

CHALLENGES AT THE FRONTIERS OF MATTER AND ENERGY:

Transformative Opportunities
for Discovery Science

On the Cover

Hybrid organic-inorganic perovskite materials have changed the way we think about solar cells. These materials were first used in solar cells in 2009 with an efficiency of 3.8%, and rapidly reached efficiencies of 20.1% in 2014, just five years later. The most common material is $\text{CH}_3\text{NH}_3\text{PbI}_3$, which is made from cheap and abundant starting materials and manufactured by simple solution processing or scalable vapor phase deposition. Inexpensive hybrid perovskites have the potential to replace expensive single crystal silicon as the dominant solar cell material. *Science Magazine* chose organic-inorganic perovskites as one of the top 10 breakthroughs of 2013 (“Newcomer Juices Up the Race to Harness Sunlight,” *Science* 342, 1438 (2013)). They symbolize the importance of new materials discovery to advancing the frontiers of science and technology. (Cover image adapted from Noel et al., *Energy Environ. Sci.*, 7, 3061 (2014).)

Challenges at the Frontiers of Matter and Energy: Transformative Opportunities for Discovery Science

A REPORT FROM THE BASIC ENERGY SCIENCES ADVISORY COMMITTEE

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John C. Hemminger (University of California, Irvine)

U.S. Department of Energy | November 2015

Prepared by the BESAC Subcommittee on Challenges at the Frontiers of Matter and Energy

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executive summary

Our progression from the Stone Age to the Bronze Age to the Iron Age reflects the increasing ability of humans to manipulate the building blocks of nature—atoms and the molecules they form through the sharing or exchanging of electrons. In 2007, the U.S. Department of Energy's Office of Science charged a panel of ranking experts with identifying key questions challenging our ability to control matter and energy, the basic currency of science, technology, and society. The panel's conclusions were presented in a landmark report titled "Directing Matter and Energy: Five Challenges for Science and the Imagination." The major contention of that report was that in meeting its five "Grand Challenges," humankind would enter a new "Control Age" in which the atomic and molecular interactions that determine material properties and the outcomes of chemical processes could be controlled on a molecule-by-molecule or atom-by-atom basis, or even at the quantum level of electrons. Controlling matter and energy at the molecular, atomic, and quantum levels could spark revolutionary changes in technologies that would help us meet some of humanity's most pressing needs, including the need for renewable, clean, and affordable energy.

While fully meeting these five Grand Challenges is still years down the road, significant advances have been made. As described throughout this report, scientific breakthroughs have not only

advanced our understanding of how nature works, they have impacted myriad energy technologies. In addition, our capabilities for probing and controlling matter have leapt forward. For example, today we have a thousand times more computational power than was available in 2007. Whereas in 2007, 100-teraflop supercomputers—meaning machines capable of performing 100 trillion floating-point calculations per second—were the gold standard, today we are on the verge of 100-petaflop machines (a petaflop is one quadrillion floating-point calculations per second). Furthermore, the Office of Science envisions exascale computing (a million trillion floating-point calculations per second) within the next decade. This enormous growth in computational power, coupled with major advances in other fields, such as the development of coherent light sources and increased imaging resolution, is accelerating the pace of materials and chemical sciences research. In 2007, the Linac Coherent Light Source and the National Synchrotron Light Source II were visions on paper; today, they are operating national user facilities bringing new, unique capabilities to materials and chemistry research. In consideration of this changed landscape, the Office of Science charged the Basic Energy Sciences Advisory Committee (BESAC) with assessing the progress that has been made on all five Grand Challenge fronts and identifying what new knowledge opportunities exist to advance energy science.

FIVE TRANSFORMATIVE OPPORTUNITIES FOR DISCOVERY SCIENCE

As a result of this effort, it has become clear that the progress made to date on the five Grand Challenges has created a springboard for seizing five new Transformative Opportunities that have the potential to further transform key technologies involving matter and energy. These five new Transformative Opportunities and the evidence supporting them are discussed in this new report, “Challenges at the Frontiers of Matter and Energy: Transformative Opportunities for Discovery Science.”

Mastering Hierarchical Architectures and Beyond-Equilibrium Matter

Complex materials and chemical processes transmute matter and energy, for example from CO₂ and water to chemical fuel in photosynthesis, from visible light to electricity in solar cells and from electricity to light in light emitting diodes (LEDs). Such functionality requires complex assemblies of heterogeneous materials in hierarchical architectures that display time-dependent away-from-equilibrium behaviors. Much of the foundation of our understanding of such transformations however, is based on monolithic single-phase materials operating at or near thermodynamic equilibrium. The emergent functionalities enabling next-generation disruptive energy technologies require mastering the design, synthesis, and control of complex hierarchical materials employing dynamic far-from-equilibrium behavior. A key guide in this pursuit is nature, for biological systems prove the power of hierarchical assembly and far-from-equilibrium behavior. The challenges here are many: a description of the functionality of hierarchical assemblies in terms of their constituent parts, a blueprint of atomic and molecular positions for each constituent part, and a synthesis strategy for (a) placing the atoms and molecules in the proper positions for the component parts and (b) arranging the component parts into the required hierarchical structure. Targeted functionality will open the door to significant advances in the harvesting, transforming (e.g., reducing

CO₂, splitting water, and fixing nitrogen), storing, and use of energy to create new materials, manufacturing processes, and technologies—the lifeblood of human societies and economic growth.

Beyond Ideal Materials and Systems: Understanding the Critical Roles of Heterogeneity, Interfaces, and Disorder

Real materials, both natural ones and those we engineer, are usually a complex mixture of compositional and structural heterogeneities, interfaces, and disorder across all spatial and temporal scales. It is the fluctuations and disorderly states of these heterogeneities and interfaces that often determine the system’s properties and functionality. Much of our fundamental scientific knowledge is based on “ideal” systems, meaning materials that are observed in “frozen” states or represented by spatially or temporally averaged states. Too often, this approach has yielded overly simplistic models that hide important nuances and do not capture the complex behaviors of materials under realistic conditions. These behaviors drive vital chemical transformations such as catalysis, which initiates most industrial manufacturing processes, and friction and corrosion, the parasitic effects of which cost the U.S. economy billions of dollars annually. Expanding our scientific knowledge from the relative simplicity of ideal, perfectly ordered, or structurally averaged materials to the true complexity of real-world heterogeneities, interfaces, and disorder should enable us to realize enormous benefits in the materials and chemical sciences, which translates to the energy sciences, including solar and nuclear power, hydraulic fracturing, power conversion, airframes, and batteries.

Harnessing Coherence in Light and Matter

Quantum coherence in light and matter is a measure of the extent to which a wave field vibrates in unison with itself at neighboring points in space and time. Although this phenomenon is expressed at the atomic and electronic scales, it can dominate the macroscopic properties

of materials and chemical reactions such as superconductivity and efficient photosynthesis. In recent years, enormous progress has been made in recognizing, manipulating, and exploiting quantum coherence. This progress has already elucidated the role that symmetry plays in protecting coherence in key materials, taught us how to use light to manipulate atoms and molecules, and provided us with increasingly sophisticated techniques for controlling and probing the charges and spins of quantum coherent systems. With the arrival of new sources of coherent light and electron beams, thanks in large part to investments by the U.S. Department of Energy’s Office of Basic Energy Sciences (BES), there is now an opportunity to engineer coherence in heterostructures that incorporate multiple types of materials and to control complex, multistep chemical transformations. This approach will pave the way for quantum information processing and next-generation photovoltaic cells and sensors.

Revolutionary Advances in Models, Mathematics, Algorithms, Data, and Computing

Science today is benefiting from a convergence of theoretical, mathematical, computational, and experimental capabilities that put us on the brink of greatly accelerating our ability to predict, synthesize, and control new materials and chemical processes, and to understand the complexities of matter across a range of scales. Imagine being able to chart a path through a vast sea of possible new materials to find a select few with desired properties. Instead of the time-honored forward approach, in which materials with desired properties are found through either trial-and-error experiments or lucky accidents, we have the opportunity to inversely design and create new materials that possess the properties we desire. The traditional approach has allowed us to make only a tiny fraction of all the materials that are theoretically possible. The inverse design approach, through the harmonious convergence of theoretical, mathematical, computational, and experimental capabilities, could usher in a virtual cornucopia of new materials with

functionalities far beyond what nature can provide. Similarly, enhanced mathematical and computational capabilities significantly enhance our ability to extract physical and chemical insights from vastly larger data streams gathered during multimodal and multidimensional experiments using advanced characterization facilities.

Exploiting Transformative Advances in Imaging Capabilities across Multiple Scales

Historically, improvements in imaging capabilities have always resulted in improved understanding of scientific phenomena. A prime challenge today is finding ways to reconstruct raw data, obtained by probing and mapping matter across multiple scales, into analyzable images. BES investments in new and improved imaging facilities, most notably synchrotron x-ray sources, free-electron lasers, electron microscopes, and neutron sources, have greatly advanced our powers of observation, as have substantial improvements in laboratory-scale technologies. Furthermore, BES is now planning or actively discussing exciting new capabilities. Taken together, these advances in imaging capabilities provide an opportunity to expand our ability to observe and study matter from the 3D spatial perspectives of today to true “4D” spatially and temporally resolved maps of dynamics that allow quantitative predictions of time-dependent material properties and chemical processes. The knowledge gained will impact data storage, catalyst design, drug delivery, structural materials, and medical implants, to name just a few key technologies.

ENABLING SUCCESS

Seizing each of these five Transformative Opportunities, as well as accelerating further progress on Grand Challenge research, will require specific, targeted investments from BES in the areas of *synthesis*, meaning the ability to make the materials and architectures that are envisioned; *instrumentation and tools*, a category that includes theory and computation; and *human capital*, the most important asset for advancing the Grand Challenges and Transformative Opportunities.

While “Challenges at the Frontiers of Matter and Energy: Transformative Opportunities for Discovery Science” could be viewed as a sequel to the original Grand Challenges report, it breaks much new ground in its assessment of the scientific landscape today versus the scientific landscape just a few years ago. In the original Grand Challenges report, it was noted that if the five Grand Challenges were met, our ability to direct matter and energy would be measured only by the limits of human imagination. This new report shows that, prodded by those challenges, the scientific community is positioned today to seize new opportunities whose impacts promise to be transformative for science and society, as well as dramatically accelerate progress in the pursuit of the original Grand Challenges.



Standing on the Shoulders of Giants—Five New Transformative Opportunities for Energy Science

“The most exciting phrase to hear in science, the one that heralds new discoveries, is not ‘Eureka!’ but ‘That’s funny...’”

—Isaac Asimov

“We are confused on a higher level, and about more important things,” wrote Earl Kelley, a professor of secondary education at Wayne State University, in his 1951 book *The Workshop Way of Learning*. Kelley was discussing the process of learning and noting that when we found answers to questions that solved problems, the answers also served to raise a whole new set of questions. Scientists face the same situation. A principal task of science is to observe natural phenomena, ask questions, and acquire answers. Learning the answers to questions, however, results in new knowledge that invariably leads to more questions. This pattern of ever deeper questions and answers is a pattern of rewards and benefits, for the knowledge that leads to new questions also often leads to new technologies—technologies that can advance our quality of life, bolster economies, and even, in some cases, transform the nature of societies.

Consider, for example, the microchip, the foundation upon which our current electronic age rests. Jack Kilby and Robert Noyce are credited with constructing the first microchip in 1958. The groundwork for this transformative technology, however, goes back many decades to questions asked and answered. Benjamin Franklin, in answering questions about lightning in the late eighteenth century, launched a new understanding of electricity. In 1897, British physicist Joseph John Thomson, in studying what were then called “cathode rays,” discovered the electron. American physicist Robert Millikan then measured its charge. Thomas Edison, in answering questions about his incandescent lamp, observed that electrons flow between conductors through a vacuum, an effect that John Fleming in 1904 exploited in the vacuum tube. The vacuum tube served as the workhorse component of electronics until the invention of the transistor in 1947 by John Bardeen, William Shockley, and Walter Brattain at Bell Labs, which

ultimately led to the integrated circuits of Kilby and Noyce. Few would take time away from their cell phones, tablets, or computers to argue against the proposition that this line of questions and answers produced knowledge and technologies that transformed our society.

In 2007, the U.S. Department of Energy’s (DOE’s) Office of Science, one of the nation’s largest sponsors of research in the physical sciences, charged a panel of ranking experts with identifying key questions about matter and energy at the quantum level. This panel, dubbed the “Grand Challenges” subcommittee of the Basic Energy Sciences Advisory Committee (BESAC), conducted a multifaceted study based on a series of workshops that had been conducted over the previous five years. The result of this effort was a landmark report titled “Directing Matter and Energy: Five Challenges for Science and the Imagination.” The five “challenges,” or questions, raised in the Grand Challenges report were as follows:

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

How do we control material processes at the level of electrons?

Chemistry can be seen as a sort of molecular melting pot in which different types of atoms swap or share electrons. As these electronic exchanges are at the heart of material properties and chemical processes, controlling the outcome of such exchanges presents an enormous opportunity for a wide range of technologies. We have evidence of this potential in the rapid advances that have been realized in areas where we have a strong foundation of theoretical concepts and experimental probes, such as crystalline solids, polymers, and certain small molecules. With sufficient control of materials properties and chemical processes at the electronic level, it should be possible for us to mimic or even improve upon the remarkable functionality of biology, such as artificial photosynthesis.

Answers to the five interconnected questions posed in the Grand Challenges report will provide fundamental knowledge to open doors to transformative technologies on several fronts, including energy, information and communication, and materials. As noted in that report, imagine a clean, affordable, and virtually unlimited supply of electrical power from solar-energy systems modeled on the photosynthetic processes utilized by green plants, and power lines that could transmit this electricity from the deserts of the Southwest to the Eastern Seaboard at nearly 100% efficiency. Imagine information and communications systems, based on light rather than electrons, that could predict when and where hurricanes will make landfall, along with self-repairing materials that could survive those hurricanes. Imagine synthetic materials fully compatible and able to communicate with biological materials.

As is befitting Grand Challenges, the quest to provide the answers that will make such technologies possible remains ongoing and formidable, a long-term venture. However, sufficient time has passed to assess the progress that has been made on all five fronts, and so the Office of Science charged a new BESAC subcommittee. This new subcommittee reviewed the scientific landscape at the time of the original report and compared it with the landscape today. The results are presented in this report, titled “Challenges at the Frontiers of Matter and Energy: Transformative Opportunities for Discovery Science.”

Just as the title of the original Grand Challenges report reflected the underlying concept of directing (controlling) matter and energy from the perspective of the Office of Basic Energy Sciences (BES) research portfolio, the title of this report reflects the breakthrough potential of current and prospective BES research, based on the advances achieved to date in answering the five Grand Challenge questions. The advances made in addressing those five original questions can now serve as a springboard to

realizing five new opportunities that have the potential to transform many of today’s energy-related technologies. These five Transformative Opportunities have been identified as follows:

- ▶ Mastering Hierarchical Architectures and Beyond-Equilibrium Matter
- ▶ Beyond Ideal Materials and Systems: Understanding the Critical Roles of Heterogeneity, Interfaces, and Disorder
- ▶ Harnessing Coherence in Light and Matter
- ▶ Revolutionary Advances in Models, Mathematics, Algorithms, Data, and Computing
- ▶ Exploiting Transformative Advances in Imaging Capabilities across Multiple Scales

Each of these five Transformative Opportunities is described in detail in an individual chapter of this report. Each chapter presents a brief overview of the opportunity, a detailed look at some of the scientific breakthroughs that will be required to capitalize on the opportunity, and the outlook for achieving the opportunity. In addition, the report provides a chapter titled **Enabling Success** that describes the resources—both people and tools—required to realize these five Transformative Opportunities. Also in the report is an appendix titled **Grand Challenges: Then and Now** that provides a status report on the five questions in the original report and the answers that have yet to be fully revealed.

The chapter titled **Mastering Hierarchical Architectures and Beyond-Equilibrium Matter** focuses on the opportunity to provide targeted functionality in materials by controlling the synthesis of beyond-equilibrium matter and its assembly into hierarchical architectures. Matter is in thermodynamic equilibrium when it does not change with time. Many of the functional materials we use today

are governed by away-from-equilibrium processes, but much of our understanding of these materials and their properties is based on at-equilibrium concepts. A number of the materials we use today are also monolithic, meaning they consist of a single material, such as conventional plastics, or a combination of materials whose individual components are indistinguishable, such as metal alloys. The successful development and deployment of sustainable energy technologies will likely depend upon transitioning from monolithic materials to materials with even more hierarchical architecture featuring multidimensional components that include matter interacting dynamically through far or even very far from equilibrium processes. Precise positioning of these components in a hierarchical mesoscale assembly will require understanding of and control over materials interactions at the nanoscale, where even a slight shift of the energetic balance affects the assembly.

With sufficient control of the hierarchical architecture of beyond-equilibrium matter, we can vastly expand the “space” to be explored for enhanced functions and processes. Within the complex multilength-scale structures of these systems are rich sets of metastable or non-equilibrium components that collectively will impact myriad applications, including energy harvesting and storage, solid-state lighting, and catalysis. The opportunity to controllably synthesize and assemble hierarchical architectures and beyond-equilibrium matter will sustain the leadership of the United States in basic energy science and technology. However seizing this opportunity will require a shift in scientific strategy. To date, the focus of research has been on understanding and manipulating the relationship between structure and function, with the goal of predicting *where the atoms should be placed* in order to achieve a desired property. We must move to an understanding of *how to get the atoms where they need to go* in order to achieve a desired structure. Developing a “science of synthesis” to precisely create targeted

hierarchical structures is a new horizon for functional matter.

The chapter titled **Beyond Ideal Materials and Systems: Understanding the Critical Roles of Heterogeneity, Interfaces, and Disorder** describes the opportunity for controlling the behavior and performance of both engineered and natural matter through a better understanding of the roles played by compositional and structural heterogeneities, interfaces, and disorder. Recent advances in theory, modeling, data science, computing, and communications, combined with new and improved experimental techniques and methods, are making it possible to study, in much greater depth, real rather than ideal materials under realistic conditions and time frames at the molecular, mesoscopic, and macroscopic levels.

Much of the materials research to date has been based on “ideal” systems, meaning they are observed in “frozen” states or represented by spatially or temporally averaged structures. Too often, this approach has yielded overly simplistic models that do not capture the complex properties and behavior of real materials under realistic conditions. Elucidating the rich, non-ideal behavior and characteristics of energy materials and systems is essential to guiding their use and adoption in the real world, improving their function, and extending their useful lifetimes. The opportunity to understand real materials under real-world conditions, including slow and statistically rare events that can dictate the success or failure of a given material, has the potential to impact a wide range of applications, including solar and nuclear power systems, hydraulically fractured systems, power conversion systems, airframes, and batteries.

The chapter titled **Harnessing Coherence in Light and Matter** explains how the ability to fully control large-scale quantum-coherent systems has the potential to revolutionize fields as diverse as information processing, sensor technology, and energy generation. Since 2007,

How do we design and perfect atom- and energy-efficient synthesis of revolutionary new forms of matter with tailored properties?

Thanks to gigantic leaps in computational power and focused national research efforts such as the Materials Genome Initiative, our ability to predict and simulate the functionality of new materials and chemical transformations has surpassed our ability to synthesize and characterize them. In other words, we are “discovering” exciting new materials we are unable to produce. What is needed to close this gap is a multipronged strategic approach. This approach includes advances in chemical synthesis approaches as well as multimodal experiments simultaneously performed on the same material sample to capture predicted new levels of temporal and spatial complexity; in situ experiments to capture the chemical dynamics and intermediate states that contribute to the outcome of interactions between different materials; and innovations in synthesis and characterization that are commensurate with the resources now available for predictions and simulations.

How do remarkable properties of matter emerge from complex correlations of the atomic or electronic constituents and how can we control these properties?

“Emergent phenomena” is the term used to describe the complex outcomes that can emerge from the correlated interactions of multiple simple constituents. The best example of this is the interactions of trillions of neurons in your brain, from which emerges your mind. Scientists have begun to unlock the mysteries of such emergent phenomena that arise from correlated electrons in metals, polymers, and hydrophilic and hydrophobic materials. They are also beginning to probe the temporal correlations of functional nanoscale systems that are mediated by electrical charge, quantum spin, or photons. The ability to predict and control the complex properties that emerge from the correlated interactions of a material’s atoms and electrons should pave the way for a new generation of materials and chemical processes that supersedes what we have available today, especially for energy and information technologies.

scientists have made enormous progress in the exploitation of quantum coherence, a phenomenon that is expressed at the atomic and electronic scale, but which can dominate the macroscopic properties of materials and chemical transformations. We have learned how to use light to manipulate atoms and molecules, and how to control and probe quantum systems such as the excited-state dynamics of photosynthetic processes in ever increasingly sophisticated ways. This progress also led to, among other achievements, a new appreciation of the role topology plays in protecting electronic coherence in key materials.

The ability to engineer symmetry-protected coherence in heterostructures that incorporate multiple types of different materials should enable us to substantially boost the coherence times of superconducting quantum bits (qubits) for quantum information processing. The ability to extend our control of quantum coherence to more complex, multistep chemical reactions will similarly transform the efficiency of artificial photosynthesis and related chemical transformations. In addition, the ability to rapidly probe coherence in increasingly complex systems, such as highly excited states, ordered mesoscale systems, or large molecular systems, should enable us to optimize photovoltaic (PV) cells for the generation of clean, renewable solar energy.

The chapter titled **Revolutionary Advances in Models, Mathematics, Algorithms, Data, and Computing** discusses a convergence of theoretical, mathematical, computational, and experimental capabilities. As shown in this chapter, we are on the brink of greatly accelerating our ability to find, predict, and control new materials, and to understand complex matter across a range of scales. Connecting theory and experiment through new computational capabilities will enable scientists to model matter and extract experimental information across a vast range of time and space scales. In turn, this knowledge should provide a better

understanding of the roles played by defects, fractures, and non-localities in the fabrication of large structures from those at the smallest scale. It should also help us better understand how the early stages of decay and failure in materials are initiated.

The rapid expansion of computational resources that continues to be realized, coupled with profound algorithmic advances that cross traditional boundaries, groundbreaking techniques to process and understand data, and a torrent of new theoretical models, has opened up the possibility of “inversely” designing materials that are incredibly strong but remarkably lightweight, resistant to failure even under extreme conditions, or able to repair themselves or adapt to changing conditions. Inverse material design will require a broad spectrum of scientific tools, working in harmony. Theory will be needed to bridge the gaps from small to large, and to model chemistry and physics across the mesoscale. New simulation algorithms will need to “go backwards” from a desired result to a proposed material. Advanced supercomputers and experimental capabilities will be indispensable. As the merging of theory and experiment continues to evolve and expand, the opportunity for integrating our knowledge of complex energy systems will blossom.

The maxim “seeing is believing” attests to the age-old reliance of humans on visual observations for asking questions and acquiring answers. Historically, improvements in imaging capabilities have always resulted in improved understanding of scientific phenomena. The case for imaging capabilities as a Transformative Opportunity and a research frontier is made in the chapter titled **Exploiting Transformative Advances in Imaging Capabilities across Multiple Scales**. A prime scientific challenge today is finding ways to reconstruct raw data from the probing and mapping of matter across multiple scales into usable images, analyze the results, and integrate those findings with other results from multiple sources. BES investments in new and improved imaging facilities, most notably synchrotron

x-ray sources, free-electron lasers, electron microscopes, and neutron sources, have greatly advanced our powers of observation. Substantial improvements in laboratory-scale technologies, such as scanning tunneling and atomic force microscopies and Raman spectroscopy, have also helped. Exciting new capabilities either planned or being actively discussed—for example, diffraction-limit upgrades to several of the nation's synchrotron light sources—will lead to smaller (nanometer), more intense, and more coherent x-ray beams extending into the hard x-ray energy range. An upgrade to the Linac Coherent Light Source at SLAC will yield probes at the attosecond timescale—the timescale at which the activities of electrons take place.

Taken together, all of these advances in imaging capabilities provide an opportunity to expand our ability to observe and study matter from the 3D spatial perspectives of today to true “4D” time-resolved maps that allow quantitative predictions of material properties. This expansion should yield answers to questions that will impact data storage, combustion science, drug delivery, computers, structural materials, and medical implants, just to name a few key technologies.

The five Transformative Opportunities described in the following chapters offer enormous potential benefits to our nation. In a world in which matter can be sufficiently controlled at the molecular and atomic levels, materials and chemical processes can be custom designed and synthesized to provide properties and outcomes that will meet specific national needs. However, each Transformative Opportunity poses questions for which the answers will not come either easily or cheaply. As the chapter titled **Enabling Success** makes clear, the successful realization of any of these five opportunities will require BES to address scientific complexities well beyond those previously contemplated. Addressing such complexities will in turn require a sustained campaign of strategic investments by BES

that initiates new research thrusts, attracts and sustains a scientific workforce with the necessary skills, and provides the appropriate facilities for carrying out the work. Developing and maintaining this campaign poses its own set of challenges for BES, especially in times of significant financial constraint.

BES has already begun this new strategic campaign with the award of 46 Energy Frontier Research Centers (EFRCs) in 2009 and a second round of 32 renewal and new Centers in 2014. As multidisciplinary, multi-institutional teams composed of the best of the best, the EFRCs are a research modality that is particularly well suited for tackling Grand Challenge and Transformative Opportunity science in a sustained and impactful manner. BES has also taken action to fuel the pipeline of researchers and cultivate a cohort of scientists focused on addressing Grand Challenge and transformational science through programs such as the Office of Science Early Career Research Program and the Graduate Student Research Program. As the rising stars in these programs reach their full potential, the impact of the BES investments will multiply.

These first steps provide a framework but not the resources to realize the Transformative Opportunities in this report. Embracing these opportunities requires much larger efforts in three broad areas—synthesis, instrumentation and tools, and human capital and resources. Synthesis is the means by which materials and chemical processes are harnessed to produce the compounds and structures that can be computationally envisioned. Instrumentation and tools, which include theory and computation, represent a continuation of BES's important history of providing large-scale user facilities that are the envy of the world, as well as the single-investigator innovation that creates lab-scale capabilities and foreshadows future facilities. With respect to human capital and resources, we are seeing the emergence of a new generation of scientists, with an awareness of both computational and experimental

How can we master energy and information on the nanoscale to create new technologies with capabilities rivaling those of living things?

Biology remains the paragon, model, and inspiration for complex, hierarchical, functional materials. Biological systems are the proof-of-concept for what can be achieved with nanotechnology. We are beginning to create nanostructures with functionality that is similar to the focused, practiced, and advanced functionality of biology. However, matching and, ultimately, surpassing nature will require a more advanced coupling of chemical, optical, electronic, magnetic, mechanical, and thermal degrees of freedom. Such advances will require increasingly sensitive experiments and sophisticated simulations of nanoscale systems, using the strategic concepts and principles of nature as our guide.

How do we characterize and control matter away—especially very far away—from equilibrium?

All natural and most human-caused phenomena occur away from equilibrium, meaning the phenomenon undergoes change over time. Away-from-equilibrium systems span scales from the very small, such as nanostructures and biomolecules, to the very large, such as earthquakes. Away-from-equilibrium processes take place over timescales ranging from nanoseconds to millennia. Although we have made great progress in unraveling the nature of non-equilibrium behavior for some specific phenomena, we have yet to characterize the universal features of non-equilibrium behavior for broad classes of phenomena. In particular, we are still not able to trap systems in metastable states or harness the transformations driven by disequilibrium. A hallmark of twentieth-century science was our learning to understand and control matter in a state of equilibrium. The knowledge to characterize and control matter when it is away, especially very far away, from equilibrium should have an even greater impact on our society and our daily lives.

capabilities that accentuates the need for collaboration: knowing what one does not know provides an exceptionally strong impetus for collaboration and partnership that BES must encourage. Synthesis, instrumentation and tools, and human capital and resources are so tightly coupled, that action in one without complementary actions in the others is unlikely to yield success. On the other hand, a concerted focus across all three areas will amplify their interdependent outcomes and accelerate progress in all three.

