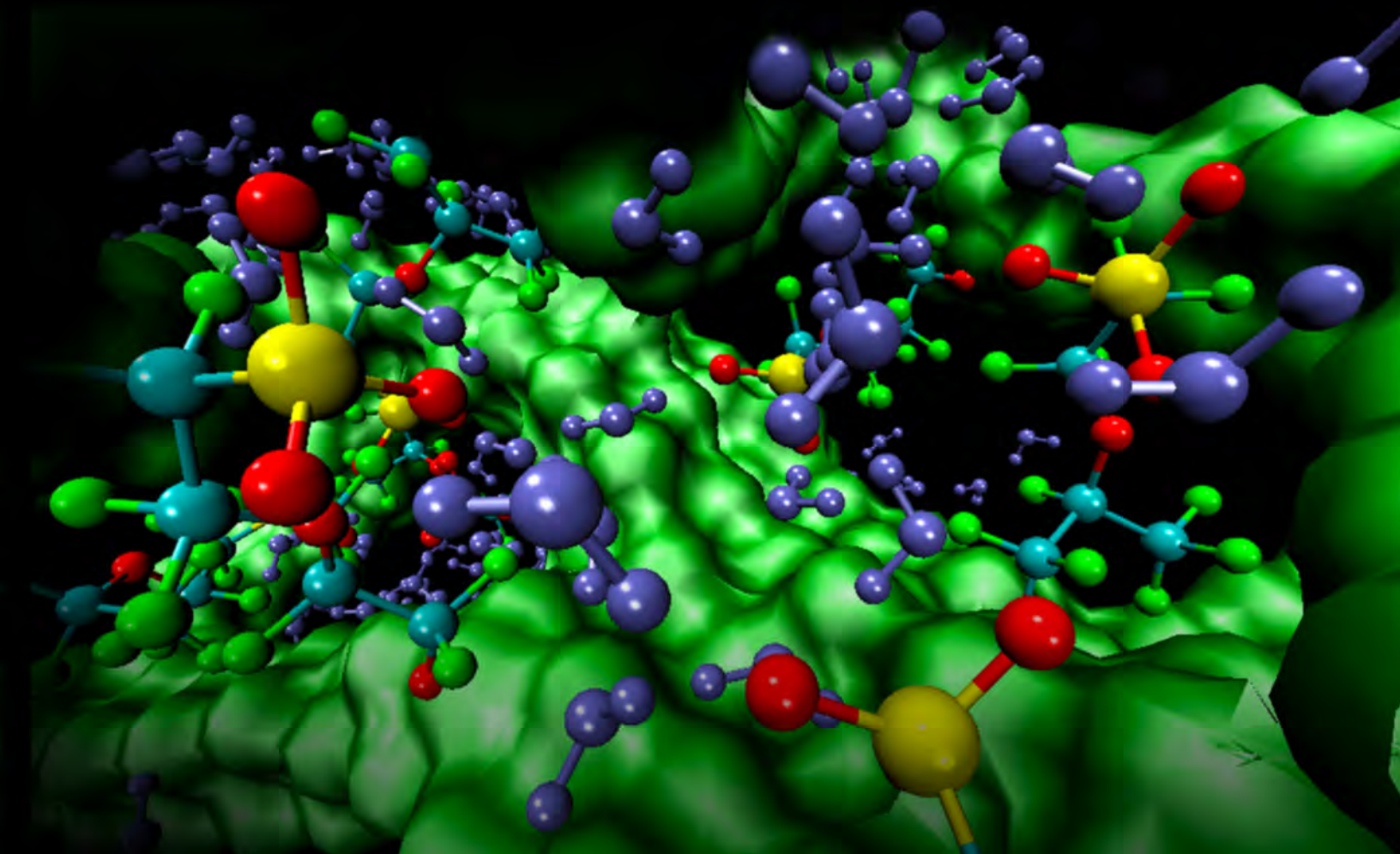SEPTEMBER 2012

FROM QUANTA TO THE CONTINUUM: OPPORTUNITIES FOR MESOSCALE SCIENCE

A REPORT FOR THE BASIC ENERGY
SCIENCES ADVISORY COMMITTEE
MESOSCALE SCIENCE SUBCOMMITTEE

About the Department of Energy's Basic Energy Sciences Program

Basic Energy Sciences (BES) supports fundamental research to understand, predict, and ultimately control matter and energy at the electronic, atomic, and molecular levels. This research provides the foundations for new energy technologies and supports DOE missions in energy, environment, and national security. The BES program also plans, constructs, and operates major scientific user facilities to serve researchers from universities, national laboratories, and private institutions.

About the "Basic Research Needs" Report Series

Over the past ten years, the Basic Energy Sciences Advisory Committee (BESAC) and BES have engaged thousands of scientists from academia, national laboratories, and industry from around the world to study the current status, limiting factors, and specific fundamental scientific bottlenecks blocking the widespread implementation of alternate energy technologies. The reports from the foundational Basic Research Needs to Assure a Secure Energy Future workshop, the following ten "Basic Research Needs" workshops, the panel on Grand Challenge science, and the summary report New Science for a Secure and Sustainable Energy Future detail the key basic research needed to create sustainable, low carbon energy technologies of the future. These reports have become standard references in the scientific community and have helped shape the strategic directions of the BES-funded programs (http://www.sc.doe.gov/bes/reports/list.html).

About this Report

Over the course of this study the Mesoscale Science Subcommittee of the Basic Energy Sciences Advisory Committee engaged hundreds of colleagues in town hall meetings, webinars, and web site interactions in order to identify important and timely priority research directions for mesoscale science, as well as the capabilities required to address these challenges. This report outlines the need, the opportunities, the challenges, and the benefits of mastering mesoscale science. Further information can also be found at www.meso2012.com.

ON THE COVER

Simulation showing water molecules (purple) and acid groups (yellow and red) in the confined environment of a separations membrane (green) relevant to many energy technologies. To understand and control the selectivity of the separation process and the degradation of membranes and electrolytes in complex electrochemical environments, we need to understand the mesoscale membrane/liquid interface in addition to understanding molecular level details of transport and reactivity. The figure illustrates these different scales. Source: Michel Dupuis and Ram Devanathan, Pacific Northwest National Laboratory.

FROM QUANTA TO THE CONTINUUM: OPPORTUNITIES FOR MESOSCALE SCIENCE

*A Report from the
Basic Energy Sciences Advisory Committee*

Chair:
John Hemminger
University of California, Irvine

U.S. Department of Energy

September 2012

Prepared by the BESAC Subcommittee on Mesoscale Science

Co-chairs:
George Crabtree
Argonne National Laboratory and University of Illinois at Chicago
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Los Alamos National Laboratory

Basic Energy Sciences Advisory Committee

Subcommittee on Mesoscale Science

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Table of Contents

Executive Summary

We are at a time of unprecedented challenge and opportunity. Our economy is in need of a jump start, and our supply of clean energy needs to dramatically increase. Innovation through basic research is a key means for addressing both of these challenges. The great scientific advances of the last decade and more, especially at the nanoscale, are ripe for exploitation. Seizing this key opportunity requires mastering the mesoscale, where classical, quantum, and nanoscale science meet. It has become clear that in many important areas the functionality that is critical to macroscopic behavior begins to manifest itself not at the atomic or nanoscale but at the mesoscale, where defects, interfaces, and non-equilibrium structures are the norm. With our recently acquired knowledge of the rules of nature that govern the atomic and nanoscales, we are well positioned to unravel and control the complexity that determines functionality at the mesoscale. The reward for breakthroughs in our understanding at the mesoscale is the emergence of previously unrealized functionality. The present report explores the opportunity and defines the research agenda for mesoscale

- Imagine the ability to manufacture at the mesoscale: that is, the directed assembly of mesoscale structures that possess unique functionality that yields faster, cheaper, higher performing, and longer lasting products, as well as products that have functionality that we have not yet imagined.

- Imagine the realization of biologically inspired complexity and functionality with inorganic earth-abundant materials to transform energy conversion, transmission, and storage.

- Imagine the transformation from top-down design of materials and systems with macroscopic building blocks to bottom-up design with nanoscale functional units producing next-generation technological innovation.

This is the promise of mesoscale science.

science—discovering, understanding, and controlling interactions among disparate systems and phenomena to reach the full potential of materials complexity and functionality. The ability to predict and control mesoscale phenomena and architectures is essential if atomic and molecular knowledge is to blossom into a next generation of technology opportunities, societal benefits, and scientific advances.

Mesoscale science and technology opportunities build on the enormous foundation of nanoscience that the scientific community has created over the last decade and continues to create. New features arise naturally in the transition to the mesoscale, including the emergence of collective behavior; the interaction of disparate electronic, mechanical, magnetic, and chemical phenomena; the appearance of defects, interfaces and statistical variation; and the self-assembly of functional composite systems. The mesoscale represents a discovery laboratory for finding new science, a self-assembly foundry for creating new functional systems, and a design engine for new technologies.

The last half-century and especially the last decade have witnessed a remarkable drive to ever smaller scales, exposing the atomic, molecular, and nanoscale structures that anchor the macroscopic materials and phenomena we deal with every day. Given this knowledge and capability, we are now starting the climb up from the atomic and nanoscale to the greater complexity and wider horizons of the mesoscale. The constructionist path up from atomic and nanoscale to mesoscale holds a different kind of promise than the reductionist path down: it allows us to re-arrange the nanoscale building blocks into new combinations, exploit the dynamics and kinetics of these new coupled interactions, and create qualitatively different mesoscale architectures and phenomena leading to new functionality and ultimately new technology. The reductionist journey to smaller length and time scales gave us sophisticated observational tools and intellectual understanding that we can now apply with great advantage to the wide opportunity of mesoscale science following a bottom-up approach.

Realizing the mesoscale opportunity requires advances not only in our knowledge but also in our ability to observe, characterize, simulate, and ultimately control matter. Mastering mesoscale materials and phenomena requires the seamless integration of theory, modeling, and simulation with synthesis and characterization. The inherent complexity of mesoscale phenomena, often including many nanoscale structural or functional units, requires theory and simulation spanning multiple space and time scales. In mesoscale architectures the positions of individual atoms are often no longer relevant, requiring new simulation approaches beyond density functional theory and molecular dynamics that are so successful at atomic scales. New organizing principles that describe emergent mesoscale phenomena arising from many coupled and competing degrees of freedom wait to be discovered and applied. Measurements that are dynamic, *in situ*, and multimodal are needed to capture the sequential phenomena of composite mesoscale materials. Finally, the ability to design and realize the complex materials we imagine will require qualitative advances in how we synthesize and fabricate materials and how we manage their metastability and degradation over time. We must move from serendipitous to directed discovery, and we must master the art of assembling structural and functional nanoscale units into larger architectures that create a higher level of complex functional systems.

While the challenge of discovering, controlling, and manipulating complex mesoscale architectures and phenomena to realize new functionality is immense, success in the pursuit of these research directions will have outcomes with the potential to transform society. The body of this report outlines the need, the opportunities, the challenges, and the benefits of mastering mesoscale science.

Introduction

The immense diversity of materials in the macroscopic world—hard, soft, viscous, conducting, insulating, magnetic, liquid, and gaseous—is made up of only a hundred or so distinct kinds of atoms representing the elements of the periodic table. The differences in the size, complexity, and operating principles of atoms and macroscopic materials are enormous. Atoms are one-tenth of a nanometer in size, have a relatively simple structure composed of negatively charged electrons circulating a positively charged nucleus in well-defined orbits, and obey the "digital" rules of quantum mechanics, where energy, charge, and mass are quantized in indivisible fundamental units. The macroscopic materials we encounter every day are tens of microns or more in size—at least 100,000 times larger than atoms—and display dramatically more complex structures and behavior obeying the "analog" rules of continuous classical mechanics, where energy, charge, and matter are, for all practical purposes, continuous and infinitely divisible. The enormous differences separating atoms and bulk materials appear at first sight to be irreconcilable. They are connected, however, by a sequence of mesoscale architectures and phenomena that form, step by step, a staircase reaching from atoms to bulk materials that can be experimentally observed, theoretically understood, and ultimately physically controlled. Mesoscale science entails the observation, understanding, and control of these intermediate-scale architectures and phenomena. It will ultimately lead to next-generation materials and technology that provide innovative solutions to pervasive societal problems including energy security, environmental sustainability, climate change, and enduring economic growth.

Hallmarks of Mesoscale Behavior

The emergence of mesoscale behavior from nanoscale origins is marked by distinctive features in the role of atomic granularity of matter, quantization of energy, collective behavior of many identical units, interaction of disparate degrees of freedom, the appearance of defects, fluctuations and statistical variation, and heterogeneity in structure and dynamics. These hallmarks of mesoscale behavior distinguish it from the adjacent realms of quantized nanoscale behavior at smaller scales and continuous macroscopic behavior at larger scales.

At nanoscale dimensions, the size of atoms (0.1 nm) and the typical spacings between them (0.5 nm) are dominant features. The atomic granularity of matter and the exact positions of individual atoms are key determinants of nanoscale structure and dynamics. At mesoscale dimensions of order ten to a hundred times the typical atomic spacing, the presence of individual atoms is less obvious and their impact less significant. Mesoscale behavior is captured by the average density of atoms in a volume containing thousands of atoms, and their associated fluctuations. In these ensembles, the exact positions of individual

atoms are often not important and may not even be known. Dependence of behavior on the average density of atoms instead of their exact positions is a hallmark of mesoscale behavior.

