically Integrated Coherent Mid-Infrared Receiver

151332

Year 3 of 3
Principal Investigator: M. Wanke

Project Purpose:

The purpose was to develop a coherent mid-infrared (MIR) receiver, with the goal of achieving mid-infrared detection, 100 times better than state of the art room temperature MIR photodetectors. Conventional MIR photodetectors suffer from excess dark current due to thermal excitation of carriers at room temperature. Our goal is to use the nonlinear electrical response of a Schottky diode detector instead of the linear optical absorption response in photodetectors and, therefore, eliminate dark current issues. Schottky detectors are commonly used at lower frequencies where they are integrated with antennas to couple light to the small diode. Although extremely sensitive at low frequencies, their sensitivity at higher frequencies has been limited due to the device capacitance, which shunts higher frequency signals from the antenna around the diode. We recently demonstrated an antenna-less method of coupling THz radiation to a Schottky diode, by inserting a diode active region directly into a laser core and using the surface plasmon to couple radiation into the diode. In this project, we will explore whether this new coupling geometry reduces the capacitive shunting and can enable highly sensitive integrated coherent mid-infrared detectors.

There were many uncertainties in this work: Does the new geometry eliminate the capacitance issue? Does the required surface plasmon coupling significantly impact the laser performance? Can planer Schottky diodes operate above a few THz? Can the mixer radio frequency (RF) response be coupled out with this geometry? While a Schottky diode heterodyne mixer could have significant application impact, this initial demonstration focused on understanding these basic questions.

Summary of Accomplishments:

We demonstrated that a Schottky diode embedded into a MIR laser could couple to the internal laser fields and mix these fields to create RF power at the difference frequency between the modes. This is the first demonstration that we know of in sensing MIR fields with a large planar Schottky diode instead of a sub-wavelength point contact. We also showed that the response of the diode depends not only on the laser power, but also the laser temperature, which needs to be taken into account when analyzing the response. Lastly, we showed that the coupling to the diode depends on the relative position of the diode compared to the standing wave pattern of the lasing modes inside the laser cavity, which will influence the ultimate design of integrated transceivers.

Significance:

This project directly addresses DOE's scientific discovery and innovation thrust by exploring novel device integration and developing sensor technology that can be applied to environmental and security challenges. Our collaborators are working on remote chemical sensing testbeds and have multiple corporate partners, providing avenues for strategic partnerships between academia, industry, and Sandia; thus enabling the developed technology out of the lab to solve national security problems, such as detecting proliferation of nuclear material.

Refereed Communications:

G.C. Dyer, C.D. Nordquist, M.J. Cich, A.D Grine, C.T Fuller, J.L. Reno, and M.C. Wanke, "Rectified Diode Response of a Multimode Quantum Cascade Laser Integrated Terahertz Transceiver," *Optical Express*, vol. 21, pp. 3996-4004, February 2013.

G.C. Dyer, C.D. Nordquist, M.J. Cich, T. Ribaudo, A.D. Grine, C.T. Fuller, J.L. Reno, and M.C. Wanke, "Position and Mode Dependent Coupling of Terahertz Quantum Cascade Laser Fields to an Integrated Diode," to be published in *Applied Physics Letter*.

Non-Abelian Fractional Quantum Hall Effect for Fault-Resistant Topological Quantum Computation

151333

Year 3 of 3
Principal Investigator: W. Pan

Project Purpose:

Modern encryption method is based on the assumption that it is impossible to prime-factorize a large digit number within a reasonable time frame. Indeed, it is estimated that factorizing a 200-digit number would require 170 CPU years using an Intel computer. This estimate, however, is drastically changed with the use of a quantum computer (QC), which could readily factorize a 300-digit number. After more than 15 years of research on quantum computation, many fundamental issues remain unresolved. For example, the strong coupling between electrons and their local environments greatly reduces electron coherence time and requires complex error-correction schemes to manipulate quantum information before it is lost. As such, there is a pressing need to identify new paradigms, which can potentially enable revolutionary advances in the field of quantum computation.

Topological quantum computation (TQC) has emerged as one of the most promising approaches. Under this approach, the topological properties of a non-Abelian quantum system, which are insensitive to local perturbations, are utilized to process and transport quantum information. The encoded information can be protected and rendered immune from nearly all environmental decoherence processes without additional error correction. It is generally believed that the low energy excitations of the so-called nu=5/2 fractional quantum Hall (FQH) state may obey non-Abelian statistics. Our goal is to explore this novel FQH state and to understand and create a scientific foundation for exploiting this quantum matter state in order to build a knowledge base for the emerging TQC technology.

We will carry out a coherent study to obtain a scientific foundation of TQC. In particular, we plan to fabricate interferometer devices and carry out quantum interference measurements in these devices. Success of this project will allow us to gain a deeper understanding of non-Abelianity and is expected to have a great impact on the feasibility of eventually building a topological computer.

Summary of Accomplishments:

1) We performed edge channel tunneling measurements in a quantum point contact device and observed a double-peak structure at the Landau level filling nu=8/3. This observation is different from that at nu=7/3. The result may have important implications in utilizing the 8/3 state in topological quantum computation, an approach currently considered by industry scientists.
2) We performed density dependent studies of the energy gap at Landau level filling nu=5/2, and observed an apparent spin transition in this state at a very low density of $5x10^{10}$ cm^{-2}. Our results demonstrate that in the low density regime the strong electron-electron interactions and large Landau level mixing effect play an important role in competing ground states in the second Landau level.
3) Our results also show that the 7/2 state, a fractional quantum Hall effect (FQHE) state in high density samples, becomes anisotropic in a sample of density n = $5.0x10^{10}$ cm^{-2}.

Significance:

Overall, our work on spin transition in the Fractional Quantum Hall Effect (FQHE) in the second Landau level (LL) has attracted worldwide attentions and led the whole quantum Hall community to re-examine the nature of FQHE in the second LL.

Germanium on Silicon Optoelectronics

151334

Year 3 of 3
Principal Investigator: P. Davids

Project Purpose:

Moore's law scaling of microprocessor technology development dictates that, within the next ten years, power consumption in large-scale computers will be dominated by their electrical interconnects. One technology that has emerged as a potential solution to this bottleneck is silicon photonics. Yet, any optical interconnect is incomplete without a light source — owing to its indirect bandgap, creating a homogeneously integrated optical source on a silicon platform has been the single most scientifically challenging problem in the field since its inception more than two decades ago. While heterogeneous wafer bonding of III-V laser sources to silicon photonic circuits has been demonstrated, this solution is ultimately undesirable due to both incompatibility with state of the art silicon fabrication and yield issues. Recently, an optically and electrically pumped strained germanium on silicon laser was reported. These preliminary results indicate that with rigorous scientific analysis, an efficient electrically pumped laser source emitting in the technologically relevant communications wavelength band may be possible. Germanium does not suffer from the same incompatibility with the complementary metal-oxide semiconductor (CMOS) process, as do heterogeneous integration technologies. Furthermore, germanium offers the ability to directly integrate a germanium receiver on a silicon platform, which enables direct integration with CMOS electronics reducing electrical parasitism and enabling high speed, low noise, and low power receivers. The combination of these two scientific achievements would enable complete low power photonic networks homogeneously integrated in silicon.

Development of an electrically pumped laser emitting at relevant optical communications wavelengths in a group IV semiconductor has never previously been achieved. Only through rigorous analysis of the band structure, strain, doping concentration, and growth conditions will a successful demonstration be possible. Demonstration of an electrically pumped germanium-on-silicon laser would be the most significant scientific and technological breakthrough in the field of silicon photonics since its foundation, an enabling accomplishment for the future of the silicon photonics platform.

Summary of Accomplishments:

We developed the best-in-class, high-speed Ge on Si photodiodes based on an integrated waveguide design. These devices have the highest bandwidth reported with low capacitance and dark current, and are fully integrated within our CMOS compatible Si photonics platform. Furthermore, we developed integrated avalanche photodetectors in the same process flow and are currently evaluating their performance.

Our efforts to examine the light emission from strained and heavily doped Ge on Si have resulted in theoretical studies demonstrating material gain in these materials, and with best estimates of Auger and free-carrier absorption rates, net gain has been theoretically demonstrated. Experimentally, we have examined light emission properties from Ge on Si and bulk Ge to quantify enhancement in emission relative to unstrained and lightly doped material. We do see a weak enhancement in N-type phosphorous-doped samples, but have not been able to validate band filling and strain enhancement models proposed to describe lasing in Ge on Si devices.

Significance:

Our results on new integrated waveguide coupled Ge on Si detectors has led to new programs to examine detection at the single photon level. This new capability could revolutionize quantum key distribution and various low light imaging and sensing applications.

Refereed Communications:

W.W. Chow, J. Kabuss, and A. Carmele, "Analysis of Lasing from Direct Transition in Ge-on-Si," *IEEE Journal of Selected Topics in Quantum Electronics*, vol.19, p. 1502309, July/August 2013.

Fundamental Investigation of Chip-Scale Vacuum Micropumping (CSVMP)

151335

Year 3 of 3
Principal Investigator: R. P. Manginell

Project Purpose:

The creation of chip-scale vacuum micropumps (CSVMP) has long been a technological goal given their essential relevance to micro-mass spectrometers, chip-scale atomic clocks, etc. Despite many years of research and funding by the Defense Advanced Research Projects Agency (DARPA) and others, high-performance CSVMP remain unrealized. Whether this shortcoming was due to fundamental limitations or technological hurdles was the subject of this project. We created micron- and nanometer-scale rectangular-cross-section flow channels comparable to CSVMP flow geometries. A gas-flow measurement capability was developed to measure flow through these channels from the continuum to the free-molecular regime in the Knudsen range of 0.03 to 1000, hitherto, unreported in the literature. Flows less than 10^{-14} kg/sec were measured. This project also developed the first validated model of flow from continuum to free molecular. Experiment and modeling led us to conclude that underperformance of CSVMP created to date is due to engineering limitations, and not due to fundamental challenges to the physics.

Summary of Accomplishments:

This project examined gas flows in rectangular channels from the continuum to the free-molecular-flow (FMF) regime, reaching to Knudsen numbers (Kn) 30 times higher than previous work and flows below 10^{-14} kg/s. This research involved three aspects: micro/nano fabrication of precision channels, development of a capability to measure such low flows, and flow modeling. This project developed the first validated flow models for such channels from continuum to Kn of ~1000.

The fabrication methods developed provided precise dimensions and channel heights down to 3 nm. The channels were hermetic and had silicon ceilings and floors, matching flow models. The vacuum flow measurement system allowed measurements more than ten times lower in flow than previously published work. This project developed the first closed-form, flow models in rectangular channels and showed model validity to Kn of 1000. These models are of fundamental importance and are of practical value as evidenced by their use by an industry leader.

This research is relevant to generic rarefied gas dynamics (RGD) and to the practical design of high-performance CSVMP. Our research shows that there is no fundamental limitation to the construction of CSVMP. The physics of flow has been measured and modeled herein from continuum to deep into the FMF with no major deviations between models and data.

Finally, we developed key fabrication methods needed to create a high-performance CSVMP, such as actuation-electrode fabrication/interconnectivity, and pump membrane fabrication and bonding. Future efforts can use these processes, and the validated flow models developed in this project, to create useful CSVMP designs.

Significance:

This research expanded the general knowledge of RGD through measurements and modeling more than 30 times higher in Kn and more than 100 times lower in flow than previous work. The models developed are relevant to fundamental RGD, flows in microelectromechanical systems (MEMS) channels and creation of CSVMP. This project developed the first validated models of flow from continuum to Kn of 1000. RGD and CSVMP have direct application to national security and nuclear weapons missions.

Refereed Communications:

M.A. Gallis and J.R. Torczynski, "Direct Simulation Monte Carlo-Based Expressions for the Gas Mass Flow Rate and Pressure Profile in a Microscale Tube," *Physics of Fluids*, vol. 24, p.012005- 12005-21, 2012.

Photodefined Micro/Nanostructures for Sensing Applications

151337

Year 3 of 3
Principal Investigator: R. Polsky

Project Purpose:

The advancement of materials technology towards the development of ultrasensitive sensors for the detection of biological and chemical agents has been a long-standing challenge. The purpose of this project is to explore various lithographic techniques to make structures in photo-patternable materials and explore chemical and material modifications to design novel sensing platforms. The key attributes that we intend to explore are as follows: 1) pattern structures for sensing applications using interference lithography and direct laser writing techniques such as two-photon fabrication and stereolithography, 2) explore patterning in photosensitive materials such as photoresist, and 3) explore methods to improve the interfacial chemistry of the electrode surface to immobilize recognition elements, signaling pathways, anti-fouling components, etc., including nanoparticle and conducting polymer modifications. The resulting electrode can be tailored for specific applications and integrated into sensing platforms for the detection of chemical and biological threats.

Summary of Accomplishments:

The final results of this project resulted in: 1) the exploration of interferometric lithographically fabricated porous carbon structures for sensing and battery applications and 2) the creation of hollow polymeric microneedles for transdermal sensing applications. We demonstrated that increased mass transport (due to hemispherical diffusion profiles) inside the open porous structures of the ordered 3D carbon had many beneficial effects including higher signal-to-noise ratios and higher energy densities for sensing and battery applications, respectively. Various material modifications, such as conducting polymer and nanoparticle depositions, were also found to be more homogeneous and uniform inside the structures. This allowed the ability to tailor the modifications for specific applications. For instance, highly faceted palladium nanoparticles (catalytic to glucose oxidation) or palladium nanocubes (catalytic for oxygen reduction) could be selected simply by controlling deposition parameters. The chemical conversion of the structures from 3D amorphous carbon to 3D graphene further improved their performance with respect to enhanced electron transfer kinetics and provides a proof of concept method to create a variety of novel 3D graphene architectures. The placement of electrochemical transducers inside hollow polymeric microneedles was also demonstrated for the first time. This included the creation of a microneedle array for the simultaneous detection of glucose, lactate, and pH to determine metabolic acidosis environments. The creation of a microfluidic microneedle interface provides the intriguing possibility to create a long-term transdermal in vivo microneedle platform capable of real time measurement for a new generation of wearable sensors.

Significance:

The significance of the project's results is twofold: sensing platforms and energy applications:

1) The enhanced mass transport observed in the porous carbon electrodes result in higher signal to noise rations (lower detection limits) and faster analysis times. The development of transdermal microneedle sensors should impact real time wearable sensor technology to monitor an individual's immediate physiological state.

2) The enhanced mass transport in the porous carbon electrodes result in higher energy densities for batteries and the development of 3D graphene presents a new paradigm for 3D battery construction.

Refereed Communications:

X. Xiao, P.R. Miller, R.J. Narayan, S.M. Brozik, D.R. Wheeler, I. Brener, J. Wang, and D.B. Burckel, "Simultaneous Detection of Dopamine, Ascorbic Acid and Uric Acid at Lithographically Defined 3D Graphene Electrodes," to be published in *Electroanalysis*.

S. Sattayasamitsathit, Y. Gu, K. Kaufmann, W. Jia, X. Xiao, M. Rodriguez, S. Minteer, J. Cha, D.B. Burckel, C. Wang, R. Polsky, and J. Wang, "Highly Ordered Multilayered 3D Graphene Decorated with Metal Nanoparticles," *Journal of Materials Chemistry A*, vol. 1, pp. 1639-1645, 2013.

X. Xiao, J.R. Michael, T. Beechem, A. McDonald, M. Rodriguez, M.T. Brumbach, T.N. Lambert, C.M. Washburn, J. Wang, S.M. Brozik, D.R. Wheeler, D.B. Burckel, and R. Polsky, "Three Dimensional Nickel-Graphene Core-Shell Electrodes," *Journal of Materials Chemistry*, vol. 22, pp. 23749-23754, September 2012.

On-Chip Coherent Qubit Operations with Microfabricated Surface Ion Traps

154195

Year 3 of 3
Principal Investigator: C. Highstrete

Project Purpose:

The objective of this project was to develop expertise and capabilities at Sandia toward on-chip, localized, and laser-less qubit operations in a scalable architecture. The initial project goals addressed three areas: 1) development and implementation of hyperfine ion qubit trapping, coherent control, and experimentation capabilities in the laboratory with legacy ion trap devices and external microwave sources, 2) design of basic on-chip microwave control test structures, and 3) implementation of these test structures in the laboratory.

Summary of Accomplishments:

This project developed expertise and capabilities at Sandia toward on-chip electronic qubit control in a scalable architecture. Laboratory accomplishments included optical system design and implementation resulting in successful trapping of the 171Yb+ ion in a microfabricated ion trap at Sandia. Additionally, a microwave control system was developed and the software to integrate the laboratory hardware for experimental control was developed.

The device modeling and design effort of the project investigated the integration of microwave control elements with surface ion traps utilizing Sandia's state of the art, four-metal-layer microfabrication process. This process is ideally suited because microwaves can be delivered by buried conductors in a stripline configuration with an overall topside metal plane held at microwave ground. Interaction regions can involve local microwave electrodes — a topside microwave ground plane covers the rest of the device, maximally shielding microwave fields from affecting other trap regions. The ultimate vision developed is microfabricated ion trap architecture with multiple control zones, each with multiple degrees of freedom for controlling to perform various operations with solely electronic control.

Toward this vision, a surface ion trap test platform capable of local on-chip microwave qubit control was developed. The trap design emphasizes efficient routing of microwave pulses to ion trap zones with maximal shielding of stray fields, utilizing buried microwave leads and surface field generating elements. Additionally, the device was designed with the ground plane (substrate) removed beneath the microwave electrodes for greater field generation. The test platform design enabled the following future experiments:

1. On-chip controlled fast single qubit rotations
2. Device coherence time characterization with shuttling
3. Local control of quantization axis
4. Cross-talk characterization between control zones
5. One dimensional cross-talk compensation experiments
6. On-chip controlled two qubit coherent operations
7. Effect of ion height on above coherent operations

Significance:

In "A Federal Vision for Quantum Information Science," (QIS) the Office of Science and Technology Policy (OSTP) identifies QIS as "a family of potentially disruptive technologies" that has the potential to "enhance discovery and economic strength" thus warranting "a cohesive national effort to achieve and maintain leadership."

The main impact of the project is that it leveraged Sandia's unique microfabrication capabilities to develop technology and expertise in the area of sophisticated on-chip ion qubit control. This benefits the QIS community in general, but specifically benefits the Intelligence Advanced Research Projects Activity (IARPA's) Multi-Qubit Coherent Operations project at Sandia.

Micro-Scale Heat Exchangers for Cryogenic Micro-Cooling Applications

158181

Year 3 of 3
Principal Investigator: A. J. Gross

Project Purpose:

There is a need to create new microscale heat exchanger structures in order to implement cryogenic cooling of low power microelectromechanical systems (MEMS) and microelectronic devices. Development of high-performance microscale coolers will enable high-performance cryogenic sensors and electronics to be deployed in systems where their size and power consumption are currently prohibitive.

Cryogenic coolers capable of reaching temperatures of 100K or lower often rely on Joule-Thomson (JT) or Stirling cycle cooling. Both types of devices require efficient heat exchangers. However, previous micro-JT and micro-Stirling coolers suffered from parasitic heat losses resulting from the fabrication techniques and materials used. Additionally, many of these devices have not been compatible with wafer scale integration. The current state of the art has, therefore, failed to address the need for a highly integrated and efficient solution to cryogenic cooling at the microscale. The project will address this problem through the development of new structures that implement microfabricated heat exchangers for use in microscale coolers.

This project focused on developing microscale counter flow heat exchangers (CFHXs) with the potential for both chip and wafer scale integration. This project is differentiated from previous work by focusing on planar, thin film micromachining instead of bulk materials. A process will be developed for fabricating all the devices mentioned above, allowing for highly integrated micro heat exchangers. The use of thin film dielectrics provides thermal isolation, increasing efficiency of the coolers compared to designs based on bulk materials, and it will allow for wafer-scale fabrication and integration. The process is intended to implement a CFHX as part of a J-T cooling system for applications with heat loads less than 1mW.

Summary of Accomplishments:

We have demonstrated a process for fabricating channels in silicon that are buried up to 10 µm below the surface of the wafer. They are formed using a combination of anisotropic and isotropic silicon etches and sealed with dielectrics deposited by chemical vapor deposition (CVD). Stress simulations of the channel profile were performed and the results showed that for channels greater than 3 µm in diameter, the profile results in high-stress regions that are likely to fracture.

Finite element simulations were performed to investigate the ability of such small channels to perform effectively as the path for the high pressure in a J-T cooler. The simulations showed that even a 3 µm diameter cross section could support enough flow to generate temperature differentials of over 50K, with pressure differentials as low 40 atmospheres. In addition, the simulations showed that with such a small channel, there is no need for an additional flow restriction in the system. Instead, the tube carrying the high-pressure flow is able to serve as the both the hot side of the counter flow heat exchanger and the as the restriction that the gas expands through. The result is a simpler overall structure for the cooling system.

Significance:

This work points the way to developing on chip J-T coolers with submillimeter foot prints. With further development this technology would enable higher performance sensors and electronics for use across a broad range of applications.

Electrically Tunable Metamaterials for Agile Filtering in the Infrared

158826

Year 2 of 3
Principal Investigator: I. Brener

Project Purpose:

Multispectral infrared imaging systems use multiple detector arrays and static filters that increase their weight, cost, and complexity. Such systems could be greatly improved through the incorporation of fast, pixilated, electrically tunable filter arrays that are tightly integrated with focal plane arrays. Previous attempts at tunable infrared (IR) filters have used Fabry-Perot cavities, photonic crystals or other multi-stacks in conjunction with microelectromechanical systems (MEMS), mechanical or temperature tuning approaches. None of these approaches can provide microscale, thin, high optical performance, and electrically tunable IR filter arrays.

In this project, we propose to create compact semiconductor based tunable infrared filters using electrically tunable planar metamaterials. We have shown that the spectral response of infrared planar metamaterials is greatly influenced by coupling to high-mobility electron sheets or intersubband transitions in semiconductor heterostructures, placed within 200 nm of the metamaterial resonators. We intend to extend these concepts to electrically tunable filter arrays in the infrared (3-12 microns) by: 1) optimizing this spectral shift through the use of gated InGaAs doped layers and heterostructures of the In-Ga-Al-Sb-As material system and 2) design, modeling, and fabrication of new matched metamaterial nanoresonators that couple efficiently to these heterostructures. Ultimately, we envision a monolithic integration of these III-V based metamaterial filters with III-V based infrared focal plane arrays.

This project combines cutting-edge research in the areas of metamaterials, nanophotonics, and semiconductor physics in order to provide a compact solution that will impact many mission areas at Sandia. It plays well into the strengths of Sandia, leveraging investments at the Microsystems and Engineering Sciences and Applications (MESA) and Center for Integrated Nanotechnologies (CINT) facilities. This combination of bandgap engineering, devices physics, metamaterial design, and nanofabrication has never been tried before and hence has risks spanning from basic science to device integration.

Understanding Tantalum Oxide Memristors: An Atoms-Up Approach

158828

Year 2 of 3
Principal Investigator: M. Marinella

Project Purpose:

Dynamic random access memory (DRAM) and Flash memory technologies are nearing physical scaling limits and are starting to require significant switching energy compared to other components of modern computing systems. A recent International Technology Roadmap for Semiconductors (ITRS) report has determined that memristive (also referred to as redox) memory is one of the two most promising new memory technologies due to its unprecedented scalability, speed, pJ/bit switching energy, endurance, and retention and has recommended that it receive increased research focus. Government customers have already invested in memristor technology for neuromorphic computing and as a rad-hard memory. However, current state of the art memristors continue to exhibit serious uniformity and reliability problems; for example, resistances can vary by several orders of magnitude for devices within the same array. Industry is using Edisonian approaches to these problems, resulting in slow, incremental progress. The physical mechanisms enabling switching between high and low resistance states is thought to involve the motion of oxygen vacancies in a region that is only tens of nanometers thick. However, we still cannot definitively answer the question — what is moving where, and how? Thus, the central scientific problem is to identify the physical and chemical changes responsible for resistive switching. This will enable us to engineer reliable devices with predictable electrical behavior. Memristors present Sandia with a time-sensitive opportunity to achieve this understanding and significantly advance the field of microelectronics as a whole, while enabling important government applications.

Industry has favored trial and error experimental approaches that often result in minor, incremental improvements. We propose a scientific approach using novel lateral structures to perform a set of linked experiments that results in a physical model of memristor switching. A comprehensive scientific model of this phenomenon will result in a groundbreaking advancement of this technology for both commercial and government applications.

Understanding and Exploiting Bilayer Graphene for Electronics and Optoelectronics

158829

Year 2 of 3
Principal Investigator: S. W. Howell

Project Purpose:

Bilayer graphene (BLG) offers advantages that its more common form, monolayer, does not. Most prominently, a dynamic, "tunable" bandgap can be readily induced in BLG using electrical fields. Understanding this tunability presents a significant scientific challenge that could enable new, potentially disruptive, graphene devices as are envisioned by the latest International Roadmap for Semiconductors. A lack of fundamental understanding, however, has limited the realization of advanced BLG devices. For example, graphene's electronic properties are exceptionally sensitive to the materials surrounding it in a device. Additionally, there is limited understanding of the factors determining the magnitude and uniformity of the induced bandgap. In response, this project leverages our capabilities in BLG synthesis, characterization, device fabrication, and modeling in order to fundamentally understand BLG properties, thereby providing a scientific foundation for future graphene electronics and optoelectronics.

This project aims to understand: 1) the interaction between BLG's 2D charge carriers and the metals/dielectrics intrinsic to device integration and 2) the many-body electronic and optical properties of the system. This understanding will allow us to demonstrate a gated BLG device having the potential for disruptive capabilities in electronics and as an infrared detector. The project operates with the belief that BLG is the best platform to study these phenomena and has the greatest promise to fully leverage graphene's inherent advantages. Most importantly, BLG exhibits a tunable bandgap when exposed to a transverse electric field. There has been no definitive realization of scalable BLG devices, however, due to the limited availability of the material itself and an incomplete understanding of how integration processes alter graphene's properties. Utilizing our differentiating competency to produce large-area, high-quality, BLG combined with our ability to fabricate, characterize, and model these structures, we are uniquely positioned to address these problems and establish Sandia as the "go to" national resource for graphene nanoelectronics.

GaN Unipolar Optical Modulators

158830

Year 2 of 3
Principal Investigator: G. A. Vawter

Project Purpose:

The purpose of this project is to create a new class of optical data modulator with high bandwidth operation at high temperature in order to bypass the limitations of existing modulator technology. Conventional optical modulators change transmitted light intensity by modulating the interband (electron-to-hole, e-h) absorption energy and are made from InGaAsP/InP materials at telecom wavelengths (~1.5 µm). The small bandgap, long carrier-recombination lifetime and smearing of the e-h energy separation versus carrier density limit the operating temperature, saturation power, and recovery time of the modulation. We are using the extremely fast phonon-assisted relaxation times (~100 fs) and the high density-of-states of the intersubband (ISB) transitions (electrons in the conduction band) in GaN/AlN quantum well (QW) structures to improve saturation power, recovery from saturation, and operating temperature in optical intensity modulators operating at ~1.5 µm.

During the second year of the project, we extended metal-organic-chemical-vapor-deposition (MOCVD) growth of AlGaN/AlN MQWs on sapphire to the new double-QW design. Experimentation with growth conditions and templates has established essentially correct absorption spectra. Improving the AlGaN MOCVD "template" has significantly reduced electrical leakage. ISB models based on III-As-P materials were significantly improved for realistic modeling of the entire modulator structure from contact to contact. This breakthrough adds detailed knowledge of the electric field, carrier concentration, and quantized energy levels including the effects of large polarization charges at multiquantum-well (MQW) cladding interfaces. Most other work in the field uses periodic boundary conditions, masking the effect of cladding material on the MQW fields and carrier distribution. Waveguide development has revealed GaN waveguides grown at temperatures known to preserve the ISB absorption are too rough for low waveguide transmission loss. Work at intermediate temperatures has yielded 10X smoother GaN. Waveguides are being prepared from this material. We are exploring alternative hybrid waveguide concepts such as wafer-bonded single-crystal Si for use as rib waveguides on top of the MQWs.

Intrinsically Radiation-Hard Nonvolatile Memory: SnO_2 Memristor Arrays

159056

Year 2 of 3
Principal Investigator: E. J. Garcia

Project Purpose:

We propose to investigate SnO_2-based memristors to create inherently radiation-hardened, ultra-dense, non-volatile memory (NVM). Radiation-hardening-by-design is an effective solution, which is based on redundancy and implemented in layout and architecture; however, it comes with the penalties of strict design constraints, lower performance (>1 Moore's Law generation), and higher cost (10,000 times more than its commercial counterpart). An inherently radiation-hardened, ultra-dense, non-volatile memory device compatible with CMOS is key to relaxing design constraints and accelerating progress in radiation-hardened CMOS.

The memristor is a new type of memory device that has the potential to combine the best characteristics of the hard drive, RAM and flash in terms of density, access speed and power, and resistance to radiation effects. Excellent switching times of ~10 ns, memory endurance of >10E9 cycles, and extrapolated retention times of >10 years have been reported. Importantly, memristors are inherently radiation-hardened since information is stored as a structural change and not as electronic charge. Although different material systems have been investigated for memristors, SnO_2 has received little attention even though it is resistant to displacement and ionizing damage and has excellent electronic properties. Furthermore, SnO_2 can be deposited on flexible surfaces.

This project builds on relevant work and technologies, and US-Mexico collaborations to make a unique and inherently radiation-hardened NVM based on SnO_2 memristors. The project will combine the intrinsic radiation resistance of both the memristor structure and SnO_2 to make inherently radiation-hardened NVM. SnO_2-based memristor memory arrays will be fabricated on silicon wafers and tested for radiation hardness for the first time. Standard CMOS input/output (I/O) electronics and microsystems will be integrated with the memristor arrays to show NVM functionality. Moderately complex functionality of pre- and post-irradiated memristor arrays with peripheral electronics will be demonstrated. The work is in collaboration with the University of Texas at El Paso.

Coupling of Quantum Dots to Nanoplasmonic Structures

159184

Year 2 of 3
Principal Investigator: I. Brener

Project Purpose:

In collaboration with New Mexico State University, the goal of this project is to investigate coherent amplification of subwavelength surface plasmons in quantum dot lasers. Quantum dot lasers are extremely attractive because of their compact size, high spectral selectivity, ultra-low power consumption, higher gain, and increased modulation bandwidth. To fully exploit the unique properties of quantum dots, such as atomic-like spectra, ultrahigh charge carrier concentrations, and wide spectral tenability via the quantum size effect, it is crucial to maximize light quantum dot interaction. Due to the diffraction limit of traditional optical systems, light confinement comparable to the physical size of quantum dots is extremely difficult. In addition, integration of quantum dots into a stable optical cavity is a major technical challenge in nanophotonics. We will address these technical challenges of quantum dot lasers by creating novel plasmonic nanocavities integrated with highly stable giant nanocrystal quantum dots (g-NQDs).

We will investigate optical gain and stimulated emission profile of optically pumped quantum dot plasmon nanolasers. The projected nanolaser will utilize distributed feedback of deep subwavelength plasmon-polaritons in a periodically coupled plasmonic nanocavity to amplify the stimulated emission of embedded quantum dots. To our knowledge, amplification of stimulated emission profile via distributed plasmonic feedback was not reported in open literature. This approach will provide a coherent nanometer scale, ultra low power, and narrow line-width optical source for fundamental scientific research as well as various applications, such as sensing and communications.

Applications of Microwave Frequency Nano-Optomechanical Systems: Oscillators, Circuits, and Sensors

159256

Year 2 of 3
Principal Investigator: M. Eichenfield

Project Purpose:

Nano-optomechanical systems (NOMS) can simultaneously localize optical photons and microwave-frequency phonons to volumes thousands of times smaller than the volume of the smallest human cell — volumes limited only by the diffraction of the two waves. At this level of localization, the light-matter interaction becomes almost unimaginably strong, with each photon exerting forces on the matter containing it larger than ten times the weight of that matter. This enables a fully engineerable and scalable platform for light-matter interactions with strengths previously attainable only when trapped atoms, trapped ions, and quantum dots interact with light from external, macroscopic cavities. Under the leadership of a Truman Fellow at Sandia, this project aims to build a research program that broadly investigates novel NOMS-based chip-scale devices as next-generation acousto-optic circuits for the manipulation and processing of information on the surface of a microchip, as well as using NOMS to develop acousto-optic transducers with unprecedented sensitivity and resolution.

Temperature Dependence of the Electronic and Optoelectronic Properties of Carbon Nanotube Devices

162907

Year 2 of 2
Principal Investigator: F. Leonard

Project Purpose:

The detection of low levels of light in the infrared region of the electromagnetic spectrum is central to many applications across Sandia. Existing approaches for infrared detection use exotic semiconductor materials (e.g., HgCdTe), which raises issues with reliability, performance, and cost. Novel approaches for optical detection that use different materials, in particular ones compatible with existing CMOS fabrication infrastructure, would be valuable. The advent of nanotechnology brings novel materials with unique properties for infrared detection; carbon nanotubes are particularly attractive, but much research and development is needed to establish firmly their electronic and optoelectronic properties. In this project, we will fabricate suspended carbon nanotube field-effect transistors and measure the temperature dependence of their electronic properties. Furthermore, we will also test the optoelectronic response using a variety of optical characterization techniques. The outcome will be a detailed understanding of the temperature-dependent phenomena in carbon nanotube devices, which is essential for them to advance from laboratory demonstrations to technology.

Summary of Accomplishments:

We developed a capability to measure the temperature dependence of the electronic and optoelectronic properties of nanodevices. The experimental capability was used to measure the temperature dependence of carbon nanotube devices. Results indicate that thermally activated processes govern device behavior and that the environment plays an important role on the device properties.

Significance:

Nanomaterials including carbon nanotubes are being explored for a number of national security applications in electronics and optoelectronics. This work establishes new capabilities for characterizing these materials, which is necessary to understand their potential performance.

Defect Localization, Characterization and Acceleration Factor Assessment in Emerging Photovoltaic and Power Electronic Materials

164183

Year 2 of 3
Principal Investigator: B. B. Yang

Project Purpose:

Thin film photovoltaic (PV) materials systems, such as cadmium telluride (CdTe) and copper indium gallium selenide (CIGS), are promising approaches to producing affordable solar energy. Their reliability and degradation rate, however, still lag behind their traditional silicon counterparts. The success of alternative technologies, such as the microsystems-enabled photovoltaic (MEPV) technology under development at Sandia depends on good reliability and quantifiable longevity. The associated power conversion systems stand to benefit from the emergence of wide bandgap materials systems, such as silicon carbide (SiC) and gallium nitride (GaN), but the long-term reliability of such devices is also untested and the failure mechanisms are not well understood. We propose to establish a failure analysis framework for these materials systems and lay the groundwork for building a reliability model for key technologies. The study will primarily focus on MEPV solar technology and GaN-based power electronic devices.

The PV and the associated wide bandgap power devices industry are relatively immature compared to their silicon-based microelectronics counterparts. As such, there is a weaker understanding of the physics behind performance degradation and device failure. In addition, microelectronics failure analysis techniques may not be the as effective in these new technologies without adjustments. This project will develop the adaptations necessary for successful defect localization and failure analysis in emerging PV and power electronics devices. In addition, accelerated testing will be used to generate data for a reliability model using a variety of stress conditions. Subsequent defect localization before and after accelerated testing will further explore whether any of these techniques can be used as a screening tool. The findings will increase our confidence in the reliability of these devices through a better understanding of failure mechanisms as well as the availability of statistics based on lab tests. This decrease in uncertainty will accelerate the maturation and adoption of these high-performance technologies.

Nano-Structured Silicon Phonic Crystals with Metal Inclusions for ZT Enhancement Proof of Concept

164672

Year 2 of 3
Principal Investigator: C. M. Reinke

Project Purpose:

Most published research on improvement of the thermoelectric figure of merit (ZT = (S^2 x sigma/k)T, where S, sigma, and k are the Seebeck coefficient, electrical conductivity, and thermal conductivity, respectively) has largely focused on only one of its components, with the hope that the other two remain favorable. However, due to the interdependent nature of the problem, efforts to reduce k by incoherent phonon scattering inadvertently create electron scattering with a corresponding reduction in sigma, and efforts to increase sigma via doping typically result in a decrease in S, in accordance with the Mott relationship. We propose to circumvent these issues by addressing all three parameters of ZT using nano-structured phononic crystals (PnCs) with metallic inclusions. The engineered scattering of phonons using PnCs reduces k, while metal inclusions increase the sigma of the PnC. Additionally, metallic nano-rings will be used to engineer the electronic band structure at the semiconductor-metal interfaces in a manner that increases S and thus the overall ZT.

Efforts to extend previous research in thermal conductivity reduction using PnCs to high-temperature, high-ZT devices raised several questions: 1) will the relative reduction in k remain constant at higher temperatures, 2) will sigma be enhanced in a semiconductor-metal PnC (rather than semiconductor-air) while maintaining the reduction in kappa, and 3) can S be enhanced using low-dimensional metallic inclusions? The first question will be answered by measuring the reduction in k relative to an unpatterned slab of the same thickness as the temperature is increased and the second will be addressed by measuring the S, sigma, and k of a Si-W PnC, using an existing thermal equilibrium test bench. The third question will require the introduction of metallic nano-rings into the PnC air holes using a focused ion beam system. All three tasks are supplemented by the theoretical expertise developed at Sandia in PnC design and thermal conductivity calculations for periodic nanoscale materials.

Gate-Controlled Diode Structure to Investigate Leakage Current and Early Breakdown in Graded InGaAsP/InP Junctions

164676

Year 2 of 3
Principal Investigator: D. Leonhardt

Project Purpose:

A number of scientifically interesting questions and technically relevant engineering challenges have arisen during recent efforts to develop PnP-heterojunction bipolar transistors (HBTs) for stockpile applications. The HBTs under development utilize group III-phosphide compositionally graded junctions and hold promise for improved device figures of merit such as reliability, base-collector breakdown voltage (BV_{cb0}), and reduced degradation in radiation environments, as compared to prevailing Si-based transistors. To date, however, the development of PnP-HBTs has been hampered by low BV_{cb0} and large leakage current. The cause of premature breakdown in these materials is not currently understood, nor is it yet known whether the problems stem from surface or bulk effects within the materials. These impediments, however, present a unique opportunity to increase our fundamental understanding of this important class of materials. Gaining a fundamental understanding of breakdown effects and surface leakage currents can suggest new avenues of research to neutralize these effects and, therefore, contribute to wider applicability of III-V devices. Moreover, surface effects are expected to increasingly dominate as device geometries reduce to the nanoscale, prompting an impetus to understand the role of surfaces in early breakdown behavior of graded III-phosphide materials.

This project, while addressing the root cause of problems specific to a class of devices with significant national security interest, also has broad scientific interest and potential for large impact to the group III-V research community. Findings are also applicable to other III-V material systems susceptible to leakage currents and surface effects, such as infrared detectors and avalanche photodiodes. In addition, achievement of a PnP-HBT with large BV_{cb0} would enable other important advances in III-V HBT device technology, such as development of complementary npn/pnp- designs analogous to Si complementary bipolar technology.

Active Plasmonics from the Weak to Strong Coupling Regime

165702

Year 1 of 3
Principal Investigator: G. A. Keeler

Project Purpose:

Plasmonics focuses on the manipulation of light using metallic nanostructures and promises to transform the field of optoelectronics, which has traditionally relied upon light guiding in dielectrics and semiconductor-based devices. Most nanoplasmonics efforts have examined passive structures with static, geometry-defined responses. We intend to demonstrate, for the first time, a range of active plasmonic devices based on guided surface plasmons coupled with electrically controlled compound semiconductor structures operating at near-infrared (NIR) wavelengths. We expect these active devices to fundamentally alter the photonics landscape and push the frontiers of nanoscale optics.

The primary scientific question examined in this project is how light-matter coupling changes when light is confined to the nanometer scale in the form of plasmons. Experimental tests of our theoretical understanding will be performed using test devices such as modulators, amplifiers, and emitters that bring about various degrees of plasmon coupling (weak to strong). Plasmonic modulators and amplifiers will be based on semiconductor quantum wells (QWs) that can be forward or reverse biased to achieve gain or loss through relatively weak plasmon-exciton coupling. Laser integration represents a more complex hybrid system, wherein the plasmonic structure will be strongly coupled within the optical cavity of a vertical-cavity surface-emitting laser (VCSEL), with plasmon interactions occurring in a high field environment.

To date, there have been no demonstrations of efficient electrical modulation and amplification techniques for NIR guided plasmons. Plasmon integration within a laser cavity represents another exciting new area of study, with significant complexity at the nanoscale. Active plasmonic devices have the potential to impact a wide range of applications, including optical communications, high performance computing, radio frequency (RF) remoting, analog-to-digital conversion, and optical signal processing.

Minority Carrier Lifetime Characterization and Analysis for Infrared Detectors

165703

Year 1 of 3
Principal Investigator: E. A. Shaner

Project Purpose:

Infrared detector performance is degraded by carrier recombination and dark current generation. The nBn device architecture, comprised of two n-type semiconductors sandwiching a barrier layer, has experimentally proved its superiority over mercury cadmium telluride (MCT) and InSb. Both parasitic generation-recombination current and perimeter currents are completely suppressed in optimized designs. However, the fundamental dark current diffusing from the absorber limits its performance to a level only marginally better than MCT. To dramatically reduce the dark current by another order of magnitude requires a new absorber material with long carrier lifetimes at mid-wave infrared (MWIR) and even longer lifetimes in the long-wave infrared (LWIR). We will study dark current and minority carrier lifetime in nBn absorbers such as InAsSb, as well as InAs/InAsSb superlattice material systems, and correlate measurements with growth conditions and crystal structure. Our goal is to develop an understanding of lifetime limiting mechanisms in these materials and work towards improvements that will impact detector performance.

The overall goal of this research effort is to characterize and understand dark current generation, the impact of defects on detector performance, and to explore solutions to these issues using either bulk or superlattice absorbers. We will focus primarily on minority carrier lifetime since material quality is the primary driver for improved performance. To fully understand an immature material system such as InAs/InAsSb, many different structures with varying layer composition and doping must be characterized over a wide range of temperatures. This fundamental effort, if successful, should enhance our efforts in other areas more closely linked to detector performance.

Refereed Communications:

B. V. Olson, E. A. Shaner, J. K. Kim, J. F. Klem, S. D. Hawkins, M. E. Flatté, and T. F. Boggess, "Identification of Dominant Recombination Mechanisms in Narrow Bandgap InAs/InAsSb Type-II Superlattices and InAsSb Alloys", *Applied Physics Letters*, Vol. 103, Issue 5, July 2013.

Electrically Injected UV-Visible Nanowire Lasers

165704

Year 1 of 3
Principal Investigator: G. T. Wang

Project Purpose:

There is strong interest in minimizing the volume of lasers to enable ultracompact, low power, coherent light sources. Nanowires (NWs) represent an ideal candidate for such nanolasers as stand-alone optical cavities and gain media and optically pumped NW lasing has been demonstrated in several semiconductor systems. Electrically injected NW lasers are needed to realize actual working devices but have been elusive due to limitations of current methods to address the requirement for NW device heterostructures with high material quality, controlled doping and geometry, low optical loss, and efficient carrier injection. We will demonstrate electrically injected NW lasers emitting in the important UV to visible wavelengths. Our approach to simultaneously address these challenges is based on high-quality III-nitride NW device heterostructures with precisely controlled geometries and strong gain and mode confinement to minimize lasing thresholds, enabled by a unique top-down NW fabrication technique developed at Sandia that provides maximum design flexibility. Our approach applies novel strategies for addressing these issues and leverages our combined expertise in III-nitride NW fabrication and characterization, nanodevices, and semiconductor laser modeling. Theory and modeling will be closely integrated with experiments to help design and demonstrate NW heterostructures with minimal lasing thresholds and to understand and predict the properties and physics from these nanolasers. Successful demonstration of a working III-nitride NW laser will potentially enable diverse new functionalities in the integration of electronics and photonics, chem-bio sensing, imaging, ultra-high density storage, nanolithography, lighting, and quantum information. External agencies are extremely interested in electrically injected NW lasers, and a proof-of-concept demonstration here first will dramatically improve the chances of successful follow-on work.

Efficient Heat Removal from Power-Semiconductor Devices Using Carbon Nanotube Arrays and Graphene

165705

Year 1 of 3
Principal Investigator: M. P. Siegal

Project Purpose:

Efficient heat removal from semiconductor-based power electronics is becoming increasingly important, especially with the growing investment in renewable energy sources that require advanced power electronics to interface with the electric grid. For example, excessive temperature reduces performance and causes failure in Si-based power-switching devices such as insulated gate bipolar transistors (photovoltaic inverters). This problem is exacerbated as voltage, current, and switching frequency scale to increase grid efficiency. This led to the pursuit of wide-bandgap SiC and GaN for next-generation power electronics. However, their advantages are obscured by reduced performance and lifetime that occur with increased temperature. To fully achieve these material gains, the thermal resistance of the system must be reduced. Therefore, this project targets the large thermal resistance occurring at the device die/package boundary where standard thermal-interface materials (TIM) (e.g., metal-loaded epoxies, with thermal conductivity ~ 1 W/m·K) act as a thermal bottleneck that can mitigate performance or even cause failure.

We seek to eliminate the TIM heat-transfer bottleneck from high-power devices to enable efficient cooling for improved device performance and reliability by creating all-carbon TIM cooling strategies to meet present/future needs. Carbon nanotubes (CNTs) and graphene can have thermal conductivities > 10x that of metals. We propose synthesizing high-quality, vertically aligned CNT arrays directly onto a metal package that directly bonds to the device die in order to reduce TIM resistance by 10 - 100X. While this alone will reduce the existing thermal bottleneck, we further propose incorporating graphene sheets onto the top of device surfaces to act as an ultimate heat spreader. By then making direct thermal contact between a graphene heat spreader and CNT-TIM in a flip-chip architecture, and with the assistance of fundamental studies of phonon transfer through each new material and interface, 1,000X improvements over state of the art TIM technology are obtainable. Planned enhancements may potentially render the device substrate thermal conductivity irrelevant, and lead to a new paradigm for high-power device performance via thermal management.

Fabrication and Characterization of a Single Hole Transistor in p-type GaAs/AlGaAs Heterostructures

165706

Year 1 of 3
Principal Investigator: L. A. Tracy

Project Purpose:

One of the leading candidates for a solid state quantum bit is the spin of a single electron confined in a semiconductor. Coherent control of individual electron spins has already been demonstrated in quantum dots. These groundbreaking experiments utilized high-mobility 2D electron systems in GaAs/AlGaAs heterostructures grown via molecular beam epitaxy (MBE). The major source of decoherence in such experiments is coupling between electron spins and nuclear spins in the host GaAs semiconductor. It has been proposed that hole spins in GaAs would be better suited for such experiments due to a lesser coupling between hole and nuclear spins. Recent experiments already show that the coherence time for hole spins in GaAs quantum dots are at least one order of magnitude longer than that of the electron spin.

Building on recent successes in the growth of high-mobility 2D-hole systems (2DHS) via carbon doping of (100) oriented GaAs/AlGaAs heterostructures here at Sandia, we plan to fabricate and characterize single-hole transistors, looking towards eventual applications in the area of quantum computing. This work will leverage Sandia's unique, world-class capabilities in MBE growth of GaAs/AlGaAs heterostructures and expertise in low temperature measurements.

To date, experiments looking at the possibility of using spins in semiconductors as quantum bits have primarily focused on electron spins. It was only recently suggested that hole spins in GaAs might provide better coherence times. One of the main reasons that there are relatively few experiments on holes in GaAs, as compared to electrons, is the difficulty of growing high-quality 2DHS that can be used to fabricate stable hole nanostructures (such as quantum dots). However, recent advances in growth of 2DHS via carbon doping provide a new possible route to obtaining material of comparable quality to current high-mobility 2D electron systems in GaAs.

Optical Polarization-Based Genomic Sensor

165707

Year 1 of 3
Principal Investigator: S. M. Brozik

Project Purpose:

Optical fluorescence-based DNA assays are commonly used for pathogen detection and consist of an optical substrate containing DNA capture molecules, binding of target RNA or DNA sequences, followed by detection of the hybridization event with a fluorescent probe. Though fluorescence detection can offer exquisite signal-to-background ratios, with high specificity, vast opportunities exist to improve current optical-based genomic sensing approaches. For instance, photobleaching, whereby fluorescent probes transition to a dark state under prolonged excitation, necessarily limits detection sensitivity. Furthermore, fluorescence detection requires relatively intense, narrow band excitation light sources, as well as expensive dichroic/band pass optical filters to isolate signal, whose alignment tolerances may preclude deployment in rugged environments. Finally, particularly sensitive applications necessitate costly detectors to attain sufficient sensitivity, further decreasing overall robustness. For these reasons, there is a clear need to explore alternative optical sensing paradigms to alleviate these restrictions.

Bio-templated nanomaterial synthesis has become a powerful concept for developing new platforms for bio sensing, as the biomolecule of interest can act as part of the sensing transducer mechanism. We will explore innovative genomic sensing methodologies based on interactions between light and nanoparticle assemblies. Rod-shaped, noble metal nanoparticles (nanorods) have been shown to strongly interact with light in a resonant fashion. This interaction can be many thousand-fold larger than fluorescent dyes and does not suffer from photobleaching. However, the full potential of this phenomenon has yet to be realized. We plan to use nucleic acid hybridization as a means to link metal nanorods end-to-end, in order to create particle chains that are predicted to display unique and useful properties for sensing specific genomic sequences. Metal nanorod chains are expected to display enhanced optical depolarization properties, over non-linked single particles, due to the coupling of individual nanoparticle plasmon resonances. This offers a method for optical genomic sensing that may be much more sensitive and stable as compared to conventional fluorescence assays.

Programmable Piezoelectric RF Filters

165708

Year 1 of 3
Principal Investigator: C. Nordquist

Project Purpose:

We plan to explore micromechanical modulation of distributed piezoelectric transducers to create the first widely tunable acoustic radio frequency (RF) filters, which will revolutionize RF filters. Currently, high-quality factor (Q>1000) reconfigurable filters cannot be achieved because of the difficulty in tuning acoustic resonators and the large size of electromagnetic resonators. The planned programmable high-Q filter will dramatically reduce size, weight, and power for RF systems and will adapt to evolving performance requirements, resulting in improved link margin.

We will combine modeling and experiment to explore the fundamental coupling mechanisms in microelectromechanical systems (MEMS)-based piezoelectric modulation switches that serve as the fingers of an acoustic filter. Varying the distance between the MEMS switch finger and the substrate from nanometers to micrometers will change the electric field in the piezoelectric film, which in turn will modify the electromechanical transduction of the signal into and out of the filter. Switching individual fingers tunes the effective width and pitch of the transducer and reflector gratings, controlling the filter center frequency, coupling, and bandshape. Additionally, designing the filter to avoid contact of the fingers with the piezoelectric film will reduce damping and increase Q.

Achieving this result requires meeting challenges in acoustic device modeling, microelectromechanics, and integration. In particular, the influence of surface contamination, roughness, and charge state on the transduction must be understood by modeling, designing, fabricating, and characterizing a robust switchable element and filters. Also, the synthesis of the filter response must be modeled and refined using coupling-of-modes modeling and optimization.

This project will enable a new class of programmable filters, advance the state of the art, and enable new, smaller, and more efficient RF systems. The envisioned integration of the MEMS switch, as a finger in a piezoelectric filter has not been attempted before and, therefore, presents novel science and engineering opportunities.

Computational and Experimental Characterization of Aluminum Nitride-Silicon Carbide Thin Film Composites for High Temperature Sensor Applications

165711

Year 1 of 2
Principal Investigator: B. Griffin

Project Purpose:

A number of important energy-related applications would benefit from sensors and electronics capable of withstanding extreme temperatures (>300 °C). Examples include pressure sensors and accelerometers for automobile engines, gas turbines, nuclear and coal power plants, and petroleum and geothermal well drilling. Military applications, such as hypersonic flight research, would also benefit from sensors capable of 1000 °C.

Silicon carbide (SiC) has long been recognized as a promising material for harsh environment sensors and electronics and SiC research has received considerable funding (e.g., from the National Aeronautics and Space Administration (NASA) and the Defense Advanced Research Projects Agency (DARPA)). Yet today, most advanced SiC devices are made from SiC films deposited on silicon wafers, which inherently limits the temperature range below 500 °C. Further, most SiC sensors to date are based on measuring capacitance or resistance shifts, which are highly temperature dependent. We plan to address these problems by developing the science and technology necessary to create sensing structures using SiC and piezoelectric aluminum nitride (AlN) thin films.

This novel material system builds upon Sandia's strengths in thin films and holds promise to be capable of withstanding temperatures to 1000 °C. SiC and AlN are stable at high temperatures and are closely matched in coefficients of thermal expansion, leading to sensor stability at high temperatures. AlN is also a non-ferroelectric piezoelectric material, enabling piezoelectric transduction at temperatures exceeding 1000 °C. Sandia has developed an AlN capability, resulting in a 2011 R&D 100 Award, and has combined SiC-AlN thin films on Si substrates for phononic crystals.

Anticipated S&T challenges consist of fabrication development, including the integration of high temperature capable electrodes. Further, in order to model a sensor's response, we will need to determine the temperature dependent properties of the SiC-AlN thin film composite, including structural stiffness, piezoelectric constants, resistivity, permittivity, damping, and noise mechanisms, at temperatures higher than the deposition temperatures (approximately 350 °C).

Development of a MEMS Dual-Axis Differential Capacitance

165823

Year 1 of 3
Principal Investigator: B. Griffin

Project Purpose:

Reduction of drag over a surface, due to both viscous skin friction and pressure separation effects, is an essential component of the effort to increase vehicle efficiency. Currently, there is no method for time resolved, direct measurement of wall shear stress at the spatial and temporal scales of turbulent flow structures inside model testing facilities. Indirect methods require extensive in situ calibration, and rely on inferred relations to produce a measurement. Some popular indirect sensors, such as hot-wires, locally act to disturb the flow by adding energy to the system. Direct sensors can circumvent these issues, although they may be prone to collecting debris or breaking under strain.

Microelectromechanical systems (MEMS) devices benefit from many favorable scaling effects which reduce overall measurement error, and can retain spatial resolution while measuring small-magnitude forces. To prevent spatial averaging over a floating element sensor, the length scale needs to remain under 20 viscous wall units, where a typical wall unit can be on the order of 10 μm for a turbulent boundary layer. Prior designs at the University of Florida have yielded sensors that either measured static or dynamic shear stress and achieved a noise floor of 14.9 μPa with 102 dB of dynamic range. Previous sensors have been constrained to single axis sensing, carrying concerns over accuracy due to alignment in testing and multi-directional flow effects.

Presently, there are no sensors capable of compliant dual-axis shear stress sensing at the microscale. Successful development of this sensor will allow for the first directly sensed vector measurement of shear forces under aerodynamic flow. Utilization of MEMS technology will yield novel information about fluid flow interaction, especially at the onset of separation that previous technologies cannot spatially resolve. This work is in collaboration with University of Florida.

In Situ Techniques to Characterize Creep and Fatigue in Freestanding Metal Thin Films

166154

Year 1 of 3
Principal Investigator: B. Boyce

Project Purpose:

Thin film mechanical properties are of critical importance in micro/nano-electromechanical systems (MEMS/NEMS). Despite increasing interests and potentials of thin film metals as the materials of MEMS/NEMS devices, their mechanical properties have been explored much less than silicon, of which diverse mechanical properties such as Young's modulus, fracture strength, and fracture toughness as well as mechanical stability such as fatigue and creep characteristics have been comprehensively studied and established. However, silicon has limitations in some important application areas. Its high resistivity (typically larger than 10 μohm·m) makes it difficult to be used in microswitches. Its relatively low optical reflectivity provides very limited opportunities in optical applications such as micromirrors. Recently thin film metals such as aluminum have been noted as a great alternative in such applications where low electrical resistivity or high optical reflectivity is critical. However, in spite of their potential, their poorly known mechanical properties and reliability characteristics remain a big hurdle. Typically, thin film metals tend to grow with much smaller grain size than their bulk counterparts, so are expected to provide higher mechanical strength and stability. In this project, we plan to explore diverse mechanical characteristics of metal thin films, particularly fatigue and creep behaviors, so that they can be used in many practical applications in various micro/nano-mechanical structures.

In collaboration with Carnegie Mellon, we will develop powerful in situ techniques to study thin film creep and fatigue using MEMS design, processing and test methods. We will work with a standard material (Aluminum) to prove out the methods. Once established, we aim to apply these tests to develop high-strength multilayer thin film metal stacks. Diverse applications for these materials are possible: 1) as low creep/fatigue materials in microrelays and micromirrors, 2) as damage-tolerant materials in extreme radiation environments (e.g., in nuclear reactor walls), and 3) as high-temperature high-strength materials, and 4) for x-ray focusing.

Quantum-Confinement Effects on Seebeck Coefficient

168506

Year 1 of 1
Principal Investigator: I. F. El-Kady

Project Purpose:

We study the effects of quantum confinement on the Seebeck coefficient of semiconducting materials in pursuit of the greater goal of an enhanced thermoelectric figure of merit, Z.T=(S^2.Sigma/κ).T, where S, Sigma, κ, and T are the Seebeck coefficient, electrical conductivity, thermal conductivity, and temperature, respectively. S can be defined as the entropy flux per unit charge at the Fermi level (Ef) and one way to increase the entropy flux is by increasing the total number of carriers at the Ef without increasing the doping level. This can be achieved by reducing the dimensionality of the system, for example from 3D to 2D, thus forcing the quantization of the electronic energy states in the reduced dimension. This, in turn, reduces the corresponding density of available states and forces the carriers to occupy the higher energy levels, leading to an increased entropy flux at Ef.

Our candidate for testing these ideas is the 2D inversion layer that can be realized in a conventional planar metal-oxide-semiconductor field-effect transistor (MOSFET) and the more exotic cylindrical sheet inversion layer in a nanowire MOSFET.

Summary of Accomplishments:

The primary goal of this project was to demonstrate the physics underlying S enhancement via quantum confinement and lay the foundation for realizing it in a practical device. We resorted to using existing MOSFET structures and attempted to apply heat using a laser beam of varying power to the source bond pad while measuring the source-drain voltage (V_{SD}) under different gate voltages (V_G). The hypothesis was that under very strong inversion (large V_G), the MOSFET channel would become a 2D electron gas (or hole gas depending on the field-effect transistor [FET] type) and we would be able to qualitatively measure a quadratic dependence of S on V_G , thus verifying the quantum confinement influence on the Seebeck coefficient. A four-axis probe station with microscope was used to perform the measurements in air using standard DC tungsten probes. The drain and body terminals were grounded and V_G was supplied using Agilent DC power supply. V_{SD} was measured with a Keithley digital multimeter. Several n-channel MOSFET devices with different widths were investigated. Our results showed a quadratic dependence of S on V_G, and hence infer a quadratic dependence of S on the channel width, thus validating the quantum confinement hypothesis. This result is quite encouraging and would imply that our route for enhancing ZT via quantum confinement is indeed viable and can lead to practical integrated on-chip thermoelectric (TE) modules.

Significance:

This project was a success and, to our knowledge, was the first direct demonstration of S enhancement in a MOSFET structure using quantum confinement. This study lays the foundation for using Si in a TE setting, thus allowing monolithic integration of TE coolers and scavengers resulting in profound impact to Si electronics. This would profoundly impact microelectronics enabling higher speeds, lower noise and unprecedented sensor sensitivity — all critical milestones for Sandia's nuclear weapons program and help maintain and strengthen the nation's technological superiority. The ability of such integrated TE devices to scavenge energy and/or reduce thermal loads increases performance efficiencies, which is at the heart of DOE missions. Finally, such TE generators may hold the key to the National Aeronautic and Space Administration's (NASA) quest for renewable energy sources in deep space exploration missions where photovoltaics are impractical, as in the Mars Rover.

Refereed Communications:

S. Alaie, D.F. Goettler, K. Abbas, M.F. Su, C. Reinke, I. El-Kady, and Z.C. Leseman, "Microfabricated Suspended Island Platform for the Measurement of In-Plane Thermal Conductivity of Thin Films and Nanostructured Materials with Consideration of Contact Resistance," *Review of Scientific Instruments*, vol. 84, p. 105003, 2013.

Decoupling Superconducting Transmon Qubits from their Quantum Bus/Readout Resonators to Enable Scaling

172334

Year 1 of 3
Principal Investigator: R. M. Lewis

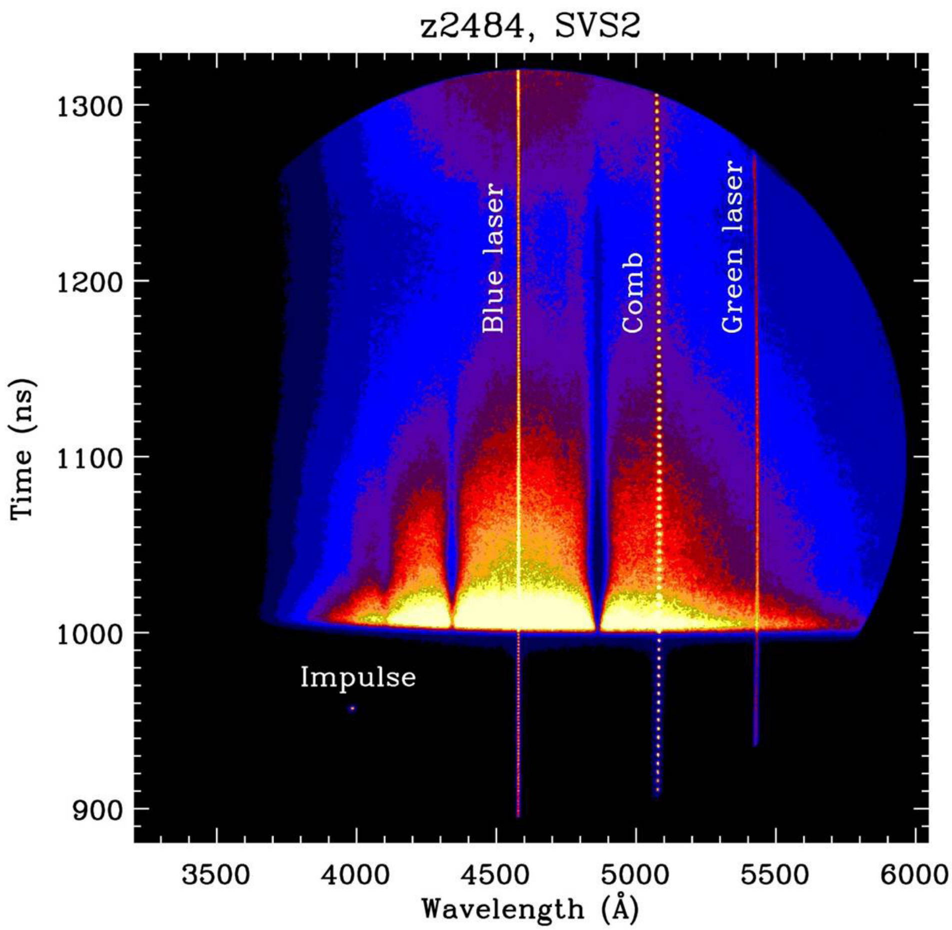
Project Purpose:

This project seeks to understand a method of decoupling superconducting qubits from their attached control circuitry. Superconducting quits have made great strides in coherence time, gating, and algorithms. However, to achieve real scalability, the ability to decouple a qubit from its control circuitry and its neighbors is required. Of the various superconducting qubit variations, the transmon is a leading design because of its long intrinsic coherence times and relative ease of coupling to other qubits. The transmon couples to its host resonator via its electric-dipole moment. We plan to use a characteristic of quantum mechanics to null the dipole moment and decouple the transmon. In doing so, we hope to study a variety of physics associated with multi-qubit operation, control, and readout. We also hope to demonstrate a path to scaling these devices to larger system sizes.

RADIATION EFFECTS AND HIGH ENERGY DENSITY SCIENCES

The Radiation Effects and High Energy Density Sciences Investment Area seeks to advance science and engineering in the areas of radiation effects science, high energy density science, and pulsed power science and enabling technologies.

The goal of the radiation effects sciences area is to ensure that engineered systems are able to operate as intended in radiation environments they encounter. Researchers are developing new radiation-resistant materials and technologies and creating technology to generate extreme radiation environments. They are advancing materials, switching, power flow, and engineering to build reliable pulsed power systems.



Example time-resolved absorption spectrum of hydrogen Balmer lines from experiment z2484. This streak image is not corrected for the optical fiber transit time delay nor have absolute calibrations been applied. We label the wavelength fiducials (blue and green lasers) and the time fiducials (comb, impulse) (Project 151366).

RADIATION EFFECTS AND HIGH ENERGY DENSITY SCIENCES

Low-Energy Electron/Photon Transport

151362

Year 3 of 3
Principal Investigator: R. P. Kensek

Project Purpose:

The purpose of the project is to create more reliable cross sections for electron/photon transport at lower energies (sub kilo-electron-volt [keV]). Radiation transport codes are limited by the accuracy of the physics models. General-purpose codes make use of tabulated independent-atom models for the cross sections which are either only evaluated down to about one keV or extend further with acknowledged large errors (estimated as 1000 percent in solids at the lowest energies). The paradigm shift we propose is to generate what would have been tabulated atomic cross sections, but now they include molecular (coherent scattering) and/or solid state effects for each material specified. The challenge of this approach is to include these materials properties for each relevant interaction cross section through a reliable numerical technique.

Interest in such a capability is motivated by applications involving low-energy electron and/or photon transport, such as transport through nanostructures, understanding experiments from x-ray sources such as Sandia's Z machine, and better understanding of the energy-resolution limitations of gamma detectors due to secondary electron emission.

The paradigm shift involves generating elemental cross sections for each material, incorporating materials effects (in particular, molecular coherent scattering and solid state effects) as they uniquely affect each element in that particular material. This involves identifying a reliable technique for each change for each relevant electron and photon interaction, which can be accomplished for a general-purpose radiation transport code.

Summary of Accomplishments:

We demonstrated that we could incorporate molecular and solid state effects for photon coherent scattering. Conceptually, the process involved obtaining a radial density function (RDF) of nuclei of the material of interest, convolving it with an isolated atom electron distribution and taking the Fourier transform to obtain a molecular/solid state form factor. The desired cross section is then the product of this form factor and the Thomson cross section. The RDF was calculated from atomistic models of the materials of interest. We used a 144-atom model of amorphous silicon dioxide (SiO_2) and a large semi-crystalline model of polyethylene. Comparisons with measurements were excellent.

Results for electron elastic scattering were mixed. We successfully demonstrated solid state oscillations in both amorphous and crystalline germanium by treating the material as effectively a large molecule through modifications of an existing tool, ELSEPA (elastic scattering of electrons and positrons algorithm). However, we were unsuccessful in attempting to demonstrate a large-magnitude difference by additionally treating the potential used for the Dirac wave functions as extending over a cluster of atoms. Furthermore, comparing measurements with ELSEPA results for molecular nitrogen (where no modifications were necessary), the results suggested use of ELSEPA's molecular capability did not produce an improvement over the independent atom option.

We demonstrated that density functional theory (DFT) could be used to compute the electron-energy-loss function for energy losses lower than perhaps 40 eV (on SiO_2). In principle, this could be extended to higher-energy losses through the use of photon-absorption cross sections, but we ran out of time. A more significant challenge lay ahead: that of extrapolating into finite momentum transfer space, which would be necessary to obtain the doubly differential electron-inelastic cross section, which was our goal.

Significance:

The success of our generation of photon coherent cross sections does suggest a real improvement in more reliable cross sections at lower energies. However, photon coherent scattering is never the dominant cross section, so the significance is ultimately rather modest here.

While we did not obtain such success with other cross sections, a greater appreciation of the challenges was achieved and communications between the practitioners of radiation transport, radiation effects, and solid state physics were enhanced tremendously. We will be looking for other opportunities to make use of this greater communication.

Modeling Electron Transport in the Presence of Electric and Magnetic Fields

151363

Year 3 of 3
Principal Investigator: W. C. Fan

Project Purpose:

Strategic weapon systems are required to survive the hostile radiation environment produced by nuclear detonations. For example, a potentially large system-generated electromagnetic pulse impinges on electrical or electronic components. Existing modeling/simulation tools assume that electron transport is totally independent from the fields created by the deposited charges, which becomes invalid if the low energy electrons are considered.

A related problem is spacecraft charging due to the accumulation of low energy electrons on the outside surface of a satellite, which can cause electrical arcing, breakdown of dielectrics, and eventually leads to the destruction of electronics and failure of mission capability. Current methods for charging predictions oversimplify the relevant physics, such as the dynamic interaction between incident electrons and electric fields generated by deposited charge. With frequent buildup of potentials on the order of 10 kV on spacecraft surfaces, the effect of the high-flux, trapped electrons in the 1-100 keV range could be significant. Current models give rough predictions, but large safety margins are required due to significant uncertainty.

The purpose of this project is to address these issues through model development and numerical simulation by creating new deterministic algorithms and implementations for multidimensional electron transport in materials in the presence of electric and magnetic fields.

Summary of Accomplishments:

We have developed a mathematical model, by including the effects of Lorentz force in the Boltzmann transport equation, for electron transport with electromagnetic fields. Two deterministic numerical techniques have been developed to treat the energy and angular redistribution due to the electromagnetic fields.

In the first approach, we apply the traditional discrete ordinates method to discretize the differential angular redistribution terms with the spatial and energy dependence treated with discontinuous finite element methods. The discrete system can be arranged into a form very similar to that encountered in standard radiation transport. More specifically, the energy and angular redistribution operators are transformed into a series of scattering matrices. However, convergence of this approach is highly problematic when applying the source iteration. In the second approach, we apply the discontinuous finite element methods to the entire phase space in which the angular flux is represented by a triple product of basis functions in space, energy, and angle. Despite its complexity, this approach offers two advantages: fewer problems in convergence of the source iteration and improved accuracy in angular flux.

We have also demonstrated full coupling between the transport and electromagnetic solvers via a staggered-time-advancing scheme on a problem involving propagation of an electron beam over a diode. However, there are significant discrepancies between our results and EMPHASIS-PIC calculation, which require further investigation.

The finite-element methods and the software components developed in this research project can be productized and incorporated into the existing radiation transport capability at Sandia. In particular,

1) Finite element in angle can improve accuracy and mitigate the notorious ray effects associated with the discrete-ordinates method for problems involving localized source
2) Finite element in energy can be extended to the continuous slowing down (CSD) approximation in electron transport and eliminate the numerical straggling associated with the finite-differencing scheme commonly applied to the Boltzmann-CSD equation

Significance:

This project has produced a computational capability to model electron transport with externally applied and/or self-generated electromagnetic fields. This capability can benefit current Sandia programs involving radiation effects on weapons, satellites, and missile defense systems from both hostile and natural radiation environments. Migration and extension of the numerical solution techniques developed in this work can improved upon the existing radiation transport capability and expand Sandia's national leadership in the area of radiation-transport and radiation effects.

Refereed Communications:

C. Drumm, W. Fan, and S. Pautz, "Phase-Space Finite Elements in a Least-Squares Solution of the Transport Equation," in *Proceedings of the International Conference on Mathematics and Computational Methods Applied to Nuclear Science and Engineering*, May 2013.

S. Pautz, C. Drumm, and W. Fan, "A Discontinuous Phase-Space Finite Element Discretization of the Linear Boltzmann Equation with EM Fields for Charged Particle Transport," in *Proceedings of the 23rd International Conference on Transport Theory*, September 2013.

Mesoscale Modeling of Dynamic Loading of Heterogeneous Materials

151364

Year 3 of 3
Principal Investigator: J. Robbins

Project Purpose:

Material response to dynamic loading is often dominated by microstructure (grain structure, porosity, inclusions, and defects). An example critically important to Sandia's mission is dynamic strength of polycrystalline metals where heterogeneities lead to localization of deformation and loss of shear strength. Microstructural effects are of broad importance to the scientific community and several institutions within DoD and DOE; however, current models rely on inaccurate assumptions about mechanisms at the subcontinuum or mesoscale. Consequently, there is a critical need for accurate and robust methods for modeling heterogeneous material response at lower length scales.

A mesoscale modeling capability would serve two essential roles. The first is to simulate in full detail the response of polycrystalline material to dynamic loading. In this case, the microstructural details appear explicitly in the simulation. This approach is computationally expensive (days on a supercomputer), but provides direct insight into the microstructural origins of material response. The second role, with potentially broader impact, is to inform lightweight (minutes on a desktop computer) continuum models with information from mesoscale simulations. At longer length scales, where direct numerical simulation (DNS) of microstructural effects is not computationally feasible, 'upscaling' techniques are a proven approach. Unfortunately, these methods typically assume static equilibrium, making them inappropriate for our applications. Further, current upscaling methods do not leverage statistical information about material response made available through mesoscale calculations. This project will address these problems using Sandia's unique computational capabilities and codes to perform DNS of a statistically significant number of microstructure realizations. Results will inform development of much needed dynamic upscaling models.

Material strength has a high priority in the dynamic materials program and yet our understanding of the fundamental processes is relatively poor. Significantly, experimentally measured dynamic strength differs substantially from what simple continuum models predict largely due to microstructural effects. We propose to develop advanced models that account for mesoscale effects on dynamic strength.

Summary of Accomplishments:

Direct numerical simulation: we developed and implemented methods in Alegra for conducting DNS of material heterogeneity: 1) implemented a local micro-plasticity model to capture the orientation-dependent single-crystal deformation behavior of individual grains and 2) implemented a microstructure initialization capability that trivializes DNS of polycrystalline materials. This virtually eliminates a substantial barrier to conducting DNS by reducing problem setup from hours or days to minutes. This approach was used to examine the effects of microstructure in metal matrix composites and polycrystalline copper.

Experimental work at the Dynamic Integrated Compression Experiment facility: we conducted plate-impact experiments on well-characterized polycrystalline copper and measured the free surface velocity using photon Doppler velocimetry (PDV). Data from these experiments were shown to be highly repeatable and were used to validate DNS results from Alegra.

Microcontinuum models: we demonstrated the efficacy of microcontinuum models in predicting the macroscale effects of material heterogeneity in dynamic applications. The model uses information from direct numerical simulation of material heterogeneity in the form of microscale material constants. The resulting method requires orders-of-magnitude fewer degrees of freedom and is, therefore, computationally tractable for component scale simulations and uncertainty quantification. The microcontinuum formulation and a general Monte Carlo sampling capability were implemented in Laslo. Follow-on funding has been secured through ASC to pursue further deployment of the method in Sandia codes.

Significance:

Sandia has considerable investment and commitments in several national programs involving prediction of material response under extreme conditions. Examples include dynamic experiments and material model development supporting the NNSA Weapon Science Campaigns and research to support the joint DoD/DOE Munitions Program to develop advanced armor, armor penetrators and energetic munitions. Success in these areas requires inclusion of material heterogeneities at the mesoscale for accurate predictions and results from this project provide a unique capability to explicitly treat natural material variations.

Refereed Communications:

R. Dingreville, J. Robbins, and T. Voth, “Multi-Resolution Modeling of the Dynamic Loading of Metal Matrix Composites,” *Journal of the Minerals*, vol. 65, 2013.

Dynamic Temperature Measurements with Embedded Optical Sensors

151365

Year 3 of 3
Principal Investigator: D. H. Dolan, III

Project Purpose:

Dynamic compression experiments provide unique insight into material behavior under extreme conditions. Full utilization of these experiments in equation-of-state and phase-diagram studies requires temperature measurements in the compressed state. Despite years of effort, dynamic temperature measurements are generally considered unreliable. This skepticism is largely due to problems with optical pyrometry. Time-resolved pyrometry measurements are technologically difficult, particularly at the modest temperatures (<1000 K) characteristic of ramp wave compression. Pyrometry also requires information about sample emissivity, a property that typically varies during dynamic compression.

Existing alternatives to pyrometry work in certain settings but not for general temperature measurements. Stokes/anti-Stokes Raman spectroscopy, for example, is extremely material-specific and is not useful for studying the temperature of metals. Neutron resonance spectroscopy can be used to probe temperature in metals, but special facilities are required to provide sufficient neutron flux. Embedded electrical gauges (thermocouples and thermistors) show some promise, but are difficult to use in conductive samples or pulsed power environments.

The goal of this project is to develop optical gauges for dynamic temperature measurements, particularly during ramp-wave compression. The use of an embedded gauge anchors the measurement to the properties of a standard material, rather than the sample of interest. At the same time, optical coupling avoids the electrical difficulties of embedded thermocouples/thermistors. To be useful in dynamic compression research, the gauges must show measurable changes in the visible spectrum (400-700 nm) on nanosecond time scales. The gauges must be very thin (<0.001 mm) for rapid thermal equilibration with the sample, yet not so thin as to be transparent to the diagnostic. Gold reflectivity has been identified as the most promising temperature gauge for this project, though other metals (notably copper and silver) may also be pursued.

Summary of Accomplishments:

We subjected gold sensors to a variety of high-pressure and high-temperature states, both statically and dynamically. In all cases, the sensors' reflectance-ratio spectra followed the same general trend: increasing at blue wavelengths and decreasing at red wavelengths. The transition between these behaviors is 500 nm at ambient pressure and moves to longer wavelength with pressure.

After many attempts at converting and analyzing reflectance-ratio measurements directly, a minimal gold model was developed for calculating more fundamental properties (dielectric function, refractive index, etc.) from which reflectance ratio can be calculated. This model allows the host refractive index to be explicitly handled so that different sensor configurations (gold in air, gold behind diamond, and gold behind sapphire) could be analyzed in a common framework. Model analysis also reduces the measured spectra, which spans hundreds of overlapping wavelength bands, to a set of six parameters. Most of these parameters have a direct physical interpretation, allowing temperature and pressure effects in gold to be understood in a meaningful way.

Heated ellipsometry measurements were analyzed with the minimal optical model, revealing how model parameters vary with temperature. Diamond-anvil-cell measurements analyzed with the same model provided estimates of the parameter pressure derivatives. Combining this information, predictions for sensor behavior during dynamic compression were made and compared with impact results obtained in this project, and plausible agreement was found. With model refinements and some diagnostic upgrades, gold sensors will be ready for deployment at Z in CY 2014.

Specific technical achievements in this project include:

- Upgrading Sandia's heated ellipsometry capability
- Initiating heated diamond-anvil-cell research at Sandia
- Developing a new capability for launching heated flyers at known temperature

Significance:

This project demonstrated that gold sensors might provide a viable temperature standard for dynamic compression research. This is similar to the use of thermocouples or thermistors in standard applications but at much faster time scales and far greater pressures. Unlike electrical sensors, gold reflectance is immune to electromagnetic noise and can be fielded in a pulsed power environment. This capability may revolutionize equation-of-state and phase-transition studies at Sandia, allowing modest temperature changes to be detected for the very first time.

Refereed Communications:

C.T. Seagle and D.H. Dolan, "Visible Reflectivity System for High-Pressure Studies," *Review of Scientific Instruments*, vol. 84, p. 066104, June 2013.

D.H. Dolan, T. Ao, and C.T. Seagle, "Reflectance Thermometry in Dynamic Compression Experiments," in *Proceedings of the International Temperature Symposium*, 2013.

Spectral Line Broadening in White Dwarf Photospheres

151366

Year 3 of 3
Principal Investigator: G. A. Rochau

Project Purpose:

White dwarf (WD) stars are potentially the most accurate independent chronometers for constraining the ages of the Galactic disk, halo, and star clusters and they provide a lower limit to the age of the universe. This accuracy depends on stellar evolution models benchmarked against observational data on WD properties: mass and surface temperature. The primary method to determine these properties is through comparison of observed optical line profiles to synthetic spectra from theoretical atmosphere models, adjusting the assumed mass and temperature to obtain the best fit. Understanding the line profiles and how they relate to the plasma conditions is critical to the precise and accurate determination of the WD properties and their inferred ages. The stellar masses inferred from this spectroscopic method, however, disagree with recent gravitational redshift measurements. In addition, the spectral analysis breaks down completely at low surface temperatures. Inaccuracy in the line-shape theory is the leading hypothesis for this breakdown at plasma conditions that span T_e = 0.3-5 eV and $n_e = 10^{(16-18)}$ cm^{-3}. We have tested the line-shape theory by accurately measuring the emergent line profiles from well-characterized hydrogen plasmas heated to WD conditions by the ~1 MJ of x-rays produced on the Z machine. Testing the line-shape theory at these densities requires the creation of a large volume of plasma with very uniform conditions in order to achieve the optical depths required to measure the full line profile. We have demonstrated the capability to create and measure H Balmer-line emission and absorption at the conditions of interest. Accurate absorption measurements have been obtained from transitions with upper levels of n>4, where the theoretical models are most uncertain.

Summary of Accomplishments:

This project achieved the following: 1) developed a radiation-hydrodynamics model for designing gas-cells on the Z facility, 2) tested the gas-cell designs on Z using time-resolved optical spectroscopy to infer the approximate plasma conditions and observe the resulting line profiles, 3) developed an understanding of the atomic kinetics in the gas cell, 4) developed the ability to measure the Balmer lines in absorption as well as emission, 5) made initial comparisons between the measured line-shapes and the leading theories, and 6) leveraged the success of this project into a DOE grant for our UT-Austin collaborators to continue these investigations on Z for the next three years. Through these activities, we have now demonstrated the ability to produce WD-relevant H plasmas across a broad range of temperature and electron density and simultaneously measure line profiles in absorption (up to H-epsilon) and emission (up to H-delta). We have also measured the gradient in electron density in the direction lateral to the measurement line of sight, and measured how the line absorption varies with path length through the plasma. These are critical parameters to demonstrate understanding of the plasma properties when comparing the measured line shapes with model calculations.

Significance:

This work advanced the DOE strategic theme of scientific discovery and innovation by expanding the capability to use the Z facility for fundamental radiation science, a growth area for all high energy density (HED) facilities across the NNSA complex. These line-shape measurements may stimulate new innovations in theoretical physics and the project has expanded the community of scientists exposed to high quality Sandia research.

Refereed Communications:

R.E. Falcon, G.A. Rochau, J.E. Bailey, J.L. Ellis, A.L. Carlson, T.A. Gomez, M.H. Montgomery, D.E. Winget, E.Y. Chen, M.R. Gomez, and T.J. Nash, "An Experimental Platform for Creating White Dwarf Photospheres in the Laboratory," *High Energy Density Physics*, vol. 9, pp. 82-90, March 2013.

Z-Petawatt-Driven Ion Beam Radiography Development

151367

Year 3 of 3
Principal Investigator: M. Schollmeier

Project Purpose:

We propose to perform laser-driven ion-beam radiography of an object during a megaJoule-driven discharge of the Z machine in order to measure the object's electromagnetic field distribution. This will allow unmatched insights into both the target performance (e.g., spherical capsule implosions, magnetic flux compression, or astrophysical jet simulations) as well as the machine performance by mapping the magnetic field distribution with micron spatial resolution. Because of the high magnetic fields and the tremendous amount of x-ray energy created during a discharge, this approach is scientifically and technically very challenging. Required is the capability of creating high ion-beam energies (10-100 MeV range) with a short pulse, high-energy laser system providing intensities well above 1020 W/cm^2. The Z-petawatt laser (ZPW) demonstrated its readiness for x-ray backlighting and it can be modified to utilize ion acceleration at the Z machine by using novel, plasma mirror focusing devices.

Summary of Accomplishments:

The final year of this project was used to finalize the HYDRA and LSP simulations and to finish data analysis of those simulations. Furthermore, we developed a relativistic, 3D particle-tracking code for charged-particle propagation in electromagnetic fields. This code was used to track protons, heavy ions, and electrons with energies between 50 MeV and 1 GeV (for electrons) in an idealized liner compression scenario at the Z accelerator. We found that, due to the mega ampere (MA) currents, the magnetic field near the liner is too strong to allow the charged particles to penetrate the liner and to generate a radiography image — 4.5 GeV energy protons are required to penetrate the magnetic field near the liner, which is well beyond the capabilities of present and near-future laser accelerators. However, 30 MeV protons can be used to measure the fringe-field region of a magnetized liner compression experiment. This proton energy can be created with the existing Z-petawatt laser. A conceptual experiment was designed and simulated with the code. Our collaboration with the Institute for Fusion Studies at UT Austin produced an article that elaborates on details of the parametric instability of laser-driven electron acceleration in an ion channel.