It was noted in the original Grand Challenges report that nature has been generous in providing us with the material resources we exploit to build and maintain our civilization. The energy that powers this civilization comes primarily from the burning of oil and coal. As we progress ever deeper into the twenty-first century, however, we are becoming increasingly aware of the finite and uneven distribution of natural materials and the high cost to our atmosphere of burning oil and coal. The original Grand Challenges report pointed the way to a brighter future in which the bounty of nature could be supplemented and perhaps even transcended by our own ingenuity. The five Transformative Opportunities described in this new report provide a road map for getting there.

2 chapter

Mastering Hierarchical Architectures and Beyond-Equilibrium Matter

The Transformative Opportunity is to realize targeted functionality in materials by controlling the synthesis and assembly of hierarchical architectures and beyond-equilibrium matter, thereby increasing dramatically the exploration space for enhanced function.

OVERVIEW

Monolithic materials are increasingly insufficient to address the many pressing global challenges in energy and sustainability. Hierarchical architectures and beyond-equilibrium matter represent a palette consisting of multidimensional materials across length scales that necessarily include materials that are not at thermodynamic equilibrium. Moving beyond equilibrium systems creates a vastly expanded space to be explored for improved functional materials and chemical processes. Embedded in many of these complex multilength-scale structures is a rich set of metastable or non-equilibrium materials with sophisticated functionality not found in materials at equilibrium.

To date, chemistry and materials research has focused on understanding and manipulating the relationship between structure and function, with the goal of predicting *where the atoms should be placed* in order to achieve a desired property. Scant attention has been directed toward the predictive science of synthesis—that is, toward understanding *how to get the atoms where they need to go* to achieve a desired structure. The creation of materials with emergent functionality that exploits multiple length scales, including interfacial metastability, and complex hybrid structures is an

emerging opportunity to meet this challenge. Figure 2-1 highlights several hierarchical structures that exemplify these principles, along with their energy-related applications.

Emerging complex materials are increasingly important for myriad applications ranging from energy harvesting and storage to solid-state lighting and catalysis. The ability to create, control, and exploit metastabilities, interfaces, and complex architectures that arise when multiple classes of materials are heterogeneously integrated is central to sustaining our nation's leadership in basic energy science and technology. To realize this opportunity, several major advances are required:

1. Predictive models, including the incorporation of metastability, to guide the creation of beyond-equilibrium matter;
2. Mastering synthesis and assembly of hierarchical structures for multidimensional hybrid matter; and
3. In situ characterization of spatial and temporal evolution during synthesis and assembly.

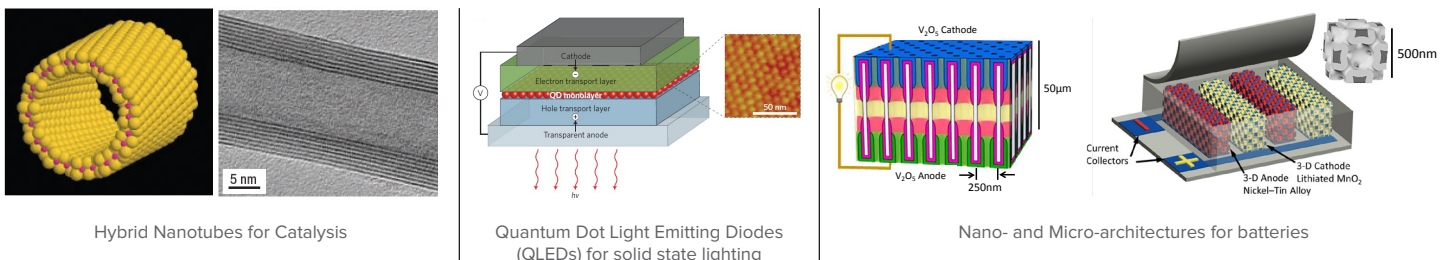


Figure 2-1. Examples of “designer” materials for energy applications. (Tenne, 2006; Coe-Sullivan, 2005; Braun and Nuzzo, 2014)

FRONTIERS

Predictive models, including the incorporation of metastability, to guide the creation of beyond-equilibrium matter

The potential diversity of this emerging class of hierarchical and beyond-equilibrium materials is daunting. Fortunately, we are entering an era of “materials by design” in which computation, integrated with experiment, can vastly accelerate materials discovery as well as our understanding of materials structure and functionality. Addressing this increasingly complex materials space requires new coupled computational and experimental tools that enable rapid evaluation of the role of such areas as materials composition, mechanical energy, thermal energy, and reaction conditions, in real time during synthesis and assembly. This fundamental gap in understanding must be addressed if robust, scalable methods for the synthesis and assembly of energy-relevant materials are to be realized. High-throughput computational, theoretical, and experimental capabilities could accelerate this process immensely.

The development of a predictive science of synthesis for metastable systems poses significant challenges, because nucleation, self-assembly, and crystallization are inherently collective phenomena that link molecular-scale interactions to ensemble outcomes. We must move beyond the computation of thermodynamic properties to capture multiple competing kinetic pathways that arise during synthesis and assembly. The fact that many of the materials along a synthetic pathway are inherently metastable enables their transformation from one identified state to another. In some cases, it may be desirable to drive the system toward an equilibrium state. Alternatively, one can envision significant advantages to driving the system toward highly demixed architectures that give rise to distinct topologies, leading to enhanced electrical, optical, magnetic, or mechanical properties. Computational tools are needed that enable understanding of the key underlying variables that determine which route is kinetically preferred, including capabilities to assess the roles of thermodynamic barriers, atomic motion, catalysts, and decomposition pathways,

and to then translate these computed solutions to synthetic reality.

The formation of nanoscale structures, such as highly branched nanoparticles, layered 2D materials, and mesoporous crystals, appears to be poorly described by the classical models of nucleation and growth. The lack of predictability is yet more pronounced for sequence-defined macromolecular materials. While their high information content enables a corresponding high level of function, it introduces conformational flexibility that can dominate the dynamics of assembly and frustrate the development of well-ordered states. In such situations, one needs to be able to calculate not only the thermodynamic ground state of the system but also low-lying excited states accessible through system excitation or controlled kinetics.

One can think of the above systems as representative examples of the growth of new functional materials that take advantage of phase space beyond that of equilibrium materials. These systems include two primary classes: materials with inherent non-equilibrium properties and interfacially driven non-equilibrium materials. Figure 2-2 illustrates a representative composition/energy landscape for a relatively simple binary system (A-B) that shows types of non-equilibrium materials by class. Multiple stoichiometries exist at thermodynamic equilibrium at low energy. More importantly, a broad range of structures and resulting functions are accessible above the ground state. Even in this simple system, one can distinguish four basic types of functional metastabilities:

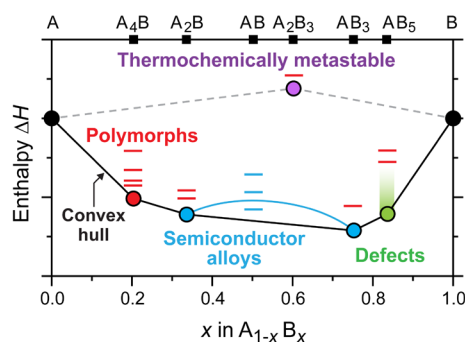


Figure 2-2. Composition/energy landscape for a binary system (A-B).

- ▶ **Thermochemical Metastability:** Materials with positive ΔH with respect to constituent elements; for example, phase-pure Cu_3N can be made, although it is unstable relative to its constituent elements.
- ▶ **Polymorphs:** Materials with the same stoichiometry, but different electronic and chemical properties; for example, the dramatically different optoelectronic properties of anatase and rutile TiO_2 .
- ▶ **Alloys:** Variable compositions whose properties scale linearly or non-linearly with composition; for example, the ZnN-GaN optically active system.
- ▶ **Defects:** Single or multiple vacancies or substitutions that determine carrier concentration, catalytic properties, and magnetic properties; for example, Zn vacancies in ZnO and dopability in CdTe.

Expanding this binary landscape to the ternary and quaternary systems that are common in inorganic synthesis today is not only graphically challenging but also indicative of the vast opportunity spaces that need to be explored predictively in order to reveal novel functionality.

The evolution of our ability to controllably synthesize molecules and matter by a wide range of chemical and physical techniques has significantly increased our access to metastable and non-equilibrium materials. Our ability to capture, computationally and experimentally, various pathways that will need to be controlled is enabled by techniques and approaches, including high-energy atoms and clusters; external fields and tunable surface energies; rapid precursor deposition and subsequent anneal cycles to create local order; vapor-to-solid direct synthesis; direct synthesis of new phase materials not on equilibrium phase diagrams; two-phase soft-soft, soft-hard, and hard-hard systems where one phase constrains the phase formation in the second; and constrained growth due to chemical and structural templates. More generally, understanding and controlling the key role of non-equilibrium interfaces in the growth of complex multidimensional materials is a central challenge.

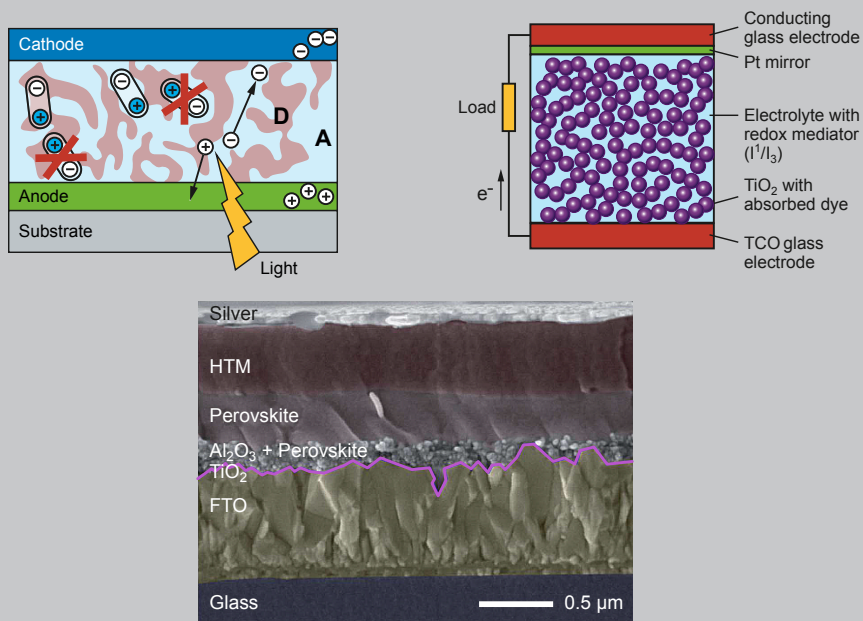
For example, in solution-based approaches, one must consider how short-range characteristics of cluster-cluster and particle-particle interactions, which are influenced by intervening solvent molecules and ions, are coupled to long-range forces and motion. Coarse-grain approaches, like Ising models, do not provide the molecular fidelity needed to be predictive, while fully atomistic computational models cannot access the spatial and temporal scales needed to simulate the formative events in extended structures. Moreover, calculations of equilibrium states are inadequate, because the complexity of formation pathways arises from the interplay between free-energy landscapes that determine the preference for a specific structure and dynamical constraints that determine whether this preferred structure actually occurs or whether an alternative kinetically controlled pathway is traversed.

A similar example is the pulsed-laser-deposition growth of materials in which very high-quality materials can be grown by an essentially physical deposition process, where initial target stoichiometry is conveyed to the substrate by clusters which then, as a function of temperature, surface energy, plasma energy, etc., can rearrange themselves across temporal and physical length scales to produce single-crystal materials. A key factor is ablation dynamics: the initial ablation pulse is on the order of nanoseconds, the subsequent ablation processes occur on the 0.1- μ s scale. The ablated clusters and plasma arrive at the substrate some 4 μ s later, followed by a relaxation and growth process that can last for milliseconds. At present, we have no good models for these time-dependent, non-equilibrium processes, which are key for generating complex materials. A critical part of developing this understanding will be to begin to understand the kinetically limiting processes along each pathway.

Coupling metastability and multidimensional structures creates a vast new landscape for identifying new functional materials and creates an even more complex problem with respect to predictive synthesis of the desired structures. Modeling and experimental

PEROVSKITE SOLAR CELLS

Hybrid perovskite materials have been attracting a great deal of attention recently because of their spectacular performance as solar cell materials, with efficiencies exceeding 20%. The perovskite cells are based on a foundation of bulk heterojunction organic photovoltaics (OPVs) and a dye-sensitized solar cell (DSSC), as illustrated in the figure.



Hybrid perovskite material based on bulk heterojunction OPVs and a DSSC. (Ball et al., 2013)

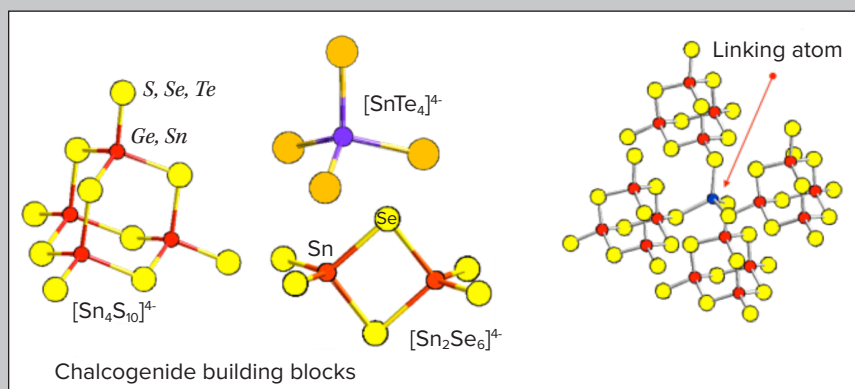
The properties of the lead-based perovskites are not observed in other analogous substituted perovskites, such as tin-based materials. The lead-based perovskites exhibit remarkable crystalline growth (demonstrating chemical anion tunability) by both solution and physical-vapor-deposition approaches, resulting in unusually long carrier diffusion lengths, extremely high absorptivity with a sharp optical onset, and ferroelectric behavior. There is also evidence of auto-surface passivation and auto-repair of defects. Though not much is understood about the interface of this hybrid material, open-circuit voltages greater than 1.57 volts have been obtained, making this system very unusual compared with typical PV materials.

Though this system has demonstrated a significant number of new and unique properties, there is presently no basic model for these materials, much less the ability to predict new materials analogous to the lead system or, more importantly, the ability to consider both the anion and cation coupled to the interface to move toward completely new materials systems. These systems are an ideal illustration of not only the rich potential of hierarchical, away-from-equilibrium functionality, but also the unanswered questions relevant to hybrid systems, for example, the need to address alternative materials, interfaces, and morphology.

CHALCOGELS: RANDOM NETWORKS WITH TUNABLE PROPERTIES

An emerging class of porous chalcogenide aerogels, also known as chalcogels, may be an ideal supramolecular structure to integrate diverse properties with various functionalities. For example, high-surface-area materials made exclusively from soft polarizable atoms for selective separations and redox-actively relevant to catalysis and solar fuels production are possible. Chalcogels, unlike the ubiquitous oxide-based aerogels, are based on chalcogenide species such as sulfides, selenides, and tellurides. This chemistry allows for interesting properties, including light absorption, from the ultraviolet to the visible to the infrared, desulfurization catalysis, heavy metal ion sequestration, and hydrogen production.

To synthesize the chalcogels, simple metathesis chemistry is used at room temperature in solution by combining anionic groups and metal cations to form metal chalcogenide networks, as shown in the figure. Chalcogenide anionic clusters such as $(\text{Ge}_4\text{S}_{10})^{4-}$, $(\text{Sn}_2\text{S}_6)^{4-}$ and $(\text{SnSe}_6)^{4-}$ can be used as building blocks and ligands to bind to metal ions such as Zn^{2+} , Sb^{3+} , or Pt^{2+} to assemble random polymeric networks which can be induced to form stable gels (chalcogels). The variety of soluble chalcogenide anions and metal cations available defines a large matrix of possible chalcogel structures. The key is to choose the proper solvents and precursor that lead to a gel and not a precipitate.



Typical building blocks and how they can bind to a metal cation (blue atom) to form an extended gel-forming network. (Bag et al., 2007)

In addition to linking metal cations, entire clusters can be used to form the chalcogenide networks. Biomimetic chalcogels can be formed by using biomimetic clusters, such as redox-active transition metal clusters and light-harvesting photoredox molecules.

The general approach to synthesizing chalcogels and the ability to use a variety of chalcogenide clusters and linking metals allow direct materials design. The porous structure and chemical diversity of framework composition are advantageous in catalysis, adsorption, and separation technologies needed for solar fuels, environmental heavy metal remediation, and nuclear waste remediation.

work are needed to understand the thermodynamics of intermediate states, including those in nucleation, self-assembly, and dynamic restructuring, and those in transient and local conditions (e.g., high chemical potentials of species established by decomposition of reactive precursors). These advances in modeling the dynamics of intermediate states will open broad new horizons in creating a science of synthesis for hierarchical and away-from-equilibrium materials and architectures that are critical for next-generation energy technologies.

Mastering synthesis and assembly of hierarchical structures for multi-dimensional hybrid matter

When disparate materials are combined with one another, they give rise to interfaces with geometries that exhibit planar to more complex topologies across the nano-, micro- and mesoscales. Examples abound, ranging from inorganic-inorganic hybrids that form the basis of thin-film copper-indium-gallium-selenide solar cells, solar thermal converters, thermoelectric materials, and topological insulators, to inorganic-organic hybrids that are used in LEDs, photovoltaics, batteries, and fuel cells. The ability to design and control these architected materials across this broad range of functionality is only now emerging. Three opportunity areas—mesoscale printing, bio-inspired and hybrid soft matter, and templated design of hard-soft interfaces—illustrate the challenge.

Printing mesoscale architectures

Mesoscale features can have a large effect on the macroscale properties of a given material. This is a result of both materials-dependent functionalities and the architectural or structural arrangements of those materials. One of the important capabilities enabled by mesoscale printing is the independent control of these two factors. Even the simplest mesoscopic structures, architected from a single material and at a single mesoscopic length scale, can enable enhanced or even fundamentally new mechanical properties at macroscopic length scales (i.e., larger than the mesoscopic structural features). Such architected materials, or metamaterials, blend the concepts

of material and structure and open a new design space. Structural motifs, structural hierarchy, and material interfaces contribute to the design of effective mesoscopic architectures for mechanical or structural applications. Functional materials can also be integrated with these architectures, raising additional considerations and opportunities. Functional capabilities can be introduced that arise from the intrinsic functionality of a particular material (such as conductivity in metals) or that emerge from interfaces between disparate materials that have been combined in mesoscopic geometries (such as electron flow in an anode-cathode system). In either case, as the system properties strongly depend on specific material functionalities, a primary research challenge in the area of functional mesoscale architectures has been and continues to be the development of printable functional materials.

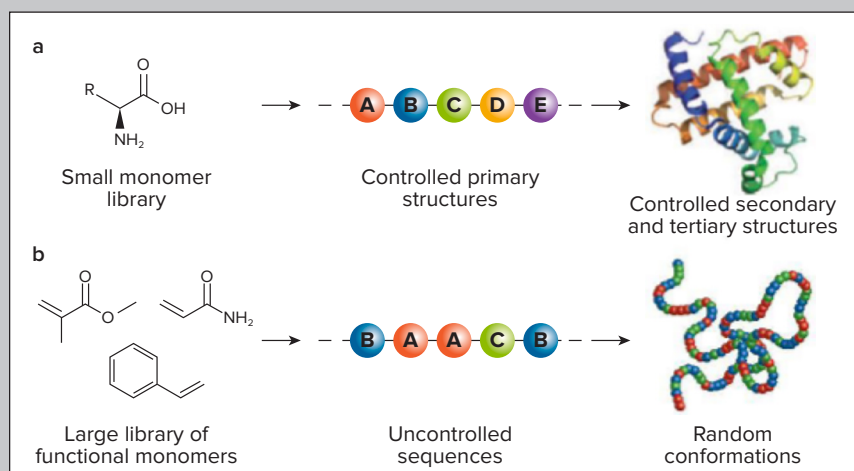
Research related to 3D printing has made significant strides in recent years. Nearly arbitrary structural motifs can now be directly printed with very fine resolution ($\sim 100\text{ nm} - 1\text{ }\mu\text{m}$). Manipulation of structure at these length scales via 3D printing enables the design of mesoscale architectures that fundamentally alter the properties of the corresponding macroscopic structure: deformation modes can be manipulated, exotic responses can be designed, and the distinctions between structure and material are blurred with the fabrication of some of the lowest density solid objects ever observed. Inspiration from nature has led to multimaterial structural materials, for example, containing combinations of soft and stiff elements that exhibit some of the same benefits as their natural counterparts. The integration of multiple materials via 3D printing is still in its infancy and again further enhances the space available for exploration. One of the benefits of 3D printing complex, multimaterial mesoscale architectures is that customizable functional systems can potentially be directly printed and integrated with complicated structures.

Bio-inspired and hybrid soft matter

The construction of new materials based on a repertoire of reversible interactions resembling those found in biology will

CHEMICAL CONTROL OVER INFORMATION CONTENT IN MACROMOLECULAR ARCHITECTURES

Biology, and all of its functionality, is controlled by the specific sequences formed from combinations of many different monomers to make linear polymers. No such level of control is even remotely possible in chemically synthesized copolymers. Biological synthesis can be commandeered to produce synthetic amino acid polymers, which can be further diversified by post-translational, or even post-polymerization, chemical modification. However, techniques that enable polymerization of a wide diversity of chemical types of monomers are currently very limited. The figure illustrates the difference in biological versus chemical synthesis.



Primary sequence control in (a) biopolymers and (b) synthetic polymers. (Lutz, 2010)

Unlike the chemical control we can now exert over polymer molecular weight and stereochemistry, general approaches to sequence-controlled synthetic polymers are very limited. For example, with certain choices of common vinyl monomers, very highly alternating copolymers can be produced, owing to the reactivity ratios of two monomers. Current approaches to sequence control in synthetic polymers (beyond amino acid polymers) include template polymerization methods and controlled free-radical polymerization methods.

enable structurally self-correcting/self-repairing materials, dynamic materials, energy- and signal-transducing materials, and new materials for information storage and processing. Complex, functional materials must necessarily integrate multiple elements to capture molecular-level signals, amplify them, and transduce them into observable macroscopic responses. Soft materials are particularly promising for achieving such functions, in that minute perturbations can induce massive molecular reorganizations. Interfaces are the gateways that allow or impede the transfer of information from one material element to another. The molecular structure of soft interfaces can be tailored to control the transfer of species or information across them, as well as their response to external cues, be they physical or chemical.

Soft materials are especially susceptible to weak forces. The interactions that hold soft matter together are often comparable in magnitude to the thermal energy; small temperature changes or the application of small stresses can therefore induce macroscopic transformations. While this attribute has traditionally presented challenges to the control of soft matter, it also provides extraordinary opportunities. Soft interfaces are compliant and can easily become sites of intimate contact between different materials. They are reconfigurable and can be tailored to achieve optimal functionality. They can exhibit orthogonal responses to multiple, simultaneous external perturbations. They are highly localized and can exhibit extraordinarily large property gradients on length scales comparable to molecular dimensions. They can allow or prevent the transfer of chemical and physical information from one region of a material or device to another. Interfaces can coordinate communication between distant elements of a material and give rise to emergent behaviors that remain unknown. The opportunity here is to gain molecular-level control of soft interfaces, thereby enabling design of truly integrated, multifunctional materials for next-generation technologies.

Synthetic soft materials have yet to exploit, in concert, the full range of interactions that give biological materials their remarkable

properties. Biological self-assembly drivers include hydrophobic, electrostatic, steric, and hydrogen-bonding interactions, deployed in spatially designed geometric relationships. Taken together, this array of joining methods leads to self-healing, exceptional deformation and durability characteristics, and useful permeability and strength-to-weight properties at the same time. Achieving this level of organization requires potency and precision placement of interactions that challenge chemical synthesis. The opportunity here is in soft-matter synthesis and characterization that build into synthetic materials a new level of information content approaching that of biological materials. Applications that could result include synthetic replacements for physiological structures, hydrogels, wet adhesion, patterned/textured soft materials for anti-reflectivity, and omni-phobicity. Biology uses many hybrid organic-inorganic materials; intimate synthetic integration of hard and soft matter can be expected to produce new materials with remarkable characteristics in the realms of toughness, optical properties, and responsiveness.

New advances in polyelectrolyte complexation, programmable self-assembly and controlled polymerization, and post-polymerization synthetic methods are making biological levels of control over materials organization conceivable. These methods are exploiting, and will continue to exploit, powerful synchrotron and neutron scattering sources, as well as new microscopy and spectroscopy techniques, as they emerge. Computational advances are leading to better predictive design capabilities.

Design and assembly of hard/soft interfaces

We are increasingly dependent on complex hybrid systems whose fundamental interactions we do not fully understand. The ability to predict, design, and control hybrid systems would enable new or improved functionalities for a wide range of applications in energy, optoelectronics, and other fields. In addition, as we gain control of chemistry, structure, and transport properties in hybrid systems over multiple length scales for stable and metastable systems, we can derive new emergent properties.

The combination of soft and hard materials can generate functionality common to neither, along with the ability to move away from empirical optimization to actual design across a range of morphologies (e.g., layered, nanoscale, and mesoscale) and composition, and could have a transformative impact on energy conversion, energy efficiency, and energy storage.

Hybrid systems composed of hard, often crystalline, inorganic materials and soft, often amorphous materials—organic, inorganic, or a combination—represent a new frontier for creating novel multifunctional systems. Recent examples of hard/soft hybrid systems relevant to energy technologies include perovskite and organic photovoltaics, organic LEDs, lithium-ion (Li-ion) batteries, polymer electrolyte membrane fuel cells, and multifunctional catalysts. These materials and structures can be in thermodynamically stable configurations, but more commonly, they are in a metastable state in hybrid systems. Understanding how to design and control the structure and dynamics of hard/soft hybrid materials and their interfaces, including transport of energy, charge, and mass across interfaces, is crucial to developing new multifunctional materials.

Perhaps the simplest approach to this challenge is enhancing known hard materials (e.g., battery or photoelectrode materials) through soft surface coatings. For example, atomic layer deposition and other deposition processes can allow for the controlled growth of thin films of organic or inorganic materials on functional substrates. Thin films of polymers, amorphous metal oxides, and inorganic/organic hybrids have been shown to enhance the stability of advanced silicon-based anode materials for Li-ion batteries. New synthetic methods are needed, not only for surface coatings but for more complex systems and architectures, including composites. New chemistries could lead to new strategies for the bottom-up synthesis of soft materials on hard substrates. Molecular approaches and new precursor concepts could lead to new composites. Understanding the mechanism of deposition processes is critical to developing the needed

control over composition, structure, and morphology. Self-assembly processes and supramolecular approaches (e.g., metal-organic framework [MOF] compounds) could provide access to a range of new hybrid materials.

In situ characterization of spatial and temporal evolution during synthesis and assembly

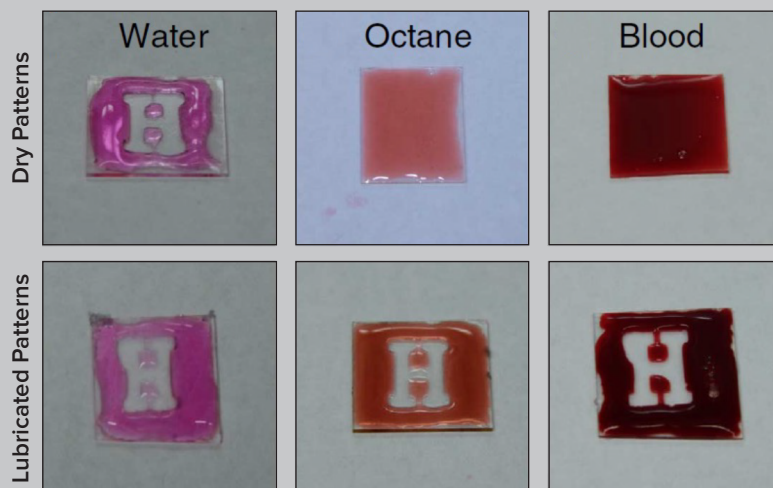
While it will always be valuable to examine a structure after the fact, it is increasingly important that we develop characterization tools to evaluate the evolution of structure and function in real time. If this capability can be achieved, it creates the critical link between computational design and experimental realization, and significantly accelerates the pace of materials discovery, especially for hierarchically assembled materials and complex chemical transformations.