Quantization of energy rules the behavior of nanoscale systems, where energies fall into discrete, quantized levels separated by large forbidden gaps not accessible to the system. The large spacing between quantized energy levels prevents the system from responding to stimuli in its environment that have smaller energies, such as temperature, light, or electric and magnetic fields. At larger mesoscale dimensions, the spacing between energy levels falls, following the "particle in a box" analogy (see sidebar "The Particle in a Box" at right), until it becomes smaller than other relevant energies. Access to many densely spaced energy levels at the mesoscale opens a broad array of potential responses of the system, significantly enriching the diversity of interactions with the environment and with neighboring components.

Collections with a large number of members such as electrons, atoms, or magnetic moments behave in ways that individual or small numbers of members cannot. Flocks of birds, schools of fish, and packs of wolves are examples from the animal world displaying collective behavior that is qualitatively different, more effective and more functional than that of individual members. Similar kinds of collective behavior apply to nanoscale components. The electric fields of point charges, for example, are screened by rearrangement of surrounding itinerant charges in metals, semiconductors, and ionic solutions. To achieve full screening, the size of the system

The Particle in a Box

Every beginning student of physics, chemistry, and materials science learns the "particle in a box," one of the few elementary and exactly solvable problems of quantum mechanics and a simple, engaging illustration of the transition from nano to meso. Quantum mechanics tells us that the energy of an electron confined to a box of width a (of nano- or mesoscale dimensions) is quantized—it can assume only discrete values, given by the simple formula indicated in the figure (see caption for details). In practice, only the lowest energy levels are occupied.

The central point is that as the size of the box increases from nano to meso, the spacing between allowed energy levels shrinks and they become dramatically denser, giving the electron much greater choice in levels to occupy and much more flexibility in its behavior. The freedom of a larger box with dense energy levels allows the electron to participate in new phenomena, a primary reason for the greater range and complexity of mesoscale over nanoscale behavior. As the box grows to macroscopic size, the spacing between allowed energy levels shrinks to insignificant values and energy becomes effectively continuous, smoothly joining to the classical mechanics that governs the familiar macroscopic world.

The higher density of allowed energy levels at the mesoscale compared to the nanoscale is the root of many hallmarks of mesoscale behavior. The collective behavior of many electrons, such as screening of point charges or strong correlation due to Coulomb repulsion, expresses subtle behavioral features that require closely spaced energy levels to convey. The statistical variation of mesoscale structure and dynamics is due to the many choices of states enabled by closely spaced energy levels, allowing small variations in configuration with little change in the energy; for nanoscale systems the wider spacing between energy levels drives up the energy cost of such variations or defects and they are correspond-

$$E = \frac{n^2 h^2}{8 m a^2}$$

with levels labeled $n=3$, $n=2$, $n=1$ and axis E, width a.
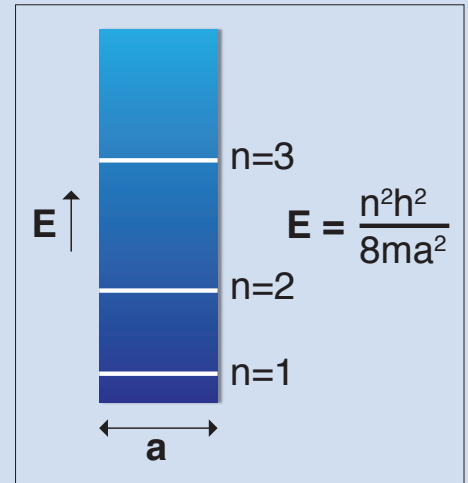
Quantized energy levels of an electron (of mass m) confined in a nanoscale or mesoscale box of width a. The electron can assume only discrete, quantized energy levels given by the formula above, where n is an integer (n=1, 2, 3…) and h is Planck's constant. For a nanoscale box, a ~ 1 nm, the electron has only a few widely spaced energy levels available to it, restricting its interactions with its surroundings. For a mesoscale box, a ~ 100 nm, the allowed energy levels are 10,000 times denser, dramatically increasing the interactions with neighboring particles and with temperature, light, and electric and magnetic fields in the environment.

ingly rare. The heterogeneity of mesoscale systems is likewise based on energy arguments: inserting a boundary between two distinct phases requires less impact on the densely packed energy spectrum of mesoscale systems than on the sparsely packed spectrum of nanoscale systems.

The particle in a box illustrates yet another connection between two key mesoscale hallmarks. The importance of atomic granularity and the quantization of energy track the size of the box and, therefore, each other as the size of the box grows. For boxes 100 times larger than atoms, for example, the positions and influences of individual atoms are hardly resolvable; simultaneously, the spacing between allowed energy levels falls to small values. Thus, these two key hallmarks of mesoscale behavior rise and fall together.

must be comparable to the screening length, which depends primarily on the density of itinerant charges. For semiconductors and ions in solution the screening length can be one to hundreds of nanometers, mesoscale lengths that modulate and enable the collective phenomena of screening. Collective behavior appears in every kind of variable, including electronic, ionic, mechanical, electromagnetic, and chemical, each described by its own mesoscale response and characteristic collective length.
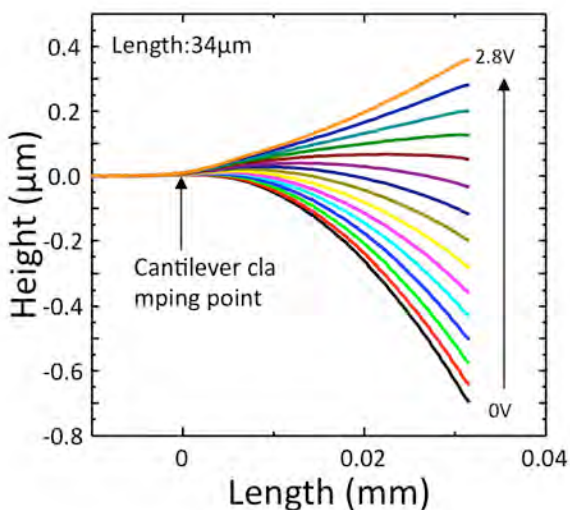
Mesoscale systems typically have many modes of response to stimuli in the environment, including physical deformation; chemical change; transport of electrons, ions, or heat; magnetic or electric polarization; and emission or absorption of light. Each of these modes corresponds to an independent degree of freedom, and within each degree of freedom the response can be mild or intense. At the mesoscale these responses become much richer and more developed, as the energy levels associated with each degree of freedom become densely packed and overlap with the levels belonging to other degrees of freedom.

The interaction of disparate degrees of freedom often produces profound outcomes. In metals, phonons associated with mechanical degrees of freedom normally scatter electrons and increase the resistivity. At low enough temperature, however, the electron-phonon interaction produces just the opposite effect—superconductivity, where the resistivity collapses to zero. Other examples of interacting degrees of freedom include electrochemistry for storage and release of electrons in chemical bonds, photochemistry for the conversion of light energy to chemical bond energy, photovoltaics for the conversion of light energy to electronic degrees

of freedom, spintronics for control of charge by magnetic fields (see sidebar "Giant Magnetoresistance: A Triumph of Mesoscale Science" on page 35) and piezoelectricity for conversion of applied voltage to mechanical displacement (see figure at left). These interacting degrees of freedom can be homogeneous, as in superconductivity where the electrons, phonons, and superconductivity coexist in the same physical space, or heterogeneous, as in solar cells where a semiconductor absorbs the photon, creates an excited electron, and passes it to metallic wires for transmission in an external circuit.

Imperfection and statistical variation constitute a mesoscale feature in sharp contrast to the relative perfection of nanoscale objects. Nanoscale systems are typically more perfect because they have fewer atoms, there are fewer ways for them to deviate from the perfect structure, and the energy cost of these deviations is relatively high. Mesoscale systems, in contrast, have many more atoms (a few thousand to a few hundreds of thousands or more) and more closely spaced energy levels, so that the energy cost of alternative configurations is relatively lower. As a result, defects are more common in mesoscale systems, and statistical variation about a mean is a universal feature of mesoscale behavior.

The variation of mesoscale systems has profound effects. While all electrons and all atoms of a given element are identical, copies of mesoscale systems vary in small details, the basis for biological mutation and evolution by natural selection. The defects in inanimate mesoscale materials are just as profound, disrupting

Interacting mesoscale degrees of freedom illustrating giant piezoelectricity, resulting in conversion of voltage to mechanical displacement. (Upper panel) Compound cantilever of Pt(60 nm)/$Pb(Mg_{1/3}$ $Nb_{2/3})O_3$-$PbTiO_3$ (270 nm)/$SrRuO_3$ (100 nm)/$SrTiO_3$ (13 nm). (Lower panel) Displacement of the cantilever tip vs. applied voltage. Source: S. H. Baek et al., *Science* **334**, 958 (2011).

the behavior of the otherwise perfect lattice by scattering electrons, preventing atoms from moving plastically in response to external stresses, and interrupting the transport of heat. Mesoscopic and larger lattices never show the mechanical, electrical, and thermal properties of a perfect lattice; instead, their macroscopic properties are determined by structural defects and imperfections separated by mesoscale distances.

On the positive side, meso- and macroscopic properties can be intentionally tailored by ntroducing specific kinds and densities of defects on meso length scales. On the negative side, the accumulation of defects at

Heterogeneous mesoscale self-assembly of a block copolymer (PS-b-PMMA) on a silicon wafer. The straight lines are patterned by a lithographic template. Source: Bryce Richter, University of Wisconsin, Madison (http://www.news.wisc.edu/newsphotos/epitaxial.html) and S. O. Kim et al., *Nature* **424**, 411-414 (2003).

the mesoscale often degrades the properties of materials, leading to crack formation and propagation and, ultimately, to macroscopic fracture and failure. This degradation can be rapid, as in the collision of two objects, or slow, as in the gradual decay of bridges and the performance of solar cells. Degradation science—observing, predicting, and mitigating degradation due to defect accumulation—is key to mesoscale science and has high societal impact.

The final mesoscale hallmark considered here is heterogeneity. Nanoscale systems are typically homogeneous, because introducing a boundary and creating two or more distinct phases costs energy. Nanoscale crystals tend to be single grain instead of multigrain, and nanoscale magnets likewise contain a single magnetic domain. Mesoscale systems, in contrast, are large enough to be heterogeneous (see figure at left) and, for example, to spontaneously break into coexisting phases at a first-order phase transition or retain an artificially constructed composite structure of two or more distinct components created by bottom-up self-assembly or top-down fabrication.

Mesoscale behavior establishes itself by many routes; there is no single hard and fast rule for defining its onset or its character. Mesoscale behavior reveals itself, however, by one or more of the hallmarks illustrated here: reduced influence of atomic granularity, diminished spacing between discrete quantized energy levels, collective behavior of many identical components, interaction of disparate degrees of freedom, the appearance of defects and statistical variation, and heterogeneity in structure and dynamics. The unifying element in these hallmarks is the very meaning of the Greek root *meso*: intermediate, in between, middle. Mesoscale behavior lies between the nanoscale world of atoms, molecules, and small assemblies with relatively perfect structure displaying simple behavior, and the macroscopic world of bulk materials with imperfect structure and endless variation, complexity, subtlety, and functionality.

Mesoscale Architectures

The staircase of mesoscale transitions from atomic, molecular, and nanoscale to the more familiar bulk macroscopic behavior is expressed through a hierarchy of architectures that organizes the constituent atoms and electrons into functional structures. At the atomic scale, two distinctly different types of architecture stand out: periodic lattices and covalent chemical bonds. At the mesoscale, a third architectgure emerges, biological membranes and cells, the building blocks for life. These architectures guide the course of the higher level mesoscale transitions, as illustrated below.

Periodic Lattices

For many materials, the basic organizing structure is a lattice of atoms, where the loosely bound outer atomic electrons are shared with many neighboring atoms to form a periodic array. The lattice of atoms creates a mechanical structure with its own mechanical responses, such as deformation and vibration, that are intrinsic to the lattice and depend on its crystallographic structure and composition. The mechanical

responses of the lattice are collective mesoscale phenomena with no analog in the behavior of individual atoms. Large enough crystals display heterogeneous structures, with grains of different orientation separated by grain boundaries, or isolated defects such as missing or interstitial atoms, dislocations, and stacking faults separated by mesoscopic distances. These heterogeneous structures and defects dramatically change the macroscopic electrical and thermal conductivity and the strength and ductility of the otherwise perfect lattice.

The mechanical structure of the lattice together with the loosely bound outer atomic electrons begets a second architecture: the electronic structure of the lattice, a set of electronic degrees of freedom distinct from the mechanical degrees of freedom. The electronic degrees of freedom appear as energy bands arising from the overlap of the outer electrons of the atoms and are capable of

producing an impressively wide range of behavior spanning metals, insulators, and semiconductors. Electrical conductivities vary over 20 orders of magnitude, depending on lattice structure and the electronic configuration of its constituent atoms. The electronic structure of lattices, like its mechanical behavior, is a collective response that is intrinsic to the lattice and has no analog in the behavior of its atomic constituents.

