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| *Author(s):* | John Sarrao, SPO-SC |
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# Decadal Challenges for Predicting and Controlling Materials Performance in Extremes

**By John Sarrao**

A Report of a Workshop held December 6-10, 2009

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**Workshop Chair**

John Sarrao, Los Alamos National Laboratory

**Panel Leaders**

Todd Allen, University of Wisconsin and Idaho National Laboratory

Robert Cauble, Lawrence Livermore National Laboratory

George Crabtree, Argonne National Laboratory

Tomas Diaz de la Rubia, Lawrence Livermore National Laboratory

Roger Falcone, Lawrence Berkeley National Laboratory

Paul Follansbee, St. Vincent's College

Rus Hemley, Carnegie Institution of Washington

Richard Lesar, Iowa State University

Malcolm McMahon, University of Edinburgh

Tony Rollett, Carnegie Mellon University

Steve Zinkle, Oak Ridge National Laboratory

**LANL Workshop Steering Committee**

Curt Bronkhorst

Micheline Devaurs

George T. "Rusty" Gray

Quanxi Jia

Jack Shlachter

Marius Stan

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## Executive Summary

The performance of materials in extreme environments is central to a number of national security challenges, including especially the need for sustainable energy solutions. From fission & fusion energy to nuclear weapons to a broad suite of renewable challenges, a science-based approach to certifying materials performance for extended lifetimes is needed. The need to develop materials that perform in new and more extreme environments is also acute. Put simply, we lack sufficient confidence in the materials we have to confidently predict or extend their lifetime. Materials often fail at one tenth or less of their intrinsic limit and we do not know why.

There is great potential to change this reality. Materials research is on the brink of a new era of science in which the traditional approach of observation and validation of materials performance is replaced by prediction and control of materials functionality. Progress in this endeavor will enable a new generation of materials solutions from a more reliable nuclear stockpile to paths to higher efficiency clean energy technologies. The urgency of the challenge extends beyond the benefits from the envisioned end uses to the fact that the next generation of materials qualification facilities is presently being contemplated and designed with known materials. Near-term progress can yield smarter, more effective facility designs as well as higher performing materials.

Against this backdrop of urgent mission need and high scientific potential, a workshop of approximately 100 international leaders in materials research was convened in Santa Fe, New Mexico to explore "Decadal Challenges in Predicting and Controlling Materials Performance in Extremes." While a number of recent workshops have recognized the challenge of materials in extremes, far fewer have focused on the means to meet this challenge. Therefore, the present workshop focused specifically on needed capabilities and tools to seize this opportunity.

To achieve the vision of prediction and control of materials functionality, workshop participants recognized that a key grand challenge is the ability to predictively manipulate microstructures to achieve desired macroscopic performance. Central to this challenge is the potency of defects, either to be exploited intentionally for enhanced performance or to suffer their deleterious effects. The role of defects is a microcosm of the broader impact of rare events that is a key stumbling block in achieving prediction and control. The extremes of heterogeneity dominate performance at the expense of the homogenous bulk.

Further, while the era of 'cook and look' Edisonian materials discovery is largely behind us and directed serendipity is a potent engine of materials discovery, there is a key difference between 'prediction and control' and 'more cooking' and 'more looking' or even 'looking while cooking' that can only be enabled by the seamless integration of theory, observation, and synthesis to achieve desired functionality.

The vision of prediction and control will only be achieved through the development of in-situ, real-time, multi-probe "tools" (including advanced theories and information science and

technology methods, high performance computing, advanced measurement capabilities, controlled environments) to enable dynamic, in-situ measurements of real materials in real environments.

A final element of the challenge relates to the workforce required to achieve success. Predictive control of materials functionality lies at the boundary between 'science' and 'engineering' and requires the integration of multi-disciplinary teams that span traditional 'chemists', 'materials scientists', 'physicists', etc. This approach necessitates broader education and training for materials researchers in which the focus is not structure→ property relationships, but rather property→ structure relationships.

In the end, workshop attendees enthusiastically concluded that achieving the grand challenge of prediction and control of materials performance in extremes was within our reach and the workshop helped to identify a roadmap of capability gaps that need to be addressed. This report documents the fruits of those efforts.

## Introduction

The performance of materials in extreme environments is central to a number of national security challenges, including especially the need for sustainable energy solutions. From fission & fusion energy to nuclear weapons to a broad suite of renewable challenges, a science-based approach to certifying materials performance for extended lifetimes is needed. The need to develop materials that perform in new and more extreme environments is also acute. Put simply, we lack sufficient confidence in the materials we have to confidently predict or extend their lifetime. Materials often fail at one tenth or less of their intrinsic limit and we do not know why.

There is great potential to change this reality. Materials research is on the brink of a new era of science in which the traditional approach of observation and validation of materials performance is replaced by prediction and control of materials functionality. Progress in this endeavor will enable a new generation of materials solutions from a more reliable nuclear stockpile to paths to higher efficiency clean energy technologies. The urgency of the challenge extends beyond the benefits from the envisioned end uses to the fact that the next generation of materials qualification facilities is presently being contemplated and designed with known materials. Near-term progress can yield smarter, more effective facility designs as well as higher performing materials.

At present we lack a sufficient multi-scale understanding of component performance and failure to enable process-aware control of materials functionality. Central to this challenge is bridging first-principles, atomic-scale understanding to integrated bulk phenomenology; the manipulation and control of defects and interfaces on intermediate spatial and temporal scales is a key opportunity. The role of theory, modeling, and computation plays a central role. Recent advances in computational power enable multi-scale modeling and co-design, the simultaneous interplay of theory, experiment, and computation. For materials research, the frontier of co-design plays out at the microsctructural level; as a result this is a exascale computational challenge and opportunity.

The purpose of this report, and the workshop from which it is derived, is to identify the scientific challenges and research directions to achieve predictive materials performance in extreme environments, focusing specifically on needed capabilities and tools. Approximately 100 researchers from across the international materials community, spanning domestic and international universities, national laboratories, and industy gathered in Santa Fe, New Mexico in December 2009 to address this challenge. Specifically, the workshop emphasized research needs in the areas of radiation-matter interactions for fission and fusion, radiation-matter interactions for energy conversion, and matter interactions in extremes. Building on previous studies by e.g., DOE's Office of Science, Office of Nuclear Energy, and National Nuclear Security Administration (NNSA) (see e.g., **Basic Research Needs for Materials under Extreme Environments**, http://www.science.doe.gov/bes/reports/files/MUEE_rpt.pdf), workshop

participants identified a series of priority research directions and the capabilities required to achieve success.

The workshop began with a series of plenary talks framing the mission challenge. George Crabtree from Argonne National Laboratory, Stuart Maloy from Los Alamos National Laboratory, Steve Zinkle from Oak Ridge National Laboratory, and Robert Hanrahan from NNSA discussed materials challenges for renewable energy, fission energy, fusion energy, and nuclear weapons, respectively. While the breadth of the challenges presented was exceptional, the common need to predict and control materials in extremes was clear and universal.

The work of translating this common vision to actionable priority research directions (PRDs) was done in four pairs of breakout panels. The charge for each panel (the titles of which are italicized) is given below:

Radiation Matter Interactions for Fission and Fusion

*Extreme-environment tolerant materials by design:* The need for higher performing materials in the extreme environments of advanced fission and fusion reactors is well documented. Approaches that accelerate the transition from the observation and validation of performance to the prediction and control of functionality through materials discovery and science-based certification remain grand challenges.

*"Watching damage happen:"* A particular challenge is the ability to make (and model/interpret) measurements of relevant phenomena in irradiation environments of interests and thereby advance fundamental understanding and predictability beyond today's 'cook and look' approaches.

Radiation Matter Interactions for Energy Conversion

*Materials discovery and processing for advanced functionality:* The need for predictive design, discovery, and growth of new materials, especially single crystals, to achieve advanced functionality is a grand challenge. Further, exploiting the full suite of synthesis, fabrication, and processing capabilities is essential if we are to discover by design next generation materials and enable the transition from observation to control.

*"Making every photon count:"* Translating quantum phenomena that arise uniquely on the nanoscale to bulk performance requires a predictive understanding of interface and microstructre effects that limit integrated efficiency and system lifetime that are central to achieving the full potential of advanced functional materials.

Matter Interactions in Extremes

*Process aware material certification in extremes:* In recent years it has become increasingly clear that how an extreme material is formed (not only the fabrication/processing techniques that created an initial structure and microstructure but also the path through phase space the material traversed to reach a given extreme condition) directly affects performance. Key challenges include rate dependence and path dependence of thermodynamic and kinetic processes.

*"When solids stop being solids:"* At sufficiently high temperature and/or energy density, solids become plasmas. In particular, warm dense matter is an important crossover regime characterized by inhomogeneities that derive from the way in which materials fail, plasma-solid interactions, and associated turbulent phenomena.

Cross-cutting Challenges

*Enabling the transition from observation to control:* A true predictive understanding of materials performance would allow us to faithfully extrapolate performance beyond regions of experimental validation and would reveal the design principles that accelerate the discovery of higher performing materials in these extremes. Such a realization of 'materials by design' is presently beyond on our reach, but key insights are being made. The means to accelerate this progress are an important focus area.

*Bridging multiple scales in space and time:* Current petascale computers and advanced algorithms are enabling the largest simulations ever performed. However, the frontier of multi-scale modeling is achieving an experimentally validated predictive understanding that spans spatial and temporal scales in an integrated framework, moving beyond the passing of parameters between distinct models.

The panel topics described above were deliberately overlapping, and as a result, much cross-fertilization of ideas and workshop participants occurred. In particular, the 15 priority research directions (PRDs) that emerged from the worskhop do not necessarily derive from a specific panel.

As one specific example, the panel on *Materials discovery and processing for advanced functionality* initially identified four priority research directions:

1. Materials design and lifetime prediction (focus on materials design)
2. Rapid materials design and synthesis (focus on synthesis)
3. Corrosion science under extreme environments (fundamentals of corrosion)
4. Controlling nucleation phenomena (nucleation as a key barrier to materials design)

The first two represented high-level research direction assessments, while the second two represented more specific topics that have not received the same attention as the first two but which were considered to be critical shortcomings of the current state of "predictive design, discovery, and growth of new materials."

Nucleation, for instance, is a fundamental process step contributing to – if not in some cases controlling – many microstructural development and failure processes. Fatigue fracture and phase transformations are largely controlled by nucleation. Yet, the theory of nucleation, in the case of phase transformations or solidification, has advanced little beyond that contained within the well-known Johnson–Mehl–Avrami–Kolmogrov equation. Innovative measurements of nucleation events – particularly using transmission electron microscopy and small-angle neutron scattering – have been published but measurements are lacking at both the spatial and temporal

scales necessary to understand the fundamentals of nucleation. New measurements are required both to validate theories and to spawn new theoretical studies.

Corrosion science also has achieved somewhat of a plateau in advancement. Yet materials performance in extreme, corrosive environments is of paramount importance to many energy applications. Panelists questioned whether this plateau was defined by the limitations of available characterization tools and that advances in spatially and temporally resolved measurements and in coupled models could move the field beyond this plateau. The emphasis of this PRD included corrosion under extreme environmental conditions.

Comparison of initial PRDs among the eight panels showed many common themes. The panel on *Extreme-environment tolerant materials by design:* also identified a corrosion-related PRD, entitled "materials design for resistance to corrosion under irradiation" with obvious overlap with PRD #3 above. What resulted was an integrated PRD on "Materials design for resistance to corrosion and surface damage in extreme environments." Similarly, "rapid materials design and synthesis" is synergistic with "accelerating materials discovery". On the one hand, there was a focus on reigniting the capability to synthesize materials – particularly test specimens – for new materials discovery, while on the other is a need for enhanced design and combinatorial tools to accelerate materials discovery.

In what follows, brief summaries of each of the four focus areas (radiation-matter interactions for fission and fusion, radiation-matter interactions for energy conversion, matter interactions in extremes, and cross-cutting challenges) are presented. As illustrated above, the breadth and diversity of these deliberations ultimately gave rise to a set of 15 priority research directions, spanning the full breadth of the workshop. The report ends with a conclusion that summarizes the main messages of the workshop is provided. Workshop participants agreed unanimously that focused effort on these priority research directions, including the development of capabilities needed to achieve success, would significantly advance our ability to predict and control materials performance in extremes.

**Panel Summary: Radiation Matter Interactions for Fission and Fusion**

The reliable performance of structural and fuel materials is central to extending the life of the current fleet of light water reactors and enabling the next generation of fission and fusion reactors. Experimentally-validated, multi-scale models are a key ingredient to realizing this potential. Capabilities are needed to expose materials to well characterized and controlled, extreme environments and simultaneously probe, measure, and manipulate interfacial reaction kinetics, transformations, and mechanisms associated with their performance.

*The Importance of Material Performance to Nuclear System Performance*

Adequate response to the significant demands on fuel and structural materials is critical to the performance of any nuclear system, either fission or fusion based. Improvements in materials science and technology will support the continued safe performance and extended lifetimes of existing light water reactors, enable building of new extended life light water reactors, advanced fission concepts, or fusion-based systems, and support a sustainable full recycle fuel cycle [1-3].

Currently, 432 light water reactors (LWR) generate 382 GWe, or about 16% of worldwide electricity demand. Doubling worldwide nuclear electricity production to 32% by 2100 will require generating about 5000 GWe, or about 4000 reactors worldwide. To take advantage of the existing LWR infrastructure in the United States, many reactor operators plan on extending the life of existing light water reactors to 60 and possibly 80 years. Operations to these extended times present challenges to materials, specifically degradation of thermo-mechanical properties and extended corrosion attack, requiring an accurate forecast of material properties beyond the current understanding. The ability to accurately forecast behavior is integrally linked to the scientific underpinnings of both radiation and corrosion material science.

In current LWR technology, <12% of the initial natural uranium is used in a reactor. The rest of the material and its associated potential nuclear energy content are relegated to nuclear waste. Existing spent nuclear fuel from LWRs could supply 75 TWe-yrs, which represents the entire U.S. electricity demand from now through 2100. A goal and a challenge are to more fully extract the energy content of nuclear fuel, thus minimizing both nuclear waste and proliferation concerns. The barrier is, to a large extent, directly related to the materials used to contain the fuel—the cladding and its robustness to the higher neutron dose concomitant with higher fuel burn-up in the fast reactor systems envisioned as the heart of a full recycle fuel cycle. To enable increasing burnup of fuels from 20 to 40% in a fast spectrum requires the development of new cladding materials. These new materials must withstand many degradation mechanisms including irradiation creep, low temperature embrittlement, void swelling, and fuel clad chemical interaction to doses up to 400 displacements per atom (dpa). Longer-lasting fuel and structural materials will make it possible to extract more energy from the fuel, reduce nuclear waste, advance the nation's nonproliferation goals, and improve our confidence in the long term safety of the nation's reactor fleet.

*The Challenge of Predicting Material Performance in Nuclear Systems*

The combined irradiation field and high temperatures under which nuclear systems operate can lead to changes in toughness, strength, ductility, fatigue, and creep resistance that shrink the allowed temperature and stress in which materials performance is adequate (Figure 1). Additionally, in a corrosive environment, materials can be attacked, leading to cracking and mass loss. The specific effects depend on the exact combination of temperature, stress, irradiation flux, and environment (corroding media), Figure 2. It is not possible to do experiments that simulate 80-years of irradiation damage and corrosion in a practical time frame. Approaches that accelerate the transition from the observation and validation of performance to the prediction and control of functionality through materials discovery and science-based certification remain grand challenges. A particular challenge is the ability to make (and model/interpret) measurements of relevant phenomena in irradiation environments of interests and thereby advance fundamental understanding and predictability beyond traditional approaches. Therefore, materials scientists will need to rely on theory, simulation, and modeling, validated by well-posed experiments to predict material behavior. As presented in Figure 3, this theory, simulation, and modeling must

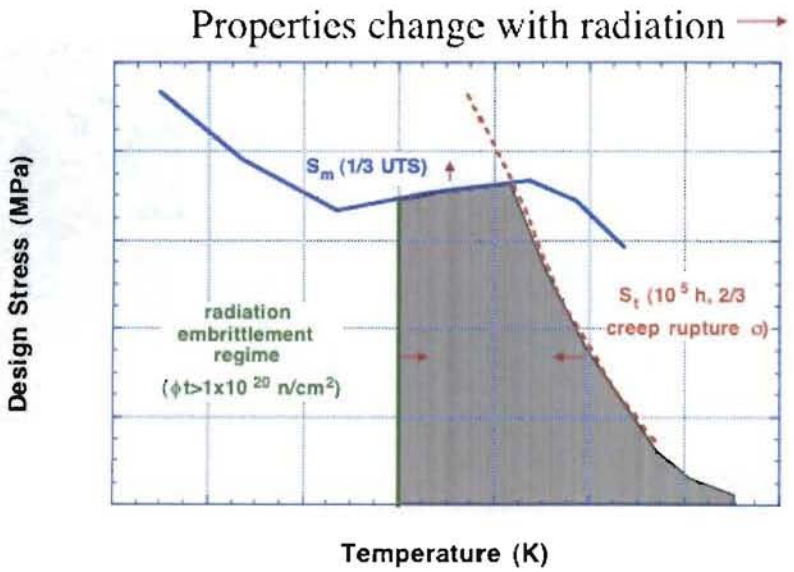


Figure 1. Each material has properties that allow it to be used in certain temperature and stress ranges and these are changed by irradiation. (Adapted from [4])

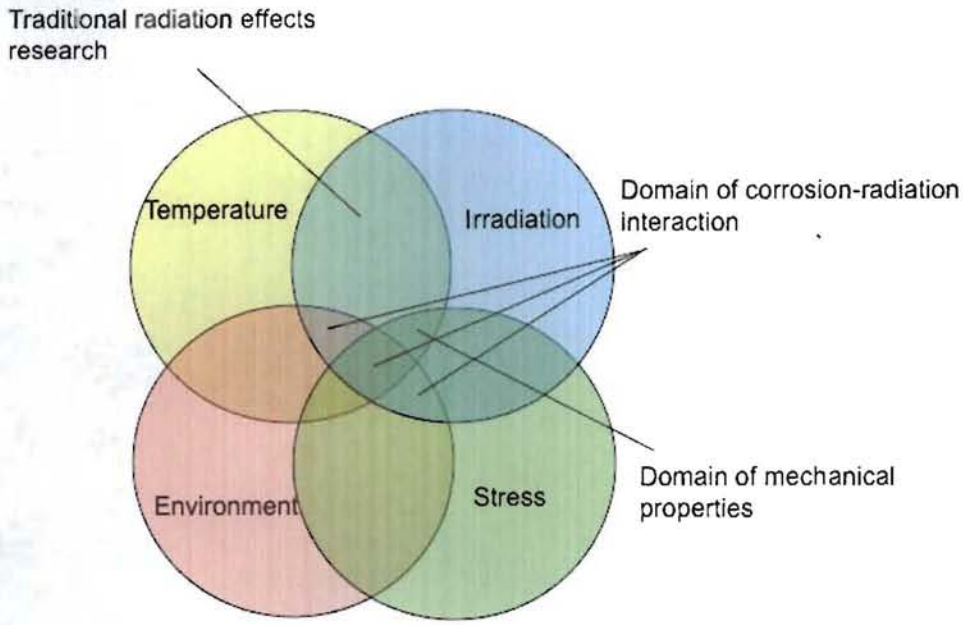


Figure 2. Radiation effects are a unique combination of temperature, stress, irradiation, and environment.

be developed on three general scales: 1) bulk material properties (strength, corrosion resistance, thermal conductivity, dimensional stability), 2) microstructure, and 3) atomic-scale unit processes. Information from the atomic-scale processes is required to understand the development of microstructures and the specifics of the microstructures determine the bulk properties. Developing the ability to predict and control the material response at each level would allow for the extrapolation of material properties beyond the existing database and control of materials properties through informed design.

As an example, void swelling is a dimensional change that occurs under radiation at intermediate temperatures (roughly 30-50% of the melting temperature of a material) -- Figure 4, left image-- and must be managed either through material replacement or material improvements. The amount of swelling is controlled by microstructural developments, specifically the nucleation and growth of voids and dislocation loops, at the mesoscale, (Figure 4, right image). Accurate prediction of the microstructural development requires a knowledge of many key processes that occur at the atomic level including the creation of radiation-produced point defects, transport of defects and atoms through the material, nucleation and growth of mesoscale defects, and interactions with sinks, as shown schematically in Figure 5 for the phenomena of radiation embrittlement and stress corrosion cracking. Understanding many of the phenomena shown in

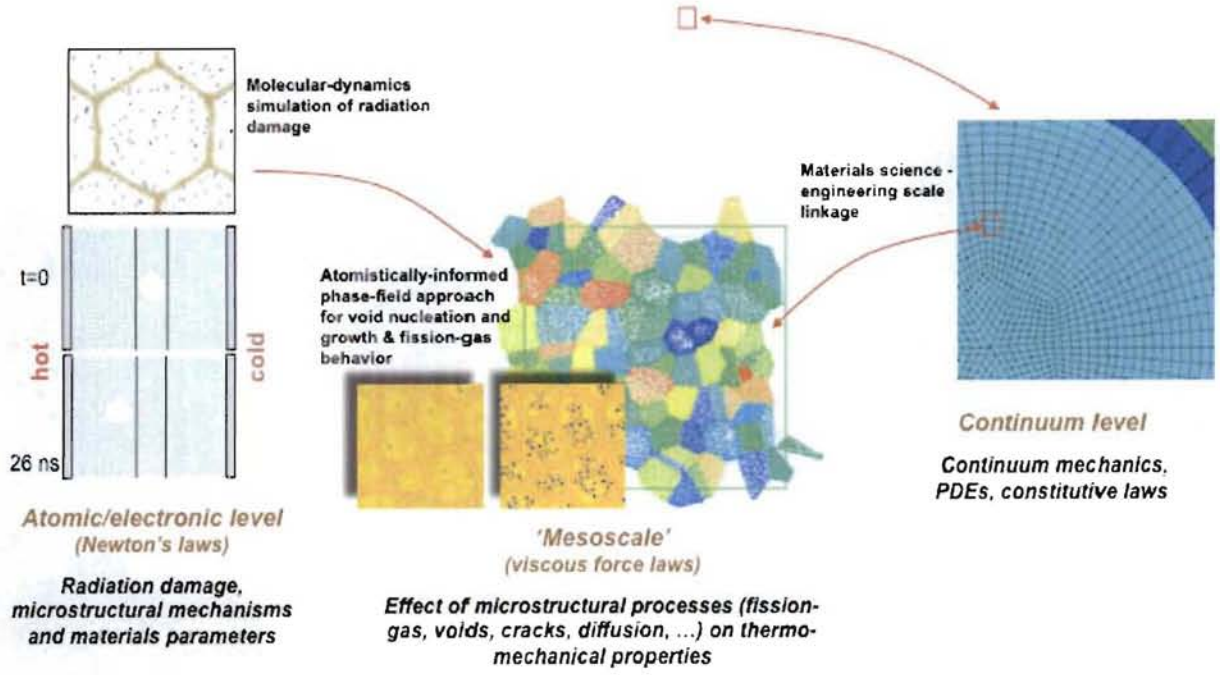


Figure 3. Material properties (continuum level) are determined by microstructural features (mesoscale), which form due to interactions at the atomic and electronic level.

Figure 5, such as point defect and atomic transport and radiation-induced segregation, is also critical in predicting other radiation-induced effects such as creep or void swelling.

For example, experiment and modeling have shown that void growth can be changed by radiation-induced segregation to the void surface and that radiation-induced segregation in austenitic iron-base materials is a strong function of bulk composition [5,6]. Therefore, to properly model radiation-effects requires understanding how structure, composition, and strain affect activation barriers in non-dilute, multi-component, crystalline solids. This is necessary to determine the complex interplay between structure and composition. Critically, all these atomic-scale effects (unit processes) occur concurrently, so establishing methods for understanding the concurrent development of many unit processes is critical to understanding the microstructure and thus bulk properties. Material solutions need to be designed to control deleterious radiation response.

One possible design to control radiation response is the use of selected interfaces to mitigate radiation damage [7-10]. Interfaces with low formation energy of vacancies and interstitials, high excess atomic volume and high density of misfit dislocation intersections are expected to be good sinks for radiation-induced defects. Thus, it should be possible to design materials with a high density of special "super-sink" interfaces to have a tailored response in extreme conditions of irradiation, stress and temperature.

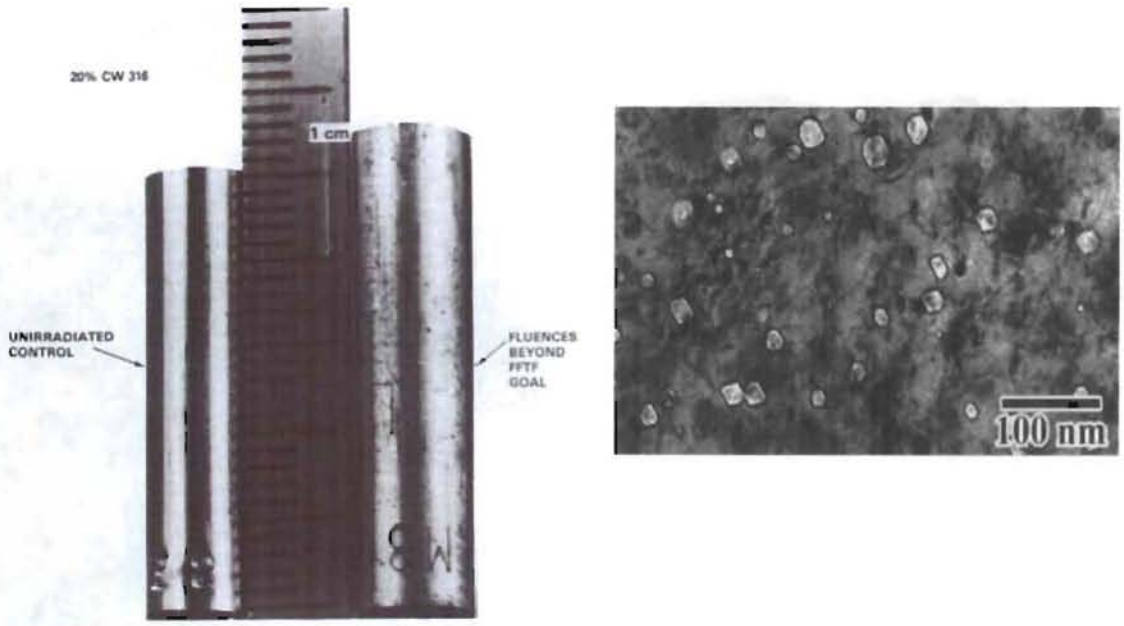


Figure 4. Swelling of an irradiated material (left image) and the underlying microstructure, a collection of voids (right image), which lead to the swelling. (After [11].)

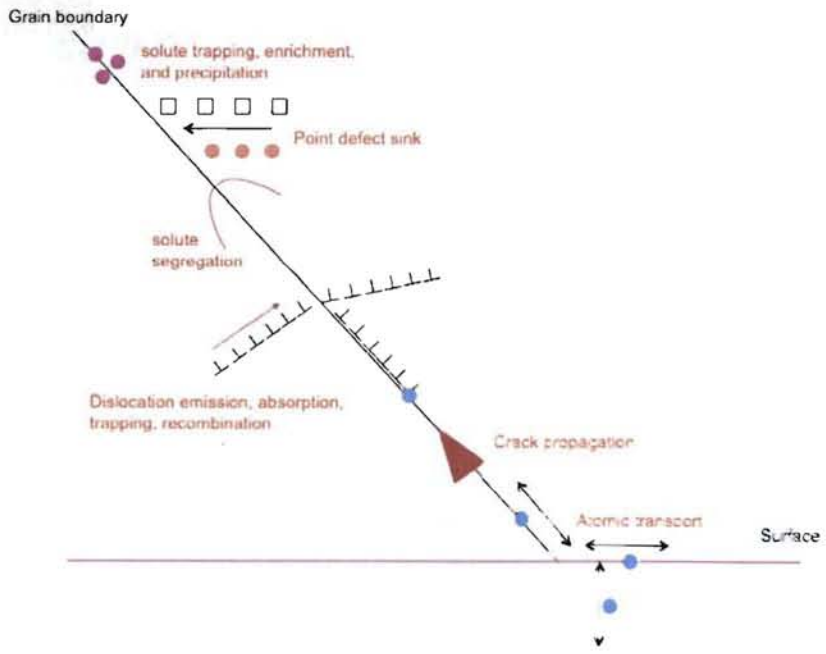


Figure 5. Many atomic scale interactions occur that lead to changes in microstructure [1].

*Tools for Studying Radiation Matter Interactions for Fission and Fusion*

Capabilities are needed to expose materials to well characterized and controlled, extreme environments and simultaneously probe, measure, and manipulate interfacial reaction kinetics, transformations, and mechanisms associated with their performance. These data and tools are essential to replacing empirical and database driven predictive models with knowledge-based models for design, prediction and control of performance, and prognostic health monitoring of materials targeted for use in extreme environments.

Unit processes, such as defect-interface interactions, strongly influence the material properties and irradiation stability of materials. For example, interfaces block slip and lead to unusually high strengths in materials with nanometer-scale spacing of interfaces. Interfaces also act as sinks for radiation-induced point defects and impurity atoms such as helium. The atomic structure of the interface is crucial in determining the number density of sites that are traps for defects and the formation energy of point defects at interfaces.

Understanding either a unit process or collective effect requires the proper tools to interrogate the proper length and time scale. Observation in-situ could significantly improve the ability to observe effects like defect production, diffusion, and nucleation. Recent advances in capability are greatly improving the ability to provide quantitative information on smaller length and time scales [12].

While many radiation effects of concern are initiated by collision between lattice atoms and high-energy neutrons, a significant amount of radiation damage in solids occurs between charged particles. Atom-atom collisions in damage cascades or interactions with fission products are two examples. Additionally, radiation interactions in liquid media can also be initiated from high-energy photons (gamma particles). Therefore, an understanding of radiation effects requires multiple tools, including test reactors, ion and electron beam facilities, and photon sources.

Typical neutron irradiation experiments in test reactors require 1-2 years of exposure in core. However, this is accompanied by additional time for capsule design and preparation as well as disassembly and cooling. Analysis takes additional time because of the precautions and special facilities and instrumentation required for handling radioactive samples. The result is that a single cycle from irradiation through microanalysis and property testing may take between 1 and 6 years. Such a long cycle length does not permit for rapid iteration on irradiation or material conditions that is a critical element in any experimental research program. Neutron irradiation is a necessity but scientific understanding can be accelerated through the complimentary use of ion beam, electron beam, and photon techniques.

In contrast to neutron irradiation, ion (heavy ions, light ions or electrons) irradiation frequently enjoys considerable advantages in both cycle length and cost. Ion irradiations of any type rarely require more than a few tens of hours to reach 1-5 dpa levels. Irradiation produces little or no residual radioactivity allowing handling of samples without the need for special precautions.

These features translate into significantly reduced cycle length. Ion irradiations can often be performed at a much lower cost per sample and in a much faster irradiation and analysis time The single energy beam energy is also suitable for controlled experiments to determine an understanding of unit effects.

The capabilities of ion irradiation, including in-situ techniques such as transmission electron microscopy, sliced pulses from synchrotron light sources, or optical techniques such as luminescence, are currently attractive in research on nuclear materials including advanced structural alloys (model and engineering), waste storage ceramics and glasses, and model fuel alloys. A strength of in situ work is the discovery and illumination of fundamental dynamic processes such as point defect clustering, dislocation loop formation, loop motion, coalescence and interactions with existing surfaces, interfaces, and microstructure, all processes that need to be understood in moving toward predictive capability of radiation stability. Additionally, ion beam techniques can be credibly adapted to include the study of synergistic interactions between radiation and environment (corrosive media in a light water reactor or plasma in a fusion system).

Additionally, there are certain cases where the phenomena of interest are the ion-matter interactions directly. For example, nuclear fuel is exposed to damage from fission fragments. These heavy projectiles with typical energy of 100 MeV produce radiation damage (tracks) that has significant different characteristics compared with defects produced by neutrons or low-energy ions in the elastic collision regime. The interaction is based on pure electronic excitation processes. Tracks formed predominantly in insulators (and only in a few selected metals) consist of amorphized or otherwise modified extended damage structures. Heavy ions irradiations could help to overcome existing problem of limited dose accumulation, however better understanding of common effects and differences in resulting defect phenomena of swift heavy ions compared to neutron and low-energy ions is mandatory.