Significance:

Most relevant is the development of a simulation methodology of intense laser-matter interaction at full scale, without free numerical parameters. We use a 3D radiation-hydrodynamics code to simulate a nanosecond laser pre-pulse matter interaction. Results are imported into an explicit 2D particle-in-cell code to simulate the main pulse interaction for over 20 ps. Never before have such detailed and large-scale simulations been performed for short pulse laser-matter interaction and ion acceleration. The model was applied to three laser systems (ZPW at Sandia, Trident at Los Alamos National Laboratory, Multi-Terawatt at Rochester University) and reproduced all measured proton and K-alpha x-ray emission data within error bars.

New Strategies for Pulsed Power Transmission Lines: from Repetitive to Replaceable to Recyclable

154060

Year 3 of 3
Principal Investigator: M. E. Cuneo

Project Purpose:

The highest risk/return application for rep-rated pulsed power is inertial fusion energy (IFE). A barrier to the use of pulsed power for IFE is the repetitive creation of a conducting path for current flow from the driver to the target. Previous research selected the recyclable transmission line (RTL) as the most promising approach for repetitive driver-to-load coupling at high fusion yields. While conceptual RTL designs exist, fully engineered solutions to a number of challenging requirements had not been explored adequately. The result of this project is a fully engineered prototype RTL facility concept that is capable of the repetitive (0.1 Hz) coupling of a conical magnetically insulated transmission lines (MITL) to a pulsed power diode. Engineered solutions to the highly coupled and challenging problems associated with pre-pumped MITL packaging, engagement and translation, and insertion into a diode have been found. The MITL is properly electrically coupled to the diode, electrically pulsed (initially a "mock" event, and eventually by a non-destructive driver), disengaged, extracted, docked, and released — all without vacuum loss in the MITL gap or in the pulsed power system. The facility is designed primarily as a mechanical test bed with an emphasis on cycle speed and component lifetime (e.g., 0.1 Hz and 10,000 cycles). The device has been designed so that future minor modifications will enable coupling to a linear transformer driver for rep-rated pulsed power testing.

Summary of Accomplishments:

The principle goal of this project was to carefully engineer a mechanical system that will allow the repetitive coupling and decoupling of a pre-pumped MITL to a pre-pumped (surrogate) pulsed power diode. Priority has been placed on cycle speed (goal of 0.1 Hz) and component lifetime (goal of 10,000 cycles, without failure). A variety of technical accomplishments have been achieved:

- Developed a MITL cassette that can be pre-pumped (to 10^{-5}-10^{-6} Torr) and sealed, awaiting insertion into a pulsed power diode
- Developed a means to deliver a pre-pumped and sealed MITL to a pre-pumped and independently sealed pulsed power diode without loss of vacuum during translation
- Designed a hydraulic "plunger" device to engage the pre-pumped MITL at a location outside the pulsed power diode, and rapidly/precisely deliver the MITL to the diode
- Developed a passive (spring-loaded) vacuum linkage system that allows the pre-pumped MITL cassette to be inserted into the pre-pumped pulsed power diode without loss of vacuum in either system
- Designed a locking system that allows the cathode to be locked into the pulsed power diode. The locking system contains separable coupling pins and cam locks so that after the cathode is locked in place, the coupling pins can be retracted, and the MITL anode cathode gap cleared for current delivery.
- Successfully extracted the MITL cassette from the diode without venting the machine, after current is delivered to the MITL. The MITL must be extracted, docked, and fully released by the "plunger." The plunger is now free to engage the next pre-pumped MITL assembly.

The primary deliverable of the completed project is a fully engineered prototype facility that simultaneously satisfies all of the above-defined objectives.

Significance:

This project has relevance to scientific discovery and innovation in pulsed power science and technology and in pulsed power fusion. The project outcomes are also relevant to energy security, environmental responsibility, and national security in laying a foundation for inertial fusion energy applications of pulsed power. Finally, the project has application to nuclear security as it provides potential solutions to environmental health and safety concerns (associated with post-shot refurbishment work) for present and future single-shot experimental facilities.

Integration of MHD Load Models with Detailed Circuit Representations of Pulsed Power Drivers

155458

Year 3 of 3
Principal Investigator: C. Jennings

Project Purpose:

State-of-the-art magnetohydrodynamic (MHD) models of loads fielded on the Z accelerator are typically driven by reduced or simplified circuit representations of the generator, while generator models typically couple to simplified representations of the load. The performance of many of the imploding loads is critically dependent on the current and power delivered to them, so may be strongly influenced by the generator's response to the rising inductance of these loads. Current losses diagnosed in the transmission lines approaching the load are further known to limit the energy delivery while exhibiting some load dependence. Studying the efficiency with which power may be coupled between the generator and the load in this implicitly linked, rapidly evolving system, therefore, necessitates the integration of detailed generator and load models. This project would develop an integrated load-generator model to establish a predictive capability that may be used to both explore how existing and next-generation pulsed power drivers may be optimized to support specific loads and how loads may be better optimized to the specific response of the generator.

Summary of Accomplishments:

Current losses were parameterized from circuit analysis of a large number of different loads, including large-diameter wire-array K-shell sources, dynamic hohlraums, compact wire arrays, gas puffs, and MagLIF-style small-diameter liners. These losses have been incorporated into a coupled circuit-and-MHD model and applied to modeling these loads. Analysis has confirmed the likelihood of a power-feed-shape-dependent additional current loss downstream of the convolute current monitors. This loss has been parameterized as a function of the convolute current-loss resistance for application to load models. Simulations of liner implosions coupled to this comprehensive circuit model have identified inconsistencies between machine electrical diagnostics and load current monitors, indicating the possibility that B-dots are underestimating the late-time current delivery in these lower-voltage implosions. The tools and analysis developed as part of this project are now being routinely used to model gas puff, liner, and wire-array loads fielded on Z.

Significance:

The work improves the capacity of existing facilities for world-class scientific research by improving the predictive modeling capability used to design new experiments.

This work will have impact in the following areas:

- Understanding convolute current loss is the first step toward mitigation and control, and modeling is critical since the losses can be difficult to measure directly
- Lower current loss (convolutes and feeds) will have an impact on multiple missions:
  x-ray sources for radiation affects nuclear weapons (NW), science, technology and engineering, (STE)
- Fusion experiments (NW, STE)
- Physics basis for scaling to new higher-power accelerators

Richtymer-Meshkov Instabilities in Cylindrical and Planar Geometries on Z

156252

Year 3 of 3
Principal Investigator: E. Harding

Project Purpose:

The goal of this project is to design an experiment that will produce the Richtmyer-Meshkov (RM) instability in dense plasma by using the large current output of the Z machine. This instability initiates the mixing of plasmas in a wide range of problems that involve large-scale systems such as astrophysical supernovae and smaller-scale systems such as imploding fuel capsules and liners in laboratory fusion experiments. Here, we aim to create a RM unstable experiment where the perturbation growth rate and the degree of mixing caused by the RM instability are diagnosable. One of the important questions is whether modern computer codes and analytical theory can accurately capture the detailed growth and mixing induced by the RM instability. In addition, from a basic science perspective, we examine whether a dense plasma transitions to turbulence in the same way as a cold, non-ionized fluid. Almost all previous RM experiments in plasma used lasers to generate the required shockwave that initiates the instability. Due to the small laser spot size and the relatively small amount of energy delivered to the target, the previous laser experiments did not capture the detailed perturbation growth nor did they achieve a fully turbulent state. We propose to generate the RM instability in one of two ways on the Z machine. RM could be generated in a planar system that involves the impact of a high-velocity flyer-plate onto a layered target with an embedded perturbation. Alternatively, by imploding a cylindrical Beryllium shell with interior perturbations and filled low-density foam, RM could be generated in a cylindrical geometry. Both the planar and cylindrical experiments would involve novel target designs and diagnostic techniques that have not been tested previously.

Summary of Accomplishments:

This project resulted in the design and simulation of an experiment that will generate RM instability from a planar interface. An experiment of this type could have a large impact in the high-energy-density plasma community. A further refinement of this experiment could lead to the discovery of a new type of interfacial instability that may be easily accessible using the existing capabilities of the Z machine.

Significance:

The instabilities investigated in this project are relevant to the nation's inertial confinement fusion program. These experiments will allow us to advance the predictive capabilities of modern computer simulations. Furthermore, these experiments are state of the art and will advance the frontiers of interfacial hydrodynamic instabilities by providing experimental data in the form of high-resolution images. There is also the potential to discover new instability modes.

Kinetics of Radiation-Driven Phase Transformations in PZT Ceramics

157693

Year 3 of 3
Principal Investigator: N. W. Moore

Project Purpose:

The purpose of the project is to understand the kinetics of phase transformation of lead zirconate titanate (PZT) ceramics following rapid heating. The only phase kinetics yet measured for PZT are those driven mechanically or electrically along the pressure axis of the phase diagram. On heating from room temperature, PZT transforms from a ferroelectric phase (FR1) to a less polarizable one (FR2), and finally to a paraelectric phase (P). A key exploratory aspect is that optical properties that could be used to discern this trajectory are not known for PZT. In particular, structural similarities issue considerable risk in differentiating the rhombohedral FR1 and FR2 phases. This work presents unique opportunities to clarify these differences. The interrogation of these optical properties is, therefore, the thrust of the project. If successful, the kinetic mechanisms could then be explored. Phase dynamics are of broad scientific and engineering importance, yet are poorly understood for many materials, including PZT.

Summary of Accomplishments:

We examined the optical properties of transparent bulk and thin films of PZT ceramics of various compositions and at various temperatures using Stokes' polarimetry and ellipsometry at atmospheric pressure. We examined structural and ferroelectric transitions using differential scanning calorimetry, x-ray diffraction, and dielectric measurements at various temperatures. We discovered that for bulk specimens, dispersed strains from local ferroelectric structure issue a larger effect on the optical properties related to crystal symmetry (e.g., optical rotation and birefringence) than the macroscopic (i.e., volume-averaged) crystal structure — a significant result for understanding the optical properties of polycrystalline materials. Based on these results, we evaluated opportunities for using optical diagnostics and various pulsed power heating sources for exploring phase dynamics.

Significance:

PZT ferroelectrics are integrated with microelectronics and microelectromechanical systems (MEMS) for use as actuators, sensors, power supplies, and optical components (e.g., for lab-on-a-chip applications). The optical properties of polycrystalline material — especially optical rotation — are yet to be universally understood. The results provide a broader understanding of the role of microstructure and polarity on the optical responses of PZT and ferroelectrics in general.

Refereed Communications:

N.W. Moore, H.J. Brown-Shaklee, M.A. Rodriguez, and G.L. Brennecka, "Optical Anisotropy near the Relaxor-Ferroelectric Phase Transition in Lanthanum Lead Zirconate Titanate," *Journal of Applied Physics*, vol. 114, p. 053515, August 2013.

Atomistic Modeling of Memristive Switching Mechanisms in Transition Metal Oxides

158699

Year 2 of 2
Principal Investigator: R. J. Bondi

Project Purpose:

In 2008, Hewlett Packard (HP) Labs described a physical implementation of the theoretically proposed, fourth passive circuit element, the memristor. This device exhibits a resistance modulated by the integral of charge transported through it with a hysteretic behavior that permits reversibility. Memristive behavior has been generalized across numerous metal oxide systems, but the TiO_2 and Ta_2O_5 systems have generated the most interest. Recent studies on the HP TiO_2 implementation identified electrochemical reduction of TiO_2 through an applied voltage bias and subsequent migration of charged oxygen vacancies (V_O^{2+}) as the likely mechanism driving transformation to less resistive TiO_x phases. TaO_x has exhibited perhaps the greatest device potential, but the inherent switching mechanisms are even less understood and appear substantially different than those proposed for TiO_x. For the memristor to evolve into a fundamental integrated circuit (IC) component, an improved understanding of the switching mechanism is beneficial to control both reliability and memory retention, achieve manufacturable device yields and uniformity, increase switching speeds, and understand radiation tolerance margins for Sandia weapons' applications.

Recent progress in phase identification suggests that V_O^{2+} migration translates the TiO_2/TiO_x ($x < 2$) phase boundary in order to change device series resistance ($R(TiO_2)/R(TiO_x) \sim 10^2$ to 10^3), but multiple oxygen-deficient Magneli phases in the phase diagram have obscured an atomistic understanding. The two phase simplicity of the Ta-O phase diagram has been credited for remarkable TaO_x device endurance and repeatability, but so little is known about this system that even the Ta_2O_5 crystal structure remains a subject of debate. Since nanometer scale in situ switching observation is impractical via experiment, this work proposes an atomistic modeling approach propagating intrinsic defect information from density functional theory (DFT) calculations in oxygen-deficient TiO_2 and Ta_2O_5 to enable first principles prediction of electrical conductivity and ultimately construct atomistic structural models of memristors for molecular dynamics (MD) simulations.

Summary of Accomplishments:

We applied first principles DFT calculations, ab-initio MD, and the Kubo-Greenwood formula to predict electrical conductivity in Ta_2O_x ($0 \leq x \leq 5$) as a function of composition, phase, and temperature, where additional focus was given to various oxidation states of the O monovacancy (V_O^n; n=0,1+,2+). In the crystalline phase, our DFT calculations suggested that V_O^0 prefers equatorial O sites, while $V_O^{1}+$ and $V_O^{2}+$ are energetically preferred in the O cap sites of TaO_7 polyhedra. Our calculations of direct current (DC) conductivity at 300K agreed well with experimental measurements taken on Ta_2O_x thin films ($0.18 \leq x \leq 4.72$) and bulk Ta_2O_5 powder-sintered pellets, although simulation accuracy can be improved for the most insulating, stoichiometric compositions. For the neutral V_O case in Ta_2O_x, the onset of finite DC conductivity was observed between 300 and 400K. Our conductivity calculations and further interrogation of the O-deficient Ta_2O_5 electronic structure provide further theoretical basis to substantiate V_O^0 as a donor dopant in Ta_2O_5. Furthermore, this dopant-like behavior is specific to the neutral V_O case and was not observed in either the 1+ or 2+ oxidation states, which suggests that reduction and oxidation reactions may effectively act as donor activation and deactivation mechanisms, respectively, for V_O^0 in Ta_2O_5.

Late in the project, we applied the same methods to generalized key aspects of dopant-like behavior in TiO_x. Our DFT results in TiO_x also suggest that dopant-like behavior is specific to the neutral V_O case. For the neutral V_O case in TiO_x, the onset of DC conductivity occurred at cryogenic temperatures between 30 and 50K.

Significance:

Memristor technologies are potential paradigm changers beyond Moore's Law in high-density memories for massively parallel, next-generation CPUs and show potential as radiation-hard, non-volatile memories; as a result, interest at Sandia spans nuclear weapons, space, national security, and high performance computing applications. Nevertheless, a basic understanding of the structural, chemical, and physical processes occurring during memristor switching is paramount to transform the memristor from laboratory novelty into fundamental IC component. This work furthers our scientific understanding of conductivity modulation in O-deficient transition metal oxides by substantiating the role of the O vacancy as a donor dopant.

Refereed Communications:

R.J. Bondi, M.P. Desjarlais, A.P. Thompson, G.L. Brennecka, and M.J. Marinella, "Electrical Conductivity in Oxygen-Deficient Phases of Tantalum Pentoxide from First-Principles Calculations," *Journal of Applied Physics*, vol. 114, p. 203701, 2013.

Laser-Ablated Active Doping Technique for Visible Spectroscopy Measurements on Z

158701

Year 3 of 3
Principal Investigator: M. R. Gomez

Project Purpose:

Spectroscopic measurements can reveal information about plasma parameters that would be otherwise extremely difficult to determine. In many cases, the spectroscopic systems observe a region of the plasma that contains sharp gradients in the plasma parameters, which obscures the intended measurement. The effect of these gradients can be minimized by incorporating a localized dopant within a relatively constant region of the plasma and observing emission from the dopant.

One goal of this project is to create an active doping system for use with the streaked visible spectroscopy (SVS) system on Z. This new capability will be particularly useful in diagnosing the plasma formation and evolution in the post-hole convolute on Z. The intense electric and magnetic fields in the convolute create an interesting plasma environment. Spectroscopic measurements of the plasma in this region may show significant Stark shifting and Zeeman splitting, as well as Stark broadening and possible Doppler shifting. Few spectroscopic measurements of plasma have been made under such extreme conditions due to the complicated nature of the measurements. With the active doping system, such measurements will become more feasible.

We propose development of a new "active doping" capability for use with the SVS system on the Z machine. In this technique, a low-density contaminant with favorable spectroscopic characteristics is intentionally inserted into the system to monitor plasma conditions. This capability will require development of a fiber-coupled laser system, design of new electrode hardware, and establishing a new triggering setup for Z.

The new system will advance a number of projects that utilize the visible spectroscopy diagnostic on Z. Primarily, we are interested in utilizing active doping to make highly spatially resolved measurements of the plasma within the post-hole convolute. The active doping capability could also be used to make independent temperature and density measurements of the plasma in the white dwarf photosphere experiment.

Summary of Accomplishments:

We discovered that laser ablation of target materials produces plasma plumes in the desired density and temperature ranges. This indicates that this technique can be used for active spectroscopic doping. The temperature and density of the plasma were established through time-integrated spectroscopy, time-integrated pinhole imaging, and time-resolved laser imaging. We also discovered that the necessary laser energy could not be coupled through the fiber as the laser was configured, but that it is possible to modify the laser to couple sufficient energy through the fiber. This is important because it allows us to use a fiber to deliver the energy to the load, which will reduce alignment times and improve safety over an open-beam setup.

Significance:

This research will allow us to use active doping on the Z machine. The most obvious project that this will positively impact is magnetic flux-compression measurements through optical Zeeman splitting. This method will allow delivery of a sodium plume to a required controlled location.

Fundamental Studies on Initiation and Evolution of Multi-Channel Discharges and their Application to Next-Generation Pulsed Power Machines

158858

Year 2 of 3
Principal Investigator: J. Schwarz

Project Purpose:

Future pulsed power systems may rely on linear-transformer-driver (LTD) technology. The LTDs will be the building blocks for a driver that can deliver higher current than the Z machine. The LTDs would require tens of thousands of low inductance (<85nH), high voltage (200kV DC) switches with high reliability and long lifetime (>>10^4shots). Sandia's Z machine employs 36 megavolt-class switches that are laser-triggered by a single channel discharge. This is feasible for tens of switches but the high inductance and short switch lifetime associated with the single channel discharge is undesirable for future machines.

Thus, the fundamental problem is how to lower inductance and losses while increasing switch lifetime and reliability. These goals can be achieved by increasing the number of current-carrying channels. The rail-gap switch is ideal for this purpose.

Although such switches have been extensively studied, each effort has only characterized a particular switch. There is no comprehensive understanding of the underlying physics that would allow predictive capability for arbitrary switch geometry. We propose to study rail-gap switches via an extensive suite of advanced diagnostics in synergy with theoretical physics and advanced modeling. Design and topology of multichannel switches as well as discharge dynamics will be investigated. This involves electrically and optically triggered rail gaps and multi-site switch concepts.

This research is aimed at gaining a full understanding of the underlying physics that drives the behavior of either optical or electrical triggered rail-gap switches. The biggest risk factors are the complexity of the modeling and the fact that some triggering techniques may turn out to be cost prohibitive on a large-scale machine. The research has tremendous payoff since it will provide a comprehensive understanding and predictive capability of high-repetition rate, high reliability, and long lifetime switches, which is an enabling technology for a realistic pursuit of next generation pulsed power fusion machines.

A New Capability to Model Defects in InGaAs and InGaP Alloys

158860

Year 2 of 3
Principal Investigator: A. F. Wright

Project Purpose:

While experimental studies during the past 50 years have yielded a nearly complete understanding of point defects in silicon, significant knowledge gaps remain for defects in III-V semiconductors (e.g., GaAs) to the extent that most of the defect properties needed to develop an atomistic model of gain degradation and recovery in radiation-hard III-V based heterojunction bipolar transistors (HBTs) will need to be calculated using density functional theory (DFT). DFT capabilities exist to calculate defect properties in III-V semiconductors such as GaAs. However, these capabilities cannot be used to calculate defect properties in ternary III-V alloys such as InGaAs because they depend on the nearby arrangement of atoms and, thus, vary from point-to-point in the alloy. The objective of this project is to develop a new capability to calculate defect properties in ternary alloys (key materials in HBTs) with DFT accuracy. The key to this new capability is a cluster expansion, which gives the energy of a defect as a function of the atoms surrounding it. Each cluster expansion (one for each defect type) is generated from a training set of DFT results for different arrangements of atoms surrounding the defect. Also, cluster expansions can be generated for both stable states and saddle points, thereby enabling kinetic Monte-Carlo (KMC) simulations of defect diffusion in alloys with DFT accuracy.

Our FY 2013 focus was on a thermal diffusion process of an As interstitial in InGaAs. A cluster expansion was developed for the stable state, demonstrating DFT accuracy and revealing that the range of defect energies in InGaAs can exceed 1 eV. While we calculated the corresponding training set for the saddle point, we used our stable-state cluster expansion to perform KMC simulations (using model activation energies), thus testing our KMC capabilities and also verifying that low-energy stable states are favored in the As interstitial diffusion process in InGaAs.

Investigate Emerging Material Technologies for the Development of Next-Generation Magnetic Core Inductors for LTD Pulsed Power Drivers

158861

Year 2 of 3
Principal Investigator: D. L. Huber

Project Purpose:

The use of magnetic cores in linear transformer drivers (LTDs) creates a significant risk to the success of realizing next-generation pulsed power drivers. Costs are extremely high and fabrication schedules are not aligned to forecasted requirements due to materials utilized and complex manufacturing methods. A breakthrough research and development effort focused on the utilization of emerging advanced high-performance materials for this critical pulsed power component is required to assure that product performance, cost, and availability meet the requirements of this critical pulsed power driver component.

This project aims to design and synthesize a novel material for a pressing need in pulsed power technology. While the work is geared to a specific application, it is of a fundamental nature and will have wide impact in the scientific community. The use of iron nanoparticle composites as magnetic core inductors (e.g., for transformer cores) has been discussed in the literature recently, but has never been realized. There are a number of scientific hurdles to the creation of this material that must be overcome. First, we must devise new synthetic methods to produce iron nanoparticles of the appropriate size (estimated to be 10-20 nm) to optimize performance. Second, we must disperse these particles into an appropriate non-magnetic matrix material, such as a polymer, to create the desired nanocomposite. Finally, we must better understand the structure/property relationships in these magnetic nanocomposites at a basic physics level, as the structural details will determine the performance of this class of materials.

Using a Nonlinear Crystal to Optically Measure Pulsed Electric Fields in Radiation Environments

159299

Year 2 of 2
Principal Investigator: T. M. Flanagan

Project Purpose:

The purpose of this project is to create a completely optical electric-field sensor to be used in a pulsed radiation environment. The advantage of an optical sensor is that it only minimally perturbs the electric field that is to be measured. There are no electronics associated with the measurement. Thus, it is less vulnerable to electrical noise associated with pulsed x-ray facilities.

We performed optical electric-field measurements on nanosecond time scales using the electro-optic crystal beta barium borate (BBO). Tests were based on a preliminary bench-top design intended to be a proof of principle stepping stone towards a modular-design optical E-field diagnostic that has no metal in the interrogated environment. We successfully demonstrated that an optical E-field diagnostic is possible on pulsed nanosecond time scales. The long-term goal is to field a modular version of the diagnostic in experiments on large-scale x-ray source facilities or similarly harsh environments.

Summary of Accomplishments:

We have demonstrated that an electric field estimate can be done optically on nanosecond time scales using a crystal of BBO. Further study could result in a reliable electric field sensor that is free of environment-perturbing metal and can track a field with an arbitrary time dependence on nanosecond time scales. Further development of a sensor that is more practical to use would require coupling to fiber optics, reducing detector noise, and packaging the crystal and polarizing optics in a module that could quickly be installed and operated in a harsh environment, such as a pulsed power facility.

Significance:

Many experiments seek to provide data that is useful for code validation, which is a critical endeavor in today's absence of underground testing. Two fundamental quantities the codes predict in pulsed radiation environments are the time-varying electric and magnetic fields. Reliable magnetic field measurements are readily available with B-dot probes. However, traditional electric field diagnostics using exposed conductors can often perturb the environment. Consequently, the majority of validation data is from magnetic field measurements alone. The successful development of an optical electric-field sensor would make possible a whole new family of data to be used for code validation.

Analysis of Defect Clustering in Semiconductors Using Kinetic Monte Carlo Methods

159305

Year 2 of 2
Principal Investigator: B. D. Hehr

Project Purpose:

The transient degradation of semiconductor device performance under irradiation has long been an issue of concern. Neutron irradiation can instigate the formation of quasi-stable defect structures, thereby introducing new energy levels into the bandgap that alter carrier lifetimes and give rise to such phenomena as gain degradation in transistors. Typically, the initial defect formation phase is followed by a recovery phase in which defect-defect or defect-dopant interactions modify the characteristics of the damaged structure. These interactions are facilitated both by thermal diffusion and by capture or emission of charge carriers — a mechanism specific to semiconductors.

The purpose of this work was to develop a kinetic Monte Carlo (KMC) code capable of modeling both thermal and carrier-injection annealing of group IV or group III-V initial defect structures. A noteworthy advantage of the KMC approach is that the spatial particularities of the initial defect distribution are faithfully propagated in 3D to the final annealed state without the need for simplifying mathematical formulae to represent the defect concentrations.

The outcome of this project is envisioned to be particularly useful in evaluating circuit performance under extreme irradiation environments. In essence, this project is designed to enhance device response calculations through a more accurate assessment of defect-specific carrier recombination rates. The technique developed herein can also be employed in studies of cluster-to-cluster interaction at high fluences, and it may be useful as well in simulations of single-event effects (at very short times).

Furthermore, the capability to perform high-fidelity annealing calculations is valuable as a means to guide experimentalists, since predictions of the important defect reactions and parameters in specific scenarios can facilitate the design of targeted experiments.

Summary of Accomplishments:

A kinetic Monte Carlo code has been developed with specific features to enable exploration of semiconductor device degradation under irradiation. The performance of the code was corroborated through a series of verification exercises. Its utility was demonstrated through comparisons against observed annealing factors in bulk p-type silicon subject to electron irradiation and also against the measured base current of a 2N2222 npn transistor irradiated at Los Alamos Neutron Science Center (LANSCE), while operating in forward active mode at emitter currents of 0.22 mA and 9 mA.

The observed agreement with experiment is partly a testament to the vast amount of work that has been devoted over the past decades to evaluating the properties of important defects in silicon. This project has built upon that existing database of knowledge by demonstrating a means to refine defect parameters that are subject to a large uncertainty (in particular, carrier capture cross sections) through analysis of experiments targeting specific defect reactions. As an example, it was shown that the annealing factors from electron irradiation experiments performed by Srour in the 1970’s effectively establish a constraint on the relative magnitudes of certain carrier-related parameters of the silicon vacancy and vacancy-oxygen defects. Consequently, it was found that parameter adjustments proposed in other studies to match bipolar junction transistor (BJT) gain degradation measurements necessitate a concomitant set of adjustments to the vacancy-oxygen cross sections.

The overall project was successful in developing a tool to explore displacement damage effects through a fundamental, atomistic-scale approach that captures the full 3D geometry of defect clusters.

Significance:

In recent semiconductor annealing studies performed at Sandia, the initial defects from a collision cascade were transformed into a simplified, spherically symmetric distribution, which was then evolved using the drift-diffusion model. This project expanded upon that work through development of a fundamental, physics-based approach, which enables a higher degree of spatial fidelity and, therefore, greater accuracy in conducting time-dependent performance assessments of systems containing an irradiated device. The tools created in this endeavor could aid in the development of system qualification evidence for the W88 Alt and W78 life extension programs.

Time-Dependent Resistivity of Millimeter-Gap Magnetically Insulated Transmission Lines Operated at Megampere/Centimeter Current Densities

164759

Year 2 of 3
Principal Investigator: B. T. Hutsel

Project Purpose:

Magnetically insulated transmission lines (MITLs) are commonly used in the final stages of pulsed power systems to transfer power at high voltage and current to the physics-package load. Future pulsed power systems, which will deliver greater power to the load, will require MITLs to transfer power at greater voltage and current. Minimizing current loss within the MITL will be a critical design issue for these larger pulsed power systems.

The proposed research will investigate current loss in a MITL at megampere/centimeter lineal current densities due to gap closure. Gap closure occurs when plasma forms within the MITL anode-cathode gap providing a conductive path for current to be shunted away from the load, resulting in reduced power transferred to the load.

Current loss within a MITL will be characterized as a function of gap distance, peak current, peak voltage, and pressure in the MITL gap. Surface chemistry will be considered and gap closure will be investigated relative to vacuum surface conditions and MITL-electrode cleaning procedures. In addition to experimental results, a theoretical model of gap closure will be developed with the aid of particle-in-cell (PIC) simulations.

The proposed research will extend existing knowledge of MITL behavior at high lineal current densities. The main technical challenges include quantitatively characterizing the vacuum surface conditions to determine their effect on MITL current loss. Development of a theoretical model of gap closure though combination of experimental results and PIC simulations will aid in the design of MITLs used in future pulsed power machines.

A systematic study focused on gap closure, combined with new simulation capabilities, has yet to be performed. The experiment will yield a more thorough understanding of gap closure within a MITL. Results from characterizing MITL performance at high current densities will aid in designs of future pulsed power accelerators necessary to extend high energy density physics (HEDP) research.

Non-Equilibrium Electron-Ion Dynamics under Extreme Conditions via Time-Dependent Density Functional Theory

165731

Year 1 of 2
Principal Investigator: R. J. Magyar

Project Purpose:

Successful approaches for materials properties at extreme conditions, led by density functional theory-based molecular dynamics (DFT-MD), lack both time-dependent electronic processes and energy transfer between electrons and ions, making them unsuitable for several applications in high energy density science. Among these is x-ray Thomson scattering (XRTS) for which interpretation of the signals limits a powerful diagnostic approach and electron-ion equilibration, which depends crucially on the transfer of energy between electrons and ions.

We propose to understand both of these phenomena by extending the machinery of time-dependent density functional theory (TDDFT) to extended systems. TDDFT is capable of accurately modeling the energy transfer between electrons and ions. We propose to demonstrate that calculated dynamic structure factors might be directly compared with XRTS experiments. This will facilitate temperature measurements off the Hugoniot on next generation pulsed power machines. We will also study systems with different initial electron and ion temperatures to determine the rate at which energy flows between these degrees of freedom. These rates are vital for accurate simulations of non-equilibrium plasmas, especially at temperatures of several eV where degeneracy affects the accuracy.

Electrical Breakdown Physics in Photoconductive Semiconductor Switches (PCSS)

165732

Year 1 of 3
Principal Investigator: A. Mar

Project Purpose:

Advanced switching devices with long lifetime will be critical components for linear transformer drivers (LTDs) in next-generation accelerators. LTD designs employ high switch counts. With current gas switch technology at ~10^3 shot life, a potential game changer would be the development of a reliable low-impedance (<35nh) optically triggered compact solid state switch capable of switching 200kV and 50kA with 10^5 shot life or better. Other applications of this technology are pulse-shaping programmable systems for dynamic material studies (Z-next, Genesis), efficient pulsed power systems for biofuel feedstock, short-pulse (10 ns) accelerator designs for the Defense Threat Reduction Agency (DTRA), and sprytron replacements in nuclear weapons (NW) firing sets.

Optically triggered photoconductive semiconductor switch (PCSS) devices have been developed at Sandia for very fast switching of electrical power. Low-cost PCSS devices are highly reliable and very compact. High-gain GaAs PCSS are triggerable by low-energy semiconductor lasers through a fiber and have demonstrated lifetimes >10^8 cycles with 20A per filament. The shot life of PCSS is predominately dependent on the switched charge as opposed to the switched voltage, as was evident in high power PCSS demonstrations up to 220kV and 8kA. Therefore, the current can be scaled without sacrificing lifetime by initiating multiple parallel filaments in multiple parallel devices. This project will develop PCSS switching modules capable of 200kV (DC) and 20kA current that can be stacked in parallel to achieve 100's of kA with 10^5 shot lifetime. The scaling of PCSS designs to switch megavolt and 10's-100's kiloamp systems will be supported by developing an improved model of the electrical breakdown physics in the device, which impacts filament diameter, peak current density, packing density (spacing), and optical trigger energy, the key parameters for scaling PCSS-based systems to the mega-ampere regime. Sentaurus device process modeling will also be employed to optimize the contact structures in the PCSS device for reliability.

Z-Pinch X-Ray Sources for 15-60keV

165733

Year 1 of 3
Principal Investigator: D. Ampleford

Project Purpose:

The purpose of this project was to develop higher photon energy x-ray sources than are currently available on the Z machine. By using emission lines produced by inner-shell absorption, we are able to create x-ray sources at high photon energies that are brighter than those that can be produced by typical thermal K-shell line emission.

Exponentially Convergent Monte Carlo for Electron Transport

165734

Year 1 of 1
Principal Investigator: B. C. Franke

Project Purpose:

The Monte Carlo technique is powerful in its accuracy, scalability, and conceptual simplicity. The primary deficiency of Monte Carlo methods is their inherently slow variance convergence (as the inverse of computation time). Residual Monte Carlo algorithms have been demonstrated to solve this precision problem by iteratively calculating an error correction to achieve exponential convergence. Remaining issues have prevented them from being deployed in production radiation transport codes. These issues appear mostly to be practical deployment of the technology. Our project aims to demonstrate practical approaches for the method in continuous angle and multidimensional calculations and to rule out other technical deployment issues. Through the development of an electron transport capability, we will tailor our investigation to address concerns for our applications. An efficient high-precision electron transport capability would permit robust iterative coupled-physics simulations for electrical effects in nuclear weapon and satellite environments.

Residual Monte Carlo is a technique that promises the accuracy of Monte Carlo methods with the precision of deterministic methods. The technique was proposed as early as 1960 and has been investigated for radiation transport problems for the last two decades. Recent advances suggest the technique may be sufficiently understood to begin implementations within production codes. However, the method has not been demonstrated with continuous angle in multidimensional problems and has not been demonstrated with energy dependence. Even attempts to demonstrate using realistic cross sections have been of quite limited fidelity. Until such demonstrations are made, the method remains very risky for production implementation. This project is proposed as a stepping stone to a larger and still risky attempt at a multi-group production capability. The unique combination of accuracy and precision will open new application space for Monte Carlo radiation transport and suggests powerful accuracy/efficiency gains that may be made in coupled deterministic/Monte-Carlo methods.

Summary of Accomplishments:

The developments under this project make it possible to extend the residual Monte Carlo method to particle transport problems with anisotropic scattering. We developed the capability to evaluate the residual with discrete scattering angles and with a screened Rutherford angular-scattering kernel in 1D calculations. These advances make it possible to implement the method in multigroup simulations. The equations developed and the approach employed can be extended to multidimensional calculations. This lowers the risk of undertaking a project to implement residual Monte Carlo in a production radiation transport code.

Significance:

This project was a feasibility study meant to advance the set of algorithms that will be needed for a production residual Monte Carlo capability in the area of particle transport. The project has succeeded in showing how residuals can be calculated for particle transport problems involving arbitrary angular-scattering distributions. These advances make a project to implement a production residual Monte Carlo capability less risky, but not all of the research challenges have been addressed.

Refereed Communications:

B.C. Franke, D.E. Bruss, and J.E. Morel, “Residual Monte Carlo with Discrete Scattering Angles in the 1-D Transport Equation,” to be published in *Transactions of the American Nuclear Society*.

Implementing and Diagnosing Magnetic Flux Compression on Z

165736

Year 1 of 3
Principal Investigator: R. D. McBride

Project Purpose:

The Z pulsed power facility offers a unique platform for producing very large magnetic fields (10's - 100's MGauss) coupled to very high energy density (HED) plasmas (>>1 Mbar). These extreme states of magnetized matter offer many rich and exciting phenomena for scientific inquiry, as was highlighted by the recent Research Needs Workshop (ReNeW) on high energy density laboratory physics (HEDLP). One interesting and programmatically important way to achieve very high magnetic field intensities on Z is through magnetic flux compression. An axially aligned, pre-imposed seed field, Bz_0, can be trapped and compressed by a fast (100-ns) imploding liner, where the implosion is driven by the azimuthal B_θ field of the Z power pulse. Flux compression can, in principle, amplify seed fields of ~30 T to more than 10,000 T (100's of MGauss). This phenomenon is exploited by the magnetized liner inertial fusion (MagLIF) concept currently under development at Sandia. However, our ability to compress flux remains unclear due to poorly understood physics. For example, the Nernst Effect (a thermo-electromagnetic effect) can cause significant flux loss in the presence of strong temperature gradients. The Nernst Effect is included in higher-order magneto-hydrodynamic theory, but the physics needs to be validated experimentally. Clearly, developing diagnostics to measure these compressed fields is required to assess whether or not adequate compression is achieved.

Producing and diagnosing such intense magnetic fields on Z is nontrivial. We, therefore, propose to evaluate and eventually test on Z the most promising diagnostic methods that have been proven to work on smaller-scale facilities. These methods include Zeeman spectroscopy, polarization and fine structure spectroscopy, miniaturized B-dot loops, Faraday rotation, proton radiography, on-axis photonic Doppler velocimetry, velocity interferometer system for any reflector (PDV/VISAR), Thomson scattering, etc.

Evaluation of Warm X-Ray Bremsstrahlung Diodes on Z

165738

Year 1 of 3
Principal Investigator: V. Harper-Slaboszewicz

Project Purpose:

The purpose of the project is to create a new type of warm x-ray bremsstrahlung source that could be fielded on the Z accelerator. Enhanced capability to understand and simulate nuclear weapons effects has become increasingly important as the stockpile is updated and data from previous underground test becomes less relevant. Warm x-ray simulation sources have been developed at Defense Threat Reduction Agency (DTRA) facilities and on the Saturn simulator to support these studies. However, the intensity and exposure volume available with existing simulators is not sufficient to access all relevant exposure conditions. The Z facility has much greater current capability than the existing simulators and so should be able to drive higher intensities and exposure volumes than existing sources. However, the drive voltage and pulse shape on Z are incompatible with present bremsstrahlung sources, so innovative bremsstrahlung diode designs will be required to get a usable source on Z. This project will develop the technical basis for a massively parallel bremsstrahlung diode that is scalable to Z.

High-Pressure Pre-Compression Cells for Planetary and Stellar Science

165739

Year 1 of 3
Principal Investigator: C. T. Seagle

Project Purpose:

Hydrogen and helium are the most abundant elements in the universe and occur in a variety of extreme environments, both natural and man-made. Mixtures of hydrogen and helium exhibit an extraordinary degree of non-ideality — the volume of the mixture is not the sum of the individual components. The relative “simplicity” of hydrogen and helium would suggest theoretical calculations of the properties of the mixture would be quite accurate; however, major discrepancies in predicted properties exist between different calculation methodologies. Few experimental data are available on the mixture, particularly at high compression. A detailed experimental study of the mixture will provide invaluable data to benchmark theoretical studies and enhance predictive capability. Applications for the data exist in several scientific disciplines including fusion research, stewardship science, and the interpretation of stellar and Jovian oscillations, which depend on the equation of state of the constituent material.

H_2-He mixtures are extremely difficult to study in laboratory settings at conditions relevant to planetary interiors because of low initial density, mixing properties, and high compressibility of the gases. In shock wave experiments, thermal pressure effects that become significant as the shock strength increases limit the maximum compression. One method to overcome these issues and obtain shock data for H_2-He mixtures at higher compressions is to pre-compress the mixtures prior to dynamic loading. For the gases, this pre-compression substantially decreases the initial compressibility and results in very different loading paths than typically achieved. The purpose of this project is to quantify the non-ideal mixing behavior and equation of state of H_2-He mixtures under shock loading by creating the ability to pre-compress macroscopic mixtures of H_2-He. Difficult challenges in the development of pre-compression for dynamic studies exist, but the reward is access to regions of phase space not previously explored.

Assessment of Load Current Multipliers to Increase Load Magnetic Pressures for Dynamic Materials and Fusion Experiments

165740

Year 1 of 3
Principal Investigator: T. J. Awe

Project Purpose:

Dynamic material properties (DMP) experiments on the Z Facility obtain equation-of-state (EOS) data for materials at multi-megabar pressures with unprecedented precision. Z's ultra-high (I~26 MA) current and advanced pulse-shaping capabilities provide a world-class platform for shock and isentropic compression experiments, yet important phase transitions remain inaccessible. A new enabling technology, the load current multiplier (LCM), will allow Z to deliver ~40% higher current to long-pulse DMP loads with minimal alteration to the generator architecture. The 40% higher current could also increase the x-ray energy radiated from z-pinches by a factor of two, and increase fusion neutron yields in inertial confinement fusion (ICF) experiments by a factor of 4 (I^4 scaling) or more.

LCMs increase the efficiency of electromagnetic energy coupling between a high-impedance generator and a low-impedance load by forcing current to pass through the load twice. Using an LCM on Z-DMP experiments could nearly double the measurable pressure along the principal isentrope, enabling first-time access to a host of multi-megabar phase transitions. While recent experiments have demonstrated current multiplication in medium-scale pulsed power facilities (~1 MA/100 ns and ~5 MA/2µs), LCM performance under the more challenging conditions (lower generator inductance, higher voltage, ultra high fast-rising current) of the Z Facility remains uncertain.

Radiation Susceptibility of Memristive Technologies in Hostile Environments

165741

Year 1 of 3
Principal Investigator: M. L. McLain

Project Purpose:

Memristor technologies show great promise as a next-generation nonvolatile memory with high endurance (one trillion cycles), long retention (> 10 years), and low power (< 1 pJ switching). In order to use memristive technologies in national security and nuclear weapon (NW) applications, it is necessary to understand the radiation susceptibility in all possible radiation environments. Currently, it is unknown how memristive technologies will operate in a dose-rate or pulsed-neutron environment and the radiation response in a total-dose, proton, or heavy-ion environment is not well understood. In this project, we will use a combined theoretical-experimental effort to probe the radiation response of memristor devices currently being fabricated by Hewlett Packard (HP) and Sandia's Microsystems and Engineering Sciences Applications (MESA) facility. We will then apply what we learn to discover other possible radiation-resistant memristive materials that are candidates to be inserted into the memristor fabrication process at MESA. Sandia is in a unique position to study the radiation susceptibility of potential radiation-hardened memristive technologies because of a cooperative research and development agreement (CRADA) that has provided us with knowledge of HP's proprietary, leading-edge memristive memory design. If successful, the proposed work will lead to an enhanced understanding of the physics and material properties that govern the radiation tolerance of memristive materials. This will enable the discovery of a radiation hardened memristive technology to be used in future NW applications.

We will use state-of-the-art radiation test facilities to investigate, for the first time in some cases, the radiation response of memristor devices. The physics of the observed response will have to be fully understood to advance Sandia's knowledge to a point at which the next generation of rad-hard circuits can be fabricated. Because there are many unknowns associated with memristors (e.g., mechanism leading to the formation of filaments), it may be difficult identifying the primary feature contributing to the radiation hardness of a memristive device.

Exploring New Frontiers in Wave-Particle Physics in Nonstationary ICF-Related Plasmas

165746

Year 1 of 3
Principal Investigator: P. Schmit

Project Purpose:

The purpose of this project is to develop new tools and models that enhance our understanding of important kinetic processes in inertial confinement fusion (ICF) experiments. Kinetic effects are identified here as any relevant target physics requiring detailed knowledge of the dynamics of individual charged particles in a fusion plasma. For both historical and practical reasons, the theoretical treatment of the plasma physics of ICF experiments typically adopts a simpler, hydrodynamic picture of the fusion plasma, either ignoring or approximating any background kinetic effects. While the hydrodynamic approach is far more computationally tractable than fully resolved plasma kinetics in integrated ICF simulations, the validity of the underlying transport, burn, and radiation models — three critical components of the simulation — relies on the satisfaction of a long and stringent list of assumptions about the overall target physics. Given the plethora of assumptions these models presume, it is no surprise that integrated simulations are often overly optimistic and/or quantitatively incorrect.

Therefore, in this project we will develop new theoretical and numerical tools to elucidate potentially important physics missed by traditional ICF multiphysics codes. Particular attention will be given to the kinetics of superthermal fuel ions, the charged particles primarily responsible for fusion in the target, within their global environment. Substantial progress has been made in FY 2013 in the development of a fully 3D particle code capable of resolving the kinetics of these ions in a wide variety of scenarios. This code will provide extensive new insights into problems relating to reactivity depletion, mix effects, magnetic confinement, and numerous other outstanding problems in ICF. Development and use of other existing codes and models will enhance and diversify the investigation of target kinetics beyond the problems mentioned explicitly in this abstract.

The PI is a Sandia Truman Fellow.

Fiber-Optic Streak Spectroscopy of Gas Cells in Extreme Radiation Environments

170977

Year 1 of 3
Principal Investigator: K. M. Williamson

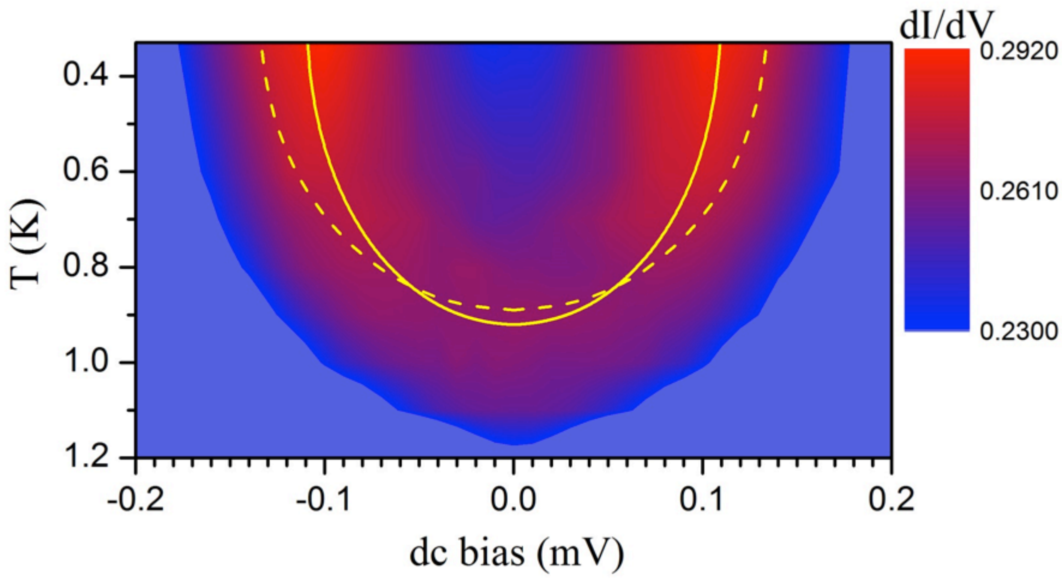
Project Purpose:

An enduring component of Sandia's core mission is to maintain our nation's nuclear deterrent in a rapidly changing technological environment. An imminent challenge to this mission is the impact of system-generated electromagnetic pulse (SGEMP) on the performance and reliability of nuclear weapons systems. The physical mechanisms involved with coupling high-energy radiation into and damaging critical system components are being studied by the Pulsed Power Sciences Center at Sandia.

These experiments utilize high intensity x-rays from z-pinch radiation sources on the Z machine to ionize a gas cell. Indirect sensing of this non-thermal plasma is presently being conducted with a B-dot sensor that results in a highly averaged measurement of the changing magnetic fields. This research will be directed at the creation of a new diagnostic and analysis technique that will enable more refined characterization of this plasma that is critical for accurate modeling and simulation of SGEMP.

NEW IDEAS

The New Ideas Investment Area provides a place to submit ideas that lie outside Sandia's current research focus, but could potentially have an impact on the Labs' strategic goals. The New Ideas Investment Area provides funding for leading-edge research that does not fit well into the research portfolio of any existing LDRD investment area. The ideas must have long time horizons with impacts that currently are uncertain, propose nascent research in a new research field that may become relevant to the mission, lie outside the current strategy space of the Research Foundations, or lie at an interface between two or more investment areas.



The temperature dependence of the contour plot of the tunneling conductance across an InAs/GaSb semiconductor and Tantalum superconductor junction with respect to dc bias voltage (solid line) deviates from that expected for a standard superconductor (dashed line), suggesting a proximity-effect-induced superconducting state in the InAs/GaSb type-II semiconductor (a possible topological superconductor) (Project 165717).

NEW IDEAS

Exploring the Possibility of Exotic Ground States in Twisted Bilayer Graphene

165713

Year 1 of 3
Principal Investigator: T. Ohta

Project Purpose:
We will examine the electronic properties of doped twisted bilayer graphene (TBG) in search of exotic ground states in this material. The following specific scientific questions will be addressed via our leading capability in this emerging material: 1) can van Hove singularities (vHs) be engineered in TBG and 2) can exotic ground states, or perhaps superconductivity, be induced by filling electrons up to, and leveraging these vHs?

The ramifications of superconductive graphene are far reaching. As its charge carriers are readily manipulated at cryogenic temperatures using the field effect (FE), gate-tunable superconductive elements, equivalent to three-terminal switches, may be realized. Importantly, such a simple switching function is currently missing for superconductor circuitries envisioned for exascale supercomputers.

Superconductivity in graphene has not been experimentally observed despite numerous predictions of its existence. The theoretical predictions have suggested the emergence of exotic ground states at vHs residing >2eV from the charge neutrality point. These energies are inaccessible using atypical FE structures, however. TBG, in contrast, has additional low-energy vHs, which are accessible by FE-gating. They evolve as a natural consequence of the two graphene sheets being misaligned. Consequently, TBG provides an exciting medium to explore the possibility of superconductivity in graphene.

The search for superconductivity is a high-risk endeavor in a low-dimensional material. TBG, however, is an emerging class of graphene whose electronic dispersion offers promise towards this end, even though its precise dispersion remains a topic of debate. Building on our leading expertise in TBG, we will strive to engineer the vHs to induce exotic ground states. Our approach is the first of its kind.

The best-case outcome is that gate-tunable superconductivity, a disruptive technology, will greatly simplify the hardware of superconductor-based supercomputers.

Closing the Nutrient Utilization Loop in Algal Production

165714

Year 1 of 3
Principal Investigator: T. Lane

Project Purpose:

Despite widespread interest in electric modes of transportation, the Energy Information Administration (EIA) projects that liquid fuels will provide more than 90% of US transportation energy through 2035, and few alternatives are on the horizon for aviation transport. Biofuels look well-positioned for this role but face daunting challenges in scale-up and sustainability. Biofuel production from algae biomass is a compelling solution for sustainable domestic production of fuels. However, recent studies suggest that replacement of domestic fuel supply with algae would require a doubling of nitrogen and phosphorus fertilizer usage. Unlike ammonia, phosphate is a non-renewable resource, and a peak in worldwide production is expected as early as 2030. Thus, without significant technological progress to recycle these major nutrients, expansion of algal biofuels to commodity scale can be expected to catalyze a food-versus-fuel crisis.

We will close the nutrient recycling loop by harnessing remineralization processes, the biological conversion of organic forms of nutrients to inorganic forms. We will develop a novel, cost-effective process for remineralization of phosphate and nitrogen from oil-extracted algal biomass and the conversion of these nutrients into forms that are captured and amenable for use as nitrogen and phosphate sources. To facilitate separation of the remineralized nutrients from the bulk phase, we will induce the co-precipitation of ammonium and phosphate as struvite (NH_4MgPO_4). Converting nutrients to solids is a low-energy means of recovering the bulk of the phosphorous and a portion of the nitrogen with maximum transportability. The remainder of the nitrogen will be recovered as ammonia. To identify scale-up concerns, we will develop models that relate the phosphate-remineralization enzyme kinetics, mixing and precipitation kinetics.

Testing the Effects of Transcranial Direct Current Stimulation on Human Learning

165715

Year 1 of 2
Principal Investigator: L. E. Matzen

Project Purpose:

Training a person in a new knowledge base or skill set is extremely time consuming and costly, particularly in highly specialized domains such as the military and the intelligence community. Recent research in cognitive neuroscience has suggested that a technique called transcranial direct-current stimulation (tDCS) has the potential to revolutionize training by enabling learners to acquire new skills faster, more efficiently, and more robustly. In tDCS, a small region of the brain is stimulated with a weak electrical current (1-2 milliamps) via an electrode placed on the scalp. This current makes the neurons in the vicinity of the stimulation either more or less likely to fire, depending on the polarity of the electrical field. Although tDCS has been used for over 50 years, recent advances in technology have created a surge of new applications, and tDCS devices are now available to the general public. Most of the research in this rapidly developing field has been focused on medical applications, such as treating migraines or assisting with rehabilitation of brain injuries. However, tDCS has many potential applications with implications for national security, and those applications have received little attention to date.

Although tDCS has the potential to have a major impact on human performance — particularly in the area of training — the research on tDCS effects in this area is in its infancy. In this project, we will study the effects of tDCS on three types of memory that are crucial for training: working memory, semantic memory, and associative memory. This work would significantly advance the science in this area and could position Sandia on the cutting edge of research into the training applications of tDCS.

Searching for Majorana Fermions in Topological Superconductors

165717

Year 1 of 2
Principal Investigator: W. Pan

Project Purpose:

The goal of this project is to search for Majorana fermions (a new quantum particle) in a topological superconductor (a new quantum matter achieved in a topological insulator proximitized by an s-wave superconductor).

Majorana fermions (MFs), predicted in 1937 by the Italian theorist Ettore Majorana, are electron-like particles that are their own anti-particles. MFs are shown to obey non-Abelian statistics and, thus, can be harnessed to make a fault-resistant topological quantum computer. Over the last decade, searching for MFs has mainly been focused on the exotic 5/2 fractional quantum Hall effect (FQHE). With the arrival of topological insulators, new schemes to create MFs have been proposed in hybrid systems by combining a topological insulator with a conventional superconductor. Compared to FQHE, this new approach of creating MFs is promised to be more versatile and the requirement of material quality is less stringent. Since 2008, a global race has been on to realize yet-elusive MFs in low-dimensional semiconductor systems.

In this project, we will follow the theoretical proposals made by Lutchyn, Sau, and Das Sarma and by Fu and Kane to search for MFs in 1D topological superconductors. A 1D topological superconductor will be created inside a quantum point contact (with the metal pinch-off gates made of conventional s-wave superconductors such as niobium) in a 2D topological insulator (such as an inverted type-II InAs/GaSb heterostructure).

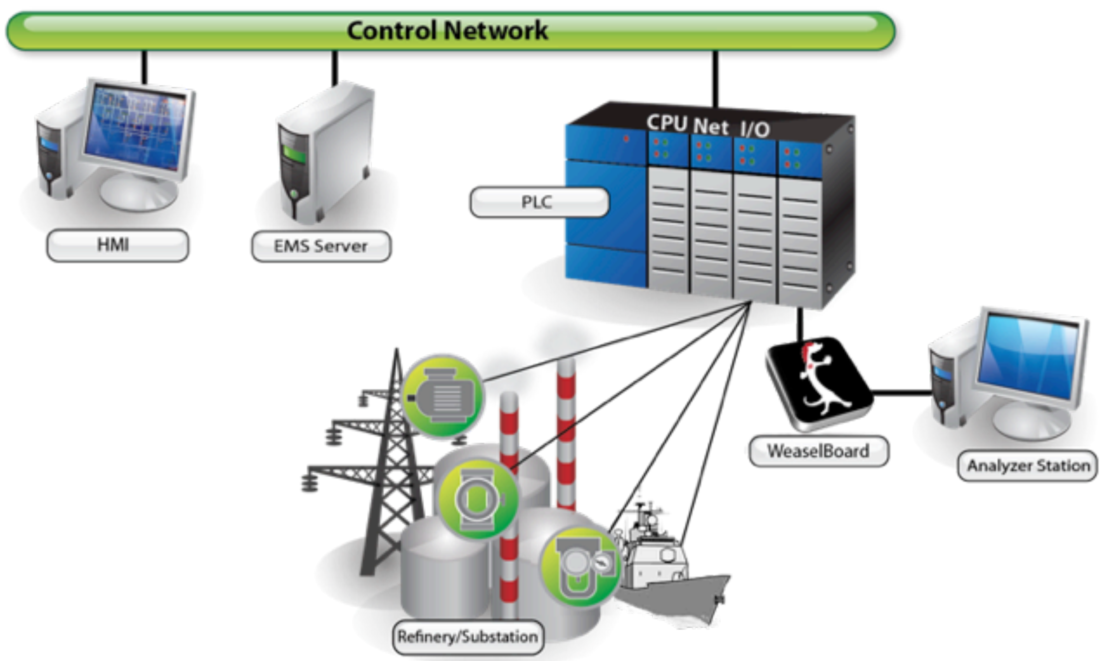
Results from this project will help to create a science-based knowledge foundation for creating, controlling, manipulating, and exploiting quantum particles in building 21st century technology. Sandia is the ideal place to perform the proposed research, which requires expertise in the high-quality MBE growth of type-II InAs/GaSb heterostructures, sophisticated device fabrication of semiconductor nanostructures, and ultra-low-temperature quantum-transport measurements, rarely found together in a single place.

DEFENSE SYSTEMS AND ASSESSMENTS

The Defense Systems and Assessments Investment Area delivers advanced science and technology solutions to deter, detect, track, defeat, and defend against threats to our national security. The work includes the development of innovative systems, sensors, and technologies for the nation's defense communities.

The investment area draws upon state of the art science, technology, and engineering capabilities (ST&E) at Sandia and from the nation's ST&E community. The work is focused in three strategic program areas: Space Mission and Remote Sensing (SMRS), Information and Intelligence Technologies (IIT), and Integrated Domain Awareness and Prompt Response (IDAPR).

SMRS is focused on next-generation satellite flight and ground systems and future challenges facing the space community. The work supports the development of enabling technologies for revolutionary remote sensing and collection systems. IIT addresses the asymmetric threats arising from our nation's dependence on information networks and on anticipating disruptive capability and technology developments that threat national security. IDAPR identifies enabling technologies that support precision knowledge, precision decisions, and precision response for the national security community.



WeaselBoard: Zero-Day Exploit Detection for Programmable Logic Controllers (Project 158752).

DEFENSE SYSTEMS AND ASSESSMENTS

First Principles Prediction of Radio Frequency Directed Energy Effects

151263

Year 3 of 3
Principal Investigator: L. D. Bacon

Project Purpose:

Radio frequency directed energy (RFDE) is demonstrating potential for application in many DoD and DOE mission areas. Systems are being developed for use by at least three services and the DOE. Its acceptance, however, is hampered by the lack of first-principles understanding of RFDE effects on electronics. At present, RFDE mission planning is semi-empirical. The uncertainty in the details of the electronic systems in modern targets of interest (improvised explosive device triggers, for example) and the very rapid rate of change in the consumer electronics used in these systems make the results from this semi-empirical approach highly perishable at best or, at worst, irrelevant by the time it is available. Empirical models give us an understanding of what happens with a specific scenario. Naturally, they are limited in how far they can be interpolated or extrapolated beyond the data upon which they are based. What is needed is the ability to predict RFDE effects from first principles, validated against measurements of example systems. First-principles models give us an understanding of why a scenario leads to the results it does. They can be interpolated or extrapolated as far as the physics they are based on remains valid. This ability will allow the details of the target that dominate the response to be identified — something that cannot be done using measurements alone — and their impact on the variability of the response and on effect margins to be addressed. This project will provide that capability as far as it is practicable today.

To our knowledge, no one has yet put together a first-principles estimate of the full RFDE effects process. Some in the community do not believe that it is possible. Our experience indicates that it is likely to be possible, and that the insights gained have been well worth the effort even if it is not.

Summary of Accomplishments:

During this project, we developed multiple techniques for accurate modeling of electronic systems, including the active Thevenin equivalent network approach (ATHENA) concept and implementation. We demonstrated principles for accurate printed circuit (PC) board modeling, by modeling and measuring structures with known radio frequency (RF) responses. We developed meshing methodologies for PC board traces that ensure accurate representations of their RF responses.

These techniques can be applied to an arbitrary PC board. We developed port representations to tie the electromagnetic response to the non-linear circuit response and we wrote scripts to generate ATHENA parameters from simulation outputs. ATHENA allows frequency-domain (FD) modeling to be applied to non-linear circuit — a significant advantage. We developed a technique for handling the non-causal precursor from band-limited FD models. This ATHENA extension allows non-linear circuit response modeling from band-limited frequency domain calculations.

We demonstrated the need for technology computer-aided design (TCAD) modeling of semiconductor devices for the off-normal operation created by RFDE. We performed wafer-scale RFDE measurements of semiconductor responses. These advances will continue to impact RFDE and other parts of Sandia's mission space.

Significance:

Acceptance of RFDE is hampered by the lack of first-principles understanding of its effects on electronics. We need the ability to predict RFDE effects from first principles, validated against measurements of example systems. This project has made progress in providing that capability as far as practicable today.

Our TCAD modeling work became part of the technical basis for a new project in Power Spectral Analysis. Our wafer-scale RFDE measurements of semiconductor responses are contributing now to a graphene project. These advances will continue to impact RFDE and other parts of Sandia's DOE and DoD mission space.

Refereed Communications:

L.D. Bacon, J.T. Williams, M.J. Walker, and A. Mar, "Progress in First Principles Modeling of HPM Effects," *Journal of Directed Energy*, vol. 5, Spring 2013.

Polarimetric Change Detection Exploitation of Synthetic Aperture Radar Data

151264

Year 3 of 3
Principal Investigator: R. Riley

Project Purpose:

Synthetic aperture radars (SARs) perform ISR (intelligence, surveillance, reconnaissance) missions by directly observing signatures of features in a scene containing activities of interest and/or by indirectly observing the evidence of activities of interest via change signatures that are present in multi-collect coherent change detection (CCD) products. The ability to detect activities via the change signatures alone is of great benefit to many applications and is utilized extensively on existing fielded airborne SAR systems. However, it can be difficult, even intractable, to classify the underlying cause of the change signatures, especially in high change clutter scenes. Disparate changes from various mechanisms frequently form one contiguous change signature, especially if several hours pass between collections, making it impossible to detect or discriminate for the change signatures of interest.

SAR systems are already fielded that exploit polarimetry to decompose a scene into terrain types, vegetation cover, and presence of man-made objects; however, we are not aware of any application of this decomposition to CCD classification. Given Sandia's current real-world experience with CCD and associated limitations when utilizing single polarization airborne SARs, it is a natural next step to consider using fully polarimetric classification to classify CCD change signatures.

This research will investigate the utility of polarimetric-based classification of scene content, as well as changes in underlying polarimetric signatures, to enable change signature discrimination and classification.

Summary of Accomplishments:

A diverse set of activities had to be performed and new areas of study had to be pursued in order to meet the objectives of this study. Some of the highlights are as follows. Before this study began, the Sandia-owned PhoeniX X-band, Sandia development radar (SDR) had the potential of full-polarization imaging; as a result of this study, the PhoeniX radar underwent hardware and software upgrades and is now a functioning fully polarimetric radar that can collect time-coherent X-band phase histories. Special calibrators were designed and manufactured for this study and these calibrators were placed, along with other traditionally used triangular trihedral calibrators, in an elaborately designed calibration array; the calibration array was needed in order to calibrate the multi-polarization PhoeniX system. Flights were needed in order to collect data to test the hypotheses of this study. To that end, ground activity plans were choreographed and flight plans were made in order to collect a meaningful and useful data set. Many algorithms were needed in order to process the collected data, everything from traditional image formation, auto-focus, and polarimetric decomposition algorithms to the new fusion algorithms that were developed for this study; a suite of end-to-end algorithms, which includes a small sampling of polarimetric decomposition algorithms, was created to properly process the data collected by the PhoeniX system.

The objectives of this study were successfully realized. It has been shown that polarimetric CCD provides a very powerful discriminator of the type of change in a scene that single-polarization CCD alone cannot provide. This study has also demonstrated that some well-known polarimetric algorithms, such as the decompositions and optimal coherency, work well with high resolution SAR imagery.

Significance:

Much of the SAR mission space depends upon the information that can be distilled from the associated image textual context; this is true even for applications that utilize derivative CCD exploitation products. Recent system design and processing advances have typically been focused on real-time fine resolution product generation. The polarimetric dimension of information exposes additional, significant context information to be observed.

Trusted Execution Methodology · Payload / Operating System (TEM·P/OS)

151270

Year 3 of 3
Principal Investigator: K. Robbins

Project Purpose:

The purpose of the project is to discover and create algorithms for advanced embedded communication architectures and to demonstrate methods to simplify development of embedded distributed event-driven systems.

Summary of Accomplishments:

We created and proved a method for constructing distributed event-driven systems that is highly scalable and that encourages reuse of proven components. The method is based on event-driven actors and software components implemented as independent, communicating state machines.

We extended the event-driven actor design discipline to hardware actors implemented in VHDL (very high speed integrated circuit hardware description language).

We discovered and proved a method for network coding that is transparent to the application layer, allowing existing and legacy applications to benefit from network coding without requiring changes.

We discovered and proved other methods for improving the robustness of embedded communication architectures.

Significance:

Sandia supports many important national security missions by delivering advanced computing systems, often operating in harsh environments. While processing requirements are increasing, performance of processors available for use in harsh environments is stagnant, lagging performance of components in consumer electronics. At the same time, computer networking continues to advance, providing greater capacity with greater power efficiency. These developments point to distributed computing systems as a likely solution to the processing requirements of next generation national security systems.

Project results, including the event-driven actor framework, the deployment planner, and methods for advanced communication architectures, greatly simplify development of distributed event-driven systems.

Matterwave Interferometer for Seismic Sensing and Inertial Navigation

151275

Year 3 of 3
Principal Investigator: G. Biedermann

Project Purpose:

In recent years, the performance of inertial navigation systems has reached a plateau due to the limits of available sensor technology. Light-pulse matterwave interferometry is widely recognized to be the next advance for inertial measurements. Demonstrations measure both rotations and accelerations with outstanding fidelity, stability, and intrinsic accuracy. In seismic sensing, a six-axis matterwave sensor can potentially discriminate between and characterize natural and manmade sources (such as underground facilities and explosions) in new ways as well as independently infer wave speed and direction to reduce event location uncertainty. Current atom interferometers are large, delicate, bandwidth-limited to a few Hz and untenable for rugged seismic and navigation applications. We plan a tabletop demonstration of the first high bandwidth (100 Hz) matterwave gyroscope/accelerometer, which may enable a broadband and reasonably rugged device. We will evaluate this technology with input from in-house experts in both the navigation and seismology user community to lay groundwork for a full system development program. We will operate the interferometer in a new short time-of-flight regime enabling a small 10 cc physics package. We anticipate two orders of magnitude gain in data rate and new opportunities for reductions in size and system requirements. A new property of this approach, heretofore unseen with matterwave sensors, is that the orientation can in principle be rotated with respect to gravity without severely affecting the performance. Using two counter-propagating, short time-of-flight interferometers we can simultaneously measure accelerations and rotations at a high data rate. During a short ~10 ms free flight, a light pulse atom interferometer sequence determines the platform rotation rate and acceleration with respect to the pristine atom proof mass. We forecast that this concept can achieve sensitivities of 10 nano-g/rtHz for accelerations and 12 nano-rad/s/rtHz (42 micro-deg/rthr) for rotations, far exceeding navigation grade metrics.

Summary of Accomplishments:

We demonstrated a dual-axis accelerometer and gyroscope atom interferometer achieving 50 to 100 measurements per second. By recapturing the atoms after the interferometer sequence, we maintained a large atom number at high data rates. Two cold ensembles were formed in trap zones located a few centimeters apart and launched toward one another. During their ballistic trajectory, they were interrogated with a stimulated Raman sequence, detected, and recaptured in the opposing trap zone. We achieved sensitivities at micro-g/rtHz and micro-rad/s/rtHz levels, making this a compelling prospect for expanding the use of atom interferometer inertial sensors beyond benign laboratory environments.

Along the way, we invented and demonstrated a recapture technique for high bandwidth atom interferometer accelerometers. We invented and demonstrated a counter-propagating atom launch and recapture technique for simultaneous atom interferometer gyroscope and accelerometer sensing. We invented and demonstrated key techniques for optimizing the performance of this approach, discovering performance and size limits along the way. Finally, we invented and demonstrated a warm vapor matterwave interferometer technique for measuring acceleration.

Significance:

Our approach to atom interferometry can enable needed advances in inertial navigation and seismic monitoring. General metrology with laser-cooled ensembles can be extended beyond benign laboratory environments using our recapture techniques. A warm vapor atom interferometer can provide a much-needed reduction in system overhead for deploying an atom interferometer device.

Spectro-Temporal Data Application and Exploitation

151276

Year 3 of 3
Principal Investigator: E. A. Shields

Project Purpose:

Prism and grating components that disperse light to produce high spectral resolution data could be used to classify or characterize objects based on spectral characteristics. These dispersive components can be contained in Sandia-built sensors without attached mission requirements due to their uncertain utilization. In this project, we will determine the potential capability of these new sensors by characterizing the range of apparent signatures of targets of interest to civilian, government, and military commanders and to assess their respective mission performance. This will be achieved through the unique position that Sandia has with respect to sensor design, testing, and data availability and through Sandia's special technical capabilities in phenomenology, modeling, and algorithm development. Project efforts will center on the technical areas of sensor characterization and sensitivity analysis, target and sensor modeling, experiment and observation, and on-orbit data analysis. The primary focus during the first year was on the short wavelength infrared (SWIR) grating band. Through analysis of test data, new high order processing algorithms were shown to be sensitive to subtle varying signals in both the spectral and temporal dimensions. In addition, a grating sensor model was developed that can simulate spectral dispersion in spatial data for use in evaluating target signatures and ultimately mission performance. In subsequent years, efforts focused on stringent assessment of spectro-temporal signatures from both the visible prism and grating dispersive bands and the polarized bands that are expected to both enhance current missions and address new missions. This was achieved primarily through forward modeling of unique spectral signatures as well as target detection and extraction algorithm development from space-based data collections and simulated data.

Summary of Accomplishments:

In the area of scene and target modeling, we advanced the state of the art in generating polarized scenes with realistic signatures for clouds. Sandia's capability of generating spectro-temporal targets was advanced as well as simulations of targets of interest were generated and processed with system simulation tools to accurately predict sensor performance. The sensor perform prediction tool (R3) was distributed to the user community and provides a valuable resource for users of Sandia's systems.

In the area of sensor modeling and characterization, multiple tools were developed. An in-house tool for modeling the polarization response of the systems was created. This tool has been used to create simulated scenes with realistic clouds to demonstrate the potential of determining cloud phase from polarimetric images. Calibrated models of the grating and prism bands were created as well. These were distributed to the user community so users can simulate system performance or optimize system parameters to optimally obtain data.

Significant advancement of spectro-temporal algorithms was achieved. We demonstrated the potential for the grating band to be used for a wide range of missions of interest to government agencies. Algorithms such as non-negative tensor factorization and principal component analyses were implemented and advanced for use with spectro-temporal data.

New mission concepts for the polarimetric and spectrally dispersive bands were found as well.

Significance:

New national security missions were enabled through the accomplishments of this project. The advances in algorithms for analyzing spectro-temporal data allow for meaningful classification and characterization of signatures of interest to be performed. These algorithms will benefit not only the programs considered in this project but other Sandia programs as well.

Adaptive Automation for Supervisory Control of Streaming Sensors

151277

Year 3 of 3
Principal Investigator: J. H. Ganter

Project Purpose:

National intelligence and security depend on effective remote sensing, the acquisition of knowledge from a distance using instruments that transform energy into information. Sandia remote sensors include the multispectral thermal imager (MTI) and synthetic aperture radar (SAR) aboard unmanned aerial vehicles (UAVs).

To improve the performance and utility of remote sensors, Sandia recently conducted studies of human labor demands located downstream of the sensing instruments. In the ground processing stage, signal processing algorithms running on large computing clusters detect signatures in noise and classify signatures into target categories. But there is a surprisingly large, and even growing, reliance on human experts to tune the algorithms to user needs, mission goals, and evolving situations. The next generation of sensors will change a labor shortage to a labor crisis. Manual labor has become the primary limiting factor in both technology rollout to national security missions and R&D investment in new sensors.

To solve the sensor labor crisis, we need a new analog to the autopilot that has become ubiquitous aboard aircraft and ships. This trusted and powerful machine aid will free human time and attention for tasks people do well. These skilled tasks include situational awareness, situational understanding, and the making of difficult choices among options. This project will invent a sensor autopilot by hybridizing methods from statistics, signal processing, control theory, and cognitive systems. A sensor autopilot must solve problems that are underspecified and thus dramatically more difficult than typical control problems. Probability density functions (histograms) of both targets and backgrounds are noisy, unknown a priori, and evolving. Solutions must be numerically generated very rapidly to remain within the time constant of the sensor control loop. We believe that creatively blending adaptive signal processing with control theory, human-supervised training, and machine learning could solve many problems currently limited by human-operator bandwidth.

Summary of Accomplishments:

The project invented the Detection Enhancement (DE) algorithm, which aids the operator in detecting low signal-to-noise ratio events. We also conducted experimentation related to the operation of a simplified interface to classify events.

Significance:

The Detection Enhancement (DE) algorithm significantly improves performance for low signal-to-noise ratio events. This has the overall effect of making the sensing system more effective against existing events and expanding it to include additional event classes.

Automated Severity Assignment for Software Vulnerabilities

151284

Year 3 of 3
Principal Investigator: G. E. Reedy

Project Purpose:

The purpose of the project is to develop tools for automated and semi-automated software analysis that are accessible and practical. The goal is to enable analysis of more complex programs and to deliver results faster than is currently possible.

Summary of Accomplishments:

We created an interactive analysis environment for program understanding tasks. This environment is built on an extensible semantics framework that enables reasoning about high-level semantic domains that can be inferred from the program's behavior. This same framework can also be used to write purpose-built fully automated analysis tools.

Significance:

The tools and techniques developed during the project deliver faster turnaround on software analysis tasks that currently require time-consuming manual effort. The approaches used give higher confidence that the results of the analysis are correct as compared to the manual analysis techniques. We have shown how this novel approach can be practically applied to problems of importance to our customers.

Command Intent on the Future Battlefield: One-to-Many Unmanned System Control

151285

Year 3 of 3
Principal Investigator: S. Buerger

Project Purpose:

The DoD faces a looming crisis in the control of unmanned systems (UMS). Acquisition trends driven by Congressional mandates ensure that forces will continue to unman. Today's multiple-operator-per vehicle remote-control methods will scale neither to meet the needs of a cost-conscious security establishment in which manpower is the single largest cost driver nor to accomplish effective, centrally commanded operations involving tens to hundreds of heterogeneous unmanned assets working together in the same battle space. DoD leaders are recognizing that, in predominantly unmanned conflict, intelligent, coordinated, man-in-loop control of multiple UMS will be the key differentiating technology. Previous approaches to multiple-UMS control have worked toward an ideal of pure autonomy, but to adopt autonomous control systems for potentially lethal assets would require certain perfection in algorithms. Instead, we envision one-operator-to-many-asset control systems that capitalize on human superiority in perception, tactics, and strategy and that compensate for perpetual imperfection in control algorithms by keeping human commanders in total control in real time while making teams of heterogeneous unmanned assets responsive to command intent.

This project is directed toward demonstrating several high-risk aspects of our long-term vision for predominately unmanned combat. A highly layered control architecture has been developed that enables the use of modular control alternatives. An efficient high-level task-assigning controller has been developed. Mid-level controls have been developed and implemented on unmanned aerial and ground vehicles to enable independent execution of behaviors including target following, line/area exploration, and obstacle avoidance. The architecture allows an operator to direct mission execution by manipulating and continually updating a single data packet that includes mission objectives and priorities. A user interface allows the operator to intuitively influence this packet. Demonstrations were conducted in which a single operator directed a team of up to three unmanned ground vehicles (UGVs) and one unmanned aerial vehicle (UAV) conducting dynamic, tactical missions in a realistic environment.

Summary of Accomplishments:

We developed a data sharing architecture and control lexicon for flexible, variable autonomy. The architecture uses a publish-and-subscribe communications paradigm, built on available open-source standards, to allow all system agents to broadcast relevant information and consume only the information needed. We created a novel set of command and control data messages that allow efficient modular control involving both centralized and distributed control elements.

We developed and demonstrated layered and distributed optimization algorithms that assign agents to specific objectives by using rapid estimates of expected performance. Mid-level control algorithms, which may be run either centrally or distributed across system agents, estimate agent performance against all relevant objectives using known agent capabilities and task characteristics. A high level optimizer, which may also be centralized or distributed, assigns agents to objectives based on these estimates. The mid level controllers then execute assigned behaviors. This structure efficiently uses limited communication bandwidth and avoids the need to run high fidelity simulations of operations in the planning phase, sacrificing optimality for speed.

We developed computationally and bandwidth-efficient algorithms for heterogeneous collaboration. These include extensions of classical swarm algorithms to accommodate heterogeneous vehicle types and multiple targets, as well as a novel formulation of hybrid, distributed model predictive control.

We integrated a team of aerial and ground vehicles and demonstrated a single operator controlling the team against a moving, unpredictable adversary. The operator simultaneously controlled the aerial and ground vehicles, focusing on high level perception and tactical reasoning by specifying tasks by their desired outcome rather than specifying low level vehicle movements. Lower level control was automated. The operator was able to reach down to lower levels of control (waypoint control or tele-operation), if desired, or to correct shortcomings in autonomy algorithms, demonstrating an adjustable level of autonomy.

Significance:

Control technology like that developed and demonstrated for this project is needed to make the unmanned systems used by the US military and other agencies effective in tactical missions in realistic environments. While others are working on common controllers, we are unaware of any existing technology that offers the equivalent of our "high level control" mode for collaborating unmanned system teams. We expect that the ability to effectively control teams conducting collaborative missions will be a key tactical differentiator in future conflict and will also be important to homeland emergency response and rescue missions.

Refereed Communications:

S.P. Buerger, J. Neely, C. Little, W. Amai, R. Joyce, and J.A. Love, "A Layered Control Architecture for Single-Operator Control of Heterogeneous Unmanned Systems," in *Proceedings of the SPIE Defense, Security and Sensing*, vol. 8387, 2012.

Multi-Mission Software-Defined RF Spectrum Processing

151286

Year 3 of 3
Principal Investigator: P. E. Sholander

Project Purpose:

The military's migration to network-centric warfare requires a robust set of airborne sensors that enable tasking directly by unit commanders. For cost and complexity reasons, these sensors will be SWaP-constrained (size, weight, and power) and flown on unmanned aerial vehicles (UAVs). These multi-mission unmanned aerial systems (UAS) can enable novel system-level applications and Concepts of Operations (CONOPS) via wideband "software-defined spectrum processing" (SDSP) that supports a wide range of surveillance (e.g., synthetic aperture radar [SAR]) and communications missions. For example, multiple, cooperating, SDSP-enabled UAS could improve communications within urban terrain and other challenging environments. They could also provide an organic high data-rate link for SAR imagery download to a ground control station (GCS), thereby enabling a more flexible partitioning between airborne- and ground-based processing on SWaP-limited UAVs. An enhanced communications capability between UAS could enable multi-static SAR capabilities and the exchange of baseline imagery between in-flight UAVs. The military utility for the exchange of baseline SAR imagery between in-flight UAVs is that it could reduce the effective off-station time for persistent surveillance missions by small UAVs.

This project focused on SDSP hardware design and implementation, which is a generalization of the "software-defined radio" concept. It also examined and analyzed a few novel CONOPS enabled by a multi-mission SDSP capability. A key goal was the ability to switch between those capabilities, in real time, while maintaining a small SWaP package compatible with deployed UAVs.

Summary of Accomplishments:

This project developed a prototype of a combined SAR and communications capability (aka, SARCOM) that leveraged existing Sandia radar hardware to provide a 233 Mbps communications capability between SDSP payloads. The project also examined a flexible set of "wide-band, low-band antennas," since antenna design is another significant barrier to multi-mission operation on SWaP-constrained UAVs. Finally, the project also explored radio frequency (RF) device characterization.

Significance:

This project will help Sandia continue to transition our existing SAR, communications, and other RF sensing capabilities to the next generation of military UAS platforms. This is critically important since UAS, and especially small UAS, may outnumber manned aerial platforms and other "national assets" in future military battle spaces. Small UAS will also be more available to unit-level commanders, and hence may provide more timely situational awareness than existing sensor platforms.

A Scalable Emulytics Platform for Observation of Windows-Centric Network Phenomena

151287

Year 3 of 3
Principal Investigator: C. T. Deccio

Project Purpose:

The purpose of the project is to create a system to understand both the behavior and the potential threat of distributed applications in large-scale networks comprised of Windows hosts. There has been some success scaling large arrays of Linux-based virtual machines (VMs) for this purpose. Due to its large memory footprint, however, Windows is at a considerable disadvantage. The goal of the project is to create ways to produce a scalable emulytics platform for Windows operating systems (OS) where it will have more impact and value to network analysts and cybersecurity.

During the first year of the project, we focused on minimizing the footprint imposed by Windows so that we could maximize use of resources on hardware to launch a large number of virtual machines per physical host. We also demonstrated proof-of-concept work in networking the VMs together on a cluster of commodity machines built for this purpose. We ended up successfully launching 65,000 instances of Windows VMs in an isolated network, in which each subsequently downloaded and executed an application.

During the second year of the project, we began work on building custom networks resembling those deployed in real enterprises to enable a more accurate network architecture. We began developing techniques for visualization and behavior analysis

During the third and final year of the project, we rewrote the VM launching configuration tool from the ground up, consolidating the disparate tool set written as proof-of-concept and using lessons learned to make it more usable and efficient. The resulting tool, "minimega," has been distributed with an open-source license and is being used by multiple projects internal and external to Sandia. Additionally, techniques for efficient categorization and visualization of network traffic have been conceptualized and developed into a web-based visualization tool for high-level analysis of network interactions.

Summary of Accomplishments:

We developed proof-of-concept work to efficiently launch VMs of various operating systems to maximize use of existing resources, built a test bed for standing up virtual networks, developed concepts and software for networking the VMs together in arbitrary topologies, and developed techniques and software for analyzing and visually representing the high volumes of inter-node traffic.

The concepts and software resulting from this work have been used by various other projects at Sandia for follow-on research and development. Minimega, the primary resulting tool for launching and configuring large numbers of VMs in a cluster environment, has been distributed with an open-source license, available at http://minimega.org/.

Significance:

The work relating to virtualization and traffic analysis in this project is, in many ways, pioneering, and the techniques and tools produced from this project will enable scientists to be informed about network activity and attacks and to take action according to their observations, both in a controlled environment and potentially in the real world. We believe this will allow additional insights into cybersecurity and lead to an Internet that is more understandable, defendable, and resilient to attack.

Relational Decision Making

151374

Year 3 of 3
Principal Investigator: L. E. Matzen

Project Purpose:

Real world planning, reasoning, and decision making require an ongoing process of mentally constructing and testing possible scenarios. This process requires: 1) binding together arbitrary collections of items, locations, and events, 2) holding multiple scenarios online simultaneously, 3) comparing between these scenarios, 4) selecting the preferred scenario, and 5) planning and executing behaviors. The goal of this project is to focus on how the brain constructs and compares alternative scenarios constructed from configurations of items. Previous research has implicated the medial temporal lobe of the brain, and specifically the hippocampus, in a mental construction system that binds together arbitrary, accidental, and heterogeneous relations between stimuli to support both declarative memory and online representation. Based on our previous research from reconstruction experiments in participants with hippocampal damage, we have developed a non-linear dynamical model of hippocampal function. This model can bind together items and relations, and unlike previous models, can update and recombine representations to construct novel scenarios. The constraints produced by these representations often result in improved performance, but sometimes representational constraints can result in systematic decision making errors. Our goal is to apply this model to the planning, reasoning, and decision-making captured by our reconstruction experiments to help to understand how this process of mental construction works, and under some circumstances, fails. The project is in collaboration with the University of Illinois at Urbana-Champaign.