Although the lattice itself has a clear atomic granularity at nanoscale dimensions, the mechanical and electronic responses associated with the lattice become continuous as the lattice grows in size, the number of quantized energy levels proliferates, and the spacing between the quantized levels becomes arbitrarily small. This continuum of mechanical and electronic energy states for large lattices allows their properties to be described by familiar continuous formulations based on elasticity theory for mechanical properties (see figure at left) and by classical electrodynamics for electronic properties, where the natural variables are density of atoms or electrons instead of the positions of individual atoms or electrons. Thus, the lattice, the most basic architecture of solids, displays atomic granularity and quantized energy levels at nanoscopic scales, transitioning to continuous matter, energy, elasticity, and conductivity at larger scales, a hallmark of mesoscale behavior.

The mechanical and electronic degrees of freedom interact by scattering to produce resistivity that dissipates energy and impedes the motion of electrons through the lattice. At low temperatures, however, the electron-phonon interaction produces a very different and striking phenomenon: superconductivity, where resistivity collapses to zero and electrons move freely throughout the lattice without loss of energy. Superconductivity is rich with new mesoscale behavior, including new mesoscale objects—Cooper pairs and superconducting vortices—whose collective behavior is described by new meso length scales, the superconducting coherence length and magnetic penetration depth. Among known superconducting materials, these superconducting mesoscale lengths range from a few to hundreds of nanometers.

Magnetism takes mesoscale behavior a step further. Each atom in the lattice may have a local magnetic moment due to the orbital motion and spin of its inner shell electrons. The lattice structure brings these local moments close enough together to interact through dipolar and exchange interactions, which cause neighboring atomic moments to point in the same direction to form ferromagnets, or in opposite directions to form antiferromagnets. The large magnetic polarization energy of ferromagnetic domains limits their size, however, introducing a mesoscale magnetic length much larger than the atomic scale of the lattice structure but smaller than macroscopic lengths.

A host of mesoscale magnetic phenomena are enabled by the
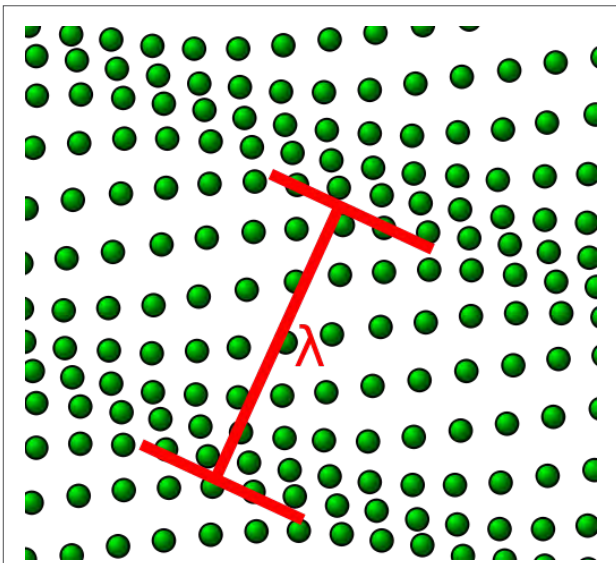
A periodic lattice of atoms showing the atomic granularity of matter in which mechanical responses such as elastic deformation are collective properties of the lattice structure. Source: Florian Marquardt, Wikimedia Commons.
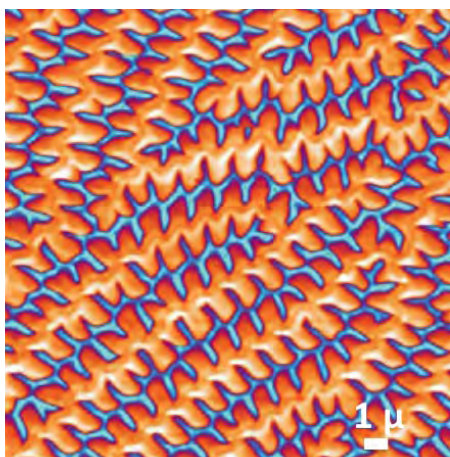
Magnetic domains on the surface of yttrium iron garnet film. Source: Del Mar Photonics (http://www.dmphotonics.com/Scanning_Probe_Microscopy/Magnetic%20structure%20of%20surface%20domains%20in%20Yttrium%20Iron%20Garnet%20(YIG)%20film.htm)

Chemical bonds between porphyrin complex on the left that donates electrons to the C_{60} complex on the right, which accepts and holds electrons for further chemical reactions. Source: Source: Liu et al, *J. Am. Chem. Soc.* **134**, 1938 (2012).

architecture of magnetic moments on a lattice, including polarization domains, polarization switching, hysteresis, and fluctuations (see figure above). The behavior of these mesoscale domains can be described by continuous formulations of magnetism, with magnetic moment density as the natural variable. These continuous formulations describe the macroscopic bulk behavior quite precisely with little or no need to reference their atomic and lattice origins.

The staircase of higher level architectures and phenomena arising from lower level structures is rich and pervasive. Ferroelectric degrees of freedom interact with ferromagnetic degrees of freedom to produce multiferroics, where magnetic fields switch electric polarization or vice versa. There are also magneto-elastic, chemomechanical, and photo-electric interactions, where strain affects the magnetic polarization or the rate of chemical reactions, and

photon absorption produces electron emission. The pattern continues throughout the mesoscale staircase: collective behavior produces new degrees of freedom and new characteristic length scales, which interact with other degrees of freedom to produce additional new levels of collective behavior and so on. Discovering the organizing principles at each level and applying them to design and control phenomena and functionality at higher levels are grand challenges of mesoscale science.

Chemical Bonds

Like the lattice, the chemical bond is a fundamental architectural element that underpins a host of macroscopic materials and phenomena. Chemical bonds fold outer shell electrons into tight configurations between two or at most a few neighbors to produce new molecules. Carbon dioxide and water are examples, the first being a linear molecule and the second, an angular molecule with hydrogen-oxygen bonds oriented at the precise angle of 105°. The rich diversity of chemically bonded structures extends from simple small molecules such as water and carbon dioxide to one-dimensional polymer chains that can be linked at their ends to form co-polymers and then cross-linked to produce two- or three-dimensional rigid or flexible networks. Solutions, suspensions, colloids, and foams are additional examples of architectures constructed of various kinds of chemical interactions.

The molecules and extended structures produced by chemical bonds differ from lattices in that they need not be periodic, and their electrons are usually confined to the bonding
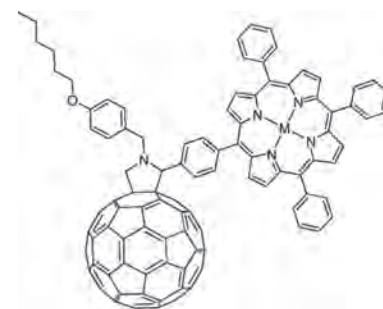
atoms. Like lattices, extended molecular structures have mechanical, thermal, magnetic, and ferroelectric degrees of freedom that interact to produce new architectures and phenomena. Unlike lattices, chemical bonds can connect chemical units of very different structure and function, such as joining porphyrin complexes that donate electrons to C_{60} buckyballs that accept and hold electrons for later use in chemical reactions (see figure above). Chemically bonded structures need not have a regular structure, allowing them wide freedom to configure locally to enhance a particular phenomena or functionality; in addition, they have chemical degrees of freedom that dynamically make or break bonds to change composition, configuration, and function and to release or store energy and electrons. The chemical bond is a primary mechanism for self-assembly of complex and functional mesoscale structures like mesoporous membranes, composites, photonic crystals, or polymer ferroelectrics. The versatility and scope of the chemical bond in molecules, polymers, and networks make it a pervasive and key architectural element for building functional mesoscale systems.

Architectures based on chemical bonds show the hallmarks of mesoscale behavior:

- polymers exhibit flexible line-like mechanical behavior that transcends atomic granularity;

- particle size directly affects spacing between quantized energy levels and the optical absorption and emission spectra of suspensions;

- electron transfer rearranges chemical bonds and couples structural, mechanical, electronic, and thermal degrees of freedom; and

- the role of defects, statistical variation, and heterogeneity is key to molecular systems such as solutions, ionic liquids, and colloids.

Membranes and Cells

Membranes composed of lipid bilayers are a basic architecture that supports an enormous number of biological phenomena and functionalities. The lipid bilayer is a derived architecture based on polymers with hydrophilic heads and hydrophobic tails, which are themselves composed of chemically bonded atoms. The presence of water encourages the polymers to line up head-to-head and tail-to-tail to form flexible membranes that can fold themselves into closed shapes

with topologically distinct insides and outsides (see figure below). The inside can be filled with proteins and other machinery that can be selected, organized, maintained and reproduced in a protected environment to accomplish specific functionalities such as energy production, locomotion, or communication with the outside by transporting ions and molecules through the cell wall.

The cell along with its internal mesoscale machinery is a remarkably versatile structural and functional module, the smallest unit of life. Single-cell bacteria are pervasive in the natural world from hydrothermal vents to radioactive waste to Antarctic ice cores, performing a host of functions such as creating and recycling nutrients; promoting digestion in humans, cockroaches, and termites; and fixing nitrogen from the atmosphere (see sidebar "Enlisting Bacteria as an Energy Workforce" on page 42). Stem cells (see figure at right) have the remarkable capability to develop into many different cell types during growth, such as a muscle cell, a red blood cell, or a brain cell.

Colonies of cells display collective behavior by signaling each other through chemical and physical means, and cells are the building
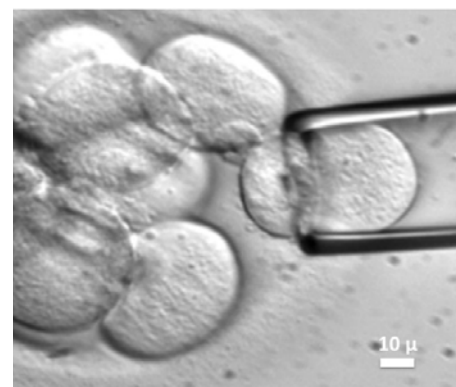
Micrograph of stem cell biopsy. Source: Y. Chung et al., *Cell Stem Cell* **2**, 113-117 (2008).

blocks of multicellular architectures that perform complex functions that a single cell cannot, such as muscle flexing and photosynthesis that require the interaction of disparate mechanical, chemical, and electronic degrees of freedom. Biology displays many compelling examples of the mesoscale staircase of architectures and functionalities (see sidebar "The Mesocale Inspiration of Biology" on page 10).

The Gap Between Top Down and Bottom Up

The assembly of mesoscale building blocks into higher level architectures and phenomena is a continuous process extending well beyond the dimensions that are natural for humans to manipulate. Biology has created living architectures as large as the Great Barrier Reef, which is over 2000 km long and dominates its regional environment by playing host to an enormous diversity of other living species. Geology has stratified the Earth's structure by density into a viscous mantle supporting floating tectonic plates that execute an intricate dance creating mountains and

Lipid bilayer folded into a closed cell with topologically distinct inside and outside. Biology uses the protected inside to contain mesoscale machinery to produce energy, transport cargo within the cell, and reproduce the cell. Source: Wikimedia Commons, http://commons.wikimedia.org/wiki/File:LiposFreome_scheme-en.svg.
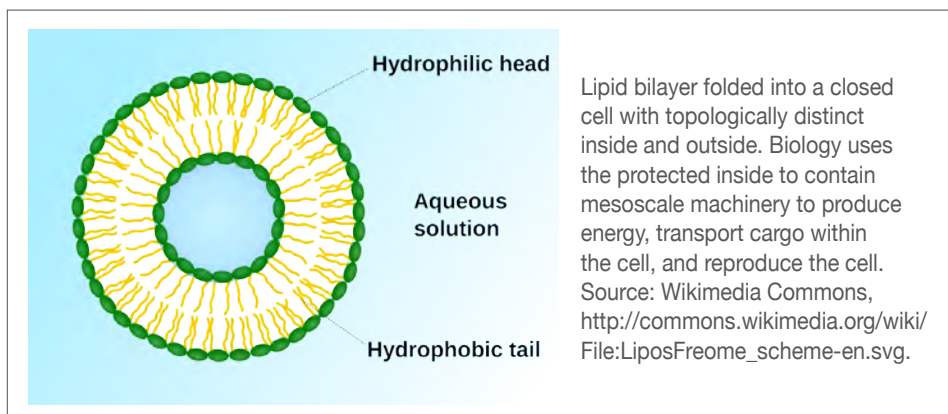
The Mesocale Inspiration of Biology

Biology displays many compelling features of mesoscale science. The building blocks of biology are cells, the smallest units of life, consisting of a lipid bilayer membrane deformed into a closed container with a collection of chemicals, polymers, and functional units on the inside and access to a diverse chemical environment on the outside. The machinery inside the cell produces energy in mitochondria to power the cell, moves cargo along cytoskeletal tracks to build and operate the cell, and transports molecules and ions like water, sugar, or calcium through channels in the cell wall to the environment.

The structures of cells—membrane, mitochondria, and cytoskeleton—define a versatile architecture adaptable to many tasks. At the same time, the cell is the building block for the next higher level of architecture: multicellular tissues such as blood vessels, bone, or muscle; the combination of disparate tissues into organs, such as the heart, the brain, and the stomach; and the combination of organs into independent plants or animals.

Each architectural level of biology produces a new level of complexity and functionality building on the levels below and contributing to the levels above. At the lowest levels, molecules and polymers obey quantum mechanics, where the granularity of atoms and the quantization of energy are dominant, features that give way to the continuous matter and energy of classical mechanics as the size of the system grows. Biology illustrates other mesoscale transitions as well:

- the interaction of disparate degrees of freedom, such as mechanical, electronic, ionic, and fluid, to create new phenomena and functionality;

- increasing complexity enabling greater functionality as the number and diversity of interacting units grow;

- the onset of statistical variation or "defects" in a collection of complex but nominally identical objects, the basis for mutation, natural selection, and evolution; and

- the integration of component parts into coordinated systems with heterogeneous structure and function that work harmoniously to produce a single composite functionality.