We have become very good at characterizing end-state materials in great detail, even—in some cases—with respect to external parameters. However, a great deal of new development needs to be accomplished to be able to use in situ characterization as a real-time probe for both nucleation and growth, directed self-assembly, hierarchical integration, and structural reordering at interfaces. In situ and real-time monitoring of growth and synthesis processes is essential to understand and ultimately control chemistry and materials synthesis. Such monitoring will allow testing and validation of predictive synthetic models and will help to accelerate materials discovery, especially into new spaces, including metastable, imperfect, and heterogeneous materials, interfaces, and high pressures. Ideally, this monitoring will address both structural and opto-electronic properties.

As an example, the national user facilities are a unique resource which can enable experiments that will build a foundational understanding of synthesis pathways over a range of length scales and will integrate these data with theory. Ultimately, this work will accelerate predictable creation of novel functional materials, including those based on abundant elements. The challenges involve developing state-of-the-

OMNIPHOBIC SURFACES VIA COLLOIDAL TEMPLATING

A transparent coating that repels a wide variety of liquids, prevents staining, is capable of self-repair, and is robust toward mechanical damage would have a broad impact. To meet this need, transparent, nanoporous surface structures have been designed using colloidal templating. A lubricant was firmly locked into the structures and, owing to its fluidic nature, the lubricant forms a defect-free, self-healing interface that eliminates the pinning of a second liquid applied to its surface, leading to efficient liquid repellency, prevention of adsorption of liquid-borne contaminants, and reduction of ice adhesion strength (see Figure). This method can also be applied to locally pattern the repellent character of the substrate, thus creating opportunities to spatially confine any simple or complex fluid. The coating is highly defect-tolerant because of its interconnected, honeycomb wall structure, and repellency is retained after the application of strong shear forces and mechanical damage. The regularity of the coating allows us to understand and predict the stability or failure of repellency as a function of lubricant layer thickness and defect distribution on the basis of a simple geometric model.



Patterning of various liquids based on surface chemistry contrasts. The upper row shows the addition of liquids to the dry, patterned substrates; the lower row shows the addition of liquids to substrates treated via colloidal templating. Rhodamine B-dyed water (left): the pattern is revealed both in a dry state and on the lubricated sample; DFSB-K175-dyed octane and sheep blood (center and right): the liquids wet and contaminate the entire surface in a dry state, while successful patterning occurs due to the repellent properties of the colloiddally templated surface on the lubricated sample. (Vogel et al., 2013)

art instrumentation and methodologies for new in situ characterization over a wide range of length and timescales, spanning atomistic to macroscopic and picoseconds to hours. Examples include rapid thermal processing, film growth by atomic-layer deposition and pulsed-laser deposition, roll-to-roll printing, and hydrothermal and very-high-pressure synthesis. Techniques will need to be developed to probe, in situ, individual nucleation and growth events.

Characterization capabilities for soft/hard hybrids are improving, not only at the national synchrotron and neutron facilities but also in the laboratory with dynamic transmission electron microscopy (TEM) and multimodal diffraction, spectroscopy, and imaging. These capabilities are increasingly allowing researchers to probe dynamically the complex structural and electronic degrees of freedom of hybrid systems. For example, many studies are providing important compositional, structural, and dynamic information on the solid electrolyte interface layer in Li-ion batteries and gas solid interfaces in catalysts. In situ characterization tools are starting to come on line, but need to be developed more broadly to study systems both during formation and during function. Spectroscopic tools are needed to probe energy, charge, and mass transport across interfaces between hard and soft materials.

OUTLOOK

Hierarchical architectures and beyond-equilibrium matter create a vastly expanded space to explore for unanticipated and enhanced materials functionality and chemical processes. The Transformative Opportunity is to synthesize and assemble such matter with spatial and temporal control to provide targeted functionality. As our understanding of the property/functional relationships for such systems becomes more complete, it will be increasingly possible to design new systems to the bond level with enhanced functionality across structural, optoelectronic, and chemical properties, and with enhanced stability. Coupling theory and experiment could eventually enable predictive synthesis. In this pursuit, we take much inspiration from biology. Achieving synthetic mastery that rivals that of nature is a grand challenge; however, the opportunity also exists to go even beyond what nature has achieved to advance the frontiers of energy science. Success will only be possible through predictive models that explicitly incorporate metastability, an unprecedented degree of synthetic mastery and directed assembly, and in situ characterization of the spatial and temporal evolution of these systems to inform materials design.

3 chapter

Beyond Ideal Materials and Systems: Understanding the Critical Roles of Heterogeneity, Interfaces, and Disorder

Developing a fundamental understanding of the roles of heterogeneities, interfacial processes, and disorder in materials behavior and chemical processes represents a Transformative Opportunity to move from ideal systems to the complexity of real systems under realistic conditions.

OVERVIEW

Advances in energy science will be achieved by understanding the roles of compositional and structural heterogeneities, interfaces, and disorder in controlling the behavior and performance of both engineered and natural energy systems. These disruptions of perfect order are often critical for materials and systems performance, yet our current understanding of their roles is in its infancy. New horizons for probing and understanding the role of heterogeneities, interfaces, and disorder in real materials under realistic operating conditions and time frames arise when recent advances in theory, modeling, data science, computing, and communications are combined with advanced experimental techniques and methods. This approach will elucidate the spatio-temporal evolution and transformations of these materials and systems in all their complexity, including the roles of slow and/or rare events and processes.

Understanding of the effects of heterogeneities, interfaces, and disorder on materials behavior and performance must span molecular, mesoscopic, and macroscopic scales, providing a fundamental predictive basis for, for example, heterogeneous catalytic reactions and their cycle lifetimes; materials degradation and failure; hydraulic fracturing of hydrocarbon-rich shales; and, in electrochemical systems, the slow (low-rate) and rare (low-frequency) events that limit the systems' lifetimes and reliability (Figure 3-1). There are many interfacial processes in heterogeneous solid-solid, solid-liquid, or solid-gas phase systems in which simple observational understanding has not been sufficient to identify the critical parameters that control dissolution, adsorption, nucleation and growth, and fatigue.

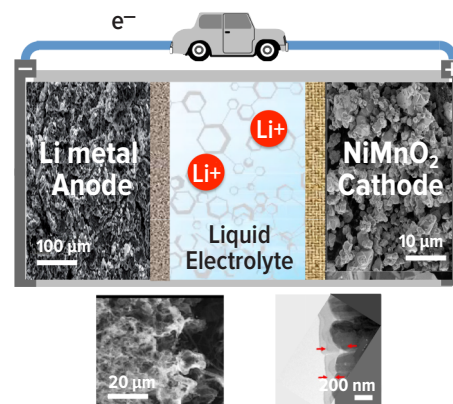


Figure 3-1. Heterogeneities, interfaces, and disorder are primary features of batteries. The Li-ion battery stores and releases energy by transferring Li^+ ions across interfaces among the anode, electrolyte, and cathode. The interfaces are not perfectly flat surfaces as often imagined in cartoons of the battery; instead, the electrodes are composed of grains that may range from nanometers to micrometers. Because of their small size, the interfaces of these grains are curved, thus exposing many atomic planes to the electrolyte, which in turn accelerates or retards specific side reactions. As Li^+ ions move through the interfaces, they expand or contract the surface, often leaving permanent strain or fractures in their wake. Each of these static and dynamic interface phenomena has the potential to help or harm the energy storage process. (Yu et al., 2015; Shi et al., 2015; Chang et al., 2015; Kim et al., 2015)

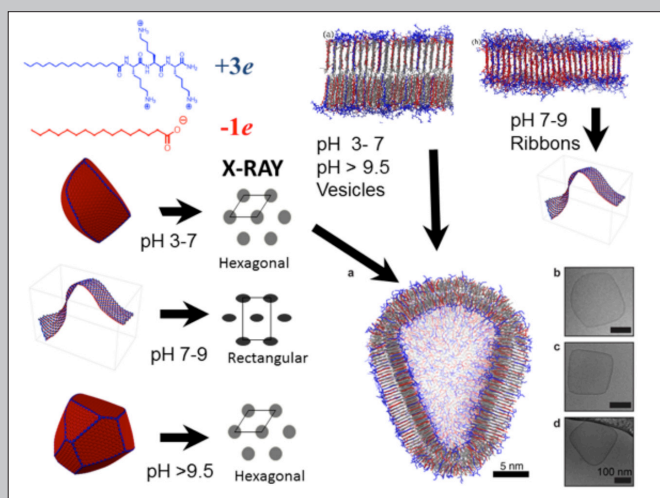
Many real materials are inherently heterogeneous across spatial and temporal scales, as evidenced by their compositional, spatial/structural, and temporal fluctuations and disorder. Defects, such as interstitial atoms and vacancies, are examples of more localized heterogeneities that are ubiquitous in real materials. Solid surfaces and solid-liquid interfaces represent another type of defect that is more extended and results in enhanced chemical reactivity relative to the idealized bulk state. These heterogeneities are deeply tied to temperature and the thermal processes that give rise to disorder and entropy. Yet we often have considered materials in idealized, “frozen” states or as represented by their spatially

CONTROLLING MESOSCOPIC MEMBRANE SHAPE AND HETEROGENEITY

Viruses, organelles, and the wall envelopes of Archaea organisms are examples of nanocontainers of diverse shapes that perform specific biological functions. These closed crystalline structures are biological reactors that control various processes; examples include controlling metabolic flow, even at very high salt concentrations (in Archaea organisms), and enhancing the fixation of CO_2 in cyanobacteria. The nanocontainers undergo transformations to perform specific functions, such as the conformational changes of viral capsids to release RNA inside cells. The mechanisms that lead to the emergence of various shapes at the mesoscale, as well as how these shape transformations couple to the functions of the nanocontainers, have been a mystery.

Heterogeneity need not be only compositional and structural. It can also refer to mesoscopic physical properties such as the shape of biomolecular nanocontainers as encountered in virus shells, organelle membranes, and wall envelopes of Archaea organisms. Self-organized nanocontainers that undergo various geometrical mesoscopic transformations are of particular interest for applications including imaging, catalysis, compartmentalization, and targeted delivery.

Co-assembly of oppositely charged lipids with variable degrees of ionization results in complex crystalline polyhedral structures that can be modified by changing the pH of the bathing electrolyte (see Figure). The coupling between heterogeneity and long-range electrostatic leads to diverse buckled geometries, including fully faceted regular and irregular polyhedra such as square and triangular shapes or mixed Janus-like vesicles with faceted and curved domains that resemble cellular shapes and wall envelopes of halophilic organisms. Furthermore, the changes in the electrolyte environment engender phase transformations between various types of heterogeneity of the nanocontainer surfaces. Understanding the coupling of shape and composition through tuning chemical and physical interactions will enable the design of polyhedral structures for various applications, including efficient nanoreactors to perform specific catalytic functions.



Changes in pH result in changes in the molecular charge distribution along the nanocontainer surface. This in turn induces changes in the molecular conformation and mesoscale shape changes. (Leung et al., 2012)

or temporally averaged structures. These overly simplistic models do not capture the nuances of structure and dynamics that often drive desired functional behavior.

The spatial, compositional, and temporal heterogeneities of energy materials, such as at interfaces and across the inherent variability of natural and manufactured populations, give rise to most of their real-world behavior and beneficial properties and produce their inherent scientific challenges. For example, interfaces among solids, liquids (e.g., water), and gases, such as in the Earth's atmosphere, dominate materials behavior and its temporal evolution, including chemical reactivity and transformations, assembly, function, and degradation, and in some cases the materials' robustness or fragility. This complexity and temporal evolution of materials across populations confounds fundamental physical modeling, which typically considers idealized average or perfect systems even when desired behaviors may arise from heterogeneities.

Aqueous solutions are common components of natural and manufactured systems and add another level of complexity in understanding real system behavior and solution processes. An example of this complexity is the electrical double layer (EDL) at solid-water interfaces, where the properties of interfacial water (e.g., its low-frequency dielectric constant) can differ considerably from those of bulk water and result in major differences in, for example, the molecular-level structure, coordination complexes, and pH of interfacial water relative to bulk water. The importance of interfaces between natural solids and liquid water in the biosphere cannot be overestimated. In spite of the importance of such interfaces, little is known from direct observation about the structure and properties of the EDL at solid/aqueous-solution interfaces. Instead, we rely on simple empirical models of the EDL developed in the early twentieth century for predictions of interfacial phenomena. In addition, although there have been recent advances in determining the structure of metal oxide/aqueous solution interfaces and of the surfaces of a few single-crystal solids in contact with aqueous solutions (using synchrotron-based surface x-ray

scattering), we have only rudimentary knowledge of the real structure of most solid surfaces in contact with liquids. This is particularly true for the surfaces of nanoparticles, which in some cases have poorly ordered surface structures. As a result, we know very little about the mechanisms of surface chemical reactions for nanoparticles and most bulk solids.

Elucidating the rich, non-ideal behavior and characteristics of energy materials and systems is essential to guiding their real-world use and adoption, improving function, and extending useful lifetime. It is also essential to understanding the effect of a material's long-term chemical and physical behavior. Heterogeneous interfaces and other defects in man-made materials and their variability and temporal evolution play a critical role in performance and limits to lifetime, whether in fuel cells, batteries, catalysts, nuclear reactor vessels, gas turbines, or other energy systems. Developing new approaches to understanding interfacial structure, its heterogeneity and disorder, chemical and long-range interactions, dynamics, and evolution under real-world conditions and time frames represents a Transformative Opportunity. The ability to couple the recent advances in modeling, communications, computation, and data science with advances in imaging, experimentation, and characterization approaches such as high-energy (synchrotron) x-rays, x-ray free electron lasers (XFELs), neutron sources, electron microscopy, and mass spectrometry (particularly under in situ and in operando conditions and at ultrafast timescales) makes this a richly compelling time to harness the opportunities arising from heterogeneity, interfaces, and disorder in multiphase energy materials under real-world conditions.

Direct experimental studies using synchrotron x-ray, XFEL, and neutron scattering and spectroscopy methods at DOE-BES user facilities represent a Transformative Opportunity to develop robust predictive models of these highly complex systems. For example, x-ray absorption spectroscopy and direct nanometer-scale imaging of the EDL have been achieved on timescales that

EVOLUTION OF SURFACE WETTING PROPERTIES OF SILICATE MINERALS DURING CO₂ STORAGE

Subsurface carbon storage, as well as oil and gas extraction, involves the flow of two- and three-phase fluids (e.g., salt-rich aqueous brine, oil, and supercritical CO₂) through the pore space of sedimentary rocks. Flow of multiphase fluids is highly dependent on the ways that different fluids “wet” mineral surfaces; hence, the properties of mineral-fluid interfaces are the key determinants of the system behavior.

Much of our knowledge of wetting properties and their effects on flow is based on non-reactive fluids such as oil, water, and air. The injection of CO₂ into the subsurface, however, results in the formation of carbonic acid from brine, and the acidified brine reacts with mineral surfaces. Consequently, although CO₂ is nominally a non-wetting phase in comparison with brine, changes in mineral surface chemistry can potentially change CO₂ into a wetting phase. Such a shift completely changes the models for trapping of CO₂ in subsurface pore space. In some cases, this change may enhance the storage properties of coarser-grained rock formations and make CO₂ easier to inject. In others, it may compromise the ability of fine-grained layers to block the rise of CO₂ back toward the surface. This phenomenon has only recently been experimentally demonstrated with specialized equipment designed to operate at realistic temperatures and pressures; however, knowledge of the specific modifications to the surface chemistry of minerals is still lacking.

Understanding the basic properties of rock formations in contact with reactive fluids is critical to ensuring safe long-term storage of CO₂ and will require new approaches to measuring the surface and near-surface properties of minerals and fluids under realistic conditions using synchrotron x-rays, combined with molecular models of the interactions. Figures 1 and 2 show examples of simulation and micromodel results, respectively.

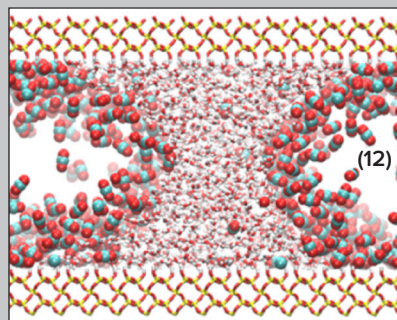


Figure 1. Molecular dynamics simulation of supercritical CO₂-brine mixture in the nanoscale planar region between two quartz surfaces, showing that CO₂ (red and teal molecules) adsorbs to the fluid-fluid interface and brine wets the mineral surface more effectively than CO₂. (Bagherzadeh et al., 2012)

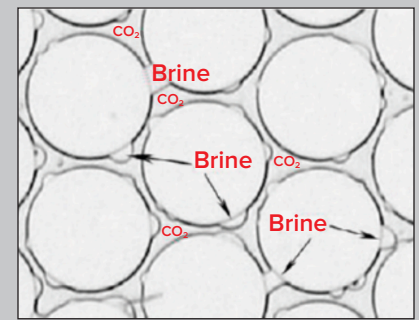
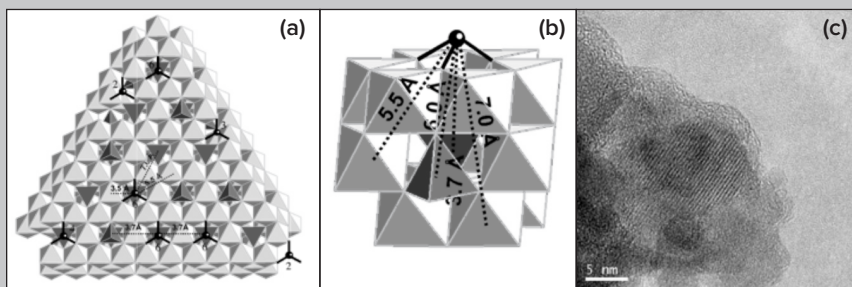


Figure 2. Micromodel image showing that after exposure to acidified brine generated during supercritical CO₂ invasion, silica surfaces are wetted by brine in preference to CO₂. (Kim et al., 2012)

HUMAN HEALTH CONSEQUENCES OF SOLID/AQUEOUS-SOLUTION INTERFACIAL PROCESSES

The exposure of more than 100,000,000 people in South and Southeast Asia to arsenic (As) in drinking water has resulted in arsenicosis and skin and organ cancers in several million inhabitants of this region. The arsenic occurs naturally in pyrite (FeS_2) and is released into surface waters as the As-pyrite undergoes chemical weathering in the Himalayas. A number of studies have suggested that released aqueous As(V) oxoanions adsorb on the surfaces of iron oxide micro- and nanoparticles (NPs), which are transported by the major rivers in this region to floodplains, where they are deposited in aquifer sediments. Bacteria are thought to play an important role in the release of As(V) from the NP surfaces by reducing the iron, which leads to dissolution of the NPs, release and reduction of As(V) to As(III), and ultimately the presence of toxic concentrations of As(III) in drinking water.

One possible solution is to remove arsenic from drinking water by using an appropriate sorbent. Magnetite (Fe_3O_4) and other iron oxide NPs as sorbents have been suggested, and filters composed of these NPs are now being used. However, the reason for the high sorptive capacity of magnetite NPs for As(III) was not known until a study using synchrotron-based x-ray absorption spectroscopy and high-resolution TEM was carried out. As shown in structural models ((a) and (b) in the figure) based on extended x-ray absorption fine structure (EXAFS) spectroscopy, arsenite (As(III)O_3^{3-}) oxoanions bind in a tridentate fashion to the trigonal cavities of magnetite (111) surfaces. Moreover, EXAFS showed that the (111) surfaces of magnetite NPs are simple terminations of the bulk structure without significant structural distortions, unlike poorly crystalline ferric hydroxides. However, these results did not explain the very high sorption capacity of magnetite NPs for AsO_3^{3-} oxoanions, which greatly exceeded complete saturation of the reactive surface sites. High-resolution TEM imaging and energy dispersive compositional analysis of AsO_3^{3-} -sorbed magnetite NPs showed an amorphous As(III)-Fe(II)-hydroxo phase on the surface of the NPs (see (c) in the figure), which helps explain the very high sorption capacity. In spite of this success and the very useful information on how AsO_3^{3-} oxoanions sorb on magnetite NPs, this study highlights the fact that the formation of amorphous nanoprecipitates cannot be predicted from first principles. Development of predictive models for sorption processes at solid-aqueous solution interfaces remains a major challenge for interface science.



Proposed structural model for tridentate As(III) on magnetite(111) surface. (a) Top view. (b) Side view. (c) TEM image reveals the existence of an additional amorphous coating. (Morin et al., 2009; Michel et al., 2010)

capture temporal fluctuations, such as ligand exchange. In biomolecular materials, the long-range interactions among bodies in aqueous solutions can lead to changes in morphology and composition and to heterogeneities, which play a critical role in the dynamics and function of natural biological systems such as viruses and membranes. Another key solution variable—ionic strength—can be very high in natural systems, such as the natural brines in subsurface systems where CO_2 is being stored, and in engineered systems, such as the solutions in high-level radioactive waste tanks at Hanford, Washington, where legacy waste from nuclear weapons production and civilian waste from nuclear power plants is currently being stored. For aqueous solutions with such high ionic strength values, we are currently limited in predicting thermodynamic activity coefficients because of the empirical nature of current models used to describe ion pairing and shielding. Another Transformative Opportunity is direct observation of the structures and lifetimes of cation-anion pairs in such solutions using x-ray scattering at the Linac Coherent Light Source (LCLS), coupled with molecular-level modeling. Such an approach could lead to a more fundamental model capable of more accurate predictions of activity coefficients and more robust models of high-ionic-strength solutions.

Heterogeneity, be it structural, compositional, spatial, or temporal, dominates real-world materials and gives them their functions and properties while determining their temporal evolution and degradation over their lifetime. For example, the interaction of both man-made and naturally occurring materials with natural waters and the atmosphere controls oxidation and corrosion at their surfaces, controls the composition of seawater and groundwater flowing past them, and plays a major role in the natural sequestration of CO_2 via incorporation into stable metal carbonates such as CaCO_3 and MgCO_3 . Sunlight, combined with the real-world environment, accelerates photolysis, thermolysis, and hydrolysis, resulting in degradation of most polymers. Dislocations confer formability and damage tolerance on metals.

Although the relevance of heterogeneity is well known, much of energy science has focused on singular, idealized materials as initial starting points for physical modeling and scientific understanding. While this approach has led to tremendous advances, it misses badly when the desired (or undesired) results arise from fluctuations, disorder, or heterogeneity. However, with recent advances in XFEL-based methods, such as x-ray photon correlation spectroscopy and scattering and ptychographic (or coherent diffractive) imaging with nanometer resolution, as well as new cryo-TEM methods, our understanding of interfacial behavior and the effects of structural, compositional, and temporal heterogeneities on the properties of natural and engineered solids has the potential to improve dramatically over the next decade, leading to robust predictive models of complex systems, including solid-liquid and solid-gas interfacial systems.

Degradation in both time and space is a clear example of a phenomenon where the mean behavior does not control the outcome. Instead, the negative outcomes arise from the members of the population that migrate to the extremes of the distribution, resulting in failures and black swan events, for example, the influence of unusually large grains and rare conformations of crystal orientation on metal fatigue. At the same time, systems can be developed that exhibit “antifragility,” that is, they benefit directly from disorder and demonstrate that the perfect material would be the least desirable. This whole field of heterogeneity and disorder at interfaces, across populations, and over real-world lifetimes is at the forefront of energy challenges that still await the development of the appropriate science.

FRONTIERS

Although advances in nanoscience and multiscale modeling and the start of the Materials Genome Initiative have accelerated synthesis of new energy materials and systems, bringing new materials into real-world use is a supreme challenge. Consider, for example, the Boeing 787, in which scaling the Li-ion battery from ounces to pounds led to the grounding of the whole fleet. As another

DEGRADATION SCIENCE: MESOSCALE EVOLUTION AND TEMPORAL ANALYTICS OF ENERGY MATERIALS

Energy materials degrade over long time frames owing to a multitude of distinct, complex, and interacting mechanisms. This degradation is critically impacted by both slow and rare events. The challenge of degradation science is to identify, model, and predict the mesoscopic evolution of structure or function in a material over the appropriate timescales while monitoring the dynamic processes that arise in the materials’ functional use and typically occur on daily timescales. It is essential to connect the mechanistic degradation pathways and their time evolution with the mesoscale science that would enable the identification of improved and longer-lived energy materials.

The major challenges facing the predictive capabilities of degradation science include linking physical and statistical models into networks of models on different spatial/temporal scales and using torrential real-time data streams. An informatics and data analytics environment such as Energy-CRADLE (Figure 1), based on cloud-based distributed computing and analytics, can support the entire data lifecycle from ingesting large volumes of real-world and lab-based data for analysis to temporal evolution modeling. For example, PMMA acrylic, or poly(methyl methacrylate), is used in PV energy system elements that reflect and concentrate light, such as back-surface mirrors and Fresnel lenses. Figure 2 shows a mesoscopic evolution model, including ultraviolet absorber (Tinuvin) bleaching, chain scission, and mechanical degradation. This mesoscopic model encompasses the three stages in this material’s temporal evolution to failure over a 25-year period. A change point is seen at 12 years for this PMMA formulation, when the concentration of Tinuvin reaches zero and mechanical degradation accelerates. This change in material degradation is the factor that defines the usable lifetime of this important energy material. The process of degradation of energy materials over time frames longer than 1 gigasecond (31.7 years) is a fundamental challenge of mesoscale science.

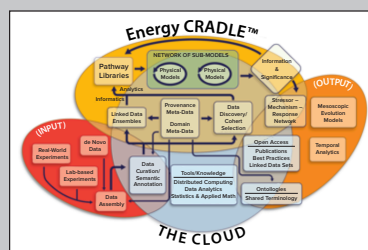


Figure 1. A schematic of the Energy-CRADLE™ infrastructure based on distributed cloud computing, data analytics, statistics, and applied math. (French et al., 2015)

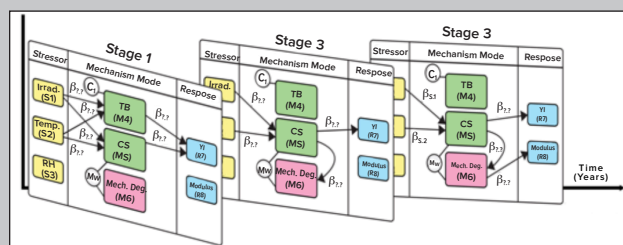


Figure 2. Mesoscopic evolution model of degradation pathways in stabilized PMMA acrylic spanning a 25-year lifetime, showing change points among multiple degradation mechanisms and modes. (French et al., 2015)

example, consider the importance of interfaces between dissimilar materials in the fabrication and functionality of spin transfer devices made with thin films, nanowires, and nanopillars.

We do not have the energy science in hand to enable new materials to be brought to scale in real-world uses, where materials behavior is dominated by interfaces and other spatio-temporal heterogeneities and their evolution. Such considerations are equally important for fracture, porosity, and the energy-efficient and environmentally safe extraction of unconventional hydrocarbons in natural materials such as tight shales, just as they are for understanding and controlling degradation in the current suite of man-made materials. This energy science of scale is one target we need to attack.

With advances in computation, communications, experimentation, scientific user facilities, lab-scale instrumentation, and analytics, it is now becoming tractable to approach these complex scientific problems without requiring simplifying assumptions. A new type of energy science can be developed to understand real materials under real-world conditions, including even the slow and statistically rare events that can dictate success or failure of materials. Instead of simply studying one sample as representative of a heterogeneous population, population-based epidemiological studies can be added to lab-based small-sample-number experiments, and thereby heterogeneity, variance, and fluctuations all become a natural part of the data, modeling, and science. This approach has similarities to the data and modeling challenges in medicine, sociology, and climate science. Both the scientific theories and models developed, and the datasets amassed, form the foundation for further studies and new and unexpected science. This new energy science can be based on open-source, open-data, open-access initiatives that combine to form the broader field of open energy science, in which progress is accelerated by the parallelization of studies to populations, of computation to distributed computing, and of science to open-source collaborative communities.