Summary of Accomplishments:

1) Developed a new experimental paradigm for testing memory for flexible configurations

2) Developed a unique reconstruction paradigm to gain better insight into participants' decision-making strategies and representations.

3) Developed an extensive suite of novel analytics to identify:
   - Performance accuracy with respect to chance
   - Performance accuracy with respect to other possible configurations
   - Performance accuracy with respect to the target of reconstruction
   - The level of constraint present in baseline pseudorandom performance
   - The level of constraint present in participants' behavior
   - How participants used these constraints to guide their performance
   - The effect of different stimulus domains on performance (e.g., spatial v. object)
   - Similarity of participants' reconstruction
   - Number of elements participants was able to treat as single items, degree to which items were chunked, and the size of the chunks in question

Significance:

This research explored cognition in complex situations where the working memory (WM) system is overwhelmed, such as situations where individuals must rapidly respond to complex and high stakes events. When WM is overwhelmed, processing shifts to slower, less accurate, but far less capacity-limited long-term memory systems. This research developed new methods to measure what sort of "compression" this entails, and gathered data on the kinds of informational shortcuts that occur to maintain high levels of performance when perfect performance is impossible. This research provides critical insight for how exposure to overwhelmingly complex tasks and problems impact decision making, creativity, and memory.

Refereed Communications:

P.D. Watson, J.L. Voss, D.E. Warren, D. Tranel, and N.J. Cohen, "Spatial Reconstruction by Patients with Hippocampal Damage is Dominated by Relational Memory Errors," *Hippocampus*, vol. 23, pp. 570-580, July 2013.

Hybrid Optics for Broadband Optical Systems

155554

Year 3 of 3
Principal Investigator: J. Choi

Project Purpose:

Optical payloads are designed and fabricated to perform in harsh thermal and radiation environments. These unique environments limit the choice of optical materials, as they need to be radiation resistant, withstand mechanical forces, and have broad spectral transmission. The limited number of radiation resistant optical materials removes degrees of freedom to correct chromatic aberration. Chromatic aberration refers to different colors of light focusing at different positions, resulting in broadband systems to appear out of focus except at one wavelength. The effect is caused by dispersion — the material separating different colors of light in different angles. Using more than one glass material enables multiple colors to be brought into focus at the same position. However, with the small number of available materials, the optical engineer is often forced to add more lenses to the optical design to achieve a high performing system. The result is that optical systems tend to be heavy, more sensitive to alignment errors and complex with many optical and mechanical elements. Diffractive optical element (DOE) is a fine periodic structure that causes dispersion of light, the degree of which can be tailored by the design of the periodic structure, independent of the material properties. Hybrid lenses — lenses with a DOE patterned into one of the surfaces — are starting to find their way into various systems. Due to efficiency and manufacturing challenges, use of these elements has generally been restricted to longer wavelength and narrow bandwidth systems. Current state-of-the-art hybrid lenses do not meet the performance demands of space-based remote sensing systems, where high efficiency and broadband operation are important. An innovative solution to expand the working bandwidth of DOEs would push the design trade space beyond what is currently possible as hybrid systems have the potential to require fewer materials, reduce size and weight, and reduce mechanical and alignment tolerances.

The goal of this project was to explore methods of overcoming bandwidth limitation of diffractive optical elements and to develop a diffraction efficiency modeling capability for broadband diffractive designs.

Summary of Accomplishments:

We demonstrated excellent image quality and transmission of diffractive elements by successfully designing and building a narrowband hybrid optical system. We also identified an important characteristic of diffractive elements, which is that they increase the secondary spectrum of an optical system. We studied two methods of expanding the spectral diffraction efficiency of diffractive elements and developed diffraction efficiency modeling tools and utilized them to design, fabricate, and test the two broadband designs. The diffraction efficiency model of the harmonic diffractive design predicted a periodic efficiency that spans over a wide range of wavelengths, while the model for the multilayer diffractive design predicted a continuously broadened efficiency curve but over a smaller range of wavelengths compared to the harmonic diffractive. Both broadband designs, requiring dimensions approaching fabrication limitations, were fabricated on fused silica and calcium fluoride. The diffraction efficiency of the two broadband diffractive elements were measured and compared to model-based performance predictions. The harmonic diffractive element design was measured at four wavelengths in the visible and from 700nm to 1000nm in increments of 10nm. The multilayer diffractive element was measured at four wavelengths in the visible. Test results showed both broadband elements to follow the general pattern of the modeled efficiencies. The harmonic diffractive design closely matched the location of the peaks predicted by the model and showed measured peak efficiencies of approximately 90% and troughs of about 40%. Results for the multilayer diffractive element also displayed the general shape of the predicted model with the efficiency at a wavelength near the designed peak differing by about 5%. We successfully developed and validated the diffraction efficiency-modeling tool for broadband diffractive elements.

Significance:

Diffractive optical elements have the potential to reduce the size, weight, and complexity of optical systems. However, conventional diffractive elements are limited in the working spectral bandwidth and Sandia lacked the modeling competency for broadband diffractive elements. We developed a diffraction efficiency modeling capability for broadband diffractive elements and have successfully validated the model by fabricating and testing the broadband designs. We applied the diffraction efficiency test method developed in this project to Sandia's next generation optical system. The broadband diffractive element model will be used to analyze the feasibility of using diffractive elements in future optical systems.

Refereed Communications:

J. Choi, A.A. Cruz-Cabrera, and A. Tanbakuchi, "Practical Implementation of Broadband Diffractive Optical Elements," in *Proceedings of the SPIE 8612, Micromachining and Microfabrication Process Technology XVIII*, March 2013.

Identifying Dynamic Patterns in Network Traffic to Predict and Mitigate Cyberattacks

155799

Year 3 of 3
Principal Investigator: J. D. Wendt

Project Purpose:

The purpose of this project is to improve cyber defenses against social engineering attacks. For attackers to craft personalized phishing (spear phishing) attacks, targeted web-based research, including research regarding Sandia web sites, will occur to identify appropriate targets. In this project, we work to visualize and analyze visit patterns to our web pages that may signal such pending attacks.

Summary of Accomplishments:

We developed various tools in support of cybersecurity analysts searching through web logs looking for potential spear phishing reconnaissance. We developed a new visualization system for finding a "big picture" view of recent visit activity and comparing specific users to overall trends. Furthermore, we developed a triaging system to help analysts quickly identify which activities seemed the most suspicious.

Significance:

The focus of this work was research to expand the analysts' potential toolkit. To that end, we developed several proof-of-concept analyses and sample tools. By sharing our results at several external venues and with external visitors, we have also spread our concepts and ideas into other government organizations.

The key R&D accomplishments have implications for the general S&T community and the national security mission areas. Spear phishing has shown itself to be quite effective at introducing malicious software that bypasses conventional cybersecurity systems; this work created new defenses against these tactics.

Alternative Waveforms for New Capabilities in Radar Systems

155802

Year 3 of 3
Principal Investigator: R. M. Naething

Project Purpose:

Synthetic aperture radar (SAR) imaging systems achieve high resolution in range by transmitting very high bandwidth waveforms. The radar's high bandwidth channel can also be used to transmit and receive information at very high data rates. The principal goal of this work is to research and develop means of allowing existing radar hardware to perform communications.

Summary of Accomplishments:

We developed several novel algorithms that enabled new features for our radar systems. An invention disclosure has been submitted for one of these novel algorithms.

Significance:

The algorithms developed in this project provided a significant performance benefit over the previous state of the art and will enable new modes and capabilities for Sandia's SAR imaging systems.

Improving Shallow Tunnel Detection from Surface Seismic Methods

156137

Year 3 of 3
Principal Investigator: N. Bonal

Project Purpose:

The purpose of this project is to improve detection of small, shallow cavities using seismic methods and to understand the effects pore saturation around cavities has on seismic wave propagation. According to theory, seismic methods should be able to identify cavities. The high impedance contrast between the rock (fast velocity, high density) and the air (slow velocity, low density) should produce strong reflections and refractions off the cavity wall. In practice, however, cavities are not always easily detected by traditional seismic reflection and refraction methods. Many cavities are located in near surface materials. The effects of pressure and other properties in the near surface are rarely investigated, and therefore, poorly understood. Changes in pore saturation, fracturing, and stress near the wall of the cavity may decrease the impedance contrast and diffuse the rock/air interface. The factors may have a greater effect in near surface materials than in deep competent rock. Therefore, we investigated the effects of cavities in the near surface environment. To determine the impact of these effects on seismic waves, we first sought to understand the hydrological processes in the medium surrounding the cavity, a shallow tunnel in this case. We simulated flow through the vadose zone to provide insight into how a cavity alters natural saturation. Next, we examined how this saturation impacts seismic velocities. Finally, we used a wave propagation code to propagate seismic waves through the models and the results were used to analyze the effects of the cavity itself and the effects of the altered material around the cavity. Also, signal processing techniques including reverse time migration (RTM) and surface wave diffraction were developed, which may be more robust than seismic reflection and refraction for detecting cavities.

Summary of Accomplishments:

We designed hydrology models representing real world conditions of small, shallow tunnels in a desert environment. The tunnels were modeled at three different depths relative to the water table and with and without a “halo” for a total of six different models. The halo is an area of higher hydrologic conductivity around the tunnel to represent actual fracture and stress conditions in near surface materials. We discovered that the hydrology response to a no-halo tunnel increases the spatial area of velocity disturbance by approximately an order of magnitude compared to the spatial area of the tunnel without considering changes in saturation. The effect when including the halo region further increases the entire footprint. The spatial area impacted when considering changes in saturation due to the presence of a tunnel with a halo is significant for all cases relative to the water table. Minor changes are also observed for no-halo cases. We learned that the halo area has a more significant impact on seismic waves than the void itself. So identifying altered material properties may be a better way to locate cavities than trying to locate a void within the material. Additionally, we improved signal-processing techniques such as reverse time migration and surface wave diffraction that do not rely on reflections and refractions form the cavity wall. These techniques have successfully located tunnels in synthetic data. Testing with real data still located the cavities but results were more ambiguous due to lower signal to noise ratio in the real data.

Significance:

This work enabled national security missions by providing insight for improved acquisition, processing, and analysis of seismic data to locate cavities. This work advanced the frontiers of science in several ways. First, hydrological modeling provided realizations of the effects of cavities on saturation of the surrounding material. Second, this work has shown that significant changes in seismic waves can be observed and used to detect cavities, especially when monitoring for new or enlarged cavities. Finally, the knowledge base of the technical workforce has been enhanced by improving signal processing techniques and increasing understanding of limitations of techniques used to locate cavities.

Refereed Communications:

N.D. Bonal and S.L.E. Desilets, “Assessment of Saturation Changes around Cavities and the Impact on Seismic Waves,” in *Proceedings of Environmental and Engineering Geophysics*, 2013.

N.D. Bonal, “Seismic Data Features Related to Tunnels,” in *Proceedings of the Joint Meeting of the Military Sensing Symposia (MSS); Battlespace Acoustic, Seismic, Magnetic, and Electric-Field Sensing and Signatures (BAMS) Session B12*, October 2012.

C.A. Zelt, S. Haines, M.H. Powers, J. Sheehan, S. Rohdewald, C. Link, K. Hayashi, D. Zhao, H-W. Zhou, B.L. Burton, U.K. Petersen, N.D. Bonal, and W.E. Doll, “Blind Test of Methods for Obtaining 2D Near-Surface Seismic Velocity Models from First-Arrival Traveltimes,” *Journal of Environmental and Engineering Geophysics*, vol. 13, pp. 183-194, 2013.

Dynamics of Point Source Signal Detection on Infrared Focal Plane Arrays

156138

Year 3 of 3
Principal Investigator: G. Soehnel

Project Purpose:

We will develop a model that describes the effects of charge diffusion and optical blooming on the point source response of infrared (IR) focal plane arrays (FPAs). Optical measurements on current systems indicate modulation transfer functions (MTFs) are incorrect due to unknown effects at the FPA pixel level. Studies observing these phenomena produced by bright point sources on visible (Silicon) FPAs are underway. The effects on IR FPAs are more severe but also less understood theoretically and much more difficult to characterize experimentally.

We will, for the first time, generate sub-pixel stimulus and develop models to describe the optical and electrical blooming occurring within the IR photodiodes and arrays as a function of spot intensity, wavelength, position, boundaries, and motion. A complete understanding of any unknown detector or read-out based anomalies will be gained by the following experimental scenarios: 1) a single sub-pixel spot, 2) dual spots resembling closely spaced objects, and 3) a bright spot with a controllable background. Measuring the response of a sub-pixel spot on an optical system and/or a detector is a notoriously difficult problem. To achieve our objectives, we will leverage recently acquired test hardware and test methodology developed for visible FPAs. The longer wavelengths, liquid nitrogen operating temperature, and the additional layers and materials present in the IR FPAs will present additional challenges. The results, however, will increase our understanding of IR FPAs and provide advanced knowledge for improved operational performance.

Summary of Accomplishments:

We built what is, to our knowledge, the most advanced infrared spot scanning measurement station in the nation. The quality of the point spread function, saturation, and blooming measurements performed with the spot scanner was very good. We learned precisely when the onset of blooming occurs which was previously unknown. In addition, the charge diffusion simulation turned out to be very accurate. It is unique in its approach, and results agreed very well with lab data from the spot scanner. We analyzed the trade space of FPA pixel designs including pixel pitch, absorber layer thickness, and mesa structures. This yielded some valuable insights on the tradeoffs when considering pixel designs. The main body of work simulating and measuring mercury cadmium telluride (MCT) FPAs resulted in a publication in Applied Optics. In addition to the MCT FPAs, the spot scanner was used to test Sandia-fabricated nBn FPAs. This uncovered an important relationship between the flux, cross talk, and bias on the detector that was previously unknown. A point source can locally de-bias the array causing far more crosstalk than normal unless there is sufficient bias applied to overcome the effect.

A number of other investigations were performed using the spot scanner. The precise translations of the stages were used to produce shifted images on the FPA to study image registration techniques. A study was performed to exploit the ripple readout property of the FPAs in order to observe time varying signals on the order of the row time rather than the frame time. Finally, heavily saturated spot scans were performed that provided an indication of the spatial variations in the carrier lifetime.

Significance:

The advanced capabilities of the spot scanner have allowed us to characterize point source related anomalies on the FPAs. This has led to several re-tunings of the FPAs that have significantly improved mission performance. This has led the program to fund developing visible spot scanning capabilities as well. The information learned has been so valuable that there are already plans to perform standard spot scanning tests on FPAs for new programs.

Refereed Communications:

G. Soehnel and A. Tanbakuchi, "Simulation and Experimental Characterization of the Point Spread Function, Pixel Saturation, and Blooming of a Mercury Cadmium Telluride Focal Plane Array," *Applied Optics*, vol. 51, pp. 7987-7993, November 2012.

Optical Refrigeration in Semiconductors for Next Generation Cryocooling

157310

Year 3 of 3
Principal Investigator: D. A. Bender

Project Purpose:

Current refrigeration technology for cooling space-based infrared (IR) focal plane arrays and sensors uses mechanical cryocoolers reaching temperatures down to approximately 75-120K. Such systems contain moving parts, which in time can wear out and contain refrigerants that can leak. These properties limit reliability and operational lifetime. Mechanical coolers produce vibrations that can lead to blurring during image acquisition. A balanced assembly minimizes vibrations, but does so at the expense of increased payload mass.

The aim of this research is to investigate challenges in optical refrigeration (or laser cooling) of semiconductors by: 1) leveraging Sandia's capabilities to grow unique highly doped GaAs/InGaP double heterostructures and 2) by partnering with the University of New Mexico (UNM) to spatially resolve the temperature profile of a sample under test in a cooling experiment. Optical refrigeration in semiconductors can potentially provide reliable, vibration-free, low-mass cooling of detectors and optics to <20K, representing a significant benefit for remote sensing applications.

Laser illumination has achieved cooling of dilute gases of atoms or ions resulting in substantial scientific progress. Within the last 15 years, optical refrigeration of solid state systems has advanced rapidly from a slight 0.3 °C temperature change, to achieving cryogenic temperatures with 150 °C of cooling. Optical refrigeration in solids was first demonstrated in 1995 using a rare-earth doped glass. Further refinement of techniques and materials research allowed cryogenic temperatures of 155K to be achieved in ytterbium-doped LiYF4 crystals. The postulated minimum achievable temperature for LiYF4 is limited to 100K. In contrast, direct band-gap semiconductors are predicted to achieve much lower temperatures with greater cooling power densities because the constituent atoms of the host material participate in cooling rather than a small percentage of dopant atoms. However, net cooling of a semiconductor has not been realized. We want to investigate possible routes to achieve this unrealized goal.

Summary of Accomplishments:

This project has achieved a world record in quantum efficiency in GaAs at 99.5%. The importance of this result has meaning in many photonic devices such as LEDs, semiconductor lasers, and solar cells. In short, material grown on this project performs its intended task with 99.5% efficiency. A laser cooling demonstration, however, was not realized due to residual parasitic background absorption. Efforts to reduce background absorption resulted in a record low background absorption in the Urbach tail of GaAs. However, despite this record low parasitic absorption, cooling was not demonstrated because the absorption was not low enough. We have been closer to demonstrating cooling than any other research performed on this material. We were approximately 30 mK away from cooling.

Significance:

With the advanced III-V growth techniques developed on this project, we anticipate applicability to photonic devices whose successful operation is particularly sensitive to quantum efficiency. Examples include photovoltaics and semiconductor lasers. Further, our efforts to reduce parasitic background absorption will hopefully serve as a foundation for a new standard in materials purity for GaAs-based devices.

Refereed Communications:

D. A. Bender, J.G. Cedeberg, C. Wang, and S.-B. Mansoor, "Development of High Quantum Efficiency GaAs/GaInP Double Heterostructures for Laser Cooling," *Applied Physics Letters*, vol. 102, p. 252102, 2013.

C. Wang, S.-B. Mansoor, J. Cederberg, and D.A. Bender, "Accurate Measurement of External Quantum Efficiency in Semiconductors," in *Proceedings of the SPIE*, 2013.

Silicon Photonics for Ultra-Linear RF Photonic Devices and Links

157633

Year 3 of 3
Principal Investigator: C. DeRose

Project Purpose:

Analog electrical radio frequency communication links suffer from susceptibility to electromagnetic interference (EMI), propagation losses which increase with the square root of frequency, and the large weight of copper lines. One way to overcome these disadvantages is with analog radio frequency photonic links (RF photonic links). RF photonic devices offer significant size, weight, and power (SWaP) advantages over traditional microwave components; moreover, RF signals transmitted on an optical carrier are immune to noise from EMI. Traditionally, external electro-optic lithium niobate modulators have been used for electrical to optical signal conversion; however, they suffer from a limited spurious free dynamic range (SFDR) and incompatibility with direct integration of optical photo detectors and complementary metal-oxide-semiconductor (CMOS) electronics.

Silicon offers the potential to create ultra-linear RF photonic devices in a process, which is compatible with rad-hard CMOS electronics and integrated germanium (Ge) photodiodes, a capability that no current RF photonic technology offers. Digital silicon photonic modulators have been demonstrated with power consumption as low as 3 fJ/bit, with an area of only a few $(\text{micrometers})^2$; therefore, it is predicted that RF silicon photonic devices will enable a significant decrease in SWaP for RF systems (e.g., RADAR). RF silicon photonics has the potential to increase system bandwidth by an order of magnitude or more, linearity by nearly two orders of magnitude, and significantly reduce susceptibility to electromagnetic interference.

Summary of Accomplishments:

We designed and laid out integrated photonic mask sets to demonstrate world-class RF photonic devices. We fabricated and tested high power photodiodes, high Q filters and low drive voltage modulators. Furthermore, we submitted four invention disclosures and one provisional invention disclosure and authored one peer reviewed journal publication this fiscal year.

Significance:

By enabling highly linear RF photonics directly on a CMOS compatible platform, RF systems with a significant size, weight, and power reduction will be possible. This may directly impact the future capabilities of many future RF systems including RADAR and satellite-based communications. Early investment in this technology positions Sandia to be a leader in future defense systems research needs.

Refereed Communications:

A.M. Jones, C.T. DeRose, A.L. Lentine, D.C. Trotter, A.L. Starbuck, and R.A. Norwood, “Ultra-Low Crosstalk, CMOS Compatible Waveguide Crossings for Densely Integrated Photonic Interconnection Networks,” *Optics Express*, vol. 21, pp. 12002-12013, 2013.

A High Voltage, High Current Thyristor Stack Command Triggered by dV/dt: An Improved MOS-Controlled Thyristor-Like Nanosecond Closing Switch

158698

Year 3 of 3
Principal Investigator: R. J. Focia

Project Purpose:

The purpose of the project was to develop an alternative high voltage, high current solid-state closing switch based on dV/dt triggering of a thyristor stack. The goals were to exceed the time rate of change of current (di/dt) limitation of thyristor switches and to make them viable options for use in fireset and other pulsed power applications. The approach taken was to demonstrate technology readiness level 4 (TRL 4) using only packaged commercial off-the-shelf (COTS) devices in a hybrid switch.

Summary of Accomplishments

- We demonstrated scientific feasibility of the proposed method to TRL 4.
- We developed a new method for triggering ordinary thyristors for high di/dt applications.
- We identified optimal COTS components for use in a chip level hybrid switch prototype.
- We identified sources for obtaining the device chips to be used in the chip level prototype.
- We identified interest in integration of the new hybrid switch into existing systems.

Significance:

The hybrid switch and thyristor triggering concepts developed in this project allow for a possibly more reliable alternative to a single source solid state switch being used in many fire set applications. The methods developed in this project can be practiced now using COTS components and may allow for advances in using solid state switching in many pulsed power applications.

Explosives Detection with Neutrons from a Short Pulse High Intensity Neutron Source

158700

Year 3 of 3
Principal Investigator: O. Doron

Project Purpose:

We will investigate the use of a short pulse high intensity neutron (SPIN) interrogation source coupled with neutron and gamma ray sensors to find buried explosives. The approach promises a powerful new method to locate buried explosives (i.e. landmines and unexploded ordinance) deeper in the ground, faster, and more accurately than is possible with current methods. The current searching depth and time to find objects with active neutron interrogation technologies is relatively shallow due to two limiting factors, the intensity and duration of the neutron pulse from a neutron generator (NG), and the poor signal-to-noise ratios (S/N). Traditionally, finding explosives in a large area requires many neutrons and a high S/N. However, it is difficult to achieve both of these requirements because as the production rate from a NG increases the S/N decreases.

Preliminary data for SPIN interrogation of fissile material shows that this may provide capabilities that require two orders of magnitude less neutrons and 100 times shorter sample time than state-of-the-art systems, including the associated particle technique (APT). The NG that we plan to use for this work has a pulse width in the 10-nanosecond range vice the microsecond range, which is standard for NGs. The narrow width of the pulse in the proposed NG can be taken advantage of in several different ways, including the increase of S/N, and with technology advancements and narrower pulse widths, time of flight (TOF) measurements will be possible as well. Currently an APT NG can provide sub-nanosecond TOF timing resolution. The neutron and gamma ray detectors that are being proposed for use are highly sensitive and selective of either neutron or gamma rays. The combination of the NG and detectors that will be used for the system will also increase the sampling depth and the probability of locating explosives.

Summary of Accomplishments:

The major accomplishments and conclusions of this work are the following:

- the APT modeling that shows the possible increased finding depth of explosives utilizing an APT NG
- the successful diesel particulate filter (DPF) NG experiments performed in collaboration with National Security Technologies (NSTec), demonstrating a reduction in the time to find explosives with SPIN
- the submission of an invention disclosure
- the establishment of a new neutron generator laboratory capability where neutron interrogation experiments can be executed, such as associated particle technique experiments.

Significance:

The successful DPF experiments demonstrating the reduction in finding time of explosives demonstrate the ability to determine the presence of carbon with one intense pulse of neutrons. This technology may greatly reduce the time to find explosives such as improvised explosive devices (IEDs).

The APT modeling that shows the possible increased finding depth of explosives utilizing an APT NG laid a solid foundation for future work.

An Adaptive Web Spider for Multi-Modal Data

158747

Year 2 of 3
Principal Investigator: J. T. McClain

Project Purpose:

While search capabilities are improving with an increased number of utilities to locate documents and images on the Internet, the task to locate data continues to be manually intensive and relies on astute search abilities. Quickly and accurately locating information is most successful when the user has a priori knowledge about the relevant search terms and domain areas. Typically, the process to locate a document involves iteratively examining the URLs and web pages returned and modifying key terms to hone the search. Searching for images is limited to the metadata a person has associated with the image, and not the image itself. We plan to develop an intelligent web spider (a.k.a. crawler) to automate human search and browsing behavior on the Internet to significantly improve the speed, accuracy, and the comprehensiveness of an Internet search. Such a capability will accelerate the data gathering tasks, thus accelerating the intended information processing, review, or analysis objective.

Acknowledging the value of data content inherent to a picture and the value of the implications of recent advancements in data comparison for text and images is at the core of this innovative project idea. We aim to develop an intelligent web spider with the capability to examine both text and images within a web page or document, as well as the capability to adapt its search strategy using machine learning algorithms. If successful, this automated search capability will allow for more efficient, more accurate, and more comprehensive search results with minimal user intervention. The potential benefit can encompass Internet users across all domains, government industry, academia, and private industry.

Vulnerability Analysis of LTE-Capable Devices

158748

Year 2 of 2
Principal Investigator: J. R. Ford

Project Purpose:

This project developed a method for utilizing digital signal processors (DSPs) to accelerate software-defined-radio (SDR) applications. The chief advantage of SDR is the ability to rapidly develop new wireless receivers and transmitters; however, this flexibility is traded against lower efficiency. This reduced efficiency typically results in the need for more computational capability, which in turn requires more power, generates more heat, and occupies more volume. As a result SDR has made limited inroads into power and/or space constrained applications. In contrast to a general-purpose processor (GPP), DSPs are very well suited to the kind of processing required for SDR.

Most users of DSPs tend to focus on one-off solutions or fixed applications rather than seeking flexibility. This project demonstrated for the first time a DSP running SDR code within the GNU Radio framework (an open-source SDR application) on real-time, streaming data. This accomplishment opens the door to investigating applications where DSP acceleration will provide substantial benefit to existing SDR implementations or enable new, low power SDR capabilities that were previously difficult or impossible on general purpose processors (GPPs), such as implementing a fourth generation long-term evolution base station in GNU Radio.

Summary of Accomplishments:

We designed and demonstrated a DSP coprocessor capability within an open source SDR framework. Our approach yielded a variety of flexible DSP-enabled SDR functions that can be used without having to know how to edit or compile DSP code. This enables the utilization of DSPs in applications where they may enhance performance or reduce power consumption.

We developed benchmarking techniques and quantified the throughput for a variety of SDR-related algorithms. This allows for comparison of DSP performance to alternative implementations so the best approach can be selected for a given application. We have also learned about the tradeoffs between the cost of transferring data to a DSP coprocessor and the benefit of power efficient DSP computation.

Significance:

The result of this project is an ability to create flexible, software-defined radios that are also low power. This will enable new applications of SDR technology in national security mission areas where SDR was previously believed to be too power intensive to be applicable.

System Level Cyber Analysis of Cellular Network Infrastructure

158749

Year 2 of 2
Principal Investigator: B. P. Van Leeuwen

Project Purpose:

Cellular networks play an increasing role in supporting critical government and private information systems. Increased capability and ubiquity of mobile devices (smartphones) is resulting in increasing cyber exploit developments targeting the smartphone and increasingly targeting the cellular infrastructure. We will advance the state of the art in cybersecurity of the cellular infrastructure.

Key factors driving the adoption of smartphones by government agencies are increasing functionality (e.g., beyond voice and texting), processing power and capability of the mobile platforms, and an increasing capability of the cellular infrastructure for data transport. With the increased infrastructure capability comes greater opportunity for cyber exploits resulting from Smartphone operating systems (e.g., Android, iPhone IOS) to manage resources, support a wealth of applications, and manage network connectivity to the cellular infrastructure. Both the infrastructure and smartphone operating systems (OS) are vulnerable to cyber exploit via network connectivity. Classical tactics, procedures, and tools, including botnets and rootkits, used to exploit fixed computer networks are being reemployed to target smartphones. Infrastructure cyber analysis methods and research platforms to assess impacts of cyber exploitation and to assess security measures are far from being satisfied.

The purpose of this project is to create a smartphone network cyber analysis capability and research platform to include smartphone and infrastructure representation. Research to date assesses smartphone hardware and OS for vulnerabilities and mitigation approaches — ignoring smartphone interaction with infrastructure. Infrastructure elements represent an important avenue for attack detection and mitigation because they control and manage connectivity. Our research will result in an analysis capability and research platform that enable analysis of exploit impact on cellular infrastructure.

The infrastructure research-platform will utilize cellular infrastructure models, emulation, and real hardware. Sandia has experience with hybrid research platform capabilities that enable combining domains into a single experiment live, virtual and constructive (LVC) capability. Building on this capability for the cellular infrastructure, our cyber analysis ability will broaden into this increasingly critical mobile communications domain.

Summary of Accomplishments:

In this project, we developed a cellular telecommunication cybersecurity analysis test bed using physical hardware, extensive virtualization and emulated machines, and simulation to answer complex system cyber questions about cellular systems and its interaction with legacy and next generation network (NGN) fixed systems. Our primary research goal was achieved; we demonstrated real, feasible, published attacks on a test bed that realistically represented a telecommunications infrastructure consisting of multiple subsystems. The purpose of the test bed was to identify if the system is vulnerable to cyberattack, creating and validating detection methods of cyberattacks, and assess the strength of security approaches to protect our network system operation. The subsystems include second-generation cellular (2G) with general packet radio service (GPRS) packet data capability, supporting global system for mobile communication (GSM)/GPRS base station connectivity, and multiple Internet protocol multimedia subsystem (IMS) infrastructures for application server connectivity. In our test bed, we successfully integrated realistic telecommunication system protocols and demonstrated some of their weaknesses in an unsecure environment. The primary weaknesses do not necessarily lie with the individual components, but in the overall system-level design.

System-level security vulnerabilities can be difficult to detect. However, using a combination of advanced networking tools and logging analysis techniques, attack characteristics can be revealed. Experimental test beds capable of faithfully representing the system-level interactions and communications are essential for these analysis methods to progress and be refined. In this research, we developed an important and capable cybersecurity analysis and experiment environment (i.e., test bed) to help perform analysis of communication networks and networked information systems. With the advent and move towards all-IP networks and NGN, these types of experiments are essential to understanding the security of future cellular telecommunications systems.

Significance:

This project addressed the asymmetric threats arising from our nation's dependence on information networks and analyzed and developed security approaches that strengthen our nation's information systems. The results of the research produced technologies and capability that provide an enhanced understanding of the security posture of complex information systems, provide information security techniques for the protection of military networks, and provide methods of measuring information security protection and the effects of adversarial activities. The resulting capability enhances cyber analysts' ability to estimate system wide impacts when specific parts of the information system are under cyberattack.

Refereed Communications:

B. Van Leeuwen, V. Urias, C. Glatter, and A. Interrante-Grant, "Testbed for Cellular Telecommunications Cyber Vulnerability Analysis," in *Proceedings of the IEEE Military Communications Conference (MILCOM)*, 2013.

PLC Backplane Analyzer for Field Forensics and Intrusion Detection

158752

Year 2 of 2
Principal Investigator: J. Mulder

Project Purpose:

The purpose of the project was to develop a backplane analysis system to examine communication between programmable logic controllers (PLC) modules. This analysis will enable field forensics, firewalling, and anomaly detection.

Critical infrastructures, such as electrical power plants and oil refineries, rely on PLCs to control essential processes. State-of-the-art security cannot consistently detect attacks on PLCs at the hardware or firmware level. This renders critical infrastructure control systems vulnerable to costly and dangerous attacks.

WeaselBoard is a PLC backplane analysis system that connects directly to the PLC backplane to capture backplane communications between modules. WeaselBoard forwards inter-module traffic to an external analysis system that detects changes to process control settings, sensor values, module configuration information, firmware updates, and process control program (logic) updates.

WeaselBoard provides zero-day exploit detection for PLCs by detecting changes in the PLC and the process. An invention disclosure was filed for the WeaselBoard approach to PLC monitoring.

Summary of Accomplishments:

We built the WeaselBoard, a device that connects to modular PLCs, to address the threat of low frequency, high impact attacks from sophisticated adversaries that use zero-day attacks against PLCs. By connecting directly to the PLC backplane, WeaselBoard has access to all traffic at a low (hardware) level, and can detect the effect of exploits against PLCs as soon as the state of the PLC changes, instead of after serious damage has occurred.

WeaselBoard introduces a new capability for PLC monitoring, and has applications for real-time monitoring of high assurance process control systems, forensics as part of an incident response investigation, and periodic system audits and maintenance.

Significance:

Industrial control system (ICS) components receive little attention as an asset requiring security monitoring. There is a critical need to inspect and monitor PLC hardware and firmware, and create an assurance platform for responding to attacks as these systems scale up in the future. Millions of dollars in equipment damage and lost uptime can be prevented by early detection.

SAR and Multispectral SWaP Reduction via Compressive Sensing

158753

Year 2 of 2
Principal Investigator: D. Thompson

Project Purpose:

Air- and space-borne sensing platforms are designed to collect data of increasingly greater sophistication while reducing size, weight, and power (SWaP) requirements. Compressive sensing (CS) is a new sampling theory that offers a unique design paradigm to reduce SWaP: it allows imaging from dramatically fewer measurements than traditional sampling. CS theory opens up new design concepts not possible with traditional paradigms. For example, a recent upgrade of the European Space Agency (ESA) Herschel/PACS (Photoconductor Array Camera and Spectrometer) instrument applied CS in order to reduce onboard computational burden, decouple onboard compression from on-ground image reconstruction, and to produce novel image products enabled by the unique characteristics of CS measurements. While the benefits of CS have been studied in many problem domains, its rigorous application to aerospace sensing platforms for national security missions is still nascent.

In this project, we will investigate how CS may reduce SWaP requirements for air and space platforms, with an emphasis on CS for synthetic aperture radar (SAR) images and for multispectral images. Our analysis and algorithms will utilize real data, drive towards mission objectives, and will help Sandia understand the novel design space that CS offers. Specifically, our research will evaluate tradeoffs between onboard and on-ground processing, using CS measurements to simultaneously reconstruct multiple image products and develop custom algorithms that approach near-real-time image delivery. The research will result in an understanding of the CS design space for SAR and multispectral sensors, algorithms to leverage novel designs in that space, and publications that document designs with experimental results.

Summary of Accomplishments:

For multispectral imagery, we demonstrated asymmetric compression/decompression and were able to show that it compares favorably to other methods studied recently in another project. We demonstrated a proof of concept for compressive background removal in multispectral imagery and tested the performance of target detection with varying levels of measurement compression.

For SAR, we collected one of the first-ever real datasets of compressive phase histories to use in our experiments. We demonstrated good results in reconstruction of SAR imagery from data under sampled by a factor of two and of ground-moving-target-indicator (GMTI) range/Doppler maps from data under sampled by factors of up to 10 and 20. We have further reconstructed SAR imagery and GMTI range/Doppler maps from the same compressive phase histories. We also demonstrated some results in charged coupling device (CCD), but demonstrated more of the challenges of CS CCD than good results.

Our university partner demonstrated a novel endoclutter GMTI target detection scheme using jittered low-rate one-channel data (a data set that traditionally could do exoclutter GMTI at best).

Significance:

The most significant result is the ability to create SAR imagery and GMTI products from the same pulses without the huge data sets or huge data rates required by other methods of simultaneous SAR/GMTI. This capability does need further development before it could be inserted into a near-real-time system. There could also be significant applications in future multi-spectral sensors or SAR or CCD imaging modes, but these require additional enhancement before they would be ready for a real system.

Two-Color nBn FPA

158754

Year 2 of 3
Principal Investigator: J. K. Kim

Project Purpose:

The purpose of the project was to develop and demonstrate two-color nBn photodetectors as well as scalability of mid-wave infrared nBn to > 1k x 1k arrays. We have successfully demonstrated two-color operation of nBn photodetectors in the short-wave and mid-wave infrared bands with dark currents meeting original specifications. We have also successfully demonstrated the scaling of mid-wave infrared photodetector arrays to 2k x 2k, using field-stitched stepper lithography.

In addition, we have demonstrated the highest performance in nBn photodetectors as measured by the dark current and the responsivity. These qualities, as well the radiation hardness, were independently verified by a government laboratory. Furthermore, the parasitic pixel perimeter current was eliminated, which resulted in efficient scaling to high-density detector arrays.

We have communicated our technical advances to various government agencies and laboratories privately and in public to maximize the impact and utility of our work.

Advanced Imaging Optics Utilizing Wavefront Coding

158755

Year 2 of 3
Principal Investigator: R. Boye

Project Purpose:

The development of small, high performance payloads has led to extreme design challenges for optical designers working on remote sensing systems. Invariably, traditional optical design is forced to consider well-known tradeoffs and must sacrifice optical performance to meet increasingly more stringent system requirements. The large operational temperature ranges result in significant changes in focus. Compensating for this focal shift is difficult and often requires active temperature or focus control, which is an expensive strategy from a system point of view. Our planned solution is the application of wavefront coding which has been shown to provide a new dimension in optical design flexibility. The use of a properly designed phase mask could be used to significantly reduce the sensitivity of the optical system to thermally induced focal changes removing the need for other expensive athermalization strategies. In addition, the use of a phase mask in the pupil of the imaging system has been shown to provide a means for extending the depth of focus (DOF), reducing the number of lens elements, or relaxing fabrication/assembly tolerances. Wavefront coding was first introduced specifically as a technique for increasing the DOF of a conventional camera. Remote sensing systems have different requirements than conventional photography (e.g., thermal environment and spectral range) and the intent of this program is to demonstrate the potential of wavefront coding for these applications. We plan to demonstrate advantages, such as extended spectral range or reduced system size, available through the use of wavefront coding. Current modeling work will be augmented by empirical validation. Phase plate implementation and experimental image capture and analysis will provide the necessary foundation for the design of a more relevant demonstration.

Nanoantenna Enabled Focal Plane Array

158756

Year 2 of 2
Principal Investigator: D. W. Peters

Project Purpose:

The goal of this project is to demonstrate a revolutionary approach to integration of optical elements with the focal plane array (FPA), using plasmonic nanoantennas. The nanoantenna allows incorporation of functionality onto the FPA itself and also can improve detector sensitivity and optical quality. This architecture works across wavelength bands, and we intend to demonstrate in the mid-wave infrared (MWIR, 2-5microns) and the long-wave infrared (LWIR, 8-12microns). It is also independent of active material. We will use InGaAsP-based material; however, the technology may be used for HgCdTe detectors also. We will incorporate a nanoantenna directly onto the FPA surface as close to the absorbing layer as possible.

The nanoantenna converts incoming light to concentrated surface waves with no reflection, thus eliminating antireflection coatings. These concentrated fields allow for a reduction in active material, as only a thin layer of active material is needed due to the concentrated fields. This reduction of material lessens the dark current, allowing higher operating temperature and a decrease in cooling load.

The nanoantenna may be designed differently for each FPA pixel, allowing spectral bands and/or polarization data to change from pixel to pixel, taking on the filter wheel's current functionality. Moreover, this new architecture would allow near 100% fill factor of active area in each FPA pixel, thus improving the optical performance of the detector.

Satellite system designs are driven by optical requirements, which are often due to limitations of the FPA itself. The requirement to operate over a broad spectral range while also being able to look at narrower spectral bands and polarizations leads to complex optical systems, while multiple FPAs require energy-hungry cooling systems. This complex system drives satellite size and power requirements. Reduction of the optical complexity and a reduction in cooling capacity would reduce satellite size, weight, power, and cost.

Summary of Accomplishments:

This project developed a design methodology for infrared detectors using nanoantennas. This design used rigorous coupled wave analysis, finite difference time domain, and other numerical codes. In addition, a circuit model approach allows for quick analytical design and has led to greater understanding of the fundamental mechanisms.

Fabrication of these devices involves growth of a thin epitaxial layer (a few hundred nanometers) of III-V semiconductor materials on a sacrificial substrate. This thin layer must then have metal applied to both sides. This is a non-trivial process with many steps. We developed different processing paths in parallel and believe we have a process that will allow the fabrication of nanoantenna-enabled detector arrays. These processing steps were developed for nbn and quantum well infrared photodetector (QWIP) structures. These structures allow us to make detectors in the mid-wave and long-wave infrared.

Initial testing of the QWIP devices demonstrated that our simulations matched experimental results. The QWIP structure that was tested was not optimized for a Nano antenna, therefore, a large space for optimization and improved performance is available.

Significance:

The nanoantenna-enabled detectors that we are striving to demonstrate have the promise to improve detectors across the infrared spectrum. While primarily an improvement in sensitivity, there are also potential improvements in areas such as crosstalk, electromagnetic interference reduction, angular tolerance, and speed.

In addition, we developed a greater scientific understanding of the interaction of the incident infrared radiation with the Nano antenna and the underlying active detector material. We also developed a suite of processing steps to fabricate this and other devices.

Training Adaptive Decision Making

158764

Year 2 of 3
Principal Investigator: R. G. Abbott

Project Purpose:

Military personnel must make consequential decisions in complex situations where the outcomes of alternative actions cannot be anticipated with confidence, and changing circumstances may cause a good decision today to become a bad decision tomorrow. Adaptive decision making remains an ill-defined concept, with little certainty of what makes decisions more or less adaptive. Without a scientifically grounded, principles-based approach for engineering training solutions, military leaders must rely upon thoughtful intentions, and some measure of faith, that their solutions are producing the desired outcomes (i.e., personnel capable of making effective decisions despite ambiguous, continually changing conditions).

Sandia's R&D addressing cognitive elements of training have focused on after-action review (AAR). While valuable, AAR is inherently a retrospective approach, with inherent limitations. There is a need to expand the scope of these capabilities to include all phases of training, beginning with instructional design. A recent project undertook a series of experiments to identify the factors that underlie effective adaptive decision making. While the resulting model has accurately predicted behavior for laboratory tasks, further research is necessary to translate these findings into technologies ready for operational settings. This project provides the essential bridge to convert scientific accomplishments into operational impacts. If successful, adaptive decision making will be transformed from a nebulous, yet important, concept into a formally defined, measurable attribute of individuals and teams. Furthermore, a scientifically grounded foundation will emerge for engineering training technologies that assess the effectiveness of adaptive decision making, provide relevant performance feedback, and manipulate training content to improve decision making performance.

A Complexity Science-Based Framework for Global Joint Operations Analysis to Support Force Projection

158765

Year 2 of 3
Principal Investigator: C. R. Lawton

Project Purpose:

The national defense enterprise constitutes a complex adaptive system-of-systems (CASoS) which coordinates the acquisition, planning, development, and deployment of national assets to accomplish effective global force projection. The military is undergoing a significant transformation as it modernizes for the information age and adapts to include an emerging asymmetric threat beyond traditional cold-war-era adversaries. This current and future operating environment will require us to cast global force projection in the broader context of a CASoS. The DoD must coordinate countless factors over a short period of time, including civilian leadership objectives, budget limitations, and adaptive adversaries, to determine the optimal tradeoffs of resources and capabilities to accomplish national security missions.

This project intends to develop an enterprise-modeling framework, which will leverage Sandia's capabilities in DoD system-of-system (SoS) and CASoS modeling and engineering for capability analysis and design of alternatives. This framework and constituent modeling objects will push the science of large-scale modeling and simulation, distributed/parallel computing/simulation, high performance computing, uncertainty quantification, and large scale optimization techniques.

In this past year, significant progress was made towards developing a scalable framework that allows for simulation of future threat and operating environment scenarios that couple with future requirement/capability evaluation at the enterprise level. Past year specific accomplishments include prototyping and calibrating an agent-based global multi-nation state simulation that allows for uncertainty quantification of ranges of possible future operating environments as well as a Java-based stochastic optimization that will assess capability at the operational level. This enterprise framework will be applied against one or more use cases (e.g., Pacific Command - PACOM, Africa Command - AFRICOM, etc.) so that real world application considerations can be identified and documented.

Validating Agent-Based Models through Virtual Worlds

158766

Year 2 of 2
Principal Investigator: J. Whetzel

Project Purpose:

As the US continues its vigilance against distributed, embedded threats, understanding the political and social structure of these groups becomes paramount for predicting and disrupting their attacks. Agent-based models (ABMs) serve as a powerful tool to study these groups. While the popularity of social network tools (e.g., Facebook, Twitter) has provided extensive communication data, there is a lack of fine-grained behavioral data with which to inform and validate existing ABMs. Virtual worlds, in particular massively multiplayer online games (MMOG), where large numbers of people interact within a complex environment for long periods of time provide an alternative source of data. For instance, Game X is an exploration-based MMOG where players interact in an open universe: conducting battles, forming guilds and trading in a market economy. Strategies employed by player groups surprisingly reflect those seen in present-day conflicts. In this project, we will address the need for fine-grained behavioral data by acquiring and analyzing game data from Game X and potentially other virtual worlds.

The goals of this project are: 1) devising toolsets for analyzing virtual world data to better inform the rules that govern a social ABM and 2) using virtual worlds as a source of data to validate ABMs established for analogous real-world phenomena. Our work will develop tools to parse, analyze, and visualize patterns of group behavior to compliment social modeling efforts where a significant lack of detailed examples of observed phenomena exists. While there has been work on studying data from virtual worlds, this project is cutting-edge in its emphasis on informing and validating ABMs. Furthermore, this research expands the capabilities in understanding the effect public communication has on group formation and potential actions. If successful, this project will establish Sandia as a leader in using virtual worlds to facilitate the study of complex human interactions.

Summary of Accomplishments:

We explored the expression-to-action (E2A) problem: given data on how people communicate within a publicly accessible forum, can we predict how these communications influence group formation and behaviors. For investigating the E2A problem, we correlated co-posting behavior of players (e.g., players who comment on each other's posts) to in-world behaviors that would indicate a closer relationship than evidenced merely from the online postings (e.g., frequency of private communications, belonging to same player groups, etc.). We examined how public rancor between two player groups would ultimately lead to an observed combat within Game X between these sparring factions. As well, we applied community detection methods for discovering hidden group formations that differ from publicly viewed relationships and interactions. Results from our research efforts on E2A have been released in several academic publications.

With this research enriching our knowledge of social dynamics of conflicting groups, our work also examined how virtual world data could facilitate in the development and validation of social ABMs. We pursued using the Game X dataset as a comparison against social behaviors previously codified within the behavior influence assessment (BIA), an established ABM framework. We determined that virtual world data shifts from traditional ABM design methodologies due to noticeable differences on the information available for the targeted domain (e.g., human intuition versus perfect information), posing a difficult challenge in using Game

X data to automate the creation of a BIA model. With ABMs rooted in generally accepted theories that govern social behavior, our research shifted at how the virtual world data could test selected theories within a BIA model by having the model predict certain group actions depending upon chosen states of the virtual world.

Significance:

This research constructs a foundation on applying virtual world data for examining national security problems that require a need for deeper understanding on the dynamics of large-scale human interactions. Through studying the relationships formed via online communities and their underlying impact, this research introduces a new capability for examining the nature of hostile groups from the proxy of a virtual world. This work provides new techniques for validating social ABMs through a high fidelity data source, demonstrating how it compliments proven methods for ABM testing. E2A research also provides more possibilities for those exploring the links between public and private behaviors.

Refereed Communications:

K. Lakkaraju and J. Whetzel, “Group Roles in Massively Multiplayer Online Games,” in *Proceedings of the Workshop on Collaborative Online Organizations at the 14th International Conference on Autonomous Agents and Multiagents Systems*, 2013.

K. Lakkaraju, J. Bernstein, and J. Whetzel, “Analyzing Effects of Public Communication onto Player Behavior,” in *Proceedings of the International Workshop on Predicting Real World Behavior from Virtual Worlds IEEE Social Computing*, 2013.

K. Lakkaraju, J. Bernstein, and J. Whetzel, “Do Public Interaction Networks Reflect Private Interaction,” in *Proceedings of the Workshop on Multiagent Interaction Networks at the 14th Autonomous Agents and Multiagent Systems Conference*, 2013.

Quantitative Adaptation Analytics for Assessing Dynamic Systems of Systems

158767

Year 2 of 3
Principal Investigator: J. H. Gauthier

Project Purpose:

The purpose of this project is to create quantitative analytic tools and discover metrics to answer specific questions concerning the efficiency, effectiveness, and adaptability of dynamic systems of systems (dSoS) that are important to national security.

Research will concentrate on four areas:

1) quantifiable adaptation metrics: possible metrics will be defined and evaluated for usefulness. Example adaptation metrics may include the average time interval for a dSoS to successfully change configuration, average cost of the changes, number of systems changed, etc.
2) rules/decisions: research will focus on what rules/decisions should be used by system models to best guide changes in their numbers and interconnections
3) analytics structure: a conceptual architecture involves interconnected system models; additional research will investigate interactions, organizational structure, etc.
4) application to a real world problem: research will focus on military deployment as an adaptive dSoS and what can be learned from modeling it.

The goal for the last year of the project is to complete and exercise a general-purpose analytic tool to evaluate adaptability of dSoS. The tool will be a process-based, discrete event simulator with provisions to incorporate rules/decisions and adaptability metrics. It will be demonstrated on a problem of national security interest. We also intend to finalize the adaptability research and present results at appropriate national security related venues.

Ultra-Stable Oscillators for RF Systems

158768

Year 2 of 3
Principal Investigator: B. L. Tise

Project Purpose:

The purpose of the project is to utilize ultra-stable clocks to improve performance of radio frequency (RF) systems and to develop new waveforms and new processing techniques to further reduce the size and power of RF receivers while increasing performance of these systems. This work stands to benefit a broad array of technologies relevant to numerous laboratory, DOE, and DoD missions.

Moving Target Detection and Location in Terrain Using Radar

158770

Year 2 of 3
Principal Investigator: D. L. Bickel

Project Purpose:

The purpose of the project is to improve detection of moving targets in difficult terrain. We have made good progress developing the antenna and radar hardware for this purpose. The antenna was designed and checkout copies built for preliminary testing. The required radar waveform generation hardware was built and tested. Initial software work to collect the large amounts of data required has begun. Algorithm development work is continuing.

Electronic Battle Damage Assessment (eBDA)

158773

Year 2 of 3
Principal Investigator: J. T. Williams

Project Purpose:

Tactically, one of the greatest impediments to the application of high power microwave (HPM) weapons is the current inability to assess their effect on the intended target, battled damage assessment (BDA). The problem is further complicated since the effects achieved by such weapons can be temporary or permanent and are sometimes not repeatable given minor changes in the engagement scenario. Hence, the BDA tools for non-kinetic weapons, and even kinetic weapons targeting electronic systems, should be based upon on-site intelligence and electronic sensing.

An effective electronic BDA (eBDA) tool should be able to detect system changes based upon electromagnetic observables, assess the operational state of the target system given the detected system changes, and classify the success of the attack. Critical to developing such eBDA tools is the identification of tactically feasible electromagnetic (EM) observables that can be exploited by either active or passive electronic sensing systems. At close ranges, we have successfully identified many such observables in realistic environments. The intent of this project is to develop the techniques to measure state-related electromagnetic observables from relevant target systems at range. The outcome of this effort should be a TRL-5 prototype system that demonstrates effective eBDA principles and techniques.

The effort is extremely challenging and fundamental in nature. Many of the passive EM observables that can be used effectively for eBDA are low power level and clustered with other less relevant emissions and background noise, making detection at range very challenging. In addition, the design of active EM signals that can be used to interrogate a specific target and produce measurable responses that can be related to its state is a relatively unexplored discipline. We intend to investigate the resolution of these issues through the development of proper measurement and signal processing techniques.

Developing Deeply Integrated GPS/INS Navigation System for High Dynamic Applications

158775

Year 2 of 2
Principal Investigator: J. D. Madsen

Project Purpose:

The purpose of this project is to develop algorithms and methods for tracking GPS (global positioning system) signals, including the carrier phase, while the GPS receiver is experiencing high dynamics. This new tracking capability will bring GPS accuracy to a new range of applications. The small weight, volume, and power requirements for GPS, along with this precision navigation capability, make it an attractive solution for many programs. GPS signal tracking has never before been demonstrated in the dynamic range this project seeks to explore. Additionally, this project will explore enhancements and upgrades to the previously developed hypersonic transition receiver (HTR). The HTR was developed under a previous project and provides a test bed for evaluating the high dynamic tracking algorithms. Improved hardware and software will be explored.

Summary of Accomplishments:

We demonstrated signal tracking in a radio frequency (RF) simulation environment that exceeded the stated goals of the project. We learned that prompt inertial navigation system (INS) aiding of the GPS tracking algorithms provides a robust and powerful method for tracking through extreme dynamic conditions. Typically, receivers designed to track under dynamics will track signals when experiencing acceleration on the order of 10Gs, and a 10G/second change in acceleration, or jerk. This research demonstrated tracking in excess of 200Gs and 100G/second jerk during a purely test environment. We also demonstrated 50G track under >200G/second jerk during a more realistic simulated flight test. As part of the study, we reviewed how various error sources and latencies impact the new algorithm's capability to track. Testing revealed the algorithm is robust to anticipated error sources while experiencing extreme dynamics. Furthermore, we were able to expand on previous work done at Sandia to enhance the custom built HTR. The developed GPS receiver now operates in a real world environment under typical GPS conditions. Real world capability was demonstrated via stationary rooftop tracking. The fusion of the developed aiding algorithms and the improved HTR receiver demonstrated the high dynamic tracking capabilities via real time hardware in the loop RF simulation.

Significance:

The resulting GPS tracking capability of this project enhances the national security mission by providing GPS accuracy to a new range of national assets. The work extended the capability of GPS tracking beyond any previous known demonstration, and enhanced Sandia's knowledge and capabilities related to GPS receivers and tracking algorithms.

Structural Kinetic Energy Warhead for Scaled and Multi-Platform Applications

158776

Year 2 of 2
Principal Investigator: L. R. Payne

Project Purpose:

The concept of the kinetic energy penetrator (KEP) warhead is to use the kinetic energy of a high velocity approach vehicle that explosively deploys thousands of penetrating fragments to destroy a target. The explosives deploy fragments in a pattern across a target; the fragments destroy it.

A large mechanical structure is required to support these preformed fragment masses in dynamic delivery environments; this structure takes up weight and volume that could be better used to generate more fragments and disrupts optimal fragment deployment patterns. We plan to develop a compact KEP warhead that eliminates the need for support structure by mechanically bonding the fragments together to create a self-supporting structure. Several concepts for bonding will be investigated. The goal is to create a self-structural system that can maximize packaging efficiency, warhead scalability, and fragment deployment pattern predictability.

Our approach departs from traditional KEP warhead concepts; the concept is to use innovative material sciences and manufacturing processes to create a bonded fragment system to support the warhead itself. Early phases will incorporate subscale testing and cost-effective surrogate materials. The major risk in this concept is whether sufficient structure can be obtained to withstand the mechanical environments of flight while preserving the desired fragment distribution patterns. Additional risks include whether complex KEPs system can be computationally modeled with high enough fidelity to provide adequate design feedback.

Summary of Accomplishments:

We designed and tested several different self-structural KEP packages. Several technologies currently exist that could provide an avenue for future applications; however, only one avenue is currently cost effective. We also discovered several technologies and applications that could become a viable avenue with some modest investment from industry but are currently underdeveloped technologies and the current level of state of the art is insufficient to provide the needed fidelity to make successful prototypes. The bonding methodology used for this project proved its application capabilities by surviving representative shock and vibration testing as well as performing as expected in explosive deployment tests.

A provisional invention disclosure has been submitted through the DOE on the viable bonding applications.

Significance:

This project has been able to reduce the parasitic mass of the KEP warhead concept significantly by removing non-lethal structural members and replacing them with bonded KEP fragments. This relinquishes underutilized mass and volume, resulting in a reduced footprint. This approach has proven its capability to survive the requisite physical environments and still function as intended. This technology could be a replacement for older, or less advanced systems providing increased packing densities with similar or better fragment deployment patterns. It could also serve as the basis for next generation weapons.

Borazine-Based Structural Materials

158777

Year 2 of 2
Principal Investigator: T. T. Borek, III

Project Purpose:

The purpose of this project was to demonstrate model chemistry that could lead to the incorporation of boron into energetic materials. Boron has the highest heat of combustion of the elements that are typically found in pyrotechnics, and access to the energy could provide more energy for energetics and propellants.

Recent theoretical calculations indicate that energetic materials that incorporate boron, in particular borazine-based materials, should have energetic properties that rival the more energetic military explosives.

The synthesis of borazine-based energetic materials has been of interest for the past 50 years, but there has been little progress in this field.

Using a systematic approach to borazine-based energetics, we attempted to synthesize and characterize model compounds that would demonstrate that this class of materials is attainable.

Summary of Accomplishments:

We synthesized a series of borazine nitrate esters; these materials were previously unknown. These chemical compounds were chemically characterized and, in one instance, a crystal structure was obtained, demonstrating the atomic structure of the molecule. We obtained other chemical characterization data that are consistent across this series of compounds. We also obtained thermal analytical data that shows latent energetic content in some of these compounds.

Significance:

This work shows that the syntheses of borazine nitrate esters are possible. This work shows that these borazine-based energetics are able to be synthesized using common techniques and reagents, and have latent energy as demonstrated by thermal analysis. No previous efforts in this arena have been successful.

Refereed Communications:

M.A. Rodriguez and T.T. Borek, "2,4-Bis(Dimethylamino)-6-(Nitrooxy)-1,3,5-Trimethylborazine," *Acta Crystallographica*, vol. E69, p. o634, 2013.

M.A. Rodriguez and T.T. Borek, "6-Chloro-2,4-Bis(Dimethylamino)-1,3,5-Trimethylborazine," *Acta Crystallographica*, vol. E69, p. o309, 2013.

Inferring Organizational Structure from Behavior

158780

Year 2 of 3
Principal Investigator: T. L. Bauer

Project Purpose:

We will advance the state of the art in algorithms for detecting networks by introducing the use of temporal correlations among behaviors, leveraging both information sources and metadata. We will validate the algorithms against two data sets. This will result in new algorithms and technology for applying them.

A lack of real word data sets with both social network and behavioral information (as opposed to poll results, for example) has impeded the development of valid models for inferring social networks. However, newer data sets and recent research suggest that this problem might now be tractable. The rapid increase in crowd-sourced applications like Wikipedia is providing a rich set of data with both a record of behaviors and a set of direct interactions among individuals. Data sets with network ground truth are needed to develop and validate models. This research will advance the state of the art by focusing on temporal correlations in behavior.

The ability to discover organizational structure from observable behavior would address multiple national security problems, such as technology surprise and nonproliferation. However it is itself a basic scientific question. The core capability for doing this is most appropriately developed and validated in the context of scientific investigation before being transitioned to specific use.

We will focus on using implicit evidence, such as two parties editing the same page, editing documents in the same topic, or participating in the diffusion of data in similar points. While none of these examples show direct connections among parties, they do show that the parties are “similar” in certain ways and may also be connected.

Frequency Translation to Demonstrate a “Hybrid” Quantum Architecture

158782

Year 2 of 3
Principal Investigator: D. L. Stick

Project Purpose:

Modern encryption relies on the computational complexity of factoring large numbers with a classical computer. In 1994, Peter Shor developed a factoring algorithm for a quantum computer, one governed by quantum mechanics, which factors numbers more efficiently and threatens to compromise modern encryption. Most experimental work in quantum computing has focused on systems of identical quantum bits. However, a large-scale quantum computer will likely be composed of several types of qubits, with each qubit selected to exploit its advantages for the overall system. Photons are a natural choice for coupling different qubits due to their ability to travel and interface with different systems.

Due to energy structure differences, one qubit type cannot be directly coupled to another of a different type. Instead, one needs a quantum interface to convert the energy (frequency) without destroying the quantum information that the photon is carrying. Using non-linear optics (NLO) and quantum frequency conversion (QFC), we plan to make photons emitted from one ytterbium ion indistinguishable from those emitted by a calcium ion. This will be the world’s first photonic coupling of different species of ion qubits, laying the foundation for coupling drastically different types of qubits, such as ions and quantum dots. If successful, this technology will enable new quantum hybrid architectures.

Converting the frequency of the photon to higher wavelengths also makes it compatible with low loss transmission via telecom fibers. This is an important regime, as the long-lived qubit states of the trapped ion plus the frequency-converted photons constitute a quantum repeater. The absence of a quantum repeater has restricted current commercial quantum communication networks that rely on fibers to 10s of km, limiting their usefulness. A viable quantum repeater would remove this restriction and would be a very important outcome for this work.

Non-Linear Decision Theory Applied to Co-Hosting Analysis for National Security Space Payloads

158784

Year 2 of 3
Principal Investigator: S. M. Gentry

Project Purpose:

Joint space programs aggregate multiple missions onto a single spacecraft or multiple agencies into a single organization. Although the primary motivation for jointness is cost savings, many joint programs have experienced significant cost growth and recently, have motivated space agency leaders to consider disaggregation, or breaking apart joint programs in order to regain cost savings. Motivated by this current interest in disaggregation, we address two research questions: 1) how does jointness induce cost growth and 2) can joint programs be more cost-effectively architected in the future? To address these questions, we use a small-N case study design and a mix of qualitative and quantitative methods. The selected case studies focus on programs for environmental monitoring from low-earth orbit and our central case study is of the National Polar-Orbiting Operational Environmental Satellite System (NPOESS).

Research has progressed on both qualitative and quantitative fronts. In terms of the qualitative research, data collection on the NPOESS program is complete and analysis is in progress. The work is in collaboration with Massachusetts Institute of Technology.

In terms of quantitative research, we have developed a system architecture model that explores a large trade space of options for future environmental monitoring systems in low earth orbit. We plan to use this model to better understand the tradeoffs between mission and agency aggregation versus disaggregation.

Learning From Nature: Biomimetic Polarimetry for Imaging in Obscuring Environments

158785

Year 2 of 3
Principal Investigator: D. Scrymgeour

Project Purpose:

Imaging in obscuring surroundings such as fog, smoke, dust, and under water is one of the most difficult environments encountered on earth. However, many key national security interests rely on communicating and seeing in these obscuring environments, such as helicopters landing blind due to obscuring dust or communicating/imaging through clouds and water. Even modest extensions in imaging ranges in these extreme turbid environments are a technological breakthrough and have wide-ranging impact on turbid-media signaling, imaging, and communications. This project seeks to develop passive optimal polarization vision, utilizing both linear and circular polarization signatures, which has been shown to increase imaging distances three times compared to standard intensity imaging. Because the environmental variables (e.g., imaging wavelength, particle size density, size distribution, and index of refraction) are so diverse, specific optimization for imaging in critical conditions have not been performed. We will systematically develop polarimetry-imaging schemes specifically tailored for obscuring environments crucial to national security applications (clouds, dust, oil plumes) through a combination of simulation and experimental techniques. This will allow the exploitation of polarimetry for tagging, tracking, and locating applications and to improve imaging in turbid media that is of interest to a broad application set including environmental monitoring, underwater communications, and rocket plume detection.

The stomatopod crustacean (mantis shrimp) has evolved an exquisite vision platform and has the capability to see in full polarization. Biologically evolved systems are often supremely adapted to their environment, solving complex problems that maximize visual information while minimizing metabolic energy consumption and signal processing requirements. These biologically evolved systems should be the inspiration for future imaging systems. Findings can be extended to both terrestrial and space-based environmental imaging systems where turbidity is introduced by pollution, smoke, and clouds. This work is in collaboration with the University of Arizona.

Enhanced Methods for the Compression of SAR Video Products

159304

Year 2 of 2
Principal Investigator: J. G. Chow

Project Purpose:

Video synthetic aperture radar (SAR) is a recent technique of persistent SAR surveillance currently employed on some manned aircraft, whereby the intelligence analyst is operating within the aircraft. The trend of manned aircraft being replaced by unmanned aircraft also means that data exploitation is increasingly being handled remotely via constrained bitrate communication networks. The compression of video SAR data is necessary to offer intelligence customers the best quality video SAR for a given allocated bitrate. We will address techniques to improve video SAR compression, the transmission of multiple simultaneous SAR products, and impacts on video quality after repeated encodings. We will also address the compression of 3D SAR point clouds. This new SAR compression paradigm drastically reduces data redundancy and facilitates model-based compression.

Summary of Accomplishments:

We designed preprocessing algorithms to improve the video SAR compression performance over conventional video encoders. The gains and losses in the current video SAR implementations compared to ones using the planned techniques were quantified. We also demonstrated the feasibility of model-based compression using point clouds derived from video SAR data as a potential alternative to the way video SAR is currently exploited and utilized.

Significance:

The results of this project directly enhance the intelligence community's capabilities in persistent surveillance, reconnaissance, and data exploitation. These results are already being applied to some programs. These results should help establish Sandia as a player in unmanned air systems rather than being limited to sensors. The 3D work opens the door for potential new applications for video SAR.

Optimal Adaptive Control Strategies for Hypersonic Vehicle Applications

161863

Year 2 of 3
Principal Investigator: J. M. Parish

Project Purpose:

The purpose of the project is to develop a reliable model-based control strategy for agile flight vehicles subject to large uncertainties and undesirable multi-body dynamic behaviors. Unlike traditional control approaches, model-based non-linear control methods are particularly well suited to construct tractable control designs for highly maneuverable vehicles subject to large aerodynamic uncertainties. In this method, non-linear vehicle dynamics are assumed to be largely "cancelled out" in an inner control loop. However, the unexpected presence of unmodeled dynamics has been shown to cause controllability issues, instabilities, and failures in both simulation and flight of actual vehicles. In general, this undesired behavior results from neglecting key non-linearities in the rigid-body vehicle model typically employed in non-linear control. Some integration of elastic effects into the control approach has been considered for similar types of vehicles, but neither multi-body nor elastic effects have been investigated for this class of vehicle. Thus, control of these more comprehensive vehicle dynamical models remains a challenging, outstanding problem. In this project, we will develop a control strategy for a multi-body dynamic model of a vehicle with consideration of low frequency body elastic modes. This hybrid approach of simultaneously investigating control of both multi-body and structural dynamics is novel for control design for this class of vehicles. This broader view synthesizes existing control methods to enhance the capabilities of advanced vehicle concepts. Furthermore, these improvements will help guide development of future vehicle concepts by providing a more holistic modeling and control approach for assessing performance of candidate flight vehicle designs.

Athermal Spectro-Polarimetric ENhancement (ASPEN)

164670

Year 2 of 2
Principal Investigator: J. C. Jones

Project Purpose:

Polarization is a fundamental optical phenomenon that provides a measurement of surface roughness, shape, and structure, but has yet to be fully exploited for remote sensing applications. Channeled spectropolarimetry (CS) is a hyperspectral polarization measurement technique that requires no moving parts, making it ideal for implementation on moving platforms. Developed extensively over the past decade, CS instruments have been demonstrated in the visible and infrared, both in the laboratory as well as with fielded instruments.

The most challenging aspect of the CS technique is maintaining system calibration. The most robust calibration procedure developed to date involves acquiring a reference polarization measurement, which is used to characterize the CS system. However, due to the effects of thermal fluctuations on CS elements, this referenced-based calibration can often introduce significant errors in the resulting data products if there is a change in the environment between the acquisition of the reference data and data for the unknown target of interest. The simplest workaround for dealing with this calibration drift is to recalibrate the system frequently, often directly before or after every test measurement. This solution can be problematic for field deployments, especially under conditions of rapidly changing environmental conditions, unknown target frequency or location, etc. Due to these calibration-related performance limitations, the potential of CS systems has yet to be fully realized.

This work will focus on demonstrating and testing a new type of CS system that will leverage an athermal crystal technology developed for another application to significantly reduce the thermal calibration errors that can be problematic with CS systems. The ultimate outcome of project success is anticipated to be a proof of concept demonstration of a thermally insensitive CS (TICS) bench top system that requires minimal recalibration, and a preliminary design for a TICS prototype that would be deployable aboard remote vehicles.

Summary of Accomplishments:

This project produced several accomplishments. First, this project designed and demonstrated the first athermal channeled spectropolarimeter based on biaxial crystals. The proof of concept prototype built in the lab provided an improvement by a factor of five in thermal stability over the previous passive state of the art. Next, the project identified and modeled how the athermalization concept could be extended to the thermal infrared using infrared (IR) crystals that provide the necessary crystal symmetries and optical properties. Finally, the initial results were leveraged to produce a design for an infrared imaging spectropolarimeter prototype, capable of capturing a complete spectropolarimetric datacube in a single camera image.

Significance:

The system development work of this project has direct applicability to a number of national security missions that require spectral and/or polarization remote sensing instrumentation. Additionally, this work advanced the field of channeled spectropolarimetry and provided a solution to a problem that affects many channeled spectropolarimeters, and in general other types of polarimeter sensors.

Refereed Communications:

J. Craven-Jones, B.M. Way, M.W. Kudenov, and J.A. Mercier, “Athermalized Channeled Spectropolarimetry Using a Biaxial Potassium Titanyl Phosphate Crystal,” *Optics Letters*, vol. 38, pp. 1657-1659, May 2013.

Investigating Dynamic Hardware and Software Checking Techniques to Enhance Trusted Computing

164671

Year 2 of 3
Principal Investigator: C. Jenkins

Project Purpose:

As the field of determined and increasingly sophisticated adversaries multiplies, the integrity of deployed computing devices comes more into question. Given the ubiquitous connectivity, substantial storage, and accessibility, the increased reliance on computer platforms make them a substantial target for attackers. Over the past decade, malware transitioned from attacking a single program to subverting the operating system (OS) kernel by means of what is known as a rootkit. While computer systems require patches to fix newly discovered vulnerabilities, undiscovered vulnerabilities potentially remain. Signature-based schemes seek to detect malware with a known signature or digital fingerprint. Signature-less schemes seek to detect anomalies within the computer system by understanding normal behavior. Both architectures are typically built on top of existing solutions or paradigms. Furthermore, these solutions tend to utilize mechanisms that operate within the OS. If the OS becomes compromised, these mechanisms may be vulnerable to being disabled.

We plan an approach to designing computer systems that inherently decouples the function of the computer system from its security specification. Instead of preventing and detecting malware attacks by patching code or using signatures (though we can use them as well), our approach focuses on the policy specification of the system and possible graceful degradation of functionality according to the policy as anomalies of security concern are detected. We believe this innovative paradigm uses existing technologies in a novel manner to determine the integrity level of the system. Based on the integrity level, the system may behave differently and/or limit access to data available at a given integrity level.

Mission Capability Analysis Environment for End-to-End Performance Assessment of Space Systems

164892

Year 2 of 3
Principal Investigator: D. P. Woodbury

Project Purpose:

By leveraging its strengths in remote-sensing-component technologies, Sandia has developed analysis capabilities to support high fidelity empirically based simulations and yield verified accurate end-to-end sensor performance estimates of electro-optical infrared (EOIR) systems. Current analysis capabilities, however, are limited only to designed and tested remote sensing assets. Furthermore, this simulation code provides mission-optimization tools only for specific systems based on experimentally determined parameters, which are unknown for envisioned EOIR designs. The combination of required mature sensor characterization inputs and a lack of parameter optimization capabilities for a variety of systems prevent utilization of the existing code for rapid mission capability performance assessments of future EOIR systems. The goal of this project is to develop a target-based design and analysis environment that bridges the gap between literal mission needs and payload design requirements, without which there is a risk of making incorrect investing decisions in future space-based EOIR systems and technologies. The key innovations of the planned analysis environment are: 1) identifying the multidisciplinary set of first-principal physical constraints which couple the mission-critical design parameters of EOIR space systems and 2) exposing this high dimensional, non-linear, mixed discrete and continuous design space for improved parameter selection capabilities to support mission requirements. First-order EOIR system requirements can be based on a finite number of fundamental physical parameters, which provide the backbone of a system's performance characterization. This multidisciplinary set of variables can be partitioned into three sets of parameters which describe the desired mission scenario, the external conditions imposed on that scenario, and the payload design itself. Along with identifying these base sets of critical design parameters, we must also ascertain the physical constraints between these parameters and how parameter uncertainty evolves through these applied constraints. Finally, the performance of the system must be related to specific mission scenarios and detectability metrics must be identified in terms of quantifiable measures of mission success.

Precision Laser Annealing of Focal Plane Arrays

165545

Year 1 of 3
Principal Investigator: D. A. Bender

Project Purpose:

Detectors of optical signals in the visible or infrared (IR) often undergo thermal annealing in manufacturing to allow dopant activation, thermal oxidation, metal reflow and chemical vapor deposition. Thermal annealing is typically done with equipment that heats the entire semiconductor wafer by using a flash lamp, hot plate or furnace. Lasers are also employed with a cylindrical lens focusing a beam into a thin line that is swept across the wafer, homogenizing the surface. These techniques, however, are performed over the entire sensor and do not discriminate between adequately manufactured and defective regions. Ideally, processing techniques would precisely target only pixels or pixel clusters that are "hot" or noisy, while leaving functional pixels and surrounding electronics untouched.

Our intent is to perform laser annealing on detectors after they have been hybridized with readout electronics (ROIC). Targeted laser annealing on packaged focal plane array (FPAs) prior to mission use represents an augmentation to the state of the art thermal annealing and laser procedures currently done during the manufacturing process. Laser annealing can be performed at any point after manufacturing and before mission commencement. If an FPA resides in flight storage or is exposed to damaging radiation for extended durations after manufacturing, laser annealing could be used to restore individual pixels or clusters that may have degraded with time or were substandard to begin with.

The time and cost associated with developing a technique to address handfuls of underperforming pixels is not economical for a volume-based commercial business. However, success in this project constitutes a method to reduce schedule delays by promoting engineering grade FPAs to science grade FPA — a procedure with high commercial value. Additionally, Sandia's mission sometimes requires a few very high performance collection platforms. Making the effort to have the best possible collection capability motivates the development of laser annealing and results in a unique, innovative capability not found in the commercial marketplace.

Computer Network Deception

165547

Year 1 of 3
Principal Investigator: V. Urias

Project Purpose:

The modern approach to computer network defense has led to an assumption that existing networks will likely be compromised. This assertion stems from the idea that the existing defense tools are challenged in defending against today's threats. Enterprises are consistently compromised by multiple classes of adversaries, despite significant amounts of money and effort. As these threats become more aggressive, there emerges a need for different, proactive strategies beyond existing plug-and-play and commercial solutions that exist to date. Research needs to focus on revolutionary and not evolutionary defenses that will affect a broader class of threats and threat vectors.

This project's purpose is to develop, implement, and test a novel computer network operations architecture that enables proactive defense by managing and monitoring the enterprises resource allocations and network flows. The architecture will leverage three emerging concepts: software-defined networks, cloud computing, and deception. It will enable the detection and identification of anomalous access and intrusions, adjust to the dynamic nature of the adversary, and provide a mechanism to discover and react to the adversary's attacks in a methodical and proactive manner.

Electrically Biased Mesh for Electron Patterning

165548

Year 1 of 1
Principal Investigator: K. W. Larson

Project Purpose:

The purpose of this work was to conduct initial research into an enhanced sensing design concept for a fast electron microscope.

Summary of Accomplishments:

We discovered that the system we were considering had a considerably greater performance envelope than we had initially thought. Furthermore, the research significantly reduced the uncertainties so that the cost/performance/risk trade-offs of proceeding to more advanced design phases are attractive.

Significance:

This work was motivated principally to address an acknowledged national security issue via a new method of sensor design that had never been applied to our domain. The outcome of the research exceeded expectations.

Graphene Survivability

165551

Year 1 of 2
Principal Investigator: S. W. Howell

Project Purpose:

The purpose of this project is to understand mechanisms that influence graphene survivability in various environments. The isolation of graphene monolayers in 2004 has spurred an explosion of international graphene research interest due to its exotic Dirac Quantum Mechanics-based electronic properties. Although intrinsically a high mobility semi-metal (~200,000 cm^2/Vs when defect-free, versus ~1500 for Si and ~8500 for GaAs), graphene's physical strength, adaptability to planar processing, micron-scale room temperature ballistic electronic transport behavior, and potential for real time bandgap manipulation (via chemically doping or application of internal/external electric fields) makes it a promising candidate for advancing and possibly replacing silicon technology in the nanoscale regime, as well as the creation of disruptive carbon-based electronic applications.

The promise of graphene as a high performance electronic material has recently attracted great interest. Currently, a large amount of research has concentrated on understanding graphene's electronic and material properties in controlled environments. However, little is known about graphene survivability in less than ideal environments. To address this lack of understanding, we will develop differentiating and synergistic approaches to: 1) characterize graphene device performance after exposure to various environments and 2) understand the root causes of graphene device failure in those environments using standard failure analysis techniques. The linkage to a complete suite of coordinated characterization/modeling efforts is another differentiating factor of our effort that assures project impact and leadership within the rapidly moving graphene research community.

Combination Bearing/Flexure Joint for Large Coarse Motions and Fine Jitter Control

165552

Year 1 of 2
Principal Investigator: P. S. Barney

Project Purpose:

High precision pointing systems are required for space applications in order to stabilize sensors to meet stringent requirements for jitter (uncompensated, high frequency motions). Minimizing the jitter is especially difficult for payloads that are flown on multi-mission spacecraft because those vehicles are not optimized to mitigate the base disturbances into the payload. The jitter requirements for new systems only get more demanding as higher density focal planes are coupled to telescopes with increasing optical power. The joints of these high precision payloads are typically supported by high quality bearings that are strong enough to ensure survival of the launch loads, yet as smooth as possible to minimize drag during moves. Even the best bearings have non-linear friction characteristics which adversely affect the control system performance. We plan to develop a combination of a bearing and a flexure that will: 1) allow large motions using the bearings across the field-of-regard (FoR) to maximize area coverage by the payload sensors and 2) allow for linear and repeatable small motions even during direction reversal thereby decreasing jitter. The combination of these two technologies will allow future systems to exceed the jitter requirements and performance of existing systems, thus increasing the capabilities and mission space.

This project will develop a new design that incorporates a bearing, a flexure, as well as a braking mechanism. The most challenging aspect in the development of such a device is to balance the flexible linear portion of the system with the large FoR non-linear portion while allowing for a robust controller. The active braking system could be the key to success. A test bed will be used to identify performance and operational limits.

Wound Ballistics Modeling for Blast Loading, Blunt Force Impact, and Projectile Penetration

165554

Year 1 of 3
Principal Investigator: P. A. Taylor

Project Purpose:

Light body armor development for the warfighter is based on trial-and-error testing of prototype designs against ballistic projectiles. Torso armor testing against blast is nonexistent but necessary to protect the respiratory and cardiovascular systems. We plan to create a modeling and simulation (M&S) capability to investigate wound injury scenarios to the head, neck, and torso of a typical warfighter. This toolset would be used to investigate the consequences of, and mitigation against, blast exposure, blunt force impact, and ballistic projectile penetration as they lead to the damage of critical soft tissue organs such as the brain, spinal cord, heart, and lungs. We would leverage Sandia simulation codes and our own M&S expertise on traumatic brain injury to develop virtual anatomical models of the head, neck, and torso and the simulation methodology necessary to capture the underlying physics of wound mechanics. We will use the toolset developed here to investigate wound injury scenarios to the head, neck, and torso with, and without protective body armor as a means of demonstrating the advantages and convenience of simulating virtual injury scenarios for the development of light body armor.

Ground Moving Target Extraction, Tracking, and Image Fusion

165555

Year 1 of 3
Principal Investigator: T. J. Ma

Project Purpose:

Real time unresolved target detection and tracking with a remote sensor is a very difficult problem. When targets are far away from the sensor, they often appear unresolved and small. Less target pixels are detected, making it very difficult to obtain characteristics such as shape and texture information to extract the target. Without such characteristics, filtering out false detections is a very difficult task. However, if our detection and tracking region is constrained, then more advanced processing techniques can be applied to solve this problem. The purpose of this R&D project is to develop automatic unresolved target detection and tracking capability that operates in a constrained environment. When designing a tracking application, we often know what types of target we are interested in and in what areas the target resides. For example, if one were monitoring animals in the zoo, we are interested in the region where the animal resides. Our constrained region is more than just simply an area where the detector should operate. It is all the possible paths that the target is likely to travel. This information can often be obtained through geographical maps. Additionally, target features and sensor characteristics are used to further discriminate target versus noise. Moreover, wavelet-based multi-sensor image fusion techniques can be applied to extract more features about the target to help improve detection and classification.

A constrained target-processing (CTP) framework has been developed to automatically detect and track objects moving along a simple path. We plan to advance our CTP capabilities to process complex multi-paths scenario. Additionally, we plan to improve existing tracking capability by adding more complex geographical constraints into our track estimation filters. Moreover, a track feature-based classification filter (TFBCF) will be developed to incorporate dynamic characteristics such as trajectory and velocity to discriminate target tracks.

Tomographic Range Imaging

165562

Year 1 of 1
Principal Investigator: M. R. Laine

Project Purpose:

Tomographic range imaging is the merging of scannerless range imaging and reflective tomography. This project examines the long-range (greater than 1000 km) object shape and orientation recognition issues by exploring laser illumination systems, sample detector performance capabilities, and signal processing shape recognition issues.

Summary of Accomplishments:

We created a highly parallel optical ray trace capability developed by incorporating custom shapes and bidirectional reflectance distribution function characteristics to produce range-resolved target projections (based off Intel's Embree code).

We characterized and compared three different detector technologies: a discrete amplification photon detector, Geiger mode avalanche photodiodes, and a high-speed linear photoreceiver.

We developed a transmitter solution utilizing an array of mode-locked Yb^{+3} fiber lasers for laser tomographic imaging

An object recognition method was established, tested and showed promising results.

Significance:

The image processing technique showed promising results for object recognition of simple geometric shapes. How well the method works depends on having adequate range and frequency resolution. Since this method is based on the ability to image the object from different orientation angles, it performs well on tumbling objects and time evolving objects.

Radio Frequency Environment Characterization through Novel Machine Learning Techniques

165563

Year 1 of 2
Principal Investigator: S. M. Patel

Project Purpose:

There are multiple scenarios that require an unaffiliated wireless RF communicator to enter an environment and establish communication with a group of affiliated RF devices with no a priori knowledge of their wireless communication protocol. This poses a difficult problem for the unaffiliated communication device because it has to learn how to establish a link based on observations of other communicators in the environment. This requires it to understand the various RF signal information such as center frequency, modulation, and signaling rate. It also needs to understand protocol behavior, such as link establishment (handshaking and authentication), and digital packet data structures such as specific identification of error correction codes, cyclic redundancy checks, and synchronization patterns. This project seeks to identify methods for autonomously detecting and characterizing this information between two or many affiliated communicators based purely on observed information. This project is topical in the area of dynamic spectrum access and cognitive radio research.

Machine learning algorithms have been studied for many years and can be considered an established science. However, the use of machine learning algorithms in certain application areas requires a qualitative and quantitative analysis of the available data and an understanding of how the data is relevant. This project is performing a study of various machine learning techniques to characterize a digital wireless communication link based on observations of the RF environment. Using techniques such as Bayesian and neural networks, we are developing a probabilistic model of a protocol and its digital data format, which will enable the unaffiliated communication device to establish communication. Machine learning techniques have been rigorously employed in the analysis of financial markets for the creation of predictive inference models. The novelty of this project is to perform similar research for sensor optimization.

A Thermo-Optic Propagation Capability for Reducing Design Cycle Time, Improving Performance Margins, and Lowering Realization Costs

165571

Year 1 of 2
Principal Investigator: K. Schrader

Project Purpose:

Due to the increasing complexity of remote sensing optical systems, performance requirements must be verified by analysis with validation. Fielded systems experience dynamic thermal loads by virtue of varying sun illumination angles subjecting them to extreme heat and cold. Since thermal loads degrade performance of an optical system by misaligning, distorting, and altering the optical properties of components, detailed thermo-optical analyses are required to complete the requirements verification.