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**Panel Summary: Radiation Matter Interactions for Energy Conversion**

The success of future energy technologies demands materials with significantly higher performance and functionality. The limits of today's materials are not imposed by intrinsic constraints: performance is often a factor of ten below theoretically possible levels. Instead, materials are limited by our knowledge and control of the structural and electronic features that govern their behavior.

*The multi-scale challenge*

Although performance and functionality are manifested at macroscopic length scales, their roots reach down to the microscopic and nanoscopic domains. Macroscopic behavior is the visible outcome of a hierarchical network of structure and dynamics that spans multiple length and time scales. Our ability to understand macroscopic behavior, therefore, is ultimately dependent on our ability to observe and connect the links in the hierarchical chain of structure and dynamics starting with atoms and femtoseconds and ending with macroscopic properties like mechanical elasticity, electrical conductivity, and optical transparency.

The past decade has seen remarkable advances in the resolution and sensitivity of experimental probes of structure and dynamics, to the point that we can now imagine observing the key links in the hierarchical chain relating macroscopic behavior to its micro- and nano-scopic origins. Such observations of the development of electronic and structural behavior at each length and time scale would mark an enormous leap toward understanding macroscopic performance and functionality.

There are, however, vital elements that remain to be implemented. Much of our observational information comes from "before and after" measurements, where we must infer a dynamic process from snapshots capturing static structure at isolated times. Often the snapshots must be taken under prescribed laboratory conditions that do not reflect the actual temperature or other environmental conditions that are central to the process. We need instead in situ measurements that watch the dynamics of the process in real time (i.e., "during" measurements), revealing the evolutionary pathways and the causal relationships that mediate them.

A second vital element is bridging the gap between length scales. For example, the propagation of light as a surface plasmon at a metal-dielectric interface is governed by interfacial structure on the scale of the wavelength, where the atomic composition and structure that determines interfacial behavior is invisible. A new macroscopic phase develops from a few microscopic nucleation sites, whose structure and dynamics are lost quickly as the new phase emerges. The output of theoretical descriptions and experimental probes for each of the relevant length scales must be interpreted within an intellectual framework connecting behavior at each scale to the neighboring scales above and below.

Dramatic advances in in situ observational tools and theoretical models linking length and time scales bring within reach a full understanding of the hierarchical chain linking macroscopic performance and functionality with micro- and nano-scopic structure and dynamics. Observation and understanding are not enough, however. To create new materials with superior performance and functionality we must make the transition from observation and understanding to prediction and control. This transition is achievable, using the advances in nanoscale fabrication of the last decade. Molecular beam epitaxy, atomic layer deposition, high-resolution lithography and directed self-assembly allow exquisite control of atomic and nanoscale architectures. Extreme environments such as high pressure, high flux irradiation with photons or particles, and high chemical corrosivity offer new levels of control over bulk synthesis of crystalline and disordered materials. Linking prediction based on in situ observation and understanding with control based on nanoscale fabrication and synthesis sets the stage for pursuing and achieving the decadal challenge of creating new materials with significantly higher performance and functionality.

*Accelerating Materials Discovery and Control of Nucleation*

The vision of "materials by design" is now three decades old and many important advances have been made toward realizing this vision. However, these have generally been materials "designs" with limited stretch beyond an existing, proven example. The grand vision of starting with a blank sheet and ending with a functioning material remains elusive. In addition to the broader elements of this vision of materials design and lifetime prediction, and rapid materials design and synthesis, two specific challenges, corrosion science and controlling nucleation phenomena, were identified as critical shortcomings of the current state of "predictive design, discovery, and growth of new materials."

Nucleation, for instance, is a fundamental process step contributing to – if not in some cases controlling – many microstructural development and failure processes. Fatigue fracture and phase transformations are largely controlled by nucleation. Yet, the theory of nucleation, in the case of phase transformations or solidification, has advanced little beyond that contained within the well-known Johnson–Mehl–Avrami–Kolmogrov equation. Innovative measurements of nucleation events – particularly using TEM and SANS – have been published but measurements are lacking at both the spatial and temporal scales necessary to understand the fundamentals of nucleation. New measurements are required both to validate theories and to spawn new theoretical studies.

Corrosion science also has achieved somewhat of a plateau in advancement. Yet materials performance in extreme, corrosive environments is of paramount importance to many energy applications. This plateau is defined, at least partially, by the limitations of available characterization tools; advances in spatially and temporally resolved measurements and in coupled models could move the field beyond this plateau.

*Light-matter interactions*

The interaction of light with matter is a promising two-way street for concentrating and shaping light through photonic crystals, plasmonic interfaces and metamaterials, and for controlling matter with light pulses that direct the course of chemical reactions and trigger phase transitions or other material responses. Both directions of light-matter interactions are in their infancy, with remarkable new phenomena like perfect absorption, perfect imaging, and quantum control of chemical reactions illustrating enormous promise for opening qualitatively new horizons.

The explosion of interest since 2001 in the classical behavior of light described by Maxwell's equations with negative permittivity and permeability has revealed a host of previously unexplored phenomena including total absorption of light, imaging below the diffraction limit of conventional lenses, and bending light along prescribed pathways in materials with a graded index of refraction. These new phenomena enable an equally remarkable array of applications, such as high efficiency solar energy absorbers, imaging with sub-wavelength resolution, cloaking of objects by bending light around them, optical lithography, high gain antennas, and high sensitivity sensors. The principles and techniques of metamaterials are now being applied beyond light to acoustic waves, opening rich opportunities in high-resolution ultrasound imaging, non-destructive structural testing, and novel underwater stealth technology [1]. The successes of metamaterials have been achieved with two-dimensional arrays of nano- and micro-scale split ring resonators, which introduce negative permittivity and permeability near resonant frequencies related to their physical size and configurational pattern. A primary challenge (Figure 6) is to reduce the size of the resonators to access the visible light regime. This requires new techniques for lithography at smaller length scales, and development of new materials and nanostructures with high frequency magnetic response that can be configured by self-assembly. A second challenge is to broaden the bandwidth of negative index of refraction response and to reduce its dependence on angle of incidence. This requires extending the two dimensional arrays to three-dimensional architectures and introducing controlled variation in the response and arrangement of the resonant elements.

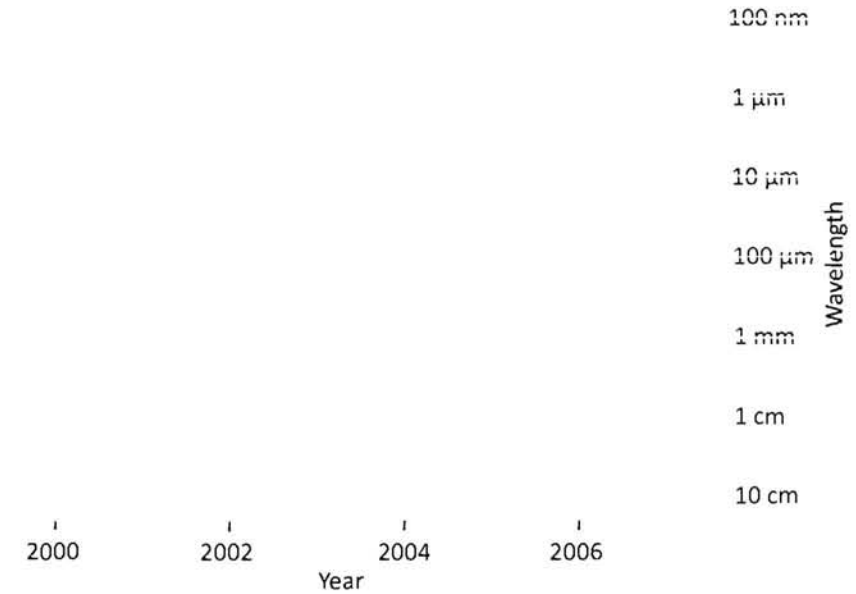


Figure 6. Advances in metamaterials. Black symbols denote negative index of refraction, red symbols denote negative permeability. Images indicate the sub-wavelength resonant structures used to control the electromagnetic response of the metamaterial. After [2].

Photonic crystals and interfacial plasmonic phenomena offer similar opportunities to manipulate light using diffraction and interference from wavelength-sized objects rather than the negative index of refraction of an effective medium composed of much smaller resonant elements [3-5]. The ability to guide, trap, reflect and intensify light from designed two- and three-dimensional structures enables applications for manipulating light with the richness and impact of semiconductor electronics. Examples include significant improvement in fiber optics for communications, high speed, low dissipation optical switching, computing with light instead of electrons, and optical data storage. Concentrating light of selected frequencies at fixed locations offers a host of opportunities for high efficiency solar photovoltaics and photochemistry. Enhanced electric fields at plasmon interfaces, up to a factor of $10^5$, promise chemical and biological sensing with single molecule sensitivity and intriguing opportunities for the electrochemical promotion of chemical reactions. The challenges are experimental exploration and understanding of the fundamental phenomena of light propagation in structured materials, and the fabrication of two and three-dimensional designed architectures to produce targeted manipulation of light.

Metamaterials, photonic crystals and surface plasmonics use Maxwell's equations and the wave nature of light to manipulate its behavior. In contrast, coherent control uses the quantum nature of light to manipulate the behavior of matter. In the quantum regime, the state of matter is described by ground and excited state energy landscapes. Photons of the right energy can drive the system into excited vibrational, structural and electronic energy landscapes that decay into a variety of final states. For example, acetophenone, $C_6H_5C(O)CH_3$, may photodissociate into $C_6H_5CO + CH_3$ or into $C_6H_5CH_3 + CO$. Subsequent pulses following the initial excitation are applied to control which outcome is achieved. Depending on the pulse sequence, either dissociation outcome can be maximized.

The concept of quantum control is illustrated in Figure 7, showing an excited state potential energy surface for a chemical or condensed matter system [6]. The reaction coordinate can be manipulated by injecting energy through tailored pulses at key points on the trajectory, driving the system to targeted locations where it will decay into desired reaction products or ground states. The new ground state could have, for example, a new crystal, magnetic or electronic structure. Coherent control has been demonstrated for over 50 systems including the dissociation of complex molecules, energy transfer in artificial photosynthesis, ultrafast optical switching, molecular rearrangement and chirality, electronic states in quantum dots, and the metabolism of biological molecules and cells. Because the effect of the external pulse on the potential energy surface cannot in general be calculated, successful pulse sequences are determined experimentally by learning algorithms based on systematic variation of pulse parameters. The success rate is impressive - of order 100 iterations of pulse parameters is enough to produce ±15% or more change in the balance of dissociation products.

Figure 7. The potential energy landscape of a chemical reaction as a function of reaction coordinates such as atomic position and orientation. Injection of tailored light pulses at critical points along the reaction trajectory selects targeted outcomes.

Despite its early successes, coherent control of chemical and condensed matter systems is in its infancy. Each situation presents its own special challenges, which often must be addressed without the benefit of experience. The iterative learning algorithms for shaping control pulses positively affect outcomes, but there is no standard for judging their success relative to a theoretical "best case scenario". As light pulses become faster and more flexible in frequency and phase control, the limits of coherent control will expand. The pulse shape and sequence that works, however, is still an empirical activity. Often the successful pulse shapes and sequences are impossible to interpret in terms of excited state potential energy landscapes and reaction coordinates, the first step toward being able to *design* a pulse sequence for a targeted outcome. The potential for coherent control is enormous, including eliminating expensive or rare catalysts like platinum in sustainable energy conversion reactions, controlling the synthesis of new high performance functional materials, and directing the solar splitting of water or carbon dioxide and its recycling to chemical fuel. Controlling the outcomes of chemical reactions, the properties of condensed matter systems, and the functionality of complex materials is a decadal challenge with high potential payoff for science and technology.

*Electronic functionality from complexity.*

The development of semiconductor electronics based on silicon is one of the primary scientific and technological triumphs of the 20th century, with life-changing impact at low cost on nearly every aspect of our personal, commercial, social and political lives. The foundation of this triumph, however, is the simplicity of silicon as an electronic material. It has two robust states, conducting and insulating, that can be switched reliably with a simple voltage. The functionality of silicon electronics comes from the complexity of large, intricately connected networks of transistors contained on tiny integrated circuit chips that transform the simple on or off states of millions of silicon transistors to sophisticated computational and decision making information machines.

For electronic functionality beyond information processing, a qualitatively different kind of electronic material is needed. Energy conversion among photons, electrons and chemical bonds requires electrons to be available in the energy states needed for excitation by a photon, for electron transfer between atomic orbitals in a chemical reaction, or for carrying electric current without loss in a superconductor. These electronic functionalities depend on strong interactions of electrons in a given system across the system boundary with states of nearly the same energy in an adjacent system. Various couplings among spin, charge, and lattice degrees of freedom are often key ingredients.

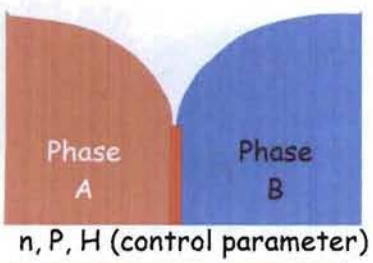


Figure 8. Superconductivity at the interface of two insulators. After [7].

An iconic example of surprising functionality arising from the interaction of closely spaced electronic states is illustrated in Figure 8: a superconducting phase appears at the interface of two insulators, $LaAlO_3$ and $SrTiO_3$. The superconductor has nothing in common with the insulators: it is neither a variation on nor an average of the two adjacent insulating states. In spite of its dramatic difference from its neighbors, the superconductivity is completely dependent on them, appearing only in the narrow interfacial region where the energy levels of the two insulating states interact.

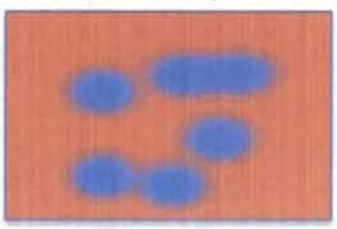

Figure 9. The competition between two phases (upper panel) can trigger fluctuating or static nanoscale phase separation (lower panel), or the emergence of an entirely new phase unlike either of its parent phases as in Figure 8.

This emergent interfacial state is an example of the rich variety of electronic behavior arising from competing phases, illustrated

in Figure 9. At the phase boundary between A and B, at least three distinct behaviors can occur. There could be a conventional phase transition, with A transforming to B sharply. If the system is inhomogeneous in the control parameter (e.g., composition) parts of it will transform before the rest, creating a mixture of two phases. Even if the system is perfectly homogeneous, however, two phases with equal energy can spontaneously phase separate, with the scale of the phase separation depending on the surface energy of A in B and B in A. A third possibility exists as well, that an entirely new phase will emerge at and near the boundary, unlike either of the parent phases.

Guided by these examples, we propose a new paradigm for electronic functionality emerging from electronic complexity. The necessary ingredients are closely spaced energy levels allowing the system to sample many levels under the influence of thermal or other environmental energies such as electric or magnetic fields or reaction with environmental reagents. The system is therefore energetically "soft." A second ingredient is interaction with closely spaced levels in a phase with different order, for example phase A might be a metal and B a magnet or insulator. The interaction of closely spaced levels from different ordered states provides the variety needed to break the symmetry of the ordered phases. A third ingredient is correlation, making the energy level structure dependent on the occupation of the levels. Correlation swings large energies with small changes in occupation; this provides a driving force for emergent phases with very different hybridized energy level structures to have decisively lower total energies.

These ingredients allow a diverse variety of emergent responses. The system can have a hierarchy of long and short range interactions, the former providing structural robustness and the latter "hot spots" of local functionality. The system can acquire a dominant physical response, such as superconductivity or a large susceptibility, or it can break into "chambers" with distinct functions that pass energy or charge from one to the other in sequential operation like an assembly line. Sequential operation is a signature of biological systems, where the division of cells, the replication of DNA, or the folding of proteins is elaborately choreographed by subtle changes in energy levels. Other features of biological systems, such as self-healing, ageing, and learning, might be introduced through repetitive cycling through closely spaced energy states with feedback to subtly alter the states.

The paradigm of closely spaced electronic energy levels interacting across competing ordered phases with significant correlation energy offers a host of opportunities for emergent functionality born of electronic complexity, in close analogy to biological functionality born of structural and chemical complexity. The decadal challenges are to develop integrated capability, including theory, modeling, synthesis, and characterization, to create prescribed electronic energy landscapes by assembling multiscale hierarchical atomic and molecular patterns, to identify the relevant degrees of freedom and length scales for controlling macroscopic functionality, and to develop a quantitative framework to relate nanoscale complexity to robust macroscale functionality.

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**Panel Summary: Matter Interactions in Extremes**

The scope of matter interactions in extremes spans the frontiers of compression science, including new chemistry enabled in extremes and the regime of warm dense matter. In all cases the ability to reliably and precisely access the extreme environment and to then be able to perform in-situ measurements at appropriate spatial and temporal scales remains a grand challenge.

**Frontiers of Compression Science**

The influence that compression science has had on national security science and its manifestation through discovery and application cannot be overstated. In addition to supporting the certification of our nuclear stockpile in the absence of underground testing and a broad spectrum of engineering and defense applications, compression science has altered our view of the material world around us. The discovery of unexpected physical and chemical phenomena and new materials through the application of compression science techniques has led to a new and refined understanding of the nature of chemical bonding in extreme environments. However, it is clear that many important aspects regarding the response of materials to compressive loading are still not understood, let alone modeled in a predictive mode. As a result, we have not derived the many benefits that a predictive understanding would bring. The scientific needs that are required to achieve full understanding and that ultimately support our ultimate goal of moving from *"observation to control"* have been documented in a recent report [see Appendix].

Making progress on these challenges will require a suite of new experimental tools and diagnostics as well as a suite of conceptual frameworks and theoretical constructs. The suite of experimental tools must include the development of diagnostic capabilities, such as next generation light sources, for peering into and achieving time-resolved measurements in compressed materials at the lowest relative length scales while simultaneously characterizing them at higher length scales. The theoretical suite must include new frameworks of computation that will allow the incorporation of the stochastic nature of matter, as well as the ability to accurately describe the essential physics without the invocation of phenomenological models, while linking the atomistic to the continuum response. Progress on these challenges will not only allow us to develop a full understanding of compression science, it will create an environment in which we can train the next generation of scientists and provide them with the tools needed to make progress and move from studying "ideal" to "real" materials.

**New Chemistry in Extremes**

The electronic structure, bonding and chemical reactivity of atoms is fairly well understood under ambient conditions. However, the rearrangement of atomic levels induced by compression can result in radically different reactivity, bonding and structure. For instance a metal such as sodium can become a transparent insulator; simple molecular systems such as $O_2$ become metallic superconductors; and a greenhouse gas such as $CO_2$ can become a solid with novel

optical properties. Such results point to the existence of a "new" density-dependent periodic table, whose control and exploitation still require a deeper fundamental understanding of the effects of density on atomic and chemical bonding. Key scientific challenges include the prediction and creation novel chemical states at extreme PT while understanding the effects of P and T on atomic structure, bonding, and reactivity; utilizing Gbar pressures to induce core-electron "kilovolt" chemistry; and to use matter/radiation coupling in concert with P and T to control chemistry and reactivity.

Such challenges will require new computational tools for describing electronic structure and thus enable a predictive capability of chemical reactivity and bonding, over wide ranges of P and T. These challenges will also require the continued development of ultrafast *in situ* diagnostics in order to observe bond breaking/formation, local energy populations and their redistribution, stoichiometry, kinetics, and to observe the production and effects of short-lived transient states. However, our current ability to control thermodynamic states with the necessary precision over a large range of T, P, and strain rate is limited, and we do not currently have the time-dependent spectroscopic diagnostics capable of *in situ* (sub-surface) probing of extreme conditions at high spatial resolution. We must continue to develop time-domain diagnostics for extreme chemistry, and to move beyond existing theories to overcome the theory/experiment timescale gap.

**Warm Dense Matter**

The dynamic behavior of materials depends on transport coefficients that relate fluxes of state variables (energy, momentum, and mass) to their gradients. Under extreme conditions the order parameters that define condensed matter change, fail, or disappear, and no longer apply to describe materials and their dynamics behavior. These conditions, have relevance to inertial fusion, stockpile stewardship, or stellar explosions, and have significant uncertainty because of these complex dynamics. Creating the extreme conditions of matter, while simultaneously measuring its state variables with sufficient spatial and temporal resolution to determine gradients and fluxes is a scientific frontier challenge. Developing theory that can explain the material behavior in these new conditions where the usual order parameters fail is the other major research need.

Recent advancements in intense, pulsed light sources provide revolutionary capabilities to subject matter to extreme conditions of pressure and temperature, creating novel conditions that span all the way from solid state to weakly coupled plasmas. Those sources also provide new powerful tools to diagnose those novel conditions. The state of matter between the solid state and weakly-coupled plasmas is known warm dense matter (WDM). Understanding the nature of WDM is one of the fundamental goals of the physical sciences associated with laboratory astrophysics, planetary dynamics, evolution of stars, and energy technologies. WDM is extrememly challenging to model, because the typical approximations (e.g., expansion parameters) used in either solid state or weakly-coupled plasmas are not applicable. Creating and diagnosing WDM is very difficult for several reasons, such as its transient nature, the need for

dynamic measurements, and the difficulty in creating sufficiently large and homogeneous samples. Understanding WDM is important in basic science (e.g., to understand the nature of giant planets) as well as in applied science (e.g., in understanding material behavior and equation of state in shocks and explosions, laser-matter interactions and non-linear optics, inertial fusion energy, etc.).

**Panel Summary: Cross Cutting Challenges**

Although a few examples exist of quantitative approaches to transitions from (empirical) observation to (quantitative) control, generalizing this transition will require substantial developments in characterization, analysis, modeling, computation and design of (critical) experiments. The magnitude of task has the potential to be a challenge on a decadal timescale and, in particular, suggests the need for multi-scale modeling. Successful development of the required models will likely be achieved by creating an experimentally-validated framework that spans spatial and temporal scales through an integrated approach that moves beyond the passing of parameters between distinct models at distinct scales.

**Decadal Challenges in Materials Development**

Materials science and engineering is at a crossroads, moving from the traditional trial-and-error methods of materials development to a new era in which materials will be increasingly designed at multiple length scales simultaneously. This change is enabled by two equally important sets of developments – the remarkable increase in our ability to experimentally probe materials at a wide range of time and length scales, and the concurrent, and equally remarkable, advances in computational capabilities and algorithms that enable modeling and simulation to describe and predict materials properties and response with unparalleled fidelity. Materials science is clearly moving from its current state as an observational science with empirical development of materials, to one in which we can design and control materials behavior. Accordingly, we need to re-think our approach to both hypothesis-driven research and goal-oriented development.

Four main areas were identified that challenge both experiment and simulation:

- Heterogeneous materials
- Bridging length and time scales
- Developing closer integration of modeling and experiment
- Developing materials design tools to manage complexity

There is a flow of these topics, from developing experimental and simulation probes of complex structures, to adding variations of length and time, to developing truly integrated experiment/simulation, and finally to the primary goal of the "observation to control" theme of this workshop, the creation of the ability to design materials across scales of length and time.

*Heterogeneous Materials*

Heterogeneities Driving Tails in Distributions

Materials in technological use have always been heterogeneous, with ranges of disorder in composition and structure. These heterogeneities occur across scales, from local atomic disorder at the nanometer level to microstructural features at the many micron level. They may involve many phases or just one, but with many orientations. What is changing is our ability to design

heterogeneities at all scales, through a range of processing paths, with desired functionalities. Many challenges remain, however, in our understanding of the role that heterogeneities play in determining materials response, especially under conditions outside the norm. To control those functionalities will require an understanding of the relations between the global properties of a heterogeneous material and the local properties of its homogenous phases. A critical gap in the current approach is it is often not recognized that obtaining the global properties is not simply a matter of computing a suitable average but may, in fact, depend on the upper tail of a distribution. This is particularly true of materials properties such as corrosion resistance, fatigue resistance, spall resistance and almost any property related to damage evolution. Moreover, we will need to predict the evolution of structure and response of these complex materials in dynamic environments.

Defect-driven variability in material response:

When materials are exposed to extreme environments (radiation, high temperature) or pushed under extreme mechanical conditions (long term fatigue, shock), the statistical variation in material failure response among seemingly identical specimens increases substantially. In these cases, the variability in response is so significant that the usual Gaussian statistical analyses that calculate mean and standard deviations are not adequate descriptors. When material response exhibits so much uncertainty, reliability in material performance in extreme environments and conditions (no matter how strong or tough the material may be in less challenging circumstances) is compromised. Approaches to reducing the uncertainty begins by first understanding how it originates, followed by the ability to predict it, and ultimately to control it.

Experimental probes

Diffraction methods are increasingly important to both 2- and 3-D characterization of heterogeneous microstructure. Innovations in x-ray and electron diffraction methods have largely driven this area through advanced user facilities such as the Advanced Photon Source for high energy x-rays and high resolution orientation scanning in the electron microscope. Nevertheless, the Vulcan facility at the Spallation Neutron Source is likely to offer new capability for neutron diffraction in the coming decade. Combining different techniques both within each area and between the two main methods may offer substantial synergistic advantages. *Comparisons of computed fields with measured ones are likely to provide valuable feedback on the importance of the intrinsic elastic properties of grain boundaries, perhaps unaccounted for in the computer simulations. And other comparisons can be envisioned that would strengthen both experimental and computational results.*

Quantifying material complexity using n-point statistics:

A rigorous framework defining the spatial correlations of local states in the microstructure already exists in the form of *n*-point correlations or *n*-point statistics. These correlations provide a hierarchy of statistical measures of the microstructure that are essentially moments of the

structure function. They preclude the need to select, either intuitively or in an ad-hoc manner, the microstructure metrics of importance in a given application. A great advantage of the use of these correlations is that they can be computed very efficiently using fast Fourier transform (FFT) algorithms. *Ultimately, our goal is to develop a science-based understanding of the properties and performance of heterogeneous materials, especially by considering variations in composition and structures to move from the "ideal" materials of the laboratory to the "real" materials in actual use.*

*Bridging length and time scales*

The impact of extreme values on modeling & simulation

The greatest challenges of materials modeling and simulation arise from the wide range of length and time scales of importance in determining materials properties. Consider first length scales, fundamental to all material structure and response is the bonding between atoms, which is quantum in nature and is typically localized to a few tens of nanometers – that metals are different from ceramics, for example, arises from this bonding. However, the properties at a larger scale, say centimeters, may also depend on structures intermediate in scale, often referred to as the mesoscale. These structures are generally distributions of defects (e.g., dislocations, grain boundaries, …) or phases. The challenge is that predicting properties at any given scale (e.g., the mesoscale) implies understanding phenomena at lower scales (e.g., electronic/atomic). Moreover, for application to many engineered structures, it is critical to create mesoscale modeling with atomistic-level accuracy yet also connected to continuum. As discussed above, often the critical issues are not well described by averages – it is the tails of the distribution that dominate some response (e.g., failure). Again, incorporation of new theories and models of the statistics of extremes is essential.

Scale Bridging:

Accurate, computationally efficient, physics-based scale-bridging relationships are critical to integrating the microstructure features from distinct time and length scales into a cohesive multi-scale modeling framework.

To successfully predict and control, it is imperative to build the following features into scale bridging: (i) the scale bridging has to transmit information accurately in both directions between the length scales. (ii) the scale bridging has to be formulated in such a way that it allows inverse solutions that are central to successful materials design.

Extending the ability of atomistic-level simulations to long times:

Capability in atomistic simulations that can reach time scales of order seconds and beyond is currently lacking. This widely recognized challenge has remained unresolved since the early days of multiscale simulations. Closing the gap requires the demonstration of an atomistic

method (using interatomic potential as an input) that can elucidate behavior such as glassy relaxation and creep deformation response, which are widely acknowledged bottlenecks in the computational materials community.

Corrosion is a ubiquitous phenomenon underlying many scientific and technological challenges. It could be the oxidation of a high-temperature ceramic component in an aircraft engine, or the hydrolytic weakening of quartz in the earth mantle. Regardless of the specificity of the phenomenon one can identify a fundamental process vital to understanding the chemo-mechanics of materials. Suppose the problem for discussion is that of corrosion initiation. The relevant process is then the formation of a passive ultrathin oxide film and its evolution to the onset of structural breakdown. At the molecular level one needs to consider charged defect transport and the role of electron transfer in the aggregation of cation vacancies that eventually lead to film-substrate decoherence and pit nucleation. This is an example of combining unit process (charged transport) to study system-level behavior (film growth). *The decadal challenge is to identify and implement extensive and intelligent combinations of TMS in order to achieve predictive insights into transgranular versus intergranular corrosion cracking in structural materials.*

*Developing closer integration of modeling and experiment*

Integrated Computational Materials Engineering

As discussed in detail in a recent National Academy Report, *Integrated Computational Materials Engineering*, much progress can be made in materials understanding and design by more thoroughly integrating experiment and modeling/simulation. From a modeling and simulation perspective, experimental data serves as part of the validation process, testing the basic physics included in the models upon which the simulations are based. More importantly, experiments serve to help define models, which may then be incorporated into large

As a minimum requirement for their integration, simulations and experiments must yield some of the same quantities (parameters) and access the same length and time scales. Better still, both simulations and experiments should be reasonably efficient to allow multiple (better numerous) measurements to enable active feedback and cross-validation for improved accuracy. Given that properties and performance are defined by material microstructure and its evolution on appropriate scales, future development should be focused on *the microscale frontier*.

Linking Experiments with Theory, Modeling and Simulations (TMS) across scales:

The validity of microstructural level (and lower length scale) theory, modeling and simulation is limited by a lack of close coupling with experimental observations at the same scale. This is particularly true for processes (ranging from very long time aging to high rate dynamical loading) in which the microscopic structure of the material changes with time. Recently, it has become possible to non-destructively measure the grain-scale microstructure in materials used 3D x-ray diffraction (3DXRD).

New tools for analyses of large datasets at multiple spatial and temporal scales.

One of the greatest challenges in materials research is how to best capture the wide range of disparate, yet connected, information that results from modeling and experiment. A new field, materials informatics, is the application of the ideas of informatics to materials science and engineering. Informatics is a field of research in which information science, processing, and systems combine to examine the structure and behavior of information, enabling new ways to access and explore that information. In materials, information comes in many forms, as does the possible use of that information. It should not be surprising that the potential applications of informatics are equally diverse. While progress has been made in applying informatics to materials, many key challenges remain. On the strictly experimental side, our ability to represent complex three-dimensional microstructures is limited [1,2]. How to include more detailed information of structures is unclear. Yet developing correlations between these structures and materials response is critical. Another frontier is to incorporate results from modeling and simulation at one set of scales along with experiment at another scale to yield a richer, more inherently multiscale, description of materials response. These are just two examples of the challenges and opportunities for materials informatics.

*Developing materials design tools to manage complexity*

Uncertainty quantification (UQ)

Usefulness of simulations to material development, insertion and certification is greatly enhanced if simulation errors and uncertainties are quantified. Agreement or disagreement between experimental data and simulations can be firmly established only if errors and uncertainties of both are known. Simulation error and model uncertainty should not be confused. Simulation error is the difference between (the usually) approximate and (asymptotically) exact simulations of the same model. Model uncertainty, on the other hand, reflects insufficient accuracy of model parameters, model incompleteness (e.g. missing mechanisms) or inadequacy of the model itself, irrespective of the quality of numerical simulation. Quantification of simulation errors (verification) may require significant computational effort but otherwise is often relatively straightforward. What it means to quantify the model uncertainty is, however, not well understood. Recent debate on the quantitative significance of Representative Volume Elements and which properties can be demonstrated to remain invariant under repeated instantiations has sharpened the focus of the discussion [3]. Thus, UQ is important not only for enabling more meaningful interaction between simulations and experiments but also for the development of the theory itself. *UQ is a wide open area of applied and computational mathematics where much progress is expected in a near future. Tight integration of theory and experiment is likely to be a major benefactor of the emerging UQ methodology.*

Inverting information flow from performance to structure to processing

Materials design has tended to proceed from the empirically possible to the discovery of plausible applications. Inverting the materials design paradigm so that materials are designed to suit known applications is a first order challenge for materials design methodology in the coming decade. Green's function approaches [1], for example, are inherently highly invertible in terms of moving from homogenized properties or localization, back to the fields of microstructure. *One much needed advance in the study of localization related phenomena in heterogeneous materials would be approaches to develop analytical Green's functions for complex geometries and complex boundary conditions.*

IS&T for Multiscale Materials Modeling and Prediction

The development of a predictive capability for materials performance with a realistic assessment of model and prediction uncertainties is one of the key challenges. Bridging the micron gap" of material properties is essential to addressing this challenge. At length-scales significantly larger than one micron, there are a number of techniques to characterize material response, albeit with averaging over material inhomogeneities and resultant fluctuations in thermo-mechanical response. Models, although nominally based on sub-scale physical processes, still rely on empirical adjustments that prevent extension beyond the range of calibration. At shorter length scales (~10 nm), the static properties of materials can be characterized or modeled with atomic precision. Unfortunately, due to limitations on size and simulation times accessible to current methods, we lack the capability to characterize the fundamental constitutive behavior that underlies the observed larger-scale phenomenology. *Bridging this micron gap is the critical roadblock to developing reliable multiscale understanding of materials that would enable truly predictive capability.*

**The Grand Challenge in Materials Modeling & Design**

A Grand Challenge is to simulate and predict materials properties and integrate the methods with those of IS&T to maximize our understanding of materials science, including aspects of: motivating, designing and analyzing experiments; achieving fully integrated multiscale modeling; data fusion of experimental and modeling results; techniques for dynamically analyzing massive data sets; and quantified measures of uncertainty applied to data extracted from both experiments and models. Our expectation is that modeling capabilities in ~5-10 years will demonstrate closure of the "micron" gap within multiscale strategies. That is, we expect that we will be able to bridge the intermediate (or mesoscale) scales in which the approximations of fast/slow or small/ large no longer apply, which will enable us to directly link electronic/atomistic and continuum scales. Success is essential to enabling a capability of "*intentionally controlled functionality*".