The staircase of increasingly complex architectures and functionalities exemplified by biology is a proof of mesoscale principles, and serves as a model and inspiration for inorganic mesoscale science. Mesoscale science, however, has the potential to go well beyond biology. Biology works primarily with bottom-up self-assembly of atoms and molecules, developing complex structures and functionalities from smaller and simpler building blocks over millions of years by mutation, natural selection, and evolution. Mesoscale science embraces not only bottom-up self-assembly but also top-down design and fabrication, starting with macroscopic materials that are cut to size as components and then assembled to a pre-conceived rational design. The promise of mesoscale science is joining bottom-up self-assembly with top-down rational design to produce targeted outcomes and functional systems using simple components, little waste, meso-, nano- or atomic level interconnects, high efficiency, and long life.

Unified bottom-up self-assembly and top-down rational design dramatically improve two features of biology: production of targeted, pre-conceived outcomes instead of random variations, most of which are ultimately discarded, and shortening of the development time for complex functional structures from the many generations required for biological evolution to a few years required for rational design and implementation.
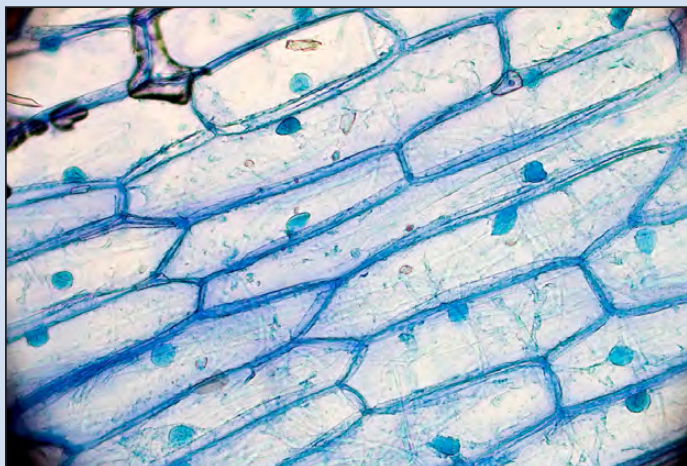
Cell structure of an onion scale, from an inner layer of the onion. Each cell is approximately 250 microns wide. Source: http://commons.wikimedia.org/wiki/File:Onion_Cells.jpg.

earthquakes as they shift and collide. Humans are learning to manipulate the bottom-up, self-assembled world, creating tools that operate well beyond the scale of our eyes and hands. Telescopes extend our vision to the very large and microscopes to the very small, while tools with greater resolution based on x-rays, electrons, neutrons, and scanning probes allow diffraction, imaging, and spectroscopy at the atomic scale.

While we can see the atomic scale with the aid of electron microscopes, we cannot yet build structures at the atomic and nanoscale with the latitude, flexibility, and precision of the top-down methods we use in the macroscopic world. These top-down methods allow the pre-conceived design of stand-alone functional units that we connect together with macroscopic links such as electrical wires, mechanical linkages, and channels for fluid flow. The smallest objects we can make with top-down methods are ~10 nm using electron beam lithography. Functional units requiring several top-down components are proportionately larger, well above the scale of bottom-up self-assembly.
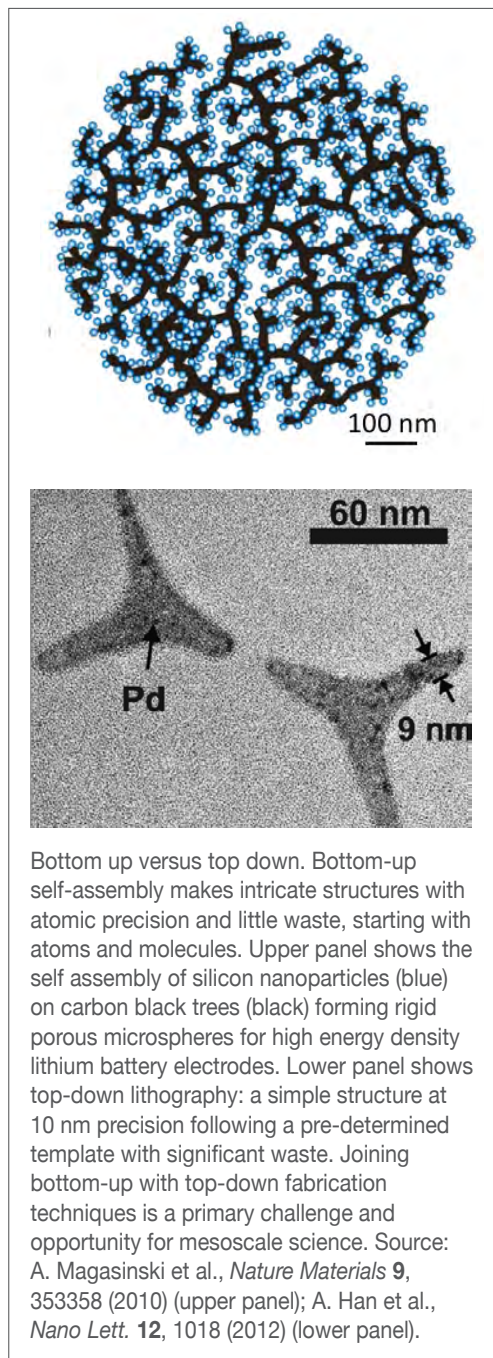
In contrast to top-down design and fabrication, bottom-up self-assembly starts with atoms and molecules to build architectures that support new phenomena and functionalities at larger scales. We are beginning to learn to use self-assembly, inspired in part by the examples of biology and geology. The complexity and functionality of the structures that we can self-assemble, however, pale in comparison to those of the natural world. Biology, in particular, has devised through trial and error a

dizzying number of types of cells and architectures for organizing them. Biological architectures accomplish a host of chemical, physical, electrical, mechanical, and energy conversion functionalities, using energy from the sun extracted by photosynthesis to power their self-assembled machinery. Biology and geology are beacons of inspiration, proving the principle and showing the way to a much richer, more functional, and more efficient self-assembly paradigm.

Top-down lithography and bottom-up self-assembly differ much more profoundly than just the size, complexity, and functionality of the structures they can make (see figure at right). They differ in operational philosophy as well. Top down starts with a large block of raw material and continuously whittles it away like a sculptor, leaving the final structure it wants and casting aside the unwanted detritus that often makes up the majority of the original block. Bottom up, however, uses only the atoms and materials that it needs, assembling them into functional units with little or no waste. Because bottom up works at smaller scales than top down, it gains the advantage of the relative perfection and reproducibility of its manufacturing process. In addition, bottom up connects functional units together directly at the atomic or mesoscale, without the need for extended wires, mechanical linkages, and channels for transporting electrons, force, and hydraulic or chemical fluids. This direct connectivity simplifies the operational design, eliminates opportunities for failure, and saves the material and assembly cost of the interconnects.

Bottom up versus top down. Bottom-up self-assembly makes intricate structures with atomic precision and little waste, starting with atoms and molecules. Upper panel shows the self assembly of silicon nanoparticles (blue) on carbon black trees (black) forming rigid porous microspheres for high energy density lithium battery electrodes. Lower panel shows top-down lithography: a simple structure at 10 nm precision following a pre-determined template with significant waste. Joining bottom-up with top-down fabrication techniques is a primary challenge and opportunity for mesoscale science. Source: A. Magasinski et al., *Nature Materials* **9**, 353358 (2010) (upper panel); A. Han et al., *Nano Lett.* **12**, 1018 (2012) (lower panel).

The gap between top down and bottom up is rich with meso opportunities. Self-assembly, though originating in atomic and nano space, quickly transitions to meso space as the architectures and phenomena to be integrated become more complex. Biology and geology are guiding

examples; much of their functionality arises from complex structures at or above the 10-100 nanometer level. Bridging the top-down/bottom-up gap is a prime meso challenge for developing sophisticated self-assembly and for controlling metastability in these systems. At present the two approaches are virtually exclusive. We do not design top down with the intention of incorporating bottom-up components, nor do we design bottom up with the intention of connecting bottom-up components with top-down links. Bridging the gap would provide many advantages, including the ability to communicate with self-assembled molecular units using conventional electronics, a task that now, for the most part, is beyond our practical reach (see sidebar "Mesoscale Manufacturing" on page 50).

The Meso Opportunity

The meso opportunity embraces and exploits the enormous foundation of nanoscience understanding and expertise that the research community has created over the last decade and continues to create. Examples include nanoscale structural and functional units such as quantum dots, core-shell nanoparticles, catalytic clusters, polymer systems, and host-guest chemistry, and nanoscale techniques such as bottom-up self-assembly and micro-beam structure determination and spectroscopy with electrons, x-rays, and neutrons. These nanoscale building blocks, phenomena, and techniques can be interfaced and integrated at the mesoscale to form new levels of architectures of greater complexity and functionality that dramatically enlarge the horizon of science and technology. The meso opportunity for new, cheaper, and more efficient technology and solutions to societal problems is significant and timely.

Beyond new technology and solutions to societal problems, the mesoscale is fertile ground for new basic science. In the bottom-up mesoscience world, the harmonious interaction of components and architectures will lead to new organizing principles that will require observation, analysis, and simulation to discover and understand. We have discovered the organizing principles of quantum mechanics for the atomic, molecular, and nanoscale and of classical physics for the macroscale, but the organizing principles

of the mesoscale remain relatively unexplored. What laws govern self-assembly, or the stability of dynamic steady states, or the localization of strongly correlated electrons? These uniquely mesoscale phenomena are pervasive in the materials world; understanding their occurrence, operation, and potential is a powerful step forward for new science and technology.

Over the course of this study the Mesoscale Science Subcommittee of the Basic Energy Sciences Advisory Committee engaged hundreds of colleagues in town hall meetings, webinars, and web site interactions in order to identify important and timely research directions for mesoscale science, as well as the capabilities required to address these challenges. Six priority research directions emerged from this study:

- Mastering Defect Mesostructure and its Evolution
- Regulating Coupled Reactions and Pathway-Dependent Chemical Processes
- Optimizing Transport and Response Properties by Design and Control of Mesoscale Structure
- Elucidating Non-equilibrium and Many-Body Physics of Electrons
- Harnessing Fluctuations, Dynamics and Degradation for Control of Metastable Mesoscale Systems
- Directing Assembly of Hierarchical Functional Materials

In exploring these priority research directions, it became clear that a next generation of synthesis, characterization, and modeling capabilities was required to enable success. These, as well as the essential challenge of integrating these capabilities, are described herein.

In what follows, each of the priority research directions is discussed in detail. The remaining chapters discuss both the integration challenge and the specific gaps in synthesis, characterization, and modeling capabilities. Workforce needs and recommendations for realizing the mesoscale opportunity are then discussed. Finally, a perspective on potential outcomes resulting from exploration at the mesoscale is offered.

Priority Research Directions
for Mesoscale Science

The present study reveals significant mesoscale science opportunities and identifies what this subcommittee has defined as the most promising emerging directions for future research. Through interactions and discussions with the community, we have identified a set of priority research directions (PRDs). In each of the PRDs, the science opportunity is discussed, the mesoscale challenge is emphasized, an approach to addressing these challenges is described, and a vision for success is articulated. These PRDs span the traditional disciplines of condensed matter physics, materials science, and chemistry, and because of their interdisciplinary nature, defy simple characterization within these traditional boundaries. They span the *Five Challenges for Science and the Imagination* that the Basic Energy Sciences Advisory Committee (BESAC) previously identified, and success in their pursuit will impact the full array of energy technology challenges.

Mastering Defect Mesostructure and its Evolution

Characterizing and controlling the patterns and evolution of mesoscale heterogeneity are key to optimizing and exploiting a wide range of materials performance and functionality.

Opportunity

Defects in materials and structures comprise a wide range of mesoscale features, including interfaces, dislocations, vacancies and intersitials. Defects are always present and distributed nonuniformly, producing mesoscale heterogeneity which is part and parcel of materials properties and behavior. Defect patterns typically extend to the boundaries of materials and are described by mesoscale dimensions. Thus, *a key element of mesoscale science is understanding and controlling the formation of individual defects on the atomic or nanoscale level and projecting their collective influence to the macroscale properties and performance of materials.*

Defects are discontinuities in material properties and behavior, which typically occur at mesoscale separation in materials systems and architectures. While defects are often associated with microstructural features that are classified according to topology (i.e., point vs. line vs. areal vs. volumetric defects), we intend a broader connotation, in two senses. First, we regard defects as features that constrain either the extent of collective behavior or the utility of mesoscale systems formed as large assemblies of components, i.e., *functional* defects, which occur in everything from crystal

lattices to magnetic domain structures. Such defects and interfacial structures may not be correlated with microstructural properties. Second, we seek to control materials functionality at the mesoscale not only by minimization of deleterious defect types but also by controlled introduction of defects that enhance properties or performance. *Without mastering science at the mesoscale, translating atomic and nanoscale phenomena into macroscopic materials solutions for society and the economy will be inefficient and slow.* Delivering value from the nanoscale requires mastery of defects at the mesoscale.