Current methods of thermo-optic analysis are extremely laborious and predominantly compartmentalized according to discipline: structural, thermal and fluid mechanics, and optical propagation analysis. The method of integrating data for final optical analysis involves mapping into a form compatible with the chosen tools. This mapping is not a true multi-physics implementation and yields only an approximate solution at best. It is susceptible to error and cannot account for effects of field-angle and compounded errors of upstream components. The S&T shortfall in thermo-optical modeling is primarily due to multi-disciplinary complexities. A true multiphysics solution requires integral collaboration at the optical modeling level.

The purpose of this project is to create a true multiphysics, thermo-optical propagation capability by developing a custom module within the Zemax optical analysis tool. This module will directly read output files of structural and thermal analyses and compute the non-linear optical propagation through components under thermal load. This capability has never been demonstrated within a validated, commercially available optical analysis product. If successful, the resulting tool will provide a new understanding of thermal effects on broad field-of-view optical imaging systems, and the compounded effects of thermal disturbances on complex, multielement systems.

Self-Powered Thin Electronic Systems

165572

Year 1 of 2
Principal Investigator: B. Jokiel, Jr.

Project Purpose:

The purpose of the project is to develop and demonstrate a quick and inexpensive way to create thin electronic systems with embedded power sources and storage that will enable quick-turn design and production of custom electronic devices.

Off-the-shelf printing technologies electronic components, printing media, and nano particle conductive inks were combined in a unique way to build a prototype simple device. The prototype device integrated a unique power system, microelectronics, and sensing/reporting attributes through the application of a novel assembly process that overcame material compatibility and assembly challenges.

This year, we demonstrated feasibility of the concept and the functionality of the overall design process. Future testing will involve more complicated and capable electronic designs with rigorous testing of the system's mechanical flexibility and survivability during temperature extremes, thermal shock, and overall lifetime of the systems at standard temperature. Future electronic designs will explore the implementation of more complex electronic circuits and antenna elements, as well as other conductive materials for lower loss traces. The mechanical flexibility and conformal nature of the devices will also be explored for potential future applications.

Large Motion High Cycle High Speed Optical Fibers for Space-Based Applications

165574

Year 1 of 2
Principal Investigator: P. G. Stromberg

Project Purpose:

Future remote sensing applications will require higher resolution, and therefore, higher data rates (up to perhaps 100 gigabits per second) while achieving lower mass and cost. A current limitation to the design space is the condition that high speed high bandwidth data does not cross movable gimbals because of cabling issues. This requires the detectors to be off gimbal. The ability to get data across the gimbal would open up efficiencies in designs where the detectors and the electronics can be placed anywhere on the system. Fiber optic cables provide light-weight high speed high bandwidth connections. Current options are limited to 20,000 cycles as opposed to the 1,000,000 cycles needed for future space-based applications. To extend this to the million+ regime requires a thorough understanding of the failure mechanisms and the materials, proper selection of materials (e.g., glass and jacket material), allowable geometry changes to the cable, radiation hardness, and other factors.

We will use advanced characterization and modeling tools to answer the fundamental question, “Are there surface or interfacial cyclic fatigue mechanisms in optical fibers?” Cyclic fatigue of fibers could jeopardize fiber reliability in remote sensing environments, either limiting design options (i.e., limiting to designs which enforce zero movement of the fibers) or reducing reliability/life in applications that require the fibers to move with a gimbaled payload. Emphasis is placed on fundamental understanding of the micromechanical origins of strength degradation in cyclic fatigue. One possibility is that fatigue strength is controlled by nm-sized surface pits formed by moisture reacting with the glass surface. Such pits could sharpen in cyclic fatigue due to effects of wedged debris or asperity contact. Another possibility is that the elastically mismatched core-clad interface delaminates during cyclic loading to cause fracture. Fundamental understanding of the degradation mechanisms and quantification of their effects will enable us to develop a model that can be used to specify safe design limits for optical fibers.

Quantum Graph Analysis: Engineering and Experiment

165577

Year 1 of 3
Principal Investigator: P. L. Maunz

Project Purpose:

In recent years, advanced network analytics have become increasingly important to national security with applications ranging from cybersecurity to detection/disruption of terrorist networks. While classical computing solutions have received considerable investment, the development of quantum algorithms to address problems, such as data mining of attributed relational graphs, is a largely unexplored space. Recent theoretical work has shown that quantum algorithms for graph analysis can be more efficient than their classical counterparts. Specifically, an adiabatic quantum version of Google's PageRank algorithm (QPR) was proposed that offers polynomial speedup in the time required to identify the most important nodes on a graph. We will pursue a combined theoretical/experimental effort to implement QPR in a system of trapped ion quantum bits (qubits). In addition, we will identify classical web-graph analysis methods and seek to develop more computationally efficient quantum alternatives.

Implementing a quantum computer is extremely difficult because qubits must be precisely controlled and well shielded from their environment to avoid decoherence. Academic groups with quantum algorithm capability are few in number and typically focus on demonstrating elements of universal quantum computing or simulating physical systems.

QGA theory is in its infancy and no QGA algorithm has been experimentally implemented. The planned goals are, therefore, at the forefront of the field. Over the past decade, Sandia has become a world leader in microfabricated surface ion trap design and fabrication. This project will develop all required ion trap quantum algorithm hardware, yield a world first QGA demonstration, advance QGA theory, and establish a strong theory/experiment quantum information processing partnership that can be adapted to meet other national security needs.

Distributed Receiver Approach to Robust Satellite Signal Reception

165578

Year 1 of 2
Principal Investigator: P. H. Probert

Project Purpose:

Many satellite-based systems rely on a microwave downlink to transfer critical information. Due to satellite power constraints, the signal at the receiving station can be very weak, and interference can delay or prevent the reception of the data. Current approaches to this problem involve: 1) robust receiver design, which is effective against certain interferers; 2) directional receiving antennas, only somewhat effective against interferers since all antennas have sidelobes; and 3) multiple independent ground stations, effective against interferers in the case of fixed ground stations and can be made effective against mobile interferers and mobile ground stations with limitations. These methods can incur significant costs, especially option 3, and are all vulnerable to certain classes of interference.

We plan to solve the problem by using a network of simple receivers scattered over a wide region and by using a digital network topology to bring the raw data to a central location where a diversity-combining scheme will add the signals together with the proper phases. This solution to the problem involves application of some newer technologies: digital high-speed networks, and digital radio frequency (RF) signal processing. There are many options to consider in this space, such as different networking methods, antenna and receiver designs, and signal combining algorithms. We plan to look at a variety of designs and determine the mix that meets the requirements of our problem.

Chemical Stability and Reliability of Petroleum-Based Products

165579

Year 1 of 2
Principal Investigator: R. D. Rasberry

Project Purpose:
Petroleum-based products are the economic cornerstone of modern society and remain essential to US economic security, stability and growth. The purpose of this project is to examine the reliability of commonly used petroleum-based materials (e.g., fuels, road materials, electrical insulators, adhesives, etc.) and how environmental changes may affect performance and utility. This work explores the potential for synergistic effects between environmental variables and chemical additives. In this topical area, product enhancement has had unanticipated secondary effects, leading to costly alterations to industrial practices and infrastructure. For example, petroleum additives that have unintended deleterious effects were previously developed as efforts to improve processing and performance (methyl t-butyl ether or tetraethyl lead increased gasoline octane number but ultimately had negative environmental impacts). The work herein represents an evolutionary departure in additive research as it is aimed to anticipate deleterious additives. Ultimately, an exploration of unintended consequences to S&T will allow for the development of detection and mitigation technologies that will ensure petroleum product supply continuity and, thus, continued domestic economic prosperity and security.

Enabling Technologies for the Development of Very Small Low Cost Interceptors

165580

Year 1 of 2
Principal Investigator: N. R. Harl

Project Purpose:

To counter emerging threats, a demand has surfaced for small, low cost ballistic missile defense (BMD) interceptors that can be used in much larger numbers than current interceptors. The small size and relative affordability of such weapons would allow for more rounds to be used, providing improved defense against large missile raids. Unfortunately, the investigation of small, low-cost, interceptor paradigms has received little attention because the Missile Defense Agency is focusing on traditional kill vehicles lofted by large boosters.

One of the primary challenges for the development of small interceptors is that, for the interceptor booster to be small and low cost, the kill vehicle must be very small. A kill vehicle of less than 5 kg could utilize a much smaller booster than current BMD interceptors. This kill vehicle size limits the technologies that can be used, and leads to limited end game divert capabilities. Through a novel and proprietary combination of new and old technologies, potential exists for the creation of new miniaturized seekers and steering systems for very small, lightweight interceptors. However, these technologies have never been applied to BMD interceptor applications.

The planned work will investigate and model technologies necessary for the development of small, low cost interceptors. Specifically, novel miniaturized seeker and steering system concepts will be analyzed. Since the development of these miniaturized technologies is a challenging problem with notable risk, several options will be analyzed and compared. The result of these efforts will be a conceptual interceptor design that is dramatically smaller than traditional BMD interceptors.

To analyze the efficacy of the miniaturized technologies, a high fidelity, model-based, simulation environment will be developed. The environment will be specifically designed and configured to support performance assessment of terminal, seeker-based, homing-guidance systems and their end-use implementation. A challenge in developing this environment will be making it useful both with broader simulation environments, such as Sandia's VEGA, and higher fidelity hardware-in-the-loop (HWIL) environments.

Turbocharging Quantum Tomography

165581

Year 1 of 2
Principal Investigator: R. J. Blume-Kohout

Project Purpose:

The purpose of the project is to develop and benchmark new protocols for quantum tomography that achieve better accuracy, reliability, and efficiency. Our results will pave the way for a comprehensive suite of tomographic “best practices” to characterize and validate quantum device technologies across many laboratories.

Quantum information processors (QIPs) promise a revolution in computing, communication, and sensing. To achieve these goals, every quantum hardware component (e.g., qubits that store quantum information and logic gates that transform them) must perform to extraordinarily high precision. Methods for characterizing, diagnosing, and verifying the behaviors of quantum devices are known, collectively, as quantum tomography.

Standard tomographic methods are very resource-intensive, thanks to the peculiar nature of quantum systems. Describing an N-qubit device requires exponentially many (2^N or 4^N) parameters, none of which can be measured directly. So, to characterize a device, an experimenter must measure many different observables, repeat many times to gather statistics, and (finally) transform the data into an estimate via some estimator. Accuracy, reliability, and efficiency all depend on the observables measured and the estimator used. Today, most tomographic experiments still use naive and inefficient protocols, due to a dearth of efficient, sophisticated methods that have been rigorously tested and validated.

Quantum hardware is sufficiently advanced that many research groups desperately need methods for reliable and accurate tomography. Our results will facilitate general progress toward the grand challenge of quantum computing and they will uniquely benefit Sandia’s experimental labs. Our tomographic capability will enable the design and evaluation of devices with higher accuracy, higher confidence, and fewer resources. This capability is critical for addressing measurement bottlenecks that stem from limited time and equipment. It will benefit a wide array of quantum information technologies developed at Sandia, while the underlying capability development will establish a leadership position in a critical area of quantum information science.

Development of a Rapid Field Response Sensor for Characterizing Nuclear Detonation (NUDET) Debris

170798

Year 1 of 3
Principal Investigator: S. Mitra

Project Purpose:

The radioactive decay of nuclear detonation (NUDET) debris samples makes rapid analysis methods highly desirable, and nuclear forensics would benefit from field response techniques for characterizing this debris, in situ. Present sample collection techniques require the samples to be returned to the laboratory for analysis. Further, the presence of high radioactivity soon after the fallout inhibits access to the affected zone. This project will conduct proof-of-principal studies to demonstrate the utility of employing low energy neutrons from a portable pulsed neutron generator for nondestructive isotopic analysis of NUDET debris in the field. In particular, interaction signatures will be established, such as the creation of prompt gamma rays. The research will model and benchmark the neutron interrogation and on-line gamma-ray detection process and lay the foundations for a field-deployable instrument, either in a static or scanning mode.

Real Time Case-Based Reasoning using Large High Dimensional Data

170800

Year 1 of 3
Principal Investigator: J. Woodbridge

Project Purpose:

The purpose of the project is to discover high dimensional search paradigms to support Case-based reasoning systems (CBR). CBR systems are an effective tool for improving decision making in many domains. CBR systems aid in decision processes by comparing current cases to past well-known cases. Current CBR systems often focus on low dimensional data or small archives of historical data. However, richer high dimensional datasets are essential in understanding many measured phenomena. Large archives of historical cases are necessary to account for variations in how a phenomenon is revealed. For example, a seismogram can be used as conclusive evidence that the source of activity was a potential nuclear test and not an earthquake, but only after properly accounting for other important factors, such as the source to receiver path through the Earth. It is necessary to analyze large archives of both types of events recorded for a variety of paths to conclusively make the distinction. Unfortunately, large high dimensional archives are not currently feasible for CBR systems due to the complexities of search in high dimensional spaces.

The planned technique learns the structure of a dataset in high dimensional space to construct an inverted index for the high dimensional space. The index is applicable to any measure of similarity with any configuration across multiple domains. This project spans many domains, giving new capabilities in machine guided decision making. Several core theoretical advancements must be made in this area over a two-year timeframe. The results of this project can then be applied to a specific domain through a direct project for the implementation of a specialized CBR system. Potential domains include any program that requires analysis of high dimensional data (such as time series, images and feature vectors). Example projects include nuclear explosion monitoring, cybersecurity (such as network behavior analysis), and satellite monitoring.

Integration of a Neutron Sensor with Commercial CMOS

170803

Year 1 of 3
Principal Investigator: W. C. Rice

Project Purpose:

Commercial microelectronics are subject to constant cosmic irradiation. These radiation fields routinely cause device interrupts known as single event upsets (SEUs) in the internal structure of the CMOS. SEUs can range in severity from individual memory bit flips to more catastrophic single event function interrupts (SEFIs), which can lead to destruction of the electronic device. The effects of the SEUs can often be resolved or mitigated by error correction codes (ECCs), which restore the device operation by, for example, rewriting the memory to correct the false bit, or cycling the power to remove a lockup condition. However, unless a precaution is taken, latency can occur in time between the SEU and its correction by ECCs. This can happen for example, when the device is operating in stand-by mode. Latencies lead to increased device damage. Therefore, it is extremely useful to be able to detect incoming radiation as soon as it occurs.

Existing microelectronics are being explored to determine the fundamental properties of device physics leading to SEUs in memories. Tests to study the response to SEUs under a variety of radiation types and energies have been designed. Some initial results have been obtained from experiments performed in Sandia's Ion Beam Laboratory. The insights gained will help improve the robustness of devices subject to SEUs. An experimental plan for FY14 has been developed that will lead to a deeper understanding of the underlying physics in these radiation environments. As a result, we will increase the possibilities for mitigating the risks to systems operated by these electronics by shortening response times and lowering power requirements for corrections.

Liquid Metal Embrittled Structures for Fragmenting Warheads

170806

Year 1 of 3
Principal Investigator: J. J. Rudolphi

Project Purpose:

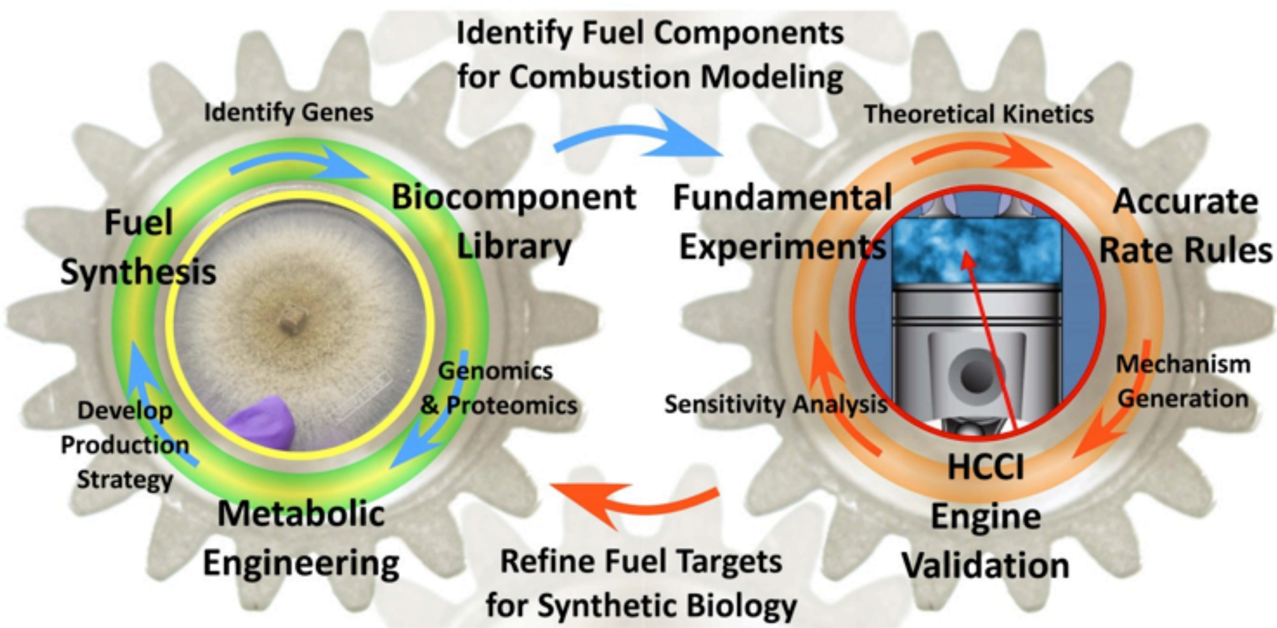
The purpose of this project is to investigate novel materials to assess their application in fragmenting structures. Specifically, the goals of the project are to 1) quantify the behavior of these novel materials when exposed to rapid material failure during explosive fragmentation and 2) assess the technology's viability to be incorporated into fragmenting devices. Typically, fragmenting devices are macroscopically weakened to create fragments of a specified shape and size. Furthermore, the ductility of the fragmenting material must be considered to determine the statistical spread of fragment sizes. This project will investigate a quasi-metallurgical technique. Through the incorporation of special agents into the fragmenting materials' microstructure, the technique creates weakened regions of variable ductility. This specific method has not been used to control fragment size and size distribution. By creating a practical method of material modification that allows a wider and more controllable range of particle sizes to be accessed, fragmenting devices could be engineered that create a wide and variable range of lethality.

Currently, there is a great interest in devices that have a more predictable and controllable fragment size and size distribution. This project could provide the warhead designer with another tool to control these important features.

ENERGY, CLIMATE, AND INFRASTRUCTURE SECURITY

The Energy, Climate, and Infrastructure Security Investment Area focuses on research and development that creates options in four areas: energy security, climate security, infrastructure security, and enabling capabilities. The goal is to enhance the nation's security and prosperity through sustainable, transformative approaches to the nation's most challenging energy, climate, and infrastructure problems. Applying science and technology from Sandia and from the Labs' broad science and technology community is critical to the success of the work.

The investment area promotes research to develop and create products and capabilities that incubate solutions for current and future national challenges. The challenges include reducing our dependence on foreign oil through R&D focused on renewable energy alternatives; increasing the use of low carbon power generation; advancing credible carbon management strategies; assuring water safety, security, and sustainability; increasing security and resiliency of the electrical grid and energy infrastructure; and, providing the foundation for a global climate treaty.



Framework for integrating combustion performance into optimization of biofuels (Project 151308).

ENERGY, CLIMATE, AND INFRASTRUCTURE SECURITY

CO_2 Reuse Innovation - Novel Approach to CO_2 Conversion Using an Adduct-Mediated Route

151300

Year 3 of 3
Principal Investigator: R. Kemp

Project Purpose:

The need to convert useless carbon dioxide (linear CO_2) into valuable products is of high interest worldwide. Performing this process at as low a temperature as kinetically possible is advantageous since it minimizes the energy input into the system and lowers the possibility for undesired side reactions. To achieve this, Sandia must explore multiple routes to CO_2 capture and fixation. We have prepared complexes that form CO_2 adducts with inexpensive earth-abundant elements such as tin and zinc. The CO_2-fragments in these metal adducts are now bent significantly from linearity in the solid-state crystal structures. We hypothesize that given the correct combination of metal and ligand structures, the bound and bent CO_2 molecule will be easier to reduce to organic products either chemically, or more likely electrochemically. If demonstrated, this is game-changing technology for DOE and Sandia. However, improvements in moisture and thermal stability of the various organometallic starting complexes are required in order to produce organic products. We have examined various valence-active main group metals with low-to-high electron counts (including electron rich ligands) to determine which metals most effectively transfer electrons into the CO_2 framework. These electrons can be provided either electrochemically or possibly chemically with appropriate reducing agents. The nature of the metal-ligand interaction (sterics and electronics) will be studied experimentally and computationally, as understanding the stability of this combination is critical to scientific advancement. Robust electron-rich ligands will be synthesized to minimize sensitivity to protic-containing solvents or reagents. From these individual component studies, an entire catalytic system will be designed to evaluate the hypothesis that chemical or electrochemical reduction of CO_2 can be facilitated by main group, or earth abundant, metal adduct formation.

Summary of Accomplishments:

Our team from Sandia, the University of New Mexico, and the University of Vermont examined a large number of complexes designed to mimic the "bent CO_2" structures seen by the less-stable compounds initially prepared. We have put forth an entirely new approach to CO_2 reduction — that of using dual Lewis acid-base pairs to bind to the CO_2 molecule in order to create a bent, less-stable complex that should be more amenable to reduction. Our team prepared >80 new metal-ligand complexes designed to complex CO_2, with more precise goals of making these metal-ligand combinations more robust and more stable to the needed electrochemical process. The numerous compounds we synthesized are of interest to other organometallic chemists outside of the CO_2 reduction chemistry. Many of these compounds have electron-rich spectator ligands and are of high interest electrochemically. Many of the new compounds react directly with CO_2 at room temperature and atmospheric pressure to form novel metal-CO_2 adducts. These adducts have been characterized by numerous analytical techniques, including nuclear magnetic resonance (NMR), infrared (IR), and single-crystal x-ray diffraction. Complexes of CO_2 with inexpensive, earth-abundant metals, such as main group metals or first/second row early transition metals, have been shown to form complexes with CO_2 and, via electrochemical studies, we have demonstrated the key hypothesis of our project — that the bent CO_2 complexes produced by the dual Lewis acid-base pairs can lead to a significant lowering (approximately 0.5 volt) of the potential required to convert CO_2 to other small molecules, such as CO. This is an extremely important finding, as expensive metals are not needed.

Significance:

The efficient conversion of excess carbon dioxide into useful organic compounds, including transportation fuel precursors, is a problem of global concern. In order to be successful, scientists need multiple approaches to CO_2 reduction. Our results have shown that using dual acid-base pairs to complex CO_2 to inexpensive, earth-abundant metal complexes can allow a significant lowering of the electrochemical energy barrier for CO_2 reduction, up to approximately 0.5 volt. Complexes such as those prepared in this study can lead to more efficacious processes for CO_2 conversion and aid in the mitigation of excess CO_2. Future work can optimize the types of ligands and metals that can be used and utilize the new compounds produced in this work. The knowledge of facilitating CO_2 reduction will be of high interest to other DOE-funded catalysis projects.

Refereed Communications:

B.M. Barry, D.A. Dickie, A.E. Wetherby, Jr., W.E. Barker, IV, C.A. Larsen, R. Waterman, W.E. Geiger, and R.A. Kemp, "CO_2 Interactions with Main Group Compounds Directed Towards Preparing Useful Organic Compounds," Preprinted Papers - American Chemical Society - *Fuel Chem*istry, vol. 57, p. 294, 2012.

A.M. Felix, B.J. Boro, D.A. Dickie, Y. Tang, J.A. Saria, B. Moasser, C.A. Stewart, B.J. Frost, and R.A. Kemp, "Insertion of CO_2 into Divalent Group 2 and 12 Amides," *Main Group Chemistry*, vol. 11, p. 13, 2012.

B.M. Barry, D.A. Dickie, L.J. Murphy, J.A.C. Clyburne, and R.A. Kemp, "NH/PH Isomerism and a Lewis Pair for Carbon Dioxide Capture," *Inorganic Chemistry*, vol. 52, pp. 8312-8314, July 2013.

D.A. Dickie, R.P. Ulibarri-Sanchez, P.J. Jarman, and R.A. Kemp, "Activation of CO_2 and CS_2 by $(Me_3Si)(i\text{-}Pr_2P)NH$ and its Zinc Complex*," Polyhedron*, vol. 58, pp. 92-98, July 2013.

B.M. Barry, B.W. Stein, C.A. Larsen, M.N. Wirtz, W.E. Geiger, R. Waterman, and R.A. Kemp, "Metal Complexes (M = Zn, Sn, and Pb) of 2-Phosphinobenzenethiolates: Insights Into Ligand Folding and Hemilability," *Inorganic Chemistry*, vol. 52, pp. 9875-9884, August 2013.

Development of Alkaline Fuel Cells

151301

Year 3 of 3
Principal Investigator: M. Hibbs

Project Purpose:

This project focuses on the development and demonstration of anion exchange membrane (AEM) fuel cells for portable power applications. For fuel cells to meet the needs of consumer electronics, significant reductions in cost are required. To meet demanding DOE portable power targets, radical approaches need to be considered. AEM fuel cells differ from proton exchange membrane (PEM) fuel cells primarily in that the operating environment is alkaline rather than acidic. AEM fuel cells offer huge potential to reduce cost and enable significant system simplification because they operate at pH conditions where nonprecious catalysts are stable and highly performing (comparable to platinum, Pt). Additionally, the ability to operate in high pH increases the number of fuel choices (alternative fuels) available and increases the efficiency of the electrochemical oxidation process. For historic reasons, these systems have not been strongly pursued, largely because they were believed to be limited by relatively poor stability and low conductivity of the membrane material and the difficulty involved in fabricating membrane-electrode assemblies from these materials.
This project leverages recent breakthrough performance of AEMs developed at Sandia and electrocatalysts developed at UNM to develop alkaline fuel cells with state-of-the-art performance and durability results.

Mass transport within the electrodes is critical to performance. However, no electrode architecture has been specifically tailored and optimized for use in AEM fuel cells. Because Sandia has developed cationic polymers for AEMs that can also be dissolved in solvents such as alcohols, we are in a unique position to work with catalyst developers to experiment with the design of electrodes for AEM fuel cells. Because this field is still in its infancy (compared to PEM fuel cell electrode design), it is too high-risk to be funded directly by DOE.

Summary of Accomplishments:

We invented the synthesis of an anion-exchange membrane (AEM) with the highest alkaline stability reported to date and have filed a patent on the composition. We also invented the synthesis of another polymer designed specifically for use as an ionomer in the electrodes of alkaline fuel cells made with the Sandia membrane. The new materials allow for both higher power outputs and longer cell lifetimes. Specifically, we demonstrated the highest reported alkaline direct methanol fuel cells (DMFC) power density (54 mW/cm^2) and a power density of 52 mW/cm^2 with no Pt in the cathode.

We also developed a novel nuclear magnetic resonance (NMR) technique for analysis of methanol and water transport in different solvent environments within membranes. This resolution allowed the measurement of diffusion rates for each different species, thus providing additional insight into the transport properties of solvents within fuel-cell membranes. This study furthers the applications of high-resolution magic angle spinning (HRMAS) NMR in materials science. It also demonstrates the benefit of this technique to the study of AEM and other similar materials by enabling diffusion measurements to be performed on mixed solvent systems that otherwise would be inaccessible utilizing standard static NMR diffusion methods. HRMAS pulsed field gradient (PFG) experiments will open new insights into the characterization of diffusion behavior of anion exchange polymer membranes and has the potential for multiple applications in fuel cell research.

Significance:

We developed a hydrocarbon alkaline fuel cell (AFC) membrane that is more stable than any reported to date. This will establish Sandia as an important institution for the development of materials for AFCs. Strategic partnerships for future DOE fuel-cell funding opportunities are in place.

The results of this research impact energy security, infrastructure security, and enabling capabilities. They support advanced electrical energy storage technologies, renewable energy systems for electricity contribution, and the development of science-based tools for the transportation fleet.

Refereed Communications:

J.E. Jenkins, M.R. Hibbs, and T.M. Alam, "Identification of Multiple Diffusion Rates in Mixed Solvent Anion Exchange Membranes Using High Resolution MAS NMR," *ACS Macro Letters*, vol. 1, pp. 910-914, July 2012.

R. Janarthanan, J.L. Horan, B.R. Caire, Z.C. Ziegler, Y. Yang, X. Zuo, M.W. Liberatore, M.R. Hibbs, and A.M. Herring, "Understanding Anion Transport in an Aminated Trimethyl Polyphenylene with High Anionic Conductivity," *Journal of Polymer Science, Part B*, *Polymer Physics*, vol. 51, pp. 1743-1750, September 2012.

M.R. Hibbs, "Alkaline Stability of Poly(phenylene)-based Anion Exchange Membranes with Various Cations," *Journal of Polymer Science, Part B*, *Polymer Physics*, vol. 51, pp. 1736-1742, December 2013.

Constitutive Framework for Simulating Coupled Clay/Shale Multiphysics

151302

Year 3 of 3
Principal Investigator: F. D. Hansen

Project Purpose:

Clay and tight shale geologic formations are increasingly promising as host media or engineered barrier materials for nuclear waste disposal, unconventional 'shale' gas resources, and as caprocks for CO_2 sequestration. Clay minerals and formations are known for compositional and structural variability. Although much effort has been directed toward understanding behaviors of clay/shale media, significant technical gaps still exist. For example, existing geochemical and geomechanical studies have been performed for a limited set of clay materials, and there is no systematic framework for modeling important aspects of system performance across the full spectrum of applications. For nuclear waste disposal, such a framework would include a set of constitutive relationships based on mechanistic understanding of relevant physical and chemical processes, and should capture the variability in clay characteristics (e.g., mineral type, pore size, and pore connectivity) and the resulting impacts on radionuclide transport. Many of these constitutive relationships have not been developed or validated.

The research effort includes both a comprehensive experimental approach to radionuclide sorption in clay and clay-bearing sediments and development and validation of a set of coupled thermal-hydrologic-mechanical-chemical (THMC) constitutive relationships using Sierra Mechanics. Hydrological physics include multiphase flow and hysteretic wetting and drying, as well as the effect of variable water properties as a function of pore and crack geometry. Thermal effects include saturation-dependent conductivity. Geomechanical effects include swelling, saturation-dependent yielding, and failure criterion, creep, and damage associated with dry-out. Geochemical aspects include reaction and sorption kinetics in consolidated clay sediments, non-Fickian transport, and clay mineral transformations. Combining these coupled mechanisms into a modeling framework for application to subsurface engineering pursuits in the national interest is a daunting challenge.

Summary of Accomplishments:

We made significant progress toward our goal to create a general Sierra Mechanics framework for clay multiphysics, comprised of both a comprehensive experimental approach to radionuclide sorption in clay and the development of coupled THMC constitutive relationships using Sierra Mechanics. A suite of clay minerals was characterized and tested for its sorption capabilities for iodide uptake. Iodide uptake experiments were completed for a range of swamping electrolytes and concentrations. Iodide uptake behaviors form distinct trends with cation exchange capacity and mineral structure. These trends change substantially with electrolyte composition and concentration, but do not appear to be affected by solution pH. We thus discovered that iodide might directly interact with clays by forming ion-pairs (e.g., NaI) that may concentrate within the interlayer space of clay particles where water behavior is more structured relative to bulk water. Ion pairing and iodide concentration in these zones are probably driven by the reduced dielectric constant of water in confined space and by the relatively high polarizability of the iodide species. This discovery has far-reaching implications to the capability of clay materials as a geo-membrane for anion exclusion and isolation. To understand radionuclide interaction with compacted clay materials under relevant geologic conditions, a high-pressure and high-stress experimental setup has been developed and successfully tested for iodide sorption and diffusion. The implementation of the Double Structure Model (DSM) in the Library of Advanced Materials for Engineering (LAME) has been accomplished. The DSM uses the Barcelona Basic Model (BBM) as its foundation for the macrostructural response and treats the net stress and suction as two independent stress variables, thus enabling simulations of clay material deformation and swelling as a function of relative humidity under partially saturated conditions.

Significance:

We have established necessary experimental capabilities for clay material studies that have led to a new level of understanding of radionuclide-clay interactions. We have developed state-of-the-art computational tools for high fidelity modeling of clay behavior in repository environments. Our work has significantly expanded Sandia's role in clay repository research. Both modeling and experimental capabilities developed in this project can also apply to other Sandia missions such as shale gas research, artic/permafrost studies, and carbon sequestration and storage. Through this project, we have established strategic university and international partnerships and integrated technical capabilities across Sandia.

Refereed Communications:

A. Miller and Y. Wang, "Al-O-F Materials as Novel Adsorbents for Gaseous Radioiodine Capture," to be published in the *Journal of Environmental Radioactivity*.

In Situ Diagnostics for Fuels Model Validation with ACRR

151303

Year 3 of 3
Principal Investigator: D. Fleming

Project Purpose:

In order to support fuels development work for advanced reactors, numerous computational models are being developed at Sandia and elsewhere. These codes aim to model the behavior of radiation-damaged materials, including the fuel and cladding, with increased fidelity over current models. Benchmark experiments are recognized as providing essential data to validate the computational models.

While the ultimate goal of these modeling efforts is to have validated codes to predict fuel performance, the current development efforts have focused primarily on code development. A reactor-scale experimental program to provide detailed validation data for current and proposed new fuel compositions during reactor transients is needed. Fuel disruption tests performed at Sandia during the 1980s obtained visual data, but no model validation data. Therefore, an opportunity exists to develop an experimental program for Sandia's Annular Core Research Reactor (ACRR) with the goal of providing quantitative validation data during transient conditions for developing computational codes.

Through this project, we use the ACRR to perform small sample, separate effects, irradiation studies during rector transients with the goal of developing benchmark experimental results (i.e., time dependent, 3D clad strain) to be used in fuel/cladding modeling codes (i.e., the Sandia iMPALE code, a previous project). Our team will establish a baseline nonfueled test capability and develop the experimental program to obtain the data. We will continue to evaluate in situ diagnostic techniques to measure strain, such as Digital Image Correlation and advanced strain gauges, on nonfuel items in ACRR to validate the experimental technique and quantify experimental uncertainty. We envision using pressurized cylinders made from fuel clad for this phase. Finally, we will seek to establish partners with other laboratories and industry to develop a transient fuel-testing program at the ACRR.

Summary of Accomplishments:

This project developed a method for understanding the limits of nuclear fuel cladding during reactor operations. Sandia researchers suggested methods for measuring strain culminating in large-scale tests in ACRR. The project successfully proved the radiative-resistant nature of strain gages and protective coatings. Extreme environments necessitate the use of supplementary materials for a temperature and radiation barrier to improve the reliability of the strain gage. The most successful developments involved optical strain mapping techniques. Recent technological improvements allowed significantly accurate results. We discovered that 2D digital image correlation (DIC) is similar to 3D DIC results when measuring circumferential strain on fuel cladding. Additionally, we designed and constructed a 35 ft. borescope to be available for testing in ACRR.

Significance:

By quantifying stress and strain in nuclear fuel, improved fuel design is possible by directly increasing performance and lifetime of the cladding. Prior to this project, the survivability of traditional strain gages in extreme environments was unknown, though ACRR testing results were positive. Future advancements in strain diagnostics will focus on optical strain mapping techniques due to improved strain resolution and reduced proximity to the sample — these had not previously been utilized in a reactor environment due to the extreme signal disruption caused by radiation. However, due to the understanding developed under this project, continued research on this technological frontier is both feasible and recommended.

Tier 2 Development of Sandia's Air Bearing Heat Exchanger Technology

151304

Year 3 of 3
Principal Investigator: J. P. Koplow

Project Purpose:

The work was aimed at transforming a recent conceptual breakthrough in air-cooled heat exchanger technology to a TRL-level-4-to-5 technology appropriate for energy sector applications. Limited work conducted prior to this project indicated that the new mechanism for heat transfer proposed for Sandia's Air Bearing Heat Exchanger (now widely known as the "Sandia Cooler") potentially represented a revolution in heat transfer technology. At the start of this project, this new technology was in its infancy. The technical challenges we faced include moving far beyond our current rudimentary understanding of the complex fluid dynamic phenomena that govern device physics — developing an engineering methodology for global optimization of the ten design parameters that govern device performance; and in support of the above goals, development of a computationally tractable fluid dynamic model that is closely coupled to experimental diagnostics such as de-rotated flow imaging, de-rotated thermal imaging, and acoustic spectral correlation. The research is cutting edge in that the air bearing heat exchanger device architecture is a radical departure from conventional air-cooling technology, whose development stagnated in the 1960s. The enormous potential of air bearing heat exchanger technology was recently demonstrated in the laboratory. However, there was significant uncertainty regarding the successful transformation of this new heat transfer mechanism observed in the laboratory into a technology base capable of providing large efficiency improvements in applications such as air conditioning, heat pumps, and refrigeration equipment. Given that such cooling loads currently account for 30% of US electricity consumption, it is imperative that we grapple with the numerous technical challenges that must be overcome to realize the potential of Air Bearing Heat Exchanger technology in real-world applications.

Summary of Accomplishments:

Major accomplishments over the course of this work included:

1. Development of optimized heat-sink-impeller geometries through a combination of computational fluid dynamic and experimental work
2. Development of self-levitating hydrodynamic air bearing
3. Implementation of a highly practical methodology for overcoming the problem of heat-sink-impeller centrifugal deformation
4. Implementation of a long lasting dry ceramic antifriction coating to enable sliding-contact start-up and shutdown of the heat-sink-impeller hydrodynamic air bearing
5. Development of a novel sensorless brushless motor controller circuit that provides the high starting torque required for device startup while maintaining the extremely small form factor of the low-profile brushless motor
6. Development of a 12-bit pulse density modulated three-phase push/pull class D amplifier to provide extremely low motor noise and torque ripple (i.e., vibration)
7. Development of closed-loop power factor control for the above motor controller that adjusts stator excitation on the basis of the voltage/current phase angle to ensure that the brushless motor operates at maximum efficiency

8. Successful incorporation of heat pipe technology into the base plate heat spreader of the Sandia Cooler
9. Development of a new device architecture (the "Sandia Heat Pump") specifically suited for large scale air-to-air heat pump applications such as building HVAC based on a novel rotating vapor compression cycle that exploits the centrifugal and Coriolis forces in the rotating frame
10. Development of new device architecture for applying the principles of the Sandia Cooler to the longstanding problem of thermal management
11. Development of a new class of thermoelectric heat pump now under development with DOE Energy Efficiency and Renewable Energy funding
12. Presentation of a 2012 R&D 100 award for the Sandia Cooler
13. Selection for an Editor's Choice award for the Sandia Cooler, one of only three chosen from among the 100 R&D 100 awards in 2012

Significance:

The impact of a fundamentally enabling technology such as the Sandia Cooler is extremely broad because heat transfer is of great importance in numerous applications. In the case of electronics cooling, impacts include higher CPU/GPU processor speeds, a viable path to proliferation of LED lighting (which has the potential to reduce US electricity consumption by 10%), and greatly improved thermal management for power electronics such as the insulated-gate bipolar transistor (IBGT) array inverters required for electric vehicles. Job creation and US economic competitiveness are also by-products of such R&D, and we have already received a great deal of interest from the private sector.

Fundamental Study of CO_2-H_2O-Mineral Interactions for Carbon Sequestration, with Emphasis on the Nature of the Supercritical Fluid-Mineral Interface

151305

Year 3 of 3
Principal Investigator: C. R. Bryan

Project Purpose:

Carbon sequestration via underground storage in geologic formations is a proposed approach for reducing industrial CO_2 emissions. There is a direct need by operators/regulators for better-informed models that incorporate coupled multiphysics processes arising from subsurface CO_2 injection and storage. Current models do not consider processes at the supercritical CO_2 ($scCO_2$)-mineral interface and their potential effects on long-term subsurface CO_2 storage. Interfacial processes control the wetting properties of minerals and the chemical reactivity at the $scCO_2$-mineral interface. The interface properties will be strongly dependent upon the activity of water in the supercritical fluid, which will change as initially anhydrous $scCO_2$ absorbs water from formation brine. As $scCO_2$ water activity increases, the water layer on hydrophilic mineral surfaces will thicken, with concomitant changes in surface properties that will affect how $scCO_2$ wets mineral surfaces, reservoir/caprock hydrological properties, and the mobility of $scCO_2$. Capillary condensation of water from $scCO_2$ and coalescence of water films may also occur. Moreover, the development of a water layer may be critical to mineral dissolution reactions in $ssCO_2$, and may affect attractive forces between clay particles. Data are currently lacking to incorporate these processes into models for CO_2 sequestration.

We will develop key theoretical, experimental, and modeling capabilities for understanding the interactions of supercritical CO_2-H_2O fluids with geologic formations. Inherent technical challenges exist in performing nanoscale studies of the $scCO_2$-mineral interface, and in upscaling nano/core-scale results to reservoir-scale processes. We will use innovative high-pressure spectroscopic methods to evaluate the $scCO_2$-mineral interface, and will develop methods for evaluating formation of surface water films in $scCO_2$ and their effect on rock hydrologic properties. This research will provide improved constitutive models and needed experimental data for evaluating and validating the long-term performance of subsurface CO_2 storage.

Summary of Accomplishments:

Major accomplishments for the project include:

1. Expanded capabilities: We have developed the capability at Sandia to perform experimental work evaluating geochemical/hydrologic processes in supercritical CO_2. Also, we developed equipment and expertise for assessing clay shrink-swell at high pressure under nonhydrostatic conditions using neutron beam and x-ray tomography techniques. Finally, we have developed models and expertise for assessing water adsorption/desorption phenomena in two-phase systems. The tools and expertise developed are also applicable to other fluid-mineral problems (e.g., enhanced oil and gas recovery).
2. Evaluated water adsorption to mineral surfaces in $scCO_2$: We have performed theoretical and experimental assessments of the formation and evolution of water films on mineral surfaces in $scCO_2$ as a function of water content. The theoretical model assesses both water adsorption and capillary condensation in $scCO_2$, and provides estimates of film thickness and of water saturation as a function of pore geometry. Water adsorption by silica surfaces and clay films was measured experimentally using both quartz crystal microbalance (QCM) and Fourier Transform Infrared Spectroscopy (FTIR) techniques. Results validated

the theoretical model, confirming that water films are thinner and saturations are lower in scCO_2 than in vadose zone systems at the same water activity.

3. Assessed mineral reactivity in scCO_2. Mineral dissolution/secondary phase formation was evaluated in hydrous scCO_2 for four silicate minerals (albite, orthoclase, labradorite, and muscovite). Results indicate that these common rock-forming minerals react readily with hydrous scCO_2, and that mineral dissolution/precipitation may have a significant effect on rock permeability in plumes of sequestered CO_2 prior to re-saturation.
4. Developed a model for the movement of CO_2 ganglia in porous media. This model evaluates residual trapping of scCO_2 as a function of effective surface tension and CO_2 injection rate, and may lead to the development of new technologies (e.g., engineered capillary entrapment) for CO_2 management.

Significance:

Carbon sequestration continues to be viewed as a critical pathway for climate management for fossil fuel mitigation. This research provides improved constitutive models and needed experimental data for incorporating processes at the mineral-scCO_2 interface into process models for CO_2 sequestration. The improved models are necessary to evaluate and validate the long-term performance of subsurface CO_2 storage. The work may also lead to the development of new technologies (e.g., engineered capillary entrapment) for CO_2 management. The tools and expertise developed are also applicable to other fluid-mineral problems (e.g., enhanced oil and gas recovery).

Refereed Communications:

Y. Wang, C.R. Bryan, T.A. Dewers, J.E. Heath, and C. Jove-Colon, "Ganglion Dynamics and its Implications to Geologic Carbon Dioxide Storage," *Environmental Science and Technology*, vol. 47, pp. 219-226, July 2012.

Development and Deployment of a Field Instrument for Measurements of Black Carbon Aerosols

151307

Year 3 of 3
Principal Investigator: H. A. Michelsen

Project Purpose:

Atmospheric black carbon (BC) consists of combustion-generated soot incorporated into atmospheric aerosols. BC particles strongly absorb solar radiation and the resulting global warming and regional climate effects are substantial. Brown carbon (BrC) particles are predominantly composed of semivolatile combustion by-products and are also suspected of having similar climate effects. In the Arctic, soot settles on snow, decreasing its albedo and leading to melting and further warming. Additionally, aerosols influence cloud properties, leading to large uncertainties in climate models. The physical characteristics of atmospheric particles and the magnitude of their climate effects depend on where they originate, how they mix in the atmosphere, and how their properties evolve as they age. Developing a better understanding of, and parameterizations for, these processes will narrow the uncertainties in climate models. Furthermore, because their physical characteristics depend on their origins and histories, the composition and partitioning among aerosol types can be used as tracers to attribute sources of greenhouse gases (GHGs) for climate treaty verification. BC and BrC particles are small and highly variable in composition and structure and existing instruments are incapable of characterizing them with sufficient sensitivity, specificity, and time response to classify populations of particles in air masses. Aerosol mass spectrometers can speciate particles with sufficient sensitivity but do not provide optical information. Filter techniques are too slow. Current optical techniques provide optical parameters but lack specificity. The purpose of this project was to develop a technique and build a field instrument that would simultaneously provide information about particle composition and optical properties. The technique involves sequential implementation of: 1) light absorption and scattering, 2) ultraviolet (UV) laser-induced fluorescence (LIF) and scattering during thermal desorption of volatile or semivolatile coatings to acquire compositional information about the volatile component and particle size, and 3) laser-induced incandescence (LII) to quantify the black-carbon component.

Summary of Accomplishments:

Over the course of this project, we designed and built a field instrument to measure atmospheric black-carbon particles. The instrument is based on LII, which is selectively sensitive to black-carbon particles. The instrument has high sensitivity to transportation particulate emissions, which tend to be too small to be measured by most state-of-the-art atmospheric instruments. We also have developed a well-characterized soot source for testing the technique and the instrument. Soot was generated in a co-flow diffusion ethylene-air flame at atmospheric pressure. Combustion was quenched with a cross flow of nitrogen. Part of the flow was extracted and sent through a differential mobility analyzer (DMA) for size selection. The size-selected soot could be sent through a condenser and coated with oleic acid. The coated or uncoated soot could also be sent through a thermodenuder to remove coating. The uncoated, coated, or denuded soot could be sent into an optical cell and heated with a pulsed 1064-nm laser. The particles were then sampled by scanning mobility particle sizer (SMPS) or centrifugal particle mass analyzer (CPMA) or collected for transmission electron microscopy (TEM) imaging. The development of the characterization source led to a number of discoveries about the effects of coatings on soot morphology and the effects of coatings and morphology on detection efficiencies using LII. Using this soot source, we compared our instrument with the current state-of-the-art.

Significance:

Our new instrument enables sensitive detection of atmospheric black-carbon particles, particularly those emitted by transportation sources. These sources are responsible for a significant fraction of atmospheric black carbon. This instrument will narrow the large uncertainties associated with abundances and distributions of black carbon in the atmosphere. The results will be used to enable the assessment of black-carbon emissions reduction as a near-term climate change mitigation approach. DOE has initiated significant expansion of its climate prediction program to support national strategic decisions, which will require expanded datasets and validation, and these measurements will also be used to support this program. This work led to two peer-reviewed publications, two talks (one invited), and four posters at national meetings. An invention disclosure is in progress.

Refereed Communications:

R.P. Bambha, M.A. Dansson, P.E. Schrader, and H.A. Michelsen, "Effects of Volatile Coatings on the Laser-Induced Incandescence of Soot," *Applied Physics B*, vol. 112, pp. 343-358, September 2013.

R.P. Bambha, M.A. Dansson, P.E. Schrader, and H.A. Michelsen, "Effects of Volatile Coatings and Coating Removal Mechanisms on the Morphology of Graphitic Soot," *Carbon*, vol. 61, pp. 80-96, September 2013.

Simulation of Component Transport and Segregation in Nuclear Fuels

151310

Year 3 of 3
Principal Investigator: V. Tikare

Project Purpose:

This project seeks to develop a model that can treat microstructural changes that are driven by both structural features (curvature of the interfaces, interfacial energies, etc.) and chemistry (changing local chemistry due to fission, temperature gradients, etc.). The two—structure and chemistry—are often interdependent. Examples of this interdependence are interfacial energies that are chemistry dependent and observation that the solubility of a component is higher in high-curvature features. The microstructures of interest are complex ones having a variety of grain sizes and shapes with multiple phases such as a second solid phase, porosity or gas bubbles, or some combination of these. The kinetics of evolution in these systems is also very complex as the transport paths and mechanism depend heavily on the local structure and chemistry. For example, the surface of a pore or gas bubble may provide high-diffusivity regions for diffusion of one or more components, or they may act as sinks for some components such as noble gases. Current models can treat either structure-driven processes or chemistry-driven process. We have started developing a model that combines elements from the two leading materials models, the Potts Monte Carlo model and the phase-field model, into a hybrid model that can treat both structure- and composition-driven materials processes. This is the first model that will simulate the coupled processes rigorously. Development of this capability will enable simulation of a host of materials and processes that are technologically important to Sandia. The model development in this project is the fundamental development of a class of models and is not specifically applicable to a particular materials technology. However, we concentrate on nuclear materials technologies, in particular, component and fission product transport and segregation in nuclear fuels. These materials systems were chosen as they are complex and couple the physics of interest.

Summary of Accomplishments:

We have developed and demonstrated hybrid models for simulation of microstructural evolution influenced by coupled processes with multiple physics. These processes are coarsening, nucleation, differential diffusion, phase transformation, radiation-induced defect formation and swelling, often with temperature gradients present. All these couple and contribute to evolution that is unique to nuclear fuels and materials. A hybrid model that combines elements from the Potts Monte Carlo, phase-field models and others has been developed to address these multiple physical processes. These models are described and applied to several processes that include the following: hybrid Potts-phase field model for simulation of coupled grain growth and diffusion in a two-component, two-phase system; hybrid Potts-cellular automation model for simulation of dynamic recrystallization; hybrid Potts-phase field model simulation of coupled microstructural-compositional evolution for Si-Al informed by thermodynamic database; simulation of radiation-induced segregation by the hybrid Potts-phase field model; and hybrid Potts-phase field model for component segregation and phase transformation in Uranium-Plutonium-Zirconium fuels. In addition to these models, supporting work was done to characterize topology and topological changes during microstructural evolution and applied to characterizing topological changes during grain growth. To enhance computational efficiency, a moving mesh capability for the phase-field model was also developed. The models developed are coded as applications within Stochastic

Parallel PARticle Kinetic Simulator (SPPARKS), a Sandia-developed framework for simulation at the mesoscale of microstructural evolution processes by kinetic Monte Carlo methods. This makes these codes readily accessible and adaptable for future applications.

Significance:

The microstructural-compositional evolution capabilities developed in this work enabled a new class of materials processes to be simulated, addressing many long-standing materials issues facing Sandia. The hybrid Potts-phase field model has already been identified as the basis for the hydride formation in nuclear fuels claddings. It has applications to many other materials of interest to Sandia and DOE such as evolution of joined regions (welds, brazes and solders), the neutron generator ceramic frame, micropores in geologic structures, compositional gradient evolution in electrical ceramics, and many more. This new capability can be used to address many long-standing materials issues facing Sandia. This work has resulted in three invited papers at international meetings, five peer-reviewed journal articles, and two peer-reviewed conference proceedings.

Refereed Communications:

J.J. Cox, E.R. Homer, and V. Tikare, "Coupled Microstructural-Compositional Evolution Informed by a Thermodynamic Database using the Hybrid Potts-Phase Field Model," *MRS Proceedings*, vol. 1524, 2013.

E. Hernández–Rivera and V. Tikare, "Simulation of Radiation-Induced Segregation by the Hybrid Potts-Phase Field Model," to be published in the *Thermec Proceedings*, 2013

B.R. Patterson, D.J. Rowenhorst, V. Tikare, R.T. DeHoff, and D.J. Rule, "Affinities for Topological Arrangements in Grain Structures," to be published in *Acta Materialia*.

E.R. Homer, V. Tikare, and E.A. Holm, "Hybrid Potts-Phase Field Model for Coupled Microstructural-Compositional Evolution," *Computational Materials Science*, vol. 69, pp. 414–423, March 2013.

B.R. Patterson, D.J. Rule, R.T. DeHoff, and V. Tikare, "Schlegel Description of Grain Form Evolution in Grain Growth," *Acta Materialia*, vol. 61, pp. 3986-4000, June 2013.

Development of a Modeling Framework for Infrastructures in Multi-Hazard Environments

151313

Year 3 of 3
Principal Investigator: N. J. Brown

Project Purpose:

The continuous operation of infrastructure systems is critical to societal welfare. Currently, much of the protection planning against natural hazards and terrorism is done separately for each infrastructure and each hazard. With limited funding, it is important to balance expenditures for terrorism and natural hazards based on potential impacts.

The key S&T problem is creating a modeling framework for investment planning in interdependent infrastructures focused on multiple hazards risks including terrorism. To develop this modeling framework, three modeling elements must be integrated: 1) sophisticated modeling of natural hazards and terrorism — for natural hazards, this includes the ability to specify a number of events (as well as their probabilities of occurrence) which are consistent with the regional hazards; 2) sophisticated modeling of the terrorist's goals and actions — this representation should admit a range of assumptions about what the terrorist knows and how they identify what to target, given their resource limitations; and 3) sophisticated models of interdependent infrastructures are needed in order to predict the impact of specific terrorist attacks and natural hazard events, as well as how the performance of these systems would change based on investments. The tools developed will be applicable across a wide range of infrastructures (Department of Homeland Security, DoD), though we initially focus on electric power and its connections to transportation. We will also explicitly identify and illustrate methods to validate each element of the framework.

The development of these tools and framework is research in nature. The success of this project rests on our ability to effectively integrate investment planning with game theory. Since natural hazards do not involve a malicious adversary, the modeling in that area does not have the same complexity (though it is critically important). Global optimization techniques and (nonzero sum) leader-follower assumptions will be used to produce a tractable formulation. The value of such a tool in this area is extremely high.

Summary of Accomplishments:

In the final year of the project, we succeeded in achieving our ultimate goal of demonstrating an investment planning optimization for multiple infrastructures (roadway and hospital networks) subject to multiple threats (earthquakes and terrorism). To this end, we developed a heuristic using a genetic algorithm, which can be run in parallel on a supercomputer cluster, and combined that with a closed-form mixed integer linear programming (MILP) formulation.

In FY 2012, the focus of the project was the development of investment planning models of single infrastructures under one threat. Because the goal of the project is the modeling of multiple infrastructures under multiple threats to support investment planning, we developed three optimization models to support investment planning under earthquake hazards. In addition, we constructed a new optimization algorithm for investment planning in electric power networks that is capable of addressing problem instances that are about two orders of magnitude larger than those found in the literature. We developed a detailed model of a second infrastructure, the US passenger air system.

In FY 2011 we developed the network modeling to support detailed analysis of the highway network for Shelby County, TN, in the New Madrid Seismic Zone, as well as the electric power system in the Eastern Interconnection (EI).

The FY 2011 work was focused on modeling the response of those systems to specific earthquake events. This included the development of a novel method to construct damage scenarios for those systems to assess the probability distribution of impacts to those systems from individual events. This year we extended that methodology to include the construction of building blocks for scenarios that support estimation of the impacts of these system events under packages of mitigation strategies and published our results along with an invention disclosure.

Significance:

The mission of DOE and DHS is to advance the security of the United States through technical means, including energy and infrastructure security. The tools developed in this project can be applied to support these missions. DHS's responsibilities to analyze and mitigate the consequences of national disasters and terrorist events are addressed by this research and the creation of modeling tools that support investment planning in infrastructure systems.

Refereed Communications:

N. Brown, J. Gearhart, D. Jones, L. Nozick, N. Romero, and N. Xu. "Multi-Objective Optimization for Bridge Retrofit to Address Earthquake Hazards," to be published in the *Proceedings of the 2013 Winter Simulation Conference*.

N. Romero, L. Nozick, I. Dobson, N. Xu, and D. Jones, "Transmission and Generation Expansion to Mitigate Seismic Risk," *IEEE Transactions in Power Systems*, vol. 28, November 2013.

J. Gearhart, N. Brown, D. Jones, L. Nozick, N. Romero, and N. Xu. "Optimization-Based Probabilistic Consequence Scenario Construction for Lifeline Systems," *Earthquake Spectra*, published online September 2013.

N. Romero, L. Nozick, I. Dobson, N. Xu, and D. Jones, "Seismic Retrofit for Electric Power Systems," to be published in *Earthquake Spectra*.

Energy Security Assessment Tools

151314

Year 3 of 3
Principal Investigator: E. D. Vugrin

Project Purpose:

Energy systems serve a keystone role, as other national critical infrastructure and key resource (CIKR) systems depend on them. Disruptions to this sector can affect civilian and military operations, so energy security assessment methodologies must consider this dependence. Current vulnerability assessment (VA) tools are limited in their ability to evaluate the role of energy security. They focus on the identification of vulnerabilities that are "within the perimeter" and may miss dependencies on civilian CIKRs and cyber components. These methods tend to be asset focused, missing mission dependencies and redundancies. Also, they generally address only protection and do not consider recovery actions. Comprehensive energy security assessment tools must be developed to address these limitations. We propose to develop the capability to evaluate energy security of military missions through the design of quantitative resilience metrics and systematic characterization of mission dependencies. The capability will enable the evaluation of energy security, provide recommendations for resilience enhancing improvements, and enable cost/benefit analysis of improvement options.

This project will advance the current state of mission assessment tools. Including dependencies on civilian CIKRs will enable the incorporation of novel design basis threats (DBTs), resulting in identification of new vulnerabilities. Identification of connections between missions across the military complex will enable application of enterprise-wide solutions for increasing mission assurance (rather than site-specific solutions). Quantitative resilience methods are rare, and we are not aware of any for military applications (not related to mental health). Development of metrics for military settings will be a significant advance in the resilience community.

This approach will be more complex than existing VA methods. Information necessary for the development of conceptual models will be sensitive and require significant interaction. Adaptation of risk metrics to resilience metrics and evaluation of systems with cross-sector dependencies are known challenges in resilience analysis. The benefit will be a more comprehensive evaluation methodology, improving energy security.

Summary of Accomplishments:

We created a set of mathematical techniques to evaluate the impact of recovery resource constraints and restoration priorities on the resilience of bulk power systems and, more generally, infrastructure systems. These techniques were implemented in two sets of computer modeling tools. The first model simulates the dynamic restoration of power for a bulk power system that experiences a disruptive event that exceeds N-1 contingencies. The model can be used by utility emergency planners to identify recovery and planning strategies that restore power faster and enhance the resilience of the system. The second numerical model simulates the impact of power outages on the ability to conduct key government missions. The model includes a mission hierarchy that represents the key dependencies between utilities, assets, critical tasks, and missions. Similarly, this model can be used for planning, assessment, and investment purposes.

Significance:

This work developed a set of mathematical approaches for modeling and analyzing infrastructure systems, electric power systems in particular. Additionally, two sets of numerical simulation tools were created to inform emergency response and restoration planning for the grid and critical government missions connected to the grid. We have demonstrated that the basic principles and metrics developed on the project for the grid can be applied to other infrastructure systems as well. Peer-reviewed publications on cyber, transportation, and other infrastructure applications demonstrate the broad applicability of the approach. This work addresses in part key R&D gaps called out in Presidential Policy and other homeland, energy, and national security policies. The methods and techniques developed on this project are/will be leveraged to support projects with the Department of Homeland Security, DOE, and the Veteran's Administration.

Refereed Communications:

M.A. Turnquist and E.D. Vugrin, "Design for Resilience in Infrastructure Distribution Networks," *Environment Systems and Decisions*, vol. 33, pp. 104-120, March 2013.

E.D. Vugrin and J. Turgeon, "Advancing Cyber Resilience Analysis with Performance-Based Metrics from Infrastructure Assessments," *International Journal of Secure Software Engineering*, vol. 4, pp. 75-96, 2013.

Development of Novel Nanoarchitectures to Enhance High-Temperature Thermoelectric Oxides for Clean Energy Harvesting

151369

Year 3 of 3
Principal Investigator: N. S. Bell

Project Purpose:

This project was performed to develop a novel processing method for porous ceramics of energy collecting materials, in which the structure would allow for improved performance over the bulk material properties. Electrospinning is known for being able to produce nanomaterials from a wide range of materials. However, high conductivity electrospinning solutions introduce a new set of challenges not previously reported. Once the electrospinning solution reaches a critical conductivity, different behaviors emerge. At high conductivities, fibers begin to deposit as 3D, low-density, structures instead of flat meshes. It was observed that this behavior begins to occur when the solution conductivity is higher than 1270 µS/cm for a TiO_2 precursor system. Above this critical value of conductivity, the shape of the collection surface begins to have a strong influence on the morphology of collected fibers. In this work, the overall structure and morphology of the fiber mesh is reported as the solution conductivity is varied. Individual fibers are also examined through scanning electron microscopy to denote changes to individual fibers. The growing interest in incorporating various compounds into electrospun fibers, which can greatly increase the electrospinning solution conductivity, makes understanding the behaviors associated with high conductivity solutions essential to future developments in a variety of applications.

Summary of Accomplishments:

This research developed a novel processing technique for forming oriented films of fiber-based materials, using simple collection geometry. This allows for the creation of 3D connected microstructures with high open space. Several sol-gel chemical approaches were investigated for developing thermoelectric materials based on these fiber-formed structures. It was learned that collecting these fibers from high conductivity solutions introduces new complications into the electrospinning process. As the conductivity increases beyond 1270 µS/cm in a TiO_2 precursor solution, fibers form 3D structures. The fibers follow the electric field lines produced by the collection surface. Since the collection surface alters the shape of the electric field, it becomes a critical factor in determining the morphology of the nanofibrous meshes. The information presented in this study details the effects of the phenomena and provides insights into methods to either diminish or exploit the low-density structures that form. The thermal processing of these materials indicated that high temperatures are required, in excess of 1200 °C in order to incorporate the doping elements homogeneously into the system. This often led to microstructural changes in the components, leading them away from the desired porous structures. Chemical routes leading to improved compositional homogeneity with low conversion temperature remain a need for further research.

Significance:

The research performed by University of Florida advanced the understanding of production of fiber-based materials. These materials, having high surface area, can be used for catalysis support, cell-growth templates, precursors to nanostructured composites, or applications in catalysis and energy technology. Several approaches that illustrate microstructural control over fiber-derived architectures were tested. These examples provide guidelines for new applications of component structure that affect component properties.

Refereed Communications:

M.J. Laudenslager and W.M. Sigmund, “A Continuous Process to Align Electrospun Nanofibers into Parallel and Crossed Arrays,” *Journal of Nanoparticle Research*, vol. 15, p. 1487, March 2013.

Reconstruction of a High-Resolution Late Holocene Arctic Paleoclimate Record from Colville River Delta Sediments

151370

Year 3 of 3
Principal Investigator: T. S. Lowry

Project Purpose:

High Arctic permafrost soils contain a massive amount of organic carbon, accounting for twice as much carbon as what is currently stored as carbon dioxide in the atmosphere. However, with current warming trends this sink is in danger of thawing and potentially releasing large amounts of carbon as both carbon dioxide and methane into the atmosphere. It is difficult to make predictions about the future of this sink without knowing how it has reacted to past temperature and climate changes. This project investigated long-term, fine-scale particulate organic carbon (POC) delivery by the high-Arctic Colville River into Simpson's Lagoon in the near-shore Beaufort Sea. Modern POC was determined to be a mixture of three sources (riverine soils, coastal erosion, and marine). Downcore POC measurements were performed in a core close to the Colville River output and a core close to intense coastal erosion. Inputs of the three major sources were found to vary throughout the last two millennia, and in the Colville River core covary significantly with Alaskan temperature reconstructions.

Summary of Accomplishments:

We discovered that the surface sediments in the system contained a mixture of POC and sediments sourced from a variety of areas, including the Colville River, the Mackenzie River, coastal peat erosion, and marine primary production. As might be expected, input from the Colville River was most important at the western end of the Lagoon, whereas coastal erosional and Mackenzie River input was most important at the eastern end of the Lagoon. For all areas of the Lagoon, terrestrial POC inputs were more important than marine POC inputs.

In addition to surface sediments, downcore sediments from two cores, one near the Colville outflow and one at the eastern end of the Lagoon, were analyzed for POC input. Higher deliveries of more degraded and older POC are found in the surface of each core when compared to downcore samples, indicating that there is currently more input of soil- and peat-sourced POC than there has been before in the Holocene. Additionally, input of fresh vegetative biomarkers correlates well with temperature changes over the North Slope for the past few hundred years, indicating that woody shrub encroachment has occurred in the past in this ecosystem. Temperature-biomarker comparisons further indicate that the current permafrost thaw and erosional input of soil and peat POC is unprecedented in the North Slope over the past 2000 years.

Significance:

This effort benefits DOE's Climate and Environmental Sciences Divisions' mission to improve the scientific basis for assessing potential consequences of climate changes by providing "the data that will enable an objective assessment of the potential for, and consequences of, global warming." The main objective of this project, to determine how terrestrial vegetation has changed in response to climate change and atmospheric oscillations over the past 2000 years on the continuous permafrost of the north slope of Alaska is directly aligned with the goals of the Office of Science Division of Biological and Environmental Research.

Refereed Communications:

K.M. Schreiner, T.S. Bianchi, T.I. Eglinton, M.A. Allison, and A.J.M. Hanna, "Sources of Terrigenous Inputs to Surface Sediments of the Colville River Delta and Simpson's Lagoon, Beaufort Sea, Alaska," *Journal of Geophysical Research: Biogeoscience*, vol. 118, pp. 808-824, June 2013.

Formation of Algae Growth and Lipid Production Constitutive Relations for Improved Algae Modeling

153236

Year 3 of 3
Principal Investigator: P. E. Gharagozloo

Project Purpose:

Algae-based biofuels have generated much excitement due to their potentially large oil yield from relatively small land use and without interfering with the food or water supply. Algae mitigate atmospheric CO_2 through photosynthetic metabolism. Production of algal biofuels will reduce dependence on foreign oil by providing a domestic renewable energy source. Important factors controlling algal productivity include temperature, salinity, and the light-to-biomass conversion rate. Lipids produced by algae are easily converted into various fuels, but they must be generated in large quantities for efficient fuel production. Parametric studies of lipid-producing marine species, typically serial experiments, that use off-line monitoring of growth, are time consuming and incomplete. These are the necessary precursors for computational models, which currently lack the data necessary to accurately simulate and predict algae growth and lipid production. This project will begin with an algae growth parametric study. Using innovative techniques to control temperature, salinity, and light within a parallel growth apparatus, we will greatly decrease the time and mass of algae required to obtain fully parameterized growth and lipid formation constitutive relations. The knowledge gained will enable computational models to optimize algae growth in real-world conditions with varying temperature, light, and salinity over the course of a day and year.

Summary of Accomplishments:

An experimental method to grow algae strains in parallel in varying conditions to complete the parametric growth study more quickly was designed. Parametric lab-scale measurements of two key algal strains were conducted and used to calibrate the model for the strains measured. The model for Nannochloropsis salina was validated by comparing the calibrated model with greenhouse/raceway measurements. The model was implemented in FLUENT for expanded options and easier interface. Our model showed which environmental factors are limiting growth. The work from this project resulted in two journal publications.

Significance:

This project has positively impacted Sandia algal biofuels program by increasing the laboratory equipment and rapid algal growth capability and developing key collaborations with Arizona State University and the University of Arizona, and through the development of a unique computational model.

Polymer-MOF Nanocomposites for High Performance Dielectric Materials

155065

Year 3 of 3
Principal Investigator: L. Appelhans

Project Purpose:

Capacitors for power electronics, pulsed power, and energy storage applications require high-energy densities, high-dielectric breakdown strengths, and high-temperature operating capability while maintaining the ability to fail as an open rather than as a short. Current dielectric technologies do not meet these requirements. Energy densities must increase by an order of magnitude in order to satisfy future needs. This goal is impossible to achieve without the development of new dielectric materials. Polymer nanocomposite dielectric materials have demonstrated superior properties relative to dielectrics based on ceramics or polymers alone. However, a major challenge in the development of nanocomposite materials is nanoparticle dispersion. Nanoparticle agglomeration severely diminishes the practical utility of dielectric polymer nanocomposite materials through degradation of dielectric properties and poor reproducibility and scalability. We propose to explore the development of polymer nanocomposite dielectric materials with metal organic frameworks (MOFs) as a possible solution to this fundamental problem. MOFs have built-in organic moieties on the surfaces that will improve intrinsic particle compatibility with polymers. Furthermore, MOFs have been little studied in terms of electrical properties and there is a wide array of interesting MOFs with promising characteristics. Polymer-MOF nanocomposites provide a very attractive solution to challenges in dielectric development that, if not overcome, will impede the realization of a practical electrical infrastructure.

Summary of Accomplishments:

This project explored the use of MOF-polymer composites of several types of polymers and MOFs. We discovered that with the commercially available P(VDF-HFP), the use of MOF fillers could result in increases in dielectric breakdown strength leading to a 45% increase in the measured energy density. The size and monodispersity of the MOF fillers were the main factors that effected dielectric breakdown strength, with breakdown strength decreasing when either larger or smaller fillers were used. Because of the relatively low permittivity of the MOF fillers used, the increase in energy density is due entirely to the increase in dielectric breakdown strength. The positive effect of MOF fillers on dielectric breakdown strength was not observed in the other polymer system studied, with all composites studied having lower dielectric breakdown strengths and lower energy densities than the controls. This suggests that the increase in dielectric breakdown strength observed in the P(VDF-HFP) composite system may be related more to changes in the P(VDF-HFP) morphology on filler addition than to the properties of the MOF fillers themselves. However, we were not able to determine conclusively the origin of the increase in breakdown strength.

The dielectric properties of the MOF fillers were also studied in this work. In particular, dielectric permittivity was compared across a series of alkaline earth tartrate MOFs. It was found that for isostructural MOFs, the permittivity decreased as the size and polarizability of the cation decreased. In addition, for two barium tartrate MOFs with identical chemical composition but different crystal structures, the noncentrosymmetric MOF was found to have significantly higher permittivity than the centrosymmetric MOF. These conclusions correspond with intuitive expectations, but have never previously been experimentally confirmed in MOFs.

Significance:

These first studies on MOF polymer composites have already yielded materials that perform as well as, or better than, many inorganic polymer composites, increasing both breakdown strength and energy density relative to the polymer alone. Advances in dielectric materials are key to several technologies of national security import, including pulsed power and alternative energy utilization (e.g., electric vehicles). Furthermore, the study and understanding of intrinsic MOF electrical properties will be essential to fully develop this burgeoning area of materials research.

Time-Resolved Broadband Cavity-Enhanced Absorption Spectrometry for Chemical Kinetics

155298

Year 3 of 3
Principal Investigator: L. Sheps

Project Purpose:

The primary purpose of this project is to develop a novel experimental probe method for gas-phase chemical kinetics: time-resolved broadband cavity-enhanced absorption spectroscopy (TR-BB-CEAS). The new method will be geared toward direct detection of transient reaction intermediates, such as free radical species, which are frequently difficult to probe by existing experimental techniques. In order to directly probe these elusive, yet important chemical species, the proposed technique will meet four specific requirements: 1) nonintrusive probing of homogenous reaction zones; 2) simultaneous detection of multiple species, especially important for complex reactions; 3) fast-time resolution for real-time monitoring of species concentrations; 4) high sensitivity. The proposed method will be complementary to other existing techniques (such as mass spectrometry or laser-induced fluorescence), which offer various advantages but do not simultaneously fulfill all four requirements.

The long-term goal of this project is to design a fully functional experimental apparatus and to integrate it into the existing chemical kinetics program at Sandia, making TR-BB-CEAS a tool in our arsenal of experimental techniques.

Summary of Accomplishments:

We successfully developed a new experimental technique as described above. From a technical perspective, we have demonstrated two important advances.

We constructed a stable medium-finesse optical resonator cavity that achieves an average factor of 100 optical path length enhancements across an unprecedented wavelength range: 300–800 nm. This enables an equivalent two orders of magnitude sensitivity increase (over single-path absorption measurements) for the entire UV-Vis spectral range, making this a viable probe technique for gas-phase samples. We demonstrated a novel transient absorption spectrometer, capable of shot-to-shot averaging of multiple time-resolved absorption spectra, each containing the full transient absorption information. The spectra are dispersed spatially (wavelength along the x-axis and time along the y-axis), projected onto a charge-coupled device (CCD) camera and averaged on the detector sensor. This ensures a simple, robust, and inexpensive experimental setup, suitable for laboratory or field studies.

From a scientific standpoint, the new method will enable direct measurements of reactive chemical species that were difficult or impossible before. We conducted studies of the vinyl radical oxidation, where we detected the short-lived reactants (vinyl radicals), chemical intermediates (formyl radicals), and products (formaldehyde) at the same time. The simultaneous detection of multiple species opens up a detailed view into this important combustion reaction.

In addition, we measured the first direct UV absorption spectrum of Criegee Intermediates, an important class of atmospheric molecules. Without TR-BB-CEAS, such measurements would have been vastly more difficult to conduct and interpret.

Significance:

This project resulted in a novel experimental technique that enables direct measurements of fundamental chemical processes that were previously impossible. Such measurements provide critical knowledge for exploration and validation of atmospheric and combustion chemistry models and mechanisms, and therefore advances Sandia's climate-science mission.

Accelerating the Development of Transparent Graphene Electrodes through Basic Science Driven Chemical Functionalization

155550

Year 3 of 3
Principal Investigator: C. Chan

Project Purpose:

Despite recent intense research on the fundamental properties of graphene, its practical widespread application remains elusive. Graphene has been proposed for use as a transparent electrode owing to the material's high in-plane conductivity, transparency, chemical stability, and elemental abundance. Large interest in this application stems from the desire to replace rare and expensive brittle conducting oxides (e.g., indium tin oxide [ITO]), unstable conducting polymers (e.g., PEDOT:PSS), and fragile optically thin metals as electrical contacts to solar cells, light-emitting diodes, and photodetectors. However, previous efforts in using graphene for electrodes have suffered from poor film quality and uncontrolled interactions between graphene and the contacted materials. Chemical functionalization is a promising means of modifying and improving graphene's interaction with other materials, but current functionalization schemes are not well controlled, characterized, or understood. The practical use of graphene as a transparent electrode material requires control over the chemical functionalization of graphene interfaces, characterizing the physical properties of the functionalized surfaces, and understanding how modifying graphene's chemical nature also affects its material and physical properties.

This work employs a comprehensive characterization methodology to understand the effects of functionalization chemistry on the material and physical properties of graphene. Of particular interest is how chemical functionalization of graphene affects its electronic band structure and its energy band alignment with other materials. These issues, which are still not well characterized or understood in graphene, greatly affect the material's conductivity and transparency, as well as charge injection and extraction in devices. We will investigate electrochemically driven covalent iodonium functionalization of graphene, which modifies graphene's work function and surface energy, improving its performance as a transparent electrode in optoelectronic devices. Using knowledge generated from fundamental surface science measurements, and correlating functionalization chemistries to material properties, this work will accelerate the systematic development of optimally functionalized graphene films for transparent electrodes and other applications.

Summary of Accomplishments:

We demonstrated electrochemically driven covalent bonding of phenyl iodoniums onto epitaxial graphene. The amount of chemisorption was demonstrated by varying the duration of the electrochemical driving potential. Chemical, electronic, and defect states of phenyl-modified graphene were studied by photoemission spectroscopy, spatially resolved Raman spectroscopy, and water contact angle measurement. In particular, we showed electrochemically driven covalent functionalization of graphene by CF_3Ph from a symmetric aryl iodonium salt solution. Unlike spontaneous diazonium functionalization of graphene, a 1 eV more negative reduction potential was required to accelerate the reaction: dissociation of the iodonium compound creates CF_3Ph radicals that covalently bonded to graphene. The functionalization coverage was varied by 1 order of magnitude from $1.6 \pm 0.5 \times 10^{13}$ to $1.0 \pm 0.3 \times 10^{14}$ molecules·cm^2 by increasing the functionalization treatment from dip treatment for one hour to aggressive electrochemical activation up to 20 s of cyclic voltammetric treatment. Shifts in the F 1s and C 1s core-level positions observed in x-ray photoelectron spectroscopy

(XPS) indicate a redistribution of electronic states toward the CF_3−graphene covalent bond. An increased functionalization-induced defect density observed with spectroscopic Raman mapping further confirmed the partial conversion of delocalized graphene sp^2 states to localized sp^3 bonds with CF_3Ph. However, the Raman data and water contact angle measurements suggest that physical damage of graphene by exfoliation does not occur. The rehybridization of sp^2 to sp^3 states was also observed as an increase in the density of C σ- bonding orbitals with respect to the C π-bonding orbitals in ultraviolet photoemission spectroscopy. Covalent anchoring of the CF_3Ph molecules on graphene resulted in a net orientation of fluorinated dipoles, increasing the work function by 0.5 eV. The increased work function and hydrophobicity of elecotrochemically functionalized CF_3Ph−graphene may have technological importance in nanoelectronics, photonics, transparent electrodes, and sensing.

Significance:

Control over the relative spontaneity (reaction rate) of covalent graphene functionalization is an important first step to the practical realization of directed molecular assembly on graphene. Demonstration of well-controlled electrochemical functionalization of graphene provides a pathway towards systematic modification of graphene for transparent electrodes, electrical energy storage, graphene electronics and optoelectronics, sensors, and other high-impact scientific studies. This work resulted in the publication of one peer-reviewed journal publication and over ten presentations at conferences and program highlights. The expertise developed throughout this work was leveraged to attract additional and follow-on funding and opportunities from DOE's Energy Efficiency and Renewable Energy, DOE's Basic Energy Science, and the National Science Foundation.

Refereed Communications:

C.K. Chan, T.E. Beechem, T. Ohta, M. Brumbach, D.R. Wheeler, and K.J. Stevenson, "Electrochemically Driven Covalent Functionalization of Graphene from Fluorinated Aryl Iodonium Salts," *The Journal of Physical Chemistry C*, vol. 117, pp. 12038-12044, May 2013.

Aerosol Characterization Study Using Multi-Spectrum Remote Sensing Measurement Techniques

155804

Year 3 of 3
Principal Investigator: C. C. Glen

Project Purpose:

Atmospheric aerosols affect climate both directly through scattering and absorption of solar radiation and indirectly by serving as cloud condensation nuclei or ice nuclei. Because of the complex spatial and temporal variability of atmospheric aerosol, measurements of the vertical structure of physical, chemical, and optical properties are necessary to understand the effects of aerosol concentrations on global climate. Light detection and ranging (LIDAR) remote sensing techniques have been employed to measure the vertical structure of atmospheric aerosol concentrations. However, due to a lack of laboratory comparisons linking LIDAR backscatter to the physical and chemical properties of in situ aerosols, empirical calculations are often used as an intermediary to estimate such properties. Furthermore, the majority of current LIDAR systems only use a few select wavelengths that limit the characterization of the chemical distribution of aerosols present, which directly impacts single scattering albedo calculations, a parameter used by climate modelers. It is my hypothesis that the wavelength specific scattering properties of atmospheric aerosols are strongly dependent on composition. Through the synergy of a multispectral LIDAR and experimental methods both the particle size distribution and more detailed characteristics of the ambient aerosol particle can be found.

By bringing together a multidisciplinary team of researchers, utilizing advanced experimental facilities, and working with powerful computational resources, we have demonstrated that this unique laboratory LIDAR system can be used to evaluate the optical backscattering and depolarization properties of both fresh and chemically aged aerosol. Our results indicate that, in some cases, organically aged atmospheric aerosol such as dust and sodium chloride can exhibit backscattering cross-sections near that of fresh black carbon. In addition, this research found that potential chemical interactions involving potassium chloride and sodium chloride exist that alters the aerosol backscattering cross-section while preserving particle shape. Further studies are needed to better quantify the results obtained through this project.

Summary of Accomplishments:

We measured the 355-nm and 1064-nm elastic backscatter cross-sections and depolarization ratios of seven different atmospherically relevant aerosols using a unique aerosol chamber and a bistatic LIDAR system. The seven species studied were ammonium sulfate, ammonium nitrate, sodium chloride, potassium chloride, black carbon, and Arizona road dust. Each material was disseminated into a chemical flow reactor where they were mixed with sulfuric acid, toluene/ozone, and m-xylene/ozone mixtures and allowed to age prior to optical scattering measurements. The measured backscatter cross sections and depolarization ratios of the aged material were then compared to their pure, unaged counterparts to aid in the understanding of aerosol optical property transformation in industrial plume transport and regional aerosol optical scattering influences.

We discovered that, in general, toluene- and m-xylene-aged aerosol exhibit a decrease in both scattering cross section and depolarization ratio. This indicates that as these particles are aged by reactive organic uptake, they become more spherical in shape. This generalized result is not consistent with the results from potassium chloride and sodium chloride organic aging, where despite an observed decrease in scattering cross section, little decrease in depolarization ratio was measured. For these chloride-based particle types, aging by toluene and m-xylene ozonolysis is likely leading to a change in the bulk chemical composition of the aerosol rather than surface uptake. Further investigation of both potassium chloride and sodium chloride aging with atmospheric organic vapors is warranted.

Despite the differences observed in reactive uptake methods, all scattering measurements for aerosol with strong scattering signatures show that aged atmospheric aerosol can have backscatter cross sections similar to pure black carbon. This leads to an indirect conclusion, supported by literature studies of aromatic hydrocarbon absorptive properties, that these aerosols can be as efficient at light absorption in the 355-nm and 1064-nm wavelengths as pure black carbon aerosol.

Significance:

Our results have potential large implications for climate related research and global climate modeling efforts, as these aerosols will likely impact atmospheric global warming coefficients. Dust in particular has an aged scattering cross section nearly equal to that of pure black carbon. Since dust is often transported globally from developing industrial areas such as Asia, particles settling in the Arctic must be included in sea-ice and artic warming models. In addition, results from this study can be applied to both biological and chemical weapons research and aid in our ability to definitively detect and discriminate from chemical and biological weapons threats.

Use of Limited Data to Construct Bayesian Networks for Probabilistic Risk Assessment

156135

Year 3 of 3
Principal Investigator: K. Groth

Project Purpose:

Probabilistic Risk Assessment (PRA) is a fundamental part of safety/quality assurance for nuclear power and nuclear weapons. As energy and defense systems change, PRA must evolve to accommodate technological changes (e.g., digital instrumentation and control, automation, passive components), and existing soft-causal risk areas (e.g., aging, common cause failure, and human reliability analysis [HRA]). Traditional PRA models are not flexible enough to accommodate these non-binary soft-causal factors.

Sandia has proven expertise in PRA, HRA, and system modeling, but new knowledge is required to analyze the risks introduced by increasingly complex systems of hardware, software, humans, and organizations. Bayesian Networks (BNs) are a state-of-the-art graphical and mathematical framework that can address these challenges.

BNs are positioned to revolutionize the practice of PRA, but the use of BNs is currently limited to applications where there is substantial statistical data available, or where no data are available; neither of these conditions is common in PRA. In PRA application areas, such as HRA, there is probabilistic information available, but it is in various forms (quantitative, qualitative) and small quantities.

Recently, there has been a push to use data to reduce the subjectivity of the HRA models currently used in nuclear power plant PRA. BNs provide the conceptual framework to combine different forms of information, but this has never been done in a HRA application. This work explores various sources of data relevant to human performance in nuclear power plants, and explores techniques for synthesizing the information into a BN. This is the first modeling effort of its kind and the resulting model will transform the way that human error probabilities are estimated for PRA.

This work will establish expertise and an analysis capability for construction and use of BNs at Sandia. This capacity is important to maintain Sandia's world-renowned reputation for advanced PRA, and positions Sandia to address the next generation of modeling challenges.

Summary of Accomplishments:

Scientific and technical accomplishments include the development of a MATLAB® tool integrating BN specification and inference into one framework, the development of a methodology for using sparse human performance data from nuclear reactors simulators to improve HRA via BN, and the development of a first-of-its kind BN-based HRA model incorporating information from three diverse sources (an existing HRA method, expert probabilities, and simulator data).