This quantitative connection between atomistic simulations and continuum response models will have a significant impact on a broad variety of materials systems and issues. This capability will be critical for integrating experimental results into true materials understanding. The coupling of

Materials Science and Information Science and Technology will demonstrate an integrated, innovative path with the following goals:

- Goal 1: Develop capability to achieve optimal use of data and design of experiments for prediction
- Goal 2: Establish the technical underpinnings of data-driven analysis and quantified predictive capability for materials performance

This strategy must focus on integrating expertise in materials modeling and condensed matter theory, existing experimental data and modern data analysis techniques to understand and predict materials behavior.

The potential impact of the challenges outlined above is manifold. Often overlooked is the crucial importance of effective frameworks for the pursuit of scientific and technological research. A serious effort to implement the integration of theory, modeling and experiment outlined above will transform the scientific environment for the next generation of scientists. More specific impacts include the development of quantitative understanding of the potency of the wide range of defects present in materials; a quantitative understanding of how populations of defects with their variable potency affect materials properties especially those with a strong sensitivity to history such as fracture and corrosion. These sorts of quantitative frameworks for materials properties in turn will enable substantially more sophisticated approaches to materials design at both the atomistic level (e.g. for catalytic activity) and at the microstructural level (e.g. toughness of artificial bone) where the performance requirements will drive the microstructure design. At the systems integration level, Integrated Computational Materials Engineering has the potential to transform materials development and refinement on the industrial scale if the right tools are provided. All these represent decadal challenges of the first order.

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## Priority Research Direction: Predictive understanding of atomistic and collective fundamental mechanisms of radiation effects in materials

### Problem Statement

Radiation effects encompass a broad range of multi-scale phenomena, ranging from atomic scale unit mechanisms to collective effects occurring at the mesoscale. In order to develop a firm predictive understanding of radiation effects in materials for advanced fission and fusion energy systems, improved understanding of these atomistic unit mechanisms and collective phenomena are needed.

### Executive Summary

Key fundamental unit processes involving solute atoms and point radiation defects, and phenomena that control their collective microstructural evolution, are poorly understood. These represent source terms for long-term development of persistent microstructures and accompanying physical and mechanical property changes due to radiation. Atomistic unit processes of atomistic and electronic defect production, their interactions, energy release pathways to materials in a radiation environment, as well as the collective impact to material properties are critical to controlling and engineering materials performance. A comprehensive research effort is needed to understand the interaction between point defects and solutes and the sinks such that quantitative predictions of sink strengths can be made. In order to access the relevant spatio-temporal scales of such processes, new measurement tools capable of simultaneous spatial and temporal resolution approaching 1 Å and <1ps are needed. These research tools include emerging enhanced capabilities in leadership-class experimental facilities utilizing X-rays, neutrons, electrons, and ion beams. Of particular importance is development of in-situ test capabilities (both during irradiation and postirradiation during heating and mechanical stressing). Acquisition of an improved understanding of these atomistic and collective radiation effects processes will enable bottom-up design of materials with unprecedented tolerance to extreme environments.

### Scientific Challenges

The understanding of fundamental unit mechanisms responsible for processes such as Frenkel pair recombination, defect clustering and precipitate nucleation, point defect interactions with interfaces, and dislocation core spreading are critical to the prediction and control needed for the bottom-up design of materials with unprecedented tolerance to extreme irradiation environments [1]. Similarly, atomistic and mesoscale phenomena that involve collective or coordinated processes may ultimately determine the overall radiation resistance of materials. Examples of poorly-understood collective phenomena include defect production via non-ballistic mechanisms such as fission fragment ionization tracks [2], dislocation annihilation of defect clusters (important for understanding dislocation channeling, radiation embrittlement and fatigue) [3,4], grain boundary sliding and pinning mechanisms at thermal creep conditions [5-7], stress-assisted

helium bubble formation at grain boundaries (basis for high temperature helium embrittlement of grain boundaries) [8,9], and quantification of the efficacy of various precipitate and grain boundary interfaces in facilitating point defect recombination and trapping of transmutant helium atoms [8-11].

The importance of interface structure in influencing these unit mechanisms cannot be over emphasized. Early work studying the interaction between point defects and grain boundaries (homophase interfaces) [12, 13] confirm qualitatively that the response of different grain boundaries to irradiation and impurity concentrations depends on interface structure [14,15] and the presence or absence of coherency. However, because experimental and modeling methods were limited, the connections between modeling and experiments were necessarily qualitative in nature. The dependence of interface response to atomistic and collective processes occurring at extreme doses, dose rates, stress and temperatures were not investigated and remain poorly understood. Improvements in computational resources and the advent of accurate inter atomic potentials have allowed atomistic modeling to provide greater insight to the connection between interface structure and response to irradiation. Modeling has shown that different atomic structures of interfaces can lead to the operation of different unit mechanisms responsible for processes such as point defect absorption, emission and diffusion at interfaces. The efficacy with which the various unit mechanisms intrinsic to a given interface operate *collectively* to mediate radiation damage can strongly affect the radiation tolerance of a material. For any interface, there exist irradiation conditions that are sufficiently severe to overwhelm that interface's ability to heal radiation damage leading to morphological and/or chemical instabilities and degradation in mechanical properties. If, however, the dependence of those limits on the collective behavior of the unit mechanisms intrinsic to that interface is well understood, then the interface structure can be tailored to obtain the kind of unit mechanisms that lead to greatest survivability of a material under a given set of irradiation conditions. Therefore, the discovery of previously unanticipated unit mechanisms, determined through atomistic modeling and validated with new measurement tools, will be important in defining the source terms for long-term development of persistent microstructures and accompanying physical and mechanical property changes due to radiation

**Research Directions**

Research is needed to acquire improved understanding of radiation effects phenomena at multiple scales, ranging from atomistic processes of defect production in displacement cascades to atomistic and collective phenomena that determine the fate of migrating point defects.

Improved understanding of electronic defect production in nonmetals, point defect interactions with extended defects in materials, energy release pathways to materials in a radiation environment, as well as the collective impact to material properties are critical to controlling and engineering materials performance. While progress has been made in modeling the dynamics of collision cascades in materials, dynamic charge effects and collective processes are much less

understood. Defect production research topics of high priority include time-resolved experiments to validate displacement cascade models, quantification of localized charge effects at defects and interfaces, rupture or changes in nature of covalent and ionic bonds, enhanced defect and atomic diffusion, and changes in phase transformation dynamics.

It is well known that dislocations and grain and interphase boundaries act as sinks for radiation-induced point defects. Also, foreign elements such as helium can migrate to microstructural sinks whereas substitutional solutes (e.g., Cr in steels) can either enrich or deplete from boundaries. A comprehensive research effort is needed to understand the interaction between point defects and solutes and the sinks such that quantitative predictions of sink strengths can be made. For example, what is the role of boundary structure and energetics on the sink behavior? This requires a coupled modeling and experimental approach. Atomistic modeling can explore the structure of sinks and interaction of point defects with sinks, both at the level of unit processes (e.g., interaction energies of *individual* vacancies and interstitials with sinks) and collective phenomena (e.g., interaction of cascades with sinks). The solubility of foreign elements such as helium at sinks can also be estimated from the atomic structure of the sink via atomistic modeling. Experimentally, the interaction can be measured in terms of defect accumulation in bulk vs. at sinks for the same irradiation condition. New *in situ* studies (e.g., ion irradiation in dynamic TEM and ultrafast x-ray diffraction analysis of cascades) are needed to elucidate the interaction of radiation-induced point defects with microstructural sinks of different atomic structure and geometry to understand which sink types interact most strongly with defects and solutes.

Improved experimental tools [16] are needed to directly observe and understand fundamental defect and solute agglomeration processes. These phenomena are the driving force for establishing the life cycle of microstructural features and their impact on material properties.

**Capability Gaps**

In order to access all relevant spatio-temporal scales of such processes, new measurement tools capable of simultaneous spatial and temporal resolution approaching 1 Å and <1ps are needed. A variety of materials characterization probes offer attractive features. X-ray sources offer the potential of ultrafast spectroscopy on a wide variety of materials. Neutron scattering provides complementary characterization of solutes, precipitates and lattice strains in bulk materials. Electron microscopy offers high spatial resolution of defect structures and solute segregation and precipitation at moderate time resolution. Ion beam analysis can be utilized to examine solute segregation and lattice locations of atoms, along with a variety of ultrafast optical spectroscopy tests. Currently only very limited in-situ test capabilities exist for examining irradiated materials in leadership-class materials characterization facilities (both during irradiation and postirradiation). The problem is particularly acute for examination of neutron irradiated materials, where daunting logistical barriers exist for the introduction of radiological materials [17].

On a decadal horizon, hard X-rays sources are very promising sources for this purpose: the short wavelength (on the order of ≈1 Å) allows for atomic spatial resolution; the high penetration into matter permits to study buried structures and bulk samples; and with the upcoming generation of hard X-ray free-electron lasers the achievable time resolution will reach the femtosecond regime. The high peak brightness of such sources will allow for single-shot imaging of non-repeatable events and for the investigation of non-periodic structures by means of coherent scattering techniques. While hard X-ray facilities are currently being developed around the world (LCLS in the US, XFEL in Germany, SCSS in Japan), their application to the study of radiation effects in materials presents special challenges. First, enabling the introduction of irradiated radioactive materials into a coherent hard X-ray facility will be crucial. Furthermore, appropriate pump-probe schemes need to be devised in order to image fast dynamic processes. Here, a capability gap exists in the technology for initiating radiation-induced dynamics with sub-picosecond precision. It will be essential to develop pulsed ion, photon, and neutron sources that can be combined and synchronized with an ultrafast X-ray source.

The combined utilization of in situ TEM and ion irradiation is a powerful technique in research on nuclear materials including advanced structural alloys, waste storage ceramics and glasses, and model fuel alloys. A strength of in situ work is the discovery and illumination of fundamental dynamic processes such as point defect clustering, dislocation loop formation, loop motion, coalescence and interactions with existing surfaces, interfaces, and microstructure. Although TEM has been used extensively in the study of radiation damage in materials, it is currently limited with regard to spatial and temporal resolution to elucidate point defect evolution in real time. *In situ* studies of ion irradiation in a TEM capture dynamics typically at rates of 30 frames/second but the defect evolution starts at sub-ps time scales. Also, sub-Å resolution is needed to resolve point defects, as opposed to defect clusters on the scale of 1 nm that is achieved currently. This represents a significant gap between experiments and modeling. Molecular dynamics simulations can reveal radiation-induced point defect interactions with interfaces at sub-pico to nano-second time scales, but experiments only resolve defect clusters (≈ 1 nm diameter) at time scales on the order of 1/30 second. Improvements in both experimental and modeling capabilities are needed to bridge this substantial difference in time scales.

A significant development is appearing which can have great impact on experimental work in irradiation effects at the 0.1 nm scale. This is the coming development of doubly aberration corrected (spherical and chromatic aberrations) electron microscopes with expanded accessible volume for *in situ* ion irradiation (1,2 or 3 beams) combined with well controlled specimen environment (temperature, stress, gas or liquid) and space for additional measurement techniques (laser based, x-ray, physical properties) beyond just the electron beam techniques (which will be quite powerful in itself: energy filtering, analytical probes, tomography, etc). Accommodation of this expanded space for *in situ* experiments will compromise the ultimate spatial resolution, but resolution limits of 0.1 nm may still be achievable. Useful temporal resolution for the study of dynamic processes should also be extended down to millisecond or shorter timescales over the

next decade. Future directions should include measurements of local chemistry changes (electron energy filtering), tomography, enhanced spatial and temporal resolutions, and the expanded experimental space afforded by aberration corrected microscopes. Capability is needed for simultaneous measurement by multiple probes (in-situ or ex-situ) in order to firmly establish links between microstructure and properties

Over the last few decades, ion beam analysis (IBA) to characterize atomic profiles and nanometer structure has developed into a mature field, and today comprises numerous techniques, including Rutherford backscattering spectrometry (RBS), elastic recoil detection analysis (ERDA), nuclear reaction analysis (NRA), and ion-beam-induced luminescence (IBIL). Perhaps the most conventional IBA technique is RBS, in which light probing ions scattered from heavy target nuclei yield information on the mass and depth of the target atoms. A powerful relative of RBS is ERDA, where recoiled target atoms are detected with near-monolayer depth resolution and good elemental, and even isotopic, identification. NRA can detect and quantify most of the light elements and their isotopes. IBIL signals are highly sensitive to defect formation, bonding changes, transient unstable states and phase transformation, as well as precipitate and nanoparticle formation. Ion beams along low-index crystallographic directions are sensitive to atomic displacements from the crystalline lattice sites, such as interstitials within channels, unaligned atoms in amorphous domains or due to local strain from dislocations. RBS, NRA and IBIL combined with ion channeling technique can provide critical information on ongoing changes of defect evolution, damage accumulation, thermal- and radiation enhanced solute diffusion, and structural transformations in a radiation environment to validate predictive models.

There is a performance gap in utilizing and advancing the ion beam tools to address relevant phenomena in radiation environments of interests for fission and fusion. Additional beamlines to deliver multiple probe ions will be needed in new multiple-beam test facilities. The *in-situ* or on-line IBA characterization capabilities, together with other spectroscopy and microscopy techniques, can effectively monitor the evolution of radiation damage (atomic migration/nucleation, interface degradation, structural stress, nano/microstructure evolution, helium and solute agglomeration, etc), therefore, are powerful diagnostic tools to understand material behavior and response to various physical and chemical processes.

**Potential Impact**

An improved understanding of the atomistic and collective processes that define the persistent microstructures in irradiated materials is essential for the development of improved high performance materials. This understanding would enable the development of validated physics-based multiscale models, which will allow accurate extrapolation beyond the current knowledge base. It would also facilitate an improved understanding of irradiation flux effects (including pulsing and accelerated testing), as well as provide the basis for understanding how to use

accelerated test techniques to more rapidly design, develop and qualify high performance materials for future advanced nuclear energy systems. Ultimately, this knowledge will enable bottom-up design of materials with unprecedented tolerance to extreme environments.

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## Priority Research Direction: Controlling thermo-mechanical properties and dimensional stability during irradiation

### Problem Statement

The service life of reactor components is frequently limited by dimensional changes and degradation of mechanical properties during irradiation. Dimensional changes, specifically swelling and irradiation-induced or –enhanced creep, result from the disposition of radiation generated defects at sinks (dislocations, dislocation loops, boundaries, voids). Degradation of mechanical properties results from irradiation induced microstructural changes including evolution of dislocation loops, voids and bubbles, and from microchemical and phase changes. In ceramic materials such as nuclear fuel, these same microstructural changes can degrade phonon and electron transport and thus decrease thermal conductivity. Though there is a good understanding of irradiation effects on thermal-mechanical properties and dimensional stability of nuclear reactor materials, the ability to predict materials performance beyond the regime of experimental experience, e.g., to higher temperatures, higher accumulated radiation damage, and higher stresses, is still lacking. The current approach in establishing high temperature design rules of nuclear structural components is practically empirical. Such an engineering approach often proves to be successful only when it is supported by a robust database and involves no data extrapolation, but can be overly conservative or problematic when the time-dependent processes such as creep and creep-fatigue are involved, and irradiation adds to a new dimension to these complex problems. A more fundamental approach based on a thorough mechanistic understanding is therefore needed to achieve the required predictive capabilities. The understanding of the origins and processes of deformation and fracture under irradiation is also critical to the design and development of advanced materials with radiation tolerance, while maintaining good thermal-mechanical properties and dimensional stability.

### Executive Summary

The performance of nuclear fuels and structural components during reactor operation is dictated by their thermal-mechanical behavior. A predictive understanding of irradiation effects on thermo-mechanical properties of multi-component, multiphase materials is essential for rational design of advanced materials for structural, fuels and waste-form applications and for development of new reactor technologies. The understanding of the complex thermal-mechanical responses of irradiated materials requires a combination of integrated theoretical, experimental, and modeling techniques from the atomic scale to the meso- and macro-scales. New experimental capabilities are required to provide insight into thermo-mechanical behavior under nuclear reactor environments at all relevant time and length scales.

Over the past twenty years in-situ mechanical testing combined with lattice strain measurements in either neutron or (more recently) synchrotron x-ray spectrometers has allowed researchers to develop a good understanding of how metals deform at the single crystal level in polycrystals.

This allows the prediction of plasticity under multi-axial, or highly constrained stress conditions like those ahead of a crack. This helps designers to understand the conditions that cause initiation and propagation of fracture, fatigue cracks, and other slow crack growth mechanisms such as delayed hydride cracking in Zr or Ti alloys. These techniques could readily be extended to the understanding of irradiated materials, if facilities were available for preparation, shipping and handling of radioactive specimens at neutron and synchrotron x-ray facilities. This capability would help the understanding of both fracture and dimensional stability of materials under irradiation.

**Scientific Challenges**

A fundamental understanding of the mechanical responses of a material to complex loading under extreme temperature and radiation environments is essential to the structural integrity and lifetime prediction of nuclear components and to the design and development of advanced materials for next-generation fission and fusion energy systems. The mechanical response of a material is a result of many competing deformation and damage processes (e.g. dislocation interactions, grain boundary motion, segregation, and diffusion, etc) that originate at atomic and microscopic scales with macroscopic consequences. A key challenge for the accurate assessment and prediction of mechanical properties in extreme environments is to integrate a number of coupled processes involving a broad range of time and length scales to capture the complex nature of real materials in real environments. In nuclear reactor environments, irradiation changes the active deformation systems (slip, twinning, climb, grain boundary sliding), causes dimensional changes including creep and swelling, and leads to the loss of fracture resistance. Many outstanding questions remain regarding mechanical properties of materials during irradiation. The physical mechanisms responsible for flow localization during plastic deformation, low-temperature irradiation embrittlement and the increase in the ductile-brittle transition temperature (DBTT) in irradiated body-centered-cubic (bcc) metals and alloys, high temperature grain boundary and helium embrittlement, irradiation-assisted stress corrosion cracking, material response under fatigue and creep-fatigue loading and irradiation are still unclear. A microstructural basis for fracture mechanism is lacking for irradiated materials.

Understanding the fundamental mechanisms of deformation and fracture will allow prediction of materials response under static or dynamic loading in nuclear reactor environments. The prediction of mechanical properties of materials, at the current stage, is still limited to a few simple cases and model configurations. The modeling of the relationship between the state of the microstructure and the deformation and damage mechanisms has remained largely phenomenological. Though there has been substantial development in understanding the deformation and fracture behavior in nuclear reactor materials, lack of understanding of contributions from structural heterogeneity is a primary limitation in the development of predictive capabilities, especially for crack initiation. The scientific challenge is to model real materials with complex microstructure and their response to complex thermal, mechanical, and irradiation conditions. Quantitative modeling is needed to incorporate individual deformation

and damage micro-processes into mesoscopic computer modeling to accurately describe the evolution and interactions of microstructural elements such as dislocations, second-phase particles, grain boundaries, radiation defects, and to produce the required macroscopic mechanical response under any external conditions (temperature, strain rate, stress and stress state) in complex material systems. An ultimate challenge is to develop a reliable computational tool that can be used for structural design of nuclear components and be accepted for qualification and licensing of nuclear materials.

In addition to understanding the changes in mechanical properties due to irradiation, changes in thermal transport and the underlying microstructural changes, are critical to understanding the performance of ceramic materials under radiation. Degradation of thermal properties resulting from microstructural and microchemical evolutions has become a limiting factor of the performance of nuclear reactor fuels. To achieve a higher burn-up, quantitatively correct modeling is critical for the development of nuclear fuel. New experimental capabilities are needed to characterize the evolution of physical and mechanical properties under the bombardments by energetic particles.

**Research Directions**

Research is required to further the fundamental understanding of nuclear materials and to develop technology required to extend the life of existing reactors and design more efficient fission and fusion energy systems. The research must address the thermo-mechanical aspects of materials performance under irradiation, including dimensional stability (growth, swelling), creep, fatigue, creep-fatigue, plasticity, crack initiation and propagation, thermal transport, and the microstructural and microchemical/phase changes that influence these phenomena.

Despite many years of research and development of materials for advanced nuclear energy applications, fundamental knowledge is still lacking in areas that are vital to the integrity and safety of nuclear reactor systems. For instance, a fundamental understanding of time-dependent deformation, dynamic microstructural evolution under thermal-mechanical loading, fatigue and creep-fatigue crack initiation and propagation, and synergistic interactions between static and dynamic loading and irradiation is still largely unknown. The current elevated-temperature structural design rules were developed in 1970s-80s, and have no fundamental physical basis. The design methodology can not provide an adequate foundation for component designs in complex stress states and for long-term service in harsh reactor environments. The qualification and licensing of any new material still requires a large experimental campaign to establish an extensive database. It is critically important, therefore, to have a basic understanding of dynamic deformation processes and material aging behavior under long-term creep-fatigue loading and irradiation to develop predictive capabilities for modeling the mechanical performance of materials exposed to high temperature, high radiation damage and complex stress states.

At present there are no models for predicting the full range of mechanical behavior of irradiated materials needed to design and operate reactors under all operating conditions. Many existing deformation mechanism models (e.g. thermal creep) and radiation effect models are semi-empirical. These models do not truly capture the fundamental physical processes of the interactions of dislocations with barriers (e.g. second-phase particles, radiation defects, grain boundaries, etc.) and not necessarily provide a good description of material behavior beyond the testing conditions. Models, such as the phase-field model that can describe the microstructure for multiple concurrent defect processes, are presently not available but are in development. Such models provide averaged physical properties, such as elastic modulus, density, thermal conductivity etc. as modified by irradiation effects, for finite element models of the macroscopic behavior. Thus they span the length scales between μm and m and are informed by processes down to the atomic length scale. Fracture mechanics models need to incorporate more physics to allow the transfer of small volume test results to complex structures involving different constrain conditions. Ultimately, a first-principle understanding of the relationship between microstructure and mechanical properties during irradiation must be developed and used for the design of components and the development of complex materials with tailored properties.

Evidently, multiscale computational modeling must be closely coupled with in-situ experiments of nano- and micro-scale structural evolution and mechanical behavior of materials. Characterization of irradiated materials requires a variety of techniques, including ex-situ and in-situ mechanical testing, metrology, neutron and x-ray diffraction and small angle scattering, strain mapping, electron microscopy, atom probe, tomography, etc. Advances in characterization techniques using electrons, neutrons, x-ray and ions provide unprecedented opportunities for investigating mechanical properties over a wide range of time and length scales. New and sophisticated capabilities are available to probe mechanical response over small material volumes. Materials can also be characterized nondestructively in-situ, during service and within actual components where material response is fundamentally different from the behavior in near-surface regions or in thin foils. Spatially-resolved characterization of stress distribution, texture, and dislocation evolution in single grains and particle distribution at structural inhomogeneities are also possible. These emerging characterization capabilities are powerful tools for validating and guiding models and for improved performance of structural components.

**Capability Gaps**

One of the key requirements for such research is long term irradiation, at the appropriate temperatures, of bulk specimens to lifetime exposures, of thermal, fast and fusion reactors, in the latter two cases to 200-400 dpa, as well as ion beam technology to allow for focused understanding of microstructural development and the relationship to deformation and thermal transport. At present there are no facilities available in the United States to expose materials up to 100-400 dpa for full scale mechanical testing. There are currently no ion-irradiation facilities combined with in-situ mechanical testing on small samples that can be irradiated through the volume. Likewise no facilities are available to irradiate materials to high dpa with fast neutrons

to simulate processes occurring in a reactor. What is needed is a copious source of fast neutrons, such as the BOR-60 source in Russia, the JOYO facility in Japan, a fusion source such as the proposed IFMIF, or a spallation source such as the Materials Test Station (MTS) at LANSCE. Full-scale mechanical testing includes tensile, fracture toughness, fatigue and creep-fatigue testing to cover present and future high temperature reactors. The additional presence of H and He ions is required to simulate the irradiation conditions in fusion reactors since these have a strong effect on embrittlement.

Studies of the dynamic effects of irradiation will require in-situ testing, i.e, simultaneous irradiation and observation using analytical techniques. This will allow the study of transient effects such as microstructure evolution and dislocation interactions with defects and irradiation-induced, or-modified precipitates and their correlation with the mechanical response under different irradiation conditions (dose, dose rate, temperature or stress, etc). Ion beam irradiation is promising for such in-situ irradiations, and facilities combing ion irradiation with transmission electron microscopy with heating and straining capabilities already exist (e.g. the IVEM-Tandem facility at the Argonne National Laboratory). Triple beam facilities combining heavy ion irradiation with light element implantation (H, He) will allow the simulation of thermal fission, fast fission and fusion conditions for mechanistic studies and rapid statistical sorting of potential new materials. However, the observations in such experiments are often affected by the specimen surfaces, and may not be fully representative of the bulk. Efforts are underway to model the surface effects in thin foils during in-situ ion irradiations with experimental validation and verification [1]. The success of such computational and experimental efforts not only allow bulk irradiation effects to be modeled, but also provides a valuable interpretation tool for small volume in-situ experiments.

One potentially useful technique is the combination of proton irradiation of "bulk" specimens (50-250mm thick), combined with synchrotron x-ray or neutron sources for diffraction, scattering, spectroscopy or imaging characterization. An ideal situation would be to have a load frame mounted on a synchrotron x-ray diffractometer so that the intergranular or type-2 strain response could be captured as well as the macroscopic strain response to applied stress while the sample is being irradiated with ions. Recent progress has shown great promise of synchrotron x-ray techniques for material characterization for nuclear energy applications. The third-generation hard x-ray beams allow measurements with high-spatial resolution and fast in-situ measurements of dynamic processes. Evolution of internal stresses for different phases or crystal families by in-situ diffraction measurements during tensile, compressive, cyclic loading provides unique experimental information about deformation mechanisms in polycrystalline materials [2]. Strain and texture mapping around a crack tip by in-situ synchrotron XRD provided a better understanding of deformation and crack propagation mechanisms under static and fatigue loading [3]. A recent work on grain structure mapping by diffraction contrast tomography and in-situ observation of stress corrosion cracking by synchrotron x-ray micro-tomography has provided insight into the dynamic interaction of a growing crack with crystal structure and the

contribution of different boundary types to cracking resistance [4]. Synchrotron radiation techniques also allow visualization of internal cracks in a material in three dimensions and to characterize stress/strain condition, grain orientation and local chemistry that provide more details critical to the understanding of the fundamental mechanisms of stress corrosion cracking. Information of spatially inhomogeneous residual stress distribution in materials and components with complex geometries can be directly applied for validating finite element modeling for stress prediction in large-scale components. These new directions in understanding deformation and fracture mechanisms in unirradiated materials are critical areas that need to be explored to understand the mechanical performance of materials in nuclear reactor environments.

Some synchrotron radiation tests can now be carried out on archived materials with low activities [5]. However, for materials irradiated to high doses, shielded facilities and remote handling will be required. Many technical questions remain to be addressed such as the set-up and shielding of the beam facilities, signal to noise issues for highly radioactive samples that may mask the diffracted signal, and affect the survival of x-ray detectors in a high $\gamma$-ray flux. New instrument technologies such as new detector and signal processing technologies may be necessary. The ability to transfer highly active material between the irradiation source and the x-ray and neutron equipment or the microscopes in which the samples will be examined, is a difficult task that must be addressed. This is easier if all the facilities are on the same site. As yet an ion accelerator to provide sample irradiation has not been set up at a synchrotron x-ray station although this has been proposed. The easiest irradiation plus observation process to implement would be on small pillars of materials milled from bulk material that can be irradiated through the whole volume by suitable ion irradiation. These can readily be examined by electron microscopy and x-ray diffraction during in-situ mechanical testing. However the question arises whether results on sub-micron size coupons are characteristic of the macroscopic response required for engineering design. Models are required to superpose the results from the two sample scales.

**Potential Impact**

A complete bridging of the capability gap discussed above will lead to substantial improvement in understanding the thermal and mechanical behavior of materials under irradiation. The development of facilities for high dosage, full-scale and in-situ thermomechanical testing could provide great benefit for the validation of advanced nuclear energy materials. This facility would also provide the best simulation to the environment that would be present in advanced nuclear reactors. A facility developed for rapid and efficient synchrotron or neutron diffraction of highly radioactive materials would be of great benefit in understanding the microstructural evolution of reactor fuels. This understanding could then be used to develop an efficient fuel with known microstructure throughout the cradle-to-grave life cycle. Furthermore, the development of a synchrotron facility that could also provide *in situ* irradiation capabilities would provide real time details of the microstructural evolution. Quantified microscale thermomechanical testing within an electron beam during helium and ion irradiation would provide a method to directly observe the defect structure development as an effect of both

irradiation and various thermal, mechanical, or other applied loads. The directly observed mechanisms would provide significant input for the development of microstructural and mechanical models. The development of correlations relating thermomechanical properties reported from various testing techniques over multiple length scales would provide great benefit in the transfer, accumulation, and access materials property description. This would drastically increase the efficiency of materials selection for a wide range of applications.

The combined impact of these new facilities, methodology, and theories will result in significant benefit to the nuclear energy industry. A thorough understanding of the life limiting effects on the thermomechanical properties may result in the suggestion of advanced materials. These materials will be better suited for the high temperature, high radiation dosage, and corrosive environment that will be present in the next generation of nuclear reactors. Advanced thermomechanical testing of new materials will be expedited and provide greater assurance during the validation process. Finally, a better understanding of thermomechanical properties in corrosive and irradiation environments will permit better maintenance practices and life prediction of current nuclear reactor facilities. A complete understanding of dimensional degradation and altered mechanical properties may permit a life extension of existing nuclear plants resulting in the savings of billions of dollars in rebuilding costs.

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## Priority Research Direction: Defining the frontiers of microstructure science under irradiation

### Problem Statement

The goal is to develop a computationally-predictive, experimentally-validated multi-scale understanding of nuclear materials (fuel and cladding) that incorporates the effects of irradiation and temperature on microstructure formation and evolution and enables prediction of how these processes affect thermo-mechanical properties.

### Executive Summary

The cumulative effect from fission-damage processes, high temperatures, high stresses, and high thermal gradients is to cause severe degradation in the thermo-mechanical properties of a nuclear-fuel assembly (fuel plus cladding), limiting its lifetime and strongly affecting operational cost. Similar effects occur in reactor core structural materials due to damage initiated by high-energy neutrons. Elucidation of the microstructural causes and mechanisms controlling this degradation behavior requires development of a comprehensive program of spatially-resolved, multi-scale computation and complementary experimentation, on commensurate length scales. The ultimate goal is the development of computationally-predictive, experimentally-validated multi-scale understanding of nuclear materials that fully incorporates all the various, concurrently occurring and highly coupled microstructural process within a unified computational and conceptual framework. The experimental limitations in the non-destructive characterization of evolving microstructures and irradiation effects provide major challenges for the community. Also, current experimental techniques, both in-situ (ion and neutron) and ex-situ, do not characterize evolving microstructures in irradiated materials with sufficient statistical detail, making the analysis of unit mechanisms very difficult.