The profound advances that we are witnessing in materials science, particularly a combination of computational capabilities and characterization tools, make this area ripe for exploitation (see figure on page 15). Both computation and experiment can now address, for the first time, a large range of the defect types and populations of interest, whether they are dislocations, pores, interfaces, grains, domains, or any other defect with mesoscale influence. The capability is such that not only individual defects but also distributions of defect features or field values can be computed and measured, including statistical analysis of rare features and correlations between quantities. Some defects and defect distributions lead to fault-tolerant behavior, while others can become sites for damage initiation and ultimately materials failure. Understanding and controlling mesoscale defects structures will lead to enhanced macroscale performance.

It is important to focus on system performance as the figure(s)-of-merit

for evaluating the positive or negative effect of defects. System performance integrates over numerous intermediate characteristics and parameters and usually declines with time as defect populations grow and agglomerate. Thus, predicting the spatial and temporal evolution of defect populations from their initial value is a key mesoscale challenge. These predictions, however, must be motivated and validated by experimental observation of defect evolution, which in real time can take decades. Therefore, *accelerated testing* modalities are needed to project long-term behavior. Unfortunately, scientific insight at the mesoscale is often inadequate to move beyond brute force approaches to accelerated testing.

Thus, the *science* requires (a) identifying defects and tracking their dynamic evolution—a major challenge—and (b) understanding the mechanisms by which defects alter system performance through their long-range/long-time behavior. The *impact* follows from the fact that, if we could establish the science, the path from fundamental understanding at the nanoscale to higher performing, longer lasting products will be shorter and more effective. Engineers can adopt such new knowledge and use it for enhanced technological solutions in, for example, advanced manufacturing.

Meso Challenges

Because defects and interfaces are by definition mesoscale constructs, the meso challenges associated with mastering defect structure and evolution are myriad. Here, we highlight three examples, spanning materials

Retained high pressure ω phase (left) and parent α phase (right) in dynamically loaded Zirconium.

Pores and pore coalescence in dynamically loaded Tantalum

Defect Evolution. Defects in materials are reflected in pore nucleation, growth, and coalescence to cause dynamic damage, failure, and phase transformations.

Mesoscale Experiment and Data Analysis

Mesoscale Theory and Simulation

New combinations of experiments, data analysis, and theory and simulation are required to understand and exploit the connection between nanoscale mechanisms and mesoscale phenomena. Adapted from C. A. Bronkhorst (Los Alamos National Laboratory).

types (mesoporous solids), relevant physical properties (strength and damage), and the consequences of fabrication approaches (top-down and bottom-up defect manipulation).

Porous and Mesoporous Solids

The mechanical and transport properties of materials containing vacancy structures and pores with mesoscopic dimensions are of practical importance to the development of high-strength, low-weight materials. In strong, light-weight materials, enhanced structural and functional performance can increase energy efficiency in, for example, transportation systems.

Integrity and Transport in Porous Materials. While the mechanical
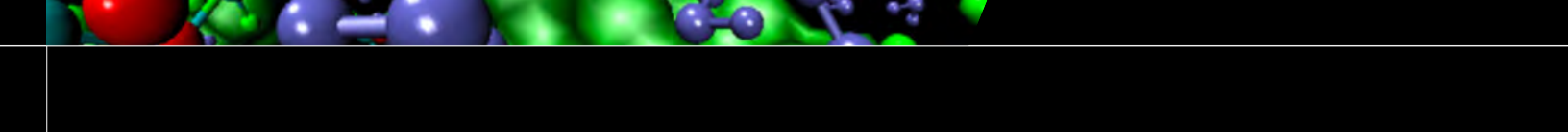
properties of the constituent materials may be known, the mechanical properties of assembled porous structures at the nano-, meso-, and microscale—including aerogels, foams, and engineered lattices—are relatively unexplored. Even the fundamental mechanisms determining the emergent strength of the bulk form are not well understood. The utility of such materials, especially in critical structures, depends on maintaining the integrity of the porous structure in the presence of extreme stresses, be they radiation-induced, mechanical, or chemical. Geological materials are a good example: understanding porous structures and their formation is crucial to improving the performance of carbon sequestration and gas extraction from hydraulically fractured or "fracked" rocks. There is

a two-sided nature to crack formation and materials failure. Considered a detriment for the built environment, it is a benefit for recovering the vast reserves of petroleum trapped in shale. *A predictive understanding of microstructure-based heterogeneity evolution and its consequences for material damage/failure and phase transformation is presently lacking.* This gap prevents us from predicting material response under severe loading conditions.

Effect of Pores on Materials Behavior. The dimensions of a porous structure, which can range from the nanoscale to microscale, affect the effective bulk elastic properties of the solid. Knowledge of the mechanical properties of mesoporous materials is essential to gaining

a basic understanding of the mechanisms responsible for strength. One must be able to distinguish pores from other defects. What is the structural stability of pores? Can pores evolve into networks of defects? How do networks evolve in the presence of environmental stresses? Dynamic damage/failure and phase transformation processes are believed to occur by a series of nucleation, growth, and coalescence events. The linkage of these events to the details of the material chemistry and microstructure of porous materials is poorly understood.

Plastic Flow, Loading Leading to Damage

Structural metallic alloys are among the most important and pervasive materials classes. Their usefulness in structures depends on their ability to distribute load via plastic deformation. Plastic strain occurs mainly via the flow of dislocations, which are line defects in crystals, and sometimes via twinning, which also depends on line defects in a complicated fashion. *Although individual dislocations are very well understood as isolated line defects at the nanoscale, their collective, mesoscale behavior remains a challenge.* By contrast to elastic moduli, which are routinely calculated from first principles, there is no avenue to compute a stress-strain curve, as required by engineers, starting at the atomistic level because we lack anything remotely resembling a statistical mechanics of dislocations.

Ductility, Dislocations, and Interfaces. One mesoscale property that is basic to metals is ductility or the ability to flow plastically without breaking, which depends on how

easily dislocations flow. The mechanisms by which alloying elements control the balance among interface strength, dislocation motion, and ductility remain unknown in many cases. Ductility is not simply a strength balance, however; it also depends on the stress-strain curve and the extent to which strain hardening occurs, once more pointing out the lack of a nano-to-meso understanding of dislocations.

Damage Initiation. Evolution of materials microstructure under loading includes accumulation of damage to the structure. This damage may be beneficial as, for example, dislocation accumulation provides strain hardening that in turn allows load redistribution in structures, or it may be life-limiting when cracks or voids form. Cracks and voids may arise through weakest-link failure such as grain boundary cracking. They can also arise through fluctuations in dislocation density. Even under macroscopically uniform deformation in single crystals, dislocations always form patterns. This behavior points to the importance at the mesoscale of distributions and the properties of their tails, where high concentrations of defects trigger rare but ultimately dominant damage events. Critical events, such as crack formation, are labeled as damage initiation at the mesoscale because, while they may result from a smooth progression at the nanoscale, they mark the beginning of a well-defined path to ultimate failure at the mesoscale. An example of a property that limits the lifetime and/or performance of many materials is resistance to cyclic loading or fatigue. In many materials, the extent of loading that leads to fatigue

crack initiation is highly variable and microstructure dependent. Improved understanding of how to control the defects would have many benefits.

Engineered Assembly and Self-organization

Our ability to understand, engineer, and exploit atomic and nanoscale phenomena is gated by how well we can *manage* defect mesostructures comprising defect populations and their correlated patterns. We intentionally say to manage defects, not to eliminate them, because defects are always present when atoms, materials, or structures are aggregated at large length scales. Defects may be created, transformed, or activated during synthesis of materials and structures, during operation of the resulting devices, or by subsequent external influences such as radiation damage and thermal or mechanical stress. The need to manage defects is critical in two domains—the engineered assembly of smaller components into mesoscale systems, and the exploitation of natural self-assembly.

Engineered Assembly. Energy applications provide rich examples of the need to manage defects in engineered systems (see figure on next page). While mesoscale architectures (assemblies of nano-wires, nanotubes, and nanoporous materials) promise power and energy benefits for electrochemical energy storage, the increased surface area that enables them offers more channels for defect generation; for example, as battery nanoelectrodes swell and shrink during ion transfer with the electrolyte, cracks may degrade essential passivation layers, leading to dendrite formation that shorts the

device and risks fire or explosion. In nanophotonic devices for photovoltaic solar energy capture, defects may trap and de-excite charge carriers or destroy the long-range nanostructure organization, degrading performance. Other examples include mesoscale heterostructures, where interfaces control properties and may enhance or damage performance.

Self-organized Assembly. Phenomena such as superconductivity, magnetism, and multiferroic behavior rely on long-range collective interactions of atomic-scale components in complex materials. Structural or compositional defects can substantially degrade or even destroy these phenomena and their utility for applications. On the other hand, the extent of long-range collective behavior is limited by other, typically unknown, mechanisms, which constitute the "defects" of importance in these

applications. These emerge spontaneously rather than being imposed externally. Our ability to identify and manage these competing interactions and the associated defects or defect mesostructures thus defines how much value these phenomena can offer in practice.

Research Directions
New experimental capabilities must be developed to observe the evolution of three dimensional defect formation and evolution *in situ* with micron-scale resolution while the material is exposed to extreme environmental conditions. New theory and simulation capability must be fostered at the length scale of these nucleation and growth events in order to best extract insight from the experiments and tangibly test hypotheses. X-ray or neutron scattering techniques are appropriate for these kinds of

measurements (see sidebar "Imaging Mesoscale Structure" on page 19). Small angle scattering is appropriate for studying the pore sizes: diffraction, for measuring interatomic spacing and strain, and radiography, for determining macroscopic dimensions. A challenge for future instrumentation is to establish the simultaneous application of such techniques. Specific directions include:

• Development of new methods to find, observe, and model functional defects evolving in three dimensions and in sub-surface systems. Such information is a prerequisite to managing and mastering the progressive evolution of isolated defects into mesoscale defect patterns that limit the range of collective response or into extended defect assemblies that locally alter the mechanical response of the system and, for example, initiate cracks that

Electrochemical Storage. Power and energy density for batteries and supercapacitors can be enhanced by using materials in nanostructured and microstructured formats, enabling fast ion and electron transport pathways. Functional defects may occur at any of these length scales, e.g., randomness at the nanoparticle scale introducing highly tortuous ion-transport paths or discontinuous electron transport paths, or dimensional variability that impedes transport in the fabricated microstructures. Adapted from Ming Tang (Lawrence Livermore National Laboratory).

grow and ultimately fracture the system. Defect evolution, i.e., an explicit focus on dynamic defect phenomena, must acquire the importance already attributed to the static study of structural defects. It is the dynamic evolution of defect structures and patterns in materials systems that directly translate to performance and reliability limitations.

- Development of defect decoration techniques, employing selective chemistry or other phenomena, for finding and watching functional defects.

- Conduct of accelerated testing in new modalities, based on advanced mesoscale characterization methods, for the prediction and controlled evolution of functional defects.

- Integration of data mining strategies, as developed for applications from security to marketing, with data-rich materials science instrumentation (e.g., computed tomography and orientation mapping), particularly at advanced user facilities, to answer questions such as the following: How do we find features in large three dimensional computed tomographic images? How do we correlate data from disparate sources such as images and acoustic emission?

Implicitly, we are always looking for an aggregate property that controls materials performance. Dislocations are a prime example. We understand individual dislocations very well at the nanoscale, even in low symmetry materials. When millions of dislocations flow and interact, however, their pattern formation is not well understood and requires supercomputing to simulate, even when only a few dislocations are present. And yet, this pattern formation controls where we find slip steps, surface roughness and cracks, void formation, and cracking of protective surfaces. *Thus, the collective behavior of dislocations controls materials performance but in a way that we do not know how to quantify or calculate.*

A key idea is that, although defects are traditionally thought of as detrimental, they can be engineered to promote useful and functional behavior. The efficient study of defects requires accelerated testing, remaining mindful that there is a trade-off

between resolution and speed. For example, in fatigue crack formation, much of fatigue life comprises waiting for crack(s) to form. Thus, a substantial fraction of materials lifetime derives from the underlying plastic deformation mechanisms, i.e., dislocation flow and localization. Ultrasonic cyclic testing is being used to perform accelerated testing, but a great deal of theoretical work needs to be done to relate these results to nanoscale understanding. This understanding and new capability will allow us to simulate these statistical events under extreme loading conditions of strategic importance and to design new materials for improved performance. We will also be able to design techniques for accelerated testing and to establish the validity of such procedures.