The prototype MATLAB tool enables researchers to use both probabilistic and deterministic information to develop and revise BNs. The tool includes multiple algorithms for passing inference in BNs, for including second-order probability on the model parameters, and for using multiple types of sparse data to update the models. The MATLAB prototype is a step toward building generic tools that can be applied to other problems, including other PRA applications. In parallel, we developed generic algorithms to enable Bayesian updating existing HRA methods using small quantities of simulator data. These algorithms enable continuous improvements to HRA as new sources of HRA data emerge, and as scientific understanding of human performance evolves. We used these algorithms and the MATLAB tool to develop a state-of-the-art HRA BN incorporating an existing HRA method (SPAR-H), simulator data from nuclear power plant operational experiments at the Halden international research simulator, and expert probabilities from existing engineering literature. This new model increases the technical basis of the widely used SPAR-H method and demonstrates the feasibility of using sparse data to improve HRA. Furthermore, since the BN framework is expandable in scope and depth, the development of a BN-based HRA method provides a focused starting point for continuous improvement of HRA.

Significance:

The MATLAB tool provides enhanced capability for development of probabilistic decision support models, which can be used to solve problems across the DOE complex. The approach to development of HRA models has wide ranging implications for both DOE and for the broader engineering community. Human reliability continues to be a weak area in the PRA. Using data to improve existing HRA methods increases the technical basis and credibility of HRA methods, which directly improves PRA result for all organizations using PRA to improve the safety of complex socio-technical systems.

Refereed Communications:

K.M. Groth and L.P. Swiler, “Bridging the Gap between HRA Research and HRA Practice: A Bayesian Network Version of SPAR-H.” *Reliability Engineering and System Safety*, vol. 115, pp. 33-42, July 2013.

Smart Adaptive Wind Turbines and Smart Adaptive Wind Farms

156702

Year 3 of 3
Principal Investigator: J. White

Project Purpose:

At the end of Q3 2010, the United States was the largest producer of wind energy with ~2% of all energy supply coming from wind. Although the percentage is single digit, wind energy is currently the most viable clean energy source and has represented ~40% of all new energy. To improve reliability and efficiency, smart adaptive wind energy plant turbines are needed that have the ability to actively measure and control the magnitude and distribution of forces applied to the rotors and drivetrain in order to maximize performance, minimize imbalance loads, diagnose and regulate the growth rate of damage, and optimize operations and maintenance costs.

This research seeks to develop operational monitoring technologies that are the primary requirement in developing smart adaptive wind turbines. Operational monitoring technologies combine sensor measurements with real-time data analysis algorithms to estimate rotor forces and deflections and the state of structural health of the turbine. None of these advancements are possible without the development of an advanced operational monitoring system that will enable smart adaptive turbines. Sensor and data acquisition systems currently deployed on turbines do not have the capability for performing these tasks. Current domestic and international research programs have been focused on the development of component level technology, but have not yet recognized the highly coupled nature of turbine structural dynamics which dictates the need for a unified turbine operational monitoring system.

Summary of Accomplishments:

The technical accomplishments of this project were:

1. A table-top experiment was performed that showed proof of concept of the application of Global Doppler Velocimetry in a small-scale to measure images of the wind flow out of a nozzle using Arizona road dust. This work ultimately led to the development of the Sandia Wake Imaging Measurement System, a system that will provide an unparalleled amount of information about the complex wind-fluid flow through a wind farm.

2. A proof-of-concept analysis was performed that showed new methods for analyzing the power performance of a wind farm. These methods analyzed the data, eliminated poor quality observations and then produced metrics that illustrated the performance and reliability issues due to turbine-turbine interaction in a utility-scale wind plant. That led to the Operational Wind Plant Turbine-Turbine Interaction and Underperformance effort to leverage the Continuous Reliability Enhancement for Wind (CREW) data from Supervisory Control and Data Acquisition (SCADA) systems on one thousand wind turbines, to study turbine-turbine interaction and underperformance on utility-scale wind farms.

Additionally, we installed instrumentation into a utility-scale wind turbine and the data showed that the methods for installation and analysis were relevant and useful to large-scale turbines. Lastly, this work successfully enabled an instrumentation strategy for the new Scaled Wind Farm Technology Facility

(SWiFT) that will lead to first-in-the-world detailed assessments of the power and fatigue associated with turbine-wake interaction.

Significance:

Through this work, Sandia performed significant technical work at both utility-scale and research-scale facilities that will be critical to the future DOE R&D in wind energy. The outcomes of this project influenced the development of a facility to not only support turbine testing but to also become the first facility in the world specifically designed to study turbine-turbine interaction and wind farm underperformance. To capture the world-class nature of this facility, it has been renamed the Scaled Wind Farm Technology Facility (SWiFT). This project contributed to the development of the Sandia Wake Imaging System and Operational Wind Plant Turbine-Turbine Interaction and Underperformance Program. Cumulatively, this helped establish Sandia as a world leader in the operational monitoring of wind energy. According to the US DOE *20% Wind Energy by 2030* report, operational monitoring could lead to a 34% increase in energy capture, and a 9% reduction in capital costs.

In total, the original investment of $500k has led or contributed to the development in $4.7M in research for FY13-FY14. The collective impact will greatly exceed the original technical work proposed in this project.

Fluid Flow Measurement of High Temperature Molten Nitrate Salts

157145

Year 3 of 3
Principal Investigator: A. M. Kruizenga

Project Purpose:

Current working fluids for concentrating solar power (CSP) applications must achieve very high temperatures, in excess of 650 °C, to meet operational and efficiency goals for power production, with nitrate salts as one suggested heat transfer fluid. Unfortunately, much of the industrially available instrumentation for flow and pressure measurement is not rated for use above 450-500 °C. The temperature limitations on most flow devices can be attributed broadly to materials compatibility. The ideal flow measurement device would be corrosion resistant, have minimal or no moving parts to minimize failures at high temperatures, and could be scaled from an R&D prototype to an industrial sized device. For instrumentation development to be realized the first challenge would be to engineer and build a flowing molten facility at Sandia Livermore. The specific technical challenge would then be to develop and test several different flow and pressure measurement devices that operate up to 700 °C with a flow error of less than 5%.

Technology currently exists for flow detection of ionic liquids at moderate temperatures (420 °C). The innovative nature of this work would expand current technologies by developing a prototype that is capable of withstanding the extremely high temperatures (~700 °C) desired for continuous operation in molten nitrate salts, while producing reliable and repeatable measurements of important flow parameters. Building an R&D molten salt loop would allow for the development of new materials suitable for use in high-temperature molten salt systems, such as packing material for valves, pressure measurement techniques, and gaskets.

Summary of Accomplishments:

We discovered a novel technique for measuring high-temperature liquid flow, which correlates surface thermal perturbations with flow rate. Intellectual property was documented in regards to an invention disclosure.

Designs and follow on experiments validated this sensing technique at room temperature conditions using water as a surrogate liquid and heated with off the shelf cartridge heaters. Scaling to high temperatures required use of advanced materials.

Materials selection for high-temperature experiments was completed for molten nitrate systems. This work was documented and submitted to the *Journal of Solar Energy* (Molten Nitrate Salts at 600 and 680 °C: Thermophysical Property Changes and Corrosion of High Temperature Nickel Alloys).

Significance:

The work that was done over this project provides an independent path to high-temperature fluid flow measurement, using some existing scientific understanding as a basis. This has implications for energy industries as power cycles continue to increase temperatures of operation.

Hydrological Characterization of Karst Phenomenon in a Semi-Arid Region Using In Situ Geophysical Technologies

157311

Year 3 of 3
Principal Investigator: K. S. Barnhart

Project Purpose:

We propose to pioneer a new geophysical method for characterizing the hydrodynamics of semiarid karst. The dissolution of soluble bedrock (e.g., limestone) results in surface and subterranean channels, called karst, which comprises 7% to 10% of the dry earth's surface. Karst serves as a preferential conduit to focus surface and subsurface water but, because of irregular structure and nonlinear hydrodynamic behavior, is difficult to exploit as a water resource or protect from pollution.

Municipal/agricultural/energy/carbon storage/waste projects are projected for location in semiarid regions, where karst often exists but is essentially impossible to characterize using standard, "wet karst" methods. Hence, the scientific challenge is to develop new techniques to gather karst hydrological information in terrains where karst features are dry except during infrequent rain and runoff events.

Ground-based geophysical tools are typically chosen to locate karst structural features when water is limited or absent. Unfortunately, past field studies have met limited success because aforementioned subsurface heterogeneities confuse low-resolution data. Even when karstic conduits are located, the original questions pertaining to conduit hydrological significance are left unanswered.

We will customize emerging in situ geophysical monitoring technology to generate time-series data during sporadic rain events. Electrical and seismic sensors will be connected to wireless "nodes" which can be left in the field for many months. Embedded software will increase sampling frequency during periods of rainfall. Further, we will develop parallel inverse code to determine subsurface parameters from this unique time-series data. We hypothesize that this contrast between no-volume flow in karst passageways during dry periods and partial- or saturated-volume flow during a rain event is detectable by these wireless sensor network (WSN) geophysical nodes.

The development of methodologies to characterize semiarid karst hydrology will benefit Sandia missions in energy technologies, waste disposal, and climate security by helping to identify safe and secure regions and those that are at risk.

Summary of Accomplishments:

Due to the realization of technical risks, specifically the durability and applicability of WSN hardware to harsh environmental conditions, we augmented the project goals to explore the feasibility of conventional geophysical techniques to characterizing shallow semiarid karst features. The challenges adapting the WSN hardware to the environment elucidated several R&D tasks for future research. For example, it is recommended that super capacitors be investigated instead of lithium-ion or other common battery types. We also recommend developing simple interfaces for users to command network data collection — a complex task for which new algorithms might be developed to automatically optimize certain parameters.

While troubleshooting WSN challenges, we diverted resources to conduct gravity, seismic, and resistivity surveys on an area with known shallow karst. The surveys were designed over small areas to enhance data resolution — a common issue with karst characterization. Additionally, we independently constructed a conceptual geological model for comparisons. Each geophysical technique offers its own advantages and disadvantages. Our results suggest that the microgravity technique offers a good cost/benefit ratio for locating general karst features. However, little confidence can be achieved using only one method; a strong conceptual geologic plus two geophysical surveys is desirable. The cost of performing multiple surveys and ensuing data analysis is often cost-prohibitive. Therefore, there is still value is pursuing time-lapse resistivity (or other methods) which may avoid multiple techniques by providing stronger information through change detection, as originally hypothesized.

Significance:

The national, economic, and energy security of the United States is reliant on locating and characterizing suitable locations for energy production and waste disposal. Karst is a common geological feature; in many places, pollutants from municipal and agricultural waste have reached crucial water supplies via karst. Improved semiarid karst characterization methodologies are crucial to the security of water systems. This research compares several geophysical techniques for achieving this goal. Since geophysical techniques can provide somewhat subjective results when performed independently, comparing multiple techniques at one location is of scientific value.

Surface Electrochemistry of Perovskite Fuel-Cell Cathodes Understood In-Operando

158702

Year 3 of 3
Principal Investigator: F. El Gabaly-Marquez

Project Purpose:

Solid-oxide fuel cells (SOFC) are electrochemical devices that convert fuels into electricity at efficiencies greatly exceeding combustion-based technologies. Operated in reverse as electrolyzers (SOEC), renewable electricity can be converted into carbon-neutral fuels by reduction of water or carbon dioxide. It is widely anticipated that fuel cells and electrolyzers will be used for storing and inter-converting energy at large scales. Key to improving SOFC technologies is eliminating the kinetic bottleneck of the oxygen reduction reaction (ORR), which occurs on the cathode. The chemical state of the cathode surface critically controls the rates of surface reactions and solid-state transport. Unfortunately, the surfaces of perovskite-structured oxides, the state-of-the-art cathode materials, are extremely complex. Therefore, developing new approaches to determining the surface chemical states during actual operation is extremely desirable.

This project represents basic research inspired to understand an important long-standing energy issue: how do SOFC cathodes function at an atomic level? The innovation that makes this approach unique is the performance of detailed, quantitative in situ measurements of the surface chemical state while the system is operating. We propose to use in situ electrochemical x-ray photoelectron spectroscopy (EC-XPS) under near-realistic operating conditions of high temperature, gas activity and in the presence of spatially dependent electric potentials to study the solid-gas interphase of state-of-the-art cathode materials over single-crystal yttria-stabilized zirconia (YSZ). This project will yield new microscopic chemical information about the processes that limit the rates and efficiencies of electrochemical energy storage and conversion. Knowing the chemical states of the surface and of the bulk and the macroscopic response of the electrolyzers/fuel cell (e.g., the current vs. voltage behavior and the impedance spectroscopy) will provide new insights into the complex processes occurring at cathode surfaces. When continuum models analyze the combined information, knowledge about which microscopic processes control device performance will be obtained.

Summary of Accomplishments:

We utilized operando soft x-ray spectroscopy to understand the chemistry of perovskite-based oxide electrodes while functioning in a device configuration.

We provided an unprecedented description of electrocatalytic reactions at the surface and described for the first time the complex interplay between chemical reaction, charge distribution, and mass transport in two important kinds of perovskite oxides: oxygen- and proton-conductors. Our results establish a link between surface reactivity and electronic orbital configuration. In particular, we show the first direct measurement of metal-oxygen orbital hybridization in working oxides.

We also have correlated proton-conductivity in perovskite oxides to valence-band gap-state formation. We find that surface properties of functioning perovskite cathodes are significantly different than their bulk structures and care should be taken not to idealize these surfaces.

Significance:

This project is part of a set of activities that are forming the basis of a differentiated Sandia expertise for in situ and in operando measurements of electrochemical energy storage and conversion. It enables detailed understanding of the specific chemical mechanisms at the core of charge transfer in electrode-solid-electrolyte energy conversion.

The new in operando diagnostics will support a broad range of S&T for Sandia and the nation for years to come. This is already enabling new, high-visibility collaborations to emerge.

Refereed Communications:

F. El Gabaly, K.F. McCarty, H. Bluhm, and A.H. McDaniel, "Oxidation Stages of Ni Electrodes in Solid Oxide Fuel Cell Environments," *Physical Chemistry Chemical Physics*, vol. 15, pp. 8334-8341, April 2013.

Advanced Materials for Next-Generation High-Efficiency Thermochemistry

158808

Year 2 of 2
Principal Investigator: J. E. Miller

Project Purpose:

Until recently, very little effort, apart from basic thermodynamic analysis, was extended towards understanding the most fundamental part of a metal oxide thermochemical cycle — the reactive oxide itself. Without this knowledge, system design was hampered, but more importantly, advances in these crucial materials were rare and resulted more from intuition rather than detailed insight. As a result, there are currently only two basic families of potentially viable materials, each of which has challenges. We applied a level of scientific rigor not previously seen to the study of thermochemical materials, enabling us to define a characteristic property space that high-performing materials will occupy. The property space includes such considerations as geometry and characteristic dimensions for transport, reaction rates, thermodynamics, and physical properties such as melting point and sublimation pressure. It is our goal to apply this hard-won knowledge to rapidly advance the field of thermochemistry to produce a material within two years that is capable of yielding CO from CO_2 at a 12.5% reactor efficiency. As materials cannot be dissociated from a system, we will also define the next generation heat engine in which this benchmark is achievable.

Sandia is a recognized world leader in the rapidly evolving field of beneficial CO_2 utilization, and in the solar thermal approach, in particular. Despite rapid progress, solar thermochemistry a remains high risk; a factor of 10–20 improvement is needed for it to reach its full potential: >12.5% life-cycle sunlight-to-hydrocarbon efficiency, which requires numerous steps beyond CO efficiency targeted in this work. Accomplishing these advances and realizing the promise for our nation requires a multidisciplinary effort and specialized expertise and equipment. Only a few organizations such as Sandia can muster a meaningful effort in this field and increase the science and technology readiness so that the risk to be assumed by a direct sponsor is acceptable.

Summary of Accomplishments:

We developed and filed a patent for a new best-of-class material that produces more fuel (nine times more hydrogen from water, or six times more carbon monoxide from carbon dioxide) under more favorable thermal conditions than the previous state-of-the-art material. The groundbreaking results were reported in a journal with high impact.

We completed the most thorough analysis of the thermodynamics of state of the art and related materials performed anywhere to date. We demonstrated that chemical modification of existing materials (i.e., by doping or atomic substitution) cannot be expected to provide the required level of improvement. We demonstrated improvements in reaction kinetics for existing materials via unique materials structuring methodology. We developed a general framework for understanding and communicating the factors that determine solar thermochemical efficiencies and applied these to establish general requirements for materials and systems. We established a new figure of merit for characterizing a thermochemical system, the utilization factor, which links materials and reactor properties. We applied engineering principles to establish overarching metrics and technical targets that must be met for solar fuels to have a global impact and limits are to be avoided. We contributed to a detailed study of the potential environmental impacts of implementing solar thermochemical fuel production. We have demonstrated the value of a comprehensive scientific and engineering approach to the development of improved materials and systems.

Significance:

Technology to produce carbon-based solar fuels will provide a pathway to a more secure, sustainable, and environmentally benign energy future. We have significantly advanced the frontiers of science and engineering, most notably by introducing a new and improved class of materials for solar thermochemistry. Our analysis provides important credibility to the topic and establishes performance targets and metrics for solar fuels in general and thermochemistry in particular. The work directly supports the DOE goal to "catalyze the timely, material, and efficient transformation of the nation's energy system and secure US leadership in clean energy technologies" (2011 Strategic Plan).

Refereed Communications:

J. Kim, J. E. Miller, C.T. Maravelias, and E.B. Stechel, "Comparative Analysis of Environmental Impact of S2P (Sunshine to Petrol) System for Transportation Fuel Production," to be published in *Applied Energy*.

N.P. Siegel, J.E. Miller, I. Ermanoski, R.B. Diver, and E.B. Stechel, "Factors Affecting the Efficiency of Solar Driven Metal Oxide Thermochemical Cycles," *Industrial Engineering Chemistry Research*, vol. 52, pp. 3276-3286, January 2013.

A.H. McDaniel, E.C. Miller, D. Arifin, A. Ambrosini, E.N. Coker, R. O'Hayre, W.C. Chueh, and J. Tong, "Sr- and Mn-Doped $LaAlO_{3-\delta}$ for Solar Thermochemical H_2 and CO Production," *Energy Environmental Science*, vol. 6, pp. 2424-2428, June 2013.

E.B. Stechel and J.E. Miller, "Re-Energizing CO_2 to Fuels with the Sun: Issues of Efficiency, Scale, and Economics," *Journal of CO_2 Utilization*, vol. 1, pp. 28-36, June 2013.

J.E. Miller, A.H. McDaniel, and M.D. Allendorf, "Considerations in the Design of Materials for Solar-Driven Fuel Production Using Metal-Oxide Thermochemical Cycles," to be published in *Advanced Energy Materials*.

I. Ermanoski, N.P. Siegel, and E.B. Stechel, "A New Reactor Concept for Efficient Solar-Thermochemical Fuel Production," *Journal of Solar Energy Engineering*, vol. 135, February 2013.

A.H. McDaniel, A. Ambrosini, E.N. Coker, J.E. Miller, W.C. Chueh, R.O. O'Hayre, and J. Tong, "Nonstoichiometric Perovskite Oxides for Solar Thermochemical H_2 and CO Production," in *Proceedings of Energy Procedia: SolarPACES*, 2013.

J.E. Miller, A. Ambrosini, E.N. Coker, A.H. McDaniel, and M.D. Allendorf, "Advancing Oxide Materials for Thermochemical Production of Solar Fuels," in *Proceedings of Energy Procedia: SolarPACES*, 2013.

M.D. Allendorf, J.E. Miller, and A.H. McDaniel, "Design of Materials for Solar-Driven Fuel Production by Metal-Oxide Thermochemical Cycles" to be published in *Interface* - a publication of the Electrochemical Society.

Designing Greenhouse Gas Monitoring Systems and Reducing Their Uncertainties

158809

Year 2 of 3
Principal Investigator: R. Bambha

Project Purpose:

A global climate treaty will likely be based on greenhouse gas (GHG) inventories supplied by participating countries. The inventory-based approach, which assigns emissions on the basis of economic and socioeconomic factors, is fraught with unacceptably large uncertainties in anthropogenic emissions. A "top-down" approach, based on atmospheric measurements, will be critical for compliance verification on countrywide or regional scales. Furthermore, US compliance with a climate treaty will require implementation of effective policies at city, state, and regional levels. To evaluate policy effectiveness, state and municipal decision makers will need estimates of GHG emissions based on emissions sectors, such as transportation, power generation, and biomass burning. Existing attribution methods are inadequate for either treaty verification or policy evaluation, largely because they focus nearly exclusively on measurements of the most abundant GHG, CO_2, which has an enormous variable natural background. Inversion of CO_2 concentration measurements to source locations provides no information on source types, and current measurement databases used for these inversions lack the necessary spatial and temporal coverage.

We will design a new measurement and analysis system for GHG source attribution suitable for treaty verification and regional or municipal policy evaluation. Our approach uses measurements of gases and particulates co-emitted with anthropogenic and biogenic GHGs, which serve as tracers of specific sources and can provide powerful information on source type and strength. This information is valuable for evaluating policy decisions and narrowing uncertainties on inversions for treaty verification, but the multidimensional nature of the associated inversion renders it intractable without co-design of the models and measurements to systematically constrain the problem. The unique approach and computational difficulty makes the project high risk. We will leverage Sandia's unique GHG mobile laboratory to characterize sources and provide an attribution testbed. Sandia's numerical simulation and analysis capabilities will be tightly coupled to support experiment design, characterize uncertainties, design sensor networks, and infer sources.

Optimization of Distributed Waste Water/Water Reuse Systems

158811

Year 2 of 2
Principal Investigator: V. C. Tidwell

Project Purpose:

In much of the semiarid Southwest, regional water sustainability (supply meeting demand) is assured only when water reuse is included as an available water resource. In such cases, integrated planning of water and wastewater infrastructures can lead to economic efficiency and increased system sustainability. For example, integrated planning can address the degree to which new wastewater treatment facilities should be spatially dispersed, particularly in rapidly growing urban areas, in order to reduce conveyance and associated energy costs for the collection of wastewater and redistribution of reclaimed water. Uncertainties in future demand and water availability add complexity to the problem.

Sandia is working jointly with The University of Arizona to develop decision support tools required for integrated water planning. This effort will build on the project "Optimization of conjunctive water supply and reuse systems with distributed treatment for high-growth, water-scarce regions," formerly supported by the National Science Foundation's Emerging Frontiers in Research and Innovation-Resilient and Sustainable Infrastructures, (EFRI-RESIN) program. This project aims to use a triple bottom line (TBL—economic, social, and environmental costs/benefits) approach to evaluate water infrastructure alternatives under uncertainty. Integrating TBL objectives involves not only quantifying economic costs and associated uncertainty for wastewater reclamation infrastructure elements, but also incorporating environmental impacts of reclamation activities through life cycle analysis and social/institutional constraints by scenario analysis. System optimization algorithms will be used to find solutions (including infrastructure location and sizing) that minimize TBL costs.

Summary of Accomplishments:

In collaboration with The University of Arizona, we worked extensively with Tucson Water and the Pima County Regional Wastewater Reclamation Department to implement a scenario-planning framework to address social and institutional aspects of the project. We identified key drivers for decisions about future infrastructure in Tucson and established bounds on these drivers. We developed scenario descriptions for each of our eight scenarios that define the range of expected future conditions. This process aided in collecting valuable data for our case study and helped refine a process that could be applied elsewhere. We also developed GIS methods for translating broad population estimates to spatial layouts of projected population over time. We identified potential sites for smaller, decentralized wastewater reclamation facilities and potential ways to model these facilities.

In the process of obtaining infrastructure solutions for each of the scenarios, we developed additions to the EPANET toolkit to modify pump parameters and pump curves so that these items can be changed by a program such as a genetic algorithm (GA). We investigated the feasibility of using a GA for simultaneous optimization of pipe and pump design parameters and found that when pump location is not fixed, GAs have difficulty converging to feasible solutions. To overcome this difficulty, we developed a hybrid approach, which uses a greedy algorithm to determine pipe sizes for a large set of possible pump configurations and then uses a GA to solve for the pump parameters (design head, design flow, and number of pumps on at peak flow). Further development of scenario infrastructure solutions is ongoing.

Significance:

Water and wastewater services are vital to communities, and planning these two infrastructures jointly can lead to more robust and sustainable systems that work well under uncertain future conditions, reduce greenhouse gas emissions, and better manage limited water resources. The tools we developed are on their way to becoming general tools that can be applied in many areas of the country to allow more efficient infrastructure planning. With the scenario planning framework, planners and engineers can incorporate unique considerations for their areas and use these general tools to take a first cut at infrastructure design, including decentralized wastewater treatment facilities.

Refereed Communications:

C.A. Scott, C.J. Bailey, R.P. Marra, G.J. Woods, K.J. Ormerod, and K.R. Lansey, "Scenario Planning to Address Critical Uncertainties for Robust and Resilient Water-Wastewater Infrastructures under Conditions of Water Scarcity and Rapid Development," *Water*, vol. 4, pp. 848-868, November 2012.

Nuclear Fuel Cycle System Simulation Tool Based on High-Fidelity Component Modeling

158998

Year 3 of 3
Principal Investigator: D. Ames

Project Purpose:

The DOE is currently directing extensive research into developing fuel-cycle technologies that will enable the safe, secure, economic, and sustainable expansion of nuclear energy. The path to successfully develop and implement an advanced fuel cycle is highly dependent on the modeling capabilities and simulation tools available for performing useful relevant analysis to assist stakeholders in decision making. This project pursued the development of a fuel-cycle simulation tool that provides consistent and comprehensive evaluations of advanced fuel cycles, including uncertainty quantification and optimization. In addition, we included the ability to incorporate policy considerations and environmental impact. The resulting simulator has unique features of being high fidelity in nature and capable of performing uncertainty analysis and optimization.

Current DOE fuel-cycle simulation tools are large-scale system dynamics models that track material flow throughout the fuel cycle at the isotopic level and include decision-making capabilities. The design and nature of these code systems limit the level of detail achievable for reactor simulation and restrict their use for uncertainty analysis applications. Therefore, there is a need to provide a greater level of detail (high fidelity) component modeling and the capability to perform uncertainty quantification. Such a tool could be used stand-alone or in conjunction with current fuel-cycle analysis tools to provide a complete set of fuel cycle evaluation data to guide decision makers.

The simulation tool fills a gap in the performance of current fuel cycle simulation tools by incorporating whole-core 3D exact geometry reactor physics models that account for specific reactor designs, variations in design parameters, and quantifying the impact on the overall fuel cycle system. A new method and analysis approach was developed and implemented to overcome limitations imposed by computational cost, which significantly restricts the ability to perform complete analysis of the system, particularly uncertainty quantification and optimization.

Summary of Accomplishments:

We developed an integrated system method and analysis approach that provides consistent and comprehensive evaluations of advanced fuel cycles. Simulation is based on the mass flow of the fuel cycle and described in terms of detailed mass flow equations. For such cases, detailed reactor physics calculations can be problematic due to computational intensity. Therefore, the simulation tool was designed to utilize specially developed multidimensional time-dependent isotopic composition databases and predictive techniques to circumvent the computational cost associated with whole core 3D reactor physics models. This approach is beneficial because it allows sensitivity and uncertainty analysis using Monte Carlo sampling to be applied, along with an optimization procedure for fuel-cycle design based on genetic algorithm optimization.

The code system tracks and produces output for an isotopic inventory, which is composed of 56 Transuranic (TRU) isotopes and ten fission product isotopes, at each fuel-cycle component and reactor interface within the system. From the isotopic inventory, time-dependent results representing material volume, mass, heat load, and radiotoxicity are generated and evaluated. In addition, a module for determining the environmental impact of the fuel cycle was developed and implemented. This module calculates the energy consumption (GJ/MWh), carbon footprint (kg CO_2/MWh), water requirements (L/MWh), and land usage (m^2/MWh) of each component and the overall nuclear fuel cycle. This capability provides a means for exemplifying the environmentally favorable aspects of nuclear energy, especially when compared to other base load electricity generation options.

Significance:

The development of a high-fidelity fuel-cycle code system provides Sandia with a tool to better understand and evaluate nuclear fuel cycle systems. The framework established and demonstrated by this simulation package can be applied to the DOE Fuel Cycle Technologies (FCT) Program's medium-term goal of conducting science-based, engineering-driven research to fully evaluate and characterize the selected sustainable fuel cycle options. It also provides a means to quantify the highly advantageous environmental impact measures associated with advanced nuclear fuel cycles.

Development of a System Model for a Small Modular Reactor Operating with a S-CO_2 Cycle on a DoD Installation that Utilizes a Smart/Micro-Grid

158999

Year 3 of 3
Principal Investigator: T. G. Lewis

Project Purpose:

The application of a dedicated nuclear power system on a DoD installation has been proposed by DoD energy security and those who are proponents of nuclear energy, but neither party has investigated how to couple the requirements of the DoD and the rigidity of nuclear power systems operational constraints. Additionally, there is an interest in using advance reactors due to their operations benefits and advanced power conversions systems. However, neither technology has been rigorously investigated in terms of applicability to DoD facilities and micro-grids. This project utilized a systems engineering approach focused on designing a model that is robust enough to accurately model the stiff equations that are produced when the slower mathematical equations in the micro-grid model are coupled to the near instantaneous physics of the nuclear reactor model. This phenomenon must be modeled with a high degree of fidelity in order to determine which nuclear power system will best fit the unique needs and challenges of a DoD installation.

Sandia has extensive expertise across the entire spectrum of technologies associated with integrating SMRs into DoD infrastructure. Particular strengths of interest to DoD are nuclear fuel-cycle management, power reactor system modeling and micro/smart grid integration. The main product developed from this project is a system model capable of simulating the impact of a load varying smart/micro grid on a SMR and vice-versa for military installations.

Summary of Accomplishments:

Most of the reactor physics analysis centered on a Sandia-developed small sodium fast reactor and a long-life core gas reactor. In the case of the sodium fast reactor, a system was developed to have an enrichment of 11.75% and having nearly zero reactivity changes over an expected life of ten years. The gas reactor was designed to use multiple fuel forms, giving it a life span in the range of three years with manageable reactivity changes. In order to have the gas reactor operate, a shuffling algorithm had to be developed. The light water reactor (LWR) modeled is similar to current technology. Results of the system model showed that SFRs worked best on demanding microgrids, followed by LWRs and gas reactors. The microgrid and Brayton cycle model were simplified in order to keep computational time to a minimum, but a literature review showed results still fell within expectation.

Significance:

The completion of this project will provide the foundation to test advanced nuclear plants in conjunction with critical infrastructure for DoD and DHS. The applicability of advanced nuclear power systems capable of working in combination with current infrastructure and unique load environments is expandable to other critical needs such as medical facilities and responding to natural or manmade disasters. The use of S-CO_2 Brayton systems improves thermal efficiencies and minimizes the size of the power system, making it possible for rapid deployment or evacuation. The modeling and analysis tools produced in this project have received interest from peer labs and the DOE. Interest in these capabilities could expand to international partners.

Toward a Predictive Understanding of Low Emission Fuel-Flexible Distributed Energy Turbine Systems

159259

Year 2 of 2
Principal Investigator: J. Oefelein

Project Purpose:

Using hydrogen derived from coal in power generation is one of the potential strategies being considered for eliminating CO_2 emissions from combustion. In a two-stage gas combustor, injection of hydrogen into a secondary combustor provides an effective means for achieving a wide range of power settings. However, when additional hydrogen is injected into the exit stream of the first stage turbine, the mixture may autoignite. This uncontrolled autoignition event is undesirable as it leads to strong acoustic waves and high levels of nitrogen oxides (NOx). Since hydrogen was not a main fuel in the past, studies of hydrogen combustion under gas turbine environments have not been extensively carried out. Autoignition of hydrogen depends on pressure in a nonlinear fashion and is sensitive to the unique transport properties of the small hydrogen molecules, making prediction of autoignition a very challenging task. For both steady and transient flames, high-fidelity Large Eddy Simulation (LES) is essential for obtaining a fundamental understanding of flame stability mechanisms. We propose a LES study, in collaboration with UC-Berkeley, to model and understand 1) key stability mechanism(s) related to flame propagation and/or autoignition, and 2) the effect of pressure on hydrogen combustion over the range of one to 20 bar.

For power-generating turbine systems, the complexity of turbulence-chemistry interactions in lifted turbulent jet flames is a key challenging issue in adopting hydrogen as a potential alternative fuel. The small size of hydrogen molecules as compared to traditional carbon-containing gaseous fuels presents engineering challenges. Hydrogen molecules have higher diffusivity than other molecules, so hydrogen combustion simulations must properly account for the different transport properties. LES, coupled with innovative capabilities in treating differential diffusion with a proper submodel, is critical in understanding the stability mechanism in lifted hydrogen jet flames. Development of these models will enable development of predictive models for design of low-carbon power systems.

Summary of Accomplishments:

The objective of the work was to study stabilization processes of a lifted hydrogen flame in a vitiated environment at elevated pressure. The second aspect of the work was to develop a combustion model capable of taking into account pressure and strain effects in high-Reynolds number flows. The present work covered these two points. First, a systematic approach was employed to define the optimal LES configuration that would provide the best accuracy while minimizing computational time. A resolution criterion was established based on the first moment of turbulence so that the optimal grid spacing was obtained when the mean and the root mean square of the velocity became insensitive to the level of refinement. Second, a flamelet approach based on tabulated chemistry was developed. Analysis revealed that the flame is thin and very robust over a large range of strain rates, which validated the flamelet assumption and allows one to simplify the modeling approach since scalar dissipation rate can be ignored in the model tabulation. In addition, it was shown that pressure has a limited impact on flame structure in mixture fraction space at supercritical pressures; therefore, it can be omitted as a table input parameter. However, pressure and strain rate fluctuations induce variations in heat release. To take these effects into account, the governing system must include a transport equation for energy. Based on these conclusions, a flamelet-like approach was developed that takes into account compressibility and strain effects. In the flame region, the enthalpy is modified by a compressible source term to recover the correct temperature field. Model sensitivity to strain rate and pressure was then tested and good agreement was obtained in comparison with detailed LES computations. This capability now provides the ability to study combustion stability in high-pressure high-Reynolds number devices.

Significance:

Development of advanced models to treat turbulent combustion processes and the LES technique will advance predictive simulation capabilities in mission-critical areas, such as energy surety. The approach will develop both a fundamental science-based understanding of critical flow phenomena and predictive design tools for combustion systems of strategic importance. With turbulent reacting flow as our target application, the proposed framework of models will has relevance a wide range of multiscale flow problems relevant in the defense, energy, and climate areas. The product of this research will also strengthen Sandia's position in the area of high-fidelity simulations.

Opportunities for Waste and Energy

159302

Year 2 of 3
Principal Investigator: J. Westbrook

Project Purpose:

Increasing concern regarding the cost, security, and environmental impacts of fossil fuel energy use is driving research and investment towards developing the most strategic methods of converting biomass resources into energy. Analyses to date have examined theoretical limitations of biomass-to-energy through resource availability assessments, but have not thoroughly challenged competing tradeoffs of conversion into liquid fuel versus electricity.

Existing studies have focused on energy crops and cellulosic residues for biomass-to-energy inputs; however, the conversion of these biomass resources is often less energetically efficient compared to fossil energy sources. Waste streams are beginning to be recognized as valuable biomass to energy resources. Municipal solid waste (MSW) is a low-cost waste resource with a well-defined supply infrastructure and does not compete for land area or food supply, making it a potentially attractive, renewable feedstock. This project will create the Waste Biomass to Energy Pathway model (WBEM) using a system dynamics approach to analyze the impact of converting MSW biomass to either bioelectricity or liquid fuel. The WBEM will incorporate macroscale feedback from supply chain costs, energy sector impacts, and greenhouse gas (GHG) production within the competing pathways of MSW to 1) landfill, 2) transportation fuel, and 3) electricity in two states with distinct electric mixes: California and Wisconsin.

Current DOE biomass-to-energy strategies focus on liquid fuel and electricity pathways separately, rather than their direct competition. Regional diversities in energy supplies, costs, and biomass resources suggest considering these pathways in competition. MSW-to-energy modeling remains in its infancy, providing Sandia an opportunity to scientifically lead within this field. The system dynamics methodology allows a quantitative exploration of trade-offs between these pathways by considering dynamics and feedback across them over time. This capability will guide understanding of how waste-to-energy technologies could more strategically advance bioenergy in the US and provide a flexible framework able to apply to waste streams beyond MSW.

Enhancing National Security to Rare Earth Element Shortages through Uncertainty Analysis

160400

Year 2 of 2
Principal Investigator: P. Sanyal

Project Purpose:

The purpose of this project was to anticipate the impacts of the Chinese rare earth export taxes on trade flows between China and its trading partners. Rare earth elements are essential to automobile manufacturing, military munitions production, and a number of "green" technologies. The United States has become totally reliant on imports of rare earth metals from China. Owing to its lower cost of production, China has collapsed the supply of rare earths through restrictive export policies, such as export taxes, export quotas, and export licensing. These export restrictions have led to export market losses for China, but also to high price differentials between export prices and domestic prices in China for rare earths.

This project developed a novel stochastic frontier estimation approach to gravity models to assess the impacts of export taxes on trade flows between China and its trading partners, and to evaluate potential mitigation strategies. Gravity models assume that bilateral trade flows between two countries are proportional to the combined "economic masses" and inversely related to geographic and economic distance. The model's popularity is driven by its empirical success, functional flexibility, and in-sample fit to predict bilateral trade flows. The central target of the project is to understand how export restrictions on rare earth elements affect trade flows between China and its trading partners.

The stochastic frontier estimation approach is chosen as the modeling approach since this approach can differentiate between "behind-the-border" trade costs, such as improvement in trade and transport infrastructure, customs and port procedures, and other infrastructure investments in China. This distinction is important as trade costs can have important influences in the volume of exports apart from relative factor abundance and comparative advantage in production.

Summary of Accomplishments:

Our results are significant in a number of ways. First, we find that the significant level of the independent variables changes over time. While geographical distance is significant in export flows in both periods, the marginal effect of per-capita gross domestic product (GDP) is attenuated over time. The significance of the real exchange rate in 2009 may signify two things: 1) it may be picking up some of the variation of export prices on export flows; and 2) successive revaluation in 2005 and again in 2010 through continuous intervention in the foreign exchange markets may have given China an "unfair competitive advantage" over its trading partners. Second, from the analysis of "behind the border" trade costs, we find export losses almost trebled over the time period. Third, our calculation of "implicit beyond-the-border" trade costs indicates that China is gaining markets in Italy, Germany, and Japan (in cerium oxide and cerium compounds). Nonetheless, it is likely that some countries are moving away from Chinese exports of rare earths by either substituting other materials for rare earths in the production function or through opening up of new mines. The implication is that although in the short run China will remain a dominant player in the rare earths industry, in the long run, the dynamics may change as countries find additional sources of supply.

Significance:

We initially investigated a network flow model of trade. However, this model was difficult to implement owing to measurement issues related to stability costs and data consistency issues related to bilateral trade flows. The modeling approach was changed to a stochastic frontier estimation approach that could be applied on a gravity model as described before. This modeling approach can address national security situations where both “behind the border” trade costs and “implicit beyond the border” trade costs are important in affecting trade flows as is the case between China and its trading partners in rare earth trade flows.

Theoretical Foundations for Measuring the Groundwater Age Distribution

161864

Year 2 of 3
Principal Investigator: W. P. Gardner

Project Purpose:

Groundwater flow rates have important implications for groundwater resources, contaminant migration, and the isolation of hazardous wastes; however, flow rates and residence times inferred from individual environmental tracers have significant uncertainties. This project will explore the high-performance simulation of groundwater age and environmental tracer concentration distribution in complex 3D aquifer systems. Groundwater ages derived from single tracer concentrations have been compared to modeled groundwater mean age, dramatically reducing parameter estimation uncertainty. However, a groundwater sample is a collection of particles with a complex residence time distribution; thus, comparison of a single modeled and tracer inferred age is fraught with uncertainty. In this project we simulate the concentrations of multiple environmental tracers and assess the formal reduction in uncertainty of subsurface parameter estimates using tracer information.

Methods to constrain the residence time distribution from the concentration of multiple tracers will be derived, and tracer information will be incorporated into formal parameter estimation and uncertainty analysis routines using synthetic data sets. By focusing on theoretical, numerical experimentation with the extensive numerical power at Sandia, this project can resolve fundamental questions of how to best utilize tracer information, the data worth of different tracers, and the computational requirements. These fundamental insights can then be applied to field data in any setting.

Chloride-Insertion Electrodes for Rechargeable Aluminum Batteries

161866

Year 2 of 3
Principal Investigator: N. Hudak

Project Purpose:

Demand for rechargeable battery systems continues to increase with the emergence of electric vehicles and the introduction of stationary energy storage to the electrical grid. Rechargeable batteries based on aluminum are attractive alternatives to those based on conventional chemistries (e.g., lithium and zinc) because of the high theoretical energy density and low cost of aluminum. An emerging type of rechargeable aluminum battery is based on room-temperature ionic liquids containing aluminum chloride. Aluminum metal has been extensively studied in such solutions, forming the basis for the negative electrode in a rechargeable aluminum battery. The purpose of this project is to explore candidate materials for the positive electrode, which have been far less explored. For this purpose, conjugated polymers are being evaluated as reversible anion-insertion electrodes in room-temperature ionic liquids. This represents a significant advance, as there has been limited investigation of positive electrode materials for nonaqueous, room-temperature aluminum batteries. This work addresses issues of energy reliability and security because of the need for new battery chemistries that are based on inexpensive, domestically produced materials. During FY 2012, the electrochemical synthesis of polypyrrole and polythiophene in chloroaluminate ionic liquids was demonstrated, and their identities were confirmed with analytical techniques. In FY 2013, reversible cycling of the polythiophene films in chloroaluminate ionic liquids was demonstrated with very little loss in capacity up to 400 cycles. Halogen substitution on polythiophene resulted in an upward shift of the battery cell's voltage. The gravimetric capacity of polythiophene in this electrolyte was measured using an electrochemical quartz crystal microbalance. A doping level of one anion per four monomer units was confirmed, which is in agreement with the doping level of polythiophene in other electrolytes. These microbalance data combined with the observed cell voltage proved that the gravimetric energy density of the proposed aluminum battery is competitive for application in grid-scale energy storage.

Hybrid-Renewable Processes for Biofuels Production: Concentrated Solar Pyrolysis of Biomass Residues

161868

Year 2 of 3
Principal Investigator: A. George

Project Purpose:

This effort improves the efficiency and reduces the cost of biorefining through developing a science and technology understanding of solar-biomass processing. The viability of thermochemically derived biofuels can be greatly enhanced by reducing the process parasitic energy loads. Gasification processes are globally endothermic, requiring 20–45% of the feedstock to be consumed allothermally. Additionally, in air-blown gasification, high CO_2 and N_2 dilute the product syngas. Integrating renewable power into biofuels production is one method by which these efficiency drains can be eliminated. There are a variety of such potentially viable "hybrid-renewable" approaches; one is to integrate concentrated solar power (CSP) to power biomass-to-liquid fuels (BTL) processes, both during pyrolysis and/or gasification operations and downstream. Barriers to CSP integration into BTL processes are predominantly the lack of fundamental kinetic and mass transport data to enable appropriate systems analysis and reactor design.

Combined CSP-for-BTL is a nascent field. It has, therefore, only been sporadically addressed from a fundamental science and a process-systems engineering perspective; many important questions need to be answered to enable uptake of this technology. This project will develop a reactor scheme by which high-quality fundamental data on the conversion of biomass-to-liquid fuels, via CSP will be obtained.

The viability of the proposed process, which would enable a significant contribution to the US renewable energy targets, has yet to be established. Our approach would be the first time fundamental process data have been obtained in an attempt to decouple reactor configuration from the behavior of biomass particles undergoing solar irradiation, in terms of kinetics, yields and product quality. The feedstock will be lignin, a copious residue derived from bioprocessing of lignocellulose. Using this waste for fuel will significantly enhance bioprocessing economics. Additionally, the process will be modeled from a process systems engineering perspective, establishing a solid basis to create a high-impact research program in this field.

Integration of SD and PRA to Create a Time-Dependent Prediction of the Risk Profile of a Nuclear Power Plant

162299

Year 2 of 3
Principal Investigator: M. R. Denman

Project Purpose:

Probabilistic Risk Assessment (PRA) is the primary tool used to risk-inform nuclear power regulatory and licensing activities. Risk-informed regulations are intended to reduce inherent conservatism in regulatory metrics that are built into the regulatory framework. It does this by quantifying both the total risk profile as well as the change in the risk profile caused by an event or action.

PRAs are currently representations of the current average risk posed to the public at the time when the analysis was conducted. Changes to the plant, either physical or managerial, are only characterized during revisions to the entire PRA. Slowly evolving changes to public risk are often not calculated until these changes are large enough to warrant a revision of the PRA. This methodology may introduce nonconservative approximations to the PRA, which produces consequences that are not always obvious to the decision maker.

System Dynamics (SD) has been used to understand unintended time-dependent feedback in both industrial and organizational settings. In SD system feedback, loops can be characterized and studied as a function of time to describe the changes to the reliability of plant Structures, Systems and Components (SSCs). While SD has been used in many subject areas, some even within the PRA community, it has not been applied toward creating longtime horizon, dynamic PRAs. Improving the estimation of a plant's continuously changing risk profile will allow for more meaningful risk insights, greater stakeholder confidence in risk insights, and increased operational flexibility.

It is hypothesized that metrics from a SD model of a nuclear plant, such as time-dependent SSC reliability, can provide input to a dynamically restructured PRA. The coupling between PRA and SD will both remove nonconservative approximations and improve stakeholder confidence in PRA.

Heavy Duty Vehicle and Infrastructure Futures

164667

Year 2 of 3
Principal Investigator: A. C. Askin

Project Purpose:

In the United States, heavy-duty vehicle (HDV) fleets comprise a significant fraction of total fossil fuel consumption, which has profound implications for national security, environmental sustainability, and economic stability. Therefore, directing the future development of this sector toward reducing petroleum consumption, while meeting the needs of fleet operators, is critical to mitigating future consequences. New alternative fuel and power system technologies in varying stages of development and commercialization comprise a broad portfolio of options for new vehicle design and current vehicle modifications. The breadth of this portfolio necessitates a tool to evaluate the interdependency of the technical, economic, and stakeholder factors driving the evolution of heavy-duty vehicle resource consumption and emissions generation. Critical questions to be answered include: How are vehicle technology innovations best leveraged to address national security, environmental, and economic concerns? What are the capability gaps and major nontechnical issues impeding industry transformation? What attractive fueling infrastructure options are available to take advantage of HDV transit patterns and fleet scales? A Heavy-Duty Vehicle Pathways Model (HDVPM) will be constructed to address these questions.

Although some modeling efforts have begun to illuminate the complexities of transforming the HDV sector, a comprehensive model accounting for the breadth of vehicle inventory, the impact of potentially transformational technologies, and the necessary infrastructure have not been developed. This project will construct a capability for evaluating the HDV fleet energy efficiency outlook based on supply-and-demand interactions between fuel and infrastructure availability, technology readiness, and primary energy sourcing. The model will incorporate the potential for both technical leaps and impediments throughout the diverse HDV fleet, culminating in the ability to assess technology development portfolios and identify critical decision points for sector transformation. Developing the model will create the capacity for identifying and understanding the principal mechanisms driving the trajectory of the HDV industry with regard to resource consumption and environmental sustainability.

Nanoscale Piezoelectric Effect Induced Surface Electrochemical Catalysis in Aqueous Environment

165464

Year 2 of 3
Principal Investigator: H. Liu

Project Purpose:

We propose advancing the knowledge of the piezoelectric-induced surface catalysis in ferroelectric nanostructures. Ferroelectrics are 'smart' functional materials whose physical properties are sensitive to changes in external conditions like electric field, pressure, and temperature. Although ferroelectrics are widely used in sensors and microelectromechanical systems, activating and catalyzing surface electrochemical reactions via the surface charges generated by piezoelectricity or pyroelectricity is poorly understood. We anticipate that advancing the scientific understanding of the reactivity of nanoscale ferroelectrics in fluidic environments will open a broad range of new applications for ferroelectric material based surface catalysis and aqueous sensing, establishing a differentiating leading edge capability relevant for addressing Sandia's future mission needs.

As an initial demonstration, we propose investigating industrially scalable electrospun ferroelectric nanofibers as a novel membrane component for mitigating membrane biofouling in water treatment (a major obstacle that decreases membrane life and prompts excessive back-washing). Embedded ferroelectric nanofibers in filtration membranes have the potential to electrochemically decompose organic matter in situ on the membrane surfaces, thereby mitigate membrane biofouling.

We propose to investigate reactivity of mechanically excited ferroelectric nanofibers in fluidic environments to identify the microscopic mechanism of effective piezoelectric effect and electrochemical reaction coupling. Electrospun nanofibers will be used because they have particularly large reactive surface areas. Nanofiber geometry can also potentially enhance the piezoelectric responses due to intensified piezoelectricity ascribed to the flexoelectric effect on the nanoscale, and nanofibers possess high sensitivity to small forces. With fabrication and materials engineering through electrospinning and sol-gel techniques, systematic studies of electrospun ferroelectric nanofibers will offer optimum size and material selection as an excellent platform to study nanoscale piezoelectricity induced electrochemical reactivity on ferroelectric surface in solutions.

Advanced SMRs Using S-CO_2 Power Conversion with Dry Cooling

165619

Year 1 of 3
Principal Investigator: T. M. Conboy

Project Purpose:

Small modular reactors (SMRs) are gaining consideration around the world to meet ever-increasing energy demands, particularly in areas where large-scale transmission is not feasible. The DOE recently announced a program of nearly $1 billion aimed at the licensing of light-water-cooled SMRs, demonstrating the high priority placed on this technology.

Light-water SMRs show promise in the near term; however, current designs require a large nearby water source for evaporative cooling, and ultimately suffer from the same waste issues and shutdown heat removal concerns as larger reactors. This project identifies two ways in which a supercritical-CO_2 working fluid is uniquely capable of addressing these problems: 1) as the secondary side of a light-water or liquid-metal reactor system and 2) as the primary coolant in a direct-cycle nuclear turbine.

Recent modeling studies have shown that the S-CO_2 power cycle is strongly compatible with dry-air cooling. Because the cycle is optimized to reject heat at temperatures above 88 °F, its efficiency with increasingly high ambient temperatures does not degrade significantly, unlike steam plants. This allows siting of plants in remote desert areas without penalty. Turbomachinery size and capital cost both strongly favor S-CO_2 power systems over steam. In addition, CO_2 near its critical point experiences sharp changes in density with small temperature changes, affecting large natural circulation flows and establishing decay heat removal for safe shutdown during accidents.

The next generation of SMRs will undoubtedly be fast reactors cooled by high-temperature gas or sodium, capable of operation up to 20 years without refueling. S-CO_2 itself can be used effectively as the primary reactor coolant for a direct-cycle nuclear turbine, as demonstrated in a recent study by Sandia researchers. These next-generation reactors will leave behind a very high value core, complementing DOE missions to advance fuel reprocessing and reduce waste.

Active Suppression of Drilling System Vibrations for Deep Drilling

165620

Year 1 of 3
Principal Investigator: D. W. Raymond

Project Purpose:

A high-reliability drilling system is needed for construction of a deep borehole disposal system reaching depths of 5 km in continental crystalline basement rock. A reference design has been developed that demonstrates viability of the engineered system (SAND2011-6749, Arnold, et al.) that can be realized with currently available drilling technology. Drillstring vibrations are one potential cause of trouble relative to deep-hole drilling as they increase the technical risks and final costs of well construction. Drillstring vibrations are a constant issue in all drilling operations and cause increases in drilling trouble and damaged components and decreases in the rate of penetration, and bit and tool life.

While the drilling industry routinely attempts to deal with these dysfunctions using fixed-rate damping tools, drilling deep wells poses particular challenges because of the increased drillstring flexibility and the greater times needed to replace worn or damaged components. Additionally, the mechanism of self-excitation depends upon the rock formation being drilled, which changes continually in heterogeneous rock. Vibrations are particularly problematic in high-strength rock where the risk of tool failure increases dramatically. Drill string stabilization is imperative for improved reliability and drilling performance.

Advanced development is needed to form an autonomous and adaptive solution for the range of conditions encountered during drilling. The supporting research and development is cutting edge as conventional drilling systems do not use this technique; it is nontrivial as drillstring property variations must be adjusted remotely and possesses high potential, as this has applicability throughout commercial drilling sectors to make deep drilling more efficient and less costly in terms of damaged equipment. Current science and technology has not solved this problem due to telemetry limitations during drilling operations making field observation of the problem challenging, difficulty with laboratory simulation of the problem due to geometric limitations in the laboratory, and the challenge of developing controls/tools with autonomous features.

Climate Induced Spillover and Implications for US Security

165630

Year 1 of 3
Principal Investigator: V. C. Tidwell

Project Purpose:

Developing nations incur a greater risk to climate change than the developed world due to poorly managed human/natural resources, unreliable infrastructure, and brittle governing/economic institutions. These vulnerabilities often give rise to a climate-induced domino effect of reduced natural resource production, which leads to economic hardship, followed by desperate emigration, social unrest, and humanitarian crises. The impact is not limited to a single nation or region but "spills over" to adjoining areas with even broader impact on global markets and security. Although the United States is forced to deal with the brunt of spillover impacts, there is a lack of tools and data to quantify the risks and access preparedness options.

We propose to develop a model of climate-induced spillover that creates and demonstrates a differentiating analysis tool set, incorporating appropriate technical and socio-economic factors of energy, water, climate, and infrastructure resiliency. The unique aspect of this work is the integration of social, economic, infrastructure, and resource dynamics/constraints to provide a comprehensive risk assessment of climate change on human welfare and security. This model will be used to perform uncertainty quantification using the climate forecasts of the United Nation's Assessment Report 5. We will quantify the risk (intensity and frequency) of "spillover" emanating from developing nations that affects US interests (or homeland security). Specifically, we will 1) identify regions at highest risk, 2) quantify the emergent risks, 3) characterize resilient solution options, and 4) provide usable and defensible information to policy makers. The resulting model and analysis will be unique in its application of a risk-based assessment framework for determining what pre-emptive adaptive measures are most necessary when and where.

Natural Gas Value Chain and Network Assessments

165631

Year 1 of 3
Principal Investigator: G. Barter

Project Purpose:

The purpose of the project is to understand the nonequilibrium dynamics that lead to natural gas (NG) price shocks in order to better assess the risk of moving to a NG-based energy economy in the United States.

Not long ago, NG prices were significantly higher and the US was increasing imports to meet demand. The discovery of extensive domestic reserves and affordable extraction techniques created a supply, and corresponding price, shock in the NG market. Such a shock can alter how an energy source is used, such as the preference for NG fueled burners in new electricity generation systems. Additionally, with its intrinsic thermal efficiency, there is enhanced interest in using NG as a transportation fuel. However, growing the market share of an alternative fuel is dependent on consumers, manufacturers, and infrastructure stakeholders having confidence that low NG prices will be a mainstay in the future, despite past volatility. Future price shocks, either upwards or downwards, could support or diminish these new uses for NG. These shocks could be the result of unforeseen economic, technological, or regulatory events. We will develop a systems-level capability that can model the growth of NG in the US economy, including the impact of any future price or supply disruptions.

Examining the impact of shocks on NG markets requires deviation from conventional economic equilibrium assumptions. We will, therefore, develop an innovative model of NG supply and demand that dynamically substitutes disequilibrium for equilibrium approaches when appropriate. Furthermore, our initial focus on NG transportation will explore the interplay between infrastructure growth and consumer adoption of alternative fuel vehicles. This focus will bridge market models with representations of technology growth and consumer behavior, creating a broad systems capability. Thus, lessons learned from this project would be applicable, broadly, to other types of “shocks,” such as disruptive technology development, or shocks in other application areas.

Novel Metal-Organic Frameworks for Efficient Stationary Energy Sources via Oxyfuel Combustion

165632

Year 1 of 3
Principal Investigator: T. M. Nenoff

Project Purpose:

Oxy-fuel combustion is a well-known approach to improve the heat transfer associated with stationary energy processes. However, its overall penetration into industrial and power markets is constrained by the high cost of existing air separation technologies for generating oxygen. Cryogenic air separation is the most widely used technology for generating large flows of oxygen, but is a complex and expensive technology. Pressure swing adsorption (PSA) is a competing technology that uses separations materials such as activated carbon, zeolites and polymer membranes. Current PSA technology is expensive and limited to moderate purity O_2 applications because of limitations of existing separations materials. Metal-organic frameworks (MOFs) are cutting edge materials for gas separation at ambient pressure and room temperature, potentially revolutionizing the PSA process and providing dramatic process efficiency improvements through oxy-fuel combustion. The purpose of this project is to produce fundamental knowledge on novel MOFs for gas separations that will be leveraged to applied studies and/or commercialization of new oxyfuel processes. Our energy analysis of MOF air separation processes coupled to oxy-fuel combustion will demonstrate greater than 5% efficiency improvement, with decreased overall carbon emissions.

Our project is both an innovative approach for developing novel high selectivity MOFs for O_2 purification and is cutting edge for: 1) optimized MOF synthesis, 2) testing of preferred O_2 sorption from multicomponent streams, 3) combined MD simulations and crystallography of gas siting in pores for structure-property relationship studies, 4) combustions testing, and 5) systems analysis to aid in real-world implementation.

Sandia's Twistact Technology: The Key to Proliferation of Wind Power

165633

Year 1 of 3
Principal Investigator: J. P. Koplow

Project Purpose:

Sandia's Twistact technology is designed to eliminate the need for rare earth magnets in multi-Megawatt (MW) wind turbines, which is the last major hurdle to proliferation of cost effective wind power. The R&D team has been making excellent progress. A central goal of this project is to demonstrate that Twistact technology can support an operating current of 1000 ampheres (A) as required for this demanding application. We have already achieved 400 A operation and will soon be testing at 550 A.

Twistact technology shows a great deal of promise. The technology will benefit the wind turbine manufacturing industry by:

1. Allowing wind-turbine manufactures to achieve their longstanding goal of eliminating rare earth magnets in multi-MW wind turbines; the magnets currently hinder large-scale investment because of anticipated rare earth supply disruptions.
2. Twistact technology may allow construction of wind turbines larger than 3 MW, to realize significantly better economies of scale that exist at 10 MW and beyond.
3. Twistact technology may reduce the weight of wind turbine nacelle by 50%, thereby reducing construction costs considerably.

Work in FY14 will continue to focus on the metallurgical belt/sheave interaction that governs current handling capacity and belt longevity. We will also continue to examine high rpm operation for applications such as electric vehicles. An ultimate project objective is to prove the merits of Twistact technology (performance specs, reliability, etc.) and field test on a multi-MW test wind turbine.

Timing is Everything: Along the Fossil Fuel Transition Pathway

165634

Year 1 of 1
Principal Investigator: P. H. Kobos

Project Purpose:

The purpose of our project is to develop a model tool that quantifies the engineering, regulatory, and market factors required to install new energy technology when trying to reach energy security and CO_2 management goals in the coming years. To address the National Energy and Climate Security challenges by lowering carbon intensity for stationary power, it is vital to understand the speed at which new energy technologies replace older ones. Research in the literature often ignores regulatory and market integration constraints.

People save for retirement throughout their career because it is virtually impossible to save all you will need in retirement the year before you retire. Similarly, without installing incremental amounts of clean fossil, renewable or transformative energy technologies throughout the coming decades, a radical change will be impossible the year before a policy goal is to be in place. Therefore, our research question is, “To meet desired technical goals, what are the barriers to installing technology at a given rate to achieve policy goals in the coming decades?”

Recent increases in the Corporate Average Fuel Economy (CAFE) vehicle fuel standards are a good example of the regulatory framework helping technology to meet fuel-economy goals. The same argument applies to US electricity sector technologies about the importance of addressing regulatory and market barriers. This difficult problem spans beyond most governmental, academic and national laboratory’s expertise. Without favorable regulatory integration factors, new stationary energy technologies may never reach their full market potential. Even with these factors in place, technologies may take years or decades to reach the installations necessary to reduce CO_2 and meet policy goals. The sooner they are being installed, the sooner these goals can be met. Therefore, the timing is everything for technology transitions in the marketplace. By developing a new quantitative modeling tool that can be used across existing technology forecasting models, this project will address this need.

Summary of Accomplishments:

The project team demonstrated that by using the modeling tool, the Technology, Regulatory and Market Readiness Simulation Model (TRMsim), one can quantify the influence a policy needs to have to help move a technology more quickly from the research space to market can take many forms. Tripling the size or influence of the key driver to the technology, regulatory and market readiness level, for example, may reduce the time to complete each stage by 63%, 68% and 64%, respectively. These working results illustrate that under the current parameter assumptions for this hypothetical example, investing three times the resources or influence in the regulatory readiness levels may help expedite the technology’s progression through the regulatory processes faster than would a similar investment in the technology’s readiness or market readiness development. These results, however, are hypothetical and very case-specific. Applying the model more widely likely requires additional real world information to adjust the model’s input parameters to help model the time it takes to move the technology from the research stages to full market adoption. With this information comes an opportunity to assess the notion that the ‘timing is everything’ when looking to meet policy goals through technology-based solutions.

Significance:
The very appealing aspect of this framework and subsequent tool is its wide applicability to not only fossil fuel energy systems as they relate to a transitioning energy portfolio in the electricity sector, but to many types of energy systems and technologies in various sectors. The research community that develops energy-economic-engineering types of models could benefit greatly from lessons developed in a tool like TRMsim. The key insights highlight how the "timing is everything" for a technology that may be ready for the marketplace in time to meet a performance in application goal.

Calibration, Validation, and Uncertainty Quantification for Turbulence Simulations of Gas Turbine Engines

165635

Year 1 of 3
Principal Investigator: J. A. Templeton

Project Purpose:

Large-eddy simulation (LES) has the potential to reduce pollutant emissions and increase the fuel efficiency of gas turbine engines through model-based investigations of engine design space. High-fidelity LES simulations have greatly enhanced our understanding of turbulent combustion. Engineering calculations, by contrast, use low-order numerical methods necessitated by the coarse, unstructured grids needed in complex geometries. High-fidelity LES often produces excellent agreement with experiments while engineering LES of the same case does not yield sufficiently accurate data for engine design. Such results lead to key questions regarding the applicability of LES models to the engineering process: 1) in what situations will they work and why? 2) Is the true solution even within the space spanned by existing models? and, 3) How will uncertainties in model parameters impact the results? This work will answer these questions using validation and uncertainty quantification (UQ) to connect science-quality LES with desktop calculations design engineers can use to improve gas turbine engine performance.

Our solution builds on the Advanced Strategic Computing (ASC) program's validation and UQ expertise while developing innovations to handle challenging chaotic flows from engine simulations. Novel UQ approaches will be created to account for the fluctuating turbulent structures. These UQ strategies will enable the calibration and validation problems to be posed in a statistical sense relative to high-fidelity solutions leveraged from existing and on-going scientific calculations. Higher risk work will utilize more complex functional forms that add more physical information but require the detail present in the well-resolved LES for proper calibration. This will determine if existing LES models are capable of the necessary fidelity at acceptable costs. Finally, models will be considered to be probabilistic rather than deterministic to measure model-induced uncertainty to demonstrate whether they retain sufficient accuracy when validation data is lacking. These approaches will greatly enhance the ability of design engineers to utilize high-performance computing to improve engine performance and efficiency.

Developing Next Generation Graphene-Based Catalysts

165636

Year 1 of 3
Principal Investigator: T. N. Lambert

Project Purpose:

We are developing next-generation catalysts based on nanoscale 3D networks of graphene and graphene-ceramic hybrids in order to establish a leading role for Sandia in graphene-based research and graphene-based catalysis. We will also develop a fully built cathode based on these catalysts for use in metal-air batteries and/or fuel cells and demonstrate their prototype use in such devices. High electrocatalytic activity, selectivity, and stability for the oxygen reduction reaction/oxygen evolution reaction (ORR/OER) is critical for successful transition of next generation fuel cells and rechargeable metal/air batteries into today's renewable energy technologies. Platinum's (Pt) high cost and overall rarity preclude it from use in larger-scale widespread commercial applications. Pt-based catalysts in fuel cells also suffer from crossover and fuel poisoning issues, which severely lowers the electrocatalytic activity and performance. Replacing Pt with less costly graphene and graphene-ceramic materials is in support of the Critical Materials Supply issues outlined by DOE. Electrocatalysts based on nanoscale 3D networks of electrocatalytic carbon represent a promising approach to developing cost effective electrocatalysts that operate at higher current densities and cell voltages, with significantly greater electrocatalytic stability in metal-air batteries and fuel cells. Practical electrocatalytic applications of graphene are still severely limited by the lack of fundamental understanding on the origin of its electrocatalytic properties graphene's and its 2D morphology, as the fabrication of practical 3D electrodes for ORR/OER is currently unestablished. What is also needed is a way to assemble these graphene-based materials into larger macroscopic 3D electrocatalysts form factors. We aim to demonstrate that such 3D structures can be prepared in a meaningful way and that they can be utilized in improving electrochemical devices.

Coating Strategies for High Energy Lithium-Ion

165637

Year 1 of 3
Principal Investigator: C. Orendorff

Project Purpose:

Many reliability and safety issues for lithium-ion batteries result from interfacial phenomena at the positive and negative electrodes. A prominent example is the solid electrolyte interphase (SEI) layer that forms on the graphite anode. This SEI layer is known to effect performance and capacity of lithium-ion batteries. Moreover, interfacial reactivity between the electrolyte and the cathode is known to initiate electrolyte combustion during thermal runaway events that compromise battery safety. Interfacial phenomena can be very sensitively influenced by ultrathin coatings on the electrodes. These ultrathin coatings can profoundly alter the interaction between the electrode and the electrolyte. This project is focused on developing atomic layer deposition (ALD) and molecular layer deposition (MLD) coatings for electrode surfaces. Alternative ALD coatings may offer improved ionic conductivity, mechanical stability, and cell performance over other ALD coatings. Advanced MLD coatings may also be devised that act to consume oxygen and decrease the potential for electrolyte combustion and high-rate thermal runaway reactions. These ALD and MLD coatings can dramatically improve lithium-ion cell reliability and safety. The work is in collaboration with the University of Colorado-Boulder.

Synthesis of Heterometallic Manganese oxo Clusters as Small Molecule Models of the Oxygen-Evolving Complex of Photosystem II

165638

Year 1 of 2
Principal Investigator: T. J. Boyle

Project Purpose:

In collaboration with California Institute of Technology (Caltech), the research will synthesize manganese complexes supported by a multinucleating ligand framework as models of the oxygen evolving complex (OEC) of Photosystem II, which is an enzyme found in plants that catalyzes the oxidation of water to molecular oxygen. These model complexes will be studied to better understand the role of the calcium ion in catalysis and the mechanism of O−O bond formation. Previous approaches have relied on self-assembly of the manganese oxo clusters, which have limited the control of cluster nuclearity and geometry.

Enabling Novel Nuclear Reactors with Advanced Life-Time Modeling and Simulation

165644

Year 1 of 2
Principal Investigator: W. J. Martin

Project Purpose:

To enable long-life advanced nuclear reactors, especially novel small modular reactors (SMRs), a study is needed into the true lifetime of the reactor system. A full-scale investigation of the lifetime of the reactor core, materials, and secondary system is necessary in order for any regulator to license the system.

This investigation will require computational tools be brought together for a type of system that has yet to have this full evaluation. All proposed advanced reactors are vastly different than the current fleet of light water reactors. Many code suites are invalid due to physics simplifications. Similarly, the power generation cycle and structural materials will require modeling to determine their lifetime performance, especially with radiation damage.

Advanced lifetime modeling and simulation will be used to assess the current concepts and determine if they match regulations and physical requirements and are feasible. An example of this is the return of the cores at the end of life after they have been exported to and operated in foreign countries. The idea of an exportable, small modular reactor is extremely attractive, but to date, there has been no full study on whether the core will be too radioactive or structurally unstable for it to be shipped after over 10 years of operation. This investigation will help guide the future design and licensing of these novel reactor systems.

Time-Varying, Multi-Scale Adaptive System Reliability Analysis of Lifeline Infrastructure Networks

166143

Year 1 of 3
Principal Investigator: J. L. Gearhart

Project Purpose:

For society's health and economic well being, a country's lifeline infrastructure must be resilient to extreme events. For effective hazard mitigation planning and maintenance based on quantified risk of the infrastructure, accurate models and efficient risk prediction methods need to be developed. This has been attempted using simulation approaches (e.g., Monte-Carlo Simulation). Unfortunately, these approaches quickly become computationally expensive or intractable as the size of the problem increases and the associated level of probability decreases. Others have used simplified approaches to model the network response (e.g., Bayesian Networks). While easier to model and able to incorporate newly available information, these may oversimplify the analysis. To overcome these computational challenges and better understand the hierarchical nature of lifeline infrastructure, a new framework for accurate and efficient risk quantification needs to be developed using a multiscale approach along with accurate computational models for vulnerability of structural components against extreme events and their deterioration. This work is in collaboration with the University of Illinois Urbana-Champaign.

The proposed time-varying hierarchical clustering approach would not only allow for the identification of critical components but also important regions or clusters based on the analysis results at multiple scales. The approach would also allow for the characterization of time-varying influence of deterioration of components and clusters on lifeline network reliability. Few have attempted to analyze large-scale infrastructure networks using such clustering and time-varying vulnerability/deterioration models of components. By incorporating the deterioration of component reliability into the multiscale analysis approach, one would be able to investigate how relative importance of components and clusters changes over time and its implication on the decision-making process.

Structural Health Monitoring for Impact Damage in Advanced Composite Structures Using Virtual Sensor Grid

166149

Year 1 of 3
Principal Investigator: D. P. Roach

Project Purpose:

As our nation's critical infrastructure and mechanical components increase in age, it is essential to introduce new measures to ensure their safe and uninterrupted operation. This research, conducted in conjunction with Purdue University, seeks to enable in situ structural health monitoring (SHM) of aircraft, wind turbine blades, bridges, and other advanced composite structures using a small number of passive and active transducers. Specifically, subsurface damage due to impacts, operational stresses or environmental conditions (e.g., moisture, lightning strike) will be identified and tracked by applying unique load identification and damage detection algorithms together with custom sensor data acquired under operating conditions. This system will allow for rapid, full-field integrity assessments of newly manufactured, and in-service structures.

Current SHM technology proposed for detecting damage or flaws in composite structures requires dense arrays of transducers to achieve the desired level of accuracy. The cost, weight, and complexity of implementing a dense grid of transducers present significant barriers to implementing systems of this type on today's large composite structures. Some SHM systems attempt to use fewer transducers to detect damage in large areas, but these technologies do not directly take into account the effects of operational loading on in situ damage detection algorithms. In other words, current SHM products are essentially nondestructive inspection (NDI) technologies installed on the structure. Therefore, these products neither acknowledge operating loads that affect the health of a structure nor take advantage of their effectiveness in aiding damage-detection techniques. This new technique will utilize the response to impacts to localize potential damage, and then measure the response to active transducers in order to assess the severity of the potential damage. This combination of operational and prescribed forcing functions could drastically reduce the required sensor density of in situ SHM systems by using a "virtual" grid of sensor locations estimated through post-processing, rather than a dense grid of physical sensors.

C2R2: Compact Compound Recirculator/Recuperator for Renewable Energy and Energy Efficient Thermochemical Processing

170805

Year 1 of 3
Principal Investigator: I. Ermanoski

Project Purpose:

This project aims to solve the problem of heat exchange between moving packed particle beds. This will be achieved by demonstrating particle conveying between reaction volumes and heat exchange, in a scalable package: the compact compound recirculator/recuperator (C2R2). To maximize productivity and the chances of success, key C2R2 features will be prototyped individually, in order of increasing complexity.

While fluid-fluid and fluid-bulk heat exchangers are ubiquitous in today's world (from microelectronics to massive power plants), the challenging, yet promising field of heat exchange between packed particle beds remains almost entirely unexplored and undeveloped. Existing applications in need of this kind of heat exchange, such as cement manufacture, employ workarounds involving fluids to achieve satisfactory results. The need, however, has been steadily increasing in emerging technologies, such as solar coal and natural gas upgrade, solar thermochemical energy storage, water and CO_2 capture, or solar thermochemical fuel production, where workarounds would be difficult, if at all possible. These technologies will benefit significantly or depend critically on the development of heat exchangers for packed particle beds. This critical need is especially well documented in the field of solar fuels.

The first goal — demonstrate elevator function with scoops compatible with compound design — was achieved in FY 2013 by shaping the rotating casing and by maximally incorporating the inlets into the casing thickness itself. These "zero-profile" inlets primarily rely on the solids pressure of the particle bed, rather than a scooping action, to feed material into the conveyor. This limiting case demonstrated the feasibility of a concentric device design. While the measured material flow rates are likely suboptimal and room for inlet improvement undoubtedly remains, the most important result is that the original premise of this novel design, namely the solids pressure feed mechanism, was supported by the experimental results. This gives us confidence that the envisioned concentric device can be successfully developed.

Development of High-Fidelity Models for Liquid Fuel Spray Atomization and Mixing Processes in Transportation and Energy Systems

170975

Year 1 of 3
Principal Investigator: R. N. Dahms

Project Purpose:

Significant inadequacies of current models for multiphase flows are a major barrier to rapid development of advanced high-efficiency low-emissions combustion devices. Liquid spray processes largely determine fuel-air mixture formation, which subsequently controls performance, emissions, and durability of a device. While substantial improvements in the design of advanced devices are possible, the processes are sensitive and require high levels of precision that can only be reached through development of advanced simulation capabilities. The present empirical understanding of sprays must be replaced by a new first-principles approach, and this need will only become more critical as requirements become more stringent. The objective of this research is to develop a first-principles approach in the context of high-fidelity large-eddy simulation (LES). We propose to systematically develop a coupled system of advanced subgrid-scale models for LES aimed at treating liquid atomization and spray phenomena. Our primary focus will be on the stringent requirements of transportation, propulsion, and power devices. However, the models developed will have wide application to a variety of multiphase systems.

Predicting multiphase flow phenomena in modern liquid fueled combustion devices is widely recognized as a critical area of research for the design of advanced systems. These needs have been consistently highlighted over many years in a variety of industry, government, and academic forums, including recent DOE workshops such as the "Workshop to Identify Research Needs and Impacts in Predictive Simulations for Internal Combustion Engines" (PreSICE), and the "Workshop on Clean and Efficient Combustion of 21st Century Transportation Fuels." Needs and priority research directions emphasize the importance of establishing a basic science foundation for the development of advanced predictive models in this area. Developing such models requires a highly specialized effort that combines detailed theory, advanced simulation capabilities, and high-performance massively parallel computing. The net results will provide the foundational models and experience required to attract external sponsors.

Development of Quality Assessment Techniques for Large-Eddy Simulation of Propulsion and Power Systems in Complex Geometries

170976

Year 1 of 3
Principal Investigator: G. Lacaze

Project Purpose:

Large-eddy simulation (LES) is quickly becoming a method of choice for studying complex thermo-physics in a wide range of propulsion and power systems. It provides a means to study coupled turbulent combustion and flow processes in parameter spaces that are unattainable using direct-numerical-simulation (DNS) with a degree of fidelity that can be far more accurate than conventional engineering methods such as the Reynolds-averaged Navier-Stokes (RANS) approximation. However, development of predictive LES is complicated by the interdependence of different subgrid-scale models, competition between modeling and numerical errors, model variability, and numerical implementation. Errors and ambiguities are multiplying, and control of accuracy has become a critical aspect in the development of predictive LES for design. When accuracy is not sufficient, results can be misleading and intractably erroneous due to factors such as poor numerics, poor grid quality, lack of appropriate spatial or temporal resolution, ill-posed boundary conditions, and inaccurate models.

The objective of this project is to create a comprehensive framework of metrics aimed at quantifying the quality and accuracy of state-of-the-art LES in a manner that addresses myriad competing interdependencies. The goal is to significantly increase confidence in the accuracy of a given solution while minimizing the time obtaining the solution. This goes well beyond the scope of isolated model development efforts and requires an integrated crosscutting approach. The approach proposed here will facilitate control of the trade-offs between cost, accuracy, and uncertainties as a function of fidelity, models, and numerical methods employed. In a typical simulation cycle, only 20% of the computational time is actually usable. The rest is spent in case preparation, assessment, and validation. This approach will significantly improve this ratio by simultaneously reducing cost while increasing accuracy. Development of these metrics will have broad impact on research supported by the DOE and significantly contribute to strengthening the role of high-fidelity simulations in the community.

Quantifying Confidence in Complex Systems Models Having Structural Uncertainties

170979

Year 1 of 3
Principal Investigator: C. S. Cooper

Project Purpose:

The purpose of this research is to enhance scientists' capabilities to characterize the uncertainties in models of complex systems. The proposed approach, grounded in nonlinear systems theory, complements direct modeling by focusing on sources of errors in models due to both structural deficiencies and external forcing. Structural deficiencies include uncertainties in parameters but can also extend to the underlying formulation of the model, especially in systems for which the mechanisms governing the behavior are not well known.

People put great effort into understanding systems that manifest complexity and defy prediction. The usual approach is incremental modeling: start with a simple model of a system that is known to be incomplete and add new components as insights about the system are discovered. The process is labor-intensive, and it is often difficult to judge whether the behaviors predicted by the model are realistic, and whether the model can no longer be substantially improved.

In particular, it is often unknown whether a model captures the essential behaviors of a system, is structurally flawed, or more terms/parameters are required. Addressing this conceptual difficulty with models will entail a new and detailed inquiry into the mathematical theory of linear and nonlinear systems. We focus here on behavioral regimes of numerical models of different types, rather than the specifics of model construction.

The goal is to develop a mathematical framework to bracket our confidence in the qualitative behaviors seen in the solutions of numerical models, given estimates of fundamental uncertainties in model structure. We envision new modeling methodologies will emerge from these studies. Ultimately, these will provide researchers with a far greater ability to characterize the range of outcomes possible in incomplete models or models with structural deficiencies caused by a lack of understanding of the underlying system.

Use of Slurries for Salt Caverns Abandonment

171525

Year 1 of 3
Principal Investigator: G. Bettin

Project Purpose:
Underground caverns leached in salt domes have been widely used and considered relatively safe for both gas and oil storage. Prior to abandonment, caverns are filled with brine and access wells are cemented. A risk associated with fluid-filled caverns is that, due to creep and thermal expansion, the pressure builds up until it hydrofractures the salt. The risk is that the cavern fluids may eventually leak into an aquifer or appear where they pose an environmental risk.

Little work has been conducted on alternative procedures for cavern abandonment as the industry relies on the standing assumption that brine will seep into the salt and reduce the cavern pressure below the fracture strength of the salt. As this assumption may be valid in some instances, it certainly cannot be held true in many cases, and as the cavern fleet is aging, the pressure from legislators to modify the requirement for cavern abandonment based on scientific data is growing.

A possible solution to mitigate the risk of hydrofracture is to refill the underground caverns or mines with buttressing material (a process called backfilling). To develop such an approach, this project will focus on the fundamental understanding of slurry fluid flow as it applies to large scales such as a 10 million barrel cavern and it will simulate the behavior of the slurry computationally as well as with bench-scale experiments.

One of the major needs for the success of the backfilling process is the choice of materials to use in the slurry and the understanding of the rheology of the chosen material. The rheology of the material is important to gauge how the material will compact in the underground opening as the material matures. Particular attention will therefore be given to the study of rheology of the slurry as it matures in the cavern after deposition.

INTERNATIONAL, HOMELAND, AND NUCLEAR SECURITY

The International, Homeland, and Nuclear Security Investment Area applies innovative science and technology research and development toward developing new and differentiating capabilities and solutions to protect the nation. That includes developing technologies to counter weapons of mass destruction, uphold nonproliferation of biological and nuclear materials, secure nuclear weapons and nuclear materials, and protect the nation's most critical assets.

The investment area's technical solutions must address current security needs and adapt to and anticipate the next generation of risks in the changing security environment. The solutions must also be responsive to the stewardship needs of our government to gain efficiencies, work effectively across the entire national security enterprise, show sustained progress and value over the long term, and demonstrate required levels of effectiveness for the tax dollars spent.

The work is divided into four program areas: Critical Asset Protection, Global Security, Homeland Security, and Homeland Defense and Force Protection.

Using Fast Neutron Signatures for Improved UF_6 Cylinder Enrichment Measurements (Project 151315).

INTERNATIONAL, HOMELAND, AND NUCLEAR SECURITY

Using Fast Neutron Signatures for Improved UF_6 Cylinder Enrichment Measurements

151315

Year 3 of 3
Principal Investigator: S. Kiff

Project Purpose:

One of the most important problems in nonproliferation is monitoring the degree of enrichment from uranium enrichment plants. Centrifuge enrichment plants are necessary to produce fuel for commercial power plants but are also capable of producing highly enriched uranium, which can be configured into a nuclear weapon. Existing technologies for measuring Uranium-235 enrichment in a uranium hexafluoride (UF_6) cylinder requires controlled conditions for accurate measurements, making them susceptible to significant systematic uncertainties. One significant uncertainty relates to the UF_6 distribution within a cylinder, which varies depending upon the filling and storage conditions. Low-energy neutrons and gammas used by current technologies have short penetration through dense UF_6, and since the UF_6 thickness near the measurement location is not known a priori, the current measurement techniques are insensitive to UF_6 in the center of the detector. Thermal neutron counting rate near a cylinder can vary by as much as 50%, depending upon the solidified geometry and the cylinder orientation relative to the detectors.

Our project aims to apply fast neutron spectrometry and imaging to ascertain the UF_6 enrichment inside the cylinder. Deeply penetrating fast neutrons allow measurements that are sensitive to materials throughout the entire cylinder. Imaging the UF_6 material distribution within the cylinder allows compensation of geometry-dependent measurements when the UF_6 mass is unevenly distributed.

This UF_6 cylinder imager is unlike any other enrichment monitor: neither neutron spectrometry nor fast neutron imaging has been applied to UF_6 cylinder enrichment measurements. Technical risks are that the neutron spectrum may degrade via scattering such that spectrometry becomes impossible; also, the benefits of imaging are unknown at this time.

If successful, this project will produce an enrichment measurement technique that is more accurate and more sensitive to diversion scenarios than current technologies.

Summary of Accomplishments:

In FY 2013, we completed two principal milestones. First, the data collected from UF_6 storage cylinders at the Paducah Gaseous Diffusion Plant in FY 2012 was analyzed fully, and was found to support the project's assertion that the measured neutron energy spectrum contains information on the uranium enrichment. This data was also used to estimate the size of a prototype measurement system, and the array of detectors for a 5% relative uncertainty measurement in ~10 minutes is very similar to the Sandia Neutron Scatter Camera, which is a mature system.

The second important result was the completion of the analysis portion of the project. Principal component analysis (PCA) was applied to simulated neutron energy spectra for an assortment of uranium enrichments, material geometries, and detector placements. The PCA technique was found to be able to classify a neutron energy spectrum by enrichment, regardless of the other systematic uncertainties impacting the measurement. Finding a technique insensitive to the systematics is an important result, as currently used techniques are highly impacted by these systematic uncertainties.

Significance:

The new fast neutron imaging system for UF_6 cylinder enrichment measurements addresses needs of the NNSA's Office of Proliferation Detection Global Nuclear Safeguards Research and Development program. For example, that program's FY 2011 proposal call requests "Advancements in unattended approaches to cylinder weighing, identification, sealing, surveillance and enrichment measurements" and "full-volume assay sensitive to heterogeneous cylinders (e.g., tails) and materials substitution scenarios," which we address by proposing an instrument that can independently measure and image uranium isotope masses inside a UF_6 cylinder. The Office of Nonproliferation and International Security would also be a potential customer of such technology.