### Scientific Challenges

A comprehensive understanding of microstructural processes is a critical component of the development of a predictive, materials-physics-based nuclear materials modeling capability. In spite of considerable experience in studying microstructural processes in nuclear materials, such as void swelling, fission-gas release and crack development, a comprehensive understanding of how microstructural processes control the thermo-mechanical properties and performance of nuclear materials remains to be developed.

Apart from large empirical databases, fundamental information that connects "structure" across the relevant length- and time-scales with fuel and cladding behavior does not currently exist. What is particularly lacking is a comprehensive multi-scale model that captures how microstructure development during irradiation (including defect generation and evolution), leads to the degradation of the fuel and cladding.

Another challenge is correlating thermo-mechanical properties to the neutron flux in the reactor. Since a certain flux can be associated with a variety of changes in the properties of the materials, depending on the history and damage mechanisms involved, solving for the irradiation level may lead to mathematically ill-posed inverse problems. On the bright side, the direct problems (change in properties versus irradiation level) can be solved using simulations.

**Research Directions**

What is needed is an experimentally validated, hierarchical multi-scale modeling approach for microstructure evolution under irradiation that combines spatially-resolved, multi-scale computation with complementary experimentation, on commensurate length scales. This unique combination will enable capturing the interplay between the material microstructure, fission products, and lattice defects and their effects on -mechanical properties. The centerpiece of the multi-scale approach (Figure 1) is a *unified* meso-scale approach that combines phase field with heat and chemical-species transport theory to predict *concurrent* formation and evolution of microstructure under irradiation, high-temperature, environment and stress. Four critical elements of this approach are:

- Development of a comprehensive theoretical and computational mesoscale approach that considers all the various, concurrently occurring and highly coupled microstructural process within a unified framework;
- Capturing irradiation effects within the mesoscale modeling framework;
- Coupling the neutron transport with the heat and chemical species transport via complex models of thermo-mechanical and chemical properties of the fuel and clad.
- Linking the microstructural simulations with continuum fuels-performance simulations via a scale-bridging approach.

The mesoscale approach receives input from the lower length scales (the atomic and electronic-structure levels (see Figure 1) and/or from experiments in the form of bulk and interfacial mechanisms and materials parameters (see also the Priority Research Direction on Predictive Understanding of atomistic and collective fundamental mechanisms of radiation effects in materials). The output from the mesoscale simulations, in the form of homogenized properties such as the elastic moduli or the thermal conductivity for a given microstructure, provide the input to the continuum level (or engineering-scale; see Figure 1).

The experimental validation of microstructural predictions requires in-situ characterization tools such as of in-situ TEM and ion irradiation, electrons, x-ray, and neutron scattering. A strength of in-situ work is the discovery and illumination of fundamental dynamic processes such as point-

defect clustering, dislocation-loop formation, loop motion, coalescence and interactions with existing surfaces, interfaces, and microstructure.

Future directions should include measurements of local chemistry changes (electron-energy filtering), tomography, enhanced spatial and temporal resolutions, and the expanded experimental space afforded by aberration-corrected microscopes.

**Capability Gaps**

• Current experimental techniques, both in-situ (ion and neutron) and ex-situ, do not characterize evolving microstructures in irradiated materials with sufficient statistical detail, making the analysis of unit mechanisms very difficult.

• Due to the very long neutron irradiation times necessary to achieve doses relevant to reactor operation regimes, ion beam (light or heavy) irradiations are used for accelerated studies. The equivalence or complementarily of the two methods requires careful consideration in the differences in damage rate and damage structure.

• The understanding of heat and chemical species transport, defect formation and evolution, and phase behavior in complex, heterogeneous materials is currently mostly based on observation and empirical correlations that involve (linear) combinations of the properties of the homogenous

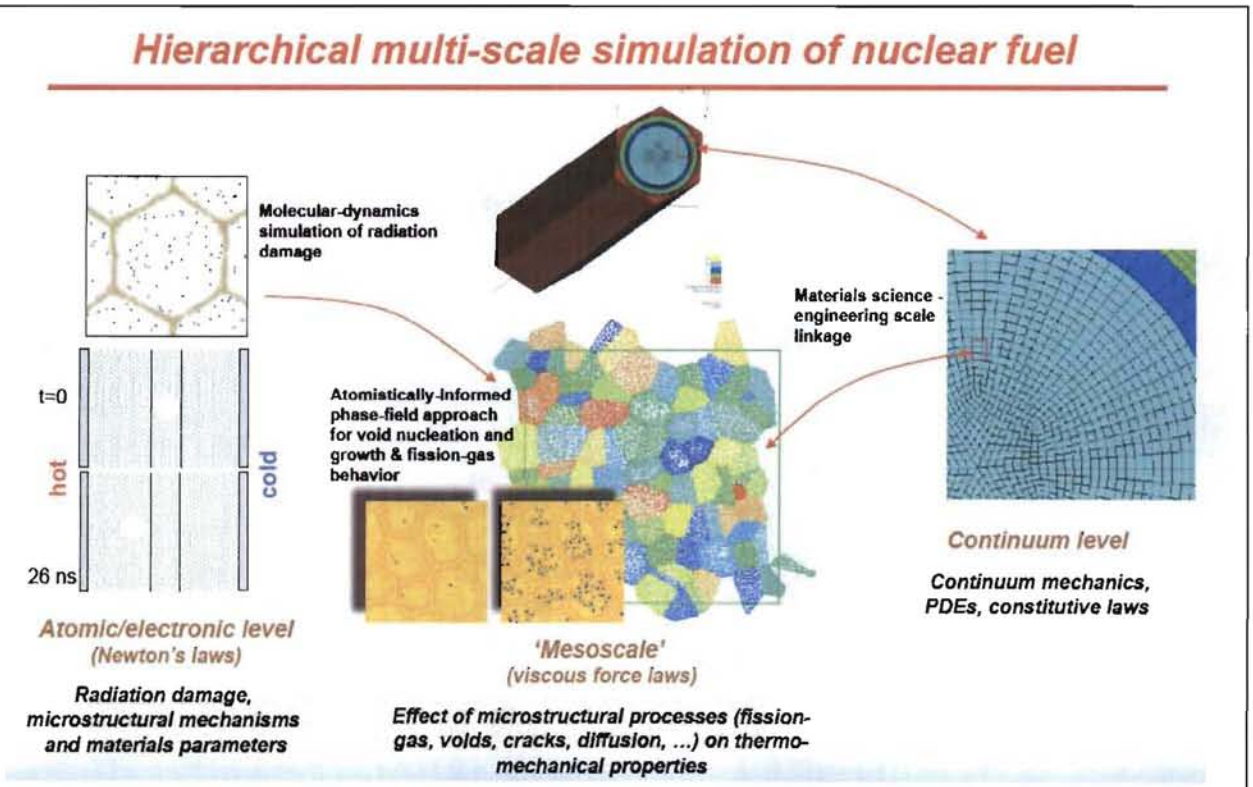


**Figure 1.** Hierarchical multi-scale simulation approach for materials-physics based prediction of the performance, degradation and lifetime of nuclear materials (see text).

phases. A more sophisticated theoretical and computational framework is necessary.

• Current reactor simulation tools perform calculations of criticality, temperature profiles and heat transport that ignore the detailed radiation-induced changes in materials properties. Although computationally intensive, the coupling is necessary for accurate predictions of both materials and reactor performance.

• Although good results are available at specific scales (atomistic, meso-scale, and continuum), there is a shortage of robust scale-bridging algorithms able to capture critical properties driving microstructural changes under irradiation.

**Potential Impact**

Understanding the relations between microstructure and continuum thermal, mechanical, and chemical properties of irradiated materials will positively impact:

- The development of fuels- and materials-performance tools capable of predicting the behavior of nuclear-fuel elements in normal and ab-normal (transients, accidents) reactor regimes.

- The design of new, innovative, fuels and structural materials with optimal functionality and performance.

**Priority Research Direction: Co-design of experiments and models of time & space dependent radiation damage**

**Problem Statement**

Twenty-five years ago experimentalists and theorists in radiation damage effects worked quite separately, and on very different length and time scales, today experiments and theory working at similar length scales are being realized. In order to take full advantage of the advances in theory, simulation, and modeling it is essential that experiments are intimately coupled at each length scale and time scale. Efforts to achieve this vision of co-design need to be accelerated and substantially enhanced.

**Executive Summary**

Experiments coupled with theory simulation and modeling will play an important role in accelerating materials development for advanced reactors, improving safety, and increasing performance in nuclear energy systems. It is imperative that in the development of multi-scale theory, simulation, and modeling (TSM) that the research plan emphasizes the intimate contact between experiments, and the TSM itself. Positive impact on the safety, reliability, and performance of nuclear reactors can be expected in 5 to 10 years as the methodologies described here become acceptable to the nuclear energy practitioners.

**Science Challenges**

Experiments coupled with theory simulation and modeling will play an important role in accelerating materials (both fuels and structural) development for advanced reactors, improving safety, and increasing performance in nuclear energy systems (both fission and fusion). During the R&D phase of development such models can reduce development costs by helping to down-select the best materials choices for further development. It is generally agreed that for those situations where materials age slowly while in service it is desirable to have simulations and models that predict performance degradation long before failures or deficiencies become evident in operation. However, there is a conundrum which is this; the development of robust models requires that there be available a large amount of experimental data covering not only the engineering space, but also the materials physics space. This data must be such that specific mechanisms of the aging process of the material can be isolated and studied in a way that it informs the models of the fundamental physics—the so called unit mechanisms. *(Side bar 1 describes the importance of unit mechanisms in more detail.)*

**Research Directions**

It is imperative that in the development of multiscale theory, simulation, and modeling (TSM) that the research plan emphasizes the intimate contact between experiments, and the TSM itself. Recently, high performance computing at the petascale and exascale for nuclear energy materials was reviewed in "Science Based Nuclear Energy Systems Enabled by Advanced Modeling and Simulation at the Extreme Scale"

(http://www.science.doe.gov/ascr/ProgramDocuments/Docs/SC-NEWorkshopReport.pdf ). Useful references focused on the materials challenges for nuclear energy can be found in this report. A central question of the report was how high performance computing might accelerate the deployment of advanced nuclear energy systems. It is noted; "(*in the past*) scientists could not credibly utilize the results of accelerated out-of-pile materials experiments to develop reliable forecasts of in-pile performance." This problem is a challenge facing TSM that must be met and resolved if validated models and simulations are to emerge from this enterprise.

Twenty-five years ago experimentalists and theorists in radiation damage effects worked quite separately, and on very different length and time scales, today experiments and theory working at similar length scales are being realized. In order to take full advantage of the advances in TSM to date it is essential that experiments are inter-digitated with physics models at each length and time scale. How this is done is an expansive topic worthy of a workshop in its own right.

What the separable elements are for both TSM and for the unit mechanistic experimental effort can be listed. In so doing, we will generate thoughtful consideration of the challenge of designing experiments that truly "inform" TSM of the underlying physics of radiation effects in materials. Such an experimental strategy might be considered, in parallel with multiscale TSM, as multi-scale experiments, experiments that are, in terms of the underlying physics, *substantially equivalent* to the multi-scale TSM.

The TSM picture reflecting time and length scales has been outlined in numerous articles. One particularly graphic representation often shown is in Figure 1. Here, simulation techniques addressing separable events at differing length and time scales are indicated. The inference is that the models at lower length scales can provide analytical models to inform longer length or time scale models about relevant properties.

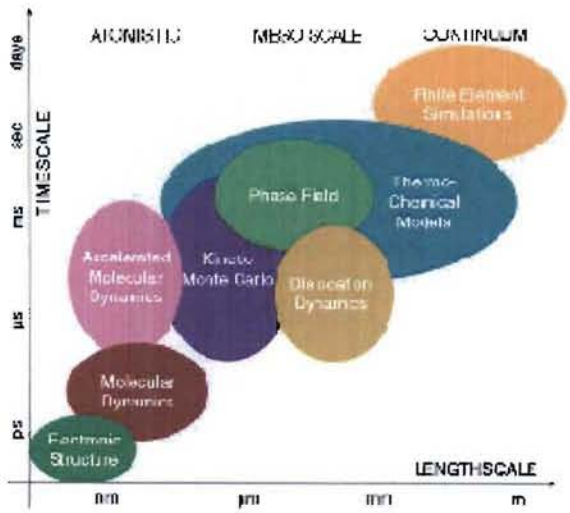


Figure 3: Multi-length and time scale modeling according to W.J. Phythian, R.E. Stoller, A.J.E. Foreman, A.F. Calder, and D.J. Bacon, "A Comparison of Displacement Cascades in Copper and Iron by Molecular- Dynamics and Its Application to Microstructural Evolution," *Journal of Nuclear Materials*, vol. 223, 1995, pp. 245-261.

These computational elements map on to numerous materials effects; hardening and embrittlement including helium embrittlement, phase instabilities, irradiation creep, and volumetric swelling that connect to critical nuclear reactor continuum code simulations such as TRACE, TRAC, RELAP and SASSYS. Examples of the underlying

unit mechanisms are; He generation (in some cases hydrogen generation), primary defect production, short-term annealing, defect recombination, clustering & migration, gas diffusion and trapping, cascade aging, local solute re-distribution, long-range defect transport & annihilation, radiation enhanced diffusion and induced segregation of solutes, nano/microstructure & local chemistry changes, and nucleation and growth of extended defects and precipitates. These physical mechanisms are examples of the experimental glue that can inform the models of the underlying physics.

If one considers, as one should, the employment of ion-beams to accelerate the research to develop a fundamental understanding of unit mechanisms, we immediately realize that while damage (dpas) can be produced 1000 times faster with ions than with reactor neutrons, we are also faced with a very intricate issue of a change in the time scale for the post cascade or displacement events. If one is not cautious, this change in rates could lead to misinterpretation of the experimental results. This point is illuminated in more detail in side bar 2.

In summary we suggest the following research direction to integrate experiments and TSM:

Design and execute the critical ion-beam experiments that will "inform" the TSM in the following areas:

1) Develop the formalisms to follow micro-structural evolution of materials at the rate of nuclear reactors and to predict macroscopic properties.
2) Identify the relevant length scales applicable to the physics mechanisms in the evolving microstructure
3) Predict the evolution of complex interfaces: corrosion, abrasion, and fuel-cladding interface

**Capability Gaps**

The discussion above brings into focus four gaps in our capability to perform multiscale modeling for nuclear energy materials.

1) Discovering, via closely coupled experiment and theory, the key factors of materials performance and including them in models
2) Bridging the time and length scales for materials evolution in the extremes of the nuclear environment
3) Dealing with the complexity of multi-component materials and their evolution due to nuclear reactions
4) Transcending ideal materials systems to engineering materials (*ideal to real*)

Closing these capability gaps will be daunting and challenging. However, we can say with some confidence, that it is essential for TSM of nuclear energy materials to establish a close, even intimate relationship with if at the end of the day the goal is predictive capabilities necessary to achieve acceptance within the engineering community. Today, multiscale-modeling links to experiments through an almost quixotic dependence on serendipitous experimental discovery. While motivation for TSM often comes from the results of integral experiments, carried out over

many years in reactor environments, the problems having been reduced to their component elements within the modeling community, are never passed to the experimental community so that specific, focused experiments are designed, executed and then serve as the basis for validation and verification of the elements of the multiscale approach. Tightening this linkage of experiment and TSM would open a new approach not currently extant in the nuclear energy area.

Indeed the goals for advanced fission systems and for fusion energy are beyond current empirical experience. Only through modeling can we hope to explore this space in reasonable time scales and at reasonable costs. Experiments are the key to assure that models developed for this exploration are physical accurate and predictive in their results.

**Potential Impact**

Experiments coupled with theory simulation and modeling will play an important role in accelerating materials development, improving safety, and increasing performance in nuclear energy systems (fission and fusion). It is generally agreed that for those situations where materials age slowly while in service it is desirable to have simulations and models that predict performance long before serious failures or deficiencies become evident in operation. Indeed during the R&D phase of development such models can reduce development costs by helping to down-select the best materials choices for further development. Separable variable and/or unit mechanism experiments coupled with time and length transcending TSM will lead to higher levels of materials reliability and faster R&D associated with application specific materials development. Positive impact on the safety, reliability, and performance of nuclear reactors can be expected in 5 to 10 years as the methodologies described here become acceptable to the nuclear energy practitioners.

*Side Bar 1: Isolating Unit Mechanisms*

Why are unit mechanisms such an important concept? This point has been illuminated in a paper titled "Mixed Atomistic-Continuum Models of Material Behavior: The Art of Transcending Atomistics and Informing Continua" by M. Ortiz et. al, *MRS Bulletin*, **26** (3) 216-221, March 2001. In this paper the connection between the atomistic world and the continuum is defined in terms of unit mechanisms. We quote from this paper:

*"It is clear, therefore, that atomistic and continuum theories need and reinforce each other. This atomistic/continuum handshake is most effectively achieved within the framework of multiscale modeling. Multiscale modeling is a 'divide and conquer' modeling paradigm. Firstly, the entire range of material behaviors is divided into a hierarchy of length scales (as well as time scales author note). Secondly, the relevant 'unit processes' are identified at each length scale. The unit processes at one scale represent averages of unit processes operating at the immediately lower length scale. This relation introduces a partial ordering of processes. In addition, the unit processes should operate roughly independently: two processes which are tightly coupled should be considered as a single unit process (author note for example the role of helium in void growth).*

*For systems for which these relations are well defined, the modeling effort reduces to the analysis of each unit mechanism in turn and the computation of averages, eventually leading to a full description of the macroscopic behavior of the material. This is an inductive process which must be given appropriate initial conditions. In many cases, such initial conditions take the form of unit mechanisms operating at the atomic scale and which are, therefore, accessible to atomistic modeling. In this manner, atomistics informs material modeling at higher continuum length scales and transcends its own size strictures.*

*Unfortunately, the multiscale paradigm is more easily stated than carried out in practice. At present, the analysis of the unit mechanisms and the characterization of effective behavior relies either on numerical schemes or a motley assortment of analytical tools. Examples of the latter are mean-field theories, statistical mechanics, transition-state theory, direct methods of the calculus of variations, and homogenization. Because of the broad scope of the field and its present state of development, multiscale modeling in general, and mixed atomistic-continuum modeling in particular, cannot be readily reduced to a self- contained and unified formal theory and remains an art as well as a science."*

So, with this definition the critical role for experiments is to inform theory simulation and modeling at every step of the multiscale process by designing experiments that capture the essential physics of the models. Moreover, it is incumbent to not only explore the engineering phase space of the application but also a wider phase space bounded by failure mechanisms or materials instabilities such as phase transformations changes in mechanical properties or the termination of mechanisms or the onset of new mechanisms. In this manner the models can more adequately inform engineering codes based on scientifically defendable methodologies.

*Side Bar 2: It is not Acceleration*

The execution of experiments that isolate unit mechanisms with the purpose of informing multiscale models of the essential physics at each step of the modeling process is not accelerated aging. While experiments that isolate unit mechanisms can and do benefit from an experimental platform where the processes are much faster than the in-service conditions they are not accelerated aging!

What then is accelerated aging or testing?. All definitions of this engineering approach to materials failure have one thing in common; they are integral experiments, where as experiments that isolate unit mechanisms are by their very definition not integral experiments. Examples of simple definitions of accelerated aging or testing are given here:

- Accelerated aging is a testing method used to estimate the useful lifespan of a product when actual lifespan data is unavailable. ...
- A test that simulates long time environmental conditions in a relatively short time.
- A set of laboratory conditions designed to produce in a short time the results of normal aging. Usual factors included are temperature, light, oxygen and water.
- A test in which voltage, temperature, etc. are increased above normal operating values to obtain observable deterioration in a relatively short period of time. The plotted results give expected life service under normal conditions.
- Procedures for subjecting pressure sensitive label material to special environmental conditions in order to predict the course of natural aging.

Accelerated aging plays an important role in product environments and in identifying weaknesses prior to their catastrophic consequences. However, it is generally believed that the acceleration rates must be modest. This arises because of a lack of understanding of the fundamentals of the underlying failure mechanism(s) – the unit mechanisms. The point to remember is that high-speed experiments designed to reveal and understand unit mechanisms are not accelerated aging experiments.

## Priority Research Direction: Materials Design for Resistance to Corrosion and Surface Damage in Extreme Environments

### Problem Statement

Corrosion and other surface degradation processes, such as oxidation, vaporization, and hydriding, are major limiting factors in the application and lifetime of materials used in extreme environments. In fact, the integrity of materials in fission and fusion systems is challenged as much by chemical aggressiveness of the environment as by radiation as most problems in LWRs and many GenIV concepts are driven by chemical interaction. The inclusion of irradiation adds a significant and new dimension to the challenge of developing materials to withstand the extreme environments of these systems, as very little is known about how radiation alters chemical processes such as corrosion and oxidation at surfaces. The problem then is one of understanding the fundamental processes of materials degradation in extreme environments consisting of high temperature, stress, irradiation and chemically aggressive species, and to use that understanding to design a new generation of resistant materials.

### Executive Summary

A scientific understanding of corrosion process has been hindered by the complex interactions of many simultaneously occurring phenomena that cover wide ranges in length and time. Critical phenomena include transport mechanisms, reaction thermodynamics and kinetics, galvanic effects, and environmental interactions in extreme environments consisting of radiation, temperature, pressure and aggressive chemical environments. Even where the overall environment may be benign in terms of general attack, localized conditions may result in aggressive attack over very restricted regions such as in the cases of pitting and stress corrosion cracking. A schematic of the various processes acting during corrosion in such an extreme environment is presented in Figure 1.

Although the details of corrosion phenomena vary widely for a given material and environment, the types of information required to construct a sound scientific model for any particular problem share a common thread. Detailed knowledge of the mechanisms of transport of point defects, electrical charge, and chemical species along with pertinent chemical reactions and phase equilibria and the effects of applied stress states are required for a complete description of any corrosion process. The development of such a knowledge base is complicated by the fact that many processes occur simultaneously and, thus, interact in unknown ways.

To elevate corrosion science to a level where confident predictions of the corrosion performance of existing and new materials can be applied to the design of components for extreme environments, several advances in capability are required. Test stations that contain the chemical environment of interest while providing the ability to apply appropriate conditions of stress, temperature and irradiation do not exist today. In addition to being able to apply appropriate environments, probes to allow for the simultaneous measurement of critical

phenomena at appropriate length and time scales are required. In addition to experimental capabilities, models for the various phenomena of interest that allow for integrated predictions of performance have yet to be established.

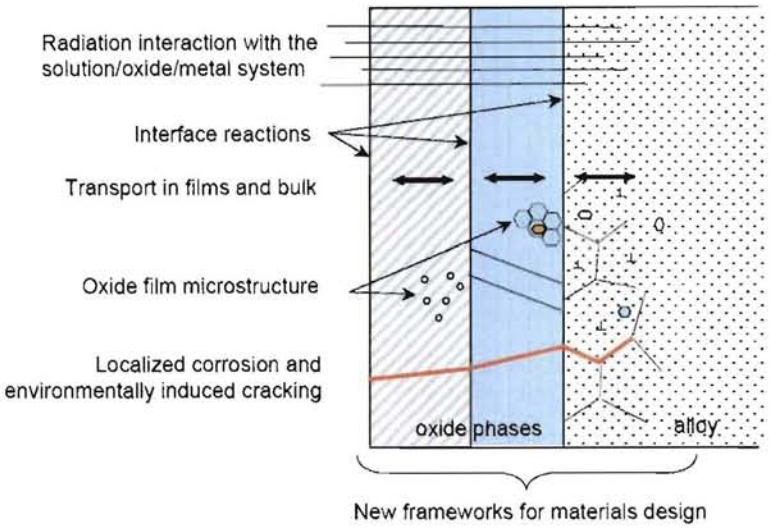


Figure 1. Schematic representation of key microstructural processes affecting corrosion in extreme environments characterized by high temperature, stress, radiation and an aggressive environment.

The general efforts described above represent a significant challenge for any given material and environmental condition. However, significant progress can be expected over a decadal time frame for a small subset of problems. An additional benefit of such an effort would be the establishment of generalized experimental and computational approaches for studying corrosion that could be applied to any particular problem in corrosion science. Examples of potential problems to focus on first include the effects of irradiation on corrosion of materials used in nuclear reactors for power generation, the pitting of landing gear alloys for fighter aircraft, and the stress-corrosion cracking of reactor components in high temperature water.

**Scientific Challenges**

Advancements are needed to simultaneously observe and measure materials structures and reaction kinetics, as well as local environmental conditions at and near interfaces through a range of length and time scales under extreme conditions. These measurements and observations are must be achieved *in situ* (combined with ex situ measurements) and must probe surface chemical reaction kinetics, transport processes, phase and defect nucleation, local stresses and strain anisotropy, and heterogeneous processes such as void and crack formation. It is critical that we measure dynamic processes over time scales from picoseconds (e.g., radiolysis time scale) to years (e.g., crack propagation time scale). The initial focus of these studies should be on

relatively simple systems to successfully model unit processes, and subsequently more complex processes.

New fundamental, atomistic and physics-based models should be developed to replace or enhance existing modeling approaches to predict materials behavior in extreme environments. Models must combine the physical properties of materials with environment. A goal of the proposed research should be to have the ability to predict materials corrosion and near-surface phenomena under complex conditions, for example, where variables such as temperature, pressure, irradiation conditions, and environment chemistry vary with time. Modeling and experiment should be done with an effort toward continuous validation and refinement predictive and design capabilities.

There is a great need for experimental and theoretical capabilities that will enable measuring and characterizing material-environment reactions under extreme conditions with the spatial and temporal resolution described in many sections of this report. Through fundamental understanding, more rapid and effective design of materials can be achieved enabling the identification of materials compositions, structures, and operating parameters with enhanced resistance to corrosion and surface damage in extreme environments.

**Research Directions**

Corrosion and interfacial reaction processes are complex, involving the need for understanding dynamic and multi-variable environmental processes and their effects on materials processes which can be extraordinarily challenging to observe directly through the length and time scales that we required to design to and understand materials performance. In particular, the following processes are areas in which a significant research effort is needed to better elucidate the mechanisms and to establish more fundamental models:

- point defect and chemical transport
- interfacial reactions, film formation and phase stability
- localized oxidation and environmentally assisted cracking
- radiation-induced corrosion

Corrosion and oxidation are still described by models that were developed decades ago. Their verification and accuracy is limited by the lack of understanding of point defect behavior and chemical transport in metal-oxide systems. Corrosion is an electrochemical process that relies on charge creation and transport. The understanding of charge transport in the corrosion process is still unclear and more robust models are required to address this important process that is often believed to be the rate limiting step in surface degradation. This is particularly true under extreme conditions. We require a far more fundamental understanding of how extreme environments, including irradiation, temperature, pressure, and a variety of chemical potential gradients, affect material-environment interfaces and processes– including chemical reactions,

charged species transport, and plasma-surface interactions. For example, a more robust treatment of point defects and the transport of chemical species via an electrochemical potential gradient in oxides is required in order to understand the growth of films.

Environmental interaction involves the formation and evolution of oxide layers, which can either protect or consume the structural material. Reactions at the interfaces are critical to the understanding of the evolution of the fluid-oxide-metal system. This involves the determination and modeling of the chemistry of molecules near interfaces, of bound interfacial species and of the near-surface solid material. It also includes the processes of oxide film nucleation and early growth. The stability of oxide phases formed far from equilibrium is important to understand for applications in extreme environments.

Localized oxidation and environment-induced cracking present unique challenges in complexity with controlling processes occurring in constrained environments influenced by local chemistry, structure, temperature, stress, deformation and radiation. Stress plays a strong role in the environmental integrity of materials by destabilizing surface films, altering oxide nucleation and growth and inducing localized cracking through films. High resolution, in-situ techniques are needed to understand the reactions that drive localized processes such as pitting, selective oxidation and stress corrosion cracking.

In the few experiments conducted to measure its effect, radiation has been observed to induce large increases in corrosion of as much as 10x that in its absence. However, as stated in the report on basic energy needs to assure a secure energy future [1], "there is insufficient fundamental understanding of radiation effects on the chemical behavior of nuclear reactor components to reliably predict component properties and thus mitigate service failures." Radiation can accelerate corrosion by a number of processes including radiolysis of the coolant, generation of surface excitons, increased diffusion through the metal-oxide couple, nucleation of oxide particles, etc. However, since radiation-induced corrosion requires that corrosion occur under irradiation, few experiments have been conducted that directly interrogate the system to elucidate the most important processes. This is a key research direction that is vital to the development of corrosion resistant materials for nuclear systems.

**Capability Gaps**

There is a great need for capabilities that that allow us to manipulate extreme environments and *simultaneously* observe, accelerate, control and mitigate kinetics, phase transformations and mechanisms. Experimental stations are, therefore, needed for in situ measurements in extreme environments that would allow us to control radiation levels, temperature, pressure, and environmental chemistry. In kinetics, proof of a mechanism is very much like a proof in a court of law and, therefore, no single method is adequate for resolving specific rate limiting mechanisms and governing processes. Therefore, these experimental stations must have a range

of diagnostic capabilities that can acquire information in parallel. Examples of the types of in-situ diagnostics required are:

- Researchers at Los Alamos demonstrated the ability to measure corrosion rates by electrochemical techniques under extreme irradiation conditions as part of the Accelerator Production of Tritium (APT) program [2].

- Oxide growth on nickel metal and stainless steel samples was measured in-situ in a microreactor cell using x-ray diffraction at APS with samples at high temperature (400°C) and high pressure (25 MPa) [3].

- Interfacing of a particle accelerator and the TEM provides for real-time imaging of defect cluster formation, evolution and destruction, that provides unique information on the fundamental processes involved as well as the time scale for their occurrence [4].

It is expected that new diagnostic tools and detectors will require development to probe and possibly survive under extreme conditions. These systems must probe the environment as well as a range of materials processes. Examples of techniques for probing materials surfaces include: synchrotron x-ray and neutron diffraction, glancing angle and bulk diffraction, XANES, XAFS, X-ray tomography, Raman spectrometry, etc.

A range of irradiation capabilities, including high flux sources (neutrons, ions, gammas, plasmas) and diagnostic tools will be required. While reactors are ideal for the study of radiation effects in relevant conditions, instrumented target chambers interfaced with particle accelerators provide accessibility that is difficult to achieve in reactors. As such, the development of a range of irradiation sources will be required to make significant progress on this objective. In particular, particle accelerators are required that are capable of producing radiation damage in targets subjected to other components of the extreme environment. Interfacing of multiple beam lines to capture additional elements of the radiation environment (e.g. formation of He) and to visualize damage as it occurs (TEM-accelerator interfaces) are also important to the problem.

In addition to the gaps in experimental sciences, computational modeling tools that simultaneously treat multiple processes in multiple phases must be developed. Chemistry effects due to radiolysis of the environment, material and point defect transport through a growing corrosion film, stress effects such as mechanical breakdown of the growing film due to volume changes between the growing film and parent material, the nucleation and evolution of irradiation damage in the underlying metal, hydrogen transport and the precipitation of hydrides under stress and temperature gradients, and the localization of chemical and mechanical effects are just some of the processes that need to be accounted for. Each of the these processes can have significant impact on material performance and need to be treated on their individual length and time scales. A complete model for macroscopically observed behavior must knit those models together in a meaningful way. As an example, phase field models for evolution of microstructural damage need to be fed information on defect interaction energies and cascade

dynamics from molecular dynamics simulations and coupled with finite-element calculations of the stress-state. The ultimate goal is a predictive tool for film growth that is based on the appropriate underlying physics that can be simplified for use in design of corrosion resistant materials. A similar model structure can be defined for more local phenomena such as stress-corrosion cracking.

**Potential Impact**

Robust materials have not been designed to survive in these extreme environments for extended periods of time because the underpinning degradation mechanisms are not sufficiently understood in the complex, high temperature environment consisting of radiation, a corrosive coolant and mechanical stress. Replacing empirical and data-based approaches to prediction of corrosion and other surface degradation processes with physics-based, experimentally-verified models will provide the capability to treat corrosion as an integral part of materials development and performance. It will also provide the capability to model the full response of materials to all components of an extreme environment and to use this knowledge to develop new, corrosion resistant materials.