This new approach allows us to start studying the large numbers of new materials compositions and structures being developed by the Materials Genome Initiative, and not only to advance physical models and theories, but also to develop large bodies of open-linked data that serve as the initial crowd-sourced open-access foundation for both pilot studies and large cross-sectional and longitudinal studies in energy science. These open-science studies also integrate diverse teams and lead to the natural formation of new teams through the nature of crowd-sourced interactions, thus allowing us both to accelerate the yield of new information from energy science and to broaden the spectrum of topics that can be studied. This approach represents a new era in the human aspect of energy science.

Improvements in synchrotron x-ray sources (e.g., increased coherence from diffraction-limited storage rings), FELs such as LCLS and LCLS-II, the Spallation Neutron Source, and developments in cryo-TEM methods, in combination with advances in computing power, modeling, and theory, will lead to new approaches for characterizing interfaces and interfacial processes in both synthetic and natural materials under in situ and in operando conditions as a function of time and variables such as temperature, pressure, and stress. To fully exploit the power of these new sources, corresponding investments in detectors, optics, and sample environments are needed to maximize the in situ and in operando opportunities.

OUTLOOK

Heterogeneity and disorder are common to the entire spectrum of energy materials, both within structures and wherever interfaces occur. One example that matters to a large fraction of the aging population is the interface between implants and medical devices and the body. Whether one is joining a metallic bone implant to existing bone or designing a biocompatible (and perhaps biodegradable) power source, the interface is crucial to success. Interfaces are a central feature of heterogeneity in matter, which carries widespread societal impact through the new energy technologies they enable. Whether one is deliberately

increasing heterogeneity, such as by hydraulic fracturing of subsurface rocks for enhanced extraction of oil and natural gas or for CO₂ storage, or constraining heterogeneity to prevent, for example, the electrochemical degradation of batteries and structural materials, understanding and controlling heterogeneity will provide a broad range of benefits for humanity.

Advancements in the science of degradation, based on the development of new theory, simulation, probes, and mapping methods, have the potential to transform how the community approaches the challenges associated with the durability and lifetime of engineered and natural materials. Potential impacts extend from increased lifetimes for solar cells, nuclear power systems, hydraulically fractured systems, power conversion systems, airframes, and batteries to a host of new applications that matter to society.

4 chapter

Harnessing Coherence in Light and Matter

Coherence is an intrinsically quantum mechanical phenomenon that has direct macroscopic implications. Recent advances have greatly enhanced our ability to observe coherence in both light and matter. The Transformative Opportunity is the potential ability to realize full control of large-scale quantum-coherent systems; success has the potential to revolutionize fields as diverse as information processing, sensor technology, and energy generation through the control of the outcome of chemical reactions or the instantaneous state of a material.

OVERVIEW

In quantum mechanics, coherence reflects the fact that individual constituents have a well-defined phase relationship among themselves so that they are synchronized in time and over extended distances and can exhibit wave-like interference effects. Although quantum mechanical in nature, coherence can be observed macroscopically; superconductivity and lasers are well-known consequences of coherence of electrons and light, respectively, with demonstrable practical benefit.

In recent years, there has been enormous progress in recognizing, engineering, and exploiting quantum coherence in atomic, molecular, and materials systems. Surprisingly, our ability to exploit and control coherence in light and matter is far more robust than we initially realized. In appropriate circumstances, a created coherent state appears to be protected and is much less fragile than naive expectations might suggest. A further unanticipated advance is that a single ultrafast laser can manipulate the quantum wave function of multiple electrons to create near-perfect temporally coherent waveforms that have complex spatial, orbital, and spin structure, and that in many cases can persist for times more than 10 orders of magnitude longer than laser pulses. Moreover, by using light to manipulate atoms, molecules, and materials, we are learning how to probe and control quantum systems in increasingly sophisticated ways. Key questions at the frontiers of chemical physics and molecular dynamics are being asked, and answered, through complementary advances in electronic structure and excited state theory. These advances enable new understanding in fields as diverse as biological photosynthesis and quantum computing, as well as fuelling new measurement capabilities spanning the entire electromagnetic spectrum from teraHertz to the x-ray region.

Photosynthesis converts solar to chemical energy with the key steps of energy absorption and charge separation playing out via ultrafast electron transfer events. It is increasingly clear that coherence plays an important role in enabling the nearly quantum-efficient evolution of this process. Further exploiting the degree of electronic coherence holds promise for the development of new energy technologies.

We have gained an important new understanding of the role of symmetry in protecting coherence in materials systems with strong coupling between orbital and spin electronic degrees of freedom. These advances are leading to remarkable new opportunities for exploration and impact, including quantum information processing.

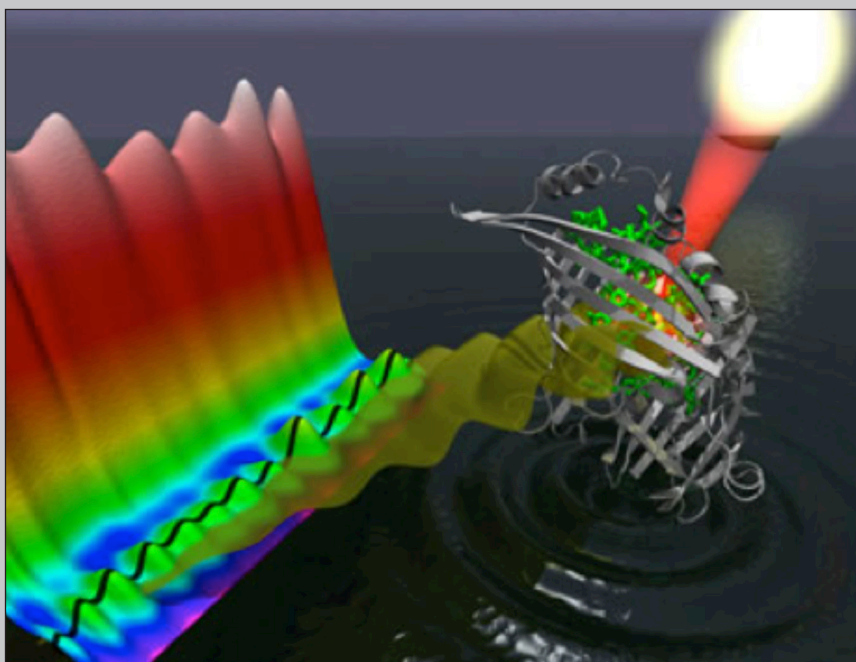
Sensors that exploit quantum coherence can be vastly more sensitive than classical ones, because the noise limiting the sensitivity of classical sensors is proportional to $1/\sqrt{N}$, where N is the number of particles detected, while the noise in a coherent quantum sensor is proportional to $1/N$, which falls much more quickly with N . This fundamental improvement has potentially transformative applications in areas such as medicine and nanotechnology.

Finally, new real-time quantum microscopes that can visualize and control quantum matter will be enabled by coherent light and electron beams to control the outcome of chemical reactions or the instantaneous state of a material. Novel bulk materials, metamaterials—artificial solids with characteristic length scales derived from photon energy rather than electron energy—and heterostructures can offer new ways to explore and exploit symmetry-protected coherent order, control charge- and spin-transport properties, or optimize the coupling of quantum-coherent materials systems to light, microwaves, phonons, and plasmons.

QUANTUM ELECTRONIC COHERENCE IN LIGHT HARVESTING

Light harvesting in photosynthetic systems occurs with nearly 100% quantum efficiency. A predictive understanding of the fundamental mechanisms responsible for this efficient conversion is challenging because of the complex electronic structure and energy transfer pathways. Long-lived quantum coherence has been observed in these systems. Coherent electronic oscillations in both donor and acceptor molecules generated by light-induced energy excitations interfere constructively, forming wavelike motions of energy that can explore multiple energy pathways simultaneously and reversibly (see Figure). The wavelike characteristic of the excitations can provide insights into the mechanisms enabling energy transfer to be so efficient. Further, evidence for quantum entanglement persists over extended time periods, even in noisy non-equilibrium systems at high temperatures.

Advanced spectroscopic methods using polarized laser pulses have revealed coherent states that decay on distinct timescales. Theoretical calculations show that these distinct timescales in photosynthesis II derive from weakly and moderately strongly coupled pigments in this system. The environment surrounding the pigments was also found to induce decoherence between excited states. Lessons being learned about the quantum aspects of light harvesting in natural systems can also be applied to the design of artificial photosynthetic systems, as well as in quantum information technologies.



Sunlight absorbed by bacteriochlorophyll (green) within the Fenna-Matthews-Olson (FMO) protein (gray) generates a wavelike motion of excitation energy whose quantum mechanical properties can be mapped through the use of 2D electronic spectroscopy. (Engel et al., 2007)

FRONTIERS

The development of quantum-coherent systems is an exciting frontier in which one can greatly suppress the decoherence effects of the environment by first understanding the relevant noise spectrum and then designing devices so that their coherence is not destroyed by it. For example, the coherence times of superconducting quantum bits, or qubits, have been increased by more than four orders of magnitude over the past several years. These advances are potentially valuable for their use in quantum information processing, in sensing and detection systems, and in enhancing capabilities for secure communication.

The ability to rapidly probe and switch the electronic and magnetic state of materials using new coherent light sources is revealing the dynamics and coupling of the lattice, charge, and spin degrees of freedom in materials. This knowledge is critical because a comprehensive quantum model of how spins, charge, photons, and phonons interact does not yet exist. Moreover, no theory can predict the properties of 3D nanostructured metamaterials that promise unique and tailored functionality as a result of quantum coherence.

In optical science, new ultrafast coherent x-ray free-electron lasers and tabletop high-harmonic generation (HHG) sources are fast enough to capture all dynamics relevant to function in matter (atoms, molecules, materials, and surfaces) on femtosecond or even attosecond timescales. These new light sources represent the first coherent beams in the x-ray region, making it possible to probe the building blocks of matter or life, as well as enabling powerful new microscopes with nanometer precision and femtosecond temporal resolution (Figure 4-1). Moreover, there are many surprising implications; for example, quantum coherence in the x-ray region is so extreme that zeptosecond waveforms are likely possible, as predicted theoretically. Such waveforms would enable precise studies of electron dynamics in processes such as photoexcitation and photoemission. However, despite these new capabilities, many questions still abound: we still do not

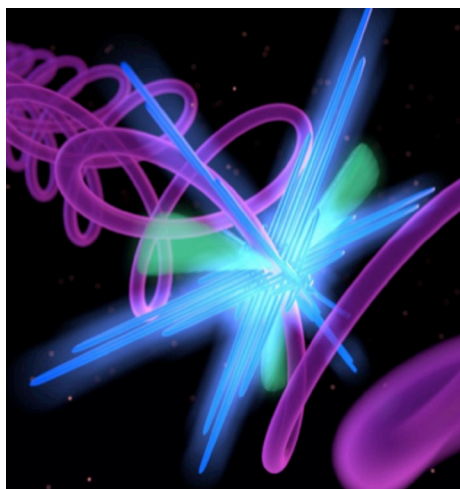


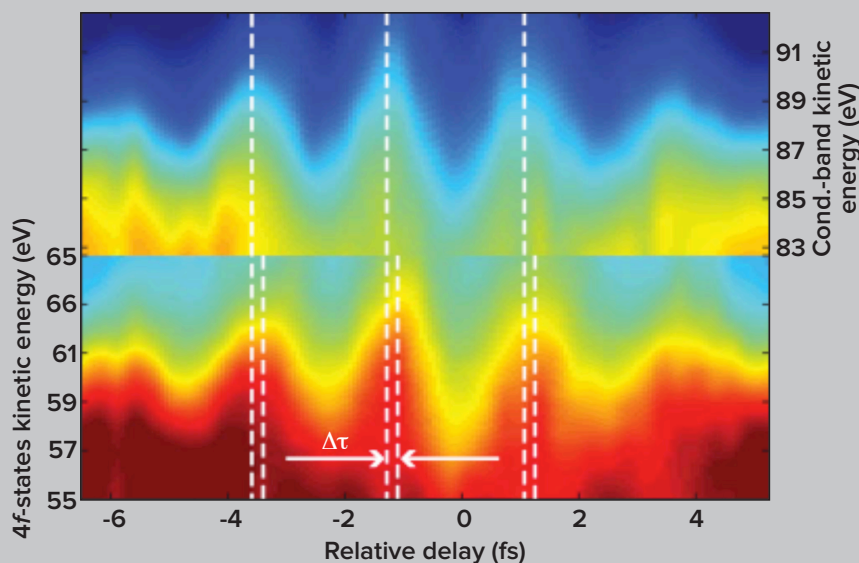
Figure 4-1. Coherent soft x-ray sources with control over the time, spectral, and polarization state. Circularly polarized coherent x-rays (blue) are driven by circularly polarized bichromatic lasers that form a cloverleaf pattern (purple). Electrons (green) are ionized three times per light cycle. Some are driven back to the parent ion, where they recombine and generate coherent x-rays.

understand which reaction channels are important for efficient catalytic function, how the nano- and mesoscale structure determines the properties of molecules and materials, or what factors determine the survival rate of a biological entity.

Importantly, the consequences and benefits of quantum coherence do not only play out in carefully engineered systems at low temperature. Nature seems to understand and use quantum mechanics. Advances in the spatial and temporal resolution with which we can observe energy flow have revealed the key role of quantum coherence, even under ambient conditions, in such systems. There is growing evidence that the efficiency of charge separation and light harvesting in photosynthetic systems results from coherence that exists between light-induced excitons and charge transfer states that are maintained by vibrational modes in the system. As such, the plant is acting as a quantum light conversion system. It is a frontier of the emerging field of quantum biology to understand and control other chemical processes in which quantum entanglement occurs in natural systems at room temperature. Further progress not only will provide deeper

ATTOSECOND SPECTROSCOPY IN CONDENSED MATTER

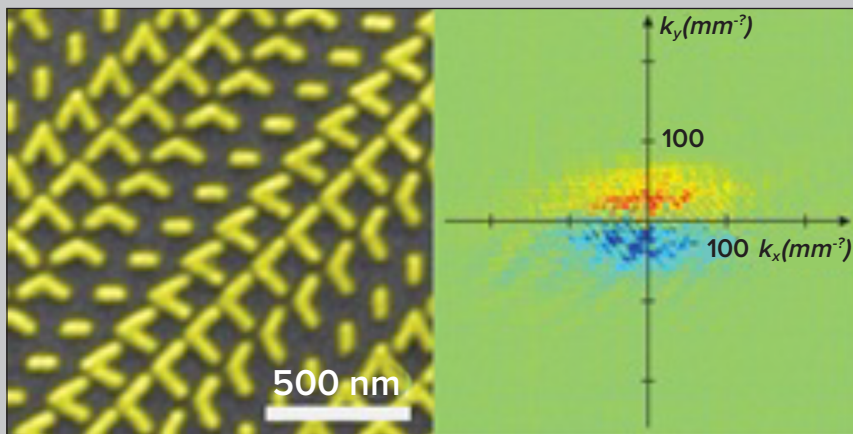
An understanding of the dynamic behavior of electrons in condensed-matter systems underpins the development of many modern technologies, such as semiconductor and molecular electronics, optoelectronics, information processing, and photovoltaics. However, it remains challenging to probe electronic processes, many of which take place in the attosecond regime. Recently, attosecond techniques previously used to study isolated atoms in the gas phase have been extended to observe electron motion in condensed-matter systems and on surfaces in real time. The ability to obtain direct time-domain access to charge dynamics with attosecond resolution has recently been demonstrated by probing photoelectron emission from single-crystal tungsten where the data reveal a delay of approximately 100 attoseconds between the emission of photoelectrons that originate from localized core states of the metal and those that are freed from delocalized conduction-band states (see Figure). These results illustrate that coherent attosecond spectroscopy constitutes a powerful tool for exploring not only gas-phase systems, but also fundamental electronic processes occurring on attosecond timescales in condensed matter systems and on surfaces. Future applications of attosecond spectroscopy center on the correlation effects in materials, exploiting unique and rich phenomena in correlated electron systems to investigate quantum multipath interference effects in the coherent attosecond response of these materials to an external electromagnetic perturbation.



The 4f and conduction band spectrograms from tungsten. A small shift in the relative delay is evident, as indicated by the white dashed lines through the fringes; the shift can be seen at each fringe maximum and minimum and corresponds to a time delay of 110 ± 70 attoseconds. (Cavaliere et al., 2007)

PUTTING LIGHT TO WORK AT THE QUANTUM SCALE

Combining quantum-based optics with artificial nanostructures has resulted in a breakthrough that could play a prominent role in the future of computing by using photon spin and orbital momentum energy transfer to encode quantum information. One possible route forward involves the use of metamaterials (artificial materials comprising precisely controlled assemblies of multiple structural elements that collectively have properties unachievable with conventional materials), in part, by incorporating structural elements that are smaller than the wavelength of the light they affect. Researchers have designed a metamaterial surface consisting of V-shaped, nanosized gold antennas engineered to generate an effect on the quantum particles of light (photons) making up the beam, somewhat akin to a spinning baseball passing through the air, thereby curving it to the left or to the right depending on the spin. The photonic spin Hall effect has been very weak and notoriously difficult to observe. In the metamaterial system, light passing through the antenna array exhibited this photonic spin Hall effect, boosting it enough to observe it using a simple camera (see Figure). The ability of metamaterials to tailor and control measurable changes in the quantum properties of light could be exploited for optical information processing and communication. Moreover, metamaterials with nanosized antennas have the potential to shrink such photonic devices to the nanometer range.



Left: Scanning electron microscope image of a silicon surface hosting a nanoscale array of V-shaped gold antennas (metasurface) with different lengths, orientations, and angles. Right: The antenna array forces linearly polarized light traveling through it into a curved trajectory, causing components with different circular polarization (red and blue) to move in opposite directions in a quantum-optical phenomena called the “photonic spin Hall effect.” (Yin et al., 2013)

insights into how biological systems work, it will provide clues for creating artificial biomimetic structures that exploit quantum coherence to enable performance that meets or exceeds that of their naturally occurring counterparts.

In quantum information science, one goal is to control many-particle systems at the quantum limit for quantum simulation and information applications. Recently, researchers have gained unprecedented control over spins in materials: single spins can be isolated, initialized, coherently manipulated, and read out using both electrical and optical techniques. Furthermore, advances have been made toward full control of the quantum states of single and coupled spins in semiconductor nanostructures, toward understanding the mechanisms through which spins lose coherence in these systems, and toward designing materials and nanostructures that are immune to the processes that lead to loss of coherence. We need to build upon this understanding by investigating pathways toward coupling many small systems together without compromising quantum coherence, which is critical for applications in quantum information processing.

Quantum networks provide opportunities and challenges such as quantum computation, communication, and metrology. The realization of quantum networks composed of many nodes and channels needs sustained investigations for generating and characterizing quantum coherence and entanglement. Researchers study, for example, quantum interconnects, which convert quantum states from one physical system to those of another in a reversible manner. Such quantum connectivity in networks can be achieved by the optical interactions of single photons and atoms, allowing the distribution of entanglement across the network and the teleportation of quantum states between nodes. There is, however, still much to be investigated. There have been advances at nanokelvin temperatures; ultra-cold quantum gases can be stored in optical lattices that consist of arrays of microscopic trapping potentials formed by laser light. Such large arrays of atoms provide opportunities for

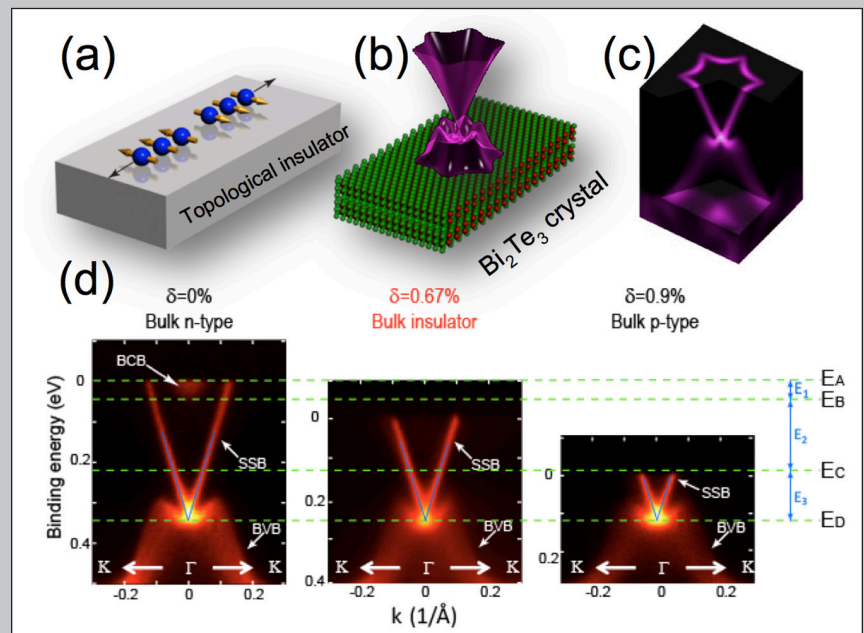
investigating quantum coherence and generating large-scale entanglement, ultimately leading to quantum information processing in these artificial crystal structures. These arrays can also function as versatile model systems to study strongly interacting many-body systems on a lattice.

The generation of attosecond pulses in the extreme ultraviolet (XUV) and soft x-ray spectral regions using HHG has ushered in a new frontier where the coherent motion of electrons can be explored, and perhaps controlled, at intrinsic timescales. Indeed, in recent experiments, attosecond pulses were used to follow the Auger decay of inner shell populations to the ground states of atoms, the time delay between the emission of photoelectrons from different atomic states, and the evolution of the wave function during molecular dissociation. In condensed matter, recent experiments have provided new insights into photoemission dynamics in metals, revealing a 100-attosecond delay between emission of electrons from localized core states and their delocalization in the conduction band.

All these studies have focused on the “two-body” problem where a single electron is promoted to an excited state, and the dynamics are captured by recording the kinetic energy of the recoil fragments. However, one of the most intriguing applications of attosecond spectroscopy centers on the correlation, or coherent, effects in materials, exploiting unique and rich phenomena in correlated electron systems to investigate quantum multipath interference effects in the attosecond response of these materials to an external electromagnetic perturbation. In these complex materials, the coherent superposition of several ionic core states may result in the hybridized mixing of energy bands where the electrons can be localized and itinerant at the same time. The electron orbital occupancy will then be of mixed character, perhaps enabling coherent manipulation through both coherent multistate excitation with x-ray pulses and exotic coherent lattice motions induced by picosecond terahertz transients.

TOPOLOGICAL INSULATORS

Topological insulators represent a new state of quantum matter. The bulk of these materials is insulating; however, the surface can conduct electric current with well-defined spin texture. In addition, the relativistic energy-momentum relationship of the surface electrons (forming an odd number of Dirac fermions) in these materials provides a great opportunity to study the physics of relativity in a condensed matter system where the velocity of massless particles is hundreds of times slower than the speed of light in vacuum. Investigations of Bi_2Te_3 by angle-resolved photoemission spectroscopy and electric transport (see Figure) revealed that Bi_2Te_3 is a 3D topological insulator with only a single Dirac fermion on the surface, making it the “hydrogen atom” of topological insulators. The single-surface Dirac fermion makes the topological effects most explicit and easiest to manipulate in Bi_2Te_3 . The large band gap observed (about seven times larger than room-temperature energy scale) with tunable carrier type and density makes it attractive for useful spintronic device applications that can operate at high temperature.



(a) Surface conduction of topological insulators: the electron spin is correlated with its direction of motion. (b) Lattice structure of Bi_2Te_3 and the predicted relativistic “Dirac cone”-like electronic structure formed by the surface electrons. (c) Electronic structure measured by angle-resolved photoemission, revealing the single Dirac cone surface state in Bi_2Te_3 . (d) Tuning of the carrier type by Sn doping in $(\text{Bi}_{1-x}\text{Sn}_x)_2\text{Te}_3$. (Chen et al., 2009)

In condensed matter and materials systems, there has been an explosion of activity identifying and investigating symmetry-protected coherence. For achieving nanoscale, room-temperature-coherent quantum systems, such as the symmetry-protected spin states of the nitrogen vacancy center in diamond or analogous structures in silicon carbide, the symmetries are point-group symmetry operations. These objects are already under intense investigation as extremely sensitive room-temperature field probes in settings as varied as local magnetism and biological systems. If the symmetry that is protected is an entanglement of spatial and spin degrees of freedom in bulk materials, then one has the potential of topologically protected coherence over long distances in bulk materials, perhaps leading to new forms of coherent electrical transport. Hitherto unsuspected topologically protected coherence exists in known materials such as cadmium-telluride/mercury-cadmium-telluride heterostructures. Density functional methods have been developed that enable possible topological properties to be calculated reliably, enabling systematic theoretical investigation of new materials. Following a general trend in materials physics, these symmetry-protected coherent systems are being incorporated into heterogeneous environments and hierarchical structures. The design and realization of topologically non-trivial materials with intrinsic strong electronic correlations is an intriguing possibility. It is recognized that strong correlations cause novel ground states, and because topological considerations constrain orbital and spin degrees of freedom, it is expected that new heretofore unknown states of matter may result in such materials. For example, theory predicts that by combining superconductors with nanowires with

strong spin-orbit coupling, networks with topological order can be made with remarkable quantum coherence properties.

OUTLOOK

Many opportunities present themselves that are exciting scientifically, while also having the potential to impact new technologies. The following are some compelling areas of inquiry: What are the spatial and temporal limits of quantum coherence? Can quantum coherence be realized in systems whose consequences play out over classical length scales? Would probing the boundary between the classical and quantum world yield far-reaching breakthroughs that can impact our society? The key to answering these questions involves probing coherence in increasingly complex systems, such as highly excited states, ordered mesoscale systems, or large photosynthetic systems.

By combining advanced nanostructure fabrication techniques with new theoretical understanding and new characterization tools, it will be possible to fabricate new materials with novel and useful chemical, mechanical, and electronic properties. Beyond static properties, we also need to control chemical and materials transformations by coherently manipulating charge, spin, and lattice dynamics—especially because we finally have the coherent light and imaging techniques to make this dream a reality. The ability to implement full control of large-scale quantum-coherent systems has the potential to advance the frontiers of chemistry and physics and to revolutionize technology in areas such as information processing, sensor technology, and energy generation/transformation.

5 chapter

Revolutionary Advances in Models, Mathematics, Algorithms, Data, and Computing

A convergence of theoretical, mathematical, computational, and experimental capabilities are poised to greatly accelerate our ability to find, predict, and control new materials and chemical processes; understand complex matter across a range of scales; and steer experiments toward illuminating deep scientific insights.

OVERVIEW

Over the past 10 years, researchers have developed powerful new theoretical frameworks to describe evermore complex mechanisms, profound algorithmic advances that reach across traditional mathematical boundaries to provide computer models of sophisticated phenomena and experiments, and groundbreaking techniques to process and understand data. Coupled to an explosion in computing, ranging from fast sensors and dedicated graphics processor units to high-performance supercomputers and massive resources for cloud computing, these advances offer unique opportunities to advance the science required to control matter and energy to meet the nation's energy needs.

Taken together, theory, computation, and experiment can help probe the structure, chemistry, behavior, and response of new and complex matter. Collectively, this data science can help us to extract information from experimental facilities, working at ever finer resolution; model phenomena across time and length scales spanning atomic to macroscopic; analyze electronic properties and disorder dynamics; understand the role of defects, fractures, and non-localities in making large structures from small ones; design new materials; and examine how the early stages of decay and failure are initiated.

As an example, imagine being able to steer through vast spaces of potential new materials, accelerating progress toward those with desired functionality. The time-honored “forward approach” manually synthesizes one material after another, trying to find one that exhibits the desired properties. However, it is hard to systematically tune a material into one with desired properties, and focusing on similar structures may well mean missing an unexpected configuration that is both radically different and highly preferred. Instead, it is tantalizing to imagine “inverse design,” which goes beyond the tiny fraction of materials that have been built

and considers almost unimaginable new configurations of matter, specifically tailored to meet crucial criteria, such as strong but lightweight, resistant to failure under extreme conditions, self-repairing, or capable of altering under changing conditions.