Predictive Modeling of Non-Ideal Explosives

151321

Year 3 of 3
Principal Investigator: R. G. Schmitt

Project Purpose:

Non-ideal explosives exhibit a strong dependence on charge configuration. The dependency manifests itself as a variation in detonation velocity with charge size and confinement properties. Non-ideal explosives have an extended reaction zone in which the unreacted explosive or nonequilibrium reaction products persist in the reaction zone for an extended period of time. To investigate these phenomena, a three-pronged effort was initiated. A framework for modeling numerically the behavior of non-ideal explosives was established within the CTH code. An experimental effort to characterize the mesoscale properties of shock-loaded non-ideal explosives was performed. A reactive molecular dynamics investigation was performed to characterize potential nonequilibrium effects, including multi-step reaction pathways and potential nonequilibrium species concentrations. The target material for this investigation was ANFO, (ammonium nitrate/fuel oil).

The large-scale heterogeneity of ANFO establishes conditions uniquely suited for observation using the spatially and temporally resolved line-imaging ORVIS (optically recording velocity interferometer system) diagnostic. The first demonstration of transmitted wave profiles in ANFO from planar impacts using a single-stage gas gun is reported. Major observations including an extended compaction precursor, post-shock particle velocity variations and between-prill jetting are reported.

A new capability within the large-scale atomic/molecular massively parallel simulator (LAMMPS) atomistic simulation package to perform reactive molecular dynamics simulations of shocked energetic materials while tracking the spatial and temporal evolution of intermediate and final reaction products was developed. We have applied this capability to ANFO mixtures, observing significant variation in reaction kinetics as a function of how the fuel oil is distributed within the ammonium nitrate matrix.

Summary of Accomplishments:

Computational and experimental capabilities to attack the complex processes that occur in the detonation of the non-ideal explosive ANFO were developed. The experimental effort produced data demonstrating the complex wave processes occurring during compaction of the highly porous ANFO mixtures. The experimental measurements provide unique data representing the distribution in particle velocity at various scales. This information is necessary for future modeling and experimental developments. In addition, new techniques were successfully developed to provide additional diagnostic information resulting in a significantly improved instrument for future use. A reactive molecular dynamics simulation capability based on the ReaxFF potential has been developed to model the behavior of ANFO under shock compression. An existing ReaxFF potential was modified to reproduce the phase behavior of ammonium nitrate crystal structures. This potential was used in multiscale shock technique and nonequilibrium molecular dynamics simulations of the reactive behavior of ammonium nitrate and fuel oil mixtures under shock loading. The reactive molecular dynamics simulations provide unique insight into the chemical processes that are occurring during shock compression. These insights are needed to guide the development of the next generation reactive flow modeling. A computational model called the multistate non-ideal explosive model was implemented into CTH. The model describes the complex nonequilibrium processes occurring when ANFO detonates. The model compared favorably to experimental data for the variation of the detonation velocity with charge diameter. Future development will focus on incorporating the distribution of states information from the line ORVIS measurements and the ideas present in the reactive molecular dynamics simulations.

Significance:

The accurate numerical simulation of ANFO allows for the simulation of this explosive under a variety of important national security related scenarios. These simulation capabilities enhance our abilities to predict response and design countermeasures to this response. Important new experimental techniques were developed that allow scientific investigation at various important time and length scales. This scientific information increases our understanding and leads to improved engineering models. The implementation and use of the multiscale shock technique into LAMMPS provides an evolving tool for addressing chemical reaction networks necessary for advancing the frontiers of scientific modeling of explosives.

Advanced High Security Command and Control Interface (AHSC2I)

151323

Year 3 of 3
Principal Investigator: D. E. Small

Project Purpose:

There exist serious, well-documented issues and deficiencies regarding the way that alarm, communication, and display (AC&D) operators interact with AC&D systems in high nuisance alarm rate (NAR) and emergency operation conditions. AC&D operators and security commanders at high-security sites use a combination of outdated systems (paper maps, books) to detect, assess, and direct the response to adversaries. It is imperative that we improve the AC&D operator's ability to handle higher event rates and more diverse set of alarm data sources (chemical-agent, electro-optical (EO), radars, traditional sensors, virtual presence extended defense systems (VPEDS), etc.). The goal of this project was to significantly improve the effectiveness of AC&D systems. By improving an AC&D operator's user interface, we can address the problems and dramatically increase their efficiency and accuracy by a minimum factor of two.

Summary of Accomplishments:

We demonstrated significant interface improvements to current Alarm, Communication and Display Systems. We completed four distinct iterations of User Interface Development:

- Individual Pages - The initial development focused on identifying what key components should exist in an AC&D system. Each component was created as its own webpage with the intent that the end user could open as many browser or tab instances of each component as desired.
- Individual Pages / Split Screen Browsing - To address these layout issues, we introduced plugins that allowed multiple pages to be shown in a single tab. This approach made refreshing the pages and restoring the layout easier, but was browser-specific.
- Mobile Application - A third generation sought to have all pages loaded with tab based browsing at the bottom of the page to move from interface to interface. This approach is common among many mobile devices.
- Dashboard - A final approach sought to recreate the dashboard use experience provided in the Apple OS. The concept was to make a webpage that allows the user to choose which components to display, where they are placed, and scale them as desired. It was written to utilize local storage on the client side to persist layout relative to the position of the page.

This enabled the entire desktop to be covered by one or more browser instances. Users have fine control on the look/feel of the layout. Refreshing of the page results in all components being refreshed in a single click. The layout is automatically recovered after a browser is closed and reopened.

Significance:

Our prototype system was integrated with our 3D simulator and demonstrated to customers from within DoD and DOE. This work resulted in the DoD and NNSA jointly funding follow-on work to examine the applicability of this technology to existing high-security missions.

Genomics-Enabled Sensor Platform for Rapid Detection of Viruses Related to Disease Outbreak

151324

Year 3 of 3
Principal Investigator: S. M. Brozik

Project Purpose:

Bioweapons and emerging infectious diseases pose growing threats to our national security. Both natural disease outbreak and outbreaks due to a bioterrorist attack are a challenge to detect, taking days after the outbreak to identify since most outbreaks are only recognized through reportable diseases by health departments and reports of unusual diseases by clinicians. The development of more rapid diagnostic assays for virus detection with high sensitivity and specificity will be very useful for the management and treatment of patients, for epidemiological surveillance, and for deployment in sensor systems for use in transportation hubs, at borders, or for threat detection by the military.

Viruses can be isolated from the blood of someone infected early on when immunoglobulin antibodies may not be detectable. However, typical methods for detection involve virus isolation through tissue culture assay with long incubation periods of a week. Molecular diagnostic systems for RNA detection are much faster but still require time-consuming steps and are not yet portable.

We will develop ultrasensitive, direct, hybridization-based RNA detection systems, requiring small sample sizes and short detection times for field and clinical use. Though detection of RNA is difficult because of its lack of stability and extraction from the virus, the pay-off of a high throughput screening capability during emergency response or outbreaks is enormous for public health and military safety. Two independent assays will be developed to address the many challenges of RNA detection.

We will also take advantage of the recent explosion of genomics data on many arboviruses, including several of those widely considered most important to public health and national security, providing a novel opportunity to leverage this data for diagnostic benefit, as well as biothreat detection.

Summary of Accomplishments:

Currently, diagnosis of acute infections requires amplification of viral nucleic acids, which can be costly, highly specific, technically challenging, and time consuming. No diagnostic devices suitable for use at the bedside or in an outbreak setting currently exist. The original goals of this project were to: 1) develop two highly sensitive and specific diagnostic assays for detecting RNA from a wide range of arboviruses; one based on an electrochemical approach and the other a fluorescent based assay and 2) develop prototype microfluidic diagnostic platforms for preclinical and field testing that utilize the assays. We generated and characterized suitable primers for West Nile Virus RNA detection. Both optical and electrochemical transduction technologies were developed for DNA-RNA hybridization detection and were implemented in microfluidic diagnostic sensing platforms that were developed in this project.

Specifically, we developed a robust silane surface chemistry coupled with multifunctional dianhydride reactions to attach high density, stable DNA probes on indium tin oxide (ITO) electrodes. Through a simple electrocatalytic redox cycle of $Ru(bpy)_3Cl_2$, we obtained viral RNA detection limits at the femtomolar (fM) to picomolar (pM) range.

We designed and fabricated a microfluidic-based electrochemical detection system consisting of ten microchannels accommodating ten microelectrode arrays per channel. The detection system includes a commercial off-the-shelf (COTS)-based MUX (MUltipleXer) electronics board intimately coupled to a custom microfluidic electrode array chip, allowing independent addressability, including activation and readout from each electrode on the array. This allows detection of multiple analytes and/or markers in each channel of the array.

Finally, we developed a microfluidic flow cell for inline RNA and DNA detection utilizing a fluorescence-based assay that we developed utilizing tethered DNA polymerases to bind hybridized stands of DNA/RNA compliments.

Significance:

Homeland Security, Defense Advanced Research Projects Agency (DARPA), and Defense Threat Reduction Agency (DTRA) could each benefit from an ultrasensitive high-throughput sensor system that could detect either RNA or DNA. Specifically, these sensor systems could be used by the military, for use in the field to detect biothreat agents in situ. Biodefense and trade agencies usage includes testing for biothreat agents during quarantine and at borders. In addition, hospitals would benefit from their use at the point of care during outbreak or emergency situations. Finally, public health surveillance and diagnostic labs could perform rapid simple detection analysis to monitor arthropod, animal, and human specimens during routine sampling.

High Energy Resonance Radiography by Double Scatter Spectroscopy

151325

Year 3 of 3
Principal Investigator: N. J. Le Galloudec

Project Purpose:

Efficient inspection of airline baggage and cargo containers at airports, seaports, and border crossings is critical to homeland security. The majority of inspection systems installed today uses x-rays or gamma rays that are primarily sensitive to the density of interrogated materials. Techniques using multiple energy x-rays, and/or fast neutrons, can achieve limited material composition identification; however, these techniques have a serious drawback in that they require expensive and complicated radiation sources. This project seeks to develop a new technique for the non-intrusive detection of explosives, illicit drugs, and radiological/nuclear threats using a combination of fast neutron resonance and gamma-ray imaging with readily available commercial radiation sources. The proposed technique will allow for high-energy neutron and gamma-ray interrogation over a large range of energies and viewing angles. As a result, material composition identification by resonance imaging and 3D tomography without rotation of the target can be achieved. This would typically require the use of a complex and expensive radiation source. We postulate that by placing a segmented plane of gamma/neutron detectors between a mono-energetic source and the target, we can interrogate with a range of energies at multiple angles. Determination of mass density is made possible by differences in the absorption of neutrons and gamma rays. Most elements have resonant features in their neutron absorption spectra allowing for further material composition identification.

To our knowledge this novel technique has never been attempted. There will be many technological issues to overcome including high interaction rates and providing adequate time resolution and neutron/gamma discrimination. The primary risk of this technique will be achieving sufficient efficiency at a reasonable cost/system complexity; however, the fidelity of the measurement should improve the signal to noise significantly mitigating this risk.

Summary of Accomplishments:

Although explosives discrimination based on elemental composition has been demonstrated by others, what makes materials identification by resonance absorption (MIRA) unique is that it simultaneously down-scatters and time tags neutrons in detectors oriented between the generator and sample, allowing for time-of-flight (TOF) measurements without pulsed neutron beams. Because this method relies on measuring the resonant attenuation as a function of transmitted energy, it is critical for the detection system to have excellent energy resolution, which is a function of the timing and spatial resolution of the detectors. The feasibility of this technique was previously demonstrated with a two-block device, after which the importance of spatial and timing resolution was fully appreciated. The results of the two-block device demonstrate overall determination of molar concentrations for the four elements of interest. Following that feasibility demonstration, our focus has been on fabricating neutron detectors with the best possible position and timing. We successfully developed neutron detectors with a spatial resolution of 5 mm and timing resolution of 5 ns, resulting in an energy resolution of ~5%. Neutron data scans using D-T, a neutron generator as the mono-energetic source, were obtained with six blocks arranged in a circle surrounding the target: two targets were tested to assess the imaging and material identification performance of the detector and our algorithms. The amount of data generated and computing resources required for the imaging and material identification algorithms did not allow enough time for detailed results by the end of this project. However, Sandia and UC Davis are in discussion to continue this work using funding from the Nuclear Science and Security Consortium.

Significance:

The MIRA device is capable of determining the elemental composition of samples by both the energy-dependent resonant neutron attenuation and the elastic scattering of neutrons within the sample. Only the measurement of elemental fractions, such as MIRA performs, can hope to distinguish between water and hydrogen peroxide, for example, due to each substance's unique elemental fraction. MIRA is also unique in its ability to image in 3D without rotation of the sample. Applications for this technology range from carry-on baggage scanners at airports and scanning at border crossings to explosives detection to inform remediation efforts at aging military storage facilities.

Coaxial Microwave Neutron Interrogation Source

154763

Year 3 of 3
Principal Investigator: W. C. Johnson

Project Purpose:

Active neutron interrogation has been demonstrated to be an effective method of detecting special nuclear material (SNM), specifically, highly enriched uranium. When the neutrons interact with SNM they induce fission resulting in the emission of neutrons and gammas that may then be detected. Current neutron generation technologies have certain intrinsic limitations, mainly related to the ion source, that lead to high voltage breakdown, excessive power consumption, and shortened operational lifetime. This project explores a revolutionary new type of sealed neutron source based on a coaxial-type microwave ion source that facilitates miniaturization, low-pressure pulsed-mode operation, long lifetime, and high neutron output. This project focuses on overcoming potential issues associated with the new type of ion source, such as: suppression of secondary electrons, production of deuterium plasma at low pressure, performance and stability of the plasma source, as well as minimization of beam power on target. Such technology could have widespread national security applications for many ongoing government funded efforts, such as DOE nuclear nonproliferation and radiological source replacement, DHS nuclear detection, and DoD nuclear material locating and tracking.

Summary of Accomplishments:

We have characterized a novel ion source for use in neutron generation. Both positive and negative ion currents have been measured and characterized in terms of gas pressures, extraction voltages, and extraction location and geometries, as well as microwave power and resonance conditions. We have shown the potential for accelerating ions from the source, as well as constructed a prototype neutron generator that has yet to be evaluated.

Significance:

The possibility of a hand-held neutron generator for the active interrogation searches of special nuclear material has been enabled through the characterization and demonstration of a low power, high ion-current, compact, sealed, deuterium/tritium ion source.

Exploring the Development of Large Area Geiger-Mode Avalanche Photodiodes

154936

Year 3 of 3
Principal Investigator: S. Soisson

Project Purpose:

There is an interest in developing technology that has a lower power requirement than a traditional photomultiplier tube (PMT) but delivers the same photon sensitivity as the PMT. Studies in silicon avalanche photodiodes operated in Geiger-mode (G-APD) with many pixels show promise for an effective solid-state PMT replacement. The G-APD shows many similarities to the PMT such as high gain and excellent photon sensitivity, but offers the advantage of having a lower power requirement. However, the size of the available G-APDs are small, on the order of 10mm x 10mm. This small size is not appropriate for replacing a PMT when large active areas are needed. Several areas in micro-pixelated semiconductor design show promise in improving G-APD performance when moving towards large active areas (greater than 2cm x 2cm).

Summary of Accomplishments:

The Microsystems and Engineering Sciences Applications facility (MESA) delivered a custom designed G-APD micropixel array. Preliminary testing was performed which showed that pixel-to-pixel optical isolation was achieved due to the detector responding linearly to varying intensity light pulses. In addition, due to fabrication procedures within the MESA facility, the dark current was lower than what is found in commercial devices. The linear response, coupled with a low dark current, shows that optical isolation techniques for micro-pixelated devices used in other semiconductor communities are viable pathways for creating a larger solid state photomultiplier for applications in the radiation detection community.

Significance:

Photomultiplier tubes are essential to many photon detection systems in a variety of fields from national security, medical imaging scanners, and applications in nuclear physics. Solid-state photomultipliers are compact and attractive alternatives to PMTs, offering features such as high gain, low bias voltage, insensitivity to magnetic fields and good timing resolution. By showing greater optical isolation between the micro-pixels coupled with lower dark current, it is possible to increase active area with high photon detection efficiency. Such a detector could provide a direct replacement for PMTs for many applications.

Characterization of Atmospheric Ionization Techniques for the Identification of New Chemical Signatures from Homemade Explosives in Complex Matrices

156400

Year 3 of 3
Principal Investigator: J. M. Hochrein

Project Purpose:

Currently, there is high demand for analytical capabilities that can rapidly identify weapons of mass destruction including homemade explosives (HME), chemical, and biological agents and at the same time obtain forensic signatures quickly, easily, and in a portable fashion. Current ion mobility spectrometry (IMS) methods, including those used in airports, are very limited in their effectiveness for these targets due to their limited resolution, ionization, and lack of biological detection. Desorption electrospray ionization (DESI) and other atmospheric ionization techniques, coupled with mass spectrometry, offer distinct advantages over traditional detection systems because of the extremely diverse range of detectable compounds, vastly improved specificity, high throughput, fieldability, and little to no sample preparation.

Although DESI has been demonstrated on some target compounds, significant technical challenges and opportunities associated with the method exist. First, there are many operational parameters that need to be optimized such as solvent selection, ionization energies, surface material selection, and identification and reduction of background contaminants. Second, many of the target compounds are analyzed as "neat" samples in very controlled environments under optimum conditions that are often very different from those in the field. In addition, many analytes of interest, including HME precursors and HME residues have not been investigated to understand if they are amenable to ambient detection.

This research will focus on enhancing scientific understanding of DESI and other atmospheric ionization techniques to address two challenging problems that currently exist in national security: 1) detection of a wide variety of HME materials in complex matrices including transport containers, soil, biological metabolites and post-detonation scenarios and 2) identification of new chemical signatures associated with HME production and investigation of the detection of HME residues to identify unique signatures that will enhance the specificity of detection. Information on specific ions that can identify particular HME can then be used to enhance the effectiveness of existing technologies including IMS and differential ion mobility.

Summary of Accomplishments:

Solvent systems were optimized for the detection of the HME residues and methanol/water/ammonium hydroxide (50:50:0.1%) resulted in the lowest background ions and highest signal for analytes of interest. These compounds were analyzed neat and as mixtures. In both cases, the molecular ions were detected and new mass signatures were identified that result from adduct formation, dimerization, and clustering. These new signatures can be used for unambiguous detection of the presence of these HME residues and, in some cases, their corresponding fuel sources. There are still challenges associated with detection of hydrocarbon fuels in negative ionization mode due to evaporation. Additional work could be done to optimize surface chemistries and solvent modifiers to potentially enhance the detection of hydrocarbon fuels. This is critical when developing field deployable instrumentation that has lower resolution and situations that may be of high consequence where false indications may result in significant cost or impact to public locations.

We successfully detected individual constituents from complex mixtures that would be similar to real-life scenarios where multiple compounds would be used in variable concentrations. Limit of detection (LODs) were determined for several surfaces and were in the pico gram to nano gram range for most target compounds and surfaces. Surfaces with low to moderate porosity and low absorption will provide the lowest detection limits. Successful automation techniques were developed for increased throughput for screening and semi-quantitation. DESI was also used on post-blast samples to identify the oxidizer used to generate the explosion and image their distributions on fragments.

There is a significant amount of follow-on work that is possible to further optimize DESI for the detection of HMEs. However, this research has led to significant findings and demonstrates that HMEs can be detected on a wide variety of surfaces at low detection limits even in complex matrices with high specificity using multiple mass signatures.

Significance:

Results from this work can significantly impact national security missions if these capabilities can be further developed and demonstrated in locations such as airports and police department labs. Rapid characterization of unknown samples or surfaces can enable one to determine if they contain the necessary chemical components to be used as an explosive. These rapid characterization techniques for homemade explosives do not currently exist but could significantly impact cost, security, and efficiency of these locations.

Development of a Sustainable Anthrax Diagnostic Test for Countering the Biological Threat

158813

Year 2 of 3
Principal Investigator: M. Finley

Project Purpose:

Anthrax poses a significant threat to US national security as demonstrated by the 2001 terrorist attacks targeting the US Postal Service and Hart Building. The causative agent, *Bacillus anthracis*, is ubiquitous. Anthrax outbreaks commonly occur in livestock, and consequently, the agent is routinely isolated, propagated, and maintained in laboratories by indigenous populations to diagnose the disease. This practice drastically increases laboratories' repositories of *B. anthracis* and escalates the risk that the agent can be stolen for nefarious purposes. To mitigate this risk, we seek to develop a sensitive diagnostic assay that will significantly reduce the amount of *B. anthracis* maintained in laboratories. The assay will use the sensitivity and cost effectiveness of culture, without producing viable cultures; samples will be automatically decontaminated after testing is complete. The project is driven by Sandia's technologies for biodetection to address global critical issues in biological threat reduction, and will develop a practical and deployable diagnostic assay that minimizes *B. anthracis* handling, isolation, propagation, and storage.

The goal of the work is to develop a portable diagnostic device for *B. anthracis* for use in low resource environments where the biological threat is elevated. Currently, commercially available diagnostic test strips are relatively expensive (~$40 per assay with control) and require propagation of the target organism prior to running the assay. In contrast, our proposed device will cost <$5 per assay (including a positive control for assay validation), will be operable by individuals with little technical training, and apply phage technology to provide access to internal virulence markers while simultaneously sterilizing the contents of the culture — a critically important aspect to minimizing malfeasant use. Moreover, the self-contained device will combine micro-culture methods to amplify *B. anthracis* with plasmon coupling among metal nanoparticles for target detection, and will not require any instrumentation/equipment.

Advanced Diagnostic and Sample Preparation Platform for Early Threat Surveillance

158814

Year 2 of 3
Principal Investigator: S. Branda

Project Purpose:

Emerging infectious diseases present a profound threat to global health, economic development, and political stability and, therefore, represent a significant national security concern for the US. The increased prevalence of international travel and the increase in globalized trade further amplify this threat. The key to preventing an outbreak before it goes global is to establish a biosurveillance network that effectively reaches even the most remote regions and provides a network-integrated, location-appropriate diagnostic capability. At present, the two main factors that prevent the extension of biosurveillance activities beyond centralized laboratory facilities are the lack of a deployable rapid-response diagnostic platform and a method to safely and consistently process infected samples in the field for analysis.

To minimize serious global outbreak events, modern surveillance requires both coordination and investment in infrastructure at the international level to enable rapid response to pathogens as they emerge. The first critical steps in the surveillance process (clinical observation, sample collection, preliminary diagnosis) typically fall to first responders around the world. However, the facilities, technology, and protocols they use can vary widely depending on the available infrastructure, which complicates efforts for a globally coordinated biosurveillance scheme. This project aims to address this identified capability gap by delivering an automated clinical sample processing platform integrating a "universal" sample collection and preparation protocol with a comprehensive diagnostic strategy. This will require: 1) the creation of a fieldable advanced diagnostic and sample preparation platform to safely and cost-effectively automate the extraction of pathogenic genomic nucleic acids (NA) from potentially infectious clinical samples for analysis, 2) the on-platform integration of a multiplex polymerase chain reaction (PCR) array for initial point-of-care diagnostic screening, and the implementation of on-platform NA formatting for subsequent off-platform microarray or next generation sequencing analysis, and 3) the transfer of the advanced diagnostic and sample preparation (ADSP) technology to identified biosurveillance collaborators for testing and integration into real-world pathogen detection and surveillance workflows.

Multi-Target Camera Tracking, Hand-Off and Display

158819

Year 2 of 3
Principal Investigator: R. J. Anderson

Project Purpose:

Individual networked cameras provide rich streams of data for monitoring physical sites but do not, in themselves, improve security response. For operators, the manual tracking of intruders takes focus and attention away from overall situational awareness (SA). Furthermore, network security cameras are becoming cheaper, more capable, and easier to deploy, but operators that monitor them are not. By combining automated tracking algorithms that share target information across multiple cameras integrated within a 3D facility model, we can radically simplify the human/machine interface and shift the cognitive focus from manual operation of the system to command and control.

To implement this vision, we have developed a high-performance computing pipeline using both multi-core computing and GPU (graphical program units) that can take the data from multiple networked security cameras and process them simultaneously on a single computer. Each pipeline includes a statistical background subtraction technique, an advanced parallel clustering technique for data reduction, and color histograms for motion tracking. Each pipeline runs within its own computing core, allowing up to 16 different camera feeds to be processed simultaneously on a single desktop computer. The live, segmented video from the individual pipelines are integrated within a single integrated game-engine model, which incorporates information about camera calibration, object occlusion, entry and exit points, and visual overlap.

The result is a system that is target focused, not camera focused. Targets are tracked around a compound, and the best available image of that target is presented to the operator within a 3D model of the facility, including advanced visual locator techniques as target rings and particle filter trails. Finally, a learning system uses visual descriptors of the targets in the field of view to enable matching of previously learned targets whenever they exit and reenter the field of view of a camera.

Rapid Affinity Reagent Development for Emerging Pathogen Detection

158820

Year 2 of 2
Principal Investigator: C. Koh

Project Purpose:

We face constantly emerging and naturally occurring global biological threats, from pandemic influenza to novel pathogens or engineered bioagents. In the event of disease outbreak or biothreat release, fast and sensitive diagnostic tools deployable to multiple point-of-care (POC) locations are crucial for effective biosurveillance and crisis management. Rapid antigen-based tests, which are the most amenable approaches to POC diagnostics, typically employ antibody affinity capture schemes for pathogen detection. However, antibody production relies on hybridoma technology that requires several months for full-scale production, making antibodies inadequate for emerging pathogen outbreak scenarios. Moreover, antibodies are not very stable to storage, especially in resource-poor areas lacking refrigeration. Polymerase chain reaction (PCR) approaches require extensive sample preparation, are very expensive because of thermal cycling needs, and often fail to detect newly emerged or divergent pathogen strains. Thus, there remains a critical need for versatile POC diagnostic approaches that are rapidly reconfigurable and deployable in emerging pathogen outbreak scenarios.

We will remove this bottleneck in biological emergency responsiveness by employing Sandia's virus-like particles (VLPs) as rapidly deployable affinity reagents. VLPs have shown efficacy in cell targeting and drug delivery applications. This project will pioneer their use as diagnostic affinity reagents. VLPs require 5-12 days for development with affinities for target analytes that rival commercial monoclonal antibodies. VLPs are less likely to denature and, hence, have much longer shelf life than antibodies. VLPs can also be loaded with "cargo", such as multiple quantum dots (QDs), facilitating a novel sedimentation assay directly targeting infectious agents using Sandia's centrifugal microfluidics platform. The proposed assay scheme will exceed the stringent limits of detection for emerging pathogens (10^3 PFU/mL), and may enable single particle resolution. This project merges two of Sandia's proven technologies to tackle the pressing challenge of emerging pathogen detection; the final product will vastly outperform state-of-the-art techniques and directly address this glaring national and global security need.

Summary of Accomplishments:

We designed methods of utilizing virus-like particles with specific affinity ligands on the surface of the constructs to bind to pathogens and subsequently detected these complexes on device. We demonstrated sensitive detection using these methods for model systems in a laboratory setting.

Furthermore, we concurrently designed non-amplified nucleic acid assay methods that were demonstrated to be highly sensitive and specific, comparing favorable with FDA-approved gold standard methods. These methods are further enhanced by deployment on the SpinDx platform.

Significance:

By developing methods of rapidly producing affinity reagents for pathogens that are poorly characterized or understood, we have enhanced the ability to respond to threats both naturally occurring and man-made. Additionally, these strategies are incorporated into Sandia's proprietary POC medical devices allowing for rapid deployment of these solutions to low-resource settings.

Intrinsic Material Elements Seal

158821

Year 2 of 3
Principal Investigator: H. A. Smartt

Project Purpose:

Seals are widely used for identifying, securing, and monitoring items. They must be unique, non-counterfeitable, tamper indicating, robust, easily applied, and low-cost. Unfortunately, US development efforts for seals ended in the 1990s, in spite of the emergence of new technical requirements such as compatibility with complex geometries, hostile environments, and remote interrogation. Currently, there is nothing in the global inventory of seals that adequately addresses all these needs. Presently employed systems suffer from slow and cumbersome readouts and require mounting of the camera system on the item being verified. Using newer technologies, better seal designs and readout options are possible. State-of-the-art cameras, modern image analysis, and new illumination approaches can be combined to produce a faster, user-friendly, non-contact readout system. This will allow more frequent verification, minimizing the time that inspectors spend in restricted or environmentally unfriendly locations.

We are developing a seal technology based on microscopic, randomly located and oriented reflective elements that possess planar optical cavities that vary from particle to particle. Each particle's reflectance spectrum depends on its cavity parameters, the local orientation of the particle, and the incidence angle of the interrogating beam. Designed to be easily applied in a coating or paint, this seal will be compatible with flat surfaces as well as complex rough geometries. Interrogation of the seal will include illumination with multiple wavelengths and multiple incidence angles and will lead to a multivariate data cube that can be analyzed using efficient multivariate image analysis algorithms. This approach expands the information collected from seals beyond simple spatial locations and orientations of the particles, to include spectral and morphological attributes.

Modeling the Contents of Radiological Devices in Real-Time

161869

Year 2 of 3
Principal Investigator: G. G. Thoreson

Project Purpose:

Modeling how radiation is emanated and transported through complex radiological sources has been limited to supercomputers in the past. This makes portable computing devices such as a laptop prohibitively slow in modeling 3D objects in reasonable time. This project's purpose is to discover new ways to approximate this solution quickly on a personal computer. Decreasing the computation time by orders of magnitude is an ambitious task. Achieving this involves applying existing radiation transport algorithms in new ways and pre-computing data as much as possible.

A major result of this project is the successful approximation of 3D photon scattering in the environment surrounding the source and radiation detector. Scattered photon radiation is computed via a Green's Functions approach. In this method, the transformation in energy, space, and direction of photons scattering from a surface is reduced to a set of transport kernels stored in a library. Using ray-tracing techniques and computational integration, the contribution of scattered photons from all the surfaces in the environment, such as a laboratory space, to the radiation detector is computed in less than a second on a personal computer. This method has been benchmarked against a wide range of experiments with good agreement.

For 3D transport within the radiological object, a new method has been developed in which the object is decomposed into a set of simpler geometries; for example, two adjacent cylinders, each with cylindrical layers of varying material inside. The photon, neutron, and electron transport are approximated as a series of 1D models to generate a volumetric source term for the entire object. This 3D source term is then ray-traced to the radiation detector to estimate the signal. The entire process requires seconds of computation time on a personal computer. These results are being compared to laboratory benchmarks with promising results.

Compressive Sensing for Nuclear Security Applications

161870

Year 2 of 3
Principal Investigator: B. J. Gestner

Project Purpose:

Special nuclear material detection has applications in nuclear material control, treaty verification, and national security. The neutron and gamma ray radiation signature of special nuclear material (SNMs) can be indirectly observed in scintillator materials, which fluoresce when exposed to this radiation. A photomultiplier tube (PMT) coupled to the scintillator material is often used to convert this weak fluorescence to an electrical output signal. The fluorescence produced by a neutron interaction event differs from that of a gamma-ray interaction event, leading to a slightly different pulse in the PMT output signal. The ability to distinguish between these pulse types (i.e., pulse shape discrimination [PSD]) has enabled applications such as neutron spectroscopy, neutron scatter cameras, and dual-mode neutron/gamma-ray imagers.

Realizations of these applications are based on conventional digitization of PMT output signals followed by PSD and statistical processing. Given that currently these pulses are sampled at 200MHz-8GHz, an enormous amount of data must be processed in real-time or stored for off-line processing. Clearly, this approach is not feasible in a resource-constrained, remote-deployment setting, such as a wireless sensor network. Therefore, reduced-data sampling and processing techniques specifically for PSD must be developed.

Compressive sensing (CS) has emerged as a mathematical method for efficiently representing and reconstructing signals. There has been considerable work in this area at Sandia for radar applications, but compressive sensing has never been applied to PSD anywhere. More broadly, the planned research is the first application of compressive sensing to radiation detection.

We will use compressive sensing to guide the development of novel mixed-signal hardware for PMT output signal acquisition. Effectively, we will explore smart digitizers that extract sufficient information for PSD while requiring a considerably lower sample rate than conventional digitizers. Given that we will determine the feasibility of realizing these designs in custom low-power analog integrated circuits, this research will enable the incorporation of SNM detection into wireless sensor networks.

Development and Field-Testing of a Diagnostics Platform for Global Syndromic Disease Surveillance

165676

Year 1 of 3
Principal Investigator: M. Finley

Project Purpose:

Infectious disease epidemics continue to threaten the homeland and international security landscape. Cost-effective global biosurveillance programs are critical for detecting and mitigating outbreak scenarios due to natural, emerging, or engineered biological threats. However, most developing countries lack the infrastructure and resources to implement effective disease surveillance. Public health and veterinary professionals lack the necessary skills to arrive at an accurate clinical diagnosis; therefore, many incidents of infection with high consequence agents go undetected, and thus, unreported. New tools are urgently needed to meet the stringent operational and economic requirements for biosurveillance in low-resource settings, including cost, speed, ease-of-use, field-deployability, and reliability. Furthermore, disease surveillance activities may be streamlined by shifting from traditional diagnosis to syndromic-based testing, in which the diagnostic tool concurrently screens for a panel of high priority pathogens and diseases based on clinical symptoms.

We seek to meet these needs with development of novel assays and an accompanying device based on Sandia's SpinDx diagnostic platform for global disease surveillance. The inherent advantages of our approach (low-cost, ultra-sensitivity, easy to use, no sample preparation, and broad assay menu) differentiate us from other conventional biosurveillance methods. Another key advantage of our approach is that rather than focus on particular pathogens, we will develop a syndrome-based screening allowing access to useful, actionable information faster. Field-portable assays for most of the diseases that we plan to target do not exist; hence, the first task will be to develop assays to diagnose a panel of high-priority zoonotic diseases. Disease of focus will be sudden death (hemorrhagic) syndrome in cattle. The assays will be developed in collaboration with the Veterinary Diagnostic Laboratory (VDL) and Biosecurity Research Institute (BRI) at Kansas State University. This work merges Sandia's expertise in microsystems development, biochemical assays, and biosecurity in low-resource settings to uniquely address this glaring need.

Processing Radiation Images Behind an Information Barrier for Automatic Warhead Authentication

165679

Year 1 of 3
Principal Investigator: C. W. Wilson

Project Purpose:

The purpose of this project is to develop enabling technologies and options that could facilitate future arms control treaty negotiations. Future arms control treaties may not be possible without the ability to utilize nuclear measurements to count warheads on delivery systems and/or measure weapon signatures to verify nuclear weapon type or status. A consensus within the arms control verification community agrees that sophisticated radiation imaging, never before used in this environment, offers the ability to measure new types of signatures of treaty-limited nuclear weapon systems or components. However, to protect sensitive information, information barriers (IB) must be used with any imaging systems. Analysis of the images behind an IB is a complex task that must be performed reliably, without human assistance. The most advanced IB systems developed to date, both developed at Sandia, perform gamma spectroscopy analysis behind an IB and have been demonstrated in several realistic exercises. The image-processing problem is far more complex, and to date, no one has demonstrated a functional system for reliable image verification behind an IB.

New radiation imaging techniques, such as the Oak Ridge National Laboratory/Sandia fast-neutron coded-aperture imager and ORNL's neutron tomography system are just becoming available. The quality, characteristics, and measurable features available in the images they produce are still uncertain. While other techniques such as radiography imaging are mature, exploration of the image features available from any of these techniques is at a very early stage. Many new and advanced feature extraction algorithms have been developed but have not yet been applied to radiation images of nuclear weapons. The risks are high since it is unclear whether such techniques can uniquely identify nuclear weapon features in the highly reliable and robust fashion needed for automated processing behind an IB; however, the potential result is a game-changing advance in the way that arms control treaties are verified.

Bubble Masks for Time-Encoded Imaging of Fast Neutrons

165680

Year 1 of 1
Principal Investigator: E. Brubaker

Project Purpose:

Fission-energy neutrons are an important signature of the special nuclear material (SNM) used in nuclear explosives, and high-resolution neutron imaging systems are desired for applications such as arms control treaty verification and emergency response. The time-encoded imaging technique produces images by inducing a time-dependent modulation of detected neutrons and is characterized by simple and robust detector elements, low channel counts, and low cost, in contrast with other imaging approaches. However, time-encoded imaging of fast neutrons has never been demonstrated in a high-resolution mode needed for these applications. There are significant conceptual and engineering challenges in building a large high-resolution mask of bulky hydrogenous material, moving in a complex controlled fashion to produce the desired time-dependent attenuation patterns. We aim to enable high-resolution, time-encoded imaging using the approach of bubble masks, in which arbitrary time-dependent neutron attenuation masks are formed by bubbles propagating through a viscous medium such as mineral oil.

DOE is currently funding a project to develop time-encoded neutron imaging and the bubble mask concept has arisen out of that work. But although the potential payoff is significant, the risks are also too extensive to justify pursuing the idea within the scope of the DOE project. Bubbles can be simply introduced into an oil column using a valve at the base of a tubing element. However, the feasibility of tuning the oil viscosity and the characteristics of the tubing (size, shape, pressure relief, etc.) to make the bubble propagation consistent and predictable is unknown. The speed of the bubble motion may depend on the spacing of other nearby bubbles via pressure and wall effects, for example, making it difficult to generate a moving mask with precise element spacing, such as the family of uniformly redundant arrays that have attractive imaging properties. If successful, the bubble mask technique would enable robust high-resolution imaging of SNM at low cost.

Summary of Accomplishments:

The goal of this project was to determine the feasibility of building bubble masks for neutron time-encoded imaging and identify any limitations on their design or performance. We have successfully demonstrated controlled introduction and propagation of bubbles through a tube of viscous hydrogenous liquid in a pattern relevant for time-encoded imaging of fast neutrons. We developed a technique for tracking bubble positions in real time and methods to reconstruct a source distribution from acquired neutron rate data. Results from a simple experimental setup provide a demonstration of the concept and give us confidence in simulation results. The simulation was then used to extrapolate beyond the experimental results to explore the potential performance of a large-scale imaging system based on bubble masks.

Two major limitations of the bubble mask technique were identified. The first is the challenge of achieving a high mask contrast, which would require tubes (and therefore, bubbles) with large cross-sectional area, and ideally a rectangular shape. The second is the inherent correlations among the response vectors of nearby source positions, due to the motion of the bubbles through the tubes. Low mask contrast and non-ideal orthogonality both contribute to slower resolving times, or the need for more statistics for a given detection threshold or image resolution.

Advantages of the bubble mask technique include the length of the encoding pattern, which is limited only by the length of the acquisition, in contrast to fixed moving masks, which must be cyclical with some finite length. In addition, the ability to respond to observations by changing the mask pattern (adaptive encoding) has potential to improve resolving times and open up a new class of algorithms for source detection and imaging.

Significance:

We accomplished what we set out to do in this small-scale project, which is to lay the technical groundwork for using bubble masks to enable two-dimensional time-encoded imaging. Since their feasibility has been demonstrated, bubble masks could be developed for applications in which ease of deployment is key (e.g., radiological emergency response). We identified what technical issues should be addressed next (e.g., increasing tube/bubble size) and developed related technical concepts that might be more optimal for some of the application space. Some of our work on adaptive encoding will apply broadly to other imaging modalities.

RGB+D for Biometrics and Physical Security

165681

Year 1 of 2
Principal Investigator: J. D. Bradley

Project Purpose:

The purpose of the project is to discover the applicability of RGB+D (red, green, blue, depth) sensors within the physical security domain. This project seeks to develop methods and algorithms to facilitate an inexpensive system for standoff biometric identification, multi-modal tracking of individuals throughout a facility, and improved intrusion detection system appliances. Novel algorithms must be developed to robustly identify individuals despite the inherent noise and inaccuracy of current commercial off-the-shelf (COTS) RGB+D sensors. Supplementary human studies are required to evaluate the efficacy of the system.

Radiography Signature Science of Homemade Explosives

165682

Year 1 of 3
Principal Investigator: J. E. Parmeter

Project Purpose:

The purpose of this project is to determine representative x-ray radiographic properties for credible threat formulations of key families of homemade explosives (HME) (i.e., x-ray attenuation parameters that bound all credible threats). This is a critical national security issue based on the need to use x-ray radiography to detect explosive threats in aviation security applications. Credible threat formulations are those that are detonable and can be readily prepared by an adversary. In this project, characteristic x-ray radiographic (attenuation) properties of key types of HME, including both hydrogen peroxide (HP)/fuel and potassium chlorate (KC)/fuel formulations will be determined. These radiographic properties will also be compared to those of various benign materials in order to gauge the ease of discrimination using x-ray radiography; hence, the likely impact of nuisance alarms resulting from benign materials in screened baggage. The work performed will be a combination of experimental measurements and computational studies. Detailed characterization of x-ray source output and detector response will be an important prerequisite to the experimental measurements of HME x-ray radiographic properties and represents an important aspect of this project. Development and documentation of ES&H procedures for working with small quantities of HME is also critical. Once data have been acquired, experimental results and computational results can be compared and both experimental and computational techniques can be refined. The theoretical work will provide us with a better understanding of the experimental results, and if excellent agreement between theory and experiment can be demonstrated, additional calculations can be carried out to obtain x-ray radiographic properties of HME formulations which we do not have adequate time or funding to investigate experimentally.

Distinguishing Bioengineering from Natural Emergence in Biothreat Genomes

165683

Year 1 of 3
Principal Investigator: K. P. Williams

Project Purpose:

Identification and characterization of engineered biological agents (EBAs) is an unsolved biosecurity challenge. Technical expertise required to generate EBAs with new gene combinations exists worldwide. Current EBA detection approaches target toolmarks of classical bioengineering (cloning vector sequences); however, advanced technology allows omission of such toolmarks. Further complicating EBA identification, novel pathogenicity gene combinations and contexts also arise naturally through horizontal gene transfer (HGT). Fortunately, biological limitations on HGT exist that enable discrimination between EBAs and HGT products. Three categories of genomic sequence information support EBA identification: 1) intrinsic gene properties (function, composition), 2) gene phylogeny, and 3) neighbor-gene context. Two aspects to our EBA identification plan are: ruling in genetic engineering by detecting its genomic signatures and ruling out a possible natural origin of the organism by comparison with the gene context characteristics of naturally emerging genomes. Current nucleic acid-based assays (PCR, microarrays) yield limited intrinsic gene data and no gene context data; the anticipated increased use of high-throughput sequencing (HTS) for biodetection enables EBA identification methods that exploit gene content and context.

So that appropriate measures can be enacted in the event of an outbreak, this work will develop tools yielding statistical evaluations of positive evidence of unnatural sequences and pathogenic potential (engineering rule-in), along with the probability that the organism emerged naturally (non-engineering rule-out).

EBA detection via the (omittable) toolmarks of bioengineering is unreliable. Our approach probes much more deeply, into the feasibility of natural emergence of the disease-relevant gene combinations found in a query pathogen. The general approach to EBA detection will directly analyze content of pathogenicity genes, and their phylogenetic and gene-neighbor contexts. This will yield a naturalness score (N) for a candidate EBA, parameterized through machine learning, and a confidence level derived by comparison with the distribution of N-scores for thousands of known non-engineered genomes.

Jam-Proof Wireless Communications

165685

Year 1 of 3
Principal Investigator: D. A. Perea

Project Purpose:

This project seeks to perform fundamental R&D for a robust and secure distributed wireless networking technology. Wireless technologies are vulnerable to denial of service or jamming attacks and, for this reason, are not allowed at nuclear weapons sites to communicate sensor or imager information from security perimeters. A few seconds of disruption in communications could make the difference between winning or losing the fight. The concept is proposing a solution combining advanced physical layers, detection, and cognitive networking to produce a new form of "jam proof" wireless communications that will meet high security needs. The exclusion of wireless networking is currently imposed by DOE and DoD policy, even though policy does not yet exist that defines the "wireless threat." This is a testimony to the progressive ideas behind this concept. It is only a matter of time before DOE and DoD address the void/absence of a definition of the "wireless threat" that sites will be required to mitigate.

The technologies necessary to create a cognitive robust and secure networking topology that is scalable to many nodes and sensors requires research and development of cognitive network controllers that can act intelligently and autonomously since the wireless threat environment is dynamic and unpredictable. The networked system requires advanced approaches in hardware/software actor based frameworks to realize the many complex tasks of managing incoming intrusion detection data, and ensuring reliable communications of networked resources. It shall incorporate attack detection and triangulation as an active component of the cognitive network, providing real-time data and geo-location of possible threats and allowing specific action to be taken by the end user. Physical layer technologies at Sandia will be advanced to allow many types of phenomenology and network layers to work as one in an adversarial environment, allowing the network to mitigate multiple attacks while providing geolocation and data on the attack to system users.

Using EEG to Understand Domain-Specific Visual Search

165686

Year 1 of 3
Principal Investigator: A. Speed

Project Purpose:

Often, national security problems demand fairly rapid decision-making in uncertain, risky situations. In such circumstances, consequences of false positives and misses can both be significant, yet high-consequence decisions are often made using "instinct," or implicit processes, as much as explicit facts. Measures of neural activity (i.e., electroencephalography [EEG]) offer mechanisms for characterizing and understanding implicit processes (e.g., some EEG signals indicate when a person makes an error, even if they are not consciously aware of that error). We will test the hypothesis that certain EEG signals have validity for improving analyst performance in a domain wrought with ambiguity and risk — visual search for weapons in x-ray images of luggage. We will use two EEG signals (the error-related negativity and N2pc)2 to help analysts identify when they might be making an error in classifying each image as threat-absent or threat-present. We will then test the hypothesis that slight direct current (DC) stimulation can reduce the overall number of errors made.

Through our relationship with the Transportation Security Administration (TSA), we will use Transportation Security Officers (TSOs) as subjects. However, the goal is not to solve a TSA problem. Rather, it is to understand whether signals observed in basic laboratory research are valid for field environments (e.g., training, checkpoints) using field-friendly commercial off-the-shelf (COTS) EEG systems.

If successful, we could significantly improve risky, ambiguous decision quality, and rapidly field EEG-based systems in numerous domains such as transportation security, imagery analysis, and materials characterization.

This work is unique in that it will generalize results from basic laboratory research on enhancing novice performance using EEG signals and electrical stimulation to field environments in order to enhance expert performance in visual search in a national security context. Furthermore, we will demonstrate the ability to enhance expert performance using $300 COTS systems instead of $50k laboratory-grade systems.

Improved Pulse Shape Discrimination in a Multicomponent Water/Organic System

165687

Year 1 of 3
Principal Investigator: J. G. Cordaro

Project Purpose:

Federal agencies seek new radiation detection technologies to detect the movement of special nuclear materials and for arms control and treaty verification. Present detectors comprise plastic scintillators that are cost-effective, scalable, and highly sensitive to ionizing radiation, yet incapable of differentiating fast neutrons from a background of gamma rays. Liquid scintillators provide efficient discrimination of these particles, although storage and toxicity concerns prevent widespread use for this application. Liquid scintillators also suffer from afterglow effects when exposed to the high radiation fields of active interrogation. Separately, inorganic scintillators based on Ce^{3+} are widely employed due to their fast decay characteristics and low afterglow effects, and improved light yield linearities that enables gamma-ray spectroscopy. Unfortunately, these materials are expensive and incapable of fast neutron discrimination. Prior attempts to combine the favorable characteristics of inorganic and organic scintillators resulted in phase-separated, opaque materials ill suited for large-scale deployment. This work overcomes many of the limitations associated with single-state scintillators by creating a highly transparent, water-based system containing both organic and inorganic components.

We will use water or a mixture of water and surfactants as our matrix for particle detection rather than a traditional organic medium. High-hydrogen content matrices are ideal for neutron detection. A two-state system for particle detection via pulse shape discrimination will be created by dissolving or suspending in water two different scintillators. The key to success and highest risk of this project is ensuring high light-yields from both scintillators upon ionization of the matrix. To mitigate this risk, we will tailor the energy transfer mechanisms within the system by modifying the matrix and scintillator characteristics. If successful, this work offers a detection system deployable by simply adding water to a powder or concentrated mixture.

Toward Interactive Scenario Analysis and Exploration: A Study on Simulation Technology Optimization and Scalability with Big-Data Analysis and their Applications

167008

Year 1 of 2
Principal Investigator: T. R. Gayle

Project Purpose:

Existing and future change will drive many national security solutions with need for a rapid tactical analysis response in ways that traditional modeling and simulation (M&S) cannot address. Issues around large data, computational requirements, delivery mechanisms, and deep analyst involvement are already challenging; any use in the field is not viable. While current solutions require hours to days to compute, rising expectations to address analysis with more depth and breadth for larger and complex scenarios will only increase difficulty. Some solutions through traditional high-performance computing (HPC) have been considered, but progress is slow, and tactical response is impractical. To overcome many of these challenges, we will develop a next-generation computational paradigm for M&S that efficiently divides the computational and storage requirements while supporting the shuttling of results between field operators, back-end analysis, and data sources. By coupling innovations in M&S software with emerging advances in cloud computing, big-data methodologies, and existing HPC, we will provide an approach that is fast (seconds to minutes), offers unique delivery options, enables a degree of rapid analysis iteration not available today, and applicable to a variety of problems for DOE, DHS, and DoD. To allow a tractable scope and effort, we will focus on force-on-force and sensor analysis in physical security as driving application domains.

Our hope is that the results of this work drive innovations and applications across several domains. Along with innovations in the underlying M&S software technology, novel technical solutions are expected in the coupling of the simulation architecture with a cloud-like resource environment that should apply to related problem spaces. Analysts will be enabled by an approach that allows fast iterative feedback on complex scenarios, allowing for rapid, deep, and broad analysis results that can be delivered in numerous ways. This type of work could enable a new class of solutions for our most important national security challenges.

Advanced Digital Microfluidic Interface for Sample Prep Automation

168507

Year 1 of 1
Principal Investigator: M. Bartsch

Project Purpose:

The R&D100-winning digital microfluidic (DMF) hub offers the potential to be a critical capability multiplier across a range of Sandia activities (see YouTube.com "Sandia Digital Microfluidic Hub"). In particular, by providing a means to modularize, interface, and automate complex sample preparation workflows at an unprecedented scale, the DMF Hub has been instrumental in establishing a toehold for Sandia in the promising new business area of DNA forensics. However, both the underlying phenomenology of digital microfluidics and the limitations of our preliminary design pose fundamental challenges which must be addressed through science-based engineering before DMF can truly become a robust and broadly applicable capability for Sandia. Accordingly, advanced development is needed to fully capitalize on the promise offered by this technology and to maintain Sandia's relevance in the burgeoning field of automated sample preparation. Three key areas for improvement have been identified: 1) increased scale for higher throughput, 2) closed-loop control for reliable automated operation, and 3) expanded interface options for increased flexibility.

Long explored in academia, DMF technology is only now entering the mainstream for bioscience and sample preparation applications. Our early successes combined with our DMF Hub intellectual property have uniquely positioned Sandia as a key player in this emerging field at just the right time. This effort will provide not just a better-engineered version of a technical curiosity, but rather the first concrete application of DMF technology in an integrated and automated context to solve real world problems in a robust, flexible, and modular (rather than self-contained) fashion. This approach is both timely and crucial to the future of automated sample preparation, and the work represented by this project will enable Sandia to continue to push the technological envelope at this critical juncture in ways that neither academia nor industry have attempted.

Summary of Accomplishments:

We constructed a self-contained, portable, and integrated demonstration system designed to allow us to effectively showcase Sandia digital microfluidic and laboratory automation technologies to potential sponsors and customers. We designed and fabricated a new generation of printed circuit board-based digital microfluidic devices offering significant improvements to scale and operational flexibility over first generation microfabricated designs. We developed an alternative fluidic interface concept as a lower-cost alternative to the more highly engineered digital microfluidic hub and initiated testing of this interface. We performed initial explorations and achieved initial proof of concept for machine vision-based closed loop control of digital microfluidic droplet manipulations. We capitalized upon work performed under this project to advance Sandia's licensing and commercialization strategies for intellectual property related to both microfluidic hub technology and the complementary rotary zone thermal cycler, gaining significant traction with a number of interested industry collaborators including Agilent, Roche, Beckman-Coulter, and Perkin-Elmer.

Significance:

This work has expanded upon microfluidic assay and sample manipulation architectures unique to Sandia which both provide novel methods for addressing critical national security needs in the chem/bio detection realm and offer potentially game-changing benefits for the laboratory automation field. We have taken what was once an academic curiosity, digital microfluidics, and leveraged it into a broadly applicable technological capability with potential to address a wide range of needs in the areas of clinical diagnostics, personalized medicine, next generation sequencing, environmental monitoring, and deployable sensing.

Refereed Communications:

A. Sinha, M.J. Jebrail, H. Kim, K.D. Patel, and S.S. Branda, "A Versatile Automated Platform for Micro-Scale Cell Stimulation Experiments," *Journal of Visualized Experiments*, vol. 78, August 2013.

High Fidelity Forward Model Development for Nuclear Reactor Spent Fuel Technical Nuclear Forensics

170995

Year 1 of 3
Principal Investigator: M. R. Sternat

Project Purpose:

Spent nuclear fuel (SNF) is an attractive material to an adversary with potential uses in an Improvised Nuclear Device or Radiation Dispersal Device. In 1977, DOE declassified the results of a 1962 test that confirmed reactor-grade plutonium could be used to make a nuclear explosive. Nuclear forensics is a major pillar of nuclear security efforts to reduce the risks from this threat. One of the key requirements of a credible nuclear forensics capability is accurate and timely characterization of material that is interdicted outside of regulatory control. Nuclear forensics typically compares signatures from interdicted materials with information from libraries to determine the source of the materials. However, in most cases adequate libraries do not exist, or not available due to restrictions on sharing information between countries.

In the researcher's doctoral work, ORIGEN is utilized in a SNF forensics system to reconstruct reactor information from spent fuel characteristics. This basic forward model does not use any geometric or non-fuel material characteristics that may be recoverable from an interdicted item and relies on predefined cross-section libraries to predict SNF characteristics. These libraries only exist for well-known power reactors and cannot accurately predict SNF characteristics in research or other reactor types. Another problem is that current database information is not always reliable since most are optimized for criticality and other purposes.

Nuclear forensics in its current state is primarily a comparative science. Unreliable database information or lack of availability causes comparative methods to be ineffective. In addition, establishment of a complete database is not practical. This work is innovative and unique as it will expand the boundaries of nuclear forensics science and will establish a predictive technique for SNF forensics. Creativity will be required to develop a practical predictive system, including the implementation of higher fidelity forward models that work with limited amount of information recoverable from an interdicted SNF sample.

Radar Detection of Personnel Obscured by Foliage

170996

Year 1 of 3
Principal Investigator: K. J. Pascoe

Project Purpose:

The purpose of the project is to create and demonstrate foliage-penetration radar for physical security and to combine the radar with other sensors via a data fusion algorithm. This system will improve intruder detection and response force timeliness, thus increasing security.

The team has performed an extensive, broad-based literature search on various aspects of radar. The team also conducted initial inquiries into radio frequency allocation, to ensure bandwidth was available for later experimentation. We have been pursuing completion of all requirements for human subject research, to enable later measurements with people in view of the radar. We started development of the radar detection algorithm as well as the data fusion and tracking algorithm. The team has started hardware design, ordered some components, and surveyed some test locations on base. The radar system design has changed over time as we moved through various design alternatives such as impulse radar, pulsed linear frequency-modulated (FM) chirp and FM continuous-wave radar.

The team is planning a study of radar clutter stability in UHF band. This study will involve both outdoor measurements and computer simulations to determine how much clutter varies over short time periods. The simulations will use computational electromagnetics codes to provide the most realistic solutions to radar scattering from targets and clutter. Field measurements have commenced and simulations are under way.

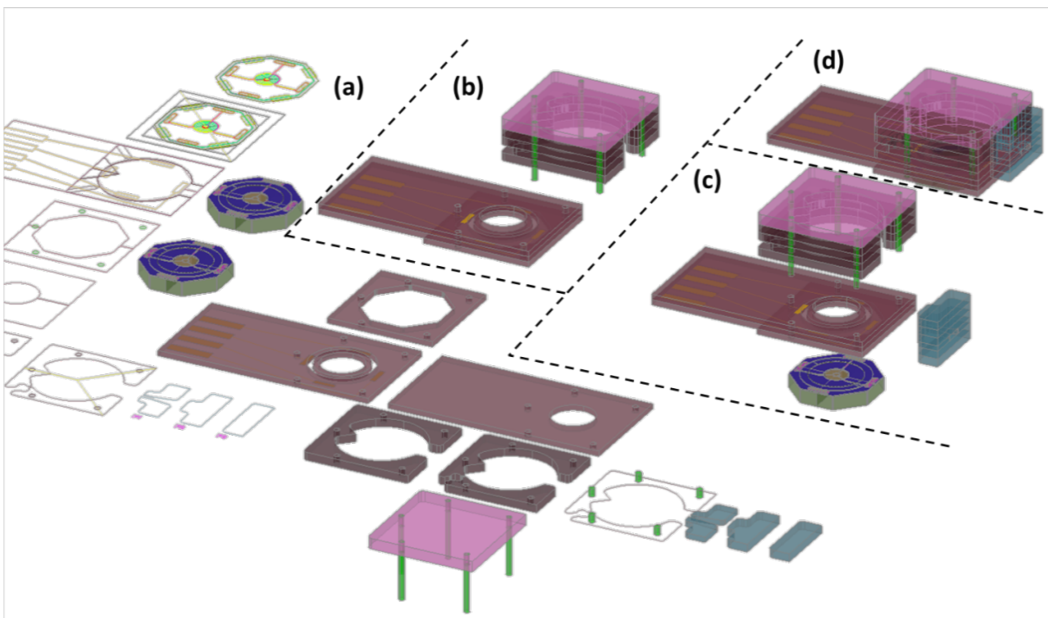
We reached out to other Sandia researchers to determine which sensors could feed target detection data into the data fusion algorithm. Video, thermal imagers, acoustic, and seismic sensors are possible candidates.

Overall, research is progressing well and the team is confident that our work will lead to a suitable design for extended detection outside a facility's perimeter in foliage and weather.

NUCLEAR WEAPONS

The Nuclear Weapons Investment Area supports Sandia's strategic objective of excellence in its nuclear weapons mission through research in leading-edge science and the incubation of new technologies and capabilities. The research is intended to promote exceptional innovation in Sandia's core products to meet future mission needs; develop new tools and technologies for design, qualification and surveillance; and nurture the seamless integration of science and engineering in all of Sandia's work.

The investment area work enables risk-taking in innovation that may not be acceptable under a weapon development effort. Such research will help ensure long-term vitality of Sandia's nuclear weapons enterprise through a creative and vibrant science, technology, and engineering base that supports a deep scientific understanding of our current and future nuclear weapons products.



Photoacoustic cell assembly in various stages: a) piece parts, including the MEMS microphone [blue octagons]; b) and c) a cell partially assembled; d) fully assembled photoacoustic cell (Project 151357).

NUCLEAR WEAPONS

Development of Ab Initio Techniques Critical for Future Science-Based Explosives R&D

151351

Year 3 of 3
Principal Investigator: R. R. Wixom

Project Purpose:

Density functional theory (DFT) has emerged as an indispensable tool in materials research, since it can accurately predict properties of a wide variety of materials at both equilibrium and extreme conditions. However, for organic molecular crystal explosives, successful application of DFT has largely failed due to the inability of current exchange-correlation functionals to correctly describe intermolecular van der Waals (vdWs) forces. Intermolecular vdWs forces are critical to predicting chemistry and physics of explosives at both equilibrium and under stimuli. For the explosive pentaerythritol tetranitrate (PETN), vdWs interactions may dominate the physics for isotropic pressures up to 10 GPa, which implies that we cannot accurately apply DFT for investigating aging, safety, or the margins associated with initiation of PETN or any high explosive. This is unfortunate since explosives research is extremely difficult, expensive, and dangerous, while at the same time essential to DOE/NNSA core missions.

We aim to construct a completely new functional using the subsystem functional scheme that was recently used to successfully include correct surface treatment into the AM05 functional. Despite decades of research, resulting in hundreds of approximate functionals, no functional treating both vdWs and stronger bonds with equal accuracy is available. Even though the vdWs problem can be circumvented by performing DFT-AM05 calculations only at very high pressure, successful investigations at equilibrium and low compression (weak shock), where vdWs forces dominate, will require a new functional provided by a more sophisticated approach such as the subsystem functional scheme. This new functional will provide an accurate first-principles link to the ongoing mesoscale and continuum physics efforts to model explosive components, and additionally will have broad dramatic impact across many fields of science including energy, biology, pharmaceuticals, and the study of any weakly bonded materials systems such as polymers and those applications involving graphene.

Summary of Accomplishments:

We discovered that DFT can be used to accurately predict the unreacted Hugoniots of molecular crystal explosives. The initial concern, the lack of correct vdWs' treatment, appears to only be a problem for predicting the equilibrium volume. Under compression, the weak intermolecular forces become unimportant and the physics are accurately described by standard DFT molecular dynamics (MD) and the AM05 functional. We computed the crystalline unreacted Hugoniot for PETN and hexanitrostilbene (HNS). The computed crystalline Hugoniot of PETN was validated by comparison with low-pressure experimental data. No such data is available for HNS. However, we were able to apply an analytical transformation that relates the crystalline and porous Hugoniots, allowing us to predict the Hugoniot of HNS at lower density where experimental data is available. The agreement between the computed and measured Hugoniots is excellent. The DFT-MD calculations also provide temperature and internal energy, which can be used to parameterize a complete equation of state. Future work will be focused on validating our predicted shock temperatures and creating a complete tabular equation of state for use in hydrocode simulations.

We also made progress in understanding the origins of vdWs' forces. While it is important to consider this origin and mechanism when developing new exchange-correlation functionals for use in DFT, this cannot be the sole focus since the equilibrium distance, for example, is determined by how the atoms interact at smaller distances. A proper functional needs to seamlessly include the van der Waals' forces at large distances while still retaining the good description of matter under compression currently available in, for example, AM05. The construction of a generally adequate functional incorporating vdWs' forces is still an elusive goal and future efforts from our team will be focused on the duality of the electron density and the local effective potential.

Significance:

DFT calculations are invaluable in many fields of science, elucidating difficult and important problems ranging from fundamental physics/chemistry to applied materials science. Previously, DFT methods have not been used in the study of explosives. Our work has opened the door for application of DFT methods in this field. Specifically, our results have produced an accurate equation of state for the explosive HNS, a key detonator material in many DOE weapon systems. That equation of state will be used in the maturation of new detonator designs, and will be critical in defining margins of operation for new life extension program (LEP) components.

Refereed Communications:

T.R. Shan, R.R. Wixom, A.E. Mattsson, and A.P. Thompson, "Atomistic Simulation of Orientation Dependence in Shock-Induced Initiation of Pentaerythritol Tetranitrate," *Journal of Physical Chemistry B*, vol. 117, pp. 928-936, January 2013.

Metal-Insulator Transition-Based Limiters

151352

Year 3 of 3
Principal Investigator: C. Nordquist

Project Purpose:

The purpose of this project was to investigate novel metal-insulator transition materials for realizing limiters with improved performance over conventional technologies. Limiters are essential, as they provide protection by passing low-level signals but blocking high-power signals that could damage sensitive electronics. Novel materials and devices provide potential for improved bandwidth, insertion loss, and power handling. Existing limiters, using semiconductor diodes, are generally restricted by capacitance that forces undesirable compromises among bandwidth, power handling, sensitivity, and survivability. Metal-insulator transition (M-IT) materials offer the potential for revolutionary improvement of these devices. One such material is vanadium dioxide, which exhibits a thousand-fold change in resistance at a specific transition temperature. Microwave heating at high power can trigger this M-IT and create a reversible short circuit, reflecting undesired energy away from the protected electronics. Because the limiting mechanism is purely resistive, these materials may enable broadband, low-loss, high-power limiters with a small footprint when compared with conventional limiters.

We have investigated reversible M-IT materials and have applied these materials to prototype demonstration devices. We have investigated material fundamentals with goals of tailoring the transition temperature, increasing the resistance ratio, and developing integration approaches. A device thrust motivated the materials requirements, applied the materials to demonstrate limiter devices, tested the limiters under continuous and pulsed power, and provided feedback for further materials development.

Summary of Accomplishments:

During this project, we developed two methods for depositing and synthesizing vanadium dioxide thin films on oxidized silicon wafers. Reactive sputtering allowed for device integration, while spin-on solution deposition allowed for rapid characterization of dopant behavior. The material structure and phase of these films were characterized electrically, optically, and with x-ray diffraction. The role of dopants in changing the transition temperature was investigated, and several dopants that raise the transition temperature were identified. Typical films deposited using this method had resistance ratios of approximately 1000 and transition temperatures near the targeted 68 °C.

The metal-insulator transition films were integrated into a microwave integrated circuit technology, which included 200 ohm/square TaN resistors, SiN metal-insulator-metal capacitors, and transmission lines. This process was used to demonstrate limiters and switches, and provided devices for characterization and modeling of the switching dynamics of these devices. This DC characterization revealed that the device switching mechanism was thermally triggered and that the device switched in stages due to current crowding and non-uniform heating. A representative limiter demonstrated insertion loss of less than 1 dB and isolation greater than 20 dB at frequencies up to 10 GHz, while a limiter optimized for high power exhibited a limiting threshold of 5 Watts and maximum power handling of greater than 50 Watts. The device switching time is power dependent and less than one microsecond.

Electrical and thermal approaches to improve power handling were investigated. In particular, the power consumption in the off-state and on-state was considered to establish design targets for minimum and maximum resistance given specific loss, isolation, and power handling goals. Modeling shows that thermal management approaches that favor lateral instead of vertical heat conduction will mitigate thermally induced current crowding and runaway. This additional knowledge is expected to allow for improved limiter devices in the future.

Significance:

By performing science-based materials development, this project supports DOE's scientific discovery and innovation mission. By impacting the size and performance of future systems, the project will support DOE strategic themes. Additionally, an innovative technology solution will appeal to other agencies and external partners that are interested in novel electronics solutions.

This new materials capability can also be applied in areas outside of the limiter, such as for reconfigurable integrated circuits, thermal and energy detection, and energy conservation initiatives such as smart windows.

Refereed Communications:

S. Scott, C.D. Nordquist, J. Custer, D. Leonhardt, T.S. Jordan, and C T. Rodenbeck, "Band-Selective Interferer Rejection for Cognitive Receiver Protection," in *Proceedings of the IEEE MTT-S International Microwave Symposium*, June 2013.

B.L. Brown, M. Lee, P.G. Clem, C.D. Nordquist, T.S. Jordan, S.L. Wolfley, D. Leonhardt, C. Edney, and J.A. Custer, "Electrical and Optical Characterization of the Metal-Insulator Transition Temperature in Cr-Doped VO_2 Thin Films," *Applied Physics Letters*, vol. 113, p. 173704, May 2013.

Thermoelectric Materials: Mechanistic Basis for Predictive Aging Models and Materials Design

151353

Year 3 of 3
Principal Investigator: D. L. Medlin

Project Purpose:

New thermoelectric devices are being developed for use as long-lived power sources. These devices rely on thermoelectric materials, based on alloys of Bi_2Te_3, to perform the active function of converting heat flow to electrical power. The long-term performance of these devices ultimately rests on the long-term properties of the thermoelectric materials. Understanding the aging mechanisms of the relevant Bi_2Te_3-based materials (including changes in the material and its interaction with contact materials) is critical if we are to confidently predict and support the 15-30 year performance of these devices. Looking forward, we also recognize that advances in nanoscience and control of electronic structure are yielding unprecedented improvements in thermoelectric materials technology — advances that are now extending to bulk materials with good performance in the temperature ranges relevant for stockpile application. A fundamental understanding of the interplay between performance and stability will be critical in developing new materials that take advantage of these recent advances while maintaining the reliability required for adoption into the future stockpile. To provide this understanding, we plan a comprehensive program of experiment and materials theory and modeling. Our goal is to discover and quantify the mechanisms governing the performance and long-term behavior of Bi_2Te_3-based thermoelectric materials and to integrate these finding into a predictive science framework. To reach this goal, we will draw on advanced tools for microscopy and transport analysis, and we will advance the state-of-the-art in modeling both materials stability and thermoelectric properties. This capability and knowledge base will be important in future years in meeting our long term responsibility for the new Bi_2Te_3-based thermoelectric power systems currently being developed and in guiding the engineering and selection of more advanced thermoelectric materials for improved reliability and tailored thermal response.

Summary of Accomplishments:

Over the course of this project, we developed a strong science base in understanding aspects microstructure, reactivity, and transport behavior of Bi_2Te_3-based thermoelectric materials. We developed new in situ transport measurements capabilities for conducting accelerated aging measurements and employed this capability for investigating the interactions of gold contacts on Bi_2Te_3. We further explored the interactions of Au with Bi_2Te_3 by conducting a detailed ab initio theoretical study of the energetics and atomic-scale diffusional mechanisms of this solute in Bi_2Te_3. These calculations help to explain observations of contact degradation in $Bi_2(Te,Se)_3$ test structures. We also developed a continuum framework for modeling the diffusive aging processes of metal contacts on thermoelectrics. This framework incorporates additional flux terms that arise in systems, such as thermoelectrics, that must operate under a temperature gradient (Soret effect) and also addresses the problem of modeling anisotropic diffusivities (as are typical of Bi_2Te_3). In the course of developing this framework, we recognized the need for an improved continuum approach for dealing with grain boundary diffusion and made advances in employing localization elements to computationally incorporate such effects into our modeling framework. Finally, we made fundamental advances in understanding t grain boundaries in Bi_2Te_3. We conducted atomic-scale observations of interfacial defect structure at a grain boundary in Bi_2Te_3, providing an advance towards a general dislocation-based model for grain boundaries in this system. We also developed a new theoretical framework for modeling thermoelectric transport properties at individual grain boundaries and applied the method to twin boundaries in Si and Bi_2Te_3.

Significance:

Thermoelectrics have diverse energy conversion and cooling applications. Existing and potential future applications include long-term, high-reliability power sources, localized cooling devices, low-temperature power scavenging, and high-temperature waste heat recovery. The present work helps to advance the basic science underpinning long-term reliability and performance of such systems and helps establish a core science and technology base for supporting and advancing this technology.

Refereed Communications:

V. Stavila, D.B. Robinson, M.A. Hekmaty, R. Nishimoto, D.L. Medlin, S. Zhu, T.M. Tritt, and P.A. Sharma, "Wet-Chemical Synthesis and Consolidation of Stoichiometric Bismuth Telluride Nanoparticles for Improving the Thermoelectric Figure-of-Merit," *ACS Applied Materials and Interfaces*, vol. 5, p. 6678-6686, 2013.

D.L. Medlin and G.J. Snyder, "Atomic Scale Interfacial Structure in Rock Salt and Tetradymite Thermoelectric Materials," *Journal of the Minerals, Metals, and Materials Society*, vol. 65, pp. 390-400, 2013.

Non-Destructive Gas Pressure Measurements in Neutron Tubes and Generators

151355

Year 3 of 3
Principal Investigator: R. S. Goeke

Project Purpose:

Neutron generators are a key limited life component in nuclear weapons and other applications requiring a neutron source to probe or activate a material for analysis. Measuring the pressure inside the tube is a difficult proposition that typically requires destructive analysis. At high pressures, a leakage current can be measured and some pressure information can also be determined during operation of the ion source. Periodically, puncturing sample tubes on the shelf is another way to infer the pressure in a population of tubes. The purpose of this project was development of a nondestructive method by which the pressure inside a neutron generator could be characterized without operating the neutron tube. An accurate measurement of the pressure over a large range of vacuum from 10^{-9} to 10^{-1} torr is desirable but has not been possible. We solved this challenge by treating the existing vacuum envelope as a Penning or Redhead style ion gauge. By creating optimized cross electrical and external magnetic fields on the existing tube design we can enhance the electron ionization path and generate a measureable signal into the high vacuum regime. This capability is also needed for vacuum switch tubes such as Sprytrons used in nuclear weapons (NW) firing sets.

While the concept of treating a neutron tube or switch tube as an ion gauge sounds simple, the materials, geometry, and small volumes had prevented previous attempts to measure high vacuum levels. We overcame this by modeling and optimizing the fields for our test system. Characterization of emission fields and ionization thresholds for existing tube geometries should allow success that was not previously possible.

Summary of Accomplishments:

We created a model that demonstrates the feasibility for creating a self-sustained Townsend discharge between two electrodes in vacuum using crossed electric and magnetic fields. The computer model was created using the physics simulation code Aleph, developed by Sandia's Advanced Simulation and Computing (ASC) Program. The Aleph model established the conditions required to trap electrons in crossed fields with enough energy to ionize gas molecules. The magnetic fields from a 2" magnetron, which was removed from a sputter cathode, was profiled with a gauss meter and used as the base design for the magnetic fields.

To validate this model, a vacuum test stand was designed and fabricated. This high vacuum system has multiple high voltage feed-throughs, which enable charging electrodes to 20kV and the measurement of electron currents down to 1 pico-amp. The system is pumped by a turbo-molecular pump and reaches base pressures of $1x10^{-8}$ torr. Also included is the capability to introduce gases such as helium at fixed flow rates, which will allow testing over a controlled range of pressures.

A simplified electrode geometry consisting of a 0.5" metal sphere and a 1.5" flat metal disk was used for the initial tests. The flat disk electrode sits on the 2" magnetron and works as the gauge cathode. Our initial testing demonstrated that a Townsend discharge can be initiated with this configuration. With a sphere to disk spacing of 0.5", a 800 gauss field at the disk surface and +2kV on the sphere, a sustaining discharge strikes with a measurable pressure varying current starting at a pressure of 10^{-5} torr of helium. These results demonstrate the validity of this research and by applying our models to neutron tube geometries, pressures inside the tubes can be measured without puncturing the vacuum envelope.

Significance:

Sandia is responsible for the full life of a neutron generator. A major degradation mechanism is the build-up of helium, from the radiogenic decay of tritium, in the neutron tube vacuum envelope. The measurement technique developed in this project can provide real-time pressure data of neutron tubes or generators to validate modeling and laboratory experiments. A number of neutron tubes are punctured each year to measure the helium pressure. The techniques developed by this project provide the required pressure information (with improved resolution), thus eliminating the cost of destroying the neutrons tubes.

All Optical Fiber Architecture for Optical Firesets

151356

Year 3 of 3
Principal Investigator: S. E. Bisson

Project Purpose:

This work addresses the desire to develop optically based methods for switching of electrical discharges. Such an approach offers enhanced safety from unintended sources of energy, however, until recently, this approach has not been practical due to the unavailability of compact, robust laser sources. In this work, we demonstrate the operation of a passively Q-switched laser based on an all-fiber architecture for switching of electrical discharges. This work is general in nature and not targeted towards a specific system, however, there are basic performance targets for pulse energy, pulse width, size, weight, power, etc. To meet these simultaneous requirements, a novel laser architecture based on scaled saturation intensity or variable mode size has been developed. This architecture has numerous advantages over a bulk laser; namely, the light is generated and propagated in a fiber, the beam quality is excellent enabling high intensity illumination on the optical switch, the laser can be fabricated in a small adjustable form factor and is robust against shock and vibration. Furthermore, it is easy to manufacture with commercial off-the-shelf (COTS) components. In this work, the basic laser design, performance, design variants were demonstrated culminating in a successful demonstration of optical switching of a sprytron switch.

Summary of Accomplishments:

During the course of this work, we designed, fabricated, and demonstrated a novel, all-fiber, passively Q-switched laser for optical switching of sprytrons. To guide this development, a highly detailed model was developed to explore alternative designs and expected performance. The model enabled multi-variable parametric studies to be performed enabling design optimization. We have also submitted an invention disclosure on the laser architecture. While the detailed requirements may vary depending on the application, attributes such as compact size, low weight, low power consumption and susceptibility to high-g loads are common requirements. To meet these challenging requirements, we developed a radically new design for optical initiation based on a highly integrated, passively Q-switched fiber laser utilizing a tapered, fiber-saturable absorber. This architecture has many potential advantages with respect to size, simplicity (only a few components) and alignment insensitivity to shock in high-G environments. The culmination of this effort was the demonstration of the triggering of an optical sprytron with an all fiber, passively Q-switched laser. Future architectures based on photonic crystal fibers have also been considered.

Significance:

This work has demonstrated a successful approach for optical switching of electrical discharges for initiation of energetic materials. This approach is motivated by the desire to eliminate the intrinsic vulnerability of existing systems to unintended coupling to external energy sources. This work addresses an important national security need for enhanced isolation of energetic materials to unintended initiation. The approach demonstrated in this work is both physically robust and suitable for integration with existing hardware. The architecture has many advantages, such as robustness, high-G capable, small size, fully integrated and represents a major advance in compact, robust laser systems.

Refereed Communications:

S.W. Moore, D.B.S. Soh, S.E. Bisson, and B.D. Patterson, "A High-Energy Cladding-Pumped 80 ns Q-Switched Fiber Laser Using a Tapered Fiber Saturable Absorber," in *Proceedings of the SPIE*, 2013.

S.W. Moore, D.B.S. Soh, S.E. Bisson, B.D. Patterson, and W. Hsu, "Cladding-Pumped Q-Switched Fiber Laser Using a Tapered Fiber Saturable Absorber," Conference on Lasers and Electro Optics, CLEO, CF1E.4, 2013.

MEMS Photoacoustic Spectroscopy

151357

Year 3 of 3
Principal Investigator: A. L. Robinson

Project Purpose:

After years in the field, materials in weapons suffer degradation, off-gassing, and chemical changes leading to measurable changes of their chemical atmospheres. Chemicals can be corrosive to electronics and other materials, causing accelerated degradation and reduced time-to-failure. Even benign compounds may indicate known or unknown age-related issues that require action. Obtaining reliable chemical information from sealed environments is difficult at best. Stand-alone embedded chemical sensors are typically limited in specificity, require electrical lines, and calibration drift makes data reliability questionable. Along with size, these Achilles heels have prevented incorporation of gas sensing.

To address this need, we have been developing all-optical mid-infrared MEMS PAS (microelectromechanical systems - photoacoustic spectroscopy) for safe, in situ gas monitoring of sealed environments. This novel research seeks to overcome limitations of optical access and insufficient absorption pathlength through the use of ever-improving infrared (IR) fiber optics, photoacoustic spectroscopy, highly sensitive MEMS microphones, and miniature acoustic gas cells. Together, these will enable gas monitoring of enclosed areas, including electrical safety exclusion regions. Meanwhile, data collection can be performed by standard analytical instruments at a safe standoff distance. This allows equipment to be sufficiently complex and sophisticated to perform high quality calibrations, measurements, and analyses.

Developing all-optical MEMS PAS presents many challenges and risks, requiring multiple disciplines for success. Success will create significant advances toward a small, yet robust, all-optical method for in situ characterization of gas composition in aging and shelf life components or full systems. This has the potential to enhance reliability of the stockpile through improved understanding of normal and abnormal gas evolution within systems or surrogates. Anomaly detection will be possible without breaching seals. Data will improve estimates of margins and uncertainties.

Summary of Accomplishments:

During this project, we made advances towards realizing all-optical photoacoustic spectroscopy for real-time monitoring of sealed environments. This started with development of miniature photoacoustic cells that can be further miniaturized to fit at the end of a fiber optic cable. Multi-physics computational simulation was used to understand the complex interactions of absorptive conversion of light to molecular motion, translation, pressure, and heat. Breathing modes of the PAS cells were modeled, enabling visualization of pressure-driven flow, flow impedance, and thermal relaxation of the system through an acoustic cycle. Modeling of the cell modes showed that the optimal photoacoustic repetition rate was below the cell's resonances, requiring greater performance of other system components. This was to be realized through microphone design.

An optical microphone with interferometric transduction of its motion was matured. With 633 laser light, picometer displacement sensitivity was observed. Another completely novel microphone was created with signal transduction by evanescent wave coupling between on-membrane waveguides. A complex parametric study was performed to correlate realized MEMS designs with empirically observed performance. Theoretically optimum designs suffer from such imperfections as nanoscale roughness of the waveguide surfaces, which shifts the evanescent transfer function for each given wavelength/width/spacing combination. We learned to manage stress in a multi-layer, multi-material stack that also required a high degree of compliance.

Additional sensitivity was obtained through gold coating of the PAS cells. Modeling of the reflector/adhesion layer/substrate demonstrated an enhancement of 3- to 100-fold, with a strong wavelength dependence over the range of 2 to 20 microns.

Significance:

This work advances our ability to monitor sealed systems in real time for chemical reactions, degradation, and materials aging. This technique can be used early in the design phase when new materials or combinations are assessed for compatibility. Interactions and changes can be observed, even when the occurrence is momentarily and would be missed by sampling only at the end of a compatibility test. Rich chemical information will aid understanding of evolving changes over extended periods. Future advances have potential to identify issues in the stockpile through embedded surveillance. This work helps ensure a reliable and responsive nuclear weapons stockpile.

AF&F Fail Safe Feature for Abnormal Thermal Environments Using Shape Memory Alloys

151358

Year 3 of 3
Principal Investigator: D. F. Susan

Project Purpose:

This project will increase nuclear safety, security, and performance margins for nuclear weapon life extension programs by creating arming, fusing, and firing (AF&F) fail-safe devices that are activated by abnormal thermal environments. This represents a revolutionary advancement in nuclear safety architectures through the development of high-temperature shape-memory alloys (HTSMAs) as mechanical safing devices. Shape metal alloys (SMAs) are metal alloys that can be mechanically deformed into complex shapes at low temperature and then, through heating, can "remember" the original trained shape. Commercial SMAs consist of alloys of nickel/titanium (Nitinol) that are application-limited due to a maximum shape-change temperature of about 100 °C, a temperature too low to be useful in abnormal thermal environments due to overlap with normal environments and production processing temperatures. Our approach will operate on the principles of inoperability and incompatibility whereby the HTSMA will: 1) fail irreversibly, 2) fail passively, 3) perform predictably, and 4) operate based on a fundamental "first principles" material response.

This research leverages an emerging materials suite that has recently attracted global attention and represents a research area yet to be developed at Sandia. The work will potentially yield an enormous enhancement in fail-safe device performance. New HTSMAs and prototype devices will be created based on a fundamental, science-based materials investigation in collaboration with NASA's Glen Research Center. This work is cutting edge and high risk as HTSMAs have not been well characterized or developed into viable devices due to such factors as cost, precision in alloying composition, and incomplete knowledge of alloy transformation properties. A tremendous amount of fundamental research is required to target alloy compositions, properties, and processing techniques that will yield useful abnormal-temperature, fail-safe devices.

Summary of Accomplishments:

In this project, we characterized the shape memory behavior of several new NiTiPt, NiTiPd, and NiTiHf alloys. This work included Differential Scanning Calorimetry (DSC) to determine phase transformation temperatures and mechanical testing such as strain vs. temperature testing to determine the effects of strain on shape memory behavior.

We discovered that these alloys exhibit superelasticity and found the temperature range for superelasticity. This is a new discovery, never before documented in these ternary alloys.

Based on prototype hardware testing, we have observed the two-way shape memory effect (TWSME), which could be useful for actuator applications. We have further characterized the TWSME as well as "negative" TWSME through strain vs. temperature testing.

We successfully collaborated with NASA Glenn Research Center and Texas A&M University (TAMU). NASA Glenn is a world leader in this technology and we will continue our work with them in the future. TAMU processed our material using equal channel angular extrusion (ECAE) to show the effects of a refined microstructure on mechanical properties and shape memory effect (SME) behavior, in particular, TWSME.

We showed that our alloys are superior to commercial binary NiTi alloys in thermal cycling and radiation environments — important for Sandia applications.

Finally, we produced several functional prototypes showing successful shape-memory failsafe operation in abnormal thermal environments.

Significance:

This research is directly related to national security because it involves failsafe materials technology. This technology improves the safety of weapons in abnormal thermal environments (fire, etc.). The technology relies on fundamental materials phase transformation and, as such, meets several criteria for robust failsafe technology.

We have advanced the scientific understanding by producing many alloys never before studied by anyone. We characterized the behavior of these materials at elevated temperatures and strains. We discovered these materials exhibit superelasticity under a certain temperature range. Importantly, our research exercised Sandia's capabilities in alloy development, materials characterization, materials testing, and prototype development.