The knowledge and capability will provide predictive models to support a range of national needs including plant life extension of nuclear power plants that employ existing materials as guidance for the more rapid development and validation of new materials for advanced fission and fusion reactor concepts, and predictive models will be developed that can be applied to nuclear weapons stockpile stewardship. Corrosion is estimated to cost the U.S. on the order of 3.1% of GDP [5]. Consequently, improved predictive and design capabilities will improve sustainability practices, reduce infrastructure costs and broaden the operating window for many materials applications in corrosive and extreme environments.

Many parallels exist between the performance of materials in extreme and environments and functional materials such as energy storage materials and gas separation membranes. Corrosion is likely to be a key issue in solar cell lifetime and wind turbine performance and will become more important in large-scale central power plants. Strategies for scrubbing emissions and capturing carbon will likely be limited by corrosion. Similarly, high efficiencies of central station plants are achieved through very high temperature of the working fluid, which means a much higher cost of corrosion than we see today. The storage and (eventual) disposal of nuclear waste are largely an issue of containment vessel corrosion rates and possible failure modes. Virtually all energy sources will see an increasing cost of corrosion and the manifestation of new forms of corrosion. Therefore, developments in corrosion technology are key to improved efficiency in energy production.

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**Priority Research Direction: Creating and Exploiting the Chemistry of a New Periodic Table Through Extreme Pressure-Temperature (P-T)**

**Problem Statement**

Compression of matter results in reordering of the shell structure of electronic levels in atoms, effectively creating a "new" periodic table with the promise of creating wholly new materials. When combined with the ability of using temperature to rearrange populations of states, the chemistry observed at extreme P-T conditions is radically different than that observed at ambient pressure and temperature. We seek to exploit the resulting novel chemistry to create new, stable materials with new functionality; understand the chemistry of planetary interiors; and facilitate the development of new theories with enhanced predictive powers.

**Executive Summary**

The electronic structure, bonding and chemical reactivity of atoms is fairly well understood under ambient conditions. However, the rearrangement of atomic levels induced by compression can result in radically different reactivity, bonding and structure. For instance a metal such as sodium can become a transparent insulator; simple molecular systems such as $O_2$ become a metallic superconductor; and a greenhouse gas such as $CO_2$ can become a solid with novel optical properties. Such results point to the existence of a "new" density-dependent periodic table, whose control and exploitation still require a deeper fundamental understanding of the effects of density on atomic and chemical bonding. Key scientific challenges include the prediction and creation novel chemical states at extreme P-T while understanding the effects of P and T on atomic structure, bonding, and reactivity; utilizing Gbar pressures to induce core-electron "kilovolt" chemistry; and to use matter/radiation coupling in concert with P and T to control chemistry and reactivity.

Such challenges will require new computational tools for describing electronic structure and thus enable a predictive capability of chemical reactivity and bonding, over wide ranges of P and T. These challenges will also require the continued development of ultrafast *in situ* diagnostics in order to observe bond breaking/formation, local energy populations and their redistribution, stoichiometry, kinetics, and to observe the production and effects of short-lived transient states. However, our current ability to control thermodynamic states with the necessary precision over a large range of T, P, and strain rate ($\eta\square$) is limited, and we do not currently have the time-dependent spectroscopic diagnostics capable of *in situ* (sub-surface) probing of extreme conditions at high spatial resolution. We must continue to develop time-domain diagnostics for extreme chemistry, and to move beyond existing theories to overcome the theory/experiment timescale gap.

However, should such capability gaps be overcome, the scientific impacts will be revolutionary. Control of the new periodic table will enable the creation of wholly new, stable materials with exotic new properties, which we imagine will be replicable at "normal" conditions. In addition,

closure of these gaps will lead to the understanding of reactivity, mechanisms and chemical processes in planetary interiors. Such knowledge is needed to understand matter where reactive energy – the energy released from chemical reactions or burn – is significant relative to other sources. We also imagine the ability to design and control the energy release in energetic materials: this could lead to safer nuclear weapons (use of on/off explosives), enhanced defeat of Improvised Explosive and Nuclear Devices (IEDs and INDs) and modern munitions with increased performance for a given mass.

**Scientific Challenges**

The key to exploiting a high-density periodic table is first to determine the effect of extreme density and temperature on the electronic structure, bonding and reactivity of matter, and then to develop new theoretical and computational tools to enable predictive capability. Accordingly, this PRD addresses the following critical scientific questions:

- How can we predict and create novel chemical states at extreme PT that potentially alter our view of the periodic table under these conditions?
- What are the effects of high pressure and temperature on atomic structure, bonding, and reactivity?
- Is chemistry and structure different at Gbar pressures, where the energy of compression is of the order of a keV, and thus high enough to promote core electrons to participate in bonding and reactivity?
- Can we control chemistry and reactivity by coupling matter and radiation coupling in concert with extreme P and T?

**Research Directions**

The goal of this PRD is to develop a detailed understanding of how electronic structure and atomic and molecular mechanisms are changed by extremes of P, T and strain rate, and to predict and control the creation of new materials formed under such conditions. Developing such an ability will have wide ranging consequences across wide ranges of materials science, defence needs, and geo and planetary science. Three key research directions are identified.

*Developing computational tools to enable prediction of chemical reactivity, bonding, over a range T, P, $\rho$ states*

The success of modern DFT and other computational methods has resulted in an ever-increasing number of non-specialists using these techniques to support and direct experimental studies of materials. Such techniques can accurately describe the properties of "normal" metals at ambient conditions, and are expected to become a still better computational tool for understanding highly-

dense matter where materials might be expected to become more free-electron like. However, such techniques cannot accurately describe atomic bonding, particularly van der Waals bonding, chemical reactivity, or the energy released from chemical reactions. Furthermore, the use of established and widely-used simulation techniques such as traditional molecular dynamics needs to be carefully examined for extreme conditions, where the ambient-pressure interatomic interaction potentials are no longer appropriate.

In order to fully exploit a density-dependent periodic table it will be essential that we develop specialized computational tools that correctly describe the exotic electronic structures and interatomic interaction potentials occurring at high density over the necessary length- and time-scales, and thereby enable a predictive capability of chemical reactivity, bonding, over a wide range of T, P, and strain states.

*Developing ultrafast diagnostics to observe bond breaking/formation, local energy creation, stoichiometry, kinetics*

In order to understand the new chemistry, reactivity and reaction kinetics that will arise at extreme densities and temperatures, it will be essential to develop a new generation of *in situ* diagnostics in order to observe bond breaking/formation, local energy populations and their redistribution, changes in structure and stoichiometry, and phase separation and kinetics over the complete range of time and length-scales. While such techniques (TEM, AFM, femto-second spectroscopy, ultra-fast electron diffraction, tomography) are well established at ambient pressures, the experimental constraints imposed by the methods required to produce high-density matter (either statically in a diamond anvil cell or via dynamic compression) impose serious constraints on experimental techniques (either geometrically or temporally) and/or the interpretability of data.

The suite of new advanced probes must include a combination of x-ray and neutron diffraction, spectroscopy, scattering, other electron and proton probes, pump-probe experiments that combine both optical and x-ray probes (or other particle probes), and advanced imaging techniques that span length-scales from angstroms to millimeters. The ultimate goal is the femtosecond imaging of chemical reactions on material surfaces, interfaces, or buried within a compressed sample with atomic-scale spatial resolution. This effort will be complemented with the development of 3D tomographic studies at relevant length- and time-scales of chemically reacting solids in extremes.

*Observing the production and effects of transient states*

While static compression techniques have had some success in determining the physical properties of final, stable states and reaction products at high density, there is little detailed information on either the existence of, of properties of, transient states that exist before the final stable state. Of particular importance are the many transient states created during dynamic compression experiments, where the reaction pathways (the many different possible routes in P,

T, strain and composition space through which the reaction can take place) which may result in very different materials.

**Capability Gaps**

While the exploitation of a new high-density periodic table has possibility to offer revolutionary breakthroughs in the understanding of matter and reactions at high density, and the creation of wholly new materials, there are a number of critical capability gaps that need to be addressed.

For example, we do not currently have the ability to control state conditions with necessary precisely over a large range of T, P, ρ. The necessary time-dependent spectroscopic diagnostics capable of *in situ* (sub-surface) probing of bonding, structure and reactions over all relevant length-scales have not yet been adapted to the study of reactions of solids and in extreme environments. Similarly, the development of time-domain diagnostics for extreme chemistry is still in its infancy. Finally, concerted effort is required to move beyond existing theories to overcome the orders-of-magnitude timescale gap that currently exists between theoretical and experiment studies of high-density matter.

**Potential Impact**

The discovery of new forms of chemical reactivity and behaviour that are promised by establishing and exploiting a new periodic table would be transformative.

We can envisage the controlled creation of new stable materials, with properties unlike those yet observed under "normal" conditions. Our understanding of high-density chemistry will enable us to understand chemical reactions within the Earth – essential to the understanding of $CO_2$ sequestration in the Earth's crust – and also at the very much higher pressure found in other planets, which will enable an ability to determine the chemical makeup of extra solar planets

The detonation and deflagration of energetic materials is still understood at a rudimentary level. Present theories lump most of the chemistry into overall reaction rates or energy release rates. The overall goal is to develop a complete time-dependent description of detonation and the evolution of the products equation of state for military purposes as well as to facilitate the introduction of new energetic materials for military, counter-terrorism, surety and industrial applications. This will lead to the design and control the energy release in energetic materials, which will lead to safer nuclear weapons (use of on/off explosives), enhanced defeat of Improvised Explosive and Nuclear Devices (IEDs and INDs) and modern munitions with increased performance for a given mass.

Finally, when reactions occur they can put or take away energy from the system. This will affect the hydrodynamics and thermodynamics of the system in new ways. Understanding how systems that are "burning" (introducing additional significant energy terms into the system)

behave and the nonlinear interactions caused by the burning will have major impact on understanding and control of applications from turbulent chemical flows to inertial fusion.

**Priority Research Direction: Predicting, characterizing, and controlling the performance of matter between solids and plasmas**

## Problem Statement

Recent advancements in intense, pulsed light sources provide revolutionary capabilities to subject matter to extreme conditions of pressure and temperature, creating novel conditions that span all the way from the solid state to weakly coupled plasmas. Those sources also provide new powerful tools to diagnose those novel conditions. The state of matter between the solid state and weakly-coupled plasmas is known as warm dense matter (WDM). Understanding the nature of WDM is one of the fundamental goals of the physical sciences associated with laboratory astrophysics, planetary dynamics, evolution of stars, and energy technologies. WDM is extremely challenging to model, because the typical approximations (e.g., expansion parameters) used in either solid state or weakly-coupled plasmas are not applicable. Creating and diagnosing WDM is very difficult for several reasons, such as its transient nature, the need for dynamic measurements, and the difficulty in creating sufficiently large and homogeneous samples. Understanding WDM is important in basic science (e.g., to understand the nature of giant planets) as well as in applied science (e.g., in understanding material behavior and equation of state in shocks and explosions, laser-matter interactions and non-linear optics, inertial fusion energy, etc.).

## Executive Summary

The area of WDM where the conventional theories of condensed matter physics and plasma statistical physics are invalid is found in the regime above the solid with high temperature and pressure in the temperature-pressure phase space. Model calculations in this regime predicts exotic states including new atomic and electronic band structure, phase transitions, anomalous transport and scattering properties and changes of opacity . However, due to the lack of the appropriate light source and robust diagnostics, experimental investigation has been limited. The study of WDM offers the possibility of exploring new material science and physics in diverse areas including solids in extreme conditions, extreme chemistry, planetary physics, and inertial fusion. In summary, we expect that the understanding WDM will have a far-reaching impact in the research of materials in extreme conditions, the overarching opportunity for a new interdisciplinary research frontier.

## Scientific Challenges

The applications of these new theoretical and experimental tools will enable an increasing understanding of WDM and an exploration of matter in extreme density and temperature conditions. Advanced scientific challenges include:

*1) What is the nature of the extreme behavior of matter (compression, shear strength, flow, structure, "solidity") at extreme conditions?*

*2) Can we predict the bheavior of matter as we traverse pathways through the phase space described by extreme pressures and temperatures.*

*3) Can we control and utilize matter under extreme conditions?*

**Research Directions**

To accomplish the goal for the understanding of this new area, we outline the research direction in two key issues.

*Measure EOS, atomic and electronic structure, opacity of WDM*

Experimentally, the study of WDM has been severely limited because the creation of WDM and its diagnosis is extremely challenging.. Characterization of WDM is the first step on the road to understanding its properties. The equation of state (EOS) is a thermodynamic expression that relates pressure, density, and temperature, describing how WDM responds to the change of those three variables. There is no general, validated EOS model for WDM. Measurement of

Figure 1. Schematic phase diagram of hydrogen.

populations of bound/free electrons will provide the information of atomic and electronic structure of WDM. Diagnosis of the opacity, conductivity and other transport coefficients, as well as compressibility also will provide fundamental information needed to characterize a given WDM system. The ability to provide different loading pathways, besides the traditional shock Hugoniots, is necessary to access and study the parameter range of interest.

For example, an illustrative experiment on hydrogen in Figure 1 shows arbitrary loading pathway. Red line notes isochoric heating to few eV with proton beam and isentropic compression to few g/cc. To characterize this WDM area, proton radiography diagnosis of $\rho r$, keV X-rays & heavy ion-beam probe, X-ray Thomson scattering, $dE_b$ / dx, and opacity diagnostics are required.

*Develop self-consistent theory that permits prediction of WDM properties*

The ability to calculate EOS is critical to predict WDM properties. Since no obvious ordering parameters exist and the theoretical uncertainties in existing models are huge, standard theoretical approaches in the WDM regime are neither validated nor reliable. The key will be in integrating the diverse, reduced models describing different phenomena at different spatial and temporal scales into a framework and tools with predictive capability. The development and validation of a more general WDM theoretical framework will have a profound impact on the study of WDM per se, as well as other disciplines where WDM plays a role. There are many systems in applied and basic science that either live in, or traverse the WDM phase space. There is also astrophysical interest in WDM modeling. A theoretical description of WDM at Mbar pressure will pin down theories of formation of astrophysical entities such as planets, brown dwarfs or neutron stars, some of which are very difficult to observe.

**Capability Gaps**

Using time- or spectrally- resolved techniques in scattering and spectroscopic diagnostic tools, we may be currently able to probe the WDM within limited conditions. However, conventional visible-light probes cannot penetrate dense matter to measure transient WDM properties volumetrically, limiting their use to surface measurements. For the successful achievement of WDM study, the following issues must be addressed.

- *Creation of homogeneous WDM using arbitrary pathways*
- *Theoretical ability to treat degeneracy, strong coupling, and quantum effects simultaneously*
- *Multi-beam sources for WDM sample and probes for simultaneous measurements of multiple state variables*
- *Develop time-dependent Thomson scattering (theory with experiment) and diffractive imaging*
- *In situ diagnostics for atomic-to-macroscopic structure higher fluence, higher energy light sources*

**Potential Impact**

The area of WDM which occurs in extreme condition of high pressure and temperature is strongly related to the other research areas, including strongly coupled plasma physics, high-temperature and pressure condensed matter physics, extreme chemistry, planetary dynamics, astrophysics, and energy technologies. When a comprehensive understanding of the nature of WDM comes, it will provide quantification of load-path-dependency of physical properties of WDM, prediction, manipulation, and control of high pressure matter. Further it will also motivate advances use-inspired research such as inertial fusion, material damage, manufacturing materials under extreme conditions.

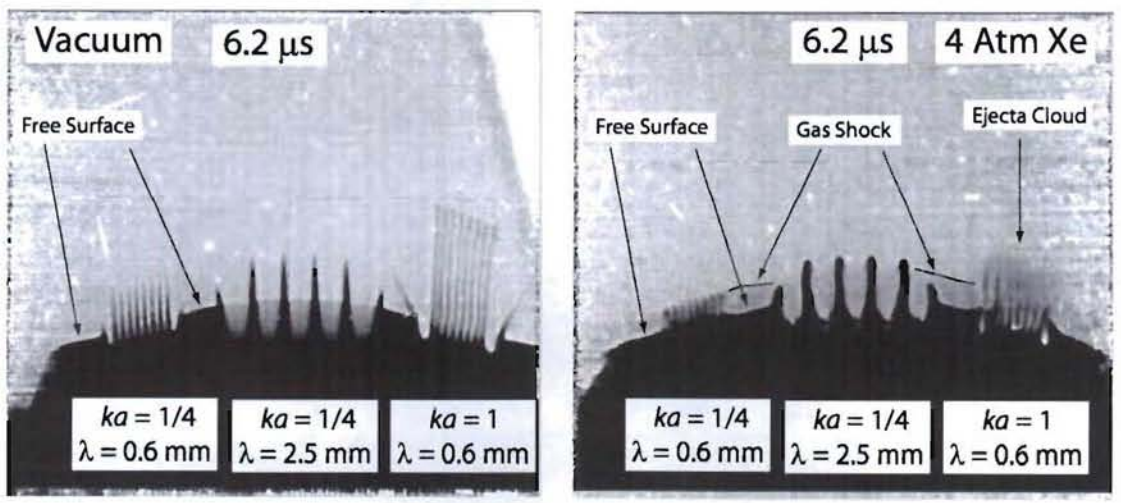
*Priority Research Direction: Determining the transport of energy, momentum and mass under extreme density and temperature*

**Problem Statement**

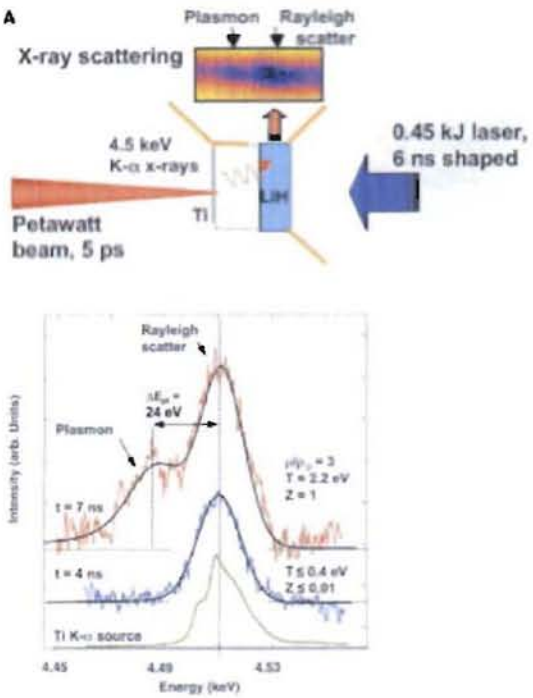
Once warm dense matter is made and characterized (matter at extremes of density and temperature where the usual order parameters fail), the next problem is determining its dynamic behavior: what are the fluxes of mass, momentum and energy in conditions where materials may lose strength, may melt and re-freeze, are in transition regimes in fluid parameters, and may introduce quantum or coupling effects that are new.

**Executive Summary**

The dynamic behavior of materials depends on transport coefficients that relate fluxes of state variables (energy, momentum, and mass) to their gradients. Under extreme conditions the order parameters that define condensed matter change, fail, or disappear, and no longer apply to describe materials and their dynamics behavior. These conditions, have relevance to inertial fusion, stockpile stewardship, or stellar explosions, and have significant uncertainty because of these complex dynamics. Creating the extreme conditions of matter, while simultaneously measuring its state variables with sufficient spatial and temporal resolution to determine gradients and fluxes is a scientific frontier challenge. Developing theory that can explain the material behavior in these new conditions where the usual order parameters fail is the other major research need.




The transition of solid material to spikes, ejecta, and eventually particulate matter. These are proton radiographs of perturbed surfaces under shocked conditions. Data courtesy of William Buttler, LANL.




Example of transient measurements needed for transport measurements in extreme conditions. This example shows x-ray scattering. spectrum from shocked LiH. From Kritcher et al., Science 322 (2008) pg. 69

**Scientific Challenges**

Making the matter in these extreme conditions of density and temperature in ways that allow *in-situ* measurements before hydrodynamic disassembly, as well as making the multiple simultaneous measurements to properly quantitatively diagnose the overall state are challenges to this field. Measurement of transport coefficients requires not just the values of the state variables, but also spatial resolution to provide measurement of the gradients or time resolution to measure time derivatives. The usual order parameters that can be used to theoretically describe the topology and behavior of the material begin to fail in these extremes; quantum effects change as pressure puts additional effects into the system.

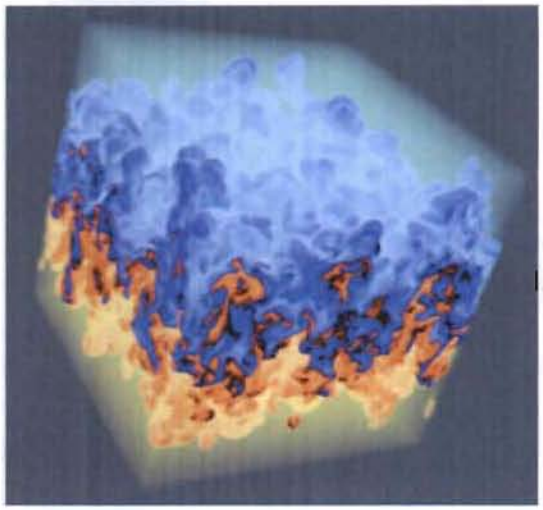
Key questions that need to be addressed include:

- What is the relationship between strength of solid materials, viscosity of fluids, and in general resistance to states of shear stress? Understanding such relationships help connect flow to constitutive properties of materials, and are vital for predictive capability of hydrodynamic behavior.
- How can accurate simulations be done in the absence of easy asymptotic parameters (parameters large or small that theories can be expanded around), and what experiments are needed to validate the underlying theories? These extreme conditions are difficult to create in a controlled manner, but vital for many applications, and so limited data will be available to develop critical theories.

**Research Directions**

In general we see two thrusts: 1) advances in theory, and 2) advances in experiments. In these conditions of extreme matter where usual order parameters fail, a self-consistent methodology needs to be developed for calculating viscosity for momentum diffusivity (similarly mass, temperature, and electrical diffusivities), thermal capacity, charged particle stopping power, and electron-ion equilibration. Based upon sound physical reasoning, new materials theories applicable to these regimes must be discovered, developed, and validated to allow accurate and efficient predictive capability.

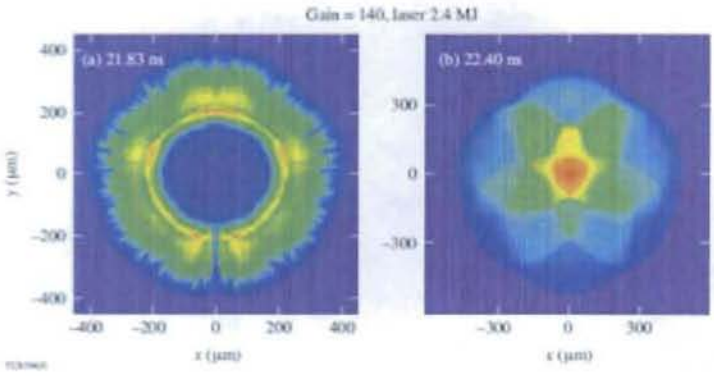
In experiments, these extreme pressure and temperature create strong gradients and therefore very rapid transport conditions. Because of these strong spatial gradients, development of experimental techniques to simultaneously create the necessary material states and measure strong gradient conditions in adequate spatial resolution the for short times are needed.



An example where turbulence meets reactive chemistry. It is proposed that for the case of this slow reaction the turbulent flame is of single-fractal character, and the distribution of temperature is strongly intermittent. Simulation from Michael Chertkov, LANL.

**Capability Gaps**

The capability gaps for determining transport behaviors and properties are even more challenging than measurement of local state variable properties because of the need for higher time and space resolution (gradients are non-local quantities). Homogeneous warm dense matter must be created using arbitrary pathways, which requires significant energy density to be applied. Multiple state variables (density, temperature, etc.) must be simultaneously (space and time) measured, which requires multiple-beam sources for making the WDM sample and then probing it. The current revolutionary tool in this field is the x-ray free-electron laser (XFEL), which provide high brilliance at sufficient photon energy to probe these states of extreme matter. They can provide *in-situ* diagnostics for atomic-to-macroscopic structure; however, gaps remain in our ability to make the matter in relevant states. A key diagnostic is x-ray Thomson scattering; the technique must be develop to include time-dependent Thomson scattering (theory with experiment) and its coupling with coherent diffractive imaging. Finally, there are significant gaps in theory and its ability to treat degeneracy, strong coupling, and quantum effects simultaneously.




An example of inertial fusion energy target implosion calculations from a two-dimensional simulation, illustrating the impact of hydrodynamic instabilities on fusion burn. Calculation courtesy A. J. Schmitt, NRL.

**Potential Impact**

Material flow is central to important energy applications, and becomes a significant uncertainty for matter in extremes. In particular, better understanding of variable density flow in rapidly transforming objects and is critical to such applications as inertial fusion energy, stockpile stewardship, stellar explosions, nuclear reactors, cooling devices, and casting.

## Priority Research Direction: Controlling photon-matter interactions: making every photon count

### Problem Statement

Applications ranging from renewable energy to advanced computation require significant advances in the scientific basis for controlling photon-materials interactions, as well as the conversion of the reluctant excitations into usable energy. Classically, this concept of 'making every photon count' involves the creation of tunable photonic materials with multifunctional, broadband electromagnetic response. In the quantum regime, we aspire towards a predictive capability for the design of materials and/or pulse sequences to coherently control the outcome of the interaction, either electronically or structurally.

### Executive Summary

The goal of this priority research direction is to develop the science and accompanying technology to enable exquisite control of photon-matter interactions over a wide range of conditions for multiple applications. To achieve this goal, we will need to understand, control and optimize photon-material interactions, spanning the classical regime of electromagnetic interactions, currently enabled through plasmonics, photonic crystals and metamaterials, to the quantum regime of coherent excitations, and materials design to control functionalities such as

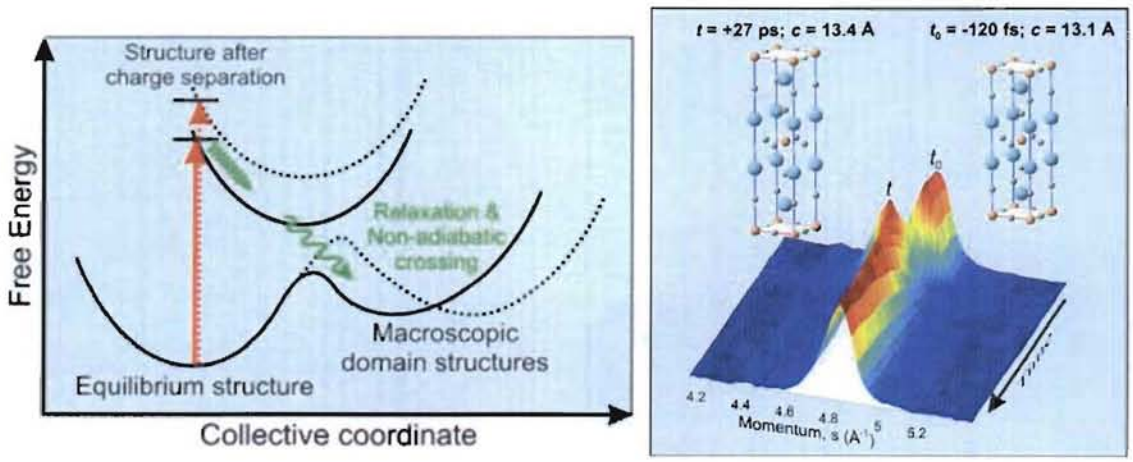



**Figure 1:** (a) New metastable photo-induced state in $La_2CuO_{4+\delta}$ that is not thermally accessible. (b) Characterization of metastable state using ultrafast electron diffraction reveals that a structural phase transition has occurred. Excitation to this state via coherent control with optimally shaped pulses should enhance access (lower threshold fluence, etc.) [From: Gedik et al, Science 2007]

charge and energy transfer and transport, charge separation, and the conversion of electronic excitations into optical signals or electrical energy. Such control will be essential for next generation renewable energy technologies, the design of catalytic materials and multifunctional materials for sensing, advanced computing and communications, the understanding of reaction mechanisms, and new directions such as the nanomechanics of Casimir force control.

**Scientific Challenges**

In the area of classical control of light, currently comprising metamaterials, plasmonic structures, and photonic crystals, we must address the following scientific challenges:

- Controlling loss or introducing gain in photonic structures in order to enable their use beyond visible frequencies.
- Developing new approaches to enable broadband electromagnetic response, rather than narrow resonances.
- Understanding and controlling bianisotropy in order to achieve magneto-electric functionality.
- Design and fabrication of 3D structures with isotropic functionality
- Understanding of the effects of inhomogeneity beyond the effective medium approximation.
- Understanding, designing and optimizing nonlinear response in novel photonic

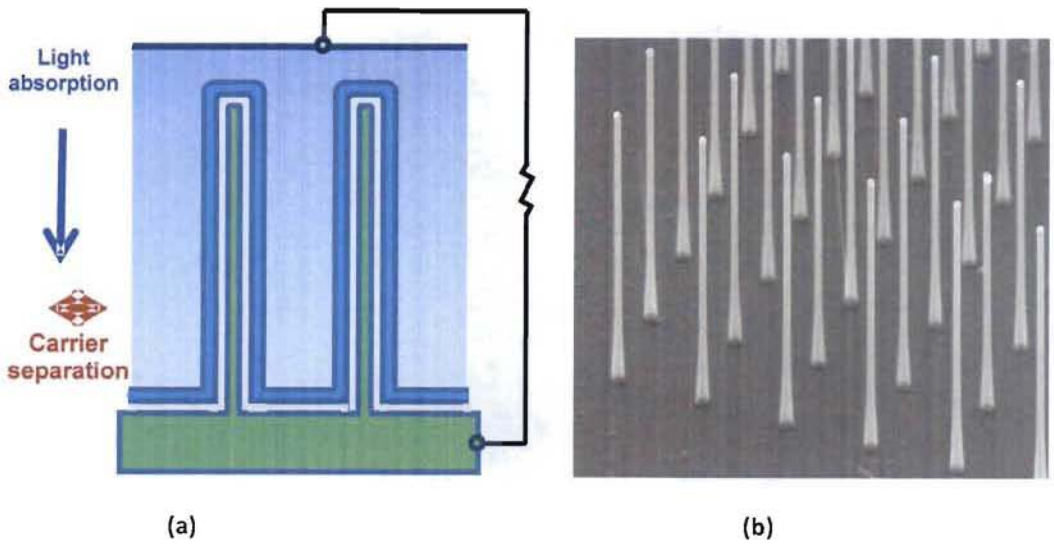



**Figure 2:** Semiconducting nanowires provide geometrically separate mechanisms for controlling light absorption and carrier separation, essential for third generation solar energy harvesting. (a) Schematic of radial p-i-n nanowire photodetector showing the separate processes. (b) SEM image of ordered array of nanowires. [Picraux et al, unpublished]

structures which would enable further functionality from these materials, including dynamic control of functionality.

- Manipulation of higher frequencies of photons (beyond visible), using smaller and smaller nanostructures, ultimately requiring manipulation on the atomic scale (and therefore merging with quantum control.

In the area of quantum control of photon-matter interactions, we must address the following scientific challenges:

- The discovery of non-thermally accessible states (Figure 1) with unusual properties and an understanding of their properties.
- Development of a predictive capability to design and implement pulse sequences to coherently control the interaction of photons with electronic (femtosecond to attosecond timescales) or structural degrees of freedom (picosecond timescales) in order to control material functionality or chemical reactions.
- Design, synthesis and fabrication, characterization and optimization of materials to control functionalities essential for photon conversion processes, such as charge and energy transfer and transport, charge separation, and the conversion of electronic excitations into optical signals or electrical energy. (See Figure 2 for an example of this challenge.)
- The combination of materials developed for specific photon-matter interactions with coherent control to optimize or provide further control for a specific functionality.
- Development of pulse shaping techniques, analogous to multidimensional NMR spectroscopy to control multiple degrees of freedom.
- Integration of classical quantum control to ultimately 'make every photon count.'

## Research Directions

Research directions here encompass the two sides of the light-matter interaction: using light to quantum mechanically control matter through its interaction with electronic or structural degrees of freedom (Figure 3) and matter to classically control light through plasmonics, photonic crystals and metamaterials (Figure 4). The first promises new functionality for matter in controlling its chemistry and bulk response (including synthesis of new materials), the second new functionality for light in controlling its intensity and propagation for communication, imaging, cloaking, switching, sensing and interacting with matter. The two are synergistic, in that plasmonics and metamaterials can be used to shape light pulses classically that are then used to quantum mechanically control matter.