Designing matter in this fashion requires a range of scientific tools working in harmony. Theory is needed to bridge the gaps from small-scale atomistic structure to macroscale phenomena, and to model chemistry and physics across the mesoscale. New simulation algorithms are needed to go backwards from the desired result to a proposed material and will rely on mathematically capturing the desired characteristics so that optimization methods can efficiently converge on potential candidate materials. Dimensional reduction techniques and machine learning algorithms are crucial to reduce the vast space of possibilities to manageable target libraries. Advanced supercomputers are indispensable in order to quickly solve the resulting large systems to help predict the stability, performance, and lifetime of new possible materials. Advanced experiments, augmented through mathematical data analysis, are required to examine prototype materials, shine light on key structure and function, and suggest new materials.

New and innovative models, algorithms, experimental capabilities, and computing environments can provide data science tools that will, for example, reconstruct structure and properties from scientific experiments; predict the behavior of new materials from the nanoscale to the macroscale; direct the hunt for new materials and new chemistries in such areas as batteries, catalysts, solar cells, and gas separation; and optimize steps in the production of biofuels. The potential impact of applying these algorithmic technologies would be enormous and transformative.

FRONTIERS

Tremendous breakthroughs are occurring in theory, algorithms, simulations, experiments, data analysis, and computational resources. These approaches are closely linked (Figure 5-1). More and more, they are merging together, integrating our understanding of energy systems.

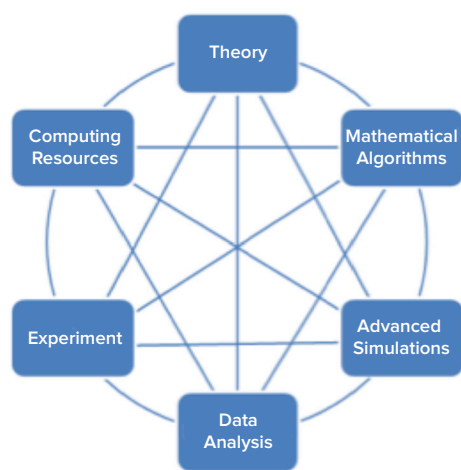


Figure 5-1. Revolutionary breakthroughs are enabled by the tight coupling among complementary data science approaches.

Theory

The fundamental theory of materials and chemistry interacts with advanced computation in several ways. Simplified models, solvable with pencil and paper or laptop-level computation, can suggest possible new phenomena whose existence in real materials is then analyzed with more powerful methods.

In the last decade, one dramatic example was the discovery of a new state of electronic materials based on spin-orbit coupling, the topological insulator. It was proposed theoretically, but its discovery in real materials was aided by computations using density-functional theory (DFT). Perhaps the main interaction of theory with computation in electronic materials, however, is in understanding how the intractable quantum mechanics of a large number of electrons can be approximated in a way that makes the problem computationally accessible without sacrificing accuracy.

DFT is the most widely used approximate treatment of electronic properties of materials because of its success in describing broad classes of molecules and materials, including many technologically important semiconductors. Its underlying theory is largely understood, but there have been significant advances in recent years in its computational implementation. Advances in ultrafast characterization methods have necessitated enhanced methodologies for calculating molecular excited states and the dynamics of reaction intermediaries. Similarly, the frontiers of theoretical quantum chemistry are being extended beyond DFT and the associated approximations that limit our predictive understanding. Recent theoretical work has constructed new approaches that go beyond DFT and other existing methods by helping researchers understand how to incorporate some of the strong electronic correlations that are neglected in the approximations underlying DFT. These approaches, two of which go under the arcane names of “density-matrix renormalization group” and “dynamical mean-field theory,” offer the potential to describe some of the most pressing quantum materials problems of our era, such as high-temperature superconductivity and complex magnetism. Relative to DFT, they are in their infancy, and an important challenge over the next decade will be to develop algorithmic standards and improvements for them as has been done for DFT.

Although the structural properties of materials are less quantum-mechanical than electronic properties, they lead to equally challenging problems in computational physics and geometry. One example is the problem of dynamics in liquids near the glass transition; even simpler versions of this problem, such as questions about static “jammed” arrangements of spheres, tetrahedra, or other units, rapidly become complicated. Finally, the division of materials theory into structural and electronic aspects in this subsection reflects a famous approximation (the Born-Oppenheimer approximation) whose validity for chemical dynamics is questionable. However, experimental advances such as free-electron lasers in the x-ray regime require accurate

computational methods for materials and chemical processes covering both fast electronic timescales and slow structural time scales.

Mathematics, Algorithms, and Simulations

More and more, traditional boundaries between various branches of mathematics are breaking down, producing powerful new capabilities. Accurate methods to solve individual components at particular time and space scales are being coupled together through multiscale modeling, and the evolution of those components is being tracked using methods from uncertainty quantification.

These algorithmic advances are leading to sophisticated computation that can help model non-equilibrium or excited states, simulate the performance of matter under realistic conditions, enable tools that guide the synthesis of new materials that exhibit target properties (such as matter with specified band gaps), model subsurface transport in complex geological systems, and predict and reduce risks associated with developing energy sources, including combustion, fracking, and seismic drilling.

New algorithms for computing electronic structure properties are building on previously unexploited mathematical tools to solve the equations of DFT. As an example, instead of finding the eigenvalues and eigenfunctions as originally required by DFT, the Pole Expansion and Selected Inversion (PEXSI) method evaluates the most important physical quantities such as the electron density, energy, and atomic force directly by computing select elements of a series of inverses of shifted Hamiltonian matrices (i.e., Green’s functions). The resulting methodologies are now being applied to systems that are orders of magnitude larger than those tackled by previous approaches.

Transforming Experimental and Simulation Data into Information

Ever more powerful experimental facilities and more and more elaborate simulations are creating vast amounts of data—far more than ever before. A tremendous body of computational tools is being developed

to handle this “big data” and to use the results to predict and steer both theory and experiments.

Simulation Data

The amount of data generated by advanced computational modeling is rapidly growing as simulations include the effects of more and more complex physics and chemistry. Examples include complex reactive simulations that track the evolution of a large number of species in a highly resolved turbulent combustion calculation, and sophisticated molecular dynamics simulations. At the same time, computation is being used more and more to explore the space of design possibilities as in, for example, large database libraries of materials generated through combinatoric approaches.

These datasets are far too massive to be analyzed through manual inspection, and high-throughput mathematical and statistical tools for automated analysis play an increasingly important role. These tools can analyze data, sometimes as they are being produced, to both steer ongoing simulations and suggest new ones. By designing mathematical similarity metrics based on exploiting information about the underlying physics, chemistry, and material properties, one might be able to use aspects of statistical, probabilistic, and machine learning methods to sift through large datasets looking for new patterns.

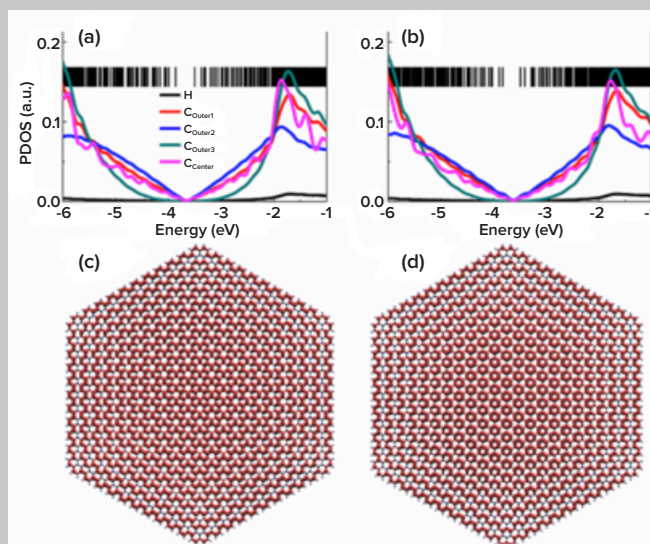
For example, imagine using combinatoric approaches to generate a library of possible chemical structures from smaller building blocks, producing a tremendous number of possible configurations. Given certain desirable properties, how can one quickly sift through this library? How can one “triage” the set of possibilities into those that warrant further analysis, those that clearly miss the target, and those in between? Evolving mathematical techniques that try to find and isolate potential materials with given target properties take advantage of new combinatoric approaches, statistical methods, machine learning, and optimization methods to sift through large databases, finding links and patterns between structure and performance.

ACCELERATING ELECTRONIC STRUCTURE CALCULATIONS FOR LARGE-SCALE MATERIAL SYSTEMS

Ab initio, or first principle, electronic structure theories, particularly those represented by Kohn-Sham density functional theory (KS-DFT), have been developed into workhorse tools with a wide range of scientific applications in, for example, chemistry, physics, materials science, and biology. The KS-DFT finds the ground state energy of a many-bodied Schrödinger equation exactly, by transforming it into a system of non-interacting electrons with an effective potential.

Although the KS-DFT makes the computation of electronic structure feasible for many quantum systems of interest, it is still computationally demanding in practice, especially for systems at the nanoscale or larger. Recent mathematical breakthroughs offer the opportunity to greatly extend the applicability and versatility of these approaches. The Pole Expansion and Selected Inversion (PEXSI) method relies (Lin et al., 2009) on a fundamental recasting of both the mathematical problem and the numerical algorithms required; it successfully reduces the computational cost of DFT calculation for generic systems, including difficult systems with a small or even zero gap between occupied and unoccupied molecular orbitals. Rather than computing the eigenvalues and eigenfunctions as originally required by KS-DFT, the PEXSI method evaluates the most important physical quantities such as the electron density, the energy, and the atomic force directly through the computation of selected elements of a series of inverses of shifted Hamiltonian matrices (i.e., Green’s functions).

This new approach, now part of Spanish Initiative for Electronic Simulations with Thousands of Atoms (SIESTA) and currently being integrated into CP2K (an open-source molecular dynamics package), regularly handles systems with 10,000 to 100,000 electrons and achieves scalability on more than 10,000 processors (see Figure).



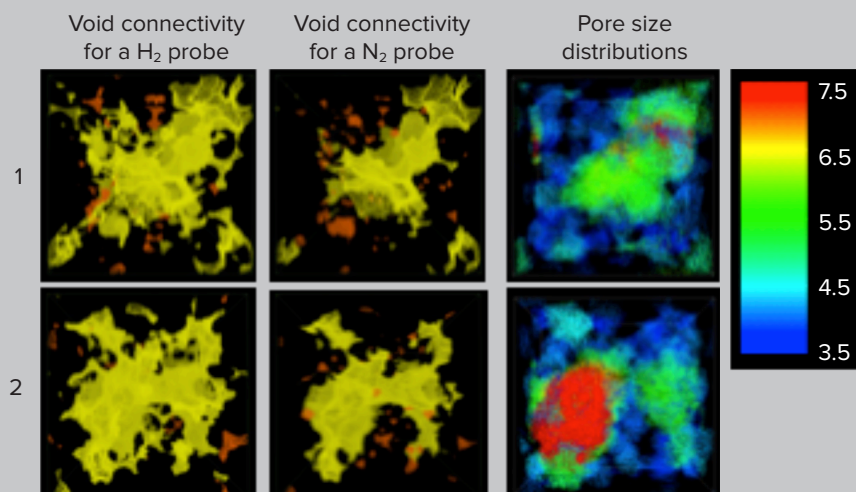
The PEXSI method as implemented in the SIESTA software package enables the investigation of the electronic structure of large-scale graphene nanoflakes using accurate ab initio methods at unprecedented sizes (up to 11,700 atoms). (a), (b) Projected density of states of two large graphene nanoflakes with armchair edges but with slightly different numbers of electrons. (c), (d) Illustrate opposite behavior of localized density of states near the highest occupied molecular orbital energy. (Hu et al., 2014)

HIGH-THROUGHPUT CHARACTERIZATION OF POROSITY IN POROUS MATERIALS

Over the last two decades, there has been a surge of interest in the design and application of new classes of advanced porous materials: MOFs, COFs, PPNs, POCs, and related families of materials. Owing to the organic nature of the components used to assemble these materials, they offer potentially limitless control over their pore geometry, size, and chemical functionality. Furthermore, these advanced porous materials hold great promise for application in many energy-related technologies, most prominently in chemical separations and catalysis. Computational approaches involving either electronic structure or molecular simulations methodology, or both, are used to make a priori predictions of the properties of materials or to seek an explanation for experimental observations through modeling. One of the challenges is characterizing porosity in these materials in order to understand structure-property relationships, to perform material similarity comparisons, or to investigate pore space dynamics upon stimuli (e.g., loading of guest species).

Recent developments in algorithms for high-throughput porosity analysis have enabled many of these tasks (see Figure). The core of these approaches is a computational geometry technique, the Voronoi decomposition. Analysis can provide parameters such as the diameters of the largest nodes and edges included and of free spheres, as well as detailed information about void space geometry and topology. For example, void space regions inaccessible to a given probe can be identified, and this information can be utilized in the calculation of accessible surface area, accessible volume, and pore size distributions.

The algorithms outlined above have been implemented in the Zeo++ package, which has been released as an open-source package. Zeo++ offers controllable sub-0.1-Å accuracy and the capability of handling a hundred thousand systems of tens of thousands of atoms each on a modern workstation.



Analysis of dynamic changes to porosity in an amorphous porous organic cage material. The two rows correspond to two selected snapshots of a molecular simulation of the system. The left and center columns present void space inside the material accessible to H₂ and N₂ molecules, color-coded for accessibility (yellow corresponds to channel systems, orange corresponds to inaccessible void spaces). The right column presents a visualization of pore size distribution (color-coded for pore diameter). The corresponding calculations are performed within Zeo++ software. (Zhang et al., 2013).

One such set of tools has recently been developed in the context of the design and application of new classes of advanced porous materials: metal-organic frameworks (MOFs), covalent organic frameworks (COFs), porous polymeric networks (PPNs), porous organic cages (POCs), and related families of materials.

Experimental Data

Experimentation is an integral part of scientific investigation, and BES facilities such as synchrotron radiation light source facilities, neutron scattering facilities, and nanoscience centers generate vast amounts of data. For example, beam science is undergoing a rapid change as facilities probe matter at higher and higher physical resolutions and rapid timescales. These experiments generate massive amounts of data; in the future, they may generate multiple terabytes of data per sample run. The data are often statistical in nature and replete with noise, poor contrast, and signal dropout.

Fundamental statistics, mathematical, algorithmic, and computational methods are needed to extract information from murky data, interpret experimental results, and provide on-demand analysis as information is being generated. In order to make sense of this information, new algorithms that fuse different branches of mathematics are at work. For example, algorithms may combine dimensional reduction, graph techniques, and computational harmonic analysis to perform robust reconstructions from scattering data, and partial differential equation methods coupled to machine learning to analyze experimental image data.

At the same time, the landscape of experimental facilities is rapidly changing. In some situations, quick and rough results are desirable while an experiment is underway. In other situations, considerable computation time can be dedicated to provide the most accurate reconstruction and analysis possible.

The desire for immediate results from algorithms embedded close to detectors spawns different mathematical questions

from those involved in post-processing aided by high-speed networks and extreme scale computing:

- ▶ One end of the spectrum aims at “on-demand” computational tools for analysis, data reduction, and feature extraction next to facilities, using embedded advanced algorithms and special-purpose hardware. Here, questions that arise include: What is the minimum/fastest computational model/algorithm that gives (at least some) useful information? Can one quickly determine whether data are useful, not useful, or in between? By taking advantage of powerful increases in core hybrid central processing units (CPUs) and general-purpose computing on graphics processing units (GPGPUs), can one quickly perform an analysis in order to steer ongoing experiments to more optimal configurations or output?
- ▶ The other end of the spectrum aims at post-processing using reconstruction, inter-comparison, simulation, and visualization using high-performance and extreme-scale computing. Here different questions arise, including: What is the maximum amount of information that can be measured, processed, organized, and displayed to help understand and shed light on further experiments? Can data be transformed to initialize computational models, with output framed to complement the experiment?

Fast algorithms embedded in hardware, special-purpose processors/graphics cards, multicore/many-core machines, and extreme-scale supercomputers are all part of meeting these user needs.

An Explosion of Advanced Computing Resources

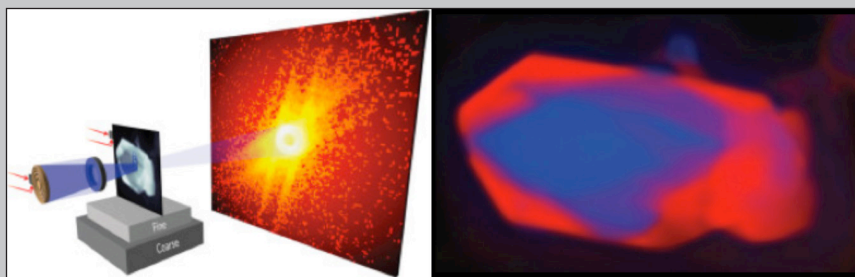
The rapid explosion in computational resources has vastly changed the landscape of scientific discovery. The most complex and resolved simulations will require harnessing hundreds of thousands (or millions) of computational processor units, and some of this computation will only be possible on the most advanced architectures offered by extreme-scale computers. Taking advantage of

PTYCHOGRAPHIC RECONSTRUCTION: PROBING MATTER AT HIGH RESOLUTION

The ability to correlate the atomic and nanoscale structure of matter with physical properties (e.g., mechanical, electrical, catalytic, and optical) and functionality forms the core of many disciplines. Until recently, however, a 3D microscope capable of diffraction-limited resolution, large field of view, and spectroscopic contrast was well beyond reach, while the need for such a microscope has become ever more urgent. High-resolution macroscale imaging enabled by diffractive imaging/ptychographic techniques will help scientists to understand evermore complex nanomaterials and self-assembled devices, or to study different length scales in the same material, when observing that the whole picture is as important as recovering the local atomic arrangement of the components (see Figure).

Ptychography enables one to build up very large images at wavelength resolution (i.e., potentially atomic) by combining the large field of view of a high-precision scanning microscope system with the resolution enabled by diffraction measurements. In ptychography, each recorded diffraction pattern contains short spatial Fourier frequency information about features that are smaller than the x-ray (or electron) beam size, enabling higher resolution. To reconstruct an image of the object, one needs to retrieve the phase, which is made even more challenging in the presence of noise, experimental uncertainties, and perturbations of the experimental geometry. The phase retrieval problem is made tractable by recording multiple diffraction patterns from the same region of the object in small increments.

Every scanning microscope can now add a parallel detector, and every diffraction instrument can add a scanning stage, quickly turning high throughput “imaging by diffraction” techniques into the sharpest images ever produced. To sustain high-throughput processing, the Scalable Heterogeneous Adaptive Robust Ptychography (SHARP) software package was optimized for the hierarchical memory bandwidth of distributed graphics processing unit/central processing unit (GPU/CPU) architectures, which is in production at four microscopes at Lawrence Berkeley National Laboratory’s Advanced Light Source and under deployment, for example, at the SLAC National Accelerator Laboratory and Brookhaven National Laboratory.



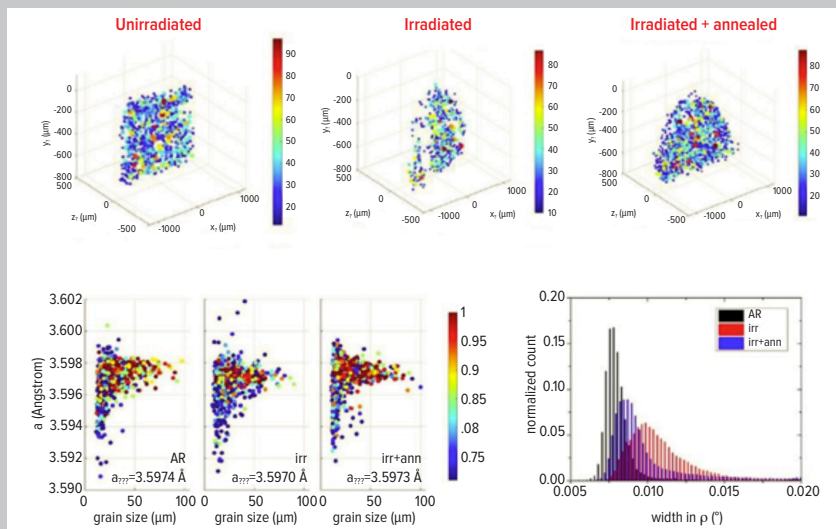
Left: A lens focuses a coherent soft x-ray beam onto the sample, which is scanned in small increments to ensure overlap of the probed areas. Right: Chemical composition of lithium iron phosphate nanocrystals after partial delithiation, mapped using ptychography. The delithiated region is shown in red. (Shapiro et al., 2014)

MULTISCALE IMAGING OF NUCLEAR MATERIALS WITH HIGH-THROUGHPUT COMPUTING

High-energy synchrotron x-rays allow scientists to peer deeply inside of materials and to non-destructively study their microstructures with high spatio-temporal resolution using either scattering or imaging. An emerging trend is to combine these modalities to provide even richer microstructural detail. The figure demonstrates the use of such a combined technique, high-energy x-ray diffraction microscopy (HEDM), to study materials evolution due to neutron irradiation and post-irradiation annealing. This imaging method provides information well beyond that provided by traditional grain-averaged diffraction measurements, thereby allowing strains, orientations, and positions of thousands of grains to be mapped simultaneously in polycrystalline materials.

HEDM datasets are collected with a high-energy (40–120 keV) x-ray beam and a large area detector (~ 4 megapixels) triggered during sample rotation similar to traditional tomography, such that each raw dataset is several gigabytes. Diffraction spots recorded in these datasets are indexed to each grain illuminated in the polycrystalline aggregate, with typically ~ 30 spots recorded per grain and thousands of grains indexed. This image reconstruction presents both a big data and big computation problem.

Real-time analysis of such complex x-ray data streams is another emerging trend with two major benefits. First, real-time feedback can allow calibration or configuration issues at the beamline to be caught during an experiment, providing increasingly robust data and enhancing the productivity of valuable beam time. Second, it promises real-time control of in situ experiments on dynamic phenomena such as additive manufacturing, electrochemical cycling, and thermomechanical deformation, allowing the user to rapidly identify key processes controlling material behavior and focus on these “hot spots” during the course of an experiment.



HEDM results from an advanced steel which is being developed for improved radiation resistance in advanced nuclear energy systems, before and after neutron irradiation to 3 displacements per atom (dpa)/500°C and post-irradiation annealing for 1 h/600°C. Spatial distribution of grains (top row; color indicates grain size), grain-specific lattice constants as a function of grain size (bottom row; color indicates completeness in data analysis), and peak width distribution for select reflections. Each dataset comprises $\sim 1,000$ grains and enables correlated and statistically representative microstructural analysis. (Park et al., 2015)

these machines may require rethinking algorithms in light of the changing balance between fast processors and inter-processor communication costs. Other calculations will be performed by cloud computing resources. Tantalizing new possibilities are being examined, including quantum computing, which makes use of quantum physics to execute operations.

At the other extreme, fast dedicated hardware, including GPGPUs, embedded close to acquisition devices such as detectors, will offer an unprecedented chance to interpret results as they are generated, steer experiments as they happen, and provide users with access to the most advanced user facilities as they run more and more optimized experiments. All of this will be accessed through a myriad of devices: sensors providing constant feedback, smartphones directing experiments and downloading processed data, and remote browsers accessing advanced computational capabilities and vast databases.

This almost seamless ubiquity of computing—ranging from handheld smartphones that can quickly relay sensor data, to fast charge-coupled devices (CCDs) acting as detectors for experiments, to fast dedicated graphics cards transformed into computational devices, to the largest-scale supercomputers—is transforming what we can now model, simulate, and detect.

OUTLOOK

Combining new models, algorithms, and advanced computing platforms will lead to new technologies. For simulation, this combination will suggest and examine candidate materials with hand-picked properties, help us understand the structure of matter, and predict the mechanics and behavior of complex chemical, geochemical, and biochemical systems. For data, it will provide critically needed tools to extract information from murky data, interpret experimental results, and provide on-demand analysis as data are generated, helping suggest and steer new experiments for discovery science. As these technologies continue to merge, they will help integrate our understanding of complex energy systems.

6 chapter

Exploiting Transformative Advances in Imaging Capabilities across Multiple Scales

Making and exploiting advances in imaging capabilities emerge as priorities because of their transformative impacts on discovery science. These impacts include accelerating the discovery of new materials and new functionalities, the understanding of combustion and other chemical processes, and progress in materials synthesis, as well as solving long-standing challenges in the relationship between the structure of inhomogeneous matter and its behavior.

OVERVIEW

The challenge inherent in probing and mapping matter across multiple scales is to find ways to reconstruct raw data into usable images, to analyze the results, to integrate data from multiple sources, and to extend the techniques to regimes that address the manifold scientific puzzles that confront us in order to advance our ability to understand and ultimately control materials and complex chemical phenomena. Our current knowledge is dominated by both vastly enhanced capability in all three spatial dimensions—alleged with improvements in time-evolution and spatially resolved spectroscopies—and the development of substantially faster probes. These advances are largely a consequence of the investment in new and improved facilities, most notably synchrotron x-ray sources, free electron lasers, electron microscopes, and neutron sources; but laboratory-scale microscopies such as scanning tunneling microscopy (STM) and atom probe microscopy, along with multimodal techniques such as Raman spectroscopy with atomic force microscopy (AFM), have also advanced imaging. Figure 6-1 provides one representative example of multimodal measurement for enhanced physical and chemical understanding.

We are now able to map variations in chemical composition, crystal orientation, structural phases, magnetic and electric domains, sprays, flames, cracks, and voids over a very wide range of length scales, from centimeters down to tenths of nanometers. Critically, we can also track the evolution of these features as a function of time and subject them to a wide variety of applied fields and operating environments (e.g., stress, magnetic, electrical, and temperature). Inner-shell atomic spectra and their fine structure may be obtained from sub-nanometer-sized regions or even individual atoms using energy-loss spectroscopy, leading to atomic-level information about chemical bonding.

In spite of this vast recent progress, challenges remain to advance, among other frontiers, attosecond methods to probe fast reactions at their intrinsic scales; methods for reconstruction of multidimensional, time-resolved images from raw data (a non-trivial problem for 3D and 4D datasets); computational sciences for data analysis (e.g., data analytics); and the integration of methods both for seamlessly computing maps of matter in user-accessible form and for combining different types of fields with different mapping methods. As the popular phrase goes, “new eyes give rise to new ideas.”

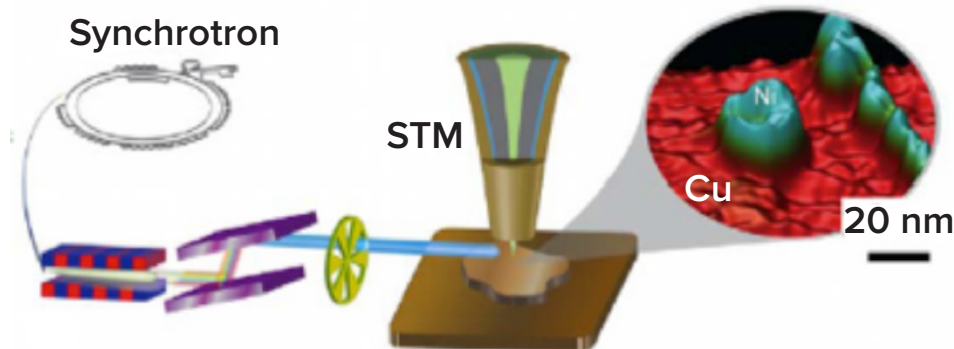
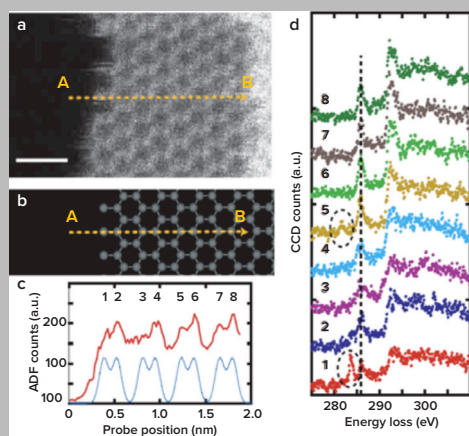


Figure 6-1. Characterization methods that combine scanning tunneling microscopy and x-ray measurements provide insight into physical topography and chemical environment of a substrate. (Shirato et al., 2014)

USING ELECTRON SCATTERING TO UNDERSTAND THE DYNAMICS OF MATERIALS AT THE ATOMIC SCALE

Dramatic advances in electron sources and sample handling environments are enabling atomic-resolution imaging, diffraction, and spectroscopy of the dynamics of materials processes over temporal ranges from femtoseconds to extended periods. Significant improvements in electron optics have revolutionized the field of electron microscopy, with aberration correction yielding spatial resolution better than 0.1 nm, and electron monochromators giving sub-10-meV energy resolution. Lasers to stimulate electron emission have enabled the development of dynamic transmission microscopy, which has, for example, enabled fast-phase transformations to be imaged. Significant opportunities exist for enhanced temporal resolution, both to understand fundamental phenomena and to observe energy-related nanomaterials under working conditions.