New Composite Separator Pellet to Increase Power Density and Reduce Size of Thermal Batteries

151359

Year 3 of 3
Principal Investigator: L. A. Mondy

Project Purpose:

The purpose of this project is to develop novel thermal battery separators using advanced ceramics manufacturing techniques to form ceramic foams that are then back-filled with electrolyte. Novel techniques include tape casting: 1) aqueous gels formed with magnesium oxide (MgO) powder, 2) pickering emulsions of aqueous suspensions of MgO particles and an oil phase, or 3) nonaqueous MgO slurries loaded with sacrificial organic particles. When dried and sintered, the resulting tapes form rigid ceramic scaffolds that are highly porous, permeable, thin, and flat. The ceramic processes must be engineered to meet the complex materials and compatibility requirements of the battery system including wetting properties, high dimensional stability, pore size and connectivity, and electrical impedance. Although similar processes have been shown to form exceptionally strong ceramics, no one has attempted to produce thin sheets needed for thermal battery separators. Pellets will be punched or cut from the sheets on demand, eliminating the slow pellet-pressing step of current technology. Despite the challenges, if successful, rigid ceramic separators will provide a revolutionary means to increase the power density, improve manufacturability and performance, as well as reduce the overall size and weight of molten salt batteries.

Summary of Accomplishments:

We showed that it is possible to manufacture a strong macroporous ceramic film that can be backfilled with electrolyte to form rigid separator pellets for thermal batteries. New ceramic manufacturing processes were developed to produce sintered magnesium oxide foams with connected porosities of over 80% by volume with sufficient strength to withstand the battery manufacturing steps. The effects of processing parameters were quantified and methods to imbibe electrolyte into the ceramic scaffold demonstrated. Preliminary single cell battery testing showed that the performance of ceramic separator pellets could be equal if not superior to current pressed pellets. Although less than optimally filled with electrolyte, preliminary samples were seen that resulted in longer voltage life with comparable resistance at the critical early times.

Significance:

This project provides a means for increasing the power density, as well as reducing the overall size of molten salt batteries. This project additionally builds a new base of scientific expertise and technical capabilities relevant to the breadth of Sandia's mission areas, including expertise in advanced materials and diagnostics. New fabrication methods for highly porous, mechanically robust ceramic foams will be useful for a wide variety of applications ranging from catalyst supports, filters for liquid metals, tissue engineering, high temperature thermal insulation, and lightweight structural supports.

Refereed Communications:

C. Roberts, L. Hughes, L. Mondy, A. Grillet, C. DiAntonio, T. Chavez, and D. Ingersoll, "Highly Porous Ceramic Foams from Magnesium Oxide Stabilized Pickering Emulsions," in *Proceedings of the 2012 AIChE Annual Meeting*, 2012.

Liquid Metal Environment Sensing Devices (ESDs)

151361

Year 3 of 3
Principal Investigator: P. C. Galambos

Project Purpose:

This project addresses integrating acceleration measurement and secure electrical switching for severe nuclear weapon environment sensing devices (NW ESD) (e.g., launch accelerometer) applications. The challenge is to create a compact, reliable, robust yet responsive, integrating accelerometer/switch component that meets stockpile to target sequence (STS) requirements and responds to appropriate g-time profiles by closing otherwise highly isolated electrical connections. While there are ESDs that address this problem, our planned alternate solution is potentially simpler, cheaper, easier to manufacture, more reliable and smaller. Our solution may also address applications not addressed by current ESDs, such as high shock resistant low-g switching. This planned ESD can be adapted to man-safety, and non-integrating accelerometer applications (alternate Rolomite).

We plan to create a novel integrating accelerometer/switch based on the motion of small (100 micron to 1 mm) liquid metal drops (mercury or mercury/thallium to meet STS specifications) in a g-field. The drops act as both high proof mass and high isolation/low insertion loss switch contacts. Contact electrode gaps are spaced for high isolation, but are closed by low resistivity liquid metal when drops move to bridge the gaps under g-forces. The component is fluidic, not mechanical, and therefore not subject to wear or fatigue. It is a non-all-electrical interface that is potentially smaller (<1 cm x 1 cm x 3 mm), lighter, and more rugged than current ESDs. Liquid metal is in hermetically sealed channels encased in a can with electrical feed-throughs. This project relies on tailored surface characteristics (roughness, surface energy) to control the force resisting drop motion and, therefore, the time to close the contacts. The concept of micro-to-nano scale surface tailoring for drop dynamic control is novel. This project is also innovative because the small scale of the contamination-free, hermetically sealed, liquid metal containment package is unprecedented.

Summary of Accomplishments:

We created a novel integrating accelerometer/switch that uses a liquid metal drop (mercury) as a proof mass. The drop is housed in a microchannel or capillary, the geometry of which greatly influences drop dynamics when exposed to steady acceleration (single digit g-loads for seconds, where 1 g is the nominal gravitational acceleration of an object near the surface of the Earth, approximately 9.81 m/s2) or shocks (10's of g's for msecs.). When the drop in the channel is subject to a prescribed acceleration for a prescribed period of time, it moves from the starting location in the channel to the ending location, where it bridges two electrical lines to close a circuit, acting as a combined sensor/switch. We presented designs, modeling and calculations that allowed us to tailor the drop size and channel geometry to meet a prescribed flight trajectory g-time history, such as one would need in a specific aerospace application. Centrifuge and shock test data show that we were able to achieve both low-g sensitivity (steady 2-5 g drop motion) while still maintaining shock insensitivity — the switch does not close–to 50 g, 10 msec shocks. The device size is on the order of cm x mm x microns and can be configured as an environment sensing component for SWaP (size, weight, and power) limited applications, such as for an unmanned air vehicle (UAV) or a rocket. Electrical testing showed the device operates without shorts when open and at low resistance when closed in the 50 to 100V switched range. Relatively well-understood design changes should increase this voltage range significantly.

Significance:

This project ties to DOE's nuclear weapons national security mission by developing novel ESD technologies with enhanced surety, reduced size, cost and complexity, and by furthering the science and engineering foundation for nuclear weapons. This technology also has man-safety applications. This project ties to the stockpile stewardship program (SSP) of the NNSA by potentially enhancing the security, reliability, and scientific understanding of a key NW component. The frontier of engineering was advanced as well, by developing a realistic production method for creating liquid metal microsystems for any number of applications.

Ultrafast Laser Diagnostics to Investigate Initiation Fundamentals in Energetic Materials

154813

Year 3 of 3
Principal Investigator: D. Farrow

Project Purpose:

Currently, the chemistry of shock ignition in energetic materials is poorly understood. Models are purely empirical and no direct measurement approach for probing of the thermochemical environment within a shocked material currently exists. The shock initiation of energetic materials progresses on picosecond time scales behind the shock wave and there exists a complex feedback between chemical and mechanical processes (changes in temperature, pressure and particle velocity) that determine the dominant pathways of ignition chemistry. Sandia currently possesses tools for measuring some mechanical properties during this process, but does not have a diagnostic to follow thermochemical evolution during ignition. The extreme temporal and spatial resolution required to monitor the ignition process makes development of appropriate experimental tools a significant technical challenge. In this research, we plan to exploit recent developments in femtosecond laser spectroscopy to probe the evolution of temperature and critical chemical species on picosecond timescales in both the gas and solid phase of shock-initiated energetic materials. Using time-resolved Coherent anti-Stokes Raman spectroscopy (CARS) and other Raman-based techniques, we plan to directly measure the material temperature and chemical-reaction dynamics behind the shock wave. Capturing the relevant physical processes will require us to deliver measurements with both extreme temporal and spatial resolution (picosecond and micron scales), in a hostile environment where response to the ultrafast Raman probe is rapidly evolving during the measurement. Time-resolved temperature measurements have never been accomplished in a reacting or inert solid material under shock loading at temperatures and pressures typical of initiation. Time-resolved measurement of chemical composition during initiation of energetic materials would provide information about the performance of energetic materials used in the nuclear weapons (NW) stockpile, and enable a transition from empirically based models to physics-based predictive simulation. This project will provide Sandia with an experimental capability that is at the forefront of the science of energetic materials and will address programmatic needs in support of NW.

Summary of Accomplishments:

We successfully demonstrated the tools required to study chemical change on fast timescales behind a shock wave in thin film explosives. We successfully implemented laser-induced shock with durations of a few hundred picoseconds with interferometric characterization unique sample identifier (USI) of particle velocity on picosecond timescales. We have also demonstrated two single-shot CARS spectroscopies that could be used to follow chemical change behind the shock wave. Preliminary measurements at room temperature suggest hybrid fs/ps CARS is the best method for this application because hybrid CARS spectrum are not strongly dependent on variations in the spectral phase of the probe field over a wide bandwidth.

Significance:

Femtosecond laser based techniques for shock generation, shock characterization, and spectroscopy allow us to measure shock properties and chemistry on ps time scales and um length scales not accessible using the current state of the art. These techniques also allow the measurement of shock properties over µm length scales. For example, a 1-inch diameter sample of pentaerythritol tetranitrate (PETN) (5 µm thick) could be used to obtain a unreacted shock Hugoniot for PETN at higher pressures traditional gas gun measurements due to the ps time scale of the measurement, further enabling the design of micro energetic devices in development at Sandia.

Ion-Induced Secondary Electron Emission and Vacuum Surface Flashover for High Gradient Ion Beam Accelerators

155409

Year 3 of 3
Principal Investigator: J. S. Howard

Project Purpose:

The primary objective of this project was to study ion-induced secondary electron emission and vacuum surface flashover as they pertain to advancements in the design of high-gradient ion-beam accelerators. This project was initially structured to follow a seemingly straightforward test plan to investigate how these phenomena affect high-voltage holdoff in such applications. However, early experimental results combined with continued literature research significantly altered the scientific approach and project goals. The test plan was reevaluated, and the path forward was focused on realizing a demountable setup to perform ion-induced single event effects (SEE) measurements on relevant metals and surface flashover experiments on insulator surfaces with representative field distributions. Significant progress was made towards realizing the demountable setup, but experimental testing towards the final project goals ultimately stalled. More significantly, equipment developed en route to achieving these project goals provided useful diagnostic testing relevant to several high-priority problem-solving investigations.

Summary of Accomplishments:

Results from the initial test plan revealed that the field distribution along the surface of a high-voltage insulator in vacuum is paramount to meaningful results for flashover threshold. It was also discovered that a particular biasing configuration was critical to the success of the ion-induced SEE yield measurements, prompting the need to design and fabricate an isolation transformer. The continued progress towards realizing the demountable setup provided diagnostic capabilities that ultimately provided significant results for various problem-solving efforts. The biasing regime permitted by the isolation transformer facilitated investigations into quasimetallize charge decay rate, wall charging phenomena, and loss-of-bias. The demountable setup also played an important role in correlating waveform features with different types of internal high-voltage breakdown.

Significance:

This project most significantly impacted national security missions through the development of diagnostic capabilities that ultimately benefited various problem-solving efforts. Characterization of quasimetallize charge-decay behavior, investigation of wall charging effects, and diagnosis of loss-of-bias made a significant impact to several high-priority problem-solving investigations. The demountable chamber realized during this project holds promise for continued investigation of plasma-source performance, ion-beam trajectories, and high-voltage breakdown.

Determination of Reaction Zone Length in Vapor-Deposited Explosive Films

156704

Year 3 of 3
Principal Investigator: R. Knepper

Project Purpose:

The purpose of this project is to determine reaction zone lengths in explosive materials by precise manipulation of the confinement conditions. Reaction zone length is a key parameter in modeling explosive behavior. However, many important explosive materials have very small reaction zones that are extremely difficult to measure using standard techniques. In this project, we plan a new method for determining reaction zone length at micron to sub-mm scales by varying the confinement conditions.

While effectively infinite confinement is known to cause a decrease in the critical thickness and an increase in detonation velocity with increased shock impedance, the thickness of confinement needed to become "infinite" and the magnitude of the effect on detonation velocity and critical thickness are largely unknown. An empirical relationship will be developed during this research that will not only elucidate this dependence, but also provide insight into the kinetics of the detonation reaction by using confinement conditions (thickness, shock impedance) to give an indirect measure of the reaction zone length.

For this work, we use vapor-deposited hexanitroazobenzene (HNAB) and copper films as a model system to study the effects of confinement on the detonation properties of secondary explosives and thus determine the reaction zone length. HNAB is chosen for the reproducibility of both its microstructure and detonation velocity when vapor-deposited, as well as for its small critical thickness and the low surface roughness of the deposited films. Both the HNAB and copper confinement layers are vapor deposited to promote intimate contact between the explosive and confinement and to provide precise control over both layer thicknesses and microstructure, creating a well-defined model system that can be easily incorporated into mesoscale computer simulations. The techniques developed for fabrication and testing of the HNAB/Cu system may be extended to additional explosive and confinement materials, time permitting.

Summary of Accomplishments:

We determined the deposition conditions necessary to fabricate metal/explosive/metal stacks with pristine, non-porous interfaces. Detonation experiments show that HNAB is effectively confined with copper layers as thin as 400 nm. Copper confinement reduces the critical thickness of explosive needed to sustain detonation by more than half, down to thicknesses of less than 30 microns. (Note that a 30 micron thick, 1 mm wide HNAB line would contain only ~0.5 mg of explosive per cm of line length). We determined the reaction zone length in HNAB films to be between 0.5 and 1.2 microns. This suggests that the relevant chemical reactions that drive detonation in these films are complete in less than 200 ps.

These results have also found immediate application in ongoing nuclear weapons (NW)-related development work featuring microenergetics and have the potential to greatly advance the state of the art in predictive modeling of explosive behavior. In addition, the methodology developed to produce high-quality, reproducible films of various explosive materials has enabled new projects studying reaction pathways in explosives and aging phenomena at interfaces.

Significance:

This work benefits Sandia's nuclear weapons mission. Utilization of microenergetic components fabricated by modern microelectronic methods has the potential to increase the precision, reliability, surety, and safety of current and future weapon systems. This work addresses key deficiencies in our understanding of energetic material behavior at the mesoscale, particularly in our knowledge of reaction zone lengths and kinetics for explosives under different confinement conditions. These experiments will significantly benefit ongoing predictive modeling efforts and create the foundations to define a path for integration of microenergetics in weapons systems.

Gas Permeation Properties of Graphene Membranes

158183

Year 3 of 3
Principal Investigator: L. Biedermann

Project Purpose:

This project investigated the potential of graphene membranes to filter gas mixtures. Graphene membranes offer a promising alternative to current membrane technologies since stable, sub-nanometer slits and pores can be formed. Overlapping graphene sheets form a thin slit of tunable width determined by the presence of functional groups. Removal of one or two benzene rings from graphene creates nanopores for molecular sieving. Furthermore, graphene can be fabricated on a commercial scale and transferred to a variety of substrates.

This project investigated how gas permeation through graphene could be optimized by careful design and assembly of graphene membranes. Exfoliated graphene, which is the highest quality form of graphene, is impermeable to helium and larger gases at room temperature and can withstand pressure differences up to 600 kPa. Density functional theory (DFT) simulations confirm that gasses cannot permeate through graphene's benzene rings. However, hydrogen can intercalate epitaxial graphene at 600-1000 °C; grain boundaries and Stone-Wales defects are likely permeation pathways.

Permeation through chemical vapor deposition (CVD)-grown graphene and graphene oxide (GO) was compared to determine how intrinsic properties of these graphene sources such as grain sizes and the presence of defects and grain boundaries affect the permeability. Graphene films were assembled via unitary transfer of CVD-graphene, directly assembled via Langmuir-Blodgett deposition, and self-assembled via vacuum filtration. CVD graphene and GO were selected since they are commercially scalable, easily transferrable forms of graphene, unlike exfoliated or epitaxial graphene. To evaluate the utility of graphene as a selective membrane, permeation of single and binary gas mixtures were measured.

We developed methods to fabricate high quality graphene membranes on porous substrates. We discovered that permselective gas transport occurred through overlapping GO sheets. Development of an alternative mechanically robust permselective membrane will directly benefit Sandia.

Summary of Accomplishments:

We demonstrated permselective gas transport through vacuum-filtered graphene-based membranes, discovered that GO Langmuir monolayers behave as planar structures, and learned that CVD-grown graphene has intrinsic defects limiting its use as a barrier material.

Using vacuum filtration, GO sheets self-assembled into a predominately planar structure directly on a target porous support. Oxygen moieties on the GO sheets control the thin-slit spacing. Vacuum-filtered GO membrane had permselective transport of hydrogen over argon by a factor of 12 over the selectivity expected for Knudsen flow (mass based separation). This high selectivity indicated that the permeation was in the flow regime of the hard-sphere correction to molecular (Knudsen) flow and that the average sheet spacing was ~0.5 nm.

To optimize the Langmuir-Blodgett (LB) deposition of GO on both solid and porous substrates, oscillatory barrier measurements were used to characterize the viscoelastic properties of the Langmuir monolayer at the air-water interface. We measured the elastic and shear moduli of GO and reduced GO (RGO) monolayers; only the GO monolayers, which had a shear modulus and thus behaved as planer structures, could be LB-deposited. LB-deposited GO monolayers selectively tore over a minority of pores in the underlying polymeric membrane support.

Minimizing the stress on CVD-graphene monolayers and controlling the draining of water minimized, but did not eliminate microscopic tearing of the graphene film. The graphene community has identified that nanometer pores are intrinsic to CVD graphene currently grown on copper foils; these defects impede CVD graphene's use as a membrane or corrosion barrier.

Significance:

Optimized vacuum-filtered GO membranes demonstrate increased permeability by decreasing the GO membrane thickness; such membranes could be used for low-energy filtration of hydrogen and helium from methane and natural gas.

Our discovery that GO monolayers behaved as planar structures led to a novel angled Langmuir-Blodgett transfer that minimized the stress on the monolayer, allowing deposition of continuous GO films.

The development of the oscillatory barrier technique to characterize nanosheet monolayers enabled the deposition of TiO_2 nanosheet monolayers for electron microscopy analysis. This characterization and assembly can be broadly extended to other 2D nanosheets.

Chemical Enhancement of Surface Kinetics in Hydrogen Storage Materials

158853

Year 2 of 3
Principal Investigator: D. Robinson

Project Purpose:

In much of the temperature range where palladium alloy powders store hydrogen, the rates of hydrogen uptake and release are limited by chemical reactions at the surface. A stable surface hydride forms that has an undesirably high barrier to transport into the bulk metal or back into the gas phase. To store or release hydrogen more quickly than this allows, engineered systems would require extra storage material, or higher pressure drops. Overcoming kinetic limits could thus improve volume and weight efficiency when fast performance is needed.

We believe that enhanced kinetics can be achieved by destabilizing the surface hydride so it more closely matches the stability of the bulk hydride. Recent modeling by others predicts that near-surface alloys — submonolayers of alloy elements at or just below the palladium surface — can cause the adsorbed states to be energetically equivalent to the bulk states, facilitating transport of hydrogen between them. We have a new and unique capability, electrochemical atomic layer deposition that allows us to make these surface alloys. We will extend our experience with film substrates, conformally applying layers of alloy elements to micrometer-scale palladium powders. Our hypothesis will be tested through measurement of hydrogen isotope exchange rates. We expect compounded improvements in exchange rates if the surface modification is applied to nanoporous powders that offer faster solid-phase transport.

Our planned work takes advantage of recent laboratory discoveries in atomic-scale fabrication, develops the new technique into a practical method, and uses it to pursue recent theoretical developments that are not yet practically demonstrated. If the risks of application of these developments pay off, we will have solved a longstanding performance problem, enabling a cascade of other improvements in hydrogen isotope storage system design that build upon new optimal flow rates and pressures.

Advances in High Dynamic Range Resonant Accelerometers

158854

Year 2 of 2
Principal Investigator: R. H. Olsson

Project Purpose:

This project addresses the fundamental challenges in simultaneously achieving the dynamic range and radiation hardness required for nuclear weapon (NW) accelerometers. Capacitively sensed accelerometers are inherently nonlinear because voltage/capacitance is a nonlinear function of proof mass displacement and beam loading results in bending (capacitive) rather than an axial strain (resonant). To overcome these inherent nonlinearities, capacitive feedback is used to hold the proof mass in a fixed position. This capacitive feedback force is highly sensitive to dielectric charging induced under radiation, creating enormous, permanent errors in acceleration measurements once exposed to NW radiation environments.

Resonant accelerometers are known to have inherently high dynamic range without force feedback, theoretically >10 million for 1 kHz accelerations, due to mechanical linearity and modulation of frequency as the transduction method. However, the dynamic range of resonant accelerometers is limited at frequencies of interest to NW by phase noise in the readout electronics. Phase noise determines the minimum frequency shift that can be measured and therefore sets the minimum detectable acceleration.

We plan a novel mechanical correlated double sampling (MCDS) approach to increase the signal-to-noise ratio (SNR), and thus the dynamic range, in resonant accelerometers. In this approach, the accelerometer sensitivity is modulated at high frequencies by a very low phase noise quartz crystal oscillator. The change is sensitivity is implemented by buckling and unbuckling a beam in parallel with the sensing beam to modulate the acceleration load applied to the sensing beam. This shift greatly reduces the $1/f^3$ oscillator phase noise used to read out the resonant sensor. This MCDS also makes the accelerometer readout insensitive to radiation. While electronic correlated double sampling has been widely applied to mitigate amplifier 1/f noise in capacitive accelerometers, electronic correlated double sampling is incompatible with resonant sensing. The planned research and mechanical implementation will enable application of this valuable technique to higher dynamic range resonant sensors.

Summary of Accomplishments:

We analyzed, designed, fabricated and measured a resonant accelerometer with mechanical correlated double sampling.

The project goals were achieved when we measured a 10 times reduction in drift and 1/f noise using the mechanical correlated double sampling approach.

Significance:

Our research enables the application of high dynamic range resonant accelerometers to NW and other missions where previously environmental drift and low frequency noise would have precluded the use of this valuable technology.

Impact of Crystallization on Glass-Ceramic to Metal Bonding

158855

Year 2 of 3
Principal Investigator: S. X. Dai

Project Purpose:

The purpose of this project is to develop a fundamental material and process science basis that can subsequently be employed to pursue high performance and reliability glass-ceramic (G-C) to metal seals. Concern has been raised when numerous leaks were recorded between G-C and stainless steel (SS) housing in intent strong link (ISL) headers. Chemical bonding is non-existent or weak at the glass-steel interface, as indicated by dissection of ISL headers. Examination of as-received G-C pressed powder preforms revealed the existence of multiple crystalline phases. Early experiments indicated that the amorphous G-C wet and bonded to SS well while pressed powder preforms (PPPs) with pre-existing crystalline phases did not.

A robust G-C to metal seal must have: 1) a strong chemical bond between G-C and metal and 2) a controlled coefficient of thermal expansion (CTE) match between G-C and metal for long-term structural integrity. Recrystallizable G-Cs have been extensively studied and widely used for such sealing applications because of their controllable CTEs by process conditions. However, while it is well known that the precipitation of multiple crystalline phases in a recrystallizable G-C substantially changes the chemistry of the residual glass, the effects of residual glass chemistry on the wetting and bonding at the G-C/metal interface remains largely unexplored.

We plan to study the interface between the G-C and the metal, and the effects of crystallization in the G-C on the bond strength. The study represents a major step forward from current knowledge on glass-metal seals, which is predicted primarily on controlling the crystallization in the G-C to achieve CTE match to the metal. The goals are to: 1) understand the interfacial reduction-oxidation (redox) process that is essential for a strong chemical bonding, 2) investigate the change of glass chemistry from crystallization and its effect on the redox process, and 3) explore paths that enhance the interfacial redox for improved glass-metal bond.

Synthesis of Wear-Resistant Electrical Contact Materials by Physical Vapor Deposition

158856

Year 2 of 3
Principal Investigator: S. V. Prasad

Project Purpose:

There are numerous components in the current NW stockpile that contain electrical contacts to ensure passage of signals or power. Issues with electrical contact degradation have been an ongoing challenge for the NW Surveillance Program. In NW safety mechanisms, maintaining low contact resistance without increasing friction is achieved by applying a thin (1-2 micron thick) layer of electroplated hard Au on contact terminals. Minute alloying elements such as Ni, Co, or Ag are known to impart wear resistance to hard Au. However, achieving the desired combination of properties via electroplated Au continues to be a problem. Besides the quality control issues and the environmental hazards associated with arsenic and cyanide baths, there are long-term materials aging and reliability issues arising from diffusion of hardeners in Au to the surface. The purpose of this project is to develop engineered materials that are radically different from the legacy materials. The major goal is to synthesize wear-resistant nanocrystalline hard Au employing minute quantities of thermodynamically stable ceramics as hardeners. The materials under consideration are processed by environmentally friendly technologies, replacing the need for electroplating and the associated environmental hazards while improving process repeatability.

Notable accomplishments during the reported fiscal year include the synthesis of nanocomposite thin films by physical vapor deposition. Using the Traid E-beam deposition system that was put in place in FY12, Au-ZnO nanocomposite films with wide range compositions (from pure Au to 100% ZnO) were synthesized. Bulk electrical resistivity was shown to increase monotonically with increasing ZnO content, falling into three regimes of behavior associated primarily with: 1) grain boundary electron scattering due to grain refinement at ZnO volume fractions (vf) below 0.3, 2) percolation theory for ZnO volume fractions at and above the percolation threshold, vf = 0.85, and 3) a transition region between these where resistivity was influenced significantly by the formation of Au-Zn complexes. A model incorporating electron scattering and percolation theory describing the composition dependence of electrical resistivity was developed. Electron backscatter diffraction (EBSD) analysis revealed that a significant reduction in grain size can be achieved even at 0.1 vol. % ZnO. Sliding electrical contact resistance (ECR) measurements with simultaneous friction data acquisition were made in regimes relevant to surety mechanism contacts using a spherically tipped Neyoro G (72Au-14Cu-8Pt-5Ag) pin. Composites with 2 vol. % ZnO were found to have practically no measurable wear with ECR below 40 mΩ, offering potential alternatives to electroplated hard Au. Nanolaminates of Au incorporating ceramic and metal layers in the Au matrix were synthesized by pulsed laser deposition and characterized by cross-sectional transmission electron microscopy (XTEM). The films, after exposure to thermal cycles, are being reexamined in the transmission electron microscopy (TEM) to identify a robust diffusion barrier for Au. A short exploratory task was undertaken to investigate the role of He ion implantation of pure Au on friction-ECR behavior, with a view to achieve similar desirable effects without incorporating the ceramic particles.

Extension of Semiconductor Laser Diodes to New Wavelengths for Novel Applications

158857

Year 2 of 3
Principal Investigator: M. H. Crawford

Project Purpose:

Extension of laser diodes (LDs) to the deep ultraviolet (DUV) is thus far unrealized but would be a major technological breakthrough. Over the past decade, advances in AlGaN semiconductor alloys have led to the first DUV light-emitting diodes. However, demonstration of DUV LDs has been thwarted by a lack of fundamental insight and solutions to formidable AlGaN materials science challenges.

Our planned effort combines Sandia's state of the art AlGaN growth and fabrication capabilities with advanced modeling to overcome these challenges. Innovative approaches to p-type doping include band structure engineering to dramatically reduce acceptor activation energies. Mitigating extended crystalline defects will involve Sandia's recently demonstrated patterned overgrowth process to promote defect annihilation. New insight into non-radiative, atomic-scale defects will be gained using deep-level optical spectroscopy, a technique mastered by few groups worldwide. Sandia-developed laser models will be used to guide AlGaN band structure engineering for maximizing material gain. Finally, LD development will include exploration of a novel laser architecture that has the potential to overcome long-standing challenges in AlGaN LD design.

Deciphering the Role of Residual Stresses on the Strength of Adhesive Joints

159749

Year 2 of 2
Principal Investigator: J. M. Kropka

Project Purpose:

The performance and reliability of many Sandia components (e.g., neutron generators, firing sets, etc.) depend upon the integrity of interfaces between dissimilar materials. Unfortunately, the ability to predict the strength of critical polymer/solid interfaces is limited. Testing and analysis of adhesive joints is often pursued to evaluate bond strength and the ability to predict debonding. However, many factors determine the strength of an adhesive joint and this often obscures a thorough understanding of the results of such efforts. To address this, we designed an approach that focuses on understanding the role of one contributor to joint strength: the residual stress built up in a polymer adhesive during preparation of a joint. Sandia's cutting-edge nonlinear viscoelastic (NLVE) polymer model has the capability to assess the residual stress state in a joint as well as evaluate the local stress/strain within the joint at the point of experimental failure, capturing the coupled effects of processing, mechanical loading, etc., on the strength of the joint. Paired with carefully designed experiments that resolve changes in joint strength with residual stress state, an understanding of when and how residual stresses become important in determining joint strength can be developed.

The project focused on two eminent challenges to developing an understanding of the role of residual stress on the strength of adhesive joints: 1) predicting residual stress associated with cure of the adhesive and 2) varying residual stress in the joint without influencing other factors that contribute to the ultimate joint strength. The first enables a more accurate definition of the residual stress state and the second allows conclusions to be drawn based on changes in residual stress versus changes in multiple factors.

Summary of Accomplishments:

The ability to parameterize the simplified potential energy clock (SPEC) model (Sandia's cutting-edge nonlinear viscoelastic (NLVE) polymer model) to account for stress developed during the cure process was examined and the resulting parameterization was tested in a validation experiment. The proximity of the model predictions to data in the rubbery cure stress validation tests was quite encouraging. The predictions of the evolution of the shear modulus with time as the material cures and vitrifies are also promising for the ability to capture glassy effects. However, the model predictions of the cure stress validation test are sensitive to a number of factors and all of these sensitivities make quantitative comparisons between the data and model predictions difficult. More data to establish tighter limits on model parameters and to more precisely define the validation test are needed. The areas that could use the most immediate attention are cure shrinkage assessment and the cure stress validation test.

Methods to alter residual stresses in the napkin-ring joint have been demonstrated. Computational predictions, representing the adhesive with the SPEC NLVE polymer model, even suggest that some of these methods would have a significant effect on the torsional response of the joint. Namely, stress controlled compressive loading, in combination with the torsional loading, is predicted to decrease the maximum in average shear stress sustained by the joint by more than a factor of two when the compressive load is of order 100 MPa. While such behavior has not been observed experimentally, work remains to verify that the experiments and computational predictions are an apples-to-apples comparison. During the experimental testing, new capabilities were developed to quantitatively resolve the torque-rotation response of the napkin-ring joint and to apply combined axial and torsion loading to the napkin-ring joint. These capabilities are important to continuing programs.

Significance:

The demonstration of the ability to parameterize and validate a physically based constitutive model with experimental measurements advances the hypotheses on which the model stands. In addition, the model's ability to account for stress developed during the cure of thermoset polymers enables the optimization of adhesive and encapsulant material cure schedules in order to reduce residual stress for more robust engineering designs that can survive the challenging environments required in national security missions. Finally, the new capabilities developed in joint testing enable more resolution in measurements that support multiple programs.

Inherent Secure Communication Using Lattice Based Waveform Design

161862

Year 2 of 3
Principal Investigator: M. O. Pugh

Project Purpose:

The wireless communication channel is susceptible to eavesdropping due to the broadcast nature of the electromagnetic medium. Traditional approaches to combat these insecurities have included encrypting the data via cryptographic methods, hiding the data in the noise floor as in wideband communications, or nulling the signal in the spatial direction of the adversary, using array-processing techniques.

Recent advances in signaling constellation design have shown that an additional level of security exists at the physical layer. By appropriately designing communication waveforms, the ability of an eavesdropper to correctly demodulate the intended secure signal can be hindered while maintaining successful communications with the desired receiver. This process increases the eavesdropper's bit error rate (BER) and inhibits successful decoding of the secure signal. This method has only been theoretically verified for simple point-to-point channels.

This research will target the design of secure communication waveforms in more complicated and realistic channels such as multipath (fading) channels and multiple antenna environments with multiple possible eavesdroppers. The effects of system constraints such as peak power consumption on the code design must also be researched.

The design of secure wireless channels has primarily focused on encryption, spread-spectrum and/or beam-forming techniques. Achieving enhanced secrecy at the physical layer through the design of communication signals is orthogonal to these existing methods. It has the following benefits:

- Unlike other secrecy techniques that either requires changes to existing systems such as additional bandwidth or the need for more antennas, this technique can be implemented with minimal changes.
- This method is broadly applicable in all environments.
- This has the potential to improve secrecy in all military and national security wireless communications, including satellite applications, fleet command and control, and even short range tactical communication.

Impact of Materials Processing on Microstructural Evolution and Hydrogen Isotope Storage Properties of Pd-Rh Alloy Powders

162522

Year 2 of 3
Principal Investigator: P. Cappillino

Project Purpose:

Palladium and its alloys are optimal storage media for tritium due to high volumetric capacity at low pressure, rapid kinetics of absorption and desorption, and resistance to poisoning. As such, development of synthetic and materials processing methods that yield reliable, optimized material is critical. Preliminary investigation of atomized Pd-Rh powders has shown that post-processing methods have significant influence on the physical properties and dimensions of Pd-Rh powders, which in turn, impacts isothermal pressure-composition-temperature (PCT) curves of Pd-Rh materials. These effects are particularly noticeable in the H-storage capacity, plateau pressure slope, and hysteresis loop upon H-cycling. The material synthesis and processing methods that have been investigated include gas atomization, cryomilling of atomized powder, and electrochemical precipitation. Further investigation using these techniques will be supplemented by spark plasma sintering (SPS) as well as other processing methods to explore the effects of texture and porosity on hydrogen isotope storage kinetics and thermodynamics.

In Pd/Pd alloys, the connection between hydrogen isotope storage properties and physical properties such as particle morphology, particle size and micro- and nanostructural aspects such as grain size, defect density and porosity remains to be fully understood. The combination of state of the art facilities for alloy syntheses, a suite of cutting-edge materials characterization techniques, and the ability to measure hydrogen isotope storage behavior provides an opportunity to break new ground in understanding this relationship. Feedback between these aspects should facilitate the tailoring of hydrogen storage properties to suit a given application. The work is in collaboration with UC-Davis.

Developing Software Systems for High-Assurance Applications

164661

Year 2 of 3
Principal Investigator: G. C. Hulette

Project Purpose:

Ordinary development practices for digital logic and embedded sensing and control programs yield unpredictable and unknowable results. While the positive function (what we intend for the system to do) is often at least partially testable, the negative function (what we don't want it to do) typically is not. We must analyze the digital system itself as a mathematical object in order to reason about what it is capable of doing under the broad circumstances required by high-assurance systems. Ascertaining negative function is particularly important in high-consequence applications such as nuclear weapons.

Conventional development practices for digital systems yield programs with large spaces of negative function. If code cannot be analyzed, providing assurances against negative function is typically impossible. The planned work will develop a language in which digital hardware or software can be created that is specifically designed to be analyzable. Writing code in this language is unlikely to be as easy as in an unconstrained language like C, but the results will provably conform to pre-defined constraints. Of course, there can be no guarantee of complete safety or security outside of what the designer has specified. However, an important artifact of the planned methodology is that, even after the digital system is complete and in use, it will remain analyzable and a posteriori newly discovered constraints can still be checked. In case new faults or vulnerabilities are discovered, planned mitigations can be proven.

Tools for developing formally verified digital systems have the potential to revolutionize high-assurance applications, enabling engineers to hold digital products to an entirely new sort of confidence — the same confidence we place in verified mathematical proofs. Our research would move Sandia closer to realizing this goal.

Understanding H Isotope Adsorption and Absorption of Al-Alloys Using Modeling and Experiments

165724

Year 1 of 3
Principal Investigator: D. Ward

Project Purpose:

The aging performance of austenitic stainless-steel reservoirs for hydrogen (H) isotopes can be limited by time-dependent H-metal interactions (e.g., embrittlement). Aluminum alloys, alternatively, have very low solubilities for H-isotopes and no evidence of embrittlement in dry H environments, suggesting improved resistance towards aging vulnerabilities. Unfortunately, the long time scales associated with effects of H-isotopes make solely experimental investigations impractical. Therefore, robust simulation tools need to be developed to strengthen our understanding of Al/H-isotope interactions and guide accelerated testing. A continuum level model capable of capturing aging of the material does not exist. Such a model requires a fundamental understanding, at the atomistic level, of H-isotope interactions with Al-metal/oxide surfaces and crystalline defects (e.g., dislocations, precipitates).

This work will focus on H-isotope interactions with binary Al-Cu containing a surface oxide. Copper is a common alloying element in Al-alloys and is the primary source of strengthening in candidate alloys such as AA2219. This project includes numerous innovations. First, we will develop the first-ever chemical-reaction-simulation-enabling high fidelity quaternary bond-order-potential (BOP). The fidelity of the BOP is achieved by extensively benchmarking with high quality density function theory (DFT) calculations, and validating with experiments. The BOP is then used in molecular dynamics (MD) and Monte Carlo (MC) simulations to study adatom trapping energies and absorption mechanisms. Second, we will develop a defect dynamics (DD) model, informed from atomistics and experiments to study effects of hydrogen and precipitates on the motion of dislocations within the binary system. Our model will be the first to combine the interactions of precipitates and the effects of H-isotopes on dislocations in three dimensions. In addition, the corresponding experiments to explore H-isotopes on oxidized binary surfaces and trapping in Al-Cu will both be firsts in the field. Sandia is uniquely positioned to solve this problem, being one of the very few institutions with expertise in all phases of this project.

Carbon Composite MEMS Accelerometer

165725

Year 1 of 3
Principal Investigator: C. M. Washburn

Project Purpose:

Our highest deliverable is to develop a carbon composite microelectromechanical systems (MEMS) accelerometer. The motivation is to understand a unique carbon-carbon blend developed at Sandia, which leverages graphene sheets embedded in an amorphous carbon backbone and development of the material to a highly sensitive-1.06 dynamic range accelerometer. Fundamentally, the graphene sheets are in random orientations (flat/folded), however, their direct interactions suggest double bond carbon-carbon templates (sp^2basal plane alterations) made during processing and needs further understanding. Recently, carbon cantilevers using graphene stiffeners demonstrated a tunable Young's modulus of 65% using 2 wt.% graphene and a 2X increase in conductivity. From literature, graphene materials show improved strength, low density (~1.4 g/cm^3), good ductile behavior, and linear responses under force. The carbon accelerometer will be designed towards a proof mass architecture for optimal displacement and view impedance vs. G-force and should require little or no dampening to the proof mass due to the low density.

A carbon composite MEMS accelerometer using graphene stiffeners drives new materials and devices into MEMS to improve dynamic range, sensitivity, lifetime, and functionality when compared to state of the art MEMS technology. The planned carbon composite structure is a replacement for single crystal/metal MEMS beams, flexures, struts, etc., at a fraction of the expense. These materials are less prone to stiction under high G-force loading and have tremendous resilience under extreme mechanical deformation and shock. The exact understanding of the science and engineering required to build a carbon composite device does not currently exist.

Organosilicon-Based Electrolytes for Long-Life Li Primary Batteries

165726

Year 1 of 3
Principal Investigator: K. R. Fenton

Project Purpose:

We aim to develop new lithium primary power sources designed to have wider operating temperatures using inherently safe materials to increase the performance and safety of power sources used in nuclear weapons (NW) testing applications. The Achilles' heel of organic electrolytes used in Li primary and secondary batteries is their instability at elevated temperatures and safety concerns including fire and explosion. In order to eliminate flammability concerns at elevated temperatures, we plan to develop a new class of 'organosilicon' electrolyte materials with high temperature stability, high ionic conductivity, which are nonflammable, nontoxic, and have low viscosities (~1.4 cP). Informed by new density functional theory (DFT) models, these compounds have the potential to offer increased temperature performance in a nontoxic, nonflammable electrolyte solvent. We are working towards fabrication of CFx (carbon monofluoride)-based Li-Primary cells with these optimized electrolytes, employing advanced packaging concepts, and focusing on NW needs for safe, high energy density primary batteries for joint test assembly (JTA)/ground controller applications.

Organosilicon electrolytes exhibit several important properties for use in lithium cells that include: 1) high conductivity/low viscosity and 2) thermal/electrochemical stability. The systematic manipulation of the silicon oxide backbone geometry and repeat unit length as well as the appended ethylene oxide moieties allows for fine-tuning of the thermal and electrochemical properties of the electrolyte. These manipulations also allow for incorporation of innovative functionalities such as anion binding agents (ABAs), which dramatically change the electrochemical properties of the electrolyte and bind the fluoride anion (a byproduct of discharge) leaving lithium ions available for incorporation into the electrolyte. This work will enable the design of unique multifunctional, thermally stable organosilicon compounds with a wide variety of tunable properties. The knowledge and understanding developed in this project is expected to have an immediate impact on battery technology but is also broadly relevant to other applications, which range from semiconductor manufacturing materials to drug delivery agents where organosilicon materials are being investigated.

Electromechanical Performance of Electronic Components in Harsh Environments

165728

Year 1 of 1
Principal Investigator: J. G. Niemczura

Project Purpose:

Ceramic capacitors are a common component found in electrical circuits. Some ceramic capacitors are piezoelectric, of which some display a ferroelectric response under certain conditions. This electromechanical coupling is not clearly addressed by manufacturers. It is important to understand this coupling as the circuits may be subjected to harsh environments, such as vibrations and/or mechanical shocks. These environments can change the performance of the capacitor. Having a capacitor model, or having a design guide based on models, would aid a designer in choosing the capacitor that will meet the design intent through all expected environments.

The goal of this project was to create an electromechanical model that could analyze and predict the performance of ceramic capacitors subjected to harsh mechanical environments. Such a model could be used to optimize a capacitor in terms of geometry and material characteristics in order to achieve a desired performance.

In order to have a predicative model for a capacitor, both a phenomenological constitutive model of the capacitor material and physical model of the capacitor are needed so that numerical simulations can be conducted. Mechanically quasi-static and dynamic electromechanical experiments are needed for model validation and for behavior analysis used towards updating the model.

Summary of Accomplishments:

A one-dimensional analysis performed on a piezoelectric device connected to three different simple circuits shows, conceptually, the circuit's electrical response to smooth, dynamic stress loading. A parameterized meshed model of a capacitor was built, which can capture most manufactured rectilinear capacitor geometries. This model has been run in the ALEGRA/EMMA finite element code with a piezoelectric constitutive model. A suite of electromechanical experiments was created for testing ceramics capacitors, which included depolarization of an unenergized, polarized ceramic capacitor at low- and high-rate mechanical loading, electrical cycling of a capacitor under quasi-static loads, and electric discharge of a capacitor under quasi-static loads. The experiments were successfully performed on C0G, R2D, and X7R capacitors.

Significance:

This project is beneficial to the NNSA as it helps assure the state of the current stockpile. The models and experiments of electrical components can be added to component assessment strategies that provide information for the annual assessment report on the stockpile. The results should also provide use in the design of replacement components for NW alterations (ALTs) or modifications (MODs), and life extension programs (LEPs) by selecting electrical components that will be assured to meet all requirements during harsh environments.

The Use of Degradation Measures to Design Reliability Test Plans

165729

Year 1 of 2
Principal Investigator: J. W. Lane

Project Purpose:

Many nuclear weapon system components display some measure of degradation. In each case, a measurable attribute dependent on component usage or age is related to the reliability of the component. In this proposal, reliability will be understood to mean the reliability with respect to a performance measurement and its associated specification limit, sometimes called margin reliability.

Our technical goal is to create robust reliability test plans for components subject to degradation. That is, given a component subject to degradation, a measure of success would be the development of an efficient reliability test plan and, if appropriate, development of replacement and maintenance plans. Models and methods may be well developed for components with significant historical data. However, additional models and methods are needed to optimize test plans for components with little or no existing data. Our goal is to design new test plan strategies for components that display degradation and have limited data. This will require extending current methodology as well as developing new theory. These new test plans will seek to optimize both time and resources needed to demonstrate reliability goals with respect to performance specifications. This approach builds on the present emphasis on quantification of margin and uncertainty (QMU) for the nuclear weapons stockpile. A related goal of testing using degradation measures is to improve component replacement and preventative maintenance strategies. The methods developed will be illustrated using actual nuclear weapons component data as well as simulated examples.

Lithium Thiophosphate Compounds as Stable, High Rate Li-Ion Separators: Moving Solid Electrolytes into High Rate Applications

166148

Year 1 of 3
Principal Investigator: C. A. Apblett

Project Purpose:

A solid phase, sulfur based lithium thiophosphate electrolyte was planned, in collaboration with the University of Colorado (Boulder). Rather than sol-gel or particle-based processing, which has been done previously, the plan was to use reactive co-sputtering to achieve the same stoichiometry in a very thin film as these other methods. The attraction of this material was the high room temperature conductivity, approaching $1E^{-3}$ siemens/cm under certain conditions. A sputtering system was procured, assembled, and activated to deposit these films. Because of the nature of this elemental system (Li-P-S), it was expected that there would be some challenges in controlling the deposition of these elements independently, and so rather than elemental versions of these targets, targets of Li, Li_2S, and P_2S_5 were pressed and assembled. It was thought that making compound targets would lower the vapor pressure of the elements to a controllable level. However, this was not observed, and instead significant contamination and cross contamination of the targets between sputtering runs by background sulfur quickly became the dominant issue. The lithium target was contaminated by background sulfur, and the P_2S_5 target quickly eroded, even at very low sputtering powers. Different combinations of power, gas pressure, temperature, compound stoichiometry, and mix ratios were attempted, but the general conclusion, after a year of effort, was that the sputter rates are too low, and the compounds too hard to control to make sputtering a good choice for this materials set.

To keep the project moving forward, we selected an alternative compound set, Li-Ge-Si-O, which also exhibits good Li conductivity ($1E^{-4}$ vs. $1E^{-3}$ for the thiophosphates), and does not suffer from high volatility elements. Li_2O, Ge, SiO_2 are target sputter compounds.

Non-Linear T-Lines for Fire-Set/EBW Drivers

169300

Year 1 of 1
Principal Investigator: J. M. Elizondo-Decanini

Project Purpose:

Present fire set designs are based on two components, which both require an investment of capacitors and vacuum switches. Much work has been dedicated to improve capacitor linearity as a function of voltage and temperature, and vacuum switch jitter. A capacitor discharge unit (CDU) is the basis of the fire set design. There have been large efforts to improve it, miniaturize it, linearize it, etc., but no radical concept has emerged to replace the legacy CDU. It is obvious that in its simplest representation, a fire set CDU is just a high voltage wave source; it takes as an input a low voltage, slowly rising wave/signal and then switches it, producing a faster rise time wave/signal as the output. The three fundamental functions are: 1) provide time-control, 2) provide a faster rise-time wave, and 3) store and provide the energy for the faster-rise wave front.

We plan a very ambitious, high pay-off effort to create a non-linear transmission line (NLTL) and demonstrate that we can compress a high-voltage pulse from sub-milliseconds, to nanoseconds. The implications may not be obvious, but dramatic — imagine a slow pulse (such as the step up pulse used to charge the CDU, or a quasi-DC front from the battery pack) converted and compressed into a sharp nano-second rise-time pulse, capable of driving a conventional exploding bridge wire (EBW) or a flyer plate; this with a passive line that uses no switches and cheap capacitors. At this point, we understand the fundamental physics that drives the concept. We plan to develop the science behind non-linear-t-line concept of voltage and current wave compression to direct and enable the engineering required to create this new concept into fire sets. The planned approach allows for more sophisticated strong/weak link approaches by replacing and/or dramatically simplifying the present baseline CDU.

Summary of Accomplishments:

The differential equation that describes a soliton using the Toda lattice approach has been solved with great detail, and we demonstrated the use of this sophisticated technique to our fire set mission. Additional observations and accomplishments are summarized below:

- The fundamental “knob” that defines the behavior of the NLTL is the wave velocity.
- The faster the wave velocity, the more compression on the initial signal width.
- A tapered NLTL (e.g., stepping the inductance capacitance [LC] values) seems to produce the best results.
- The driving parameters are basically the inductance and capacitance on the transmission line (TL). If a TL with descending capacitance values (or LC pairs) is used, the result is compression from an initial entering wave width to an exit wave width.
- A formal introduction to the dielectric constant and the dispersion relation, which is entirely a frequency dependent effect, was explored.
- An NLTL will compress the input signal; losses still need to be introduced.
- A few circuit-equivalent models that show the same results as the differential equation have been produced.

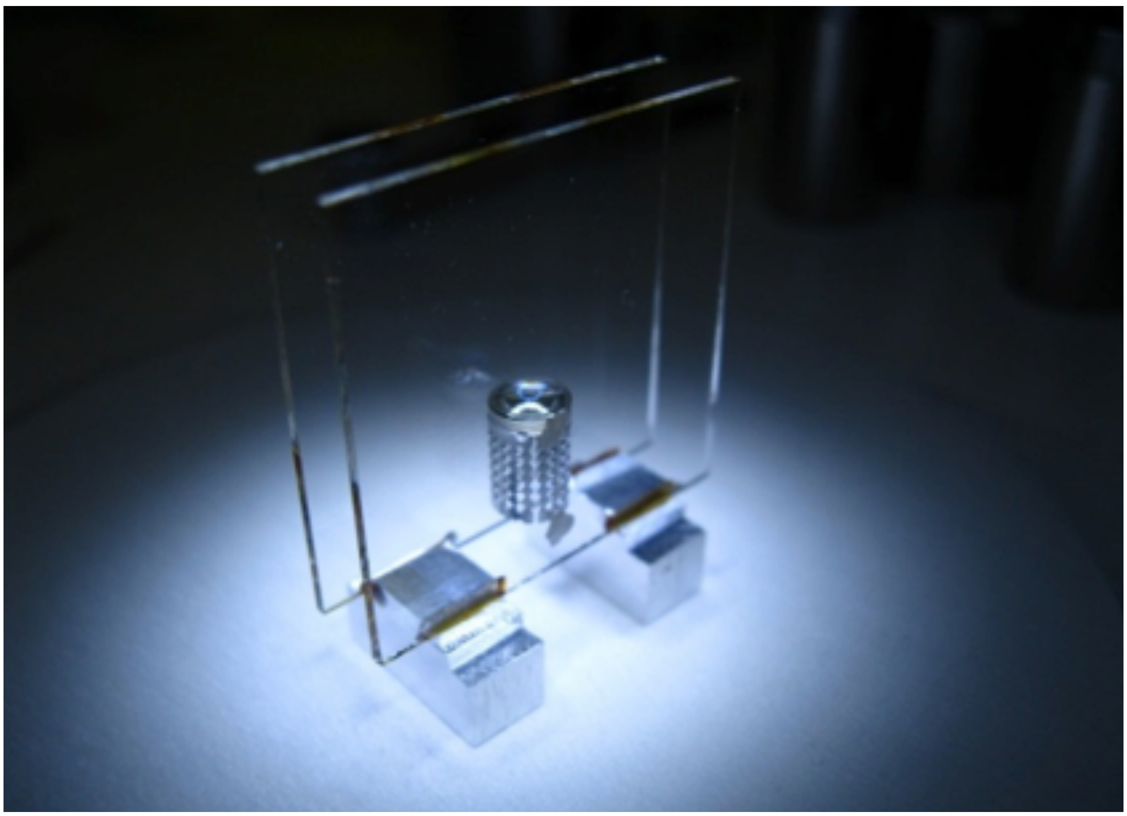
Significance:

This technique has been demonstrated to open the door for a new fire set concept, as well as a number of new strong-link developments that require a more advanced fire set concept.

The use of non-linear techniques opens the door for a new "game changing" approach to fire sets and detonator technology, this by enabling in a compact micro-engineered package the inclusion of multiple elements relevant to nuclear safety.

GRAND CHALLENGES

LDRD Grand Challenges are bold, game-changing ideas with the potential for enormous impact to the security of the nation through significant advances in science and engineering. Grand Challenge Investment Area projects are expected to drive the future of Sandia by providing new directions, capabilities, and solutions to provide long-term impact to multiple areas of the Labs' mission work. These projects result in a long-term science, technology, and engineering legacy for Sandia, from breakthrough scientific discoveries through the development of unique and differentiating technical capabilities. These projects are multimillion dollars in size and utilize multidisciplinary teams, often including external collaborators.



Optical assembly of indium tin oxide-coated surfaces to mitigate electric field fluctuations. The side of the optical tweezers lens facing the atom is coated with a l/4 thickness of ITO at l = 852 nm, whereas the backside is AR-coated and thus shielded with a conductive cylinder. The large square plates have indium tin oxide on the surfaces facing the atom (Project 152501).

GRAND CHALLENGES

AQUARIUS: Adiabatic Quantum Architectures in Ultracold Systems

152501

Year 3 of 3
Principal Investigator: A. J. Landahl

Project Purpose:

AQUARIUS's vision is to develop a quantum computing architecture whose resource requirements are more achievable than conventional approaches because of the intrinsic noise immunity offered by adiabaticity. A quantum computer is capable of speeding up the solution to numerous problems in our national interest, including those in simulation, energy, and cybersecurity.

To achieve this vision, AQUARIUS' goals are to experimentally demonstrate an adiabatic quantum optimization (AQO) algorithm in two technologies: 1) neutral atoms trapped in an optical-trap array and 2) electron spins in semiconductor nanostructures, and for these technologies to evaluate the potential for fault-tolerant universal adiabatic quantum computation (AQC) architectures.

The key experimental challenges are characterizing and adiabatically controlling "always-on" qubit interactions and integrating high-fidelity qubit readout. The key theoretical challenges are developing realistic noise models and adapting fault-tolerance concepts from quantum circuit architectures to AQC architectures.

Previous experimental research has predominantly focused on superconducting qubit technology, which may not be best suited to AQC architectures. Previous theoretical research has predominantly focused on bringing error-correction to AQC instead of AQC to error-correction. AQUARIUS will diversify the AQC technology base and explore new ways of making AQC architectures fault-tolerant. This project leverages several unique Sandia capabilities, including the Microsystems and Engineering Sciences and Applications (MESA) fab, the Center for Integrated Nanotechnology (CINT) fab and High-Performance Computing (HPC) facilities.

Most existing quantum computing efforts are pursuing the quantum circuit architecture, in which an algorithm is expressed as a sequence of simple operations. The price for this simplicity is high — each operation must be error-free to at least one part in 10,000 to operate fault-tolerantly. An experimentally proven resource reduction and a design path forward for scalable universal fault-tolerant AQC could reshape how quantum computing R&D is approached.

Summary of Accomplishments:

Our principal accomplishments, by task, include:

<u>Neutral atoms</u>:
We built a system for trapping and controlling individual cesium atoms. With it, we executed single-qubit AQC algorithms and demonstrated quantum adiabatic behavior unequivocally. We also demonstrated entangling

Rydberg-blockade coupling between two atoms. For our system, we developed an innovative special-purpose 318 nm laser, an indium-tin-oxide-coated vacuum cell, and a field-programmable-gate-array control system.

We designed and fabricated numerous world-first diffractive optical elements for trapping, control, and readout of neutral-atom AQC, including three-atom traps, bottle-beam traps, collection lenses up to F/0.025, and grayscale lenses up to 80% efficiency.

Semiconductors:
We demonstrated near-atomic precision hydrogen lithography of silicon devices using scanning-tunneling microscopy, including a phosphorous-donor incorporation phase. With it, we fabricated Hall bars, nanowires, tunnel barriers, and a charge qubit suitable for AQC. Our fab capability is world-second after Australia's University of New South Wales.

We fabricated a charge-qubit silicon device using e-beam lithography. With it, we established single-electron occupation and executed single-qubit AQC algorithms. We developed and executed an experiment that distinguished relaxation effects from adiabatic effects, which also measured the qubit's energy-dependent relaxation rate. We fabricated a two-charge-qubit device, with which we measured the exchange-interaction coupling strength between two charge qubits.

Architecture:
We proved dynamical decoupling and energy-gap protection provide equivalent AQC quantum error suppression (QES). For AQC, we established quantum error correction (QEC) requirements and created non-equilibrium QES/QEC dynamical models. We devised new AQC QEC solutions to accommodate 1) planar hardware and 2) imperfect qubit couplings.

We identified flaws in AQC variants, such as holonomic- and ground-state quantum computing. We improved AQC path robustness using optimal control theory and proved that quadratic gap amplification is possible for frustration-free AQC. Finally, we developed new AQC algorithms for combinatorial-constrained partial differential equations and identified isothermal quantum physics as a key limiter to AQC algorithmic speedups.

Significance:
Quantum information science "has the potential to expand and strengthen the US economy and security in the 21st century just as transistors and lasers did in the 20th century" as stated in the White House Office of Science and Technology Policy, "A Federal Vision for Quantum Information Science," December 2008.

AQUARIUS directly supports US leadership in computer technologies, far beyond tomorrow's high performance computers and exascale computing. Potential applications of interest to Sandia, DOE, and other agencies include:

- Detection, image classification, and pattern matching;
- Simulation of complex systems including biological materials, proteins, and pharmaceuticals;
- Optimization of complex systems.

Refereed Communications:

W.C.T. Lee, N. Bishop, D.L. Thompson, K. Xue, G. Scappucci, J.G. Cedeberg, J.K. Gray, S.M. Han, G.K. Celler, M.S. Carroll, and M.Y. Simmons, "Thermal Processing of Strained Silicon-on-Insulator for Atomically Precise Si Device Fabrication," *Applied Surface Science*, vol. 265, pp. 833-838, January 2013.

T.-M. Lu, N. Bishop, T. Pluym, P. Kotula, M. Lilly, and M. Carroll, "Enhancement-Mode Buried Strained Silicon Channel Double Quantum Dot with Integrated Electrometer," *ECS Transactions*, vol. 50, p. 837, 2013.

X. Gao, et al., "QCAD Simulation and Optimization of Semiconductor Quantum Dots, to be published in the *Journal of Applied Physics*.

L.P. Parazzoli, A.H. Hankin, and G.W. Biedermann, "Observation of Free-Space Single-Atom Matterwave Interference," *Physical Review Letters*, vol. 109, p. 230401, 2012.

K.C. Young, M. Sarovar, and R. Blume-Kohout, "Error Suppression and Error Correction in Adiabatic Quantum Computation: Techniques and Challenges," *Physical Review X,* vol. 3, p. 041013, 2013.

V.V. Ivanov, J.A. Isaacs, M. Saffman, S.A. Kemme, A.R. Ellis, G.R. Brady, J.R. Wendt, G. Biedermann, and S. Samora, "Atom Trapping in a Bottle Beam Created by a Diffractive Optical Element," to be published in *Applied Physics Letters*.

R.D. Somma and S. Boixo, "Spectral Gap Amplification," *SIAM Journal on Computing*, vol. 42, pp. 593-610, 2013.

T. Keating, K. Goyal, Y.Y. Jau, G.W. Biedermann, A.J. Landahl, and I.H. Deutsch, "Adiabatic Quantum Computation with Rydberg-Dressed Atoms," *Physical Review A*, vol. 87, p. 052314, 2013.

Enabling Secure, Scalable Microgrids with High Penetration Renewables

152503

Year 3 of 3
Principal Investigator: S. F. Glover

Project Purpose:

The electric power grid is evolving to a state not yet defined. Bi-directional power and information flow will replace uni-directional flow as the future electric grid incorporates new distributed energy sources. Renewable and other distributed energy sources cannot be economically and reliably integrated into the existing grid because it has been optimized over decades for large centralized generation. The current grid is based on excess generation capacity (largely fossil fuel), static distribution/transmission systems, and limited closed-loop control of the power flow between sources and loads. This design leaves the grid extremely vulnerable to terrorist attacks, natural disasters, and infrastructure failures. Developing cost-effective and reliable energy systems has been a concern of both the DOE and DoD in the past, but energy surety — providing cost-effective, reliable, safe, secure, and sustainable supplies of energy — is becoming increasingly important to both agencies. This offers an exceptional opportunity to introduce and validate the transformational concepts presented for existing Sandia DoD customers and the broader national arena.

We pursued the development of a novel intelligent grid architecture — the secure scalable microgrid (SSM) — based on closed loop controls and agent-based architectures to support intelligent power flow control. An open architecture control has been chosen to increase the impact on the technical communities and industry adoption of microgrids. Unlike the scope of program funded initiatives, this bold approach will enable self-healing, self-adapting, self-organizing architectures and allow a trade-off between storage in the grid versus information flow to control generation sources, power distribution and, where necessary, loads. Incorporating agent-based distributed nonlinear control to maintain reliable energy distribution while minimizing the need for excessive storage or backup generation will be a revolutionary step towards greater renewable energy penetration. Developing dynamic nonlinear source models, scalable agent based architectures, and multi-time-variant simulations are key to this solution.

Summary of Accomplishments:

In the third year of the SSM project, a DC microgrid collective was constructed. This collective consists of three DC microgrids: two with diesel, wind, load and energy storage components and one with diesel, solar, load and energy storage components.

Informatics and Hamiltonian-based distributed control research has resulted in mathematically scalable structures and algorithms that will enable the microgrid building block concept. Even more critical to broad utilization of technologies developed in this project is the successful identification of a structure that will allow the migration of our distributed Hamiltonian-based control to AC systems.

Cyberattack scenarios and appropriate countermeasures for the most critical collective microgrid assets were identified and evaluated within an innovative simulation environment. The Army's network exploitation and evaluation testing threat (NETT) tool was used to provide verification that the agent platforms were able to maintain adequate system performance during attempts to acquire vulnerable target information and execute denial of service threats.

Significance:

Our continued focus will be on expanding our capabilities in the SSM mission space within the DoD. By developing advanced control theories and architectures to enable secure and reliable high penetration of renewable energy into the power grid, this research also has the potential to significantly impact the design of the future US power grid as well as the evolution of Smart Grid technology, both of which are major DOE's Office of Energy Efficiency and Renewable Energy missions and multi-billion dollar industries.

Refereed Communications:

J. Neely, K. Ruehl, R. Jepsen, J. Roberts, S. Glover, F. White, and M. Horry, "Electromechanical Emulation of Hydrokinetic Generators for Renewable Energy Research," in *Proceedings MTS/IEEE OCEANS' 13, 2013.*

J. Frolik, A.L. Lentine, A. Seier, and C. Palombini, "Dynamic Communications Control for µGrid Agents," in *Proceedings 3rd IEEE PES International Conference and Exhibition on Innovative Smart Grid Technologies (ISGT Europe)*, pp. 14-17, 2012.

Science-Enabled Next Generation Photovoltaics for Disruptive Advances in Solar Power and Global Energy Safety and Security

159257

Year 2 of 3
Principal Investigator: G. N. Nielson

Project Purpose:

With the development of a decentralized electricity grid, the emerging electrification of personal transportation, growing dependence on mobile devices, natural disasters that take centralized power plants off-line, and persistent concerns about atmospheric emissions from fossil fuel use, there is a drastic need for clean, convenient, and decentralized ways to generate electricity. However, there are no suitable energy harvesting technologies that have the ability to produce electricity from a variety of light sources, the scalability for multi-megawatt to gigawatt electricity generation, and the versatility to be incorporated directly into devices that need power. While solar energy can meet national and global energy consumption with orders of magnitude to spare, the collection and conversion of light to electricity remains two to three times more expensive than fossil fuel electricity generation. Until this cost barrier is broken, new energy storage and smart grid technologies will not have an enabling, mainstream role.

Our team has conceived a photovoltaic (PV) system design that consists of microsystems enabled PV cells in an independently wired configuration, a microlens concentrator array, optics that allows coarse sun tracking, and massively parallel assembly to produce low cost, packaged PV energy systems. Together, these design elements decrease the need for high cost PV materials by three orders of magnitude, increase conversion efficiency per gram of utilized PV material by a factor of 30, and reduce overall system cost by a factor of two to three. These components, combined with our new manufacturing and installation concepts, have never been put together into a complete PV system, but have a real chance of solving all key elements of this problem. It is the high cumulative risk along with the prospect of achieving the elusive cost breakthrough that has brought our team together to design, prototype, and test a complete microsystems enabled PV (MEPV) system with the capability to disrupt current fossil fuel and renewable energy generation paradigms.

Extreme Scale Computing Grand Challenge

159258

Year 2 of 3
Principal Investigator: K. S. Hemmert

Project Purpose:

Leadership in computing has been a critical factor in our nation's security for the last seven decades. This is particularly true for intelligence, nuclear weapons stewardship, the design and employment of military systems, and the scientific advances that underpin them. US leadership is now threatened by China, which supplanted us on the Top500 this year. Consequently, the US government, led by DOE, is making a significant investment in exascale technology to ensure overall superiority. This investment rests on Moore's Law, which continues unabated. Energy consumption now constrains the performance of very-large-scale integration (VLSI) circuits. Without significant innovation, an exascale computer in the 2018 timeframe will consume hundreds of megawatts (versus approximately five today). Therefore, we aim to address the problem of data movement at all layers of computing from device technology through applications.

We have two overarching goals: first, leverage Sandia's unique capabilities to demonstrate a path to low-energy data movement operations, and second, facilitate rethinking computing from embedded systems through supercomputers to address energy issues.

Data transport energy will dwarf compute energy. Fixing this requires a rethink of high performance computing (HPC), including finding the most efficient implementation devices, integrating them in a system, and developing new computational models that allow deep but manageable data movement insights. Computational science must shift from minimizing run time to minimizing the entire energy-delay product of an application. Sandia is uniquely qualified to examine disruptive approaches to creating an exascale system. It alone has the expertise in microelectronic technologies, computer architecture, systems software, and applications that will allow it to pursue the comprehensive atoms-to-applications research needed to overcome the energy challenge posed by data movement in an exascale system. Market forces are directing major computer companies towards hand-held devices and large-scale cloud servers, and away from the large-scale tightly integrated systems required for HPC.

Pattern ANalytics To Support High-Performance Exploitation and Reasoning (PANTHER)

165535

Year 1 of 3
Principal Investigator: K. R. Czuchlewski

Project Purpose:

PANTHER will advance the science of remote sensing to exploit critical patterns and relationships in high-volume, pixel-based national decision systems. These systems detect the subtlest of features, including spatially and temporally distributed cues associated with gradually unfolding events. However, by focusing on pixels, current exploitation infrastructure enables only a fraction of sensors' full potential in sensitivity, specificity, and magnitude. Furthermore, this paradigm does not scale to the increase in pixel-based data volumes anticipated in coming decades.

To maximize remote sensing capability, scientific advances are required across three key technical domains:

- Sensor Exploitation, where innovative algorithms extract and characterize relevant entities from raw data streams in real time;
- Discrete Analytics, where semantic graphs and tensors represent, index, and correlate entities, enabling complex spatiotemporal queries; and
- Human Analytics, where empirical studies of visual cognition inform technologies that support rapid, data-based situational assessment via pattern-based content query, retrieval, hypothesis formation, and testing.

The current paradigm utilizing "data fusion" technologies results in implementations that are neither scalable nor support detection of intricate threat patterns. Analysts continue to operate in sensor space, where spatiotemporal cues are buried in pixel data. The results of this research will bring analysts into information space, where concise, feature-based data representations of activities, objects, and transactions allow the detection of complex threat patterns.

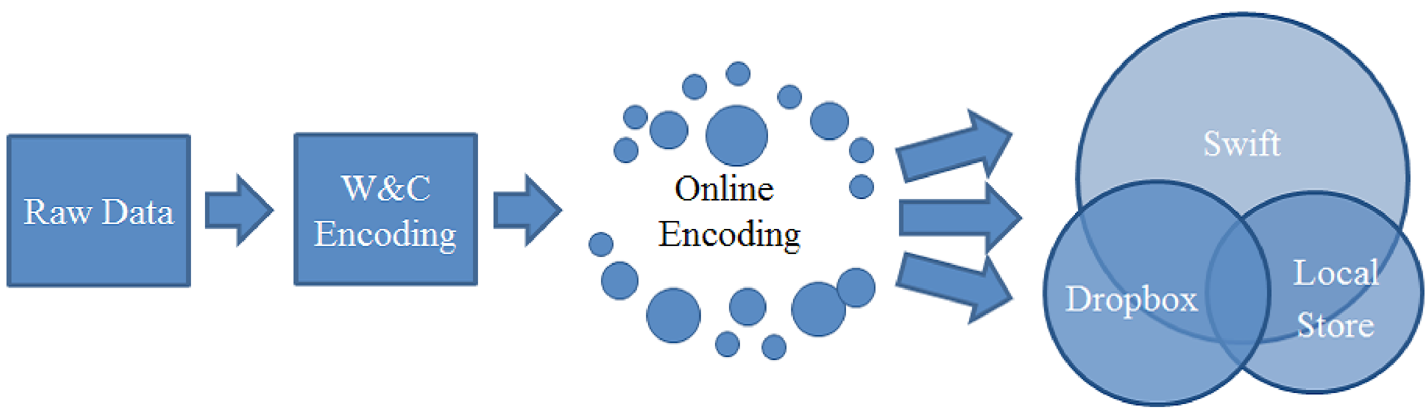
Our studies of analytic cognition will enable iterative design and evaluation of systems that demonstrably support real time, high-consequence decision making in challenging operational environments. This research will develop a fundamental, interactive, pattern-based approach that supports the identification, tracking, and ongoing assessment of spatiotemporally distributed activities. We will establish the scalable mathematical, computational, and cognitive science required to transform pixel-based data into interactive spatiotemporal information representations, measurably improving human abilities to perceive, understand, and communicate activities of national security significance in near real time.

CYBERSECURITY

The Cybersecurity Investment Area develops robust strategies and technologies designed to address and mitigate the significant vulnerabilities of our nation's cyber information infrastructure, on which critical government, military, critical infrastructure, and social functions rely.

Sandia uses its significant computing resources and works with computing experts around the nation to advance an understanding of the network and environment that affect information systems, including network traffic, intrusions, implanting of malicious code, and exfiltration of information. The work includes developing an ability to control the network environment, assuring user identities, maintaining resilience in the face of sophisticated attacks, developing an ability to recover quickly, and developing methods and strategies to counter the willingness of naïve users to comply with attacker instructions.

The work applies aspects of computer science, physical science, mathematics, and social sciences, and is exploring novel and near-term applications of quantum information technologies and quantum algorithms that support national security needs.



Data Encoding Process (Project 156435)

CYBERSECURITY

Hybrid Methods for Cybersecurity Analysis

154197

Year 3 of 3
Principal Investigator: W. L. Davis, IV

Project Purpose:

The discovery of threats in computer networks is a critical task in cybersecurity. Because of the volume and complexity of the data, most deployed methods rely on signature detection and simple statistics and are guided more by time and hardware constraints than by the needs of the problem. This gives an adversary many degrees of freedom within which to hide.

We propose research that will broaden analysts' views and deepen their capabilities with respect to the always-on torrent of data. We will bridge real-time tools and compute-intensive high performance computing (HPC) algorithms by allowing the "human in the loop" to transfer insight freely between on- and offline capabilities, thus continually refining their ability to automatically analyze incoming data.

We focus on the following goals:

- Malicious email detection: Moving beyond simple signature detection to accurately identify mutations or variations of malicious email attacks.
- Malicious behavior detection: Aggregating information to detect multi-stage attacks, analyzing systems for potential vulnerabilities, and detecting rare events.
- Malicious activity attribution: Determining the source of malicious code or behavior through analysis of network topology and traffic in the presence of internet protocol (IP) spoofing, compromised machines and mutating malware.

The challenge of placing the analyst at the center of advanced capability consists of casting each algorithmic component as part of a coherent, accessible whole. Our work will fuse real-time techniques (rule-based intrusion detection and frequent item-set analysis) with large-scale offline methods (graph algorithms, text analysis and statistical modeling). At a high level, this requires model and data fusion as we enlist diverse algorithms in support of cybersecurity. We find a corresponding engineering challenge as we federate diverse software into a coherent system. Our innovation lies in integrating these parts into a whole that can affect and be quickly affected by expert users and decision makers. Our success will give cyber defenders much of the same agility enjoyed by their adversaries.

Summary of Accomplishments:

We created data ingestion interfaces with open source and proprietary packet capture utilities, as well as data of altogether different content and format. We created data export mechanisms to utilities such as Splunk, as well as Sandia proprietary interfaces.

We designed and implemented a software framework, the Hybrid Framework, for processing, modeling, and analyzing large-scale data sets associated with cybersecurity tasks. We integrated analytical modules from toolkits such as Titan, as well as creating new analytical capabilities within the Hybrid Framework, itself. The framework was advanced to the point where customers and other researchers outside the project team were able to create new functionality using our tools. We applied the framework to a multitude of domains, such as the detection of phishing attacks, analysis of web traffic, and the detection of sensitive data exfiltration.

We created a database extraction layer that allows users to not have to worry about a majority of extract/transform/load (ETL) issues associated with a majority of database servers.

We integrated default multi-threading capability, allowing users with no knowledge of parallel computation to take advantage of multi-core processing.

Significance:

The project aligns with the goals outlined in Sandia's Cybersecurity Strategy report — namely, quick detection and attribution of attacks, ensuring cyber infrastructure integrity, and utilization of scalable threat analytics.

The modular nature of this framework enables researchers to explore new approaches to detecting malicious events by swapping in new technologies as they are developed. Such extensibility is critical in developing effective solutions for the ever-evolving nature of network attacks.

Our framework drastically reduces the time needed to take research algorithms to production. We presented our framework to professional peer groups at two international conferences on large-scale data analysis and visualization.

With this new framework in place, advanced analytics developed throughout Sandia can be deployed to analysts' desktops and incorporated into their workflows seamlessly, facilitating future collaboration between key organizations.

Leveraging Complexity for Unpredictable yet Robust Cyber Systems

154199

Year 3 of 3
Principal Investigator: J. Mayo

Project Purpose:

Attempts to secure computer systems have consumed decades of effort, resulting in little net progress and a continuing flood of successful attacks. This frustrating outcome strongly suggests that finding a solution requires rethinking the problem and addressing the basic reason that defenders currently cannot assure security. This reason is the inherent complexity of computer systems, made precise by theorems that no general algorithms exist for answering questions about the behavior of an arbitrary program. Although engineers try to implement intended behaviors and no others, the theorems imply that unintended behaviors, including vulnerabilities, are generically present and there is no practical procedure for detecting all of them. On the other hand, to compromise a system, attackers need only find a single vulnerability or introduce one in the supply chain — tasks that are quite feasible. Thus, complexity currently gives attackers an asymmetric advantage by affording them a rich environment to exploit vulnerabilities while making protection an effectively unsolvable task.

We propose to investigate methods for leveraging complexity against attackers so that their task becomes effectively unsolvable, reversing today's asymmetry. We will develop designs, based on diversity and redundancy, for systems that perform their intended function reliably but present a "moving target" to frustrate attackers. Enabling research will focus on automated code transformation, genetic programming, and ways of supporting diversity in compilers, runtime environments, and microelectronics. Our approach aims at generating unpredictability sufficient to thwart entire classes of attacks that rely on implementation incidentals. The strategy applies equally to hardware, software, and the boundaries between them; it will enable fortifying against vulnerabilities heretofore unknown or even introduced subversively. If successful, our work has the potential to alter the balance of power in cybersecurity and restore control to system owners.

Summary of Accomplishments:

We developed a prototype approach for creating diverse implementations, by using genetic programming to "grow" simple circuits represented as Boolean networks. This approach applied recombination and selection of Boolean networks to find many circuits that perform well (but not always perfectly) in meeting a specification, similar to more complex hardware and software. Value from this genetic programming work accrued not only to the diverse redundant voting system approach that we focused on, but also beyond it. For voting systems, we found that diversity can provide a dramatic improvement in fault rates, especially when multiple populations are used in the genetic programming. Evaluation via fuzzing for a 24-bit "string recognizer" circuit showed that a 5-fold voter has 85% fault reduction and 15-fold voter has >99% reduction. Evaluation via formal verification for an 8-bit string recognizer showed that a 15-fold voter is almost always perfect (fault-free), whereas the individual circuits almost never are. Broader application of these insights included our published work developing a general complexity scheme to generate good test inputs for fuzzing. In addition, we used formal analysis of many systematically created, flawed circuits to explore and demonstrate the benefits of using formal methods in addition to testing for high-consequence systems. The project then sought to enable pragmatic applications of diversity. We demonstrated a fault-tolerance boost for hardware with a technique to create a voting system with better cost-resilience tradeoffs than triple modular redundancy. We also demonstrated code transformations on real software, by developing an extended C compiler that randomizes function signatures, and successfully executing a partially diversified PDF reader library.

Significance:

Insight and examples from this project have informed broader digital design approaches, including formal methods and resilience analyses, and their use for Sandia missions. By pursuing a broader scope, we have provided new options for hardware reliability. Also, experience from this project is providing guidance to future cybersecurity research strategy and efforts regarding the role of complexity in digital systems.

Reliable PUFs for Supply Chain Assurance

154693

Year 3 of 3
Principal Investigator: T. Bauer

Project Purpose:

Supply chain security to prevent, detect, or deter subversion by substitution of both networked and stand-alone integrated circuits (ICs) is critical to cybersecurity. Previous Sandia work has leveraged physically unclonable functions (PUFs) as an enabling technology for authentication of ICs throughout the supply chain, which enhances the trust of high-consequence and high-exposure cyber systems by reducing the risk of subversion by substitution. Demonstrating PUF concepts with simple circuits in field programmable gates (FPGAs) or application-specific integrated circuits (ASICs) is easy. It is difficult to assure that these circuits exhibit sufficiently high inter-device variation and sufficiently low intra-device variation over a range of environmental conditions. This project is to develop methods of consistently achieving PUFs with required variation characteristics in FPGAs and ASICs.

PUFS are emerging as a technology that can improve supply chain assurance, but no reliable methodology for achieving the required variation exists. Previous Sandia work has developed methods for using PUFs to generate unique ID numbers for ICs, generate Public/Private keys while eliminating nonvolatile key storage and playback attacks through the use of signed lists, authenticate ICs to detect subversion by substitution, electronically bind ICs together to detect substitution, and combine with other unique factors to achieve multi-factor authentication. Now, to widely apply these techniques, we need reliable PUFs that are easily instantiated in FPGAs and ASICs.

In addition to developing methods for improving variation characteristics, we will investigate "PUF Perturbation Devices" such as antifuses to "tweak" PUF output during an "enrollment" operation in the supply chain. By establishing PUF-based chip IDs and tweaking the ID when collisions are detected, entropy is added and combined with PUF-based interdevice variation via a hash function. Other applications include key generation. We will explore "watchdog" circuits to activate the PUF Perturbation Device or alarm to indicate insufficient entropy without revealing the PUF measurement.

Summary of Accomplishments:

We conducted the evaluation of PUFs circuits on FPGAs and ASICs.

For FPGAs, we designed, programmed, and tested an area-optimized ring oscillator PUF.

For ASICs, we designed, fabricated, packaged, and tested PUFs in three distinct ASICs.

On the first ASIC, we explored four variations of arbiter delay-based PUFs in a 0.35 μm complementary metal oxide semiconductor (CMOS) technology.

On the second ASIC, we explored the following PUF circuits: ring oscillator, capacitor, voltage divider, integrating oscillator, cross-coupled latch (two instances to explore intra-chip variation), threshold voltage (two instances at one gate length, to explore intra-chip variation, and one instance at another gate length), and an arbiter. With this design, we also included a true random number generator, a fuzzy extractor to correct errors on our PUFs, and a watchdog circuit to monitor the output of the PUFs. State machines control the PUF circuits. We fabricated this design in a 0.35 μm CMOS technology.

On the third ASIC, we explored the following PUF circuits: capacitor, voltage divider, cross-coupled latch, threshold voltage (two instances at different gate lengths), and an arbiter. We fabricated this design in a 0.13 μm CMOS technology.

For FPGAs, our area-optimized ring oscillator implementation shows inter-device variation that is close to 50% across 12 devices, and intra-device variation on the order of 1%. These statistics are consistent with the state of the art.

For ASICs, our threshold voltage and voltage divider circuits show inter-device variation that is close to 50% across scores of chips, and intra-device variation less than 5%. Again, these statistics are consistent with the state of the art.

We explored the radiation response of a subset of our ASIC PUFs, which to our knowledge is the first study of its kind.

Significance:

Our work has advanced the state of the art for authenticating ICs to protect against subversion by substitution. Over the duration of this project, we have established a strong intellectual property (IP) position by filing three invention disclosures. We have licensed that IP to an industry giant who has included our designs on their own exploratory ICs. We are preparing to engage another industry giant. Publications are in preparation. Our PUFs technology was selected for the DHS Transition-to-Practice Program.

Uncertainty Quantification and Substantiation for Machine Learning in the Context of Cybersecurity

154815

Year 3 of 3
Principal Investigator: M. A. Munson

Project Purpose:

Cybersecurity is critically important in safeguarding the networks that support our national interests. Malware and targeted cyber intrusions constantly threaten to disable major systems, exfiltrate sensitive information, etc. Not only must Sandia protect its own networks, we are playing an increasing role in cybersecurity as it relates to DOE's core nuclear weapons mission and the critical national security missions of other government agencies.

Detecting malware and other cyber threats is difficult due to the massive volume of data. Machine learning has the potential to detect these threats, but it is not widely used because it provides detections without explanations. The goal of this project is to make machine learning more usable to analysts by quantifying the uncertainty associated with events of interest and identifying cases where machine learning is unreliable. This research will lay the groundwork for tools that reduce information overload by allowing analysts to: 1) prioritize data by both threat level and confidence interval and 2) focus on events that require human analysis (vs. automated analysis).

To maintain our strong reputation in cybersecurity, we need to continue to advance the state of the art. Little research has been invested on quantifying the uncertainty in machine learning results and checking the reliability of blackbox outputs because average-case accuracy and reliability is sufficient for most industrial and academic applications. Stronger guarantees are required for cybersecurity and other domains of interest. Our approach is to develop two diagnostic capabilities: confidence intervals and extrapolation detection.

Summary of Accomplishments:

A key assumption in supervised machine learning is that future data will be similar to labeled historical data. Real-world applications often violate this assumption to a greater or lesser extent. In these cases, the learned prediction model is not qualified to make a prediction — any prediction is an extrapolation beyond its experience. It is important to detect when a model's prediction is an extrapolation so that domain experts can intervene and provide a qualified analysis.

We, therefore, investigated the problem of quantifying extrapolation risk. Prediction models can be built automatically with no pre-processing and without specifying variable distributions; we sought a similarly automatic method for assessing extrapolation risk.

We analyzed and tested four approaches to estimating extrapolation risk for mixed data. The first two approaches, Margin Risk and Forest Dispersion Risk, are based on information in an ensemble of decision trees trained for classification, so we call them built-in risk detectors. The second two approaches, CERT and Chaos Forests, construct an external, auxiliary model to explicitly model risk.

Using synthetic and real data sets, we compare how well the four methods estimate extrapolation risk. Our main findings and contributions are:

- Extending forest proximity for extrapolation risk detection
- Showing that pruning is not needed for chaos emergency response teams (CERT) forests, but it is for chaos forests
- Thoroughly testing forest-based outliers and CERT, resulting in a better understanding of how the algorithms behave.
- Demonstrating that neither built-in nor auxiliary approaches are a complete solution. Both strategies should be used to safeguard against extrapolation.

Significance:

Machine learning models are central to many national security missions, such as cybersecurity, counterproliferation analysis, and assessment of supply chain risk. National security applications, by their nature, generally involve high consequence decisions; thus, it is important to detect when a model's prediction is not solid — is an extrapolation — so that domain experts can intervene and provide a qualified analysis. The current project has generated practical advice and deepened our theoretical understanding concerning the detection of extrapolations and the assessment of the risk therein.

Peering Through the Haze: Privacy and Monitoring in the Cloud Computing Paradigm

156435

Year 3 of 3
Principal Investigator: D. J. Zage

Project Purpose:

Cloud computing is becoming the infrastructure of choice for hosting data and software solutions for many organizations, necessitating the need for research to understand the vulnerabilities of this paradigm. While some security risks, such as the vulnerability of data during transport, are obvious, the infrastructure introduces new non-obvious threats, particularly those due to the lack of control of the physical hardware. These threats pose significant risks to the integrity of data and user privacy during both data storage and data usage. For example, an untrustworthy cloud service provider has access to all of an organization's data stored on the cloud, and it can monitor device usage to further learn about a user. Although some of these risks can be mitigated by leveraging solutions from current research (e.g., cryptographic techniques), creating solutions that maintain the performance and utility of cloud computing while preserving privacy and data integrity remains a challenge. Mitigating these risks is essential for organizations working with sensitive data — failure to do so can result in the compromise of information. This can lead to fiscal loss, embarrassment, and in the case of critical data, even the loss of life.