Potential Impact
Bulk material properties need to be quantitatively connected to atomistic, fundamental understanding in a predictive manner. The gaps in
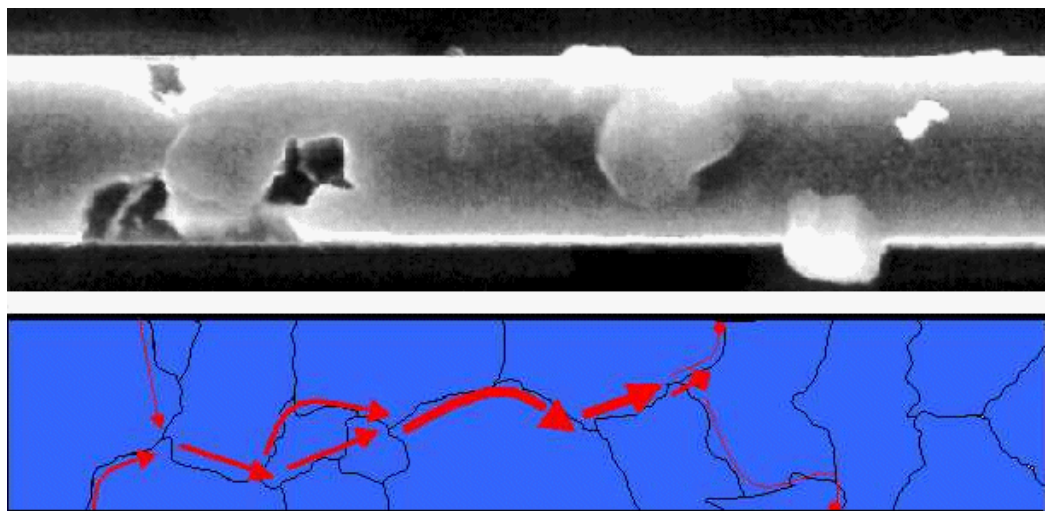
Electromigration Failure. At high current density, metal atoms can diffuse along grain boundaries, leading to void formation, elevated current density and heating around the void, and ultimately breakage of wiring. In a serendipitous event, Francois d'Heurle (IBM) discovered that dopants (e.g., Cu or Si) introduced into Al wiring segregate at grain boundaries and retard electromigration.Mesoscale science offers promise to dramatically shorten the time between such advances. Given the proposed combination of largescale simulation and advances in characterization, this represents a problem that might have been solved far more rapidly. Photo from forum.xcpus.com.

our current mesoscale knowledge severely limit our ability to optimize materials performance.

Advancing the connections between individual defects at the nanoscale, which are mostly well understood, and defect systems and architectures at the macroscale, which limit materials performance and are poorly understood, will accelerate discovery and enable active defect management. Today, materials performance in relation to mechanical/thermal/electrochemical cycling is a highly empirical field in which macroscale behavior is measured and variability accounted for by means of safety factors, for example, by limiting operational stresses to half the projected limit. Improved understanding would help to define more-resistant, more-reliable ways to assemble materials while maintaining beneficial microstructure. Quantitative formulations of the links between defect distributions and materials performance will promote innovation of new products and services with enhanced materials reliability (see figure on page 18). For example, development of a scientific basis for accelerated testing would be immensely valuable. An old but still relevant example is how Paul D. Merica's theoretical description of phase diagrams for aluminum alloys in the early 20th century rapidly accelerated development and utilization of diverse aluminum alloys in industry. There is a similar potential impact from mastering defect mesostructure and evolution on almost the whole range of manufactured devices and machinery from fuel cells to airplanes.

Imaging Mesoscale Structure and Materials Response Using High Energy X-rays

High Energy X-ray Diffraction Microscopy (HEDM) has emerged as a powerful measurement technique that probes mesoscale structure and evolution inside of bulk materials. The ability to see inside of millimeter-sized samples with microscale resolution of polycrystal orientations and strain states promises to allow rigorous tests of computational models of materials response to thermal, mechanical, and chemical stimuli. This new and unique capability can be expected to lead to deeper understanding of structure-property relationships and to predictive models of materials responses. Coupling HEDM to modeling can play an important role in shortening the time scale for development of new materials and better understanding of service lifetimes in a broad spectrum of applications.

HEDM and similar techniques are implemented at third-generation synchrotron facilities such as the Advanced Photon Source at Argonne National Laboratory. These sources yield high brilliance beams at energies >50 keV that can be focused to the microscale and that penetrate millimeter distances into materials across much of the periodic table. State-of-the-art area detectors allow collection of large terabyte data sets that probe complex materials problems in unprecedented detail. The reduction of these data sets to physical quantities relies on the availability of high-performance computing systems. Making comparisons to model calculations or employing models to compare directly to observed diffraction images also requires advanced computational techniques and will require the development of statistical methods of comparison and the use of the mathematics of optimization.
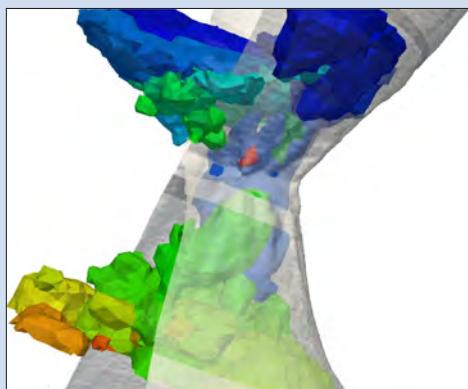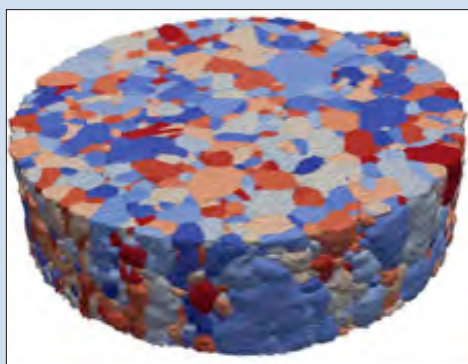
The images at left show two representative data sets illustrating the power of HEDM microstructure mapping, a method that yields the orientation field that specifies the orientation of crystal unit cell axes over three dimensions. Future work will combine these measurements with elastic strain sensitivity. The top figure shows a volumetric map of ~0.3 mm^3 of nickel as mapped with HEDM. This same volume of material has been re-measured successively as the sample was annealed five times. The data sets are being used to test traditional models of grain growth, a central problem in microstructural science for at least 60 years. The data allow the evolution of the grain boundary network to be tracked both by statistics and through the tracking of individual boundaries. The lower figure shows a combined HEDM map and tomographic measurement of a copper wire being deformed in tension in the experimental setup. The gray tomographic image (cut away on the left side) shows the shape of the wire after substantial strain. The small red object in the center of the puckered narrow section of the wire is a void that formed during ductile deformation. The colored regions represent crystalline grains. These measurements will allow the correlation of damage (intragrain defect accumulation and void formation) with specific microstructural features. Very recently, the resolution of HEDM has been dramatically improved by a series of new lensless x-ray imaging tools, such as tomographic ptychography, and diffractive imaging. Source: R.M. Suter, Carnegie Mellon University.

Regulating Coupled Reactions and Pathway-dependent Chemical Processes

Characterizing and controlling the mechanisms and kinetics of pathway-dependent chemical processes on the mesoscale are central to a broad spectrum of important technological areas such as carbon sequestration, heterogeneous catalysis, energy storage systems, functional materials, and reactive transport and interfacial chemical processes in the subsurface (see figure on next page).

Opportunity

Multiphase physicochemical transport and interfacial processes are pervasive in synthetic permeable media for energy conversion and in natural systems such as the Earth's surface. The photo of Earth from the 1972 Apollo 17 mission shows that the Earth's surface is dominated by interfaces involving solids, liquids, and gases on a global scale and provides a hint of the enormous importance of interfacial chemical reactions among these three phases of matter in Earth's highly fractured crust. These coupled reactions control the composition of our environment, including the atmosphere, oceans, groundwaters, and the soils derived from interactions of atmospheric gases and natural waters with solid phases. Aqueous fluids, liquid hydrocarbons, and gases flow through soils, sediments, and permeable rocks along pathways that

can be exceedingly complex at the nano- to microscales. Adding to this complexity are the chemical reactions occurring along these pathways that can irreversibly alter permeability and porosity as well as the compositions of fluid, gas, and solid phases, depending on the physicochemical conditions. Subsurface mesoscale colloidal and interfacial phenomena are another area of critical importance. The current theories of colloidal stability are not adequate for accurate predictions of the behavior of colloids under the extreme conditions in subsurface environments; in particular, we do not know how to trigger their different functionalities in mesoporous media.

An example of the important role played by the flow of natural fluids and gases through solid media is the recovery of oil and shale gas from subsurface reservoirs through enhanced recovery methods involving injection of water/CO_2 mixtures under supercritical conditions. Another is the sequestration of CO_2 in subsurface rocks, through either physical trapping in depleted oil and natural gas reservoirs or chemical trapping by reaction of CO_2 with appropriate minerals such as Mg silicates; these processes result in mineral carbonation and permanent CO_2 sequestration. One of the key issues in CO_2 sequestration through physical trapping is leakage through tight fractures and well grout in the subsurface environment. This problem could be mitigated significantly if we had a

better fundamental understanding of emergent mesoscale colloidal and interfacial phenomena. Armed with such knowledge, we might be able to determine how to trigger colloidal instability under the extreme chemical and physical conditions typical of the subsurface environment such that fractures are sealed by aggregation of nanoparticles. One of the key issues with chemical trapping of CO_2 is the slow kinetics of mineral carbonation reactions, resulting from low reactive surface areas as well as surface passivation caused by formation of unreactive layers of silica. Solutions to these problems could potentially lead to commercial CO_2 sequestration operations on a scale large enough to sequester the billion-plus metric tons of CO_2 produced annually from the burning of fossil fuels.

In the synthetic world of materials and catalysis, pathway-dependent mesoscale chemical processes are also of enormous importance. An excellent example is the polymer electrolyte membrane (PEM) fuel cell, which uses H_2 fuel and O_2 from air to produce electricity by catalytic splitting of H_2 into protons and electrons on the anode side of the membrane, then transport of only the protons through the membrane to the cathode side while the electrons travel along an external circuit to the cathode, producing an electrical current. For practical application, the PEM fuel cell requires a variety of improvements, including better-performing catalysts and membranes.

Geological CO_2 sequestration

Pathway-Dependent Chemical Processes.
Understanding such processes on the mesoscale would have many benefits, including accurate prediction of interfacial chemical reactions in natural systems such as the Earth's surface, mitigation of leakage associated with carbon sequestration in the subsurface, and development of improved membranes for fuel cells.

$$H_2 \rightarrow 2H^+ + 2e^-$$

$$2H^+ + 2e^- + \tfrac{1}{2}O_2 \rightarrow H_2O$$

Hydrogen polymer elctrolyte fuel cells

There are many mesoscale challenges associated with membranes in various applications, such as those used for H_2 fuel cells and for reverse osmosis in the purification of drinking water. For example, integrating nanomaterials into mesoporous architectures would allow the benefits of the high surface area of nanomaterials to be combined with the efficient mass transport in mesoscale architectures. We do not know how to engineer this integration at present. An opportunity in this area is the design and synthesis of hybrid materials that combine "hard" inorganic nanocrystals with "soft" polymeric materials in one, two and three dimensional mesoscale architectures that could be used in CO_2 capture, H_2 generation and storage, and gas separations. Another example is the emerging field of reticular chemistry, which includes the design and synthesis of a new class of mesoporous materials known as metal-organic framework structures, which can be used for gas storage, purification, separation, catalysis, sequestration, hydrogen storage, and other applications.

We have little fundamental understanding of the properties of liquids in confined geometries. An example of an opportunity in this area is exploitation of the self-organization of water around small molecules such as methane, resulting in clathrate hydrates, and around protein molecules, affecting their binding, recognition, and enzyme catalysis. Local solvent organization must also play a role in non-enzymatic catalysis, but we have no systematic understanding of how or when this occurs. This lack of understanding of the structure and properties of confined water and other solvents opens new opportunities for novel approaches to promote and control chemical transformations that take into account local solvent organization and interactions.

Another example of how understanding pathway-dependent chemical reactions could help advance energy-related needs is the use of hierarchically structured porous electrodes for energy storage in batteries. Most batteries today consist of porous electrodes produced by simple random packing of nanoparticles and microparticles. The central question that needs to be addressed is how to organize porous channels at different length scales in battery electrodes to maximize charge transport efficiency and minimize chemical and mechanical degradation. The tailoring of porous electrodes on the mesoscale is a largely unexplored research direction that, if successful, could accelerate advancement in energy storage systems and push the performance and lifetime limits of batteries by optimizing "degrees of freedom" at the mesoscale that have rarely been explored.

The design of mesoscale catalytic processes presents an opportunity for major advances in the control of pathway-dependent chemical reactions that could lead to entirely new catalytic processes for the efficient conversion of complex feedstock materials into fuels and chemicals based on new understanding of how to control coupled reaction/transport processes. Molecular science has made great strides in understanding how individual active sites promote bond breaking/making processes. Control of catalytic conversions, which involve multiple coupled reaction steps, will require an understanding of how to transport intermediates between active sites with differing functions and to design active sites for specific transformations. Although progress toward understanding catalytic processes at individual active sites has been significant, we currently do not know how to control interactions between active sites that are needed to direct the cascade of reactions in complex, multi-step catalytic conversions. Biology has mastered such complex conversions by using a variety of mesoscale processes to control coupled reaction and transport processes at the level of enzymes and cells. We have the opportunity to learn from nature how to design new inorganic catalytic materials and processes. Another area ripe with opportunity in heterogeneous catalysis addresses the question of how electronic structure is correlated with the morphology and mesoscopic structural stability of catalysts. Moreover, understanding how mechanical and electronic properties evolve as the surface chemistry of solids is manipulated is one of the fundamental questions in

designing new porous materials for energy harvesting, energy storage, stored-energy actuation, or catalytic applications. In many cases, unique charge-transfer-induced changes in physical properties are observed as surface chemistry is manipulated. Addressing this important question will lead to predictive capabilities and feedback loops for designing new mesoporous materials for energy storage and catalysis.

This is the right time for addressing some of the challenges associated with pathway-dependent chemical processes at the mesoscale because of major advances in high-performance computation and development of new molecular-level and mesoscale simulation codes. This is also an opportune time for advancing our understanding of mesoscale phenomena because of new developments in imaging tools, such as coherent diffractive imaging, synchrotron-based 3-D tomography, and x-ray absorption nanospectroscopy that is element and chemical-state specific and provides information not obtainable with laboratory x-ray sources.