The ultimate spatial limits of imaging have been largely reached with the latest electron scattering instruments. However, these capabilities are generally limited to materials that are imaged in high-vacuum environments, at room temperature, and with an image acquisition time of seconds. In operando experimentation on the changes that occur in the interfaces in a working battery, a heterogeneous catalyst, or a deforming material, requires nanoscale information over the relevant lifetimes of these working systems. With further development of ultrafast electron sources and advances in stimulating samples during experimentation, it becomes possible to push from the present state of the art—atomic-resolution images and spectra obtained from materials under mostly static conditions (see Figure)—to real-time understanding of atomic-scale phenomena over timescales that span from a few femtoseconds to days or even longer. Such advances can be expected to revolutionize our understanding of emergent quantum phenomena (e.g., high-temperature superconductivity) and to enhance our ability to create improved systems for energy capture, conversion, and storage.



Atom-by-atom spectroscopy in graphene. (a) Annular dark-field (ADF) image of graphene edge. The dotted arrow indicates where the spectrum-line was made (A to B). Scale bar, 0.5 nm. (b) An atomic model of the investigated edge. (c) Line-profile of the ADF counts (in red) recorded simultaneously with the spectrum-line. For comparison with the simulated ADF counts (blue), the number of each atom is indicated (from 1 to 8). (d) The carbon K-edge energy-loss near-edge structure obtained from each atom. The single-coordinated carbon atom (numbered 1) clearly shows peak S. (Suenaga and Koshino, 2010)

Experience teaches us that improvements enable improved understanding of phenomena and, ultimately, new science. Recent reviews of accelerator physics and aberration-corrected electron microscopy, in particular, combined with the current state of the major facilities, point unambiguously to exciting new capabilities either planned or being actively discussed. For example, diffraction-limit upgrades to several of the nation's synchrotron light sources will lead to smaller, more intense and more coherent x-ray beams, which will extend into the hard x-ray range. New understanding of scattering under conditions of high energy, high coherence, and timing control indicates that it is possible to probe at the attosecond timescale. Atomic-resolution mapping of surfaces, for example, with STM combined with other tools such as synchrotron x-rays, is revealing many new insights about mass transport, magnetic state, etc. From the perspective of needs, that is, technology pull, initiatives such as the Materials Genome Initiative motivate the need for more complete characterization methods for matter, especially during synthesis and assembly in order to shorten the time required for introduction of new materials. Whether the application is data storage, aircraft turbine blade design, advanced catalysts, combustion science, drug delivery, computers, structural materials, or medical implants, 4D maps of matter (in three spatial dimensions plus the fourth dimension of time) are essential to quantitative prediction of materials properties and behavior. The timeliness of seizing the opportunity to advance imaging methods and, most especially, to integrate different modalities is beyond question.

FRONTIERS

Attosecond measurements

Recent advances in ultrafast laser and x-ray sources now make it possible to produce bursts of light spanning all timescales relevant to function down to the femtosecond, and even attosecond, regimes. The LCLS, for example, has provided atomic-resolution imaging and simultaneous chemical spectroscopy of the reactions involved in photosynthesis on a sub-picosecond timescale, allowing the oxidation state of species identified in

the image to be tracked in time. Similarly, it is now possible to probe the magnetic and electrical response of materials subject to ultra-short (and intense) pulses of light. Tabletop high harmonic generation (HHG) sources have already produced femtosecond and attosecond pulses in the extreme ultraviolet (XUV), and more recently in the soft x-ray region, while several designs have been published for lab-scale compact light sources and free electron lasers. Owing to their ability to probe dynamics at multiple sites simultaneously, HHG sources have been used to uncover the fundamental mechanisms governing how materials change their magnetic or electronic states on a timescale of a few femtoseconds. With further improvements in the coherence and brightness of x-ray sources, there is the prospect of being able to make a movie that captures a functioning nanoscale, chemical, or biological system in 3D.

High-resolution and multiscale mapping with chemical information

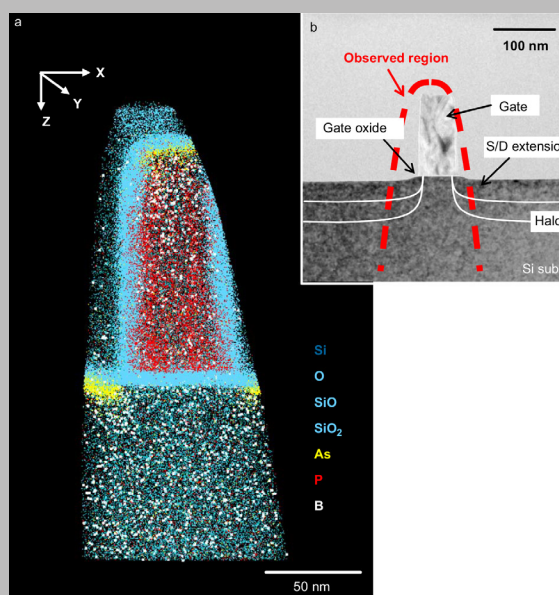
Energy loss spectroscopy, in combination with atomic-resolution imaging, has become an essential feature of electron microscopy to map composition at the atomic level using the sub-angstrom-diameter coherent beam of the scanning transmission electron microscope. Similarly, it is possible to map compositional variations in organic, inorganic, and hard materials at the nanoscale, using x-ray zone plate imaging tuned to various absorption edges. In addition, it is possible to create 3D maps of both chemical composition and structural phase at the meso- and macro-scale, through advances in neutron sources and detectors. Overcoming the challenge of 3D imaging with chemical specificity at atomic resolution for non-periodic structures, using either electron or x-ray beams, is now close at hand. Atom probe tomography provides a partial answer to this need in hard materials, and tunneling microscopy has an impressive number of variants for probing surfaces of all kinds. This field benefits greatly from related developments in computed tomography and cryo-electron microscopy, where 3D reconstruction algorithms have matured.

3D ATOM MAPPING FOR FUNCTIONALITY AND UNDERSTANDING

Atom probe mapping was developed from the field ion microscope, as a combination of laser-assisted removal of individual atoms from sharp tips and mass spectroscopy, to measure mass and deduce the element. Although one is able to collect far fewer than all the atoms that are removed, the crystal orientation can often be inferred, especially when the samples are also characterized with TEM. The method has revealed many aspects of nanostructures in metallic materials, most notably the clusters of solute atoms in pressure vessel steels that give rise to hardening from radiation damage, which in turn decreases the fracture toughness and limits service life. The characterization has become more sophisticated as solute interactions with defects, such as dislocations and grain boundaries, are quantified. The applications of the method have broadened to include analysis of complex mineral structures such as bone and dentin.

3D atomic mapping has revealed how oxidation and corrosion occur on zirconium alloys. Even non-conductive materials such as semiconductors have become accessible. The figure shows an application of the atom probe to mapping out an individual gate in an n-MOSFET (metal-oxide-semiconductor field-effect transistor). The samples were long-gate-length n-type MOSFETs, with a polysilicon gate, a gate-oxide film, and a silicon substrate with source/drain extension and halo regions, and boron implanted into the channel region. The results show that segregation of the phosphorus to grain boundaries in the polycrystalline silicon has occurred.

Further refinements of the technique will derive from improved detectors that can distinguish species with the same nominal charge-to-mass ratio, and modeling of the atom trajectories to take account of the markedly anisotropic characteristics of the near-tip regions. The future of the technique clearly lies in combinations with electron microscopy. One can imagine scenarios in which electron tomography alternates with atom probe mapping along with, for example, electron energy loss spectroscopy, energy-dispersive spectroscopy, high-resolution electron microscopy, or diffraction.



(a) 3D elemental map of an n-type MOSFET showing the concentration of the phosphorus (red) in the gate and the oxide layers. For visual clarity, only 0.1% of Si atoms were plotted. (b) Cross-sectional transmission electron microscopic image. (Inoue et al., 2009)

SPATIALLY AND TEMPORALLY RESOLVED CHARACTERIZATION OF INDUSTRIAL-SCALE CATALYSIS

Industrial catalysts are typically materials that are highly complex in both composition and structure, with minority surface species often dominating catalytic properties. Such catalysts are made by empirical recipes that are often intricate and proprietary. In an investigation of industry-like catalysts for methanol synthesis from H_2 and CO or CO_2 , neutron diffraction found that the copper in the catalyst had defects such as stacking faults, providing steps where catalysis was facilitated much more readily than on defect-free copper, and thin layers of zinc oxide near the step sites, detected by x-ray photoemission spectroscopy, enhanced the activity. Density functional theory calculations support the interpretation, and images determined by high-resolution electron microscopy (Figure 1) showed evidence of these unique surface sites. This work points the way toward further enhanced catalyst performance.

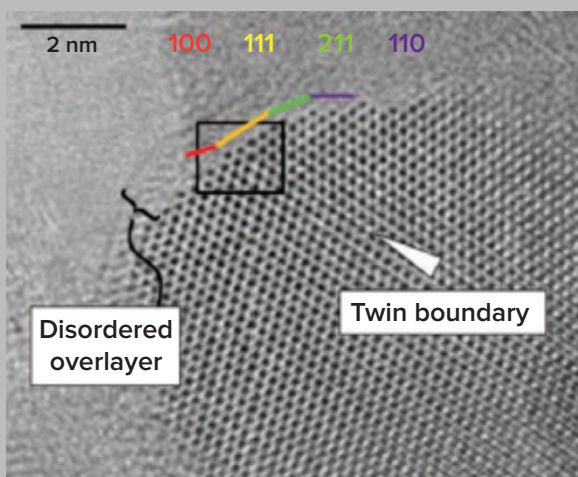


Figure 1. Aberration-corrected, high-resolution TEM image of a high-performing $Cu/ZnO/Al_2O_3$ catalyst revealing the defect structure and partial surface layer that lead to enhanced catalytic activity. (Behrens et al., 2012)

Spatially resolved surface studies of catalysts are now being complemented by time-resolved studies. Using the LCLS, researchers have made the first observations showing how bonds break and form in a reaction (CO oxidation) on a catalyst surface (ruthenium). The free electron laser and atom-specific spectroscopic tools showed how O atoms and CO molecules change positions on the surface at picosecond timescales and undergo changes in the transition state region, providing new insights into the electronic states of molecules reacting on surfaces (Figure 2).

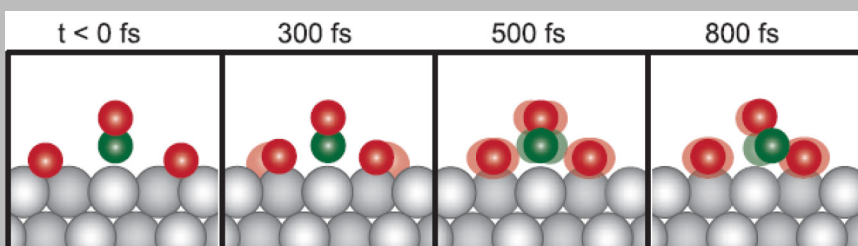


Figure 2. Pictorial view of the reaction sequence (oxygen atoms are red and carbon atoms are green) with corresponding timescales for oxygen activation, CO translation, collision, and CO_2 reaction product formation. (Öström et al., 2015)

Advances in the understanding and exploitation of coherence allow the use of phase information to replace multiframe tomographic image reconstruction. As an example of the need for continued progress, imaging fuel sprays for combustion is currently limited by the challenges of resolving fast-moving micrometer-scale droplets that may be evaporating into the surrounding atmosphere as they propagate. Continued advances in energy-sensitive mapping using synchrotrons, x-ray free electron lasers, electron microscopes and neutron sources, allied with advances in computation for data reduction and analytics, are needed. New tools are also needed to expand this approach for high-resolution imaging under controlled environmental conditions, including electromagnetic fields, chemical environments, and applied stresses.

4D characterization

The ability to view molecular to mesoscale structures in 3D, using either electron, neutron, or x-ray beams, has revolutionized structural biology and can be expected to do the same for materials science and condensed matter physics in the near future. The most important and challenging problems concern imaging of defects. For example, past errors in interpretation of rock structure have been corrected by 3D characterization.

Including the fourth dimension, that is evolution in time, is crucial, especially when it can be combined with external loading or other environmental variation. To understand and quantify the initiation of damage in structural materials, for example, we need the capability to map both structure and elastic strain in the time domain. In fact, 4D characterization more generally means following the evolution of structure under any kind of loading, (e.g., temperature, radiation, or chemical). This, in turn, drives needs for advances in both the sources of radiation and the detection of scattering as well as in the data processing (i.e., computation).

The development of miniature laboratories within microscopes has made rapid progress: an example is the use of wet-cells, fabricated by

semiconductor lithography techniques, in electron microscopy for the study of electrochemistry by time-resolved imaging at near-atomic spatial resolution. Similar technologies allow atmospheric imaging of catalysts in their working environment. New mathematical approaches and new algorithms have a substantial role to play, not least because of the size of the data flows. Faster data analysis and acquisition is qualitatively important in order to improve the capacity of our national facilities and to allow access to them by more users.

Spectroscopy

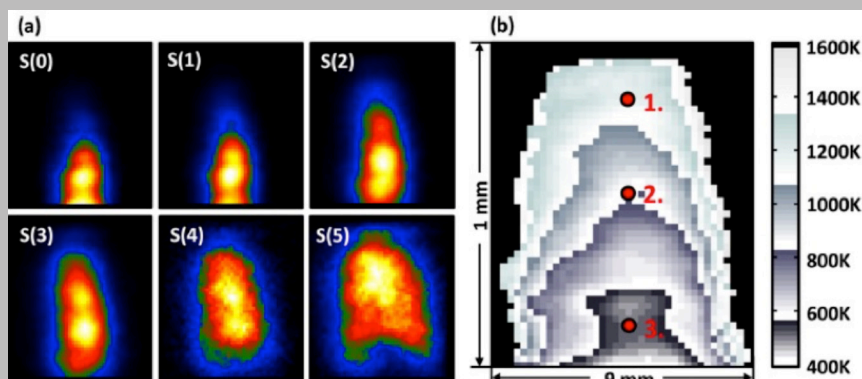
Chemical information about materials is crucial to understanding function. Considerable innovation has occurred in recent years, especially with respect to combinations of techniques, for example, lasers or synchrotron radiation with mass or infrared spectrometry, and the development of energy-loss spectroscopy with atomic resolution in electron microscopy. The latest instruments have demonstrated energy resolution of less than 10 meV, allowing the acquisition of vibrational spectra with a 1-nm electron probe: expected resolution improvements to 5 meV will yield nanoscale measurements of phonons. These techniques allow the observation of chemical reactivity and excited-state dynamics with sufficient energetic and spatial resolution to reveal the effects of, for example, heterogeneity in catalytic processes.

OUTLOOK

The potential impact of imaging advances is clear both for current challenges, such as quantifying the origin of damage in meso-structured materials, and for discovery of new and unanticipated phenomena and behavior. Predicting the unanticipated is a risky extrapolation from past experience; however, it is also the frontier of imaging advances most likely to deliver large unexpected benefits—that which we have not yet seen and thus not yet imagined. Easier to predict are impacts that address known problems, as well as the substantial need for characterization of new materials as part of the Materials Genome Initiative, where accelerated development of

IMAGING OF SPRAYS IN COMBUSTION SCIENCE

Imaging in combustion science has focused in recent years on quantifying the sprays that emerge from fuel injector systems, because understanding and predicting the resulting combustion is very sensitive to the droplet size and dispersion. Diesel spray combustion, for example, is dominated by air entrainment rates and gas-phase turbulence generation via spray/gas interaction. These processes are not directly coupled to primary breakup. The physical characteristics of the sprays are daunting in contrast to some of the solid-state examples shown in other sidebars in this chapter because of the dimensions and speeds involved. The droplets are a few micrometers in diameter by the point at which the spray is fully formed; they move at speeds on the order of meters per second, and a field of view such as that shown in the figure may contain hundreds of droplets. The current state of the art uses both laser shadowgraphy, with many adjustments for the substantial absorption of the beam(s) by the spray, and x-ray radiography, with high-energy synchrotron sources providing excellent penetration. Recent advances include chemically selective mapping in the gas phase with a single laser source. Coherent anti-Stokes Raman spectroscopy (CARS) permits the analysis of the temperature contour of a reacting fuel species as it evolves at a flame-front.



Spatial maps of specific H₂ CARS transitions and the derived temperature contour. (a), (b) Two separate recordings from imaged transitions of the pure-rotational H₂ S-branch and the vibrational H₂ Q-branch distributed in a wide spectral region. The recordings are performed at different positions in the flame. The distributed intensity across the transitions depends on the thermal population of the specific states involved, governed by the different zones of the reaction. (Bohlin and Klierer, 2014)

materials depends so crucially on quantitative prediction of behavior based on structure.

In Chapter 3, we addressed the issue of heterogeneity and its pervasive influence on the behavior of matter, whose understanding is again dependent on improved probes to deliver quantification and understanding of defect structure. For example, improved probes of interfaces in novel devices for transistors and other microelectronic components will be crucial for proving/disproving hypotheses about their behavior. Improved 4D capability will be essential to understanding how microstructural evolution changes and limits performance in electrochemical systems, combustion, biological (and biologically inspired) materials, solid state devices, and structural materials. It will also be crucial for delivering new understanding in dynamic systems. As another example, the ways that damage is initiated under fatigue and creep of advanced high-temperature materials for energy conversion and production remain wide-open topics of investigation.

Enabling Success

This report has identified a set of compelling opportunities for scientific advances that must be addressed to obtain truly transformative new energy technologies for our country. These Transformative Opportunities require us to address scientific complexities well beyond those contemplated in the 2007 Grand Challenges report in order to accelerate discovery science and conquer the barriers to practical and economical implementations of the discoveries we expect. Success will require a sustained campaign of strategic investments by BES that initiates new research thrusts, attracts and sustains a leading scientific workforce having the necessary skills, and provides the innovative instruments and tools with which to carry out the work. This chapter outlines some of the specific needs that are apparent now. First, however, it is essential to establish the organizing principles for a successful BES strategy to reach the goals we have identified here.

BES's strategy for scientific success has long been based on finding the appropriate balance among investment priorities, which BES has developed a number of modalities to preserve. Specifically, balance between single-Principal Investigator (PI) and research-center modalities, balance between large-scale facilities and lab-scale inquiry, and balance between high-risk, high-payoff opportunities and sustained and steady progress are all necessary. It is a continuing challenge for BES to maintain this strategic balance, especially in times of significant financial constraint.

The exciting progress and breakthroughs discussed throughout this report were made possible by the creativity and ingenuity of the scientific community, but they were also enabled by the strategic resource choices of BES. The 2007 Grand Challenges report not only identified Grand Challenges for science and the imagination but also articulated important opportunities and the steps that should be taken in order to realize them. In particular, the following needs were identified:

- ▶ A highly trained, diverse, and empowered scientific workforce whose members possess depth in one or two areas and are able to collaborate across a breadth of scientific and technical fields;
- ▶ A group of theorists, concentrating on the very difficult and demanding fundamental questions that arise in such problems as systems far away from equilibrium, nanoscale communications, or strong correlations; and
- ▶ Appropriate new experimental and computational facilities and a balance of funding mechanisms that permit development of new instruments, tools, and materials capabilities for single PIs, team science, and major user facilities.

The strategic actions taken by BES following the 2007 report's recommendations enabled the progress discussed throughout the present report. Perhaps most dramatically, 46 EFRCs were created in 2009, and these were succeeded by a new set of 32 EFRCs in 2014, intended to sustain the momentum created by the inaugural class. As multi-disciplinary, multi-institutional teams composed of the best of the best, the EFRCs are a research modality that is particularly well-suited for tackling the Grand Challenges in a sustained and impactful manner.

In addition to the EFRCs, BES has taken action to fuel the pipeline of researchers and cultivate a cohort of scientists focused on addressing the grand challenges. These investments include the Office of Science Early Career and Graduate Student Research programs. The benefits from these investments will be seen for decades to come in the careers of the BES Early Career Research Program recipients who have been selected in the first six years of the program, as well as the graduate students who were introduced to energy science through graduate student fellowships. As these rising stars reach

their full potentials, the impact of the BES investments will multiply through new research directions and future generations of scientists.

In assessing the advances of the last decade and critically evaluating the opportunities looking forward, it becomes clear that strategic and deliberate actions will be required in order to realize the potential that lies before us. Just as the scientific frontiers have evolved by virtue of the progress of the last eight years, so too have the needs for accelerating progress and impact. The required actions, discussed in detail below, span three broad areas: synthesis; instrumentation and tools, including theory and computation; and resources and human capital. These areas are intimately coupled, and action in one without complementary actions in the others is unlikely to yield success. Equally important, a concerted focus across all three will yield significant advances far beyond isolated investments in only one or two, owing to synergies that have developed since 2007. In order to seize the Transformative Opportunities before us, we make the following observations and recommendations:

- ▶ A central element of control science is the ability to make materials and chemical processes behave as we desire through the realization of functionality by design. The science of synthesis includes not only knowing what one wants to make but also knowing how to make it. BES should lead the way in embracing computational materials and chemical sciences, advanced synthetic approaches, and their integration as critical initiatives to accelerate materials discovery.
- ▶ Multi-modal and in situ imaging measurements, closely coupled to advanced analysis methods and algorithms, are required to observe and exploit the complex functionality we seek to control. BES should enhance its commitment to investigators skilled in instrument development and technique creation in order to plant the seeds for the next generation of experimental, mathematical, and computational capabilities that will advance the frontiers

of discovery science and inspire future large-scale facilities.

- ▶ Especially in times of fiscal constraint, BES should ensure a balanced portfolio of investments, with a particular focus on enhancing its “seed corn” for discovery science. Over the last decade, the seeds of a new generation of energy scientists have been planted. Networks of scientists spanning synthesis, characterization, theory, and simulation are necessary for effectively meeting the Grand Challenges and accelerating the pace of discovery science. BES should strive to strengthen the connections among energy scientists who can span disciplines through collaboration.

SYNTHESIS

Synthesis is an essential step in translating observation to controlled functionality. Most simply and directly, synthesis is the means by which we demonstrate control science, harnessing material and chemical processes to produce matter that does what we want it to do. Further, the science of synthesis provides the means to actually produce the compounds and structures we envision computationally. One consequence of realizing significant large-scale characterization facilities is the need to synthesize materials whose quality and functionality are commensurate with the power and fidelity of the measurements that are now possible. The five Nanoscale Science Research Centers are a foundational contribution to filling this gap, with their pioneering development of nanoscale observation, theory, and materials growth. However, we now face a new era of integrated synthesis, characterization, and simulation that reaches far beyond the remarkable advances in nanoscience of the last 15 years. Much more needs to be done to meet the challenges for next-generation synthesis for our energy requirements and our existing characterization and computational capabilities.

As one considers the dramatically enhanced space of hierarchical architectures and beyond-equilibrium matter, the gaps in our synthetic capabilities become even more evident.

We need to extend our current ability to understand and control from the nanoscale to the mesoscale and beyond. In particular, synthesizing non-equilibrium structures and hierarchical architectures requires in situ manipulation of the synthesis process itself. The science of synthesis requires a groundswell of invention and discovery focused on the new horizons of hierarchical and beyond-equilibrium opportunities. Close coupling of synthesis with advanced modeling, theory, and characterization enables predictive design, which will rapidly outpace serendipitous exploration.

INSTRUMENTATION AND TOOLS

Over the past decade, BES has delivered, and is delivering, a suite of large-scale national user facilities that is the envy of the world. The Spallation Neutron Source (SNS), Linac Coherent Light Source (LCLS), and National Synchrotron Light Source II (NSLS-II) build on the success of the Advanced Light Source (ALS), Stanford Synchrotron Radiation Light Source (SSRL), NSLS, Advanced Photon Source (APS), High Flux Isotope Reactor (HFIR), and the Lujan Center. Important upgrade projects are underway at the LCLS and APS. The five Nanoscale Science Research Centers (Center for Functional Nanomaterials [CFN], Center for Integrated Nanotechnology [CINT], Center for Nanoscale Materials [CNM], Center for Nanophase Materials Sciences [CNMS], and the Molecular Foundry) have played a major role in advancing the frontiers of Grand Challenge research. To fully exploit this suite of facilities, continued attention is required to maintain their world-leading status, as is a renewed emphasis on lab-scale and single-investigator innovation to fuel the next generation of instrument development.

As pervasive and impactful as large-scale facilities are, their origins are in the innovations of researchers working in individual labs developing new tools and capabilities. The ingenuity of individual investigators underlies essentially all of the breakthroughs that have enabled the enhanced brightness, resolution, and sensitivity that have been realized in large-scale facilities. To seize the Transformative Opportunities that are

before us, we need to ensure that a culture of invention/innovation and instrument and algorithm development is sustained. In the education and funding of researchers, a specific focus on cultivating technique development, including advanced analytics to foster effective data utilization, is needed. Such efforts not only lead to unique small-scale capabilities, but also inspire future large-scale facilities. Similarly, recapitalization and upgrades of existing mid-scale instrumentation are essential for maintaining scientific leadership and providing modern tools to researchers and students, the vast majority of whom spend only a small fraction of their research career at large-scale user facilities.

A particularly promising opportunity for capability development is in the area of in situ/multimodal imaging measurements (e.g., in situ synthesis and characterization, “labs in a microscope” that enable a variety of sample environments, and universal sample holders for multimodal imaging among a range of instruments and spectrometers). The successful understanding and control of complex materials and functionality discussed throughout this report require much more than static, single-mode characterization. Finally, as simulation and software tools mature and become accepted by larger communities, standardization and unification of data/analysis tools have been shown to have wide impact.

In parallel with fostering single-investigator innovation, it is important to ensure that the world-leading facilities of BES remain state-of-the-art. Investments in detectors, end stations, and sample environments can multiply the investments already made in facility sources and impact scientific domains not previously imagined. As an example, the single synchrotron ring at the APS provides photons for more than 50 measurement stations. Regular end-station recapitalization ensures that the photons are well used. While we may be entering a period in which fewer large-scale sources and accelerators are actively being built, it is important to retain and sustain state-of-the-art instrumentation at existing facilities for both current operations and future development.

Finally, in order to use large-scale facilities well and efficiently, development of technical support and research scientists is essential for stewarding capabilities. As measurements become more complex and multimodal, the need for highly trained instrument scientists will become even more acute. As highlighted above, access to computing resources and analysis techniques, data capabilities, and storage and archival approaches, including potentially automated analytics, can have a transformational influence on the rate of scientific productivity, further amplifying the impact of existing facilities.

HUMAN CAPITAL AND RESOURCES

The most important resource the community has for advancing the Grand Challenges and Transformative Opportunities is its researchers. A positive legacy of the 2007 report is the Early Career Research Program, which is important for fostering creativity in rising stars. Sadly, the current success rate (fewer than 10% of proposers are successful) distorts reality relative to the potential of the community. Sustaining early-career success to mid-career is important to allow maximum payoff from the initial investment. As these early-career researchers advance successfully through their careers, the initial investments will continue to pay dividends.

Another positive outcome of the 2007 report is an emerging new generation of scientists who are aware of both simulation/computation and experiment capabilities. This awareness does not obviate the need for collaboration, but rather strengthens it. Knowing what one does not know provides an exceptionally strong impetus for collaboration and partnership. To bring a full suite of experts to bear on any particular problem, multidisciplinary PI networks for lectures, training, and focused schools, integrating both students and established researchers, are needed. One practical consideration is that residence programs, such as short sabbatical and visitor programs, enable diverse teams to “live” together, greatly accelerating communication and productivity beyond that which occurs

during short workshops and conferences. As noted above, synthesis and instrument development are two key areas where demand exceeds supply and which are particularly ripe for human capital investments.