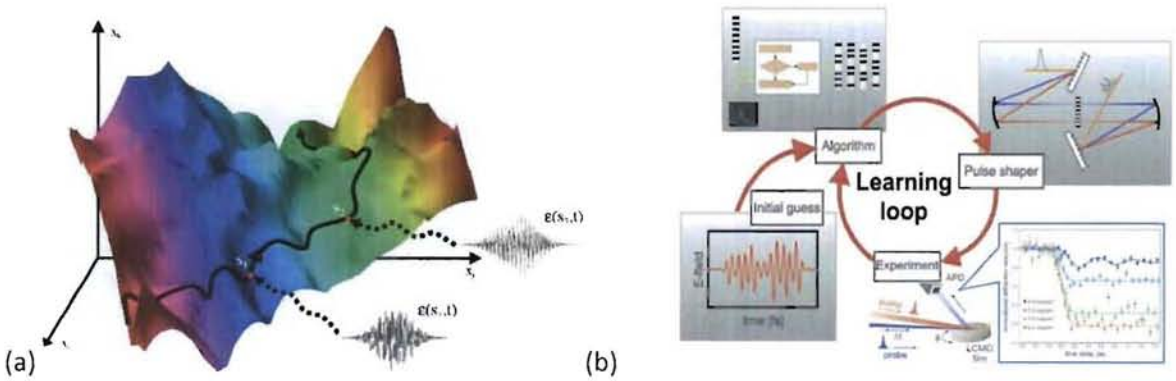
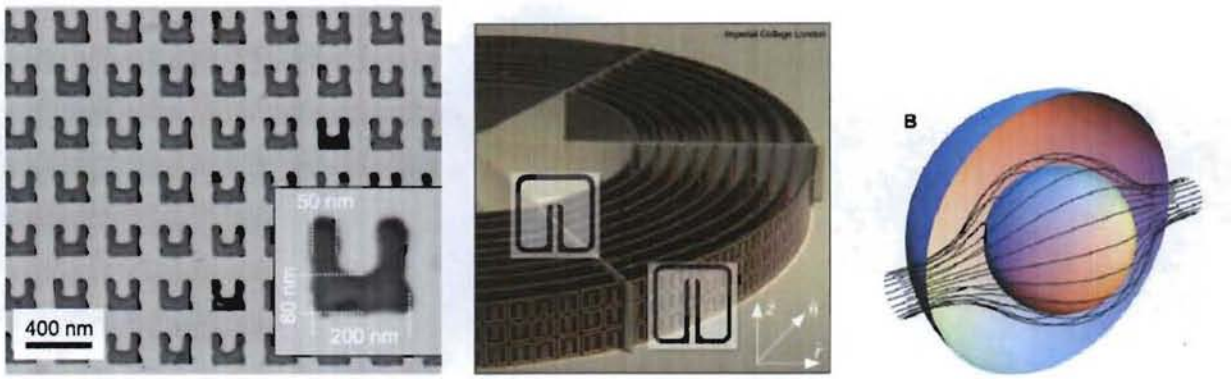



**Figure 3:** Quantum coherent control is a quantum mechanical process that exploits the fact that the evolution of a quantum system is a result of constructive interference between multiple available routes connecting initial and final system states. If the laser pulse has a broad enough spectrum to overlap with several paths (states), it will impose its spectral phase and amplitude distribution on the corresponding path probabilities. (a) Proper selection of the laser pulse phase and amplitude profiles provides a way to guide a system along a particular path through destructive interference of all alternate routes. (b) In general, the tremendous complexity in modeling sizable quantum systems precludes *a priori* identification of optimal pulse shapes; instead, an adaptive coherent control method is used to extract the desired pulse shape from the analysis of pulse-system interactions. Diagram of an adaptive coherent control experiment is shown where a randomly chosen initial pulse shape is iteratively optimized to eventually provide the desired experimental outcome.




(a) (b)

**Figure 4:** Metamaterial based structures enabling classical control of electromagnetic radiation. (a) Negative index metamaterial, optimized for infrared frequencies. (b) Structure enabling electromagnetic cloaking at microwave frequencies and simulation of cloaking based on the concept of transformational optics.

To date, the fields of plasmonics and metamaterials have allowed rudimentary control over classical interactions of light with matter, while a combination of materials design and coherent control has enabled optimization of quantum mechanisms and/or wavefunctions for specific functionality such as control of reaction products, phase transformation or energy conversion. In the classical regime, research directions required 'to make every photon count' include developing new approaches to next generation photonic materials to address issues of bandwidth, loss, isotropy, dispersion, inhomogeneity, bianisotropy, active control, and nonlinearity. In the quantum regime, research should be directed towards the development of a predictive capability to design materials and/or pulse sequences to coherently control the interaction of photons with electronic or structural degrees of freedom.

## Capability Gaps

Specific capability gaps required to achieve control of photon-matter interactions include:

- A predictive theory of nanoscale electromagnetic interactions beyond effective medium theory, ultimately incorporated into simulation tools for design of functional electromagnetic structures
- A predictive theory of coherent photon-matter interactions.
- Fabrication of complex 3D nanoscale architectures
- Integration of diverse nanoscale materials to achieve the desired functionality
- Nanoscale materials' characterization with ultrafast temporal resolution.
- Coherent spectroscopic techniques with ultrafast temporal and nanoscale spatial resolution, as well as specificity to functionality (electronic, magnetic, structural, photonic, chemical, etc.).

- Design/implementation of ultrafast pulses (attosecond to picosecond) to control structural and/or electronic excitations.

**Potential Impact**

'Making every photon count' will impact multiple application areas from renewable energy to global security to discovery science. The development of a predictive capability to control photon-matter interactions, spanning classical to quantum regimes will impact the following areas:

- Renewable energy and environmental security: the creation of materials tailored for unique photon conversion applications efficient catalysis.
- Global threat reduction: design and development of sensors and detectors involving photons, quantum and classical, optimized for specific applications and materials for advanced communication systems.
- Nuclear deterrent: next generation materials for advanced computation.
- Discovery science: novel materials and phenomena and detailed understanding reaction mechanisms.

These research directions, coupling advanced synthesis, characterization and theory, are poised to provide answers to the five Grand Challenges posed in the BES report "Directing Matter and Energy: Five Challenges for Science and the Imagination."

- How do we control materials processes at the level of electrons?
- How do we design and perfect atom- and energy-efficient synthesis of revolutionary new forms of matter with tailored properties?
- How do the remarkable properties of matter emerge from complex correlations of the atomic or electronic constituents and how can we control these properties?
- How can we master energy and information on the nanoscale to create new technologies with the capabilities rivaling those of living things?
- How do we characterize and control matter away--especially very far away--from equilibrium?

The proposed research directions will apply the methods and tools of control science to advanced photonic materials with the goal of controlling functionality, an explicit requirement for next generation materials research, as described in the BES report, "New Science for a Secure and Sustainable Energy Future." This capability is required to attain the goal of controlled functionality in materials that will enable a secure future for our Nation.

**Priority Research Direction: Control Functionality from Electronic Complexity**

**Problem statement**

To develop a science-based framework for the design and fabrication of high performance functional materials based on multiscale electronic complexity in classes of inorganic, organic and hybrid materials through understanding the origins, consequences and control of complexity. Bringing together recent advances in theory, modeling, multiscale probes and synthesis will enable the required prediction, characterization, control and design .

**Executive Summary**

The last three decades have seen remarkable advances in the discovery of complex inorganic, organic, biological, and electronic materials with unexpected function and performance. Examples include superconducting oxides, pnictides and borides, giant and colossal magnetoresistance materials, plastic conductors and superconductors, carbon nanotubes, and graphene. The last decade has seen a similarly remarkable explosion of new and improved experimental probes of structure and function for multiple spatial and temporal scales, including scanning probe microscopies, focused x-rays, angle resolved photoemission, a variety of pump probes, time resolved crystallography, EXAFS, and diffuse scattering. There have also been remarkable enabling advances in synthesis including, for example, atomic layer control and directed self-assembly. These materials and probes increasingly reveal novel electronic functionalities that exist at several distinct scales organized into robust hierarchical, self-consistently supported systems. Creating new high performance materials with designed functionality requires understanding and controlling the link between complexity and functionality.

Harnessing electronic complexity for new levels of functionality will mark a qualitatively new era beyond the familiar Bloch theory applicable to periodic systems and small deviations therefrom. The Bloch framework has been remarkably successful for describing and controlling many simpler scientific and technologically important materials such as silicon. However, creating materials with higher levels of performance and functionality requires creating and controlling higher levels of complexity. Achieving this goal for the next decade is now feasible because of major advances in:

- Synthesis
- Multiscale space and time probes
- Simultaneous probes of multiple properties
- Theory of nonlinear, nonadiabatic, far from equilibrium phenomena, including systems with coupled spin, charge, and lattice degrees of freedom
- Modeling and simulation, including a new generation of high performance computing and visualization tools

In short, we can now build the "science of electronic complexity" – understanding its origins, measures, and consequences - and exploit this new knowledge to create radically new forms of electronic materials with greatly enhanced multifunctionalities, tunability, control and performance.

**Scientific Challenges**

The principal scientific challenges are

- Develop integrated capability, including theory, modeling, synthesis, and characterization, to create prescribed electronic energy landscapes by assembling multiscale hierarchical atomic and molecular patterns.
- Identify the relevant degrees of freedom and length/time scales for controlling macroscopic functionality.
- Relate nanoscale complexity to robust macroscale functionality

**Research Directions**

The functionality of electronic materials is linked to specific ingredients of their electronic complexity: closely spaced energy levels (e.g., electronic, phononic, magnetic) belonging to two or more competing and interacting phases. These ingredients can lead to ordinary phase transitions, nanoscale phase separation, emergent phases, or spontaneously generated hierarchical spatiotemporal patterns. The research direction is to control the outcome of these competitions and to design their functionality.

The major achievements of the research direction are

- Creating and understanding design principles for controlling the energy landscapes of interacting, competing states and the new phases they produce
- Identifying model systems with sufficiently rich energy landscapes to enable the above emergent features. particularly those arising from various couplings among spin, charge, and lattice degrees of freedom. Examples include relaxor ferroelectrics, heavy fermions, emergent phenomena near quantum critical points and at interfaces in multilayer systems.
- Developing experimental tools to correlate the local structural, spectroscopic and functional behavior of electronically complex systems. These must include a range of

time and length scales, using, for example, ultrafast spectroscopic techniques, fluctuation spectroscopy, and multi-color excitations such as multidimensional NMR.

- Developing appropriate theory and modeling tools for describing landscapes of closely spaced energy levels and interpreting the experimental probes.

The conceptual framework linking electronic complexity to functionality integrates the following challenging elements:

- Near degenerate energy states
- Far from equilibrium theory
- Time resolved dynamics, beyond simple relaxation time and effective temperature approaches
- Competing phases and the emergence of novel states
- Charge transfer driving structurally embedded electronic phases, e.g. Zintl phenomena
- Hieracrchical long and short range interactions
- Self-consistently organized local "hot spots" which collectively mediate functionality.

**Capability Gaps**

- Diffraction, imaging and spectroscopy tools for characterizing closely spaced energy landscapes with resolution approaching nanometer length and femtosecond time scales.

- Description of materials beyond Bloch theory ("thinking outside the Bloch"!): electronic structure techniques including nonadiabatic techniques for closely spaced electronic energy landscapes with nanoscale spatial inhomogeneity.

- Tools for working "outside the Boltzmann box": computational techniques to address far from equilibrium electronic, lattice and spin states using, for example, nonequilibrium Green's functions and quantum Monte Carlo methods.

- Understanding and achieving robust functionality, learning, self-healing, and ultimately sequential functionality via feedback from nonlinearity.

**Potential Impact**

- Creation of a new paradigm for the design of functional materials, starting with a targeted functionality, choosing the constituent competing ordered phases and designing the closely spaced energy landscape, wave function symmetry and competing interactions,

followed by iteration of the energy landscape inputs to converge the desired functional outcome.

- Creation of radically new forms of electronic materials with greatly enhanced mutifunctionalities, tunability, control and performance.

- Designing new materials with unprecedented performance for solar, fission, fusion and biofuel energy applications.

- Next generation multifunctional materials for sensing, communication and computation.

**Priority Research Direction: Controlling nucleation phenomena**

**Problem Statement**

Nucleation is a fundamental process step contributing to – if not in some cases controlling – many microstructural development and failure processes. Fatigue fracture and phase transformations are largely controlled by nucleation. Yet, theory of nucleation, in the case of phase transformations or solidification, has advanced little beyond that contained within the Johnson–Mehl–Avrami–Kolmogrov equation. Innovative measurements of nucleation events – particularly using TEM and SANS – have been published but measurements are lacking at both the spatial and temporal scales necessary to understand the fundamentals of nucleation. New measurements are required both to validate theories and to spawn new theoretical studies.

**Executive Summary**

Too little is known about the "form", i.e., the structure, composition, dimensions, etc., of a pre-embryo, nucleant, and nuclei. New time-resolved measurements with the required spatial and temporal resolution could provide information that would feed theoretical developments and compare to numerical simulations. A formidable challenge in nucleation is heterogeneous nucleation, in which interfaces, defects, stress concentrations, etc., can provide a site for nucleation before a homogeneous event would occur. This introduces a stochastic aspect and an uncertainty in where to look for the event. Ultimately, a predictive capability, requires representation of heterogeneous and unlikely events in models, which remains a grand scientific challenge in general and a critical challenge to the understanding of nucleation.

A predictive capability in nucleation would remove one of the key barriers to predictive design. Such a capability would need to be followed with theories and models for growth and, ultimately, coalescence to enable predictive design of microstructure or growth of dominant cracks leading to failure. Of all the material processes that contribute to development of microstructure and properties, nucleation is one of the most important and least understood.

**Scientific Challenges**

Nucleation phenomena play a key role in fatigue fracture and phase transformations as well as many other processes. To motivate the broader challenge, we discuss in detail the specific role of nucleation phenomena in initiating phase transformations.

*Nucleation Phenomena Controlling Phase Transformations*

Because of its atomic-scale origins and attendant difficulties in making direct observations, nucleation — the formation of the smallest amount of a new phase that is kinetically resistant to dissociation — remains one of the least-understood phenomena in phase transformations. The atomic rearrangements needed for nucleation pose an energetic barrier, except in special instances such as spinodal decomposition. The reaction path needed to surmount this barrier and achieve nucleation and subsequent growth has yet to be directly observed. Hence, existing quantitative nucleation theories and models must rely on a set of unverifiable assumptions, some of which are likely to be vast oversimplifications of the actual underlying physical processes.

Diffusional nucleation theory is premised on the spatio-temporal evolution of clusters, a generic term for any localized region of the system that differs from the matrix phase in terms of crystal structure, composition and/or degree of order. Prospective nuclei, termed embryos, are initially unstable n-atom clusters that must climb up an energetic hill if they are to grow, since the creation of a new matrix-embryo interface requires more energy, at small sizes, than is liberated by the chemical driving force. Cluster evolution is therefore biased in favor of dissolution, not growth. Given time, a favorably-growing embryo will eventually reach the peak of the energetic hill once it attains a critical number of atoms, n*, at which point it is called the critical nucleus. Adding one more atom to the critical nucleus is considered to render the cluster safe against dissolution. All such clusters having >n* atoms are considered to be stable precipitates that then proceed into the growth stage, for which there is always a net energy release, as the chemical driving force now outweighs the energy sinks of interfacial (and strain) energy.

To date, quantitative studies of nucleation have been done through ex-situ nucleation rate measurements using the indirect methods of electrical resistivity and small angle scattering, and the less indirect methods of electron microscopy and atom probe. The generalized steady-state nucleation rate $J_{ss}^*$ of second-phase precipitate from a supersaturated matrix (in units of nuclei per unit volume per unit time) is as follows [1]:

$$J_{ss}^{*} = \beta^{*} C_{n^{*},ss} = \beta^{*} NZ \exp\left[-\Delta G^{*} / kT\right] \qquad [1]$$

where:

- $\beta^*$ = frequency factor, the rate at which atoms attach to critical nuclei
- $C_{n^*ss}$ = steady state concentration of critical nuclei
- N = number of available nucleation sites per unit volume
- Z = Zeldovich non-equilibrium factor
- $\Delta G^*$ = free energy required to form a critical nucleus
- k = Boltzmann's constant
- T = absolute temperature

The concentration of critical nuclei is expanded into its three major components in the right side of this equation. The most important of these is the height of the energetic barrier, $\Delta G^*$ (Figure 1), which depends on the nucleus configuration (to be described later) and the driving force.

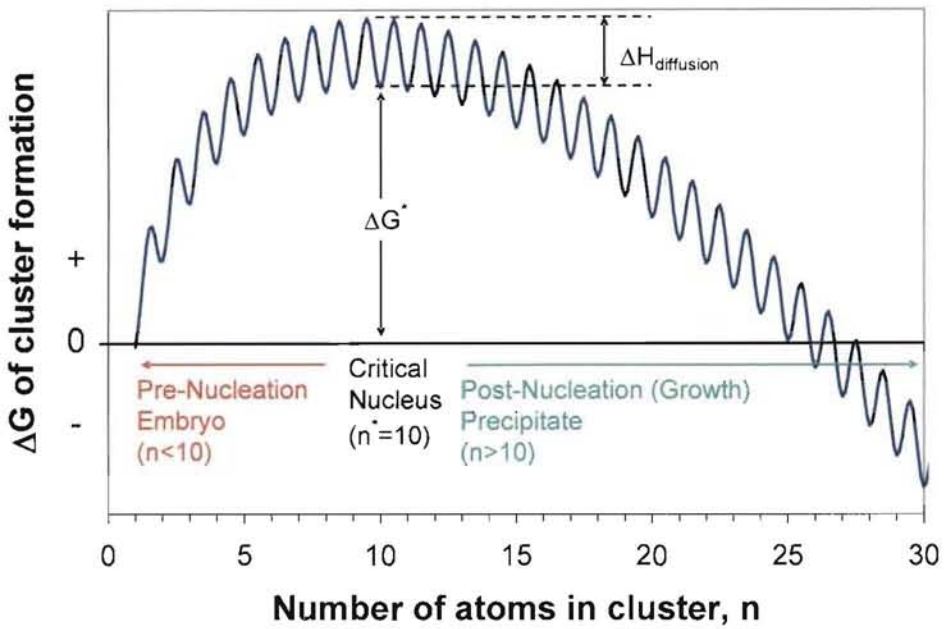



Figure 1. Schematic energy landscape for a cluster expanding/shrinking via diffusional jumps of atoms to/from any given n-atom cluster, one atom at a time. The cluster initially travels up the free energy hill, since for $n<n^*$ the surface energy sink (scaling as $n^{2/3}$) outweighs the negative volumetric energy source (=chemical driving force less strain energy, and scaling as $n^1$). The cluster is considered nucleated when it expands to $n>n^*$, crossing the top of the energy hill, $\Delta G^*$.

The energy landscape depicted in Figure 1 is specific to a cluster having a particular configuration — defined by its crystal structure, shape, matrix-embryo interfacial energy (or energies, in the non-isotropic case), composition, and degree of order. One would suppose that any given supersaturated matrix could try out an enormous number of prospective nuclei (via trial combinations of crystal structures, shapes, interfaces, compositions, and degrees of order), with the likely result that only one such combination will win out (the others being kinetically uncompetitive owing to higher $\Delta G^*$ values). Furthermore, the kinetic winner is not necessarily the equilibrium phase, as embryos of metastable phases may be able to assemble faster.

The most ambitious experimental goal would be time-resolved observations of all cluster configurations. For example, there may be patterns as to how the fluctuations in these different attributes are coupled to one another, for example, interfacial energy and composition. At a minimum, it would be desirable to sort out the fluctuations attributable to phonons from those attributable to electronic interactions. Detailed experimental information on the complex sequence of atomic rearrangements by which an embryo evolves to critical size would spark a renaissance in nucleation theory, modeling, and ultimately prediction.

Lacking any observations of this kind of pre-nucleation activity — the system "trying out" different clusters configurations through random, statistical fluctuations — nucleation theory and modeling has resorted to making the following key assumptions:

1. the critical nucleus is the equilibrium crystal shape, determined by simultaneous, independent minimizations of the total interfacial and strain energies
2. clusters grow or shrink by one atom at a time; mutual interactions among multi-atom clusters are considered negligible.

The time evolution of n-atom clusters (of a specified configuration) for $2 \leq n \leq n^*$ in a supersaturated matrix is schematically depicted in Figure 2. The one-atom-at-a-time rule severely constrains the actual shapes of the $C_n$ curves. *The acquisition of in-situ experimental data on cluster populations, which could be plotted as in Figure 2, is a key goal of future experimental efforts to understand nucleation.* Even if all the details of the cluster configuration were not known, if there was certitude that a given population had the same configuration (whatever it might be), such data would be of tremendous use in refining existing atomic potentials and cluster-evolution models and prompt the development of improved ones.

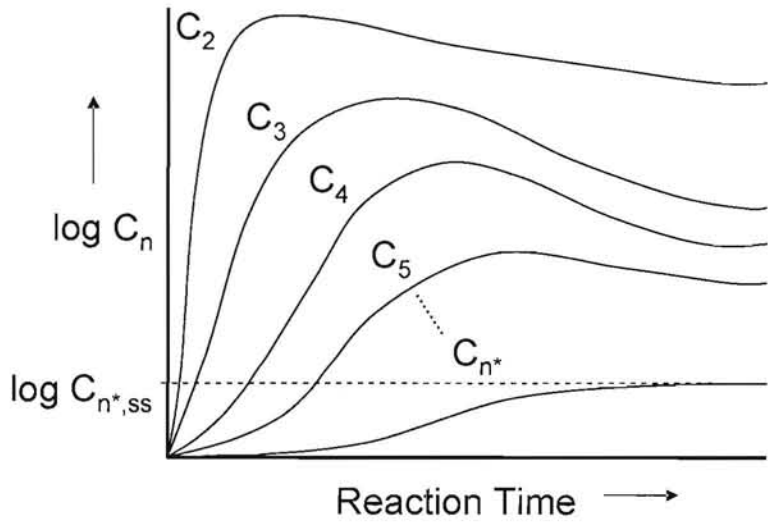



Figure 2. Schematic of the concentration $C_n$ of n-atom clusters as they evolve with reaction time in a supersaturated solution. The concentration of critical nuclei is given by $C_{n^*}$, for which there is an initial transient prior to the achievement of a steady-state population $C_{n^*,ss}$. (cf. Equation 1)

The lack of accurate ancillary experimental data has precluded closure between nucleation theory and experiment, and new spatially and temporally resolved experiments would be instrumental in closing this gap. The simplest case of homogeneous nucleation of a spherical precipitates with an isotropic interfacial energy will be used to motivate this discussion. For this simplest case, Eq. 1 reduces to:

$$J_{ss}^{*} = \frac{2Dx\gamma^{1/2}}{a^{4}(kT)^{1/2}} \exp\left[-\frac{16\pi\gamma^{3}}{3(\Delta G_{V}+W)^{2}kT}\right] \qquad [2]$$

where:

- D = applicable diffusivity in the matrix phase
- x = atom fraction of solute in the matrix
- $\gamma$ = specific interfacial energy between the matrix and the embryo/nucleus/precipitate
- a = averaged lattice parameter of the matrix and precipitate phases
- $\Delta G_V$ = chemical volumetric free energy change per unit volume of precipitate formed (negative quantity; the more negative, the higher the driving force)
- W = elastic strain energy work per unit volume of precipitate (positive quantity)

Lacking any better information, nucleation studies have had to make do with continuum measurements and models of D, $\gamma$, $\Delta G_V$, and W, even though their applicability to clusters containing only tens to thousands of atoms should be immediately suspect. Realistic measurements under the actual conditions of interest to nucleation and growth problems would be valuable in driving the next generation of theory. Opportunities for improving two of these parameters will be highlighted.

The most important parameter in Eq. 2 is the nucleus-matrix interfacial energy $\gamma$ [2]. Unfortunately, this suffers from the greatest error in its measurement, on the order of factors of 2-10, which is greatly compounded by the cube power in the exponential term of Eq. 2. Such is the case that most experimental studies of nucleation conclude by back-calculating the value of $\gamma$ and considering of whether this is a reasonable value. Improved back-calculation of $\gamma$ through highly accurate $J^{*}$ measurements, or better yet, some alternate means of measuring $\gamma$ more directly at more realistic temperatures and alloy compositions would enable true closure.

The second most important parameter is the applicable diffusivity D. Classically, D is extrapolated down from higher-temperature measurements, creating uncertainty as to whether such extrapolation is legitimate, given the likelihood of short-circuit diffusion paths at the lower temperatures of interest to nucleation (and perhaps more importantly, to growth). Time-resolved

and/or high-throughput measurements of atomic motion would constrain the value of D needed in nucleation and growth equations, and in all likelihood would result in the upsetting of conventional wisdom about diffusion and prompt the development of better models.

A brief consideration of the issues surrounding heterogeneous (defect-mediated) nucleation is in order before closing this section. Heterogeneous nucleation occurs at/near structural defects (dislocations, grain/twin boundaries, other interfaces) whose local interfaces, strain fields, and compositions differ from the perfect matrix in such a way that reductions in $\Delta G^*$ and $n^*$ (vs homogeneous) are realized. Given the ubiquity of defects such as dislocations, grain boundaries, and free surfaces (e.g., in powders) and the kinetic benefits of such defect mediation, heterogeneous nucleation is assumed in experimental studies unless proven otherwise. Unfortunately, since nucleation events cannot be directly observed with current capabilities, the defect and its local character (or "sweet spot", e.g., local grain boundary structure or local dislocation line direction) that are actually responsible for heterogeneous nucleation cannot be identified. Observations made of actual precipitates typically take place ex-situ, long after nucleation, and with only a narrow 2D view of a 3D microstructure. Given these experimental limitations, the correlation of the nucleation event with specific defects touching the precipitate can often be misleading. A nucleation model cannot possibly succeed if the nucleating defect is mis-identified. In-situ experiments would be in a position to correctly identify these defects as they interact with growing embryos, and help generate relevant maps of the energy landscape containing such features. Such data would refine and update atomic potentials and cluster evolution models, in addition to having the immediate benefit of constraining N in Eq. 1.

**Research Directions**

In order to realize the vision articulated in the previous section, the following research directions should be pursued:

- Determine the form of the pre-embryo, nucleant and nuclei and interrelationships (structure, composition, strain).
- Determine methods to characterize these various forms.
- Develop theories for heterogeneous nucleation that account for multiply distributed nucleant potency.
- Experimentally characterize and quantify distributed heterogeneous nucleation behavior.
- Explore methods for seeding the structure with defect controlling nucleation
- Use undercooling techniques to watch embryo development at time scales that we can measure.

**Capability Gaps**

Current state of the art theoretical and experimental methods are inadequate to address the research directions listed above. Success would require the following advances in capability:

- Development of experimental probes and models that can probe nuclei at small length scales (10 nm) and time scales (~ps-ns) but sampling large volumes (microns – mm) over time scales (secs to days).
- 3D X-ray diffraction measuring lattice strain (~10 nm res.) to detect onset of nuclei (current state 2D, 20 nm).
- Compositional and structural fluctuations can be measured via TEM down to nm scale, but not at time scales needed. How do we improve temporal resolution?
- Connection of theoretical models with real heterogeneous fluctuations.
- Develop theoretical models, models and experimental probes aimed at understanding interfacial mechanisms: nucleant interface and nucleus interface.

**Potential Impact**

Nucleation is a fundamental process step contributing to many microstructural development and failure processes. A first-principles, experimentally validated theory of nucleation would remove a key barrier to predictive capability for microstructural control across numerous application areas. Success would enable control of novel distribution of phases for improved functionality.

**References**


1. H.I. Aaronson and J.K. Lee, "The Kinetic Equations of Solid-Solid Nucleation Theory and Comparisons with Experimental Observations," in "Lectures on the Theory of Phase Transformations," H. I. Aaronson, ed. (TMS, Warrendale, PA, 1999), p. 165.

2. R.K. Trivedi, "Theory of Capillarity," in "Lectures on the Theory of Phase Transformations," H. I. Aaronson, ed. (TMS, Warrendale, PA, 1999), p. 135.

## Priority Research Direction: Accelerating Materials Discovery

### Problem Statement

The discovery of new materials is essential for the discovery of new science. The 1986 discovery of high temperature superconductivity in the cuprates changed the face of condensed matter science. More recently, the development of electrodes based on lithium iron phosphate has transformed battery technology. Impressive as these discoveries are, they occur far too rarely to sustain the steady advance of the frontier of science and technology innovation. A new paradigm for accelerating materials discovery is needed: a tight integration of theory, synthesis and physical property measurement. The advantage of this closed loop is strong feedback that guides synthesis towards interesting and useful materials. The feedback is enabled by developments over the last decade in characterization of materials and first principles based theory. Theory is now capable of quickly providing detailed information about properties and their origins in increasingly complex materials, thus enabling a marriage of experiment with theory that is reshaping how new materials research can and is being done. The challenge is to leverage these developments to establish materials discovery teams that effectively integrate these modern capabilities. The promise is an accelerated pace of discovery, enabling new technologies that will underpin our future competitiveness and energy independence.

### Executive Summary

The striking technical progress in materials characterization capabilities and computation of materials properties calls for their effective incorporation into a tight synthesis-characterization-computation loop to transform the nature of new materials discovery. Achieving this will require a steep learning curve to integrate the advanced tools into a new materials loop free from bottlenecks. We have the ability to not only learn more in microscopic detail about real materials now than ever before but also at a rate which is fast enough to influence a typical synthesis protocol. The integration of theory, computation and characterization with synthesis will give new focus to the search for new materials and can be expected to lead to qualitatively new ways to think about structure-property relations, the overarching agenda of new materials research.

### Scientific Challenges

The next generation of energy technologies is dependent on the discovery of new materials that will enable revolutionary and transformative advances in how we generate, use and store energy. The process of materials discovery requires a new paradigm, from an expert-based intuition-driven process to a more comprehensive approach that closely integrates theory, synthesis and characterization.

**Research Directions**

*Discover guiding principles for materials functionality.* Traditionally, solid state chemists have used empirical guiding principles to find new materials, such as crystal structures that harbor interesting functionality, exemplified by ferroelectricity in perovskite-related structures. Another example is Zintl-based ideas of charge transfer triggering covalent reorganization of polyatomic anions guiding the discovery of interesting new intermetallic compounds. The interplay of modern theory and experiment enables guided searches for new materials by developing detailed microscopic understanding of trends connecting structure with properties. This guided approach should be exploited in focused searches for materials with specific properties needed for energy technology, including, for example, high performance magnetic materials, superconductors and thermoelectrics.

*Synthesis and process modeling of novel phases from extreme conditions.* The systematics of materials properties often suggest new materials with enhanced properties which do not form under normal preparation conditions. As example, there is a trend towards higher superconducting critical temperatures in less stable phases and there is a strong association between phases that form under high pressure and super-hard materials. Further, the recent advances in high pressure research find quite unexpected structures and properties in elements and compounds. Materials synthesis under extreme conditions expands greatly the phase space available for the deeper understanding of structure/property relations. These methods include high pressure, intense radiation fields and large electric potential gradients that occur in electrolytic processes. Effective exploitation of methods for synthesis under extreme conditions is needed.

*Exploration of unstable and metastable phases.* The properties of unstable and metastable phases vastly expand the phase space of interesting materials. Glass is an ancient example with extensive continuing interest. Diamond, which is now finding multiple applications in thin film form, is another example. Metastable materials usually require special synthetic routes which process modeling can address. Furthermore, they often support anomalous atomic valence states and these in turn can lead to novel properties. Finally, these materials show functional possibilities that can be designed into new stable but as yet unknown materials via appropriate functional units. For example, discovery of novel properties in unstable high pressure phases may lead to realization of these properties in metastable or stable phases. Exploitation of modern techniques for the discovery of new metastable phases is needed.

*Identification of Synthesis Routes for Promising Materials.* Methods, both theoretical and experimental, that inform the synthesis process must be developed and integrated into the materials discovery process. These advances include computational methods based on first principles theory and the development of experimental screening probes for thin films as in combinatorial searches. For instance, studies of thin films with compositional spreads using a combination of appropriate probes, such as laser melting coupled with x-ray diffraction, can

rapidly elaborate solid-liquid phase relations and the resultant microstructural development leading to a more complete realization of multi-component phase diagrams. These experimental methods coupled with computational prediction of multi-component thermodynamics and kinetic pathways will lead to rapid identification of synthesis routes.