Meso Challenges
In the natural world, pore-scale (~μm to cm) and field-scale (~10 cm and larger) heterogeneity has long been recognized as a source of complexity and uncertainty in subsurface fluid transport. It is clear, however, that the largely ignored mesoscale (100 nm to μm) plays a critical role in multiphase flow of CO_2 and brine in subsurface rocks. It is also becoming clear that chemical reactions between these gas-fluid mixtures and the

mineral-lined pathways though which they flow can have a major influence on (i) the connectivity of the pathways, (ii) the ability to recover oil and natural gas more efficiently and with less detrimental environmental consequences (e.g., serious groundwater pollution from fracking of shale-gas reservoirs), and (iii) the safe, long-term sequestration of CO_2 in subsurface rocks. Understanding reactive transport at the mesoscale provides the opportunity to develop a rigorous understanding of the major controls on CO_2 migration at the lower end of the spatial scales where quantum meets continuum descriptions of the multiphase physics needed to bridge between mesoscale and field-scale theory and experiments. A number of challenges must be addressed if progress is to be made in solving these problems. We must develop better ways of characterizing mesoscale pore structures of complex, heterogeneous geological media and their evolution under field-relevant conditions. In addition, we must be able to follow chemical reactions with elemental specificity at the mesoscale in real time in order to understand how reaction intermediates and final products affect porosity and permeability in a dynamic fashion.

The same mesoscale challenges discussed above are also true for the synthetic world. For example, in mesoscale catalytic processes, the goal is to learn how to control coupled reactions and transport over 10s to 100s of nanometers, rather than at the macroscopic levels encountered, for example, in scale-up of catalytic processes. New emergent behavior is expected from reaction/transport coupling at the mesoscale. The

challenge is to develop a fundamental understanding of the microscopic processes that occur on the surfaces of porous materials (or meso-scale constructions of nanomaterials) under various environmental conditions. In this context, it is crucial to understand the role of charge transfer on surface stress, as well as the correlation between the change in electronic structure and morphology or structural stability. In the area of energy storage, the mesoscale challenges are how to fabricate and characterize mesostructures in porous electrodes with flexibility, precision, and efficiency, and how to accurately model charge transport and degradation in electrodes containing multi-scale (nano, meso, micro) porous channels. In the area of fluid and gas transport through mesoporous media, the challenges include the following: (1) better observation, characterization, and quantification of complex and coupled meso- and micro-pore scale processes, (2) more effective ways to translate, abstract, and simplify their collective behavior to achieve predictive continuum models, (3) new approaches for understanding gas flow in mesoporous media (the continuum description of fluids is not adequate in the slip or transitional flow regimes, and molecular dynamics simulations are prohibitively expensive due to the large number of molecules that must be considered), (4) improved knowledge of the optimum architectures and bonding motifs for efficient gas transport through mesoporous inorganic-organic hybrid materials, (5) better integration of nanomaterials into mesoporous architectures using robust synthesis approaches based on templating and self-organization, and (6) optimization

of nano-meso architectures through mesoscale simulations and advanced characterization.

Research Directions

Experimental, theoretical, and modeling approaches are needed to address the challenges discussed above and thereby lead to new understanding of pathway-dependent chemical processes and coupled reactions at the mesoscale. In all of the areas involving flow of liquids and gases through mesoporous media, ultra-high resolution imaging capable of distinguishing between different elements and different chemical states of a given element is needed. Conventional x-ray tomography methods using commercial computerized tomography (CT) scanners are widely used to provide 3-D images of rock cores and other porous media, but spatial resolution is limited, and there is no element or chemical-state specificity. Recent developments in synchrotron-based CT scanning at different x-ray energies coupled with diffraction-based microscopy as well as improvements in resolution to the few-nanometer level through tomographic ptychography and scanning microscopies, coupled with simultaneous nano-XANES (x-ray absorption near edge structure) spectroscopy, are beginning to provide unique information on compositional heterogeneities at the mesoscale and complex 3-D nano-meso architectures that can be optimized for fast mass transport. These studies will provide the necessary feedback for nanoporous materials synthesis. A similar imaging approach will provide new insights to the design and functioning of catalysts and battery electrodes under *in*

operando conditions (see sidebar on "Synchrotron-Based High-Resolution 3-D Tomography *In Operando* Conditions" on page 25). Based on these early successes, new hard x-ray synchrotron beam-line facilities are needed in the U.S. to facilitate *in situ* characterization studies of mesoporous materials. In addition, small angle x-ray and neutron scattering will be useful in characterizing the mesoscale pore structure of membranes as well as shales, clay rocks, and sandstones under the extreme conditions of the subsurface. New functional optical probes, such as nanotubes with tunable optical and physical properties, as well as high-speed near infrared microscopy, can be used to visualize transport through mesoporous media.

In theory and modeling, advances in high performance computing now allow a variety of approaches, including use of the lattice Boltzmann method to model transport and interfacial processes in mesoporous permeable media, as well as kinetic Monte Carlo modeling of complex catalytic processes. At a more fundamental level, density functional theory (DFT) studies coupled with ab initio thermodynamics of solid surfaces in contact with liquids and gases can be used to provide critical information on the solid-liquid interface structure and its properties under reactive conditions. In addition, controlled synthesis, assembly, and deposition of catalytic scaffolds are critical to model development. Experimental studies of the kinetics of reactions and mineral

transformations occurring during the flow of liquids and gases through porous geological media are needed to understand how to enhance the kinetics of mineral carbonation reactions required for permanent sequestration of CO_2 as well as the long-term integrity of shale and clay caprocks that prevent the leakage of CO_2 from deep saline aquifers. There are many fruitful research avenues that will lead to major advances in our understanding of pathway-dependent chemical processes in mesoporous media of all types.

Potential Impact

There are many potential impacts of mesoscale research on pathway-dependent chemical processes. In the area of geological sequestration of CO_2, successful commercial-scale physical and/or chemical trapping of CO_2 will help solve one of the major environmental problems facing humankind (see sidebar "Earth Science: A Meso Frontier" on page 26). In a more general sense, understanding what drives mesoporous flow and transport will potentially benefit areas as diverse as drug delivery, ultrafiltration, and nanofluidic energy conversion. In synthetic mesoporous systems, novel polymer-nanocrystal hybrid materials with controlled nanoscale to mesoscale architectures represent a new form of matter that could potentially enable unprecedented control over selective gas storage, separations, and transport. The broad range of gas solubilities in polymers, when combined

with gas-specific binding modalities in nanocrystals, enables targeted end-use design not possible today. New metal-organic framework structures have similar potential for enormous improvements in selective gas storage.

In the area of heterogeneous catalysis, detailed understanding of how to control coupled reaction/transport processes will enable the design of entirely new catalytic processes for efficient conversion of complex feedstock materials to fuels and chemicals. In addition, new understanding of solvent organization in enzymatic and non-enzymatic catalysis, as well as intentional encapsulation of catalysts, has the potential to enable more general control of reaction selectivities and rates.

In the area of energy storage, fundamental understanding of how nanoscale surface properties of battery electrode materials affect macroscopic performance will lead to development of a predictive capability and feedback loop for designing new porous electrode materials. This understanding will also accelerate advancement in energy storage systems and push the performance and lifetime limit of battery electrodes by optimizing "degrees of freedom" at the mesoscale that have rarely been explored. The development of nanomaterials with integrated mesoporosity will improve the power density, efficiency, and throughput of next-generation energy storage and conversion materials, and thus has game-changing potential.

Synchrotron-Based High-Resolution 3-D Tomography under In Operando Conditions
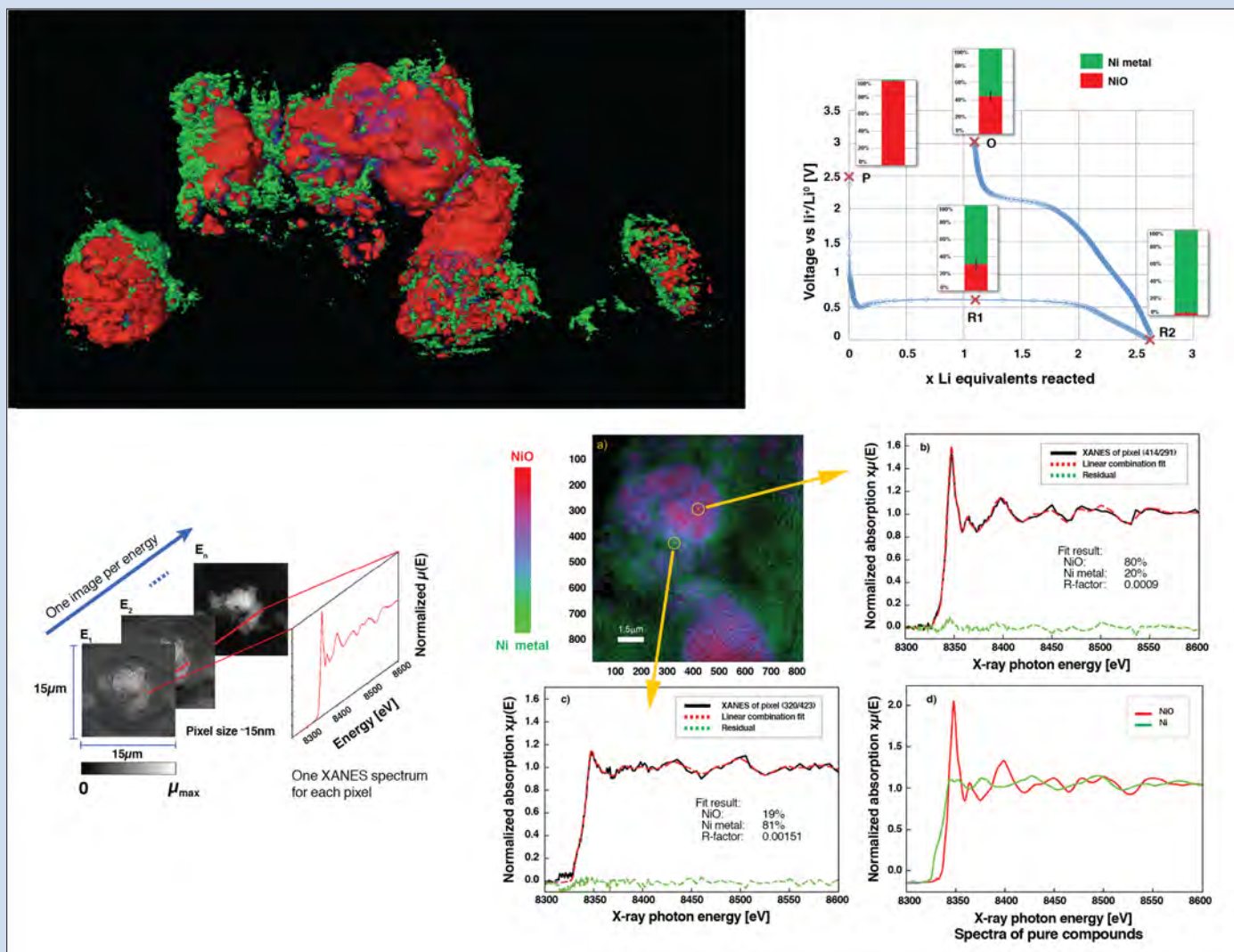
A research team from SLAC National Accelerator Laboratory (Piero Pianetta *et al.*), Lawrence Berkeley National Laboratory (Jose Cabana *et al.*), FBK in Povo, Italy (F. Meirer), and Xradia has characterized NiO/Li battery electrodes under *in operando* conditions in an electrochemical cell using 3-D tomography and elemental mapping at the 40-nm resolution level. Detailed, spatially resolved information on the chemical state of Ni was provided by x-ray absorption near-edge structure (XANES) spectroscopy at a pixel size of 15 nm. The transmission x-ray microscope on beam-line 6-2 at the Stanford Synchrotron Radiation Lightsource (SSRL) was used for this imaging and nanospectroscopy. The 3-D x-ray tomograph and Ni K-edge XANES spectrum of the NiO battery electrode below show that NiO (red) is being reduced to Ni metal (green) during the first charge cycle of the operating battery, and that Ni metal is not fully reoxidized to NiO, which shortens battery lifetime and function. This state-of-the-art 3-D tomographic imaging that is element and chemical-state specific has provided important new insights about the irreversible changes that occur in the battery electrode materials that directly address the important problem of how to organize porous channels at different length scales in battery electrodes to maximize charge transport efficiency and minimize chemical and mechanical degradation.

This same 3-D tomographic approach has provided critical new information on mesoscale changes in Fe_2O_3-Fe_2TiO_5 catalysts in a project led by Bert Weckhuysen and Frank de Groot at SSRL, and it is likely to provide important new insights about path-dependent chemical processes at the mesoscale in all of the other areas discussed in this section, including CO_2 capture and sequestration and gas-phase separations. Current laboratory-based x-ray tomographic imaging using commercially available CT scanners is limited to spatial resolutions of ≈ 0.5 μm and is not capable of element- or chemical state-sensitive mapping. Thus, this new synchrotron-based tunable energy, hard x-ray tomographic imaging, represents a major new development that is potentially transformative.

Earth Science: A Meso Frontier

From groundwater flow to petroleum formation and extraction to carbon sequestration, mesoscale phenomena control the Earth's dynamics and its human impact.