With the increasing push in governmental sectors towards cloud computing solutions, continued research is needed in creating solutions that maintain data and user integrity even when considering malicious actors. This project has developed a methodology to enable cloud users to store and access sensitive data while maintaining security and privacy in terms of the data stored at the provider and in relation to a user's service usage. Our approach exploits mathematically based protocols and advances communication paradigms to create secure solutions. Additionally, the research brings us closer to understanding the cloud-computing paradigm in general and further Sandia's leadership in understanding technology critical to the nation.

Summary of Accomplishments:

We created a linear subspace-based encoding solution that combines stored data confidentiality and service level agreement (SLA) verification in one cohesive protocol. The storage solution incorporates the use of wheat (legitimate data) and chaff (bogus data used for verification purposes) through projections into various algebraic subspaces to provide desired security properties. Additionally, we created a novel technique for encoding large amounts of data while minimizing storage and processing overhead termed matrix block chaining (MBC). The work has been extended to allow for encodings both over real value numbers as well as finite fields, each of which provides interesting tradeoffs between security and system operation. The security proofs have been extended to be complete proofs of security and include both mathematical variants. To make distribution to multiple clouds easier, a dynamic distribution system was developed utilizing online codes, which allow for easy partition and data resiliency as the codes can tolerate partial data loss. Effectiveness has been demonstrated in a prototype implementation that stores information over Dropbox, an internal deployment of the OpenStack Object Storage Swift, and a local hard drive. This can easily be extended to additional cloud-storage services.

Significance:

Our work has advanced the state of the art and understanding in cloud storage, including the creation of provably secure storage protocols. Additionally, our publications and presentations play an important role in raising awareness of security and deployment issues surrounding cloud computing and its impact on national security. Due to this project, there is continued interest from internal and external customers in terms of protocol usage and collaboration.

Refereed Communications:

D. Zage, D. Franklin, and V. Urias, “What Does the Future Hold for Cloud Computing?” *CrossTalk: The Journal of Defense Software Engineering*, pp. 4-8, September/October, 2013.

Secure and Efficient Privacy Preserving Program Obfuscation

156436

Year 3 of 3
Principal Investigator: J. H. Solis

Project Purpose:

OBSCURE (Oracle Based Software Concealment for Untrusted Runtime Environments) is a provably secure code obfuscation technology developed at Sandia that operates under a new model called "obfuscation with respect to oracle machines". Given a program based on the x86 or ARM instruction sets, OBSCURE outputs: 1) encrypted obfuscated code functionally equivalent to the original and 2) an oracle capable of executing the obfuscated code.

The encrypted obfuscated code can be distributed to any number of (untrusted) users or devices and is executed through a two-party protocol with the oracle. Oracles may exist as stand alone devices (e.g., Gumstix board, or as an online trusted server). No information can be leaked because the encrypted obfuscated code is indistinguishable from random without knowledge of the decryption key. This holds even if a malicious adversary has compromised the user device.

This core capability, the ability to securely execute code in untrusted environments, impacts the ability of the federal government to utilize secret or sensitive information in internal operating environments that are potentially compromised — a problem with which every government agency is concerned. As an example, this technology can be used to build tools that search user machines for classified material without revealing the algorithm performing the classification or its results.

We propose to continue investigating methods that improve overhead and extend general applicability while still preserving cryptographic security and integrity. For example, private information retrieval and oblivious transfer schemes could retrieve program instructions without revealing any information about the instructions being fetched.

Summary of Accomplishments:

We developed a modular framework for constructing a secure and efficient program obfuscation scheme. Our approach retains an interactive online protocol with an oracle, but relaxes the original computational and storage restrictions. Furthermore, we relax the information-theoretic security requirement to give us the flexibility to explore advanced cryptographic primitives. In particular, our framework combines the security and integrity properties of authenticated encryption with the query privacy of private-information retrieval. We present implementation results and show that non-trivial sized programs can be realized in practice. These results were incorporated as new capabilities into the existing CodeSeal effort for broader applicability. In particular, our scheme is compatible with x86 and ARM instruction sets.

Significance:

Our technology was one of eight cybersecurity technologies selected by the DHS S&T Transition-to-Practice program from across all DOE labs. This resulted in an invitation by the DOE Chief Technology Officer to present security solutions to DOE Program Directors and Managers in Washington, DC. We are also in the planning stages of a real-world pilot with a major California energy provider to demonstrate the feasibility in securing critical energy infrastructures.

Instrumenting Nation-Scale Networks with Hierarchical, Peer-to-Peer Communications

158479

Year 2 of 2
Principal Investigator: T. M. Kroeger

Project Purpose:

The purpose of this project is to understand and create methods for large-scale distributed resource management. We have been working with researchers at University of California (UC) Santa Cruz and Santa Clara University to explore graph-based models for data distribution and resilience. This work provides a technique for mapping data distribution to a graph-coloring problem. Initial work has focused on using this to provide reliable peta-scale storage system, but these same techniques can be used to provide data resilience as we instrument and collect monitoring data.

Beyond large-scale storage systems, we also focus on using secret splitting to enable secure long-term archives. Our intent here is to create and understand design parameters for a system that enables secure operation in spite of partial system compromise. Additionally, our model offers a unique resilience to insider threat.

Summary of Accomplishments:

This work initially focused on large-scale distributed resource management via graph coloring. Collaborating with researchers at UC Santa Cruz, we produced a method to abstract distributed resource management to a graph-coloring model. We use this technique with fault tolerant encodings to create a resilient storage cluster we call RESAR (Robust, Efficient, Scalable, Autonomous Reliable). Through emulations, we show that this system scales to more than one million disks and recovers from a disk failure in less than four minutes, while current systems take hours.

From here, we examined secure long-term data archival in a project we called Percival. Percival focuses on the use of secret sharing as the basis for a distributed data archive that is resilient to insider threats and able to operate securely in spite of compromised members of the system. Additionally, this system provides an information-theoretic level of data protect that is resilient to crypto-analytic. We provide a detailed system design and a proof of concept implementation. From those foundations, we have explored operational capabilities of such an environment and methods to enable secure blinded search within such an archive.

Significance:

Our Percival project enabled a secure long-term data archive that is both resilient to insider threats and able to operate securely in spite of partial system compromise. These are key attributes needed for a broad range of national security missions. Beyond secure archival, this work also explored and developed secure blinded search across such archives. This capability provides a foundation for secure information sharing.

RESAR provided a unique ability for reliable exascale storage with dramatically less overhead than current systems. This has key impacts around both power consumption and cost for exascale system design.

Refereed Communications:

M. Sabolish, A. Amer, and T.M. Kroeger, “A Distributed Approach to Taming Peak Demand,” in *Proceedings of the 2012 International Green Computing Conference (IGCC), IGCC ’12*, pp. 1-6, 2012.

Y. Li, N.S. Dhotre, Y. Ohara, T.M. Kroeger, E.L. Miller, and D.D.E. Long, "Horus: Fine-Grained Encryption-Based Security for Large-Scale Storage," in *Proceedings of the 11th USENIX Conference on File and Storage Technologies (FAST)*, 2013.

T.M. Kroeger, J.C. Frank, and E.L. Miller, "The Case for Distributed Data Archival Using Secret Splitting with Percival," in *Proceedings of the 1st International Symposium on Resilient Cyber Systems*, 2013.

S. Peisert, E. Talbot, and T.M. Kroeger, "Principles of Authentication," to be published in the *Proceedings of the 2013 New Security Paradigms Workshop (NSPW)*, 2013.

Memristor Evaluation and Optimization for Cybersecurity

158740

Year 2 of 3
Principal Investigator: M. Marinella

Project Purpose:

Dynamic random access memory (DRAM) and Flash memory technologies are nearing physical scaling limits and are starting to require significant switching energy compared to other components of modern computing systems. Excitement surrounding memristor (or resistive random-access memory [ReRAM]) technology led Sandia to begin investigating possible government applications of this device, which led to the following conclusions: 1) government customers are interested in using this device for security related applications and 2) we found that these applications require devices to have several electrical and physical characteristics that are not of interest to companies involved in memristor technology development, and thus have not been thoroughly studied. Sandia has the necessary expertise, infrastructure, and partners to evaluate and optimize this technology and potentially gain a very large string of security-related business. In this research, Sandia will continue to develop a state of the art memristor process, design a memristor controller application-specific integrated circuits (ASIC), and develop a robust set of characterization methods to evaluate these properties.

Sandia is uniquely positioned to carry out this research. We have the necessary facilities and background expertise to fabricate and characterize memristors and the necessary infrastructure to perform sensitive work related to national security.

A Thin Hypervisor for Dynamic Analysis and Reverse Engineering of ARM Based Embedded Systems

158742

Year 2 of 3
Principal Investigator: B. K. Eames

Project Purpose:

The center of personal computing is gradually shifting toward commercial mobile devices like smart phones and tablets that act as a window to large scale networked services. Separately, networked embedded control devices are often deployed to sense and manage distributed critical infrastructure. Together, these mobile and embedded devices have tremendous security relevance as they are increasingly used for personal, commercial, and government business. Mobile systems and networked embedded systems have a key similarity. An overwhelming majority of mobile devices and a significant fraction of power-sensitive embedded systems that require high performance are based on the ARM CPU architecture. To understand and counter the threats posed to such devices, one must be able to observe and influence their runtime behavior. The task is not straightforward due to obscurity, limited standards, and intentional removal of debugging and analysis features by manufacturers. This project seeks to build a virtualization-based dynamic analysis platform for ARM-based mobile devices to facilitate security assessment and to serve as the basis for host-based monitoring and intrusion prevention research on mobile and embedded devices. A robust ARM-based dynamic security and analysis platform directly supports Sandia's role in driving innovation in cybersecurity, particularly considering the emerging ubiquity of mobile computing.

Encryption Using Electrochemical Keys (EEK)

158743

Year 2 of 3
Principal Investigator: D. R. Wheeler

Project Purpose:

We will develop an electrochemical-based memory for storing small amounts of valuable data such as encryption keys. Our data storage will rely on changes in chemical interaction with surfaces, rather than bulk stored charge. Electrochemical data will be stored as a liquid phase above a number of differently treated (monolayer) conductors, and the interplay between chemistry and surface will give rise to a chemical potential change. Since this is a surface-only effect, very little charge is stored (femtocouloumbs/mm2). This non-traditional method for key storage will make readout of the data only possible by specific electrochemical interrogation methods, thus increasing the security of any encrypted data.

Cross-Domain Situational Awareness in Computing Networks

158783

Year 2 of 3
Principal Investigator: S. A. Mulder

Project Purpose:

The purpose of this project is to understand the potential for semantic labeling of individual programs executing in system memory, characterize the behavior of specific machines over time based on this labeling, and develop a framework to provide this information to an analyst in a clear format. Semantic understanding of programs and system characteristics of machines operating on our networks is a huge gap in the situational awareness picture. If we are to have any hope of advancing the state of awareness, this gap must be addressed. This project builds on expertise and tools developed over years in the center, university collaboration and machine learning expertise, and ongoing engagement with real systems to develop new frameworks for representing the functionality contained in executable content, model system behavior over time with respect to this functionality, and help an analyst gain an accurate representation of what is going on in computing resources. Allowing cybersecurity at high security sites to monitor and maintain awareness about the computer programs operating in their environment creates a potential to identify and respond to significant changes and threats on their network.

Modeling and Development of Nondestructive Forensic Techniques for Manufacturer Attribution

159303

Year 2 of 2
Principal Investigator: R. Helinski

Project Purpose:

Counterfeit integrated circuits (ICs) are a recognized hazard of utilizing commercial off-the-shelf (COTS) components. The purpose of this project is to develop and demonstrate integrated electronic circuits for counterfeit IC detection. Counterfeit ICs have been sourced from decommissioned systems (recycling), are genuine but unauthorized copies of the IC (over-production), or have been built from the ground up to imitate the genuine IC (cloning). Our focus was on cloning, where an IC may operate the same as a genuine IC, but is built in a different fabrication facility (fab) and may have a different design.

Integrated electronic circuits that measure their own process variations could be used as a screening tool to indicate that a part is anomalous based on its characteristics. These types of circuits (known as process monitors) are well known, however, they have not been used in this way or in a product in general. They are usually scribe-line structures designed by the fab so that they can verify their manufacturing process. They are tested throughout the manufacturing process and are cut out during wafer dicing. These types of circuits could be used as a screen to verify, with some level of confidence, that a part originated from the expected manufacturer based on previously made measurements of that manufacturer. Furthermore, they should be able to determine if two ICs are from the same lot. These tools are suited to serve as a screen because they are nondestructive, fast, and accurate.

Summary of Accomplishments:

In order to understand the feasibility and to prove the concept, we developed an IC design with prototype circuits on it. We considered many different types of circuits in this process. This IC was manufactured by two separate facilities, and also twice at one facility in order to understand the fab-to-fab and lot-to-lot variations. We utilized machine-learning techniques in order to estimate the accuracy with which we can distinguish fabs and lots in practice. We discovered that these circuits allowed us to distinguish these two fabs with up to 97% accuracy and also distinguish the lots from the second fab with up to 98% accuracy. These two indicators would give system integrators good reason to trust parts that appear to be manufactured as expected and allow them to exclude parts that appear to be outliers. Our treatment of these ICs also included preliminary environmental and aging characterization. This serves as an excellent demonstration of the feasibility of this approach.

Significance:

The goals of this project — to design, build, and measure an IC for counterfeit IC detection — are unique by comparison to other work being done in this area. Our results have a significant impact for national security missions by providing new tools for enhancing supply chain integrity. These tools will add to the comprehensive coverage of the possible solutions to the supply chain integrity problem, and enable confidence to be enhanced in systems that use COTS parts as well as those that design their parts and have them fabricated externally.

An Empirical Assessment of the Factors Underlying Phishing

164764

Year 2 of 3
Principal Investigator: M. C. Kimura

Project Purpose:

Recent phishing attacks on various institutions have underscored the need for research on the human dimension of cybersecurity. Phishing generally refers to the use of electronic communication (typically email) by an adversary to pose as a trusted source for which a person is willing to provide information or perform actions.

Currently, there is no effective solution for countering phishing. The vast majority of work in cybersecurity today focuses either on engineered solutions, which are appropriate for mitigating technical vulnerabilities, or on managerial policy, which provides support for mitigation but not effective techniques. Previous published research attempting to address phishing mitigations has largely relied upon user-reported data and responses from artificial role-playing scenarios; however, studies have found that subjects of realistic phishing exercises have expressed strong anger and denial upon discovering they have been phished, which indicates that user-reported data is likely to be unreliable. In addition, the studies did not account for the likelihood that users will behave differently in an artificial situation such as a lab-based experiment.

We postulate that focusing on core causes is more likely to aid in the development of mitigations that are both effective and robust to adversary adaptations. Therefore, the goal of this project is to build a science-based cognitive model that enables a comprehensive understanding of both the underlying factors that cause a victim to fall for a phishing attack and the mitigations that address them.

Flexible and Scalable Data Fusion using Proactive, Schemaless Information Services

164869

Year 2 of 3
Principal Investigator: P. Widener

Project Purpose:

Exascale data environments are fast approaching, driven by diverse sources such as system and application telemetry streams, open-source information capture, and on-demand simulation output. Storage costs having plummeted, the question is now one of converting vast stores of data to actionable information. The prevailing data management environment in most government agencies is still one of high manual effort, low degrees of awareness across domain boundaries about what related data may exist, and write-once-read-never (data generation/collection rates outpacing data analysis and integration rates). Increasingly, technologists and researchers need to correlate previously unrelated data sources and artifacts to produce fused data objects serving domain-specific purposes. New tools and approaches for creating actionable knowledge from vast amounts of data are vitally important to maintaining research and operational momentum.

We propose to research and develop tools and services to assist in the fusion and analysis of different types of data, allowing users to flexibly create scalable, tailored information streams and objects. A central design principle is specifically not to follow the "build a big fused database of everything" approach by providing a general index over all data. Instead, we wish to make possible a distributed "forest" of loosely connected user-defined index structures (flexible multi-indexing) and provide a mechanism (data proactivity) by which those structures can advertise not only changes in data state (new data collected), but also changes in the state of the information service (new data type exists). In so doing, we hope to encourage discovery and reuse of already-computed indexes and metadata. We envision a decentralized, component-like toolset that allows fine-grained control and is easily customized and/or extended for integration into applications. This research has the potential both to dramatically accelerate individual and cooperative data analysis and management tasks, and to assist in Sandia's transition to a data environment that will scale with the critical data demands of 21st century national security research.

Robust Decision Making Despite Compromised Data

165536

Year 1 of 1
Principal Investigator: T. G. Kolda

Project Purpose:

We intend to enable robust decision making, even when sensor data may be corrupted by adversaries. Distributed sensors are essential to monitoring critical systems such as the nation's cyber infrastructure, power grid, ports of entry, security of facilities, etc. Given their importance, ubiquity, and the ease of remote access, such sensors are obvious targets of cyber attacks. Assuming the security of our sensors is imperfect, our challenge is to design more robust monitoring systems without greatly increasing complexity or cost. The end result will be a set of "best practices" for designing and deploying sensor systems.

There has been a great deal of research on reconstructing signals contaminated by noise, assuming that the noise is somehow "natural" in the sense that it is only a small perturbation to the original data and is well-described by a Gaussian. In the case of adversarial noise (i.e., the Byzantine General problem), research has focused on the probability of exactly decoding a signal for various data exchange scenarios. We are interested in robustly reconstructing signals (mostly continuous) contaminated by adversarial noise. We aim to recover whatever is needed for correct decision making; we do not hope for perfect reconstruction. Accordingly, we will appeal to the techniques of signal processing, but extend them to handle non-Gaussian and possibly unbounded noise.

Our approach is premised on judicious redundancy. Recent developments in compressed sensing have revealed that most data can be compressed orders of magnitude beyond what standard Nyquist-Shannon coding theory bounds suggest. This compression exploits inherent structure in the data and can be incorporated directly into the physical sensor. We suggest that extra compressed sensing measurements yield sufficient redundancy without adding much complexity or cost. Assuming that at least some of the data is uncontaminated, we propose to develop consistency metrics to detect tampering and reconstruct the signal by filtering altered measurements and identifying regions of high uncertainty.

Summary of Accomplishments:

We provided an overview of compressed sensing (CS) and considered its potential for adding robustness to sensor readings.

The main application we considered is remote imaging for site security. Compressed sensing may be useful because it offers the simultaneous benefits of compression, encryption, and robustness to lost packets in transmission. A method called "justice pursuit" can even separate out additive noise so long as the noise is sparse in some basis — this means CS is robust to more than just additive white noise. It is robust to large magnitude noise so long as it has certain specific features.

Compressed sensing may be particularly appropriate for remote video assessment where the images are communicated via microwave signal. An example of a specific application is security at a nuclear weapon complex.

We also studied the potential for the smashed filter classification method, which is able to do classification directly on the compressed signals without reconstruction. This means that we can do decision making without the extra work to rebuild the original signal.

Another potential application where CS may be useful is in monitoring power systems. How can the system be protected from tampering? The methods used currently are struggling to deal with the growth in the system (any home may generate power via solar cells) and growing threats of cyber-attack that may attempt to cause failures in the system. The state of the system can only be determined by taking remote measurements.

Significance:

Compressed sensing may be useful to national security because it offers the simultaneous benefits of compression, encryption, and robustness to lost packets in transmission. Such features are critical for collecting data from remote sensors, which are used to monitor everything from ocean currents to secure entryways.

Composing Formally Verified Modules to Analyze Security and Reliability Properties of Large-Scale High-Consequence Systems

165537

Year 1 of 3
Principal Investigator: J. Ruthruff

Project Purpose:

The complexity of modern electronics, computer systems, and digital networks in cybersecurity domains has given rise to numerous unintended logic flaws in high-consequence systems, providing significant behavioral spaces that adversaries can exploit or intentionally introduce flaws. Traditional testing and simulation techniques, while important, only scratch the surface of behavioral spaces for large-scale systems, necessitating alternative and rigorous methodologies for verifying cyber systems.

Formal methods analyze digital designs to prove specific security or reliability properties, or locate flaws compromising these properties. These techniques apply advanced logic-based algorithms to rigorously verify the absence of specified flaws in hardware and software, thus offering improved technical foundations for security and reliability assessments. However, the time and space complexity of formal methods scale poorly with increasing problem size, commonly prohibitive to the analysis of realistic systems. Practitioners, therefore, commonly verify smaller subsystems individually — the verification methodology, for example, behind Intel's Core i7 processor. Even absent formal verification, human programmers of digital systems address complexity and cost with divide-and-conquer strategies using modular or component-based designs; this includes the next generation of adaptable nuclear warheads. Similar component-based schemes for formal verification are also needed.

We propose research to develop a framework allowing smaller formal methods analyses at module or subsystem levels to be composed to the full system level. We will initially support probabilistic assessments of full system correctness, accepting the limitations of reasoning about an entire system based on piecewise verifications. We will then explore rigorously sound compositions where, given certain assumptions or discoveries in system designs, definitive statements about entire systems are possible based on individual verifications.

Though there is work on modular formal verification of object-oriented languages, there is little specifically targeting modularity to achieve scalability, even though this vision is desired by the research community. In fact, this goal was specified in the Cybersecurity R&D strategic plan issued by the Executive Office of the President.

Line Element Electron Source for High-Speed Electron Microscopy

165539

Year 1 of 1
Principal Investigator: K. W. Larson

Project Purpose:

The purpose of this work was to conduct initial research into a concept for a fast electron microscope utilizing compressive sensing as an integral part sampling strategy. The compressive sensing would be implemented in microfabricated components that impart a pattern on a 1-D line of electron beamlets, illuminating many pixels of the sample simultaneously.

Summary of Accomplishments:

We designed a linear patterning system for compressive sensing in electron microscopy and demonstrated that it is compatible with a COTS electron detector. Our design incorporates novel microfabricated components that could be built in Sandia's microFAB, and COTS electron beam lenses. This is a notable outcome that could lead to one or more invention disclosures. A high-risk aspect of this research was the difficulty of designing an objective lens for compressive patterns longer than about 10,000 pixels. We were unable to identify such a lens. The design we invented had about 10% of the performance that would have been possible if we had solved the risky element.

Significance:

This work was motivated principally to address an acknowledged national security issue via a new method of sensor design that had never been applied to our domain. The research was partially successful. Although the technical accomplishment in science and engineering is significant, the results may not be compelling toward further development of this particular design concept.

Cyber Graph Queries for Geographically Distributed Data Centers

165541

Year 1 of 2
Principal Investigator: C. A. Phillips

Project Purpose:

The project considers a new model of distributed graph algorithm motivated by cyber-related operations. In our model, two or more institutions gather graph data independently, and store that data in data centers that they own and operate. Because the institutions are observing the same set of objects, the graphs intersect at nodes. However, because the data was collected independently, no institution initially knows which nodes it shares with others. The institutions would like to cooperate to solve global problems on the graph formed from the union of all these local graphs. However, there are barriers to that computation.

We model that in two ways: a limited amount of communication (very small compared to full set of observations), or limited trust. In the latter case, the institutions do not want to reveal any more information than is necessary to solve the problem. This models fundamental privacy issues and fundamental data movement issues in modern distributed data centers. We will develop algorithms for one or more fundamental graph problems in these models.

Applying Cognitively Inspired Computing Systems to Create a Robust Cyber Protection Architecture

165542

Year 1 of 2
Principal Investigator: J. H. Naegle

Project Purpose:

Current technologies offering protection from cyber attacks have many limitations including:

1) Computational Horsepower: Use of commodity processors is a poor fit for security rule sets that are unfortunately parallel, typically byte aligned, and require large randomly accessed memory images.
2) Cost: The cost of security is increasing as a percentage of the overall cost of computing. The emerging cloud exacerbates this problem.
3) Vulnerability to Direct Attack: Coresident security software can be compromised by malicious code.
4) Management Complexity: Improper management of distributed, diverse software packages can compromise their functionality.

Typical cyber problems can be broken into two categories: threat detection and high-speed matching (or filtering). We propose to address the latter category because it is typically ill suited for von Neumann architectures and can be used to build more advanced detection mechanisms.

A new approach that provides orders of magnitude more compute capability and isolates the security function from systems would improve the dynamics of cyber protection. The cyber Work for Others programs are producing analytics that are beyond the capabilities of current compute systems. It is important to create an affordable, distributed security infrastructure to solve problems like security in cloud computing. New streaming compute architectures that promise orders of magnitude improvement in processing and memory performance in a small form factor with less power could be a major differentiating capability for Sandia. Other programs with streaming compute problems, such as space computing and remote/mobile sensors, would also greatly benefit from a breakthrough in the processing of streaming data. Sandia and Blue I Systems are collaborating on a very simple, cognitive inspired data processing unit based on a cortex model. The design utilizes massively parallel, simplistic compute elements coupled to a uniquely configured, very high bandwidth memory.

This research effort will enable a new class of streaming architectures capable of addressing the growing cyber threat and massive volumes of data (that today grow faster than processing capabilities). This work will apply to the strategic goals of DHS, DOE, as well as other government agencies.

Nested Narratives

165543

Year 1 of 2
Principal Investigator: A. T. Wilson

Project Purpose:

There is a great deal of research and development around vulnerability assessment and anomaly detection in a network. Far less focuses on effective communication of these anomalies. Almost none concerns the path from data to insight and decision support. A list of 125 widely used cybersecurity tools includes 60 for vulnerability assessment, 17 for monitoring and 10 for forensics, only 6 of which are meant specifically for cybersecurity. Moreover, all six of those focus on fine-grained detail and leave analysts to construct the bigger picture without further assistance. Only one tool provides any support for modeling scenarios instead of data.

We will bridge this gap by addressing the following research challenges:

- Attribute traffic on a testbed network to the processes and user actions that caused it
- Help analysts construct stories from that data that tell what is happening and also why
- Preserve those stories in multi-layered artifacts that can be used to tell the story at any level from strategic intent down to actual data

We will create algorithms and tools that enable flexible narratives of "how" and "what" backed by original data captured from a network. We will measure success by the richness of the scenarios we can capture as well as by quantifiable benefits to cybersecurity analysts.

Success will narrow the gap between data and understanding, between an event and situational awareness. It will allow richer communication by bringing data and story closer together and give analysts powerful new building blocks for what they do best.

The idea of narrative has received close attention recently as an accessible representation of complex information. Our innovation stems from embodying narrative in the cyber domain by combining Sandia's unique cyber capabilities: TracerFIRE for data collection, RECOIL for human studies, plus the visualization, cognitive science and analysis experts. These capabilities position Sandia uniquely to make this leap.

Active Learning for Alert Triage

165544

Year 1 of 2
Principal Investigator: J. E. Doak

Project Purpose:

In cyber operations, data from multiple sources are typically logged to a centralized database. When certain conditions in the data are met, an alert is generated in an alert management system. Analysts inspect these alerts to decide if any deserve promotion to an event requiring further scrutiny. This triage process is manual, time consuming, and detracts from in-depth investigation of events. Our goal is to develop an automated alert ranking system that is fully integrated into analysts' workflow. We will conduct this research by leveraging access to Sandia's cyber operational data, because we feel this is a superior alternative to theoretical or synthetic data.

We propose the use of active learning to selectively query the analysts for labels on alerts. Empirical and theoretical evidence indicate that active learning can outperform passive learning (i.e., randomly selecting instances for labeling) on a variety of learning tasks. In addition, our literature review indicates that the field of active learning is well established in terms of its theoretical underpinnings, but the application of active learning to real-world problems is in its infancy. Thus, the primary research challenges associated with this project will be how to map active learning theory onto our particular problem and how to address the various practical concerns that will undoubtedly arise.

Our literature search indicates that active learning has not been applied to a cybersecurity problem comparable to ours. Thus, there are many unknowns, for example, which active learning scenarios and query strategies are most appropriate for our problem? What practical, unanticipated considerations will we need to address? Despite the risks, the need is great as cyber analysts are struggling to effectively triage the ever-increasing flow of alerts. This project has the potential to greatly assist analysts by providing a ranked list of alerts so that only the most important alerts need to be inspected.

Highly Efficient Entangled Photon Source for High-Speed Secure Quantum Communication Network

166151

Year 1 of 2
Principal Investigator: D. B. Soh

Project Purpose:

The purpose of the project is to develop a new single photon source for high-speed quantum communication. An ideal quantum communication protocol provides an unconditional security against eavesdropping attempts utilizing quantum mechanical principles. Such attempts will exhibit the presence of eavesdroppers through the photon statistics and properties, which the communicating parties can immediately detect. For unconditional security, the photon source needs to be highly non-classical, ensuring only single photons per communication qubit. One can generate such single photon sources through wave mixing in optical fibers, which unfortunately suffers from unwanted photon scattering through the Raman process. Once a Raman scattered photon enters the communication, eavesdroppers may utilize their presence and seriously disturb the security of the communication. There have been security attacks reported, utilizing such defects. Thus, it is imperative to subdue such unwanted rogue photons.

This new class of single photon source can dramatically improve the speed and the security of quantum communications. We estimate the improvement will be orders of magnitude. This source also provides a broad impact on all branches of quantum information science applications, including quantum repeaters, quantum memory, optical quantum computation, and quantum teleportation.

Model Reduction for Quantum Technologies

170973

Year 1 of 3
Principal Investigator: M. Sarovar

Project Purpose:

The purpose of the project is to develop methods for reducing the complexity of simulating the dynamics of quantum mechanical systems.

Precisely controlled, engineered quantum systems will be critical to next-generation measurement, computing and communication technologies. However, as we attempt to design and construct larger and more complex quantum devices we quickly approach a difficult impasse — namely, the task of modeling and simulating such large-to-medium scale quantum mechanical devices becomes computationally challenging since the size of modeling state-space increases exponentially with the number of degrees of freedom. This difficulty severely limits our ability to perform predictive simulation of quantum technology devices.

In this project, we will take a systems-level approach to this problem and develop techniques for reducing the modeling complexity of a broad class of potential quantum devices. The primary thrust of the research will be to extend rigorous model reduction techniques from engineering and applied mathematics (e.g. proper orthogonal decomposition, unsupervised manifold learning) to the quantum realm. Properties such as structure preservation will be incorporated into these classical model reduction techniques in order to make them suitable for quantum systems. The successful formulation of such quantum model reduction methods will enable rigorous performance analysis of quantum devices, including application of methods for uncertainty quantification (UQ) and verification and validation (V&V). This, in turn, will enable more rapid development of near-term quantum technologies for tasks such as precision measurement and secure communication.

The proposed research is highly inter-disciplinary and develops methods that bridge engineering, physics, and computer science. It has the potential to have broad impact on the quantum information sciences by generating new insights into the modeling and simulation of quantum mechanical systems.

Supply Chain Lifecycle Analytics

172335

Year 1 of 1
Principal Investigator: G. K. Kao

Project Purpose:

The purpose of the project is to develop a decision analytic framework to perform trade-off analysis for understanding the end-to-end supply chain lifecycle risk. To date, there is a lack of analytics and decision support tools to analyze supply chain security holistically, and to perform tradeoff analyses to determine how to invest in or deploy possible mitigation options for supply chain security, such that the return on investment is optimal with respect to cost, efficiency, and security. Decision makers have limited control and influence on supply chain networks due to the complex and distributed nature of the problem. We will develop a framework and an initial tool suite to address this issue by examining the system lifecycle phases (requirements, design, implementation, testing, deployment, maintenance, and retirement) of supply chains that complements the typical "flow-of-goods" analysis. This R&D effort will develop decision-support technologies that enable decision makers to perform risk-based cost-benefit prioritization of security investments to manage supply chain integrity and risk. To do so, we are leveraging a new security risk metric based on the degree of difficulty an adversary will encounter to successfully execute the most advantageous attack scenario. This metric will enable decision makers to overcome the complexity of quantifying security risk, and is suited for cost-benefit optimization. Furthermore, our approach enables us to decompose the supply chain problem hierarchically. The information based hierarchical approach in modeling the supply chain allows analysts to manage the complexity of the problem more effectively. To further streamline the problem, we will develop functional grammar to help bound the problem in order to perform vulnerability assessments. By design, the hierarchical and recursive nature of our methodology can be expanded so that our techniques address the supply chain problem holistically at various depths.

Summary of Accomplishments:

We designed a new full spectrum supply chain lifecycle decision support tool that enables decision makers to perform risk-based cost-benefit analyses to optimally apply mitigation options to address vulnerabilities in supply chains. The tool consists of four components:

1) Hierarchical Supply Chain Representation
2) Sandia's Difficulty and Consequences Risk Based Assessment
3) Semi-Automatic Grammar Based Vulnerability and Mitigation Assessment
4) Optimization Based Decision Analytics

The tool is a proof-of-concept demonstration for our framework. We applied this framework to a model problem and a real-life electronic component for an initial use-case analysis.

We created a tool suite with some visualization capabilities.

Significance:

Our research builds the capabilities to help strengthen the foundation of the nation's information and communication technologies critical infrastructure supply chain. This problem addresses issues that will not only have a national impact, but will also have a global impact. The models developed will help federal agencies (e.g., DOE, DoD, DHS), to evaluate security impact in designing and developing a viable and secure global supply chain. This research will, no doubt, provide insights to the national security risk on the reliance of the global supply chain.

RESEARCH CHALLENGES

Research Challenges seek to create a differentiating capability by the active engagement of expertise from fundamental science to technology application, resulting in a long-term science and engineering legacy for Sandia. Research Challenges consist of major science and engineering pursuits that bring together an interdisciplinary cross section of Sandia's capabilities and research foundations to surmount a critical path technical obstacle important to Sandia's mission, and to advance the state of the art in science and engineering. These projects are intended to have impact on a spectrum of time scales, and require developed roadmaps that identify priorities for investment in the context of the Research Challenge goals.

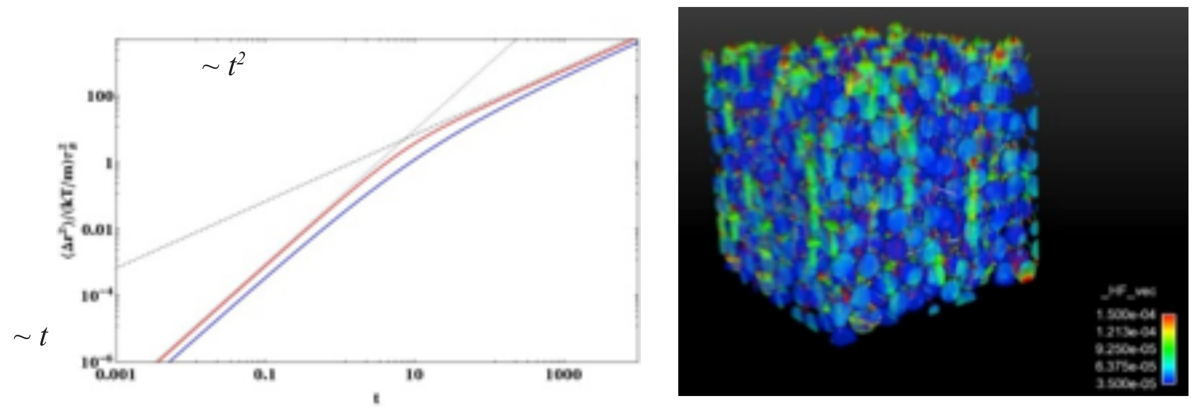


Figure 1 (left) mean-squared displacement vs. time for OU processes showing two distinct regimes of behavior relative to $\tau_B = 1$ (red line is for Markovian, blue non-Markovian). (Right) Numerical simulation of thermal conduction in mono-sized, random dispersion of conducting spheres in insulating matrix. Colors (red = "hot", blue = "cold") and vectors indication magnitude and direction of heat flux. Note inhomogeneity of heat flux field (Project 171054).

RESEARCH CHALLENGES

Revisiting the Applied Mechanics Paradigm: Multi-Scale Modeling of Transport Processes in Complex Materials

171054

Year 1 of 2
Principal Investigator: J. B. Lechman

Project Purpose:

The complex response of inhomogeneous materials to mechanical and thermodynamic loads results from multiple dynamical/stochastic processes, anti-correlated and correlated, occurring over multiple length and time scales, leading to significant variability in performance. Current challenges in predicting this behavior include: 1) identifying and characterizing physical and/or chemical processes and their couplings across multiple length and time scales, 2) modeling information transfer between scales, and 3) resolving inhomogeneities in order to quantify uncertainty. Overcoming these challenges to create engineered solutions requires multiscale materials theory/modeling and experimental discovery/characterization. Many multiscale modeling efforts employ a hierarchy of governing equations and simulation tools each specific to a particular scale; however, this approach is limited by a priori assumptions of the degree of coupling between scales and a posteriori methods of restoring this coupling. In practice, these so-called "hierarchical" approaches rely on one-way propagation of information: atoms-up. Moreover, although numerical simulation with "concurrent" coupling of, say, classical atomistic dynamics and macroscale partial differential governing equations is possible, transfer of information can be significantly hampered by scale mismatch, and becomes computationally intractable when a series of mesoscales with associated phenomena are present.

This project's goal is to discover and create modeling techniques for predicting the behavior of inhomogeneous materials. Hence, we will develop a novel scale-consistent modeling framework for formulating governing balance equations, coupling spatial and temporal correlations from micro through meso to macroscales. Scale-consistent models reduce complications associated with multiscale data transfer and coupling between simulation tools because multiple scales are embedded in the model formulation. However, this requires advancing experimental discovery and characterization tools for complex materials and processes spanning relevant scales. If successful, this project will demonstrate a methodology that provides multiple scale effects in one approach. While demonstrating the approach for thermal properties (identifying "hot spots" in pyrotechnic applications), it can be extended to fracture, additional energetic materials applications, and beyond.

Breaking Antibiotic Resistance: Use of High-Throughput, Multi-Dimensional Data Analyses and Revolutionary Advances in Engineered Nanoparticles to Design and Deliver Antisense RNA

171055

Year 1 of 2
Principal Investigator: E. C. Carnes

Project Purpose:

Antibiotic resistance has become a major public health and national security concern and is now considered by the National Institute of Allergy and Infectious Disease (NIAID), the DHS, and the Center for Disease Control (CDC) to be a Category C priority. There is, therefore, an urgent need for strategies that reverse resistance and restore the efficacy of widely available, clinically proven antibiotics. Attempts to use antisense strategies for this purpose have failed, however, due to poor RNA design and inherent limitations of many state of the art RNA delivery vehicles. To this end, we plan to use high-throughput bioinformatic approaches to identify genes that contribute to antibiotic resistance and design antisense RNAs that interfere with drug resistance mechanisms. In parallel, we will engineer mesoporous silica nanoparticle-supported lipid bilayers (protocells) for high capacity delivery of antisense RNA and antibiotics to drug-resistant bacteria. Our effort will result in generic bioinformatic approaches that can be used to rapidly characterize emerging threats and design highly effective RNAs with minimal off-target effects. Furthermore, due to the protocell's enormous cargo capacity, high degree of stability, and exquisite targeting specificity, our R&D promises to result in a universal delivery vehicle that is capable of both verifying predictive genomic analyses and effectively treating infections caused by the so-called superbugs, such as multidrug-resistant *Klebsiella pneumonia* and methicillin-resistant *Staphylococcus aureus* (MRSA), and by bacterial threats with engineered antibiotic resistance.

Our planned effort combines two high-risk, high-impact research avenues to address a problem with serious biosafety, biosecurity, biodefense, and public health implications: 1) high-throughput development of predictive models using multidimensional data sets and 2) use of engineered nanoparticles to translate predictive model output into actionable knowledge. Our approach should prove effective against the highly antibiotic-resistant superbugs and will provide the ability to identify links between genomics and function for various microorganisms of interest to Sandia's biodefense and bioenergy research thrusts.

Flexible, Adaptable, Full-Spectrum Imaging via Nanoantenna Enabled Two-Dimensional Detectors

171056

Year 1 of 2
Principal Investigator: D. W. Peters

Project Purpose:

End users always demand improved infrared detector performance. Likewise, energy conversion efficiency always needs to be increased. In this effort, we design and fabricate low-loss nanoantennas on a proven infrared detector, integrate nanoantennas with a thermal energy harvesting rectenna, and integrate nanoantennas with a bilayer graphene (BLG) based detector. Nanoantennas are subwavelength structures that offer an enabling technology for visible to terahertz components; here we focus on the infrared. Nanoantennas offer existing infrared detectors a means to make the detector much thinner and thus lower the dark current and pixel crosstalk and increase performance. Bilayer graphene offers a new tunable detector platform, however, it is only two atomic layers thick. For detection efficiencies over a few percent it must have a method of light concentration: the nanoantenna is unique in its ability to concentrate light into a small volume and makes BLG detectors possible. Similarly, the rectenna is reliant on the light concentration that the nanoantenna offers to squeeze light into a very thin tunnel diode; past efforts at rectenna fabrication without a nanoantenna yielded 0.1% efficiency.

Nanoantenna fabrication and integration with the disparate materials used in each technology is nontrivial. Initial attempts to fabricate nBn detectors in the geometry required for a nanoantenna has proved extremely challenging. For this reason, this effort will not only improve upon nanoantenna design, but as importantly, examine advanced integration of these novel concepts into actual devices in order to realize improved detector performance. Sandia's Microsystems and Engineering Sciences and Applications (MESA) facilities are unique in their capability and flexibility to handle silicon, III-V semiconductors, and silicon carbide substrates and the various other materials then deposited on them. The rewards from this project are high: high-performance midwave infrared (MWIR) detectors, tunable longwave infrared (LWIR) graphene detectors, and the first demonstration of heat into electrical power with a rectenna.

Comparative Approach for a Physics-Based Understanding of Power Spectrum Analysis Signatures

171057

Year 1 of 2
Principal Investigator: P. Tangyunyong

Project Purpose:

Power spectrum analysis (PSA) technique is an electrical technique developed at Sandia to detect electrical differences in devices. The goal of this project is to develop a fundamental understanding of the physical mechanisms that generate PSA signatures. We plan to develop a physics-based understanding of component level PSA signatures using first principle modeling and simulation.

To date, we have accurately simulated the dynamic operation of simple devices with several theoretical models; the modeling results agree very well with experimental PSA data. The modeling results also provide an insight into the non-linear processes that generate PSA signatures, as well as a better understanding of the limitation and detection sensitivity of PSA.

We plan to simulate more complex devices. The complexity of the devices used in the modeling will be gradually increased to determine the effectiveness and limitations.

Counter-Adversarial Data Analytics

171059

Year 1 of 2
Principal Investigator: W. P. Kegelmeyer

Project Purpose:

Sandia makes critical use of data analytics in defense of national security. Our adversaries, therefore, seek to sap, even suborn, those analytics. Through understanding our methods, they seek to produce data that is evolving, incomplete, deceptive, and otherwise custom-designed to defeat our analysis. Further, we cannot prevent them from doing so. We live in a changed world, in which we frequently must depend on data over which our adversaries have unprecedented influence.

We will develop and assess novel data analysis methods to counter that adversarial influence. We will also generate implementations and at least one prototype deployment in support of a national security challenge.

We must do data science, discovering generalizable and quantifiable counter-adversarial principles. Our national security mission requires methods that are relevant, applicable to analytics that matter, with realistic assumptions, useful uncertainty assessments, and practical implementations. We are also trying to counter dedicated, agile, intelligent adversaries who will closely observe and learn from our behaviors.

The ability to anticipate and defeat attacks on the data analytics at the heart of, for example, cybersecurity, stockpile assurance, counter proliferation, and biotechnology for threat detection is critical to a range of national security concerns.

Beyond Moore's Law Computer Architecture

171060

Year 1 of 2
Principal Investigator: E. Debenedictis

Project Purpose:

The challenge is to extend what is popularly called "Moore's Law" for both national security and economic productivity. To do so will first require identifying or inventing a replacement for computers' underlying device technology that is faster and more power efficient. In addition, computer architecture must be created that is both tuned to the new device and to the evolving nature of computer applications.

This is a widely recognized problem, but industry is looking at a solution space dominated by "drop in replacements" for the complementary metal-oxide-semiconductor (CMOS) current devices in current architectures (multi-core microprocessors). In order to satisfy specific needs of the US government, this project will look more broadly.

The project will focus on a few device types, yet looking beyond "drop in replacements" for CMOS as has been done in other projects. The project will also provide a fair, rigorous assessment of a broader range of devices. The solution will go beyond the common practice of analyzing devices in isolation, developing an entire "technology stack" of circuits, architectures, and software. This will yield realistic vision of the end result, as opposed to a thorough analysis of just the first step.

The solution will consider alternatives or enhancements to the preeminent Von Neumann architecture. A requirement of the planned solution will be execution of today's "legacy" software, yet the solution may be optimized for code that uses non-Von Neumann features such as learning.

Two stretch goals will be considered:

1. Cyber security and supply chain trust are very important. Subject to available resources, this project will consider whether the underlying physical technology and architecture can help address these issues.

2. A "Beyond Moore" physical prototyping capability will be considered. MESA or a new fab at Sandia could be considered for a role analogous to the DARPA-sponsored prototyping service that bootstrapped CMOS.

First to High Yield Fusion

171061

Year 1 of 2
Principal Investigator: S. A. Slutz

Project Purpose:

In the broadest terms, the purpose of this project is to find a low risk path toward high yield (~GJ/pulse) inertial fusion in the laboratory. Such an achievement would be a transformative capability for our country. History has shown this to be an extremely challenging multi-disciplinary problem. Our approach is based on a new concept — magnetized liner inertial fusion (MagLIF) in which the Z pulsed power facility implodes a cylindrical liner filled with deuterium fuel. The fuel is heated during the implosion with the Z-beamlet laser and magnetized with external field coils in order to reduce thermal losses between the hot plasma and cold liner. Detailed numerical simulations indicate the pressure required to achieve fusion with this concept is only about 5 Gbar as compared to the standard radiation driven capsule, which has a stagnation pressure of about 400 Gbar. In addition, the fuel convergence ratio for the standard capsule is about 35 while the point design MagLIF capsule has a convergence of 23. Since the effects of hydrodynamic instabilities are amplified as a capsule implodes, high convergence is a significant risk factor for inertial fusion. We have performed numerical simulations predicting high fusion yields with low convergence ratios (~15) are possible by increasing the fuel preheat energy. We have performed numerical simulations indicating that the fuel preheat energy could be increased significantly if a large energy laser were available. We expect to upgrade the Z-beamlet laser to 6 kJ within the next three years, but this will not be sufficient for low convergence implosions with large drive currents and high yields. Therefore, we are looking into pulsed power approaches to providing the fuel preheat. Simulations have been performed on two approaches that look promising. We plan to experimentally test these ideas in the coming year.

EXPLORATORY EXPRESS

Exploratory Express provides a vehicle to explore novel ideas that are generated by researchers spontaneously through the year, rather than in response to a specific proposal call. A small amount of funding ($50K) is provided to Exploratory Express projects over a period of no more than a few months to answer a key research question in an area of current or future strategic importance to Sandia. An added benefit is that funding allows for innovative R&D with rapid attainment of objectives, offering a means to cultivate a challenging and rewarding work environment for the Sandia workforce.

The asteroid that fell to earth near Chelyabinsk, Russia, gave scientists new insights into the risks of smaller asteroid impacts (Project 171074).

EXPLORATORY EXPRESS

Experimental Validation of a High-Voltage Pulse Measurement Method

170983

Year 1 of 1
Principal Investigator: S. Cular

Project Purpose:

Within the Nuclear Weapon Enterprise (NWE), there are requirements to measure high-voltage pulses precisely; however, no currently available method is capable of delivering with the uncertainty that is desired. Over 10 years ago, National Institute of Standards and Technology (NIST) discontinued the calibration service and provided Sandia's Primary Standards Laboratory with the resistive voltage divider to which all pulse high-voltage measurements are traceable, the NIST-N1. This divider has an uncertainty (~0.5%, k=2) that permits the calibration of working standards and other voltage dividers to >1%, typically 4-6% due to positional, cable, and terminator sensitivities. The measurement science to lower the uncertainty of this measurement is extremely limited; thus, outside the NWE there is no generic work that can be applied.

In the proposed work, a piezoelectric crystal, $LiNbO_3$, will be monitored with an acoustic wave before, during, and after a high-voltage pulse is applied. The change in piezoelectric crystal properties as a result of the high-voltage pulse is proportional to the voltage applied. Utilizing this method, the pulse high-voltage measurement becomes a function of measuring a low-voltage signal that can be accomplished with very low uncertainties. Initial estimates indicate an uncertainty of 0.1% (k=2) using standard high-bit, high-bandwidth digitizers. Application-specific follow-on work to develop an optimized measurement circuit has potential to lower the uncertainty one to two orders of magnitude further.

Although this work is specifically intended to address the needs of the NWE, the technology has broad application outside to the electrical and electronic industries. Two significant application areas include: use in power distribution/metering and analysis of transient high-voltage signals in electronics (surge circuit protection).

Summary of Accomplishments:

We designed and began testing a novel pulsed high-voltage sensor that ultimately will only require a change in duration measurement to determine the applied voltage. The work focused on using X-cut lithium niobate ($LiNbO_3$) for voltage sensing by monitoring the acoustic-wave propagation changes through $LiNbO_3$ resulting from applied voltage. Direct current (DC), alternating current (AC), and pulsed voltage signals were applied to the crystal. The measured values ranged from 10 – 273 ps and 189 ps – 2 ns for DC and non-DC voltages, respectively. Data suggests $LiNbO_3$ has a frequency-sensitive response to voltage. Through analysis and modeling of the physics involved, it is possible to eliminate the voltage source as a contributor to the error of the measurement. Based on the present experimental results, the method's U95 estimated combined uncertainty would decrease to ~0.025% for DC, AC, and pulsed voltage measurements.

As part of the experimental data analysis, we compared the results to those of simplified multiphysics finite-element model simulations and found the model and experimental results did not agree. Within the allotted time, a study was started to determine the possible reasons for the differences. Conclusions from this study indicate either that the model did not contain enough detail to fully account for the material properties or that the $LiNbO_3$ used in the experiment was not the cut stated by the manufacturer. Further work is necessary to make a final determination.

Significance:

The results of this project have set a new foundation for pulsed high-voltage measurements, similar to the results of the 1970's where Sandia led the way in this field that was and still is greatly needed for the weapons we support. By reducing the measurement uncertainties, products can be built and tested with greater confidence. Additionally, it becomes possible to feed theoretical models data that is accurate enough to increase the confidence in predicting the longevity of current and future products.

Reconfigurable Threat Emulation Attitude Control Strategy

170985

Year 1 of 1
Principal Investigator: J. M. Parish

Project Purpose:

The purpose of this project is to develop a family of "proof-of-concept" near-optimal attitude control strategies that are applicable to a large class of vehicles and mission requirements (i.e., reconfigurable). A need exists for a generalized optimal attitude controller that can be easily applied to arbitrary endo- and exo-atmospheric spacecraft, such as threat-emulation flight vehicles. The nonlinear nature of rotational mechanics, coupled with real-world effects including uncertainties, time delays, and time-variant system properties, presents a significant challenge for researchers desiring flight-admissible control solutions.

This problem is multi-dimensional. First, it is desirable to develop a control strategy that is not restricted by significant constraints on the configuration of the flight vehicle. That is, the control strategy should be applicable to a "generic" vehicle. However, to develop a controller that applies to any conceivable vehicle is out of the scope of this work; rather, a large class of flight vehicles with generally unspecified control allocation or mass properties is considered. Here, the primary reconfiguration parameters of interest are system inertias because these vary significantly from mission to mission and often have a high degree of uncertainty throughout the flight-control design process. Next, nonlinear multi-axis dynamics must be considered in the control design. It is desirable to take advantage of these nonlinear dynamics rather than constrain controllers to single-axis maneuvers. Third, a realistic set of flight controls must reject disturbances, including aerodynamic force perturbations, actuator delays, and uncertainties in system properties. Essentially, this requires the proposed solutions to have a real-time feedback element that makes control decisions based on the current state of the flight vehicle. Collectively, these three elements together make the attitude control design process innovative and challenging.

Summary of Accomplishments:

In this project, we developed and demonstrated the feasibility of a family of near-optimal multi-axis attitude control solutions. Each controller investigated directly addresses the problem of attitude control design for reconfigurable threat emulation flight vehicles. To tackle this complex design space, the typical operations handled by an attitude control system (rest-to-rest, spin-to-spin, and spin-to-rest pointing maneuvers) were independently investigated. Five control designs resulted and were tested in simulation: two for spin-to-spin, one each for spin-to-rest and rest-to-rest, and an all-inclusive (but non-optimal) solution that covers all three maneuvers. These five solutions include three near-minimum-time Eigenaxis-based controllers; a near-minimum-fuel impulse-based coning control; and a Lyapunov-based spinning reorientation controller. The three Eigenaxis maneuver-based controllers can be collapsed into a single control solution for axisymmetric bodies. Though some of these control solutions have restrictions from the fully generalized tumbling rigid body (such as axisymmetry), each still covers a large class of flight vehicles (and more importantly each covers those of interest for threat emulation). The state-dependent form of these controllers, which is primarily closed-loop feedback, gives them greater stability in the presence of perturbations such as aerodynamic effects, mechanical disturbances, and time delays. Also, the generalized structure of these control designs allows them to be implemented with minimal gain tuning, which can often be a time-intensive, iterative process with other control strategies. The most important aspect of the proposed control solutions is that each accounts for the coupled, nonlinear dynamics of rigid body rotational motion. This "multi-axis" approach helps avoid some of the pitfalls associated with single-axis control, such as strict limitations on off-axis rates and large sensitivities to inertia uncertainties. This research lays the foundation for future work in flight software design using multi-axis attitude control as well as for advanced control design using new numerical optimal control methods.

Significance:

This research impacts defense mission objectives to develop and demonstrate advanced technologies and deliver responsive technical solutions. The work addresses this goal by providing control solutions that facilitate: faster response to time-sensitive customer requests for vehicle design, simulations, and analysis; development of reconfigurable flight control software; extension of the performance envelope of existing vehicles; expansion of Sandia's aerospace control expertise and related visibility in the technical community. The goal of this work, to investigate the feasibility of generalized, multi-axis, optimal control, is accomplished and provides a technical foundation for pursuing advance controller implementations in flight test vehicles.

In Situ TEM Study of $LiMn_2O_4$ Stability

170986

Year 1 of 1
Principal Investigator: N. A. Missert

Project Purpose:

This work explores techniques to address a unique question in Li ion battery science: how does the underlying microstructure influence the stability of $LiMn_2O_4$ during cycling, specifically, what are the dissolution and reaction mechanisms? Understanding cathode stability is crucial to achieving the performance and reliability required for the next generation of Li ion batteries in the transportation sector. $LiMn_2O_4$ is one of the most promising cathode materials, and our films provide a state-of-the-art, controlled microstructural template for in situ studies of stability using in situ transmission electron microscopy (TEM) platform. Previous in situ TEM studies using nanoparticles (or wires) have not had the resolution to study stability and the influence of microstructure. Our novel thin films, combined with the reduced window size of our TEM platform, should allow the first in situ TEM studies of cathode stability. The results obtained in this project provide guidelines for using this new capability to understand stability in a wide variety of materials and environments.

Summary of Accomplishments:

In order to ensure compatibility of the Center for Integrated Nanotechnology (CINT) platform with the 550 °C growth temperature of the $LiMn_2O_4$ films, annealing studies were performed on the platform. CINT platforms with Al leads were unstable after annealing to 600 °C, where widespread de-adhesion occurred. CINT platforms using W/TiN leads were stable, with no de-adhesion observed, after depositing 25 nm of Au and then 10 nm of $LiMn_2O_4$ at temperatures of 550 °C. A stainless steel mask was designed and fabricated to align the Au evaporation and pulsed-laser $LiMn_2O_4$ film deposition to the Si_3N_4 window on the CINT platform.

In situ TEM studies of $LiMn_2O_4$ stability during cycling require that the W/TiN leads, two of which can be used for reference and counter-electrodes, do not undergo reactions at the potentials required for Li cycling. The stability of the W/TiN was tested by measuring the current-voltage characteristics between 3.8 and 4.3 V in EC:DMC:1M $LiPF_6$ of a 1-cm^2 film grown in the same system as the CINT platform. The C-V curve shows that the W/TiN is indeed stable. In situ TEM studies also require that the Au/ $LiMn_2O_4$ film cycle Li at the expected potentials. We showed that 10 nm of $LiMn_2O_4$ on 25 nm of Au cycles Li in EC:DMC:1M $LiPF_6$ at the expected potentials.

Our final task was to demonstrate that 10 nm of $LiMn_2O_4$ on 25 nm of Au shows well-defined structural features and would be electron transparent in order to enable the in situ TEM studies of stability. Atomic force microscope (AFM) images of a 10-nm $LiMn_2O_4$ film on 25 nm of Au showed individual faceted grains. TEM images of another 10-nm $LiMn_2O_4$ film on 25 nm of Au deposited on a Si_3N_4 window showed the moiré fringes associated with $LiMn_2O_4$ grains with specific alignment relative to the underlying Au.

Significance:

Obtaining a mechanistic understanding of Li-ion-battery cathode stability would have an enormous impact on our ability to use this technology for electric vehicles, addressing one of DOE's main goals: to "catalyze the timely, material, and efficient transformation of the nation's energy system and secure US leadership in clean energy technologies."

Pathogen Capture: Using Sandia Technology to Understand Host-Pathogen Interactions

171001

Year 1 of 1
Principal Investigator: Z. Bent

Project Purpose:

The purpose of this project was to develop and optimize pathogen-capture technology and to use this technique to better understand the suite of genes that are expressed by a pathogenic bacterium as it infects a host cell. Current techniques to analyze bacterial gene expression during an infection are extremely limited and typically focus on a single known gene or set of genes thought to encode virulence factors. Over a decade ago, these limitations were thought to be overcome with the advent of microarray technology. However, it was quickly discovered that hybridization of the pathogen sequences to the array was severely inhibited by the presence of host transcripts. This problem was again believed to be resolved by second-generation-sequencing (SGS) of RNA (RNA-Seq) with the added benefit that RNA-Seq decreases the price, increases sensitivity, dynamic range, and the ability to detect un-annotated and non-protein-coding transcripts. However, even with the read depth provided by SGS, it is extremely difficult to get enough pathogen reads for an effective gene level analysis. At Sandia, we have invented and developed a novel capture-based technique and device that considerably enriches for bacterial and viral transcripts from infected samples, thus overcoming the limitations of both microarray and current RNA-Seq technologies.

Summary of Accomplishments:

Through the course of this project, we were able to significantly optimize not only the process, but the efficacy of the technique as well. Prior to the start of the project, the pathogen capture technique, while effective, was extremely labor intensive due to the cumbersome equipment and low throughput of the system. A single sample at a time had to be processed by a technician taking about two hours to process a sample, allowing no more than four samples a day to be run. Because of this, it could take weeks to process all the samples required for a complete study. During this project, we were able to increase the number of samples that could be processed at once from one to twelve and the time from two hours down to as little as one hour. It is now possible to process more than 48 samples in one day, representing a 12-fold increase in daily throughput and allowing complete studies to be processed in less than two days rather than several weeks. We were able to increase the effectiveness and consistency of the technique while lowering the cost of equipment needed to run the protocol. Using the new methods, we are able to achieve a consistently higher level of pathogen transcript enrichment without the sample-to-sample variation we observed before. In addition, through the course of this project, we were able to publish a paper studying *Francisella tularensis* pathogenesis and are currently preparing another paper about *Yersinia enterocolitica*.

Significance:

The newly developed pathogen capture technique represents a significant advancement in the field of host-pathogen interactions for several reasons. First, this technique is able to enrich pathogen transcripts from an infected sample enough to enable a full transcriptomic profile of the bacteria to be achieved, a feat that was previously only possible through costly brute force approaches. Second, the improvements in equipment and protocol allow this technique to be used by any lab interested in sequencing. Finally, as documented in the published manuscript, this technique will lead to a much more complete picture of bacterial pathogenesis.

Refereed Communications:

Z.W. Bent, D.M. Brazel, M.B. Tran-Gyamfi, R.Y. Hamblin, V.A. VanderNoot, and S.S. Branda, "Use of a Capture-Based Pathogen Transcript Enrichment Strategy for RNA-Seq Analysis of the *Francisella tularensis* LVS Transcriptome during Infection of Murine Macrophages," to be published in *PLoS ONE*.

Modeling the Chelyabinsk Airburst: a New Benchmark for Radiation Hydrocodes

171074

Year 1 of 1
Principal Investigator: M. B. Boslough

Project Purpose:

Sandia has developed a special version of the CTH shock physics code (radCTH), which includes two radiation transport processes: radiation diffusion and photon energy leakage. The transport algorithms are validated with several radiation-dominated benchmark problems, each problem addressing particular aspects of the transport algorithms. Several of these benchmarks are atmospheric nuclear tests (surface and free airbursts) from the 1950s and early 1960s. Such validations are limited due to the small number of useful tests and the mid-20th-century instrumentation. Moreover, nuclear explosions are all essentially point-source, low-mass, low-momentum events. The range of nuclear-explosion-scale “simulation space” that can be validated is narrow.

The Chelyabinsk airburst of February 15, 2013 had an equivalent explosive yield of about a half megaton and represents a mechanism of radiation-dominated energy deposition that is fundamentally unlike that of a nuclear explosion. Because it effectively has “line source” geometry, its hydrodynamics and radiation transport are different from that of a bomb. It, therefore, provides an opportunity to: 1) apply radCTH to model the event and understand the observed phenomena and 2) use data collected from the event to validate radCTH on nuclear-explosion energy scales but under radically different conditions from the atmospheric nuclear-test data currently used. We intend to perform the first 2D and 3D radCTH simulations of the event and compare the results to observational data to assess the use of the Chelyabinsk event as an independent means of validating radCTH for high-energy explosive atmospheric events.

Summary of Accomplishments:

We performed the first physics simulations of the Chelyabinsk airburst to be initialized with accurate energy deposition derived from observations. We developed the techniques to do energy insertions to enable these simulations. This Chelyabinsk explosion occurred about 40 km SSW of the Russian city of that name. Its proximity to a population center led to many injuries and widespread blast damage, but also yielded a plethora of data from security and dashboard cameras. Combined with seismic, infrasound, and satellite records, this provides a rich and multi-faceted means to determine the projectile size and entry parameters and to develop a self-consistent model.

The shallow entry angle led to a long bolide duration (16.5 s) and energy was deposited over 100s of km leading to an extended, near-horizontal, linear explosion. The blast was distributed over a large area and was much weaker than for a steep entry and a more concentrated explosion closer to the surface. The orientation also led to different phenomena than expected for a more vertical entry. There was no ballistic plume as observed from SL9 impacts (45°) or calculated for Tunguska (~35°). Instead, buoyant instabilities grew into mushroom clouds and bifurcated the trail into two contra-rotating vortices.

We have modeled the airburst using both 2D and 3D simulations and using both radCTH and hydrodynamics-only versions. We have compared blast overpressures to those inferred from observations and have also compared the evolution of the wake and other phenomena. Our simulations provide a framework for understanding this event and explain the anisotropy of the blast wave on the ground, the cylindrical nature of the wave, and the wake.

Significance:

Sandia was already a leader in the very small field of asteroid airburst modeling, and our models have become the most widely-cited sources of yield estimates for the largest such historical event (Tunguska, in 1908). The Chelyabinsk event has drawn enormous attention to our modeling effort, and gives us the opportunity to cement our reputation as the lab of choice in "all matters airburst." We anticipate that an enhanced reputation will boost our related efforts in nuclear explosion effects modeling. Moreover, we expect that our role as airburst modelers will lead to NASA funding to assess airburst consequences and risk.

Refereed Communications:

P.G. Brown, et al., "A 500-Kiloton Airburst over Chelyabinsk and an Enhanced Hazard from Small Impactors," *Nature*, vol. 503, pp. 238-241, November 2013.

Graphene Liquid Crystals: Novel Building Block for Anisotropic Oriented Materials

171128

Year 1 of 1
Principal Investigator: T. M. Alam

Project Purpose:

This project will develop a general and scalable route to produce polymer-graphene nanocomposites with molecular-level control of the graphene orientation. Many of the physical and chemical properties in nanocomposites are controlled by the anisotropy and orientation of the nanomaterials imbedded within the polymer matrix. Control of this anisotropy has been demonstrated to impact the electrical and thermal conductivity, transport and permeability, photovoltaic activity, and improved mechanical properties. The ability to precisely control the orientation of nanoparticles in composite materials remains an important enabling technology for future material science advances. Current methods for producing anisotropic materials include electrical fields, magnetic fields, mechanical shear, melt stretching, and gel extrusion. While advances have been made in these areas, the performance is highly dependent on the size, asymmetry, and susceptibility of the nanoparticle being incorporated and has proven particularly problematic for orienting nanocomposite thin films. In this project, liquid-crystal (LC)-modified graphene building blocks will be developed that allow for precise magnetic field control of the graphene orientation in polymer systems containing LC domains. The ability to produce surface-modified graphene will be demonstrated using a thermotropic/nematic LC. This method is generalized, scalable, and only limited to the applied magnetic field dimensions. Oriented LC-modified graphene particles as a generalized building block could be incorporated into a variety of materials including nano-reinforced polymers, separation membranes, electrolyte membranes, and solar cells. Development of this capability will expand Sandia's expertise in producing the next generation of advanced materials.

Summary of Accomplishments:

The results of this project involving the production of graphene/liquid crystal materials include:

1) Graphene/liquid crystal nanocomposites have been prepared and characterized. The orientational order of the LC phase as a function of graphene concentration has been directly measured using ^{2}H nuclear magnetic resonance (NMR). For all the nanocomposites investigated, magnetic ordering of the nematic phase is complete with the director-oriented parallel to the external magnetic field. No large distributions or large defects were observed. The graphene was also oriented parallel to the magnetic field.
2) For these composites, the nematic-to-isotropic phase transition is lowered in the graphene/5CB nanocomposite but is increased in the graphene/benzene/5CB nanocomposite as a function of increasing graphene concentration. The latter material shows an almost 40% increase in orientational order near the phase transition with the addition of graphene. These results demonstrate that surface interactions play a large role in these graphene/LC nanocomposites.
3) A series of functionalized graphene materials have been synthesized to address these surface interactions. Preliminary results show a dramatic improvement in alignment with the benzene and hexyl benzene derivatives.
4) A series of 5CB/PDMS polymer nanocomposites were prepared and characterized. For a narrow LC concentration range, it is possible to produce LC domains dispersed in the polymer matrix that can still be magnetically oriented. These magnetically oriented phases will allow for the control of the graphene orientation in these polymers.

Significance:

This research demonstrates graphene/LC nanocomposites can be incorporated into polymer matrices with magnetic alignment. These nanocomposites provide generalized building blocks for DOE-relevant materials including nano-reinforced polymers, separation membranes, electrolyte membranes, and solar cells. This effort developed diazonium chemistry for graphene functionalization impacting other graphene composite efforts at Sandia. These results provide preliminary data for future proposals on graphene nanocomposites directed towards DOE, Basic Energy Sciences, and Office of Electricity to support future nanocomposite material development and energy-related materials.

A Micro-Engineered Human Blood-Brain Barrier (u-BBB) to Study Host-Pathogen Interactions

171129

Year 1 of 1
Principal Investigator: M. Wu

Project Purpose:

The blood-brain barrier (BBB) is a highly specialized barrier that separates the central nervous system (CNS) from circulating blood. The primary purpose of the BBB is to protect the brain and spinal cord from fluctuating ionic concentrations in the circulation and to regulate the CNS microenvironment. The delivery of therapeutic agents or prophylaxis into the CNS is also excluded by the BBB, making CNS drug development and screening highly challenging. Consequently, the highly specialized nature of the BBB interface is a subject of great interest both for biodefense and for therapeutic research. This project aims to leverage Sandia's engineering expertise to develop an ex-vivo BBB model on a microfluidic format, where primary human brain microvascular cells can be cultured and differentiated into a functional BBB to provide a scalable, low-cost mimic of the physiological BBB. The ex-vivo BBB model will provide an important organ mimic to enable screening the effects of neurotoxic compounds as well as countermeasures for neurotoxic agents.

Summary of Accomplishments:

We designed a microfluidic two-compartment system to culture brain microvascular endothelial cells and astrocytes and fabricated devices that can be interfaced with a peristaltic pump to generate a media circulatory system to create tunable shear stress inside the device for proper differentiation of brain microvascular cells into phenotypes representative of the blood-brain barrier in vivo.

Significance:

The microfluidic blood-brain barrier system serves the National Security Biodefense mission by enabling the study of the effects of neurotoxic chemical weapons, as well as enabling the screening of countermeasures against neurotoxic agents.

Study of Gallium Nitride High Electron Mobility Transistor Degradation through Comprehensive Characterization

171926

Year 1 of 1
Principal Investigator: B. B. Yang

Project Purpose:

The purpose of the project is to develop the methodology to characterize gallium nitride (GaN) high electron mobility transistors (HEMTs). This development will help improve the design and reliability of these devices. The techniques explored in this project focus on infrared (IR) thermography, Raman thermography, and deep-level optical spectroscopy (DLOS).

GaN HEMTs are wide-bandgap switching devices that can provide substantial performance improvement over current power-electronics technologies. On a system level, the promise of reduced system size, decreased weight, and higher operating power densities broaden the potential impact of GaN HEMTs beyond electrical grids to include improvements to weapons, radar, and radiation-hardened systems. The superior switching speed and low on-state resistance of GaN HEMTs over their silicon (Si) counterparts make them widely used in radio-frequency applications. Extending the application of GaN HEMTs from radio-frequency communication to power-conversion systems involves increased electric-field stress. This increased stress brings out severe field-induced degradation that limits GaN HEMT reliability.

Previous reliability research involves several characterization tools used in isolation. The techniques include electrical characterization, IR thermography, Raman thermography, and deep level optical spectroscopy. The limited number of characterization methods largely stem from lack of availability. Sandia is uniquely positioned to address this shortcoming with its access to a large number of characterization tools. By utilizing a comprehensive set of characterization and failure analysis methods, Sandia can leverage its extensive capabilities to contribute to the understanding of GaN field-induced degradation physics. This project seeks to lay the groundwork for a broader GaN HEMT research program by streamlining the use of the above techniques. In addition, the project uses these capabilities to explore thermal profiles and the effects of carrier traps in these devices.

Summary of Accomplishments:

We successfully developed the process to characterize normally off GaN HEMTs using high-magnification IR thermography, Raman thermography, and DLOS. The accuracy of IR thermography was verified by comparing the results with those from Raman thermography. The measured temperatures of the two techniques were within 5 °C. This calibration provides the confidence to primarily use IR thermography to quickly characterize samples, reserving Raman thermography to situations where extreme accuracy, material specificity, and spatial resolution are required. In the case of Raman thermography, a technique of utilizing the silicon substrate's Raman line to measure the GaN device temperature was developed to overcome the interference caused by surface passivation layers. The IR thermography results found a relationship between heat distribution and gate leakage, suggesting an uneven current or electric field distribution that could be related to the degradation of the device.

DLOS measurements were taken in the device triode and saturation regions. In both cases, the primary deep level response was between 1.8 eV and 2.8 eV. Triode region measurements found electron photoemission that produced excess accumulation in the 2DEG. Measurements taken in the saturation condition found indications of minority-carrier traps under the gate. The overall results suggest that dielectric or barrier trapping at the gate is a critical issue and could be a dominant cause behind threshold-voltage fluctuation.

The development and refinement of the characterization process has led to faster turnaround times for IR thermography, Raman thermography, and DLOS, making these tools more affordable to a greater number of ongoing research projects at Sandia. Methodology improvements resulting from this project strengthen Sandia's leadership role in wide-bandgap devices and also enhance its value proposition to collaborators in the field.

Significance:

As a result of the work in this project, turnaround time for characterization of packaged GaN HEMTs has been reduced to one business day per technique. This increases the affordability for future researchers to perform these characterizations in their wide-bandgap research. The findings from the characterized devices will be incorporated into a future study on their reliability and failure mechanisms. The results will help accelerate the maturation of these technologies. Earlier adoption will hasten their impact on renewable energy, communications, and radiation-hardened electronics.

Carbon Nanotube Thermal Interface Materials for Satellite Systems

172316

Year 1 of 1
Principal Investigator: R. Sayer

Project Purpose:

The purpose of the project is to demonstrate the thermal performance of carbon nanotube (CNT) thermal interface materials (TIMs) as superior to metallic foils. Heat transfer across the interface of contacting materials is of fundamental importance in the design and simulation of thermal systems. Due to the microscopic roughness found on all manufactured materials, heat is restricted to flow through a small number of contact spots formed between two mating surfaces, which give rise to a thermal contact resistance (TCR). For typical surfaces, the actual contact area (sum of the contact spot areas) is typically two to six orders of magnitude less than the apparent area of contact. As a result, TCR can be quite large, often accounting for a significant fraction of the total thermal resistance of a heat path. TIMs are interstitial materials that are inserted at the contact interface to increase contact area for conduction and, hence, decrease the overall TCR of the joint. TIMs serve a critical role in thermal management by enhancing heat transfer across contact interfaces, thus allowing higher heat fluxes to be removed from the system and lowering device operating temperature.

In satellite systems, gold foils are commonly used as TIMs. Although these foils provide an improvement in heat transfer across an interface, at a cost of approximately $200 per square inch, they are quite expensive. Also, because gold is a precious metal, special handling and tracking procedures must be followed when working with and installing the TIMs. This research focused on testing CNT based TIMs that offer superior thermal performance, reduced weight, and lower cost in comparison to gold TIMs. CNT TIMs can provide heat transfer performance that is superior to metallic foils. Additionally, the potential cost savings are significant — a commercially produced CNT TIMs should only cost $1 to $5 per square inch.

Summary of Accomplishments:

We demonstrated that CNT TIMs offer superior performance in comparison to metallic foils. This work represents the first report of pressure-dependent thermal contact resistance of radiation-aged CNT TIMs. Additionally, vibration isolation characteristics of these TIMs were measured and reported for the first time. It is shown that the TIMs provide good coupling across the interface.

Significance:

This work provides a basis for improved thermal performance of satellite systems allowing for the implementation of sensors with greater performance and higher heat-dissipation requirements to be utilized. Ultimately, improved satellite designs will lead to improved surveillance techniques and improved defense capabilities.

Exploring Graphene Field Effect Transistor Devices to Improve Spectral Resolution of Semiconductor Radiation Detectors

173297

Year 1 of 1
Principal Investigator: J. B. Martin

Project Purpose:

We propose to investigate the concept of a semiconductor-graphene radiation energy spectrometer. This spectrometer will amplify and measure the electron-hole pairs produced in semiconductor materials by interaction of gamma ray, x-ray, neutrons, or alpha particle radiation.

Graphene, a planar, atomically thin form of carbon, has unique electrical and material properties that could enable new high performance semiconductor devices. Graphene could be of specific interest in the development of room temperature, high-resolution semiconductor radiation spectrometers.

In our new graphene-electrode concept, a few-layer graphene film, which is extremely sensitive to charge, is deposited on a thin insulating layer on top of a thick absorbing semiconductor substrate. The incident ionizing radiation creates electron-hole pairs in the semiconductor material. The resulting free electrons, which have a faster drift velocity than holes in semiconductors of interest, will be collected at the insulator/semiconductor interface, producing an electric field that modifies the conduction of the graphene readout layer in a field effect transistor (FET) device architecture. This low-capacitance, single-polarity charge-sensing configuration is similar to semiconductor drift detectors which have demonstrated excellent energy resolution. The difference in electron and holedrift velocity can degrade the energy resolution possible with these semiconductor materials. Our electrode concept eliminates the dependence on the holedrift velocity.

We investigated our graphene-field-effect-transistor (GFET) detector read-out in a silicon carbide detector. We believe that we can improve room-temperature semiconductor spectrometer resolution with our proposed low-capacitance GFET architecture.

We plan to pursue follow-on funding to investigate other room-temperature semiconductor detector materials such as HgI_2 and cadmium zinc telluride (CZT), which enable room-temperature gamma-ray spectrometry.

Summary of Accomplishments:

We designed and fabricated a field effect transistor in SiC material with a graphene readout circuit. We applied a bias voltage to the back gate of the device to transport free electrons to a point where they would be fixed and detected by the transistor circuit.

We first tested the GFET by illuminating it with ultraviolet (UV) and measuring the device current. We were able to detect the presence of the UV light as an increase in the device current.

Our next test was to irradiate the GFET with alpha particles from a polonium-210 (Po-210) source. We were also able to detect the interaction of the alpha particles with our GFET as an increase in the device current.

While our SiC GFET sensor has a small collection of depth on the order of 1 micron, we have measured data that indicates the capability of the GFET to measure the energy deposited in the SiC. Future work would involve using high-purity semiconductor material to increase the collection depth and perform energy spectroscopy on the interacting ionizing radiation.

Significance:

Our work advances the capability of room-temperature semiconductor detectors to accurately measure the energy spectrum of gamma rays. These detectors are widely used in research and development, industry, and academia. They are also used in national security missions to detect and track radiation sources that may be a safety threat, and to detect special nuclear materials. Our work would make these room-temperature semiconductor detectors more effective, less expensive, and more widely used to improve our nation's security.

Enabling the First-Ever Measurement of Coherent Neutrino Scattering through Background Neutron Measurements

173302

Year 1 of 1
Principal Investigator: D. Reyna

Project Purpose:

The purpose of this project is to determine if an experiment to discover coherent neutrino nucleus scattering (CNNS) is possible at the Spallation Neutron Source (SNS). CNNS is a theoretically well-grounded, but as-yet unverified process. DOE's NA-22 has funded work on developing detector technology that may ultimately be able to monitor nuclear reactors using this process, but nuclear reactors are a particularly challenging environment for a first measurement. The SNS at Oak Ridge National Laboratory (ORNL) provides a unique source of neutrinos that may provide an optimal platform for the first detection of CNNS. A proto-collaboration of groups supported by DOE's NA-22 and the DOE Office of Science/High-Energy Physics has come together to investigate this option and propose an experiment to these two agencies. Currently, the largest risk to such an experiment comes from an unknown background of high-energy neutrons that penetrate the existing SNS shielding. We have deployed a neutron scatter camera at the SNS during beam operation and performed preliminary measurements of the neutron backgrounds at a promising experimental location and report the results of those measurements.

Summary of Accomplishments:

We measured the neutron backgrounds at a promising experimental location inside the SNS experimental hall. In addition to our existing capability of measuring neutrons from 1-10MeV, we were able to extend the operational range of our neutron scatter camera to record and image neutron backgrounds in excess of 100MeV. The represents a powerful achievement for our detector and has provided a wealth of information for our proto-collaboration. These measurements now enable the other scientific groups to determine whether sufficient neutron shielding could be provided to allow the sensitive neutrino detectors to operate in that environment. Our preliminary estimates suggest that such an experiment should be possible. Furthermore, these measurements will allow neutron shielding designs to be optimized and the neutrino source simulations to be bench marked.

Significance:

DOE's NA-22 has identified CNNS as a promising technology for reactor monitoring. The results from this experiment help us to determine if a demonstration experiment at the SNS is possible, thus greatly supporting the technology development for this mission. Furthermore, the measurement of CNNS would be a first-ever detection of a theoretical interaction that is at the forefront of basic neutrino physics. Participation in this effort has allowed us to extend the operational capabilities of our existing equipment and has furthered our status within the international neutrino detection community.

Unpublished Summaries

For information on the following FY 2013 LDRD projects, please contact the LDRD Office:

Laboratory Directed Research & Development
Sandia National Laboratories
Albuquerque, NM 87185-0123

Project Number	Title
151266	Ultra-Thin, Temperature Stable, Low Power Frequency References
151354	Software-Defined Telemetry Using a Programmable Fuzing Radar
151360	Multi-Phase Laminates: A Study of Prompt Transformations in Abnormal Environments
155408	Leveraging Safety Applications for Global Revocation and Congestion Control in Vehicular ad hoc Networks
158751	Assessment of Windows Integrity Levels for Sandboxed Systems
158757	Applying Discrimination Methods to Collected and Synthetically Modeled Explosive Signatures
158759	Remote Optical Sensing of Ionizing Radiation
158772	Acoustic Tag for Maritime Location and Tracking Applications
158774	Ablation Chemistry Effects on Boundary-Layer Transition
158779	Novel Memory Analyses
158781	Breaking the Language Barrier
158850	Miniature Tritium Free Neutron Generator
158859	New Radiation-Resistant Materials
165546	Bus Assessment
165549	Precise and Persistent RF Detection, Tracking, and Location
165550	Hardware Solution to Flash Memory Accessibility Problems
165553	Advanced Prototyping Using Composite Materials
165557	Dynamic Invariant Inference for Binary Analysis
165559	Board and System Level Spectral Analysis
165565	Sintering Kinetics and Latency of Silver Nanoparticle Conducting Layers
165566	Electromagnetic-Wave Probing of Electrical Circuits
165570	Exploration of the Thunderbolt Bus Protocol

Appendix A: FY 2013 Awards and Recognition

Award Description	LDRD Contribution
R&D 100 Award, *R&D:* *Membrane Projection Lithography: Bruce Burckel*	Project 131302, "Metamaterial Science and Technology"
R&D 100 Award, *R&D Magazine:* *Mantevo Suite 1.0: Michael A. Heroux*	Project 105815, "HPC Application Performance Analysis and Prediction"
R&D 100 Award, *R&D Magazine:* *ADIOS: Gerald F. Lofstead II*	Project 120479, "Advanced I/O for Large-Scale Scientific Applications"
Asian American Engineer of the Year: *Jeffrey Tsao*	Project 27328, "A Revolution in Lighting: Building the Science and Technology Base for Ultra-Efficient Solid State Lighting," and others
Federal Laboratory Consortium: *Mid-Continent Region awarded the Outstanding Regional Partnership Award*	Project 151379, "Biodefense and Emerging Infectious Disease (BEID) Applications of Engineered Nanoparticles," and others
Federal Laboratory Consortium: *Award for Excellence in Technology Transfer for the Removal of Radioactive Cesium from Seawater Using Crystalline Silico-Titanate*	Project 3530050, "Radioactive Waste Processing Using Titanate Ion Exchangers"
IEEE Fellow: *for contributions to thermal management and 3D electronics packaging technologies: Subash L. Shinde*	Project 159258, "Extreme Scale Computing Grand Challenge," and others
American Institute of Aeronautics and Astronautics Fellow: *Basil Hassan*	Project 67044, "Adaptive Force Feedback Surface Control," and others
American Ceramic Society Fellow: *William Hammetter*	Project 165609, "The Engineering and Understanding of Nanoparticle/ Cellular Interactions," and others
American Ceramic Society Fellow: *Paul G. Clem*	Project 117761, "Flexible Thin Film Battery Development," and others
American Chemical Society: *Nancy Jackson*	Project 3532010, "Chemical Feedstocks for the Future: Oxidative Dehydrogenation," and others
American Society for Metals (ASM) International Fellow: *for revolutionizing microelectronics failure analysis: Ed Cole*	Project 165559, "Board and System Level Spectral Analysis," and others
Alameda County Women's Hall of Fame Inductee: *for soot diagnostics in combustion and the atmosphere: Hope Michelsen*	Project 151307, "Development and Deployment of a Field Instrument for Measurements of Black Carbon Aerosols," and others
TechConnect Innovation Award: *Microsystems Enabled Photovoltaics (MEPV)*	Project 159257, "Science-Enabled Next Generation Photovoltaics for Disruptive Advances in Solar Power and Global Energy Safety and Security"
Society for Experimental Mechanics Brewer Award: *for "Outstanding Practicing Experimentalist": Randy Mayes*	Project 165659, "Development of Non-Intrusive Methods to Measure Static and Dynamic Forces and Motions in Mechanical Joints"
IEEE Photonics Society Quantum Electronics Award*: for contributions to semiconductor-laser theory: Weng Chow*	Project 117825, "Four-Wave Mixing for Phase-Matching-Free Nonlinear Optics in Quantum Cascade Structures," and others
ACerS/NICE Karl Schwartzwalder-Professional Achievement in Ceramics Engineering (PACE) Award: *Geoffrey Brennecka*	Project 158828, "Understanding Tantalum Oxide Memristors: An Atoms Up Approach," and others