*Morphological control of crystal growth.* Proper characterization of complex materials depends to a large extent on measurements on suitable single crystals. An example is provided by materials for radiation detection, where it is essential to perform experiments on large single crystals to determine the performance of a given material. Producing single crystals, especially with high perfection, remains a significant challenge. Generally imperfections such as point and line defects, compositional gradients and second phases, are generated at the advancing solid-liquid interface and depend on the morphology and stability of this interface. Greater understanding of the growth conditions, such as growth temperature, velocity and supersaturation levels, will lead to stable growth morphologies and allow greater manipulation of the growth process which can significantly speed progress in the study of new materials.

**Capability Gaps**

Advances in the past decade in characterization tools, in particular in intense sources of photons and neutrons for scattering experiments, now allow sample analysis of a sort never before possible and promise a new era of materials discovery. Realizing this promise requires not only utilizing the tools fully but also coupling their output into the synthesis-characterization-theory loop in an immediate way that does not bottleneck the flow of ideas and results.

Scientific approaches that integrate the ground breaking scattering capabilities of user facilities with modern capabilities in theory and synthesis, and harness them to accelerate the pace of materials discovery are needed.

The tremendous extent of the space of materials that can be made and the tiny fraction of these materials that are known underscores both the challenge and the promise of materials discovery. This is exemplified by the many recent unanticipated discoveries in superconductivity, such as two-band superconductivity in $MgB_2$ and iron-based superconductivity in pnictides and chalcogenides, which continue to occur even after decades of research in the field. Methods for effectively exploring the materials space are needed. Promising approaches include guided materials synthesis in which theory, characterization and synthesis are tightly integrated to discover trends and guiding principles and use them to find useful materials, and combinatorial synthesis where large numbers of materials are synthesized and rapidly screened for interesting properties. Theory and computation can also be used in a combinatorial fashion to suggest interesting materials for experimental synthesis and characterization.

Within the past decade, advances in combinatorial thin film methods and reliable detailed theoretical descriptions of materials functionality have lead to a rapid identification of many potential new useful materials. Trends identified from experimental and theoretical studies

suggest regions of materials space that should be explored for advanced materials. However, synthesis of bulk samples is often challenging and in many cases is the limiting factor of such approaches. The low capacity of materials synthesis capabilities in the US further limits the pace at which materials discovery can advance. Rapid methods for assessing synthetic routes and process modeling to optimize synthesis are needed. At this time, development of synthesis routes remains iterative and serial, requiring multiple syntheses and time-intensive characterization to identify and optimize synthesis. Combinatorial approaches generally stop short of providing sufficient information to assess appropriate bulk synthesis routes and similar considerations apply to computational searches for new materials. For example, most solidification based synthesis methods require a set of material parameters that inform the growth conditions needed to stabilize the morphology of the solid-liquid interface and allow full control of microstructural and compositional development.

A new generation of in situ probes to monitor and control synthesis is needed, allowing real-time feedback as growth occurs to manipulate defect structure formation and/or impurity level and distribution, and to control long range homogeneity, and/or local inhomogeneity.

Combinatorial approaches either through experimental thin film methods and/or by computational approaches are beginning to demonstrate success in guiding searches for new materials discovery by refining the limits of phase space. Thin film methods that utilize chemistry spreads to sample a portion of a phase diagram essentially provide an infinite number of samples limited only by the spatial resolution of the characterization probes. This powerful approach can be developed further by minimizing the unwanted stress during growth that leads to crystallographic textures that can hide intrinsic behavior. New high-resolution characterization probes of materials functionality that are applicable to thin films need to be developed. Similarly, tools to characterize very small bulk samples will be very helpful for materials discovery in general but are lacking for many key properties.

**Potential Impact**

The continuing surprises in new materials discovery sends the resounding message that we are far from even remotely knowing the full range of nature's possibilities. One has only to look at the small sub-field of superconducting materials to realize just how unexpected the findings are. Superconductivity in the high transition temperature cuprates, $MgB_2$ and now the iron pnictides are the prominent tip of a much larger iceberg. The fact that elemental Li at one million atmospheres pressure is a 20K superconductor is a finding that defies conventional understanding. The focused search for new superconductors, as for many other materials classes, is in need of guiding principles. Establishing a paradigm for new materials research based on full utilization of the state-of-the-art characterization tools, advanced computational capability, modern theory and a complete suite of synthesis techniques has the potential to define entirely new perspectives for materials discovery. An important collateral impact is a vastly enhanced set

of skills, competencies and promising new horizons for the next generation of materials synthesizers.

The accelerated identification of new materials with novel properties will result in the rapid introduction of new materials into the basic research and technology streams that define and enable scientific and economic competitiveness. Capitalizing on discoveries of new materials is very much a matter of timing, both in basic research and in technological application. The element of immediacy should not be underestimated in its relation to maintaining scientific health, both for the enterprise and for attracting the finest students to the field to maintain future capabilities.

**Priority Research Direction: Realizing materials design and performance: lifetime prediction**

**Problem Statement**

Empirical discovery techniques can achieve incremental advances. Steel-making for example dates back over thirty centuries, but the strengths of most present-day empirically-developed commercial steels are less than a factor of two higher than that used in swords during the medieval-era. While this empirical description has some success in describing the simple tests in which the response was sampled, their applicability outside this regime is based on extrapolation to fits not to observed behavior. As new manufacturing techniques are developed, processes are better understood and new mechanisms are accessed. Equally probing and accessing new extreme loading paths takes matter through a suite of new mechanisms. These are different in each phase, in each class and each component of a material system, and until they are mapped and analytically described there is no possibility of accurately describing behavior nor controlling fabrication and design of new materials.

**Executive Summary**

The only means of achieving the ambitious goal of realizing materials design and lifetime prediction is to evolve a suite of tools and a knowledge base that is built upon the physical mechanisms that operate both in the formation and processing of the materials at their inception, but also in the means by which the microstructure responds to loads delivered in the environment in which the material must operate. At present mathematical descriptions are derived from a limited suite of tests in a small part of loading phase space and fitted to the responses observed. Thus a vital, science-based challenge is to engineer materials based upon a cadre of knowledge founded on scientific mechanisms as opposed to empirical relationships fitted to testing.

**Scientific Challenge**

Understanding of the relationships between processing, structure and properties will give rise to the integrated performance of the material in the range of applications and environments that the twenty-first century will require and which the new environments man accesses will impose. This interrelation of structure to processing and its connection to the response achieved in use, must be understood to exploit materials for the extreme but also to design new processing routes for the modern world. These paradigms offer an exciting forefront for the future advance of materials and structures constructed from them through the next century.

To advance on these fronts requires accelerated qualification and testing for the use of these optimized materials to acquire performance through life. To do so safely and reliably requires a new means of qualification and testing to be developed to allow rapid assessment and licensing of the materials. Such schemes and structures already exist (e.g. Accelerated Insertion of Materials; AIM) to ensure assurance for performance through life. But full development of these

will allow more rapid use of materials from the drawing board through to a safe and productive life in a particular application.

**Research directions**

*Materials Design*

Materials Design focuses on the development of *inverse* solution methodologies geared to identifying new materials and microstructures that are theoretically predicted to meet a set of designer specified performance criteria. Broadly, the tasks involved in materials design can be broken into two main components: (i) Identify the complete set of microstructures that are theoretically predicted to meet or exceed a combination of desired material properties or performance characteristics. (ii) Identify processing routes that are theoretically predicted to physically realize elements of set of the desired (presumably optimized) microstructures. Developing a rigorous mathematical framework that facilitates these inverse solutions constitutes an important decadal challenge that can transform the current practice in the field of materials science and engineering and provide a clear pathway forward for the rational design and processing of high performance materials.

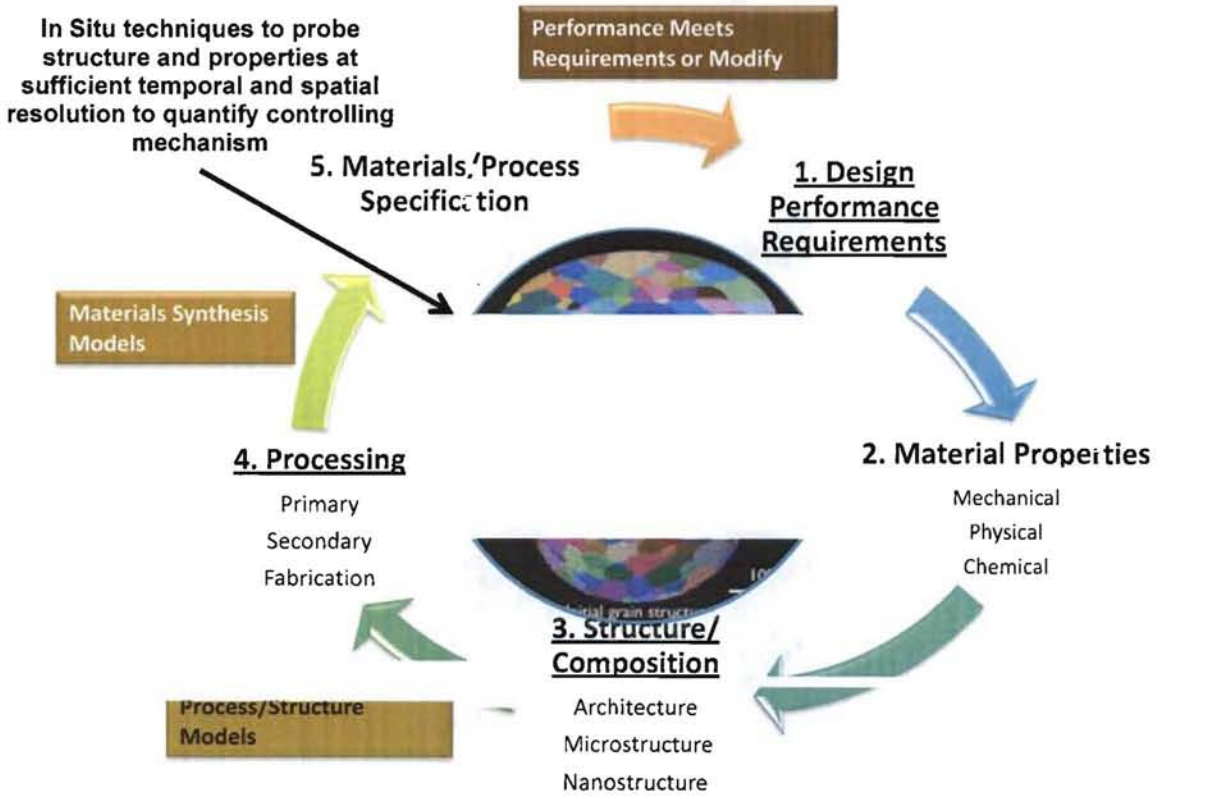
A critical element for success in materials design is the availability of validated forward models that predict the structure-property-processing relationships in the material systems of interest to desired accuracy. Given that the materials phenomena of interest often span distinct time and length scales, it is imperative to develop a cohesive multi-scale modeling framework that is also critically validated with direct experimental observations. Additionally, to facilitate materials design, it is critical that the scale-bridging in the multi-scale modeling framework is designed to transmit information accurately in *both directions* between the constituent spatial and temporal scales. It should be noted that the focus in most of the current multi-scale approaches is homogenization (going up in scales). For success in materials design, it is imperative that we focus equally on localization, i.e. passing information to the lower length scales.

There could be tremendous benefits from employing established concepts in Digital Signal Processing and Systems Engineering in developing a mathematical framework that can address the challenges described above. Using these ideas can lead to FFT-based computationally efficient procedures for (i) fast retrieval of important microstructure statistics (e.g. defined in terms of $n$-point statistics), (ii) rigorous extraction of representative volume elements, (iii) automatic objective classification/cataloguing of microstructures, (iv) real-time searchable and shareable microstructure databases that can lead to improved collaborations among materials researchers and scientists worldwide, (v) computationally efficient data-mining tools that can extract the underlying knowledge in the large experimental and numerical datasets being assembled by materials scientists and produce a new class of modern *Materials Knowledge Systems*.

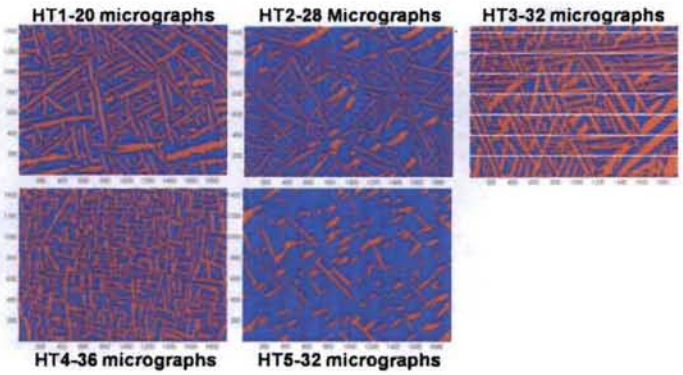
On the processing side, combining known manufacturing options into hybrid processing routes to develop targeted new materials is a particularly promising approach that deserves focused attention. However, the very large number of available manufacturing options, combined with the huge space of possible microstructures on which they operate, precludes process design by a purely combinatorial experimental approach. Once again a database approach that captures important details of microstructure evolution in a broad range of processing options can help deliver process design solutions much more efficiently than the brute-force methods.

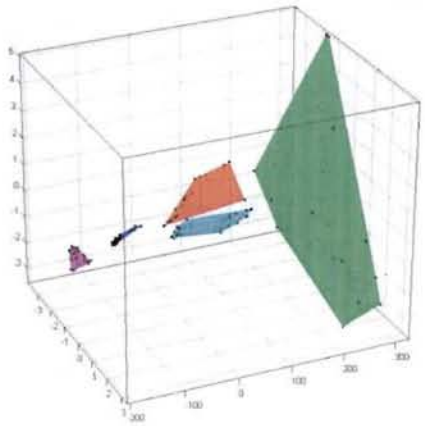
Throughout the design process, it is vital that the system of theoretical prediction is tightly coupled to an efficient experimental system of model calibration and validation to define accuracy through the quantification of model uncertainty. This is especially important for the application of modern probabilistic design methods to achieve reliability and safety with reduced reliance on macroscopic empirical statistics.

The following figures provide some examples of possible materials design research directions described above.




Microstructure image courtesy of E. Lauritsen



$$\frac{p_s}{\bar{p}} = \left( \sum_{h=1}^{H} \sum_{t \in S} \alpha_t^h \, m_{s+t}^h + \sum_{h=1}^{H} \sum_{h'=1}^{H} \sum_{t \in S} \sum_{t' \in S} \alpha_{tt'}^{hh'} \, m_{s+t}^h m_{s+t+t'}^{h'} + \cdots \right)$$

Microscale strain rate fields from a section of a 93x93x93 two-phase RVE subjected to rigid-viscoplastic deformation simulated by both FE methods and the spectral methods developed in our work. The FE results required 94 processor hours of supercomputer time, the spectral linkages took 32 seconds on a desktop PC.

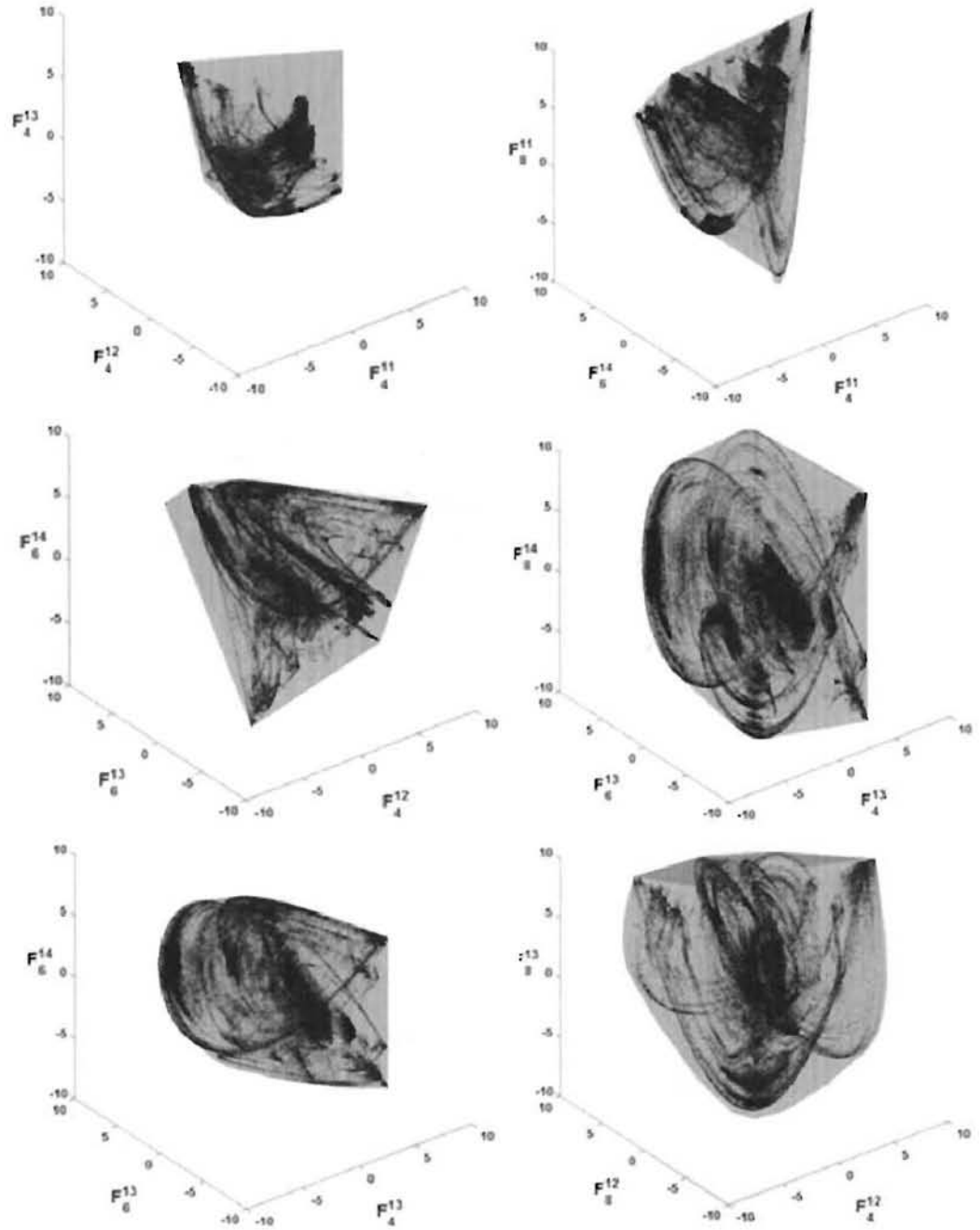
FEM

MKS

Phase Field

MKS

Spinodal decomposition of a binary alloy



Texture evolution networks of deformation processing showing a database of process networks projected in selected three-dimensional subspaces. The pathlines depict the various options available to transform a given initial texture in a sample into a desired texture. Every point in this space denotes a distinct texture. Therefore, process design reduces to finding a pathline in this network that starts at a selected initial point and gets to a selected final point, much like how a GPS system plots a route between any two selected destinations.

*Materials Lifetime Prediction*

The DARPA-AIM initiative of 2001-2003 represents an important milestone in demonstrating the power of deterministic modeling of complex multiscale microstructural evolution during processing, using statistically defined process variation to accurately predict probabilistic material property variation arising from multistage manufacturing [1]. The modeling approach and supporting tools were driven in this case by the need to accelerate process optimization of a new material at the component level and to forecast minimum property "design allowables" with greatly reduced reliance on empirical data. A recent NMAB study of best computational materials engineering practices [2] identified the AIM demonstration as the highest achievement in acceleration of materials technology transition. The example opens the way to a broader predictive probabilistic science of materials with emphasis on behaviors controlled by distributed heterogeneous nucleation, such as high-cycle fatigue (HCF) life. A firm foundation for such an approach lies in the well developed theory of heterogeneous nucleation of first-order phase transformations, particularly the cases of martensitic transformations and solidification. Here quantitative nucleation theory has defined deterministic multi-parameter structure/property relations at the level of a single nucleant, and thorough fundamental experiments have quantified the statistics of nucleant potency distributions from which probabilistic properties can be predicted. Ongoing efforts to apply the approach to HCF life modeling incorporate path dependent behaviors both in terms of the role of processing history on nucleant damage state and the role of load path history on properties emerging from anisotropic microstructural distributions. While significant research investment will be required to fully develop this new probabilistic materials science, the ability to predict low probability behaviors from fundamental mechanistic knowledge with minimal calibration from empirical data offers a major technological breakthrough in the life-based robust design, qualification and accelerated certification of safe reliable engineering systems.

**Capability Gaps**

*Accelerated Discovery of Controlling Mechanisms*

Addressing deficits in materials understanding that pace our predictive design capability requires the means to more quickly find the operating physical mechanisms that occur in a loaded microstructure. When these fundamental processes are understood, exciting opportunities to use extreme thermo-mechanical conditions to design and manufacture new classes of materials open up. Such advances may allow extremes such as the theoretical strength to be achieved through confinement effects on dislocations. Thus a shift in perception and boundary conditions is necessary to bridge the gap between materials today and the theoretically achievable. Further, these processes differ across material classes. Metals respond differently to polymers and they in

turn behave differently to brittle solids. The response is driven not by pure compression of atoms but by shear between agglomerations of atoms, that slide on planes as dislocations in metals or flow like spaghetti formed from polymer chains. In brittle solids inelastic response is preceded by fracture where cracking must first fragment the solid before compression can follow. In all of these cases it is flaws and defects that determine the nature of the behavior. Thus each of these varying behaviors must be probed with suitable sensors that are optimized to deliver the required data to understand the operating mechanisms. A series of deformation mechanisms are triggered by extreme loading, each having different operating kinetics. The various operating regimes for the devices limit the relevant mechanisms that can be accessed. This means that new loading devices and facilities need to be designed and operated to allow the accelerated discovery of controlling mechanisms.

*Ability to quantify the full spectrum of the Dynamic Statistical Distribution of the Structure and Properties with the Required Spatial and Temporal Resolution*

Diffraction methods are increasingly important to 2- and 3-D characterization of heterogeneous microstructure. These remarks pertain primarily to x-ray and electron diffraction methods. A case can be made for combining the two methods to take advantage of both.

Probes based upon electron diffraction are capable of resolving lattice orientation differences down to $0.005^0$ and elastic strain/rotation to ~0.0003. It is expected that order-of-magnitude improvements in these current resolution limits can be achieved with appropriate emphasis (funding) with improved hardware and calibration of the electron optical systems within ~ 5 years. Spatial resolution of these techniques is approximately 20nm for the semi-infinite samples examined by SEM-based systems, and sub-nm in the thin sections prepared for TEM-based observations. Thus, the electron diffraction methods are essentially 2-D in nature.

X-ray probes, based upon the synchrotron light sources such as APS, offer 3-D imaging capability typically over cubic millimeters of volume. Current spatial resolution is ~ 1 micron. These systems have not yet been fully developed for resolution of the elastic fields, and at this point it is difficult to speculate on achievable angular resolution.

Both x-ray and electron diffraction methods require substantial experimental time frames to characterize extensive microstructure and response fields. EBSD-based electron diffraction can currently occur at rates of up to 1000 points per second for lattice orientation determination. High-resolution methods are currently implemented off-line, and the EBSD patterns are stored for subsequent analysis of the elastic and defect fields. It can reasonably be expected that with sufficient emphasis the high-resolution methods could be made real-time, so that ~ 1000 patterns per second could be fully analyzed for lattice orientation, elastic strain/rotation and their derivative – continuum dislocation density.

X-ray campaigns also require substantial time frames for extensive characterization of the microstructure fields. Thus experimental campaigns in excess of 24 hours are typical for a full

3-D characterization of volumes containing several thousand grains. The main recovery at this point is lattice phase and orientation, although one can reasonably expect that resolution of local first-order elastic properties (i.e., elastic strain and rotation) may be possible in the future. One large advantage of the x-ray probes is the ability to apply temperature and mechanical loads more readily than can be accomplished within the chamber of an SEM or TEM.

Temporal resolution is currently a serious issue for both x-ray and electron-diffraction systems. Strategies for rapidly noticing changes in the fields during in-situ experiments, and then focusing the probe in to the nearby region where the change is occurring are contemplated, and limited experience has been achieved. But this is an area where much work needs to be undertaken, if these instruments are to be optimally efficient for the study of localization-related events (e.g., nucleation events).

It is interesting to contemplate a hybrid instrument that would couple electron diffraction capabilities with x-ray diffraction, and with computer simulations. One can imagine, for example, an EBSD-based SEM introduced into a beam line at APS. Simultaneous probing with the x-ray and electron beams seems quite possible. The 3-D x-ray capability, with resolution on the order of 1 micron, could provide required information for simulation of the mechanical fields, identifying where "hot spots" should occur near the surface. Samples could be placed under thermal and mechanical loads. After these determinations the electron beam could be trained in the neighborhood of predicted surface hot spots, and these could be characterized at much higher resolution by SEM-EBSD methods. Comparisons of computed fields with measured ones would provide valuable feedback on the importance of the intrinsic elastic properties of grain boundaries, perhaps unaccounted for in the computer simulations. And other comparisons can be envisioned that would strengthen both experimental and computational results. Finally, for selected areas it would be possible to use FIB methods to cut TEM samples for further, even higher-resolution characterization.

*Predictive capability for inverting information flow from performance to structure to processing:*

There is a strong case for using Green's Function (GF) methods as much as possible for predicting the response fields in heterogeneous microstructure. The GF methods result in localization relations that are integrations over space (and time) of the product of GF operators acting on the microstructure fields. These microstructure fields include elastic polarizations that can be computed from knowing the elastic constants of the phases present in the material, and the local lattice orientation. But they also include the fields of dislocation density at grain interiors and at grain boundaries.

This basic *separable* character of the influence functions and the microstructure fields is of great advantage to inverse problems, because it enables the investigator to consider how the analytical form of the microstructure influences the tensorial nature of the response field. And since the integral equations are essentially sums, the effects of various components of the microstructure

can be summed up. Even non-linear constitutive behaviors can be treated in this way by considering perturbations away from an average response that can be conveniently selected from averages.

The GFs themselves are solutions to the equilibrium equations (for example), and they are of simplest form for infinite media under uniform boundary conditions. However, some progress has been made in terms of generalizing the approach to BCs, to make things more realistic.

Invertibility of the materials design paradigm is an important attribute of design methodology GF approaches are inherently highly invertible in terms of moving from homogenized properties or localization, back to the fields of microstructure. One much needed advance in the study of localization related phenomena in heterogeneous materials would be approaches to develop analytical Green's functions for complex geometries and complex boundary conditions.

*Required changes in education*

While the power of computational materials design has now been well demonstrated [3], the principal barrier to further materials design technology development is the relative lack of a design tradition in the materials research community. This fundamental cultural barrier is best addressed by significant educational reform at both the undergraduate and graduate levels. Notable examples that can serve as templates for this reform are the educational initiatives at Northwestern University and Brigham Young University (BYU).

An upper undergraduate course in Computational Materials Design has been underway at Northwestern since 1989 [4]. Building on the systems view of materials proposed by the late Cyril Smith, the course develops the application of general practices of systems engineering to materials as multiscale interactive hierarchical systems. With projects drawn from funded graduate research, materials majors incorporate research findings from allied disciplines of applied mechanics and quantum physics applying a microstructure-based parametric design approach to the specification of materials composition and processing, employing computational thermodynamics as the principal integrative tool. Since 1993, national undergraduate design competitions of the TMS and ASM materials societies have fostered design curriculum development, and showcased best practices of winning teams, for which Northwestern has been a leading contributor. The program at Northwestern has been further strengthened by the development of an engineering school-wide Freshman Design and Communication course sequence that has built a common design practice foundation across disciplines. Taught jointly with writing faculty, this "techmanities" education initiative integrates communication skills to enhance both client/user interactions and team creativity [5]. With this foundation, the upper-level Materials Design course can focus more on technical design principles. Further technical depth in design projects is fostered by a hierarchical coaching system in which graduate students engaged in doctoral design research serve as mentors to the undergraduate design teams [6]. The course employs 5 computer laboratory sessions to develop basic proficiency in the computational

tools employed in the design projects. Greater comfort with the tools is fostered by an ongoing initiative to introduce the tools in core courses where the associated scientific principles are taught. Under auspices of an engineering school-wide Design Institute, a sequence of upper-level Interdisciplinary Design project courses brings together undergraduate students from multiple departments to engage in systems engineering projects, including the concurrent design of materials and structures [7].

For approximately 3 years activities at BYU have also fostered undergraduate and graduate level education in materials design. The approach has been to integrate materials design into the larger design enterprise. Engineering designers have little difficulty in understanding that materials design could increase their design space, affording greater flexibility in design and allowing novel and unusual designs. However, there exist significant barriers to be overcome. The investment of mechanical designers in ordinary strength of materials concepts (which nearly always invoke unwanted assumptions about material, such as homogeneity and isotropy) is considerable, and it is difficult to get them to move away from these ideas. Anisotropy is difficult to teach, because it requires the use of tensors – and the concept and manipulation of tensors is not usually taught at the undergraduate level. Introducing tensorial concepts at the undergraduate level is widely viewed as difficult. Materials design can be introduced without anisotropy, but this limits the potential benefits that can accrue from materials design.

One of the more effective educational tools is to form design teams surrounding an interesting design problem. Some examples taken on by BYU undergraduates include the design of a flywheel for energy storage, combined geometry and heterogeneous microstructure design for an electrostatic MEMS switch, and the design of an orthopedic implant for the femur, with the aim of minimizing the elastic mismatch between bone and implant. These teams were typically about 6 students + 1 faculty member. BYU's experience is that these experiences need to be at least 2 semesters in length, given that the concepts and methods of microstructure design must be introduced before students can work with them.

It is interesting to contemplate an alliance with the national labs in this educational process. High end, highly-constrained design problems are typical within the DOE labs, and there will be an ongoing need for materials design. The institute program, with alliances to selected universities emphasizing materials design, could be a useful vehicle for promoting materials design as an important discipline.

**Potential impact**

These benefits are the applied consequences conceived now without all of the advances in new physical science and engineering gained from understanding the new behaviors occurring and modeling the controlling mechanisms. The range of conditions that can be addressed apply to loading that comes from a specific environment but also stimuli that can be used to engineer new designer microstructures. The stimuli under this umbrella span high energetic fluxes, intense

electromagnetic- and extreme mechanical loading. If these can be adequately controlled then materials can be created with tailored performance and further accelerated transition into application will result.

When such knowledge has been assembled, one will be able to apply the designed materials or use existing stock outside of the existing design envelopes accepted in modern engineering. This will allow extension of the abilities of materials both in service life for existing components but also to access new operating conditions for use in the field. The future will see faster, better structures capable of lasting longer times in safety to address the challenges of the modern world.

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## Priority Research Direction: Bridging Length and Time Scales

### Problem Statement

One of the most challenging problems facing the integration of modeling and simulation with experiment to advance materials development is that of scale. The physical phenomena that govern materials response range over many orders of magnitude in both length and time. The current approach, in which we develop methods that are applicable over small ranges of length and time, and then attempt to link those together, is often inadequate. New approaches that take advantage of advances in material theory, computational resources and information science, are needed. Strategies for attacking such problems are proposed. Linkage with experiment will be critical, both for validation of the physical models as well as to provide information not available from calculation.

### Executive Summary

One of the basic challenges in multiscale materials design is the wide range of length and time scales that govern the properties of materials. The standard modeling approach is to identify the various phenomena that govern a specified property at given ranges of length and time, and to identify the fundamental "unit" whose behavior dominates the materials response at that scale.[1] For example, at the smallest scale, the bonding between atoms dominates, which arises from the underlying electronic structure, with the electron as the fundamental unit. To describe this bonding requires the use of a specified set of computational tools geared to solve that problem. At larger scales, where the behavior of multitudes of atoms dominates the response, simulation methods based on those atoms (e.g., molecular dynamics) may be most appropriate. At still larger scales there are too many atoms for us to consider, so we must find new approaches that focus on the dominant "units." These units often may be dislocations, grain boundaries, or some other defect, and the simulations would use these defects as their fundamental entities.