The pores in rocks and soils play a primary role in the formation and dynamics of the earth's crust. Sedimentary rocks that cover much of the earth's crust are formed by accumulation of mineral and organic material that were created by weathering and erosion and transported to the place of deposition by water, wind, ice, or glaciers. The mineral and organic grains form strata that are compacted by pressure from above to form rocks of various porosities, depending on the size, composition, and dispersity of the constituent grains and the pressure and heat applied to the buried strata.

The pores in sedimentary rocks are critical to the dynamics of the earth, including the availability of groundwater, the formation and extraction of oil and gas, and the sequestration of carbon dioxide. Groundwater, the largest source of available freshwater, flows through pores in sedimentary rock to replenish aquifers that provide water for agriculture, drinking, and sanitation. As groundwater flows, it reacts with and dissolves the surrounding porous rocks, providing nutrients for plants and increasing or decreasing pore size and flow properties. The mesoscale dynamics of groundwater flow are critical to solving challenges of freshwater supply, aquifer replenishment, and contamination with toxic pollutants.

Oil and gas form by chemical reaction of organic matter in sedimentary rock promoted by the high pressure and temperature of buried strata. After formation times of millions to hundreds of millions of years, these fossil fuels may be released if the rocks are sufficiently permeable and rise through pores until stopped by an impermeable cap rock to form reservoirs that can be tapped by drilling. Less permeable organic shales retain their oil and gas, a rich source of unconventional fossil fuel that can be tapped by hydraulic fracturing to produce porosity that releases the trapped petroleum to flow to a reservoir or well.

Carbon sequestration in the pores of sedimentary rock provides an opportunity to store, for thousands of years, the carbon dioxide produced by fossil fuel combustion that now supplies over 80% of the world's energy. Migration of carbon dioxide underground, the possibility of leakage to the atmosphere where it would contribute to global warming and climate change, and reaction with the rocks in which it is sequestered are critical issues that require mesoscale science to resolve before sequestration can be implemented on a significant scale.
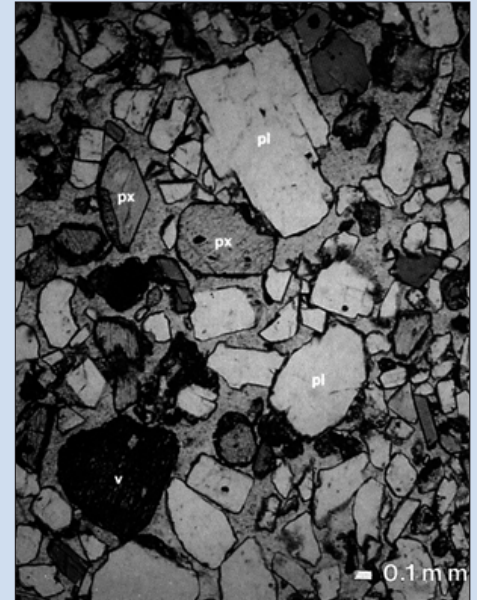
Pores in sandstone, a sedimentary rock formed by accumulation of many sizes and shapes of mineral and organic grains. The pores range in size from nanometers to microns, depending on the dispersity of the grains and the pressure and temperature of formation. Source: http://darkwing.uoregon.edu/~drt/Classes/201_99/Rice/Seds.html.

Optimizing Transport and Response Properties by Design and Control of Mesoscale Structure

Competing degrees of freedom and system constraints involving coupled electrons, photons, and atomic structures determine intermediate length scales that can potentially be exploited in functional mesoscale systems.

Opportunity

In the process of optimizing materials for energy-related applications, a compromise between competing requirements often leads to structural architecture on an intermediate length scale. This observation is especially true when one needs to couple light or electric and magnetic fields, with the motion of electrons, ions, or spins. For example, in designing an efficient solar cell to convert sunlight to electricity, one has to balance the challenges of using as much of the incident light as possible to generate electrons (or electron-hole pairs) while effectively collecting the electrons at an electrode (and sending the holes to the opposite electrode). The light absorption and electron transport functions put different demands on the architecture. Another example involves the design of improved batteries for storage of electrical energy (see figure on next page). The coupling of ion transport to ion insertion and removal from electrode material results in competing demands. To get ions into and out of the electrode material, one would like a large surface area relative to the volume, pointing to small-grained electrode material,

but high charge density favors large-grained material. The constraints of reproducible cycling and good electrical connectivity provide further challenges.

There are other situations in which the important functional property of a material emerges from the self-organized mesoscale structure in response to competing interactions. For example, high-temperature superconductivity appears in materials in which antiferromagnetism competes with the mobility of the charge carriers. Competition among antiferromagnetic and Coulomb interactions and the tendency of electrons to delocalize frequently lead to electronic modulations on an intermediate length scale. Somehow, superconductivity emerges with long-range order. Another example is the case of colossal magnetoresistance materials. There, interactions involving magnetic moments, electronic charges, and lattice distortions result in mesoscale structures that are very sensitive to temperature and applied magnetic field, resulting in a strong coupling between electrical conductivity and applied magnetic field.

The importance of mesoscale structure to the design and optimization of functional materials and systems has become increasingly apparent in recent years. Experimental and theoretical tools have developed to the point that we have an opportunity to make substantial progress in determining and understanding the rules behind external and intrinsic mesoscale structure, so that we can design and control materials and systems to improve their performance.

Meso Challenges

The research challenges are best described in terms of specific examples; in all cases, a common theme emerges: the need to discover, design, fabricate, and probe mesoscale-ordered superstructures and architectures. We begin with a problem relevant to batteries and supercapacitors. The transport of ions, such as lithium, into and out of the electrodes of a battery causes expansion and shrinking of the electrodes. The repetition of these processes as a battery is cyclically charged and discharged tends to cause the electrodes to deteriorate, thus reducing the amount of charge that can be stored. To improve the performance and lifetime, the strain effects can be reduced if the electrodes are formed from small grains of material. At the same time, the grains of the mesostructured electrode require good electrical conductivity to allow electrons and ions to separate or recombine in an efficient fashion. At present, the design of electrodes proceeds by trial and error. By characterizing and modeling such systems, we will develop the capability to design and control the mesoscale structure and composition in order to optimize capacity and sustainable performance simultaneously.

Semiconductor quantum dots have shown great promise as the active material for light-harvesting and light-emitting devices that are efficient and have low cost. Plasmonic metal nanoparticles can greatly enhance absorption, emission, and transport of excitations in such devices. Full exploitation of these effects requires advanced understanding and control over the interactions among disparate nanoscale ingredients in an extended structure. The challenge is to design,

fabricate, and probe mesoscale-ordered superstructures, arrays, and architectures.

The transport of heat by electrons in thermoelectric materials allows one to convert thermal energy to electrical energy or, conversely, to cool an object by running an electrical current. For this process to be efficient, there must be little heat transport by lattice vibrations. Experiments have shown that this condition can be achieved by the suitable nanostructuring of an appropriate material. The artificial nanostructuring of materials is not realistic for a practical thermoelectric device as the device must be quite large compared to the substructure, which would be expensive to create. The challenge is to find suitable materials with natural mesoscale structure or to find processes for effectively assembling smaller objects into a practical device.

Self-adaptive Electrodes. Conventional battery electrodes with predetermined crystalline structures often undergo phase transitions upon intercalation of transporting ions. These phase transitions cause swelling of the electrode materials, resulting in local atomic rearrangements, limited diffusion of ions, and ultimately capacity degradation. In recent work, a new bio-inspired evolutionary approach has been demonstrated. Starting from amorphous, low-crystallinity materials, repeated voltage cycling leads to interconnected porous mesoscale electrodes that undergo self-organization into an optimized crystalline phase. This is a promising approach that requires further testing and study. Source: H. Xiong et al., *J. Phys. Chem. C* **116**, 3181-3187 (2011); S. Tepavcevic et al., *ACS Nano* **6**, 530-538 (2011).

Resistance-free transport of electrons in high-temperature superconductors typically coexists with self-organized electronic heterogeneity that exists on a length scale of ten times the interatomic spacing. By controlling the chemical and lattice structure, one should be able to enhance the current-carrying capacity and operating temperature of superconducting compounds. There is no theoretical consensus on the nature of the electronic heterogeneity or its effect on superconductivity. Experimental characterizations of the electronic inhomogeneity are challenging and incomplete (see figure at right).

Ferromagnets couple their magnetization to an external magnetic field. In a multiferroic material, the magnetic order is coupled to a ferroelectric modulation of the lattice, thus allowing the magnetic order to couple to an applied electric field and the ferroelectric order to respond to an applied magnetic field (see figure at far right). The response of real materials is complicated by the formation of domains, with the orientation of the magnetization and/or electric polarization varying from one domain to the next. For example, a ferromagnet tends to break up into domains with the magnetization reversing direction from one domain to the next; the size of the domains is determined by the competition between the energy cost of forming domain walls and the dipole interaction energy between the domains. The domain structure occurs on an intermediate length scale that impacts the way in which the material couples to applied fields. An improved understanding of such domain structures is necessary to enable control of functional properties.
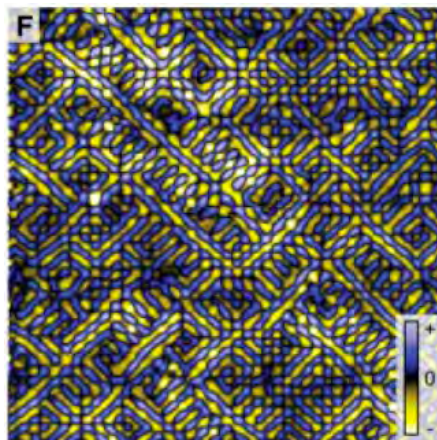
Superconductivity. Correlated-electron materials can exhibit self-organized mesoscale structures. This image shows electronic modulations in the copper-oxide high-temperature superconductor $Bi_2Sr_2CaCu_2O_{8+\delta}$, obtained by spectroscopic-imaging scanning-tunneling microscopy. Image is 12 nm on a side. The relationship between the modulations and the superconductivity remains to be understood. Y. Kohsaka et al., *Science* **315**, 1380 (2007).

Research Directions

Synthesis

Exploratory synthesis remains key to discovering new possibilities in material behavior and performance. While we aspire to gain the theoretical understanding that will allow rational design of optimal systems, the science of materials with mesoscale structure is presently dominated by experiment. A broad range of synthesis efforts is necessary, from growth of single crystals, to atomic-scale growth of multilayered films, then to assembly of nanoparticles. The performance of particular materials can often be tested in the laboratory with measurements of conductivity, photoabsorption, etc. Characterization of the mesoscale structure often requires unique and specialized equipment available at national user facilities.

Characterization

A range of characterization techniques is needed. One certainly needs to be able to map the spatial structure with diffraction techniques that employ x rays, neutrons, and electrons. One would also like to obtain chemical and electronic variation, as determined by spectroscopic techniques such as photoemission and optical absorption, with the same spatial resolution. In some cases, one needs to map magnetic order and orientation. It is important to be able to measure variations in order or structure when various fields are applied, and to follow the time dependence of such variations.
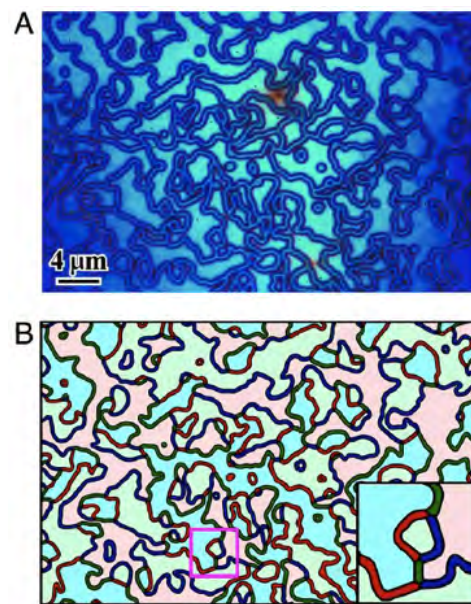
Polarization. A multiferroic material can have a complex domain pattern. The top image shows the ferroelectric domain pattern at the surface of a crystal of $YMnO_3$, obtained with an optical microscope after selectively etching the surface to distinguish domains of upward and downward polarization. The domain areas are not equal because the crystal was cooled from a higher temperature in an electric field. The coloring of the lower figure reflects the existence of three inequivalent structural domains, each of which can have two polarization directions. One would like to be able directly to measure both the structural and magnetic characteristics of each domain. Source: S. C. Chae et al., *PNAS* **107**, 21366 (2010).

Theoretical Modeling

Multiscale modeling is essential. Many accurate theoretical techniques have been developed for modeling the properties of materials on the nanoscale, but it is challenging to scale up these methods to span mesoscale structure. Granular models must be developed and tested against experiment. The goal is to develop predictive capabilities across scales.

Potential Impact

The importance of mesoscale structure to the design and optimization of functional materials and systems has become increasingly apparent in recent years. In the process of optimizing materials for energy-related applications, a compromise between competing requirements often leads to structural architecture on an intermediate length scale. The ability to design and control meso-scale structure of materials could lead to a more efficient electrical grid, improved energy storage, efficient conversion of waste heat to electrical energy, improved photovoltaics and light-emitting diodes, and better electrical motors and generators (see sidebar "Mesophotonics for Energy Applications" below).

Mesophotonics for Energy Applications