The urgency and potential impact of the Transformative Opportunities discussed above motivate increased financial investment. However, in times of fiscal constraint, maintaining an appropriate balance is increasingly essential for ensuring maximum impact. Over time, BES has developed a number of modalities to ensure this balance. In particular, balance between single-PI and center modalities, balance between large-scale facilities and lab-scale inquiry, and balance between high-risk, high-payoff opportunities and sustained and steady progress are all necessary. The EFRCs have had a dramatic impact on BES science. At the same time, funding for the core research programs that gave rise to the ideas behind the EFRCs has remained rather static. Similarly, BES’s large-scale facilities are the wonder of the world, but additional investment in those scientists who innovate for and utilize these facilities is necessary. Finally, while it is important to pursue new directions, a sustained attack on decadal challenges is necessary for success. Therefore, in addition to the magnitude of the budget, duration is also important. Put plainly, decadal challenges cannot be solved on a three-year funding cycle. BES’s robust peer review processes create an opportunity to ensure that steady progress continues to be made through prolonged investment.

Centers have emerged as a key modality for advancing the frontiers of research over the last decade. The impact of these centers is clear; however, as we plan for future research investments, enthusiasm for center-based research should not be unbridled, as it may lead to the proliferation of centers without clear intent, which could disrupt the balance between centers and single investigators. Centers have been used effectively for at least three mission purposes: fostering team science, leveraging central infrastructure, and providing seed funding for the exploration of new ideas. Each of these activities has

merits, but it is important that the goals and objectives are well understood both by BES and by the researchers supported when centers are created.

As the ultimate compliment to BES's vision and as a threat to its leadership, private foundations and many non-U.S. funding agencies have been emulating BES's pursuit of the Grand Challenges and have explored a variety of funding modalities, from large-scale centers to sustained investment in single individuals. An opportunity exists to extend the best of these modalities (and to avoid the least successful). By innovating and stewarding a growing and balanced portfolio of research modalities, BES can enable sustained and dramatic progress by the research community.

In summary, focused and strategic investment in synthesis, instrumentation, and people through appropriate resource balance can dramatically accelerate the research community's potential to advance the Grand Challenges and Transformative Opportunities. Our confidence derives substantially from the success story that has played out since the 2007 report. The community is even better positioned to seize the opportunity today, and the impacts promise to be transformative for science, society, and the imagination.

appendix

Grand Challenges: Then and Now

The five interconnected questions posed in the 2007 “Grand Challenges” report proved to be a compelling prod for the scientific community in the United States and beyond. Through their analysis and pursuit, significant progress has been made in advancing the frontiers of science. Notably, the breadth and depth of the challenge in each case is more compelling today than it was at the time of the report. A scientific community deeply focused on these grand challenges will continue to generate fertile new directions for further breakthroughs and discoveries for many years to come. In the narrative that follows, we discuss the advances that have been made and the challenges that remain for each of the five Grand Challenges:

- ▶ How do we control material 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 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 capabilities rivaling those of living things?
- ▶ How do we characterize and control matter away—especially very far away—from equilibrium?

A.1

How Do We Control Material Processes at the Level of Electrons?

OVERVIEW

Electrons govern nearly all aspects of a material's behavior, from atomic bonding and architecture to static and dynamic performance, to natural and designed functionality. Much of the last century was spent observing how electrons shape the behavior of matter through their charge, spin, and dynamics. Recent advances in ultrafast x-ray and optical pulses have revealed previously hidden intermediate states; high-spatial-resolution diagnostics probe the interfacial and local dynamics of charge, spin, and mass transport; and high-energy-resolution spectroscopy, coupled with sophisticated electronic simulation schemes such as time-dependent density functional theory and dynamic mean field theory, allow deeper understanding of evermore complex materials and phenomena.

We are turning our attention from the static behavior of electrons in relatively simple bulk and thin-layer materials to the dynamic behavior in complex materials, where electrons connect with many other degrees of freedom. The charge and spin carried by each electron, combined with the richness of their Fermi-Dirac statistics and ultrafast dynamics, enable an infinite horizon of complex behavior embracing optical, mechanical, magnetic, and chemical dimensions. We are just beginning to fathom and control these complex electronic perspectives in single-layer, soft, amorphous, and heterogeneous materials that go well beyond traditional crystalline solids and small molecules.

BREAKTHROUGHS

Exciton Fission

Sunlight delivers cheap and abundant energy to Earth, more than enough to satisfy human energy needs many times over. The Sun delivers its light in a range of energies, as we see in rainbows; capturing more than one color is necessary for efficient solar energy production. More than half a century ago, William Shockley showed that a single solar absorber

that captures only one color of the solar spectrum has a maximal efficiency of about 31%.

Several creative routes have been proposed to overcome this barrier. In the 1970s, Arthur Nozik suggested that a process called exciton fission could produce two electrons from capturing a single high-energy photon, boosting efficiency above 45%. The mechanisms for generating two electrons from a single photon require high temporal and physical organization. Electrons couple sequentially first to photons to absorb the energy of sunlight, then to organic molecules to store the energy in excitons, to neighboring molecular clusters to promote fission of the exciton into two derivative excitons of lower energy, and finally to an interface or other structure that drives the separation of each exciton into free electrons and free holes. These challenges have blocked rapid progress on exciton fission.

Recent progress in exciton fission has been remarkable, particularly among the Energy Frontier Research Centers (EFRCs). One example is shown in Figure A.1-1. Conventional solar cells generate a maximum of one electron per photon incident on the solar cell's surface and waste the remaining energy as heat. Singlet exciton fission can produce up to two electrons per photon using some of the energy normally wasted as heat to generate extra power. Using pentacene as the exciton media, researchers demonstrated in 2013 that 109 electrons can be generated from 100 photons of incident red light. The solar cell absorbs only 70% of incident photons, translating to 160 electrons generated per 100 photons absorbed. Modulating the photocurrent with a magnetic field, the researchers showed that the fission yield is two triplet excitons per photon for pentacene layers greater than five nanometers thick. Their work opens the door to pairing singlet exciton fission with highly efficient solar cells to substantially raise their efficiencies without significantly increasing costs, as

the processing of singlet fission materials occurs at room temperature with common materials and standard deposition techniques.

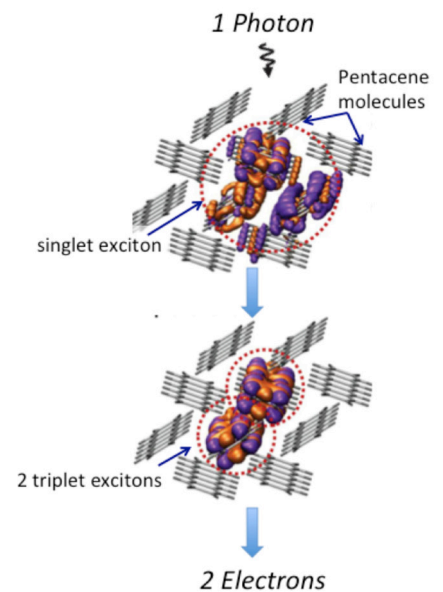


Figure A.1-1. Organic pentacene molecules capture high-energy photons from the solar spectrum, producing a singlet exciton consisting of a bound electron-hole pair. The singlet exciton decays spontaneously into two triplet excitons of approximately half its energy, each also consisting of a bound electron-hole pair. Each of the two triplet excitons can then be dissociated into unbound electrons and holes, which can then be used as input to chemical reactions that produce solar fuels such as hydrocarbons from water and CO₂, or directly as solar electricity to replace carbon electricity in the grid. (Congreve et al., 2013).

Work elsewhere has shown that fission efficiencies close to 200%, the maximum that can be attained by splitting an exciton from one photon into two electrons, can be attained with appropriate molecular chromophores. Exciton fission promises to substantially increase, at lower cost, the efficiency of solar collection of energy, which can then be channeled to artificial production of fuel or to generation of photovoltaic electricity.

Ultrafast, Multistep Catalysis

Controlled electron transfer is the beating heart of catalysis, the promotion of beneficial chemical reactions to the exclusion of unwanted side reactions. Most catalysts are found by trial and error and operate by mysterious means that have remained stubbornly invisible to our experimental probes. Often several steps and intermediate states are involved, some on ultrafast timescales that elude observation and thus preclude understanding that could lead to rational design of catalysts for critical needs.

Recently, ultrafast visible and near-infrared transient absorption spectroscopy has resolved the intermediate states in multicomponent catalysts and allowed a detailed understanding of their temporal and spatial dynamics. An example is the multicomponent donor-bridge-acceptor triad shown in Figure A.1-2, designed to absorb light energy in the donor, triggering the release of an electron that flows through the bridge to the acceptor, which is coordinated with a new proton-reducing cobalt diimine-dioxime catalytic complex. The catalyst complex on the right in the figure reduces protons to diatomic hydrogen molecules, H_2 . The remarkable features of this donor-bridge-acceptor-catalyst combination are its rational design and self-assembly from component molecules, the ultrafast transfer of photoexcited electrons from the chromophore absorber on the left to the catalyst on the right, and the much slower speed of detrimental recombination of the transferred electron back to the absorber. This asymmetry in transfer rates is directly attributed to the spatial separation of the constituent parts of the system and the designed mismatch of internal energy levels of the component parts. The long residence time of the transferred electron on the catalyst allows ample time for it to reduce the catalyst and for the catalyst to perform its proton reduction to diatomic hydrogen.

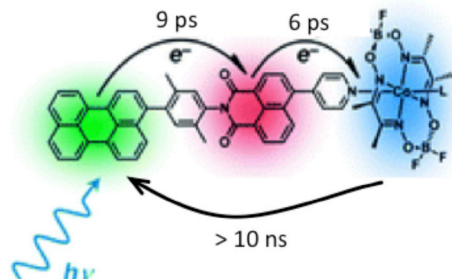


Figure A.1-2. The temporal transfer sequence of photoexcited electrons from a chromophore absorber (perylene, green) through a xylene bridge (uncolored) to a naphthalene imide acceptor (red), which is coordinated with a new proton-reducing cobalt diimine-dioxime catalytic complex (blue). (Veldkamp et al., 2013)

The details of the intermediate states revealed in ultrafast transient absorption spectroscopy like this allow the guiding principles governing the timing and spatial coordination of high-performance multistep electron transfer to be discovered. This basic information is the key to a new era of designed catalysts for critical needs.

Multiferroic Spin Valves

The simultaneous presence of charge and spin on an electron creates fertile ground for coupling these two rich degrees of freedom, allowing charge-related orbital and transport effects to be controlled by spins and magnetic fields, and spin-related magnetism to be controlled by charges and electric fields. The many combinations of multiferroic materials, where electric and magnetic polarizations either coexist in the same lattice or interact across an interface, create even more fertile opportunities for new phenomena and new functionalities. The field of spintronics, where spins play a central role in controlling electronic behavior, has seen dramatic advances in the last few years. The combinations and permutations of materials, polarizations, and interactions are endlessly rich and productive.

Rapid advances in multiferroic spintronics are well illustrated by the discovery of a novel phenomenon that exploits ferroelectric polarization to switch magnetic order, which then switches transport current conductivity by over an order of magnitude. Even more impressive is the precise theoretical design and prediction of this effect before it was observed experimentally, showing the sophistication of electronic structure simulations of complex geometries.

The three-part multiferroic assembly is shown in the lower panel of Figure A.1-3. On the left is a stable ferromagnetic and metallic $La_{0.7}Sr_{0.3}MnO_3$ electrode; in the middle are five layers of insulating ferroelectric $BaTiO_3$, thin enough for electrons to tunnel through; and on the right is an unstable $La_{0.6}Sr_{0.4}MnO_3$ electrode, in which the La content is adjusted to the brink of a phase transition between ferromagnetism (with approximately isotropic metallic conductivity) and antiferromagnetism (with highly anisotropic metallic conductivity). In the antiferromagnetic state, the right electrode is insulating in the horizontal direction and conducting in the transverse direction. The electric polarization of the $BaTiO_3$ dopes the adjacent right and left magnetic electrode layers with either excess holes or electrons, depending on the electric polarization direction. The two nearest magnetic layers on the right, having been prepared to be near the phase transition, switch between their conducting ferromagnetic state and insulating antiferromagnetic state; the adjacent layers on the left are unaffected, having been prepared to be far from the phase transition. Density functional theory simulations reveal the distribution of conductivity of the electronic states in the Brillouin zone, shown as the upper panel in the figure. Gray areas do not conduct, red is highly conducting, and yellow and green are moderately conducting. The average conductivity over the Brillouin zone changes by over an order of magnitude between the ferromagnetic and antiferromagnetic states on the right; it is the polarization of the five layers of ferroelectric $BaTiO_3$ in the middle and the

consequent hole doping of the right-hand electrode that controls this significant switch.

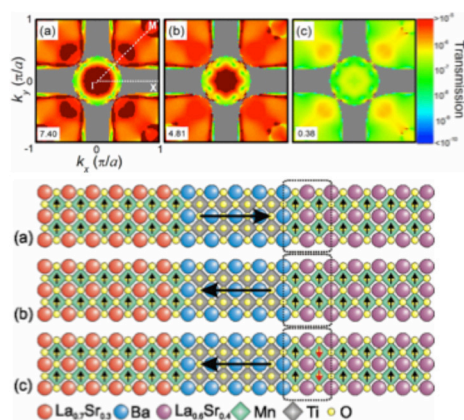


Figure A.1-3. Lower panel: Sandwich of ferromagnetically ordered $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ electrode on the left, five layers of ferroelectrically ordered BaTiO_3 in the middle, and ferromagnetic or antiferromagnetic $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ electrode on the right. The electric polarization of the five layers of BaTiO_3 in the middle dopes the first two layers of the electrode on the right, switching them between the conducting or insulating states and changing the conductivity by over an order of magnitude (upper panel). (Burton and Tsymbal, 2011)

This example shows the richness, complexity, and functionality of interacting spin and charge degrees of freedom in multiferroic architectures and demonstrates the sophistication of density functional theory, rivaling experiment in capturing such complex behavior. We are beginning not only to understand, but also to design and control electronic behavior for targeted functional outcomes in complex assemblies of interacting materials.

OUTLOOK

The examples above show the transformational shift in our understanding of electronic behavior, from observation in relatively static and simple crystalline and small molecule or polymer formats, to design and control in dynamic and complex materials assemblies. Despite these early successes, our journey has just begun. The ultrafast timescale of electronic excitation and transfer demands much more sophisticated tools, such as the free electron lasers that are just now beginning to emerge, capable of producing sub-picosecond pulses of coherent, high-energy x-rays. Such x-ray lasers hold the promise of not only revealing the most secret and previously invisible ultrafast behavior of electrons, but also exerting quantum control over the direction in which a multistep chemical reaction proceeds. This revolutionary kind of catalysis, where coherent, high-energy photons replace traditional catalytic materials, is within sight but not yet within reach.

Controlling processes at the level of electrons has an enormously wide horizon. We have seen rapid advances in areas where we have a strong foundation of theoretical concepts and experimental probes, such as crystalline solids and small-molecule and polymer chemistry. The broader challenges remain to be explored in single-layer, soft, amorphous and heterogeneous materials that enable the remarkable functionality of biology and promise to bring similar complexity and functionality to artificial energy materials.

A.2

How Do We Design and Perfect Atom- and Energy-Efficient Synthesis of Revolutionary New Forms of Matter with Tailored Properties?

OVERVIEW

The progress of civilization depends on our ability to design and manipulate the properties of natural and synthetic materials. The periodic table contains more than 100 elements, yet only a tiny fraction of possible chemical compounds have been synthesized and characterized; many more materials and phenomena remain to be discovered than we now know. Predictive materials simulation has reached a level of sophistication and accessibility that allows it to bring order and structure to the vast space of unmade materials. The Materials Genome Initiative takes advantage of this ripe opportunity, using predictive materials simulation to identify the most promising new materials with a portfolio of targeted properties before they are made. This “materials by design” approach has the potential to rapidly accelerate the pace of materials discovery and innovation. Such qualitative and quantitative acceleration puts pressure on materials synthesis and characterization, which have not advanced as far or as fast as predictive simulation. Innovation and resources are required to bring the sophistication and power of synthesis and characterization to levels commensurate with the new horizons of predictive simulation. The three activities must be “joined at the hip” to provide the highly interactive crosscutting fertilization that advances and refines our collective materials wisdom. Predictive synthesis and materials by design provide a conceptual framework for creating revolutionary new forms of matter with tailored properties. However, identifying the basic building blocks and creating the complex architectures that impart functionality to these building blocks require equal participation from synthesis and characterization.

BREAKTHROUGHS

The Materials Genome Initiative

Materials are at the very center of scientific discovery and innovative technology, from Dirac fermions in graphene to high-performance, low-cost energy storage in lithium-ion (Li-ion) batteries. Often, new materials and new phenomena are intimately linked: the discovery of high-temperature superconductivity focused attention on the copper oxides, which triggered discovery of entirely new classes of highly correlated normal state electronic behavior in the copper and manganese oxides. On the technology side, progress to higher performance and lower cost is often constrained by materials limitations and advanced by new materials discovery. The successive replacements of rechargeable nickel-cadmium battery technology with nickel metal hydride and then Li-ion, and the current drive for a new set of battery materials and technologies to transform transportation and the electricity grid bear witness to this truth. Despite the critical importance of materials to advancing the frontiers of science and technology, we typically discover new materials by very traditional means: intuition, serendipity, and trial and error.

A new paradigm for materials discovery is emerging: the Materials Genome Initiative is based on the continuing revolution in computer performance and advances in software and cloud-based open-access information technology. Sophisticated computer codes now predict materials properties before those materials are synthesized in the laboratory, dramatically enhancing and exceeding the power of traditional materials discovery methods (see Figure A.2-1). Scientists have begun to survey tens of thousands of materials for specific portfolios of properties, often selecting as few as 5 or 10 as promising enough for further simulation or synthesis in the laboratory. Such wide search and pre-selection procedures dramatically reduce the time needed to find the best materials for a given set of targeted

properties, often finding counterintuitive materials that would otherwise have been overlooked. Large openly available platforms also serve needs beyond their initial purposes, enabling, for example, re-running prior simulations to search for properties not targeted in the initial portfolio, or searching several databases for property trends that support or refute new concepts.

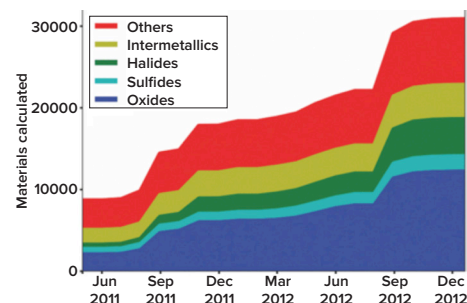


Figure A.2-1. Number of compounds available on the Materials Project website, from its initial release in October 2011 through December 2012, broken down by type of compound. (Jain et al., 2013)

Although the Materials Genome Initiative grew from simulations of crystalline materials, its approach is being applied to other classes of materials, including liquid organic electrolytes for next-generation batteries, and ionic liquids for a variety of scientific and technological directions. One can imagine the day when freely available databases of simulated materials properties become *de rigueur*, as regularly consulted as we now consult the Internet for news, history, and technical and cultural information. Like the Internet, the uses and impact of such an extensive and easily available resource of materials information are likely to be surprising and transformative.

Materials simulation must be coupled to materials synthesis and characterization to enable critical comparison of measured and simulated properties and to advance our understanding. Synthesis and characterization may soon be overwhelmed by the rapid growth of

predictive simulation. There is a growing need for additional innovations and resources to bring these activities to a level commensurate with predictive simulation.

A ripe innovation for synthesis is the intimate incorporation of simulation with materials formation. We now use predictive simulation for materials by design, predicting where the atoms must go to produce a given portfolio of properties. We can equally focus predictive simulation on how to put the atoms where they must go, that is, “synthesis by design.” This vast and rich area is largely unexplored and only beginning to emerge, much as materials by design was beginning to emerge a decade or more ago. Synthesis by design is an inherently non-equilibrium enterprise, because gradients of temperature, electric and magnetic fields, chemical compositions, and the flow of mass, charge, spin, and energy are required to create new materials. These challenges are a level above the predictive simulation of equilibrium properties commonly used in materials by design, but are being increasingly developed for the design of materials functionality, which, like synthesis, requires harnessing non-equilibrium behavior. Developing the predictive science of synthesis is a natural next step for the Materials Genome Initiative.

Directed Self-Assembly

Directed self-assembly has advanced rapidly in recent years, allowing ever more complex structures and architectures to be created from molecules, nanotubes, polymers, quantum dots, and other nanoscale components. In some cases, these structures arise naturally in response to relatively small adjustments to the environment, such as temperature or composition changes or gradients. Biology has mastered a far more sophisticated directed assembly process, using, for example, digital information stored in DNA to replicate nearly identical proteins that in turn control assembly and functionality of more complex structures. By comparison, our artificial, directed self-assembly is at a more primitive level; we are learning how to place individual nanoscale objects at

targeted locations where they may link with other nanoscale components in a complex architecture. Our challenge is creating a “nanoscale assembly line.”

One of the biggest challenges in nanoscale assembly is grasping and moving objects smaller than approximately 100 nm in size. Conventional optical tweezers grasp objects with intense non-uniform light beams that create energy gradients and forces on targeted objects that are grasped and then follow the motion of the inhomogeneous light beams. The smaller the object, the more intense the light beams must be to grasp it. Intense beams produce local heating around the object to be grasped, and they create unwanted thermal gradients and hydrodynamic flows of gases or liquids in which the targeted object resides. These forces typically compete with and weaken the forces grasping the object.

Recently, researchers developed a new form of “nanotweezers” (Figure A.2-2) based on photonic crystals that can trap, move, and release nanoscale objects a few tens of nanometers in size, while limiting the local temperature rise to approximately 0.3 K. The photonic crystal nanotweezers, which are made from silicon nitride instead of conventional silicon, can be operated at optical wavelengths near 1,064 nm, where water and biological molecules have dramatically lower energy absorption rates. This reduces the energy input of the tweezers for nanodots and biological molecules in solution, a common medium for self-assembly, limiting the temperature rise and resultant heat and fluid flows. The silicon nitride nanotweezers can manipulate polymers as short as 22 nm.

Advances in directed self-assembly increase the range and precision of the assembly process, bringing the concept of nanoscale assembly lines within reach. Such assembly lines are a key step toward reliable and reproducible production of complex nanoscale architectures and functionality that will initiate a new era in nanoscale manufacturing and may someday challenge biology in the sophistication and intricacy of its methods and products.

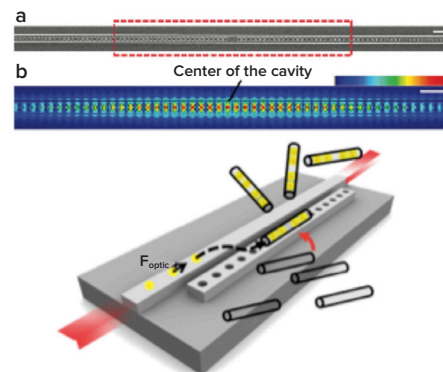


Figure A.2-2. Optical nanotweezers based on photonic crystals of silicon nitride. The upper panel (a) shows the physical structure of the photonic crystal and the simulated gradient of light intensity across the tweezers (b), with steep gradients in the vertical and modest gradients in the horizontal directions. Nanoscale objects are attracted to the center of the cavity where the light intensity is strongest. The lower panel shows the tweezer action: nano-objects are captured from flowing water and trapped on the photonic crystal, where they can be moved to another location and released. (Chen et al., 2012)

In Situ Characterization

Characterization has taken major leaps forward in higher spatial, temporal, and energy resolution across a host of probes, including photon, neutron, and electron scattering and spanning diffraction, imaging, and spectroscopy. These characterization techniques are now significantly more powerful than they were a decade ago. Free electron lasers and high harmonic generation (HHG) of ultrafast highly coherent photons, high-intensity neutron pulses, and time-resolved and aberration-corrected electron microscopy continue to advance the frontiers of science.

These and other characterization techniques share one common and still underdeveloped opportunity: in situ measurements. Observing the dynamics of materials as they function creates a new level of analysis, discovery, and understanding, often revealing intermediate states and reaction pathways that are invisible to ex situ characterization of the static final state.

The power of in situ characterization is illustrated by electron microscopy in an electrochemical cell, where multimodal diffraction, imaging, and spectroscopy tools can be brought to bear on an electrochemical process such as charging and discharging battery electrodes. Recently, several groups designed such in situ electrochemical electron microscopy cells. Figure A.2-3 shows the results of one such set of experiments on the conversion reaction of lithium with nanoparticles of FeF_2 to produce LiF and elemental Fe , the discharge reaction at the cathode of a proposed battery chemistry. Three measurements were applied sequentially to the discharge reaction: real-time imaging by transmission electron microscopy (TEM), electron diffraction, and electron energy-loss spectroscopy recorded at sub-second temporal resolution. These multimodal experiments were combined with first-principles density functional theory calculations and phase-field simulations to interpret the origin of the observed morphology and phase evolution.

A major discovery of Fang's study was the surprisingly fast reaction rate within individual nanoparticles, complete within 3–12 minutes. This discovery contrasts sharply with conventional wisdom, which holds that conversion reactions are inherently slow, limiting the maximum charging and discharging rates of batteries. In situ experiments that capture dynamics are critical to exploring the validity of this common, and now challenged, belief. Time-resolved TEM was also performed on films of FeF_2 reacting with Li , revealing a reaction front moving across the film and confirming the fast reaction rate.

Increasingly complex and heterogeneous materials such as battery electrodes challenge characterization to provide a complete picture of nanoscale interactions, mesoscale impact, and macroscopic performance. Multimodal experiments are needed to capture the interactions among many charge, spin, structural, and morphological degrees of freedom, and in situ experiments are needed to capture the dynamics and intermediate states that contribute to the outcome. Both multimodal

and in situ characterization need greater innovation and deployment to keep up with rapid advances in materials complexity and functionality.

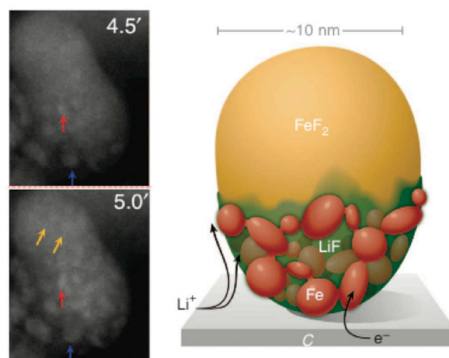


Figure A.2-3. Left: Time-lapse transmission electron microscopy images of a nanoparticle of FeF_2 reacting with Li ions and electrons to produce LiF and elemental Fe , after 4.5 and 5 minutes. Elemental Fe appears as sub-nanometer particles on the surface of the larger, 10-nm FeF_2 particle, quickly covering its surface. Right: Cartoon of the proposed reaction dynamics, with a fast reaction on the surface, followed by a slower reaction as Li ions penetrate the bulk. (Fang et al., 2012)

OUTLOOK

As predictive simulation and the Materials Genome Initiative drive toward ever more complex materials and functionality, synthesis and characterization are in danger of falling behind, unable to progress fast enough to capture the new levels of temporal and spatial complexity that are rapidly emerging. Multimodal experiments performed on the same material, on the same sample, and in the best cases simultaneously, have the potential to capture the complexity; in situ experiments have the potential to capture the dynamics and intermediate states that contribute to the outcome. Innovation and resources are needed for synthesis and characterization to reach a level commensurate with predictive materials by design, allowing all three activities—discovery, synthesis, and characterization—to work collaboratively to advance our collective materials wisdom.

A.3

How Do Remarkable Properties of Matter Emerge from Complex Correlations of Atomic or Electronic Constituents and How Can We Control These Properties?

OVERVIEW

Emergent phenomena driven by correlated behavior of many atomic or electronic constituents are pervasive in science and engineering; they offer the prospect of creating new macro- and mesoscale functionality from the interaction of nanoscale components. Uncovering the fundamental rules of correlation and emergence is the first part of the challenge. The second is to achieve control over these correlations, a prospect that only now can be contemplated with the advent of tools that probe and reconfigure atoms and electrons on the nanoscale. By understanding and controlling correlations, we can put emergence to work for us.

BREAKTHROUGHS

Since 2007, new kinds of correlations have been discovered in electronic behavior within a single unit cell of metals, in the dynamic behavior of flexible superconducting vortex lines, and in large assemblies of charged polymers. These discoveries reveal new features of the large-scale collective behavior of correlated systems and new ways to harness correlation for targeted outcomes.