Thus, each scale is generally dominated by a different set of fundamental microvariables, which typically describe some sort of collective behavior of sets of microvariables from smaller scales. To model each scale generally requires unique methods and is usually done by different research groups. While much progress has been made in modeling at many of the individual scales, especially with respect to length, bridging from one scale to another is still a major challenge.

Modeling of multiscale materials systems encompasses a broad range of increasingly challenging phenomena and physics. While there are currently many efforts focused on developing techniques for multiscale modeling, there are no proven methodologies to creatively *design* multiscale materials and processes and there are few research efforts to develop these needed design techniques. The design of multiscale materials is unique in several ways - by working across scales, additional degrees of freedom are introduced into the design space and small changes at one scale can have a significant impact on other scales relevant to the intended purpose of the design. The methodologies and tools to do this type creative engineering design do not, however, currently exist. Here we describe a research direction that would help create these tools.

More progress has been made in bridging length scales than in bridging time scales. Too many of the physical processes governing materials behavior are not easily separable in time. Thus, a great deal of effort has gone into developing new approaches that extend the time scale of existing methods. While these efforts are essential, new theoretical approaches are also needed. It is these two primary tasks that are the focus of this PRD.

**Scientific Challenges**

Development of accurate, computationally efficient, and physics-based approaches to bridging scales in length and time are critical to integrating the microstructure features from distinct time and length scales into a cohesive multiscale modeling framework. While there are specific challenges to be met for distinct classes of methods, there are general requirements. To successfully predict and control, it is imperative to build the following features into scale bridging: (i) scale bridging has to transmit information accurately in both directions between the length scales. (ii) scale bridging has to be formulated in such a way that it allows inverse solutions that are central to successful materials design.

It is an especially important challenge to **extend** atomistic calculations to long times that capture rare events. The most-used approach, molecular dynamics, is limited by the requirement that it resolve the fastest motion, which limits the time scale of a simulation to the nanosecond regime. While advances have been made for systems dominated by infrequent, and activated, events (e.g., hyderdynamics [2], etc.), new approaches are needed that can elucidate behavior such as glassy relaxation and creep deformation response which are widely acknowledged bottlenecks in the computational materials community.

Ultimately, however, the key challenge is to develop new ways to integrate whatever information is needed for a given problem, at a given moment and at whatever scale, to describe materials behavior and response. That information could be from experiment, modeling, and/or simulation. What information is needed to describe one region of a structure may be different than that needed for another; the structure could be under complex stress states or in varying chemical environments. One approach is to take a broad view of information across scales and to employ new approaches to describe and use that information. Thus, new methods to catalog and characterize such information, from a variety of sources and at a variety of scales, are essential

**Research Directions**

Research activities needed to meet the scientific challenges can be loosely grouped into three categories: theory, simulation, and computation. These are not entirely separate categories, however, and the ultimate goal is to incorporate this broad range of activities into a unified package, creation of which will require a fourth category of research: information science.

First and foremost, there must be a strong effort in the theory of multiscale materials behavior, especially with respect to the bridging of scales. For materials, perhaps the most critical area is at the microstructural scale (i.e., the mesoscale), i.e., at the scale of the ensembles of defects that often dominate materials response. With the advent of high-resolution structural probes, for

example, a central challenge is the development of theories or models that describe the self-organization or collective behavior that emerges in evolving microstructure. Theories need to be based on identifying the important driving modes or "order parameters" for a given phenomenon, and then to relate those order parameters to the appropriate energy terms. The merit of such an approach is that questions may be answered by the methods of statistical physics. More importantly, one can add disorder to these theories and study transitions to more complex behavior. To date, there are very few examples where this approach has been demonstrated. However, developing such theories is crucial if we are to understand and predict the complexity of materials issues.

Coupled with new theory is a need for advances in the fundamental models and simulation methods applied to materials. There are many important areas of research in this area, many that are underway in various places around the world and others that have not yet been identified. One of the most important would be the development and characterization of infrequent-event sampling algorithms for extending scales, especially in time. Many events are stochastic, involving activated processes and occurring only rarely. Better methods for handling such events are essential. As an example, a primary research direction would be to perform benchmark simulations to determine the viability of existing atomistic methods (e.g., hyperdynamics [2], first-passage Monte Carlo [3], and metadynamics [4-5]). Appropriate problems to be considered include calculating the viscosity of supercooled liquids, for which experimental are available for comparison, and the stress relaxation of a solid under fixed strain deformation. A metadynamics method in the form of a series of activation-relaxation involving the use of an energy penalty function has been demonstrated to close the capability gap in predicting the temperature of glassy liquids [4]. This approach, in which the system is able to climb out of any potential well, shows promise as a sampling method for the potential energy surface of a material system in a study of deformation response at strain rates from $10^{4}$ $s^{-1}$ to $10^{-11}$ $s^{-1}$, a range that is beyond the capability of MD simulations [5].

It is also necessary to create an increased ability to link methods across scales. Given the stochastic nature of many processes, and their importance in determining materials behavior (e.g., fracture, failure, materials aging), this will require the development of statistically reliable accelerated algorithms for cross-scale simulations, by which we mean that the probability of rare-events is appropriately incorporated at all scales. Many methods to address this challenge have been proposed (e.g., Bayesian statistics [6], etc.), but much development remains. Another critical need is to be able to track uncertainties across scales, i.e., how inaccuracies at one scale affect the prediction of materials behavior at larger scales. Usefulness of simulations to material development, insertion and certification is greatly enhanced if simulation errors and uncertainties are quantified. Agreement or disagreement between experimental data and simulations can be firmly established only if errors and uncertainties of both are known. Simulation error and model uncertainty should not be confused. Simulation error is the difference between (the usually) approximate and (asymptotically) exact simulations of the same model. Model uncertainty, on

the other hand, reflects insufficient accuracy of model parameters, model incompleteness (e.g. missing mechanisms) or inadequacy of the model itself, irrespective of the quality of numerical simulation. Quantification of simulation errors (verification) may require significant computational effort but otherwise is often relatively straightforward. What it means to quantify the model uncertainty is not as well understood. Few robust methods exist to date, yet it is a critical need for predicting materials behavior.

All of these methods and algorithms must take advantage of new computational architectures. As of now few methods are well optimized for current architectures with massive numbers of processors, especially for some of the more innovative computers (e.g., the Roadrunner). As we move to exascale computing, optimizing computations is likely to be even more challenging. It is critical that we start now to develop new approaches to take advantage of these machines.

To link these disparate activities together in a unified package for materials prediction and design will require new and innovative ways to organize information across scales. These needs arise in computational algorithms, e.g., optimal multiscaling via adaptive model refinement and self-learning algorithms, as well as in flowing information from one scale to another, e.g., incorporating microstructure-based simulations into engineering modeling systems. The recent focus on semantic ways to handle information may offer a productive way to think about information flow in materials in that it does not prescribe linkages, but rather enables the information to self-identify and self-organize, eliminating redundancies and optimizing the ability to have the needed information at the desired fidelity at the right time. Given the complexities of the information flow needed to describe the multiscale nature of materials, this feature of the data flow may be essential.

**Capability Gaps**

The reach program described above will be made more difficult by gaps in our knowledge and capabilities. These include:

A lack of theoretical and computational approaches needed to bridge length and time scales. One approach has been to average properties at one scale (either from experiment or modeling) and to use those averages to develop models for behavior at larger scales. There are a number of limitations to this approach. The averaged models tend to be limited in range and applicability, they are often time-consuming to produce, they typically are limited in the quality of physics they can represent, and they cannot represent "abnormal" or rare events, which are stochastic in nature and not generally amenable to an averaged description. For example, we cannot couple properties at the mesoscale with the underlying dynamic electronic structure, as needed for multiscale predictions. This "message passing" approach is, however, the most common way people attempt to link simulations from one scale to another. An alternative is to embed one simulation method within another, i.e., different methods are employed to model different regions of the material. The most common example in materials is the incorporation of atomistic simulations within finite-element calculations, which has been accomplished by a number of

groups. What has been done to date has, however, been limited. Moreover, the design is static, with fixed interfaces between the simulations. Thus, they do not provide flexibility to handle the information inherent in a multiscale description of material properties nor to describe the range of physical states different parts of a material might have in use. Thus, they cannot be the basis of the systematic approach needed for full multiscale design.

The ability of atomistic simulations to reach time scales of order seconds and beyond is currently lacking. This widely recognized challenge has remained unresolved since the early days of multiscale simulations. Closing the gap requires the demonstration of an atomistic method (using interatomic potential as an input) that can elucidate behavior, such as glassy relaxation and creep deformation response, which are widely acknowledged bottlenecks in the computational materials community.

We currently lack methods to perform inverse mapping from larger to smaller scales, largely because the problems are underdetermined, i.e., many representative microstructures, for example, could yield the same average response at a higher scale.

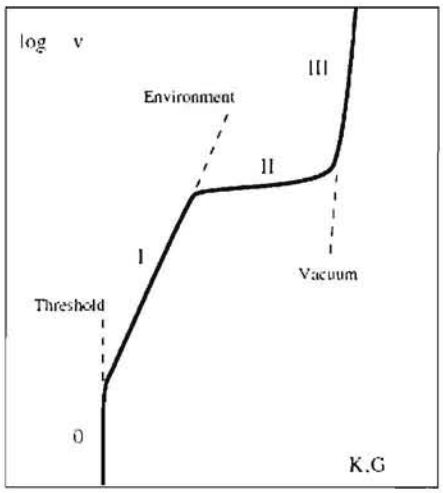


Figure 1. Schematic view of stress corrosion cracking, plotting the log of the crack velocity versus load.[7]

Many materials system exhibit behavior in which their properties show a marked change in character over a very small range of applied conditions, e.g., a large change in stress strain behavior over a small range of applied stress. This is an example of a threshold phenomenon, which generally arises when there is a competition between nonlinear physical processes. There are other threshold phenomena that are more catastrophic, for example a sudden change in behavior in radiation damaged materials. In Figure 1 we show an example of a threshold in a schematic view of stress corrosion cracking. We lack a general theoretical understanding of such behavior and, because of limitations in modeling/simulation capabilities, can rarely predict such behavior computationally.

We lack a set of robust algorithms required to make the best use of petascale and exascale computing. Methods developed when the computation employed a few thousand processors are unlikely to be most efficient when used in a platform in which there are tens of thousands of processors that may or may not behave similarly. How data is stored and transferred between processors, how loads are balanced, etc, are all questions yet to be answered

**Potential Impact**

The potential impact of successful completion of the research thrusts in this PRD is enormous. Currently, we rely mostly on experiment to observe material behavior, especially when that behavior is stochastic and rare. With the multiscale modeling and simulation methods suggested here, it will allow robust extraction of underlying physical principles across scales, with an emphasis on physics at the mesoscale, which often dominates materials behavior. Indeed by bringing a mathematically grounded approach to materials science and engineering, we will create capabilities that will allow the transformation from observation to prediction and control of materials properties properties.

Perhaps the greatest impact will be on the creation of a new ability for integrated computational materials design. Engineered designs are generally based on the use of a constrained, and fixed, set of materials. However as multiscale materials behavior is understood, and new computationally-based predictive tools are developed, we will be able to design the material properties of each part, providing enormous freedom in the design of new processes and products. The need for such capabilities are outlined in detail in a recent National Academy study entitled *Integrated Computational Materials Engineering: A Transformational Discipline for Improved Competitiveness and National Security.*[8]

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**Priority Research Direction: Exploiting materials complexity**

**Problem Statement**

Materials exhibit considerable complexity and especially those used in engineered applications. The natural tendency in hypothesis-driven research is to identify one aspect at one length or time scale and investigate it or engineer with it. In reality, however, many of the important properties of materials are sensitive to the full complexity of the microstructure. As examples, consider the properties of corrosion resistance, radiation damage resistance and fatigue resistance. All these depend on synergistic interactions between such features as grain structure and chemical heterogeneity and responses to loading such as mechanical response. These sorts of properties reveal another important subtlety, which is that all the features and responses are populations with varying strengths and that the members of these distributions that concern us are often not the mean values but rather the extremes. Strategies for attacking such problems are proposed. Advances in instrumentation, simulation and analysis will all play a crucial role in allowing such issues to be addressed.

**Executive Summary**

If all that is required in a given situation is the average response of a material then microstructure often plays a minor role. For the more complex but important materials properties such as fatigue, corrosion, and spall resistance, however, safety often dictates that minimum values must be used. This means that one must understand the variability in materials response at least and in some cases the extremes values ("tails") of distributions. With this mind, careful examination of materials response under extreme conditions reveals some important characteristics.

- Heterogeneity-dependent variability in material response, more so under extremes of loading.
- Size dependence (microstructure, sample size) based on weakest link statistics.
- Time (or strain) dependence: scatter is most apparent at either end of life (e.g. in creep, fatigue or shock) and this scatter is linked to microstructural variability.
- Where multiple processes are concurrent, such as in materials subjected to irradiation and mechanical load, the interactions of defect production, defect loss to sinks and defect-mediated deformation, coupled with anisotropy, can result in counterintuitive behaviors.

The sources of such variability in materials response are manifold. Whatever the nominal composition of a material, it is rarely the same from one point to another because of the segregation that commonly occurs in thermomechanical processes (or analogous variability in other synthesis routes). Consequently the population of second phase particles can be highly variable. Most metals and ceramics are polycrystalline (along with the semicrystalline polymers), which means that a grain boundary network exists in the material. Thus there is

variability associated with crystal orientation (texture), grain shape, grain boundary character (nearest neighbor correlations in orientation) as well as potentially higher order correlations.

**Scientific Challenges**

We currently lack methods that can accurately model dynamic situations in which the electrons and the ions are not in equilibrium, e.g. ion bombardment in radiation damage. The scientific question is, therefore, to postulate that there are computational methods that address such problems in reasonable times. The opportunity is to be able to go beyond, say, hard sphere models for calculating radiation damage plumes.

We currently also lack probabilistic theories of material failure that relate the 3D statistical distribution of defects to the statistical distribution in material performance. Although there are a number of statistically based models available (e.g. peridynamics) we do not have theories that take microstructure directly as an input and make predictions. The scientific question is to devise experiments, both physical and numerical that can provide the necessary links.

We lack efficient computational schemes for evaluating the impact of microstructure on material response, especially in 3D. This also brings up the issue of a Representative Volume Element (RVE) versus a Statistical Volume Element (SVE). The scientific question is therefore how best to bound the distributions of properties, especially where it is the upper (or lower) tail of a distribution that controls the material property.

We lack ability to accurately model multi-component systems, e.g. phase relationships and diffusion. The scientific question, at least at present, is how best to combine *ab initio* calculations with computational thermodynamics (Calphad) and produce arbitrarily complicated phase diagrams. Even more challenging is the need to be able to predict diffusion in multi-component systems since this is a non-equilibrium property that requires long simulation times, relative to atomic vibration frequencies.

We lack robust approaches to quantify the uncertainties (and/or distributions) of materials properties, e.g. thermal properties, voiding, cracking. In some cases, such gaps can be addressed by numerical experiments, keeping in mind the need to analyze the variations from successive instantiations and the need to understand at a scientific level where that variability arises in the microstructure. There is an opportunity to establish a methodology for predicting not just the mean value of a (microstructure-dependent) property but also its distribution.

**Research Directions**

*Heterogeneities Driving Tails in Distributions*

Materials in technological use have always been heterogeneous, with ranges of disorder in composition and structure. These heterogeneities occur across scales, from local atomic disorder

at the nanometer level to microstructural features at the many micron level. They may involve many phases or just one, but with many orientations. What is changing is our ability to design heterogeneities at all scales, through a range of processing paths, with desired functionalities. Many challenges remain, however, in our understanding of the role that heterogeneities play in determining materials response, especially under conditions outside the norm. To control those functionalities will require an understanding of the relations between the global properties of a heterogeneous material and the local properties of its homogenous phases. A critical gap in the current approach is it is often not recognized that obtaining the global properties is not simply a matter of computing a suitable average but may, in fact, depend on the upper tail of a distribution. This is particularly true of materials properties such as corrosion resistance, fatigue resistance, spall resistance and almost any property related to damage evolution. Moreover, we will need to predict the evolution of structure and response of these complex materials in dynamic environments.

*Defect-driven variability in material response*

When materials are exposed to extreme environments (radiation, high temperature) or pushed under extreme mechanical conditions (long term fatigue, shock), the statistical variation in material failure response among seemingly identical specimens increases substantially. In these cases, the variability in response is so significant that the usual Gaussian statistical analyses that calculate mean and standard deviations are not adequate descriptors. When material response exhibits so much uncertainty, reliability in material performance in extreme environments and conditions (no matter how strong or tough the material may be in less challenging circumstances) is compromised. Approaches to reducing the uncertainty begins by first understanding how it originates, followed by the ability to predict it, and ultimately to control it.

Non-negligible variability in material response in extremes is the result of a combination of enhanced sensitivity in two components: distributions of defects, inherently linked with 'microstructure' (including atomic structure, nano-structure) and variability in the forcing component (stress, radiation, temperature). When and where defects nucleate and how slow or how fast they coalesce depend on a combination of these two components: material and mechanical. As a simple illustration of how these two components interact, consider the two illustrations in Figure 1 (first cartoon with all 'red' defects) and Figure 2 (second cartoon with red and blue defects).

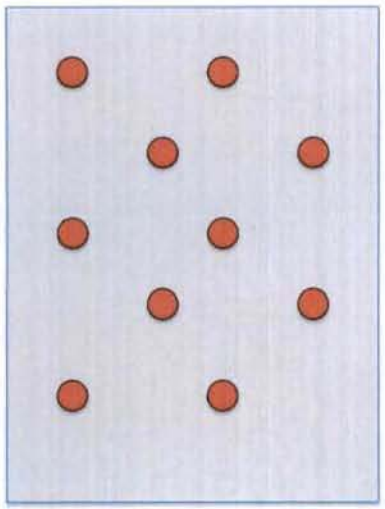

*Figure. 1. Illustration of the effect of variable spatial distributions of defects at constant volume fraction.*

In Figure 1, the stress state is uniform across the sample and the same for all three samples. The only difference is the spatial distribution of these defects. Although the mean volume fraction is the same for all three, the distribution in the first picture is uniform (no correlation-class A), the distribution in the second picture is highly correlated in 1D (class B), and in the third it is highly correlated in 2D (class C). The response among many samples of class A would exhibit very little variation and little size effect. The responses of many samples of class C, however, would vary significantly. The macroscale response of material C would be highly sensitive to the likelihood of activating several 'potent' defects in close proximity as shown. The chance this cluster appears increases as the size of the sample C increases. As a result the response (its mean, variation, and lower tail) would change as the sample size became larger. Last, samples of class B would likely exhibit even more variation than samples of class C. We can imagine that the 1D defect distribution in class B is far worse than the defect distribution in either A or C, yet the chance of such a well aligned defect configuration being present is smaller. Moreover, the chance it exists increases rapidly as the sample size increases and hence the size effect for samples of class B will be the most pronounced.

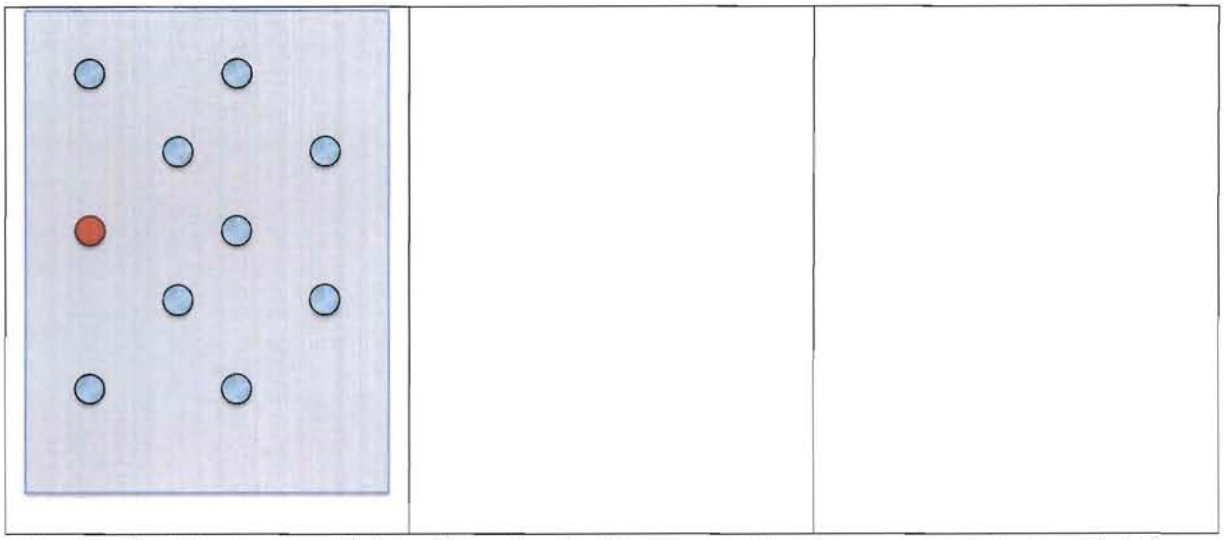

*Figure. 2. Illustration of the effect of variable potency for the same population of defects; The loading increases going from left to right thereby increasing the fraction of defects that originate damage, leading to variation in outcomes in finite size samples.*

In Figure 2, the defect distribution is the same; however, the stress level is different. In (a), the stress level is low (creep, high cycle fatigue) and hence failure processes and ultimate failure would occur over large time scales. In (c), the stress level is high (shock, low cycle fatigue) and failure processes and ultimate failure would occur in relative short times. Case (b) represents an intermediate level, in which, uncertainty in failure time and stress is perhaps the greatest. In all three cases, variations and size effects would manifest. However, the mechanisms and sequences of events leading to failure are different between (a), (b), and (c). Thus, the distribution in the response of many samples exposed to stress condition (a) cannot be expected to be the same as that for many samples exposed to stress condition (c).

Such variations have been observed in, for example, tests of thin films by Rupert *et al.* [1]. They inserted two holes into free-standing nanocrystalline thin films of aluminum and performed tensile tests. Two different arrangements of the holes were made, one with the holes in line with the tensile axis, and one with the two holes at 45° to the axis, somewhat akin to the variations in Figure 1. Not only were the response in terms of damage very different between the two arrangements but they also detected stress-driven grain growth. For the latter, the different stress patterns induced by the two different arrangements were crucial in permitting the deduction to be made about the driving force for grain growth.

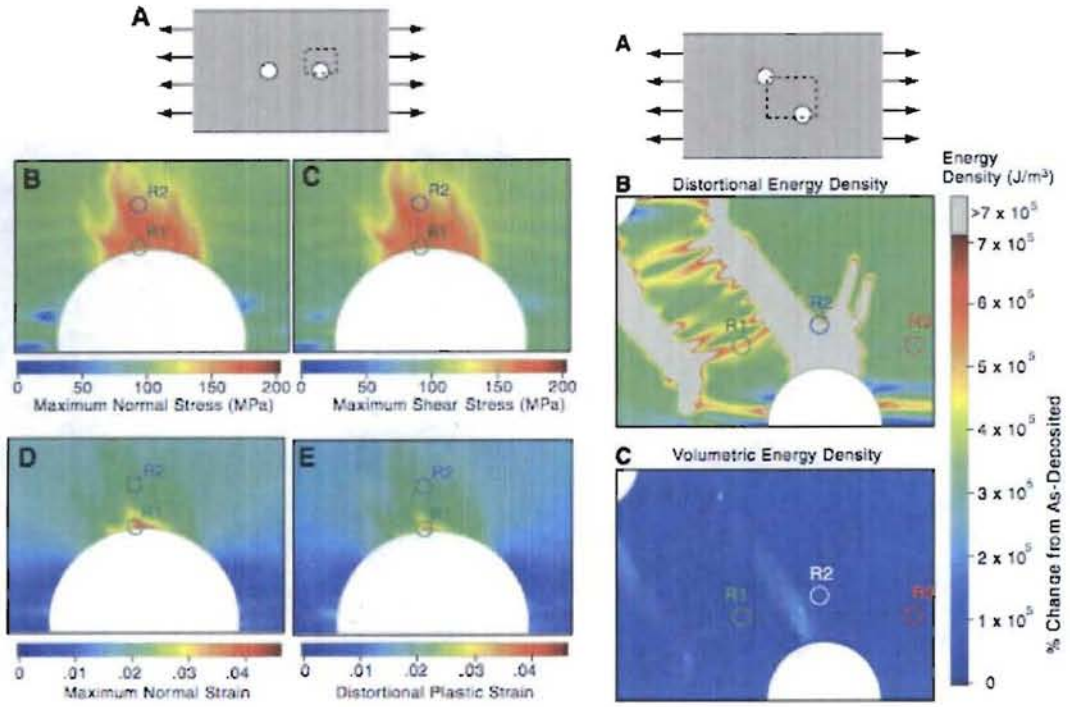


Figure 3. Diagrams showing two different arrangements of holes inserted into nanocrystalline thin films of aluminum, with finite element calculations of the stress and strain fields, showing significant variations between the in-line (left) and diagonal (right) arrangement of holes. [1] These different hole arrangements resulted in different localizations of (stress-driven) grain growth in the material.

## Capability Gaps

*Experimental probes*

Diffraction methods are increasingly important to both 2- and 3-D characterization of heterogeneous microstructure. Innovations in x-ray and electron diffraction methods have largely driven this area through advanced user facilities such as the Advanced Photon Source for high energy x-rays and high resolution orientation scanning in the electron microscope. The Vulcan facility at the Spallation Neutron Source is likely to offer new capability for neutron diffraction in the coming decade. Combining different techniques both within each area and between the two main methods may offer substantial synergistic advantages. *Comparisons of computed fields with measured ones are likely to provide valuable feedback on the importance of the intrinsic elastic properties of grain boundaries, perhaps unaccounted for in the computer simulations. And other comparisons can be envisioned that would strengthen both experimental and computational results.*

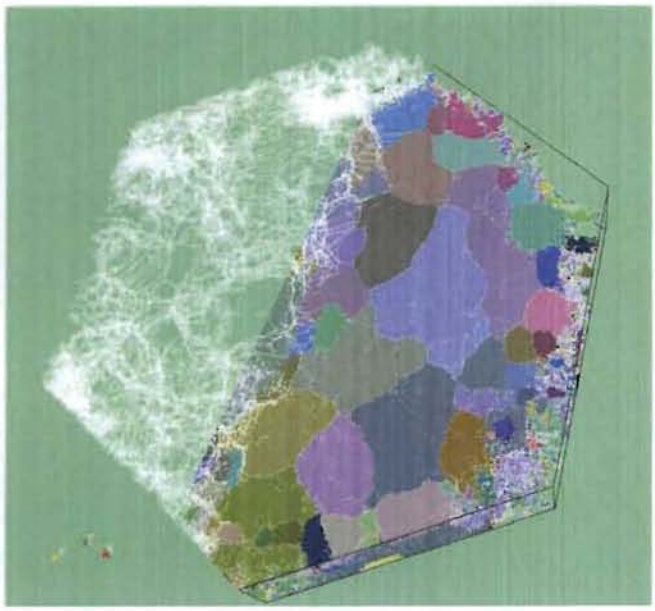

Figure 4. Combined 3D orientation color map and grain boundary outline (lines on successive layers) in a commercial purity aluminum measured by high energy x-ray diffraction at the Advanced Photon Source (APS). Image courtesy of R. Suter, CMU.

*Quantifying and predicting material complexity using n-point statistics*

A rigorous framework defining the spatial correlations of local states in the microstructure already exists in the form of *n*-point correlations or *n*-point statistics. These correlations provide a hierarchy of statistical measures of the microstructure that are essentially moments of the structure function. They preclude the need to select, either intuitively or in an ad-hoc manner, the microstructure metrics of importance in a given application. A great advantage of the use of these correlations is that they can be computed very efficiently using fast Fourier transform (FFT) algorithms. Given the strong contrast in properties among the various components of materials microstructure, there is also a need for more efficient methods of computing the response of materials to various types of loading. To complement the established finite element methods, there is increasing interest in image-based methods and these are likely to be increasingly useful as 3D characterization of materials produces ever larger datasets. To concretize this remark, we note that recent reports on 3D microstructure characterization have shown (individual) images of order $300^3$ (as a number of points or voxels), whereas it is clear that we will soon be working with images of order $1000^3$. As acquisition speeds increase and resolution increases, the image sizes may soon reach $10{,}000^3$. These image-based methods also exploit FFT algorithms for computational efficiency.

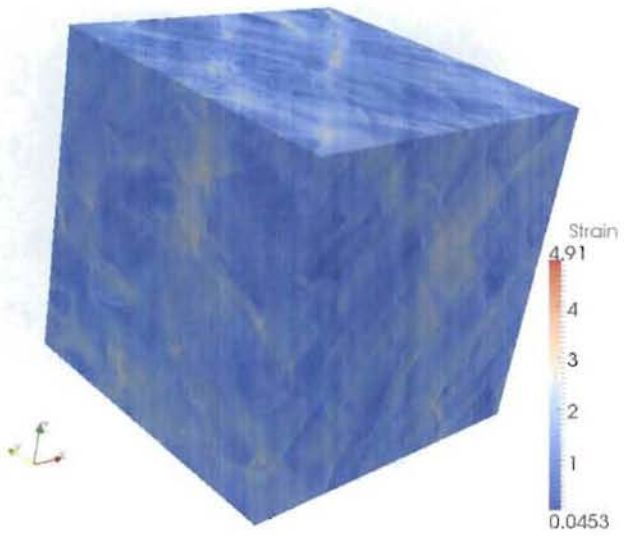


Figure 5 Image of the strain rate field from a full-field solution using the FFT viscoplastic method for unaxial tensile deformation of a randomly oriented polycrystal. [Rollett, unpublished work 2009]

*Ultimately, our goal is to develop a science-based understanding of the properties and performance of heterogeneous materials, especially by considering variations in composition and structures to move from the "ideal" materials of the laboratory to the "real" materials in actual use.*

**Potential Impact**

The potential impact of success in quantifying materials complexity includes the following:

- We will be able to quantify the reliability of engineering components based on validated theoretical models that fully capture the heterogeneous character of materials and handle realistic boundary conditions and gradients.

- We will have statistically-based definition of properties and performance characterized in terms of distributions that are based on materials history. Where appropriate to the material property of interest, these distributions will include quantified tails.

- Size & Time Scaling Laws will have been developed quantitatively. For example, we will be able to describe quantitatively how fast 'strength' decreases as sample size increases, or as microstructural length scales (grain size) increase. In terms of component performance, this should permit failure times in the laboratory to be correlated to failure times in service.

**References**

1. Rupert TJ, Gianola DS, Gan Y, Hemker KJ. Science 2009;326:1686.

## Conclusion

Materials are central to every national need, and future technologies will place increasing demands on performance in a range of extremes: stress, strain, temperature, pressure, chemical reactivity, photon or radiation flux, and electric or magnetic fields. To lower fuel consumption in transportation, future vehicles will demand lighter-weight components with increased strength and damage tolerance. Next-generation nuclear fission reactors require materials capable of withstanding higher temperatures and higher radiation flux in extremely corrosive environments and for longer service lifetimes without failure. To counter security threats, defense agencies require the means to field protection for the populace against terrorist attack and to protect critical facilities and buildings against human or atmospheric extremes. Finally, nuclear weapons represent among the most extreme environments that can be achieved.

Empirical discovery techniques can achieve incremental advances. Steel-making for example dates back over thirty centuries, but the strengths of most present-day empirically-developed commercial steels are less than a factor of two higher than that used in swords during the medieval-era. However, 21$^{st}$ century challenges demand the ability to move beyond empiricism to predictive control.

A key grand challenge to achieve this vision is the ability to predictively manipulate microstructures to achieve desired macroscopic performance. Central to this challenge is the potency of defects, either to be exploited intentionally for enhanced performance or to suffer their deleterious effects. The role of defects is a microcosm of the broader impact of rare events that is a key stumbling block in achieving prediction and control. The extremes of heterogeneity dominate performance at the expense of the homogenous bulk.

The vision of prediction and control will only be achieved through the development of in-situ, real-time, multi-probe "tools" (including advanced theories and information science and technology methods, high performance computing, advanced measurement capabilities, controlled environments) to enable dynamic, in-situ measurements of real materials in real environments with the spatial and temporal resolution of microstructures, interfaces, and defects

Workshop participants concluded that the grand challenge of prediction and control of materials performance in extremes was within reach. Success requires the pursuit of the priority research directions defined in this report and the development of needed capabilities required to achieve success.

**Appendices (to be inserted in production)**

Agenda

Attendance List

Earlier reports (4x)