Electronic Liquid Crystals

The long-range electrostatic Coulomb repulsion among electrons in metals leads to many dramatic effects, including the localization of normally itinerant electrons—turning metals into insulators—and the creation of local magnetic moments on atoms that then interact through long-range dipole and short-range exchange interactions to create a new layer of emergent macro- and mesoscale magnetic behavior.

Recently, a new kind of short-range electronic correlation, dubbed an “electronic liquid crystal,” has been discovered in the normal state of cuprate high-temperature superconductors. Unlike well-known long-range electronic correlation phenomena, this correlation occurs at short range: within a single unit

cell of the metal. As shown in Figure A.3-1, the new correlation appears visually in scanning tunneling microscopy (STM) images of the phase of the electronic wave function at the oxygen sites in the normal state of high-temperature superconductors; it can be seen in neutron scattering, thermal transport, and polarized x-ray scattering, as well. Intriguingly, the d-wave symmetry of the new short-range correlation matches the d-wave symmetry of the neighboring high-temperature superconducting state, suggesting that short-range electronic correlation in the normal state may be a precursor or a prerequisite for formation of the high-temperature superconducting state.

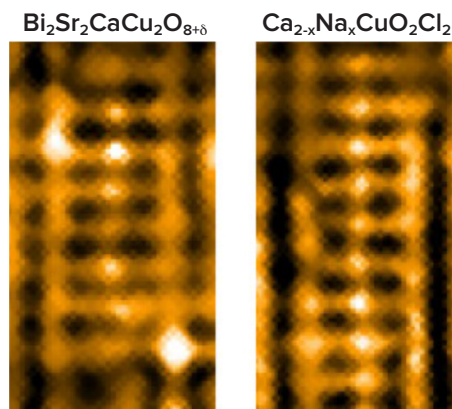


Figure A.3-1. Subunit cell-phase-resolved images of the d-wave symmetry in the normal state of two cuprate high-temperature superconductors. The rectangular symmetry of the electronic states in both images reflects d-wave symmetry, breaking the expected square symmetry of the copper oxide crystal lattice. (Fujita et al., 2014).

This new, short-range electronic correlation within a single unit cell is yet another fundamental discovery in the rich behavior of strongly correlated electrons, and a step toward a comprehensive description of high-temperature superconductivity.

Superconductivity: Breaking the Glass Ceiling and Predictive Vortex Simulation

The most dramatic feature of superconductors is their unique ability

to carry large electrical currents without resistance or energy loss. This feature, if fully understood and controlled, has transformative potential for the generation, delivery, and use of energy in the electric grid. The maximum resistance-less current, or “critical current,” however, is limited by the correlated motion of superconducting vortices, flexible tubes of magnetic field surrounded by circulating supercurrents (see Figure A.3-2). Vortices experience two kinds of correlation: long-range mutual repulsion and short-range attraction to pinning defects such as impurities, dislocations, or second phases that take the form of points, lines, and extended volumes. The critical current of superconductors has always been limited to 25–30% of its theoretically expected value, for both conventional and high-temperature superconductors, sometimes called the “glass ceiling.” Mastering this artificial glass ceiling requires understanding and controlling the interplay of these two powerful correlations.

The glass ceiling was convincingly broken in 2013, when Jia et al. doubled the critical current of state-of-the-art commercial superconductors by introducing additional

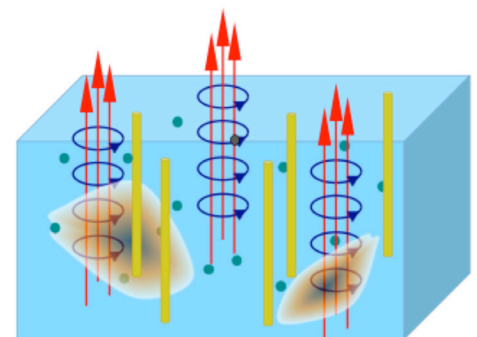


Figure A.3-2. Superconductor (blue) containing line-like vortices (red magnetic field lines) surrounded by blue circulating supercurrents and defects in the form of points (green), lines (yellow), and extended 3D second phases (shaded brown). Correlation among vortices due to their mutual long-range repulsion and the combined interaction of many defects on a single vortex controls the critical current of superconductors.

point pinning defects by irradiation with 4-MeV protons. The critical current rose monotonically with point defect density to twice the value of the best unirradiated commercial superconductors. This is a landmark discovery for basic science, revealing the unexpected power of point defects to control the critical current. It is also a landmark discovery for applications, with the potential to cut the cost of commercial deployment of superconducting wire by nearly a factor of two, opening a new horizon of inexpensive superconducting applications. These results introduce new scientific challenges: understanding why point defects have such a dramatic effect on vortex correlation in an already complex pinning landscape, and what the ultimate limit on critical current actually is.

A new approach to simulating the dynamic behavior of large arrays of vortices and pinning defects promises to answer these fundamental questions of correlation. Time-dependent Ginzburg-Landau simulations avoid the complications of parameterizing the position and motion of each vortex in a large array; instead, they describe the superconductor by its superconducting order parameter expressed as a continuous field, with vortices tracked as zeros of the order parameter and pinning defects represented by depressions of the order parameter. This approach puts correlations due to long-range mutual vortex repulsion and short-range vortex attraction to pinning defects on the same footing, allowing their interactions to be captured much more precisely than has been previously possible. The order parameter approach automatically includes many other critical effects such as elastic vortex line flexibility, vortex line cutting and reconnecting that often accompany vortex motion, and the temperature dependence of pinning strength; these features are normally left out of simpler formulations. Recent advances in high-performance computing enable this new approach.

The time-dependent Ginzburg-Landau formulation promises a new horizon in predictive simulation of superconducting vortex dynamics and rational design of pinning landscapes containing a diversity of pinning defects that produce macroscopic critical currents with targeted magnitude, temperature dependence, and anisotropy.

Charged Polymers

Charged polymers, or “polyelectrolytes,” display a host of striking correlation phenomena, driven by the long-range electrostatic attraction and repulsion of the charges attached to their backbones. The flexibility of the polymer chain dramatically enhances the range of possible structural correlations, including folding in polymers with opposite charges on the same chain and extension or straightening of polymer chains with like charges. The addition of simple salts to the charged polymer solution introduces local screening by point-like counterions that mediate the longer-range interactions between charged polymer chains. A single charged polymer chain in a solution of counterions undergoes phase transitions between collapsed and extended states mediated by the shielding of the counterions. An array of charged polymer chains in solution displays collective behavior such as precipitation to an ionic solid or liquid phase separation into a polymer-rich liquid phase, or “coacervate,” and solvent-rich liquid phase (Figure A.3-3). The strong electrostatic correlations can be designed to drive layer-by-layer growth of polymer composites or self-assembly of hierarchical structures (Figure A.3-4). Molecular dynamics simulations are beginning to describe the rich structural, dynamical, and functional complexity of polyelectrolyte complexes.

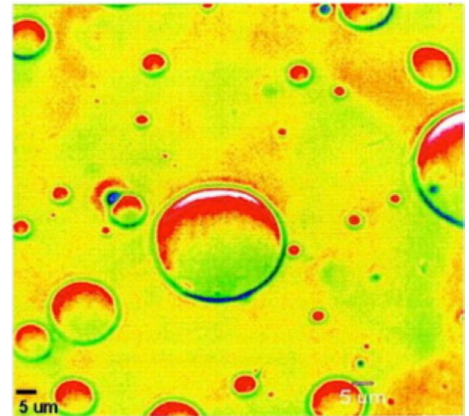


Figure A.3-3. Fluorescence microscopy of coacervate suspension composed of the polyelectrolyte poly(dimethyldiallylammonium chloride) (PDADMAC) and bovine serum albumin (BSA). (Kizilay et al., 2011)

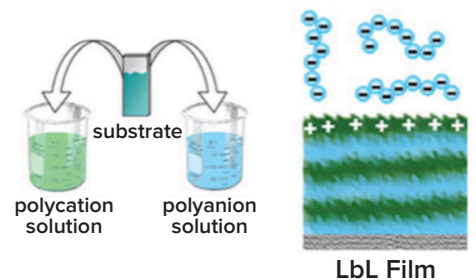


Figure A.3-4. The construction of layer-by-layer films from the alternating adsorption of positively and negatively charged polyelectrolytes from water solutions on a substrate. (Hammond, 2011)

The possibilities for understanding, and ultimately controlling, electrostatic correlation among charged polymer chains and point-like counterions are fundamental science challenges with rich application potentials. Polyelectrolyte complexes display a remarkable range and versatility, promising the development of “smart” materials that respond to electric fields, the creation of selective ion-conducting membranes, the design of electrochemical interfaces, and the enabling of flexible protective encapsulation. This emerging field is just beginning to yield its rich basic science and application secrets.

OUTLOOK

Correlation arising from long- and short-range interaction presents a broad, fertile, and exciting horizon. We are beginning to unlock the mysteries of electrostatic correlation due to Coulomb interaction in correlated electrons in metals and charged polymer chains in solution, and of electrodynamic correlation among superconducting vortices and pinning defects. There are many additional sources and outcomes of correlation, including spatial correlations among charge orbitals and spin states, chemical correlations from hydrophilic and hydrophobic interactions, and temporal correlations of functional nanoscale components mediated by exchange of charges, spins, or photons. Correlation and the emergence of the new phenomena it drives are wellsprings of scientific discovery and innovation, ripe for the harnessing of new functionalities and applications.

A.4

How Can We Master Energy and Information on the Nanoscale To Create New Technologies with Capabilities Rivaling Those of Living Things?

OVERVIEW

The nanoscale contains a diversity of attractive and repulsive forces capable of supporting a host of complex architectures. These forces span electrostatic, magnetic, hydrophilic, hydrophobic, van der Waals, hydrogen bonding, and mechanical, elastic, and plastic deformations. At the nanoscale, many of these interactions operate on approximately the same energy scale, comparable with the energy of thermal fluctuations. This rich variety of energetically compatible interactions and fluctuations among many degrees of freedom is a virtual “Lego® playroom” for assembling complex architectures. Biology exploits this playroom to build complex architectures with remarkable functionality using the simple guiding principles of mutation and natural selection. Although mutation produces a host of complex architectures, natural selection eliminates most of them, relentlessly choosing for survival only those with superior functionality. Artificial nanostructures cannot yet compete with biological nanostructures in complexity or functionality, perhaps because we have not yet tried all the mutations that biology has sampled in four billion years of evolution, and because we do not rigorously impose functionality as the single condition for continued development.

BREAKTHROUGHS

In recent years, we have begun to exploit coupled degrees of freedom at the nanoscale with a sophistication reminiscent of biology. Mechanical degrees of freedom allow clear distinctions among morphologically distinct states, such as “stretched,” “collapsed,” or “rotated.” These mechanically distinct states can then control other chemical, thermal, or electronic degrees of freedom. Biology often uses mechanical motion to mediate other functions, such as producing the chemical fuel adenosine triphosphate (ATP), folding proteins, and regulating

temperature. In the last five years, we have learned to accomplish similar functions in artificial nanoscale assemblies.

Artificial Molecular Motor

Figure A.4-1 shows an artificial, stand-alone molecular motor attached to a gold (111) surface. The motor can be made to rotate in a clockwise or counterclockwise direction by injecting an electron into different arms of the rotor. The motor consists of a tripodal molecular stator for vertical positioning and a five-arm molecular rotor resting on a ruthenium atom that acts as a ball bearing to permit rotation. Electron tunneling from a STM tip induces rotation. The rotation of the rotor is quantized in units of 24° , the angular period of the 15 energy minima formed by the three-legged stator and the five-armed rotor. The direction of rotation is determined by which arm receives the injected electron: clockwise for the single phenyl arm and counterclockwise for any of the four ferrocene arms. Unlike classical macroscale motors, the artificial molecular motor is quantized: tunneling of a single electron induces a single 24° rotational step.

This artificial molecular motor is reminiscent of the biological molecular motor that mediates the chemical synthesis of ATP, the fuel for many biological functions. The biological molecular motor drives motion with chemical fuel, a chemo-mechanical coupling. The artificial molecular motor described above drives motion with electron energy, an electro-mechanical coupling. The functionality of the artificial molecular motor resembles that of biological motors, a clear sign that we are beginning to learn the arts of design, synthesis, and operation of complex molecular machines. We are still far from biology’s level of sophistication, which not only creates such molecular motors, but also incorporates them into intricate hierarchical architectures that display multiple functionalities, such as

muscle contraction and temperature sensing in a finger or hand.

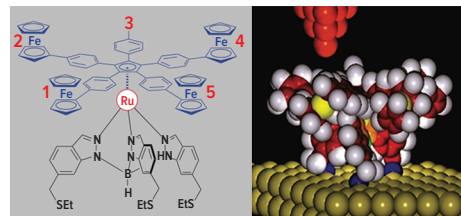


Figure A.4-1. A stand-alone artificial molecular motor consisting of a tripodal stator anchored to a gold (111) surface and a five-membered rotor consisting of four phenyl ring-ferrocene ring arms (labeled 1, 2, 4, and 5) and one phenyl ring arm (labeled 3) to provide structural asymmetry. The rotor turns on the stator through an atomic ruthenium ball bearing when activated by electron injection from a STM tip. Left: The molecular structure of the motor. Right: An atomic visualization, including the gold surface beneath and the STM tip above the motor. (Perera et al., 2013).

Folding Polymer Binds to Chlorine

Protein folding is a pervasive functionality in biology, relying on a single simple concept elaborated in many formats. Protein folding brings the isolated “active sites” of a coded linear polymer into close proximity, where they can interact with each other and perform specific functions such as selective catalysis of targeted chemical reactions or selective transmission of potassium ions or water molecules through a channel. Figure A.4-2 shows an artificial folding polymer or “foldamer” that wraps around isolated chlorine ions and removes them from the water solution, binding them with a strength six orders of magnitude higher than that of other mechanisms.

The foldamer is a chain of 15 rings with nine conventional carbon rings and six interspersed non-traditional hydrogen-bonding rings (triazoles, in red, see Figure A.4-2). In the presence of an isolated chlorine ion in solution, a combination of electrostatic and hydrophobic forces triggers the collapse of

the foldamer around the chlorine ion, with the hydrophobic faces bonding inward to the chlorine ion and the hydrogen bonding edges interacting outward with water molecules in solution. The remarkable effectiveness of the foldamer binding to chlorine arises from a combination of chemical degrees of freedom that promote bonding and mechanical degrees of freedom that promote folding, a common theme in biology.

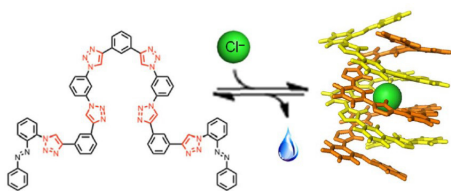


Figure A.4-2. Unfolded structure of an artificial polymer consisting of nine carbon rings and six nontraditional hydrogen bonding rings (triazoles, in red, left). In the presence of isolated chlorine ions, two foldamers wrap around each ion in a double helix formation, driven by hydrophobia of the ring faces and hydrogen bonding of the edges. (Hua et al., 2013).

Artificial Temperature Self-Regulation

One of the most sophisticated biological functionalities is sensing and regulating a targeted condition. The temperature regulation of the body and the regulation of blood sugar and blood pressure are examples. Recently, temperature self-regulation has been achieved in a system of artificial microscale materials exploiting chemo-mechanical coupling. The basic design and function are shown in Figure A.4-3. Flexible microfibers are partially embedded in a thermo-responsive hydrogel. In the “hot” or “on” condition, the hydrogel swells and expands vertically, pushing the tips of the microfibers into the top layer of a liquid bilayer. A catalyst that coats the tips of the microfibers makes contact with reactants in the top liquid layer and triggers a strong endothermic reaction, which absorbs heat and cools the hydrogel. The hydrogel shrinks to the “cold” or “off” configuration, the microfibers contract, their tips are removed from the upper liquid layer, and the reaction

stops, allowing the system to warm up. When the hydrogel swells and expands again, the cycle is repeated.

This kind of chemo-mechanical coupling controls temperature to within 2.6°C at 28°C and is made from simple artificial materials. Like many biological constructions, this hydrogel-catalyst-liquid bilayer architecture can be adapted to self-regulate a variety of targeted conditions including, for example, pH, light, glucose, and pressure. These variations in regulated condition are achieved by changing the parameter to which the hydrogel responds and the chemical reaction that is catalyzed in the “on” state. This rather sophisticated and versatile example of self-regulation based on chemo-mechanical coupling begins to have the look and feel of biological functionality.

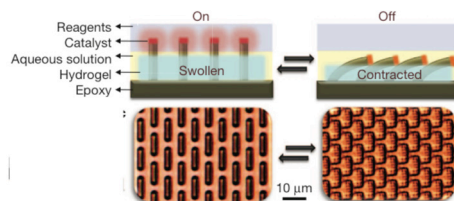


Figure A.4-3. A self-regulating system exploiting chemo-mechanical coupling to self-regulate temperature. Left: When hot or “on,” the hydrogel stiffens and expands vertically, pushing the exposed tips of the microfibers into the top layer of a liquid bilayer. On cooling, the hydrogel shrinks and the microfibers contract, stopping the reaction and allowing the system to warm, and the cycle is repeated. (He et al., 2012).

OUTLOOK

Biology remains the paragon, model, and inspiration for complex, hierarchical, functional materials architectures. Artificial materials are achieving remarkable new levels of complexity, though still far from the elaborate hierarchical complexity of biology. Beyond complexity, we are beginning to create functionality, reminiscent of the more focused, practiced, and advanced functionality of biology. Such complexity and functionality require coupling chemical, optical, electronic, magnetic, mechanical, and thermal

degrees of freedom. We are beginning to master these rich and endlessly creative opportunities, taking advantage of the unusual overlap in energy scales of these interactions in nanometer-scale settings. Biology is an excellent inspiration, yielding its strategic concepts and guiding principles, as well as its operational tactics, to our ever more sensitive experiments and sophisticated simulations. As we develop the tools to unravel biology’s most important secrets and remarkable successes in harnessing complexity for functionality, we can look forward to equally rich and expansive achievements in applying biology’s lessons to artificial energy materials, and even ultimately exceeding biology’s capabilities.

A.5

How Do We Characterize and Control Matter Away—Especially Very Far Away—from Equilibrium?

OVERVIEW

The equilibrium state of matter, where there are no gradients or flows of matter, charge, spin, or energy, is characterized by a simple and elegant principle: the free energy of the equilibrium state is lower than all other states of the system. This singular condition uniquely identifies the equilibrium state and allows it to be found by minimizing an analytic or numerical expression for the free energy. By contrast, there is a profusion of non-equilibrium or excited states of matter, each with its own lifetime and decay routes to the equilibrium state. There are no guiding principles for identifying which of the many possible non-equilibrium states an excited system will occupy, or which of the many possible decay routes the system will take to achieve equilibrium. Although we know much less about them, non-equilibrium states are much more prevalent in nature than equilibrium states. Virtually everything interesting that happens in the universe is a result of departures from equilibrium. Such departures represent energy that is available to drive system dynamics and create functionality. The question is how to understand enough about far-from-equilibrium evolution to be able to harness it for useful purposes, or to design around it where it cannot be controlled or accurately predicted.

Beyond the non-equilibrium state itself, the return of the non-equilibrium state to equilibrium is of high interest and critical importance. Typically, there are a host of possible return paths, many of which contain metastable intermediate states that are long-lived and impart special character to the system. The laser is an example of relaxation to equilibrium through long-lived intermediate states that synchronize their decay to produce coherent light of precisely defined energy. Other familiar examples of non-equilibrium states include artificially layered materials, supercooled and supersaturated liquids, and glasses of various kinds, all of which display behavior that cannot be accessed in equilibrium materials.

The behavior of non-equilibrium systems is a broad topic and an enduring challenge because non-equilibrium systems cannot be effectively treated with a small set of general principles. Numerous methods are used to describe them, each tailored to essential aspects of the behavior at an appropriate scale. Although this Grand Challenge is driven by the lofty quest for general guiding principles applicable to all non-equilibrium behavior, progress comes in smaller increments associated with understanding the behavior of particular non-equilibrium materials. With the advent of x-ray free electron lasers, we are gaining access to non-equilibrium electronic behavior on ultrafast timescales; computer codes simulating non-equilibrium behavior are becoming ever more powerful; and we are learning to use smart materials to harness non-equilibrium behavior.

BREAKTHROUGHS

Over the past decade, impressive progress has been made in understanding, characterizing, describing, and controlling non-equilibrium systems. These advances have been facilitated by new characterization techniques combined with specially designed experimental equipment, and by continually improving computational capabilities. The breadth of non-equilibrium behavior spans a large range in spatial and temporal scales, in scope, and in approach.

Ultrafast Non-equilibrium Behavior

Probing short-time, inherently non-equilibrium pathways of fast chemical reactions or electron transfer requires ultrafast spectroscopic techniques. The new capabilities of free electron lasers to carry out femtosecond time-resolved x-ray photoelectron spectroscopy provide an atomic-scale perspective of ultrafast interfacial charge transfer. Figure A.5-1 shows charge transfer dynamics in hybrid molecule-semiconductor interfacial materials monitored with time-resolved pump-probe experiments on femtosecond timescales, and simulated with constrained

density functional theory. The ultrafast experiment and simulation show evidence of a transient, excited electronic state formed at the interface within the first picosecond after excitation. This interfacial, transient, excited electronic state mediates transfer of the photoexcited electron from the dye to the semiconductor substrate, providing a mechanism to tune the efficiency of the process and an explanation for the large differences in electron transfer efficiency for different substrates paired with the same dye molecule. These results show the promise of free electron lasers to elucidate the behavior of far-from-equilibrium charge-transfer systems at their extremely small spatial and temporal scales.

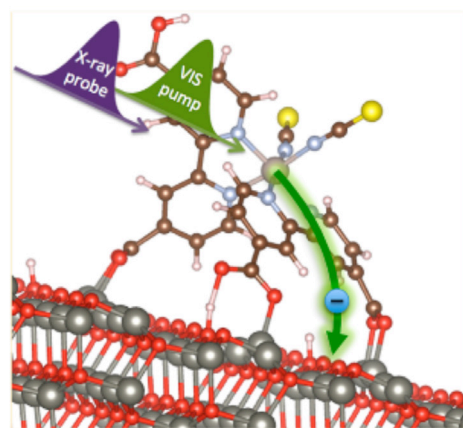


Figure A.5-1. Excitation of the interface between a ruthenium-based dyed N_3 molecule and a ZnO semiconductor excited by a laser pulse (green) and probed by ultrafast x-ray pulses from the Linac Coherent Light Source (LCLS) free electron laser. (Siefermann et al., 2014)

Unconventional Precipitation

Precipitation of solids from solution is one of the oldest, most pervasive, and most important non-equilibrium phenomena in chemistry, spanning growth of single crystals, reactive flow of subsurface water in geology, absorption of nutrients in the blood, and biomineralization of shells, bones, and teeth. Computer simulations have recently revealed a novel far-from-equilibrium precipitation

mechanism in highly oversaturated calcium carbonate aqueous solutions, illustrated in Figure A.5-2. Instead of directly forming crystalline calcium carbonate from solution by conventional nucleation and growth, molecules of calcium carbonate cluster in the liquid to form dense regions of nanoscale hydrated calcium carbonate. These dense regions then aggregate further and dehydrate, producing an amorphous solid that is the precursor to the crystalline solid. This non-equilibrium precipitation route is entirely different from conventional fluctuation-driven nucleation and growth of crystalline structures, going through dense liquid and amorphous solid stages before the crystalline material emerges. This advance implements sophisticated molecular dynamics simulations coupled with advanced algorithms to efficiently search the free-energy landscape to identify likely accessible intermediate, metastable states. It illustrates the power and utility of state-of-the-art simulations as discovery science tools.

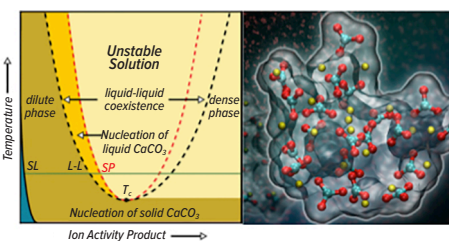


Figure A.5-2. Cartoon showing the clustering of calcium carbonate molecules in solution to form a dense liquid phase before dehydrating to form an amorphous solid phase that converts to the crystalline phase (right), and the liquid-liquid phase diagram of the new phenomenon (left). (Wallace et al., 2013)

Combustion

Combustion for energy generation is an example of a far-from-equilibrium and highly complex process that begs for control. A recent advance was achieved through the use of soft x-ray synchrotron methods to identify reaction intermediates, which can then be used to verify computer codes that model the multistep, multipathway process by which butanol is combusted. Butanol is a potentially important biofuel, and the ability to accurately predict combustion chemistry with verified computational models will speed assessment of proposed new fuels.

Arresting Thermal Runaway

The Li-ion battery is a quintessentially far-from-equilibrium system. Its design and performance depend on harnessing departures from equilibrium, while the extreme non-equilibrium phenomena needed for high power create a challenge for safety and reliability. Overheating of Li-ion batteries triggers a runaway chemical reaction between metal oxide cathodes and liquid electrolytes that can cause fire and explosion. A novel approach to arresting this extreme non-equilibrium behavior uses thermoresponsive microspheres of polyethylene or paraffin wax as a smart barrier to Li-ion transport. Microspheres incorporated onto the anode of a Li-ion battery (see Figure A.5-3) leave abundant inter-sphere pores for electrolyte-electrode contact and do not adversely affect normal battery performance. On heating above a preset threshold, however, the microspheres melt, and the liquid polyethylene (PE) or paraffin coats the anode with an ionic insulating layer, producing rapid irreversible shutdown of battery operation.

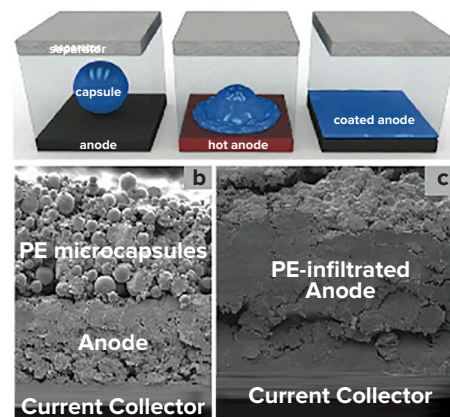


Figure A.5-3. Top: Concept for autonomous shutdown of Li-ion battery operation on overheating by melting polyethylene (PE) microspheres, which then infiltrate the anode and block Li-ion conduction. Bottom: Scanning electron microscopy images of the pre-melted (left) and post-melted (right) states of the anode. (Baginska et al., 2012)

OUTLOOK

The advances described above show foundational progress in understanding and controlling far-from-equilibrium behavior in specific cases. Ultrafast, highly coherent laser and x-ray pulses are a major advance, with the potential to transform our knowledge and understanding of non-equilibrium electron behavior, including electron transfer in chemical reactions; excitation and relaxation of electrons in atoms, molecules, and solids; and coupling of ultrafast electron motion with much slower atomic motion. Liquid-liquid phase separation points the way to a new class of non-equilibrium precipitation phenomena mediated by entirely different principles than conventional nucleation and growth. Combustion and Li-ion batteries are far-from-equilibrium phenomena of fundamental importance to energy efficiency, conversion, and use. As we understand the behavior and extract the governing principles of these phenomena, we extend the breadth and depth of our far-from-equilibrium knowledge base.

Critical universal questions, however, remain to be solved in this Grand Challenge.

- ▶ By what mechanisms and how fast do far-from-equilibrium systems evolve?
- ▶ Are there barriers to reaching equilibrium or metastable states in which the system can be trapped?
- ▶ How can we harness or manipulate transformations driven by disequilibrium?

Although we have made great progress in unraveling the nature of non-equilibrium behavior for particular phenomena, we still face ripe challenges and opportunities to identify universal features of non-equilibrium behavior spanning broad classes of phenomena. These challenges and opportunities have much greater potential to impact science and our daily lives than the pioneering advances in understanding and controlling the equilibrium states of matter that were hallmarks of twentieth-century science.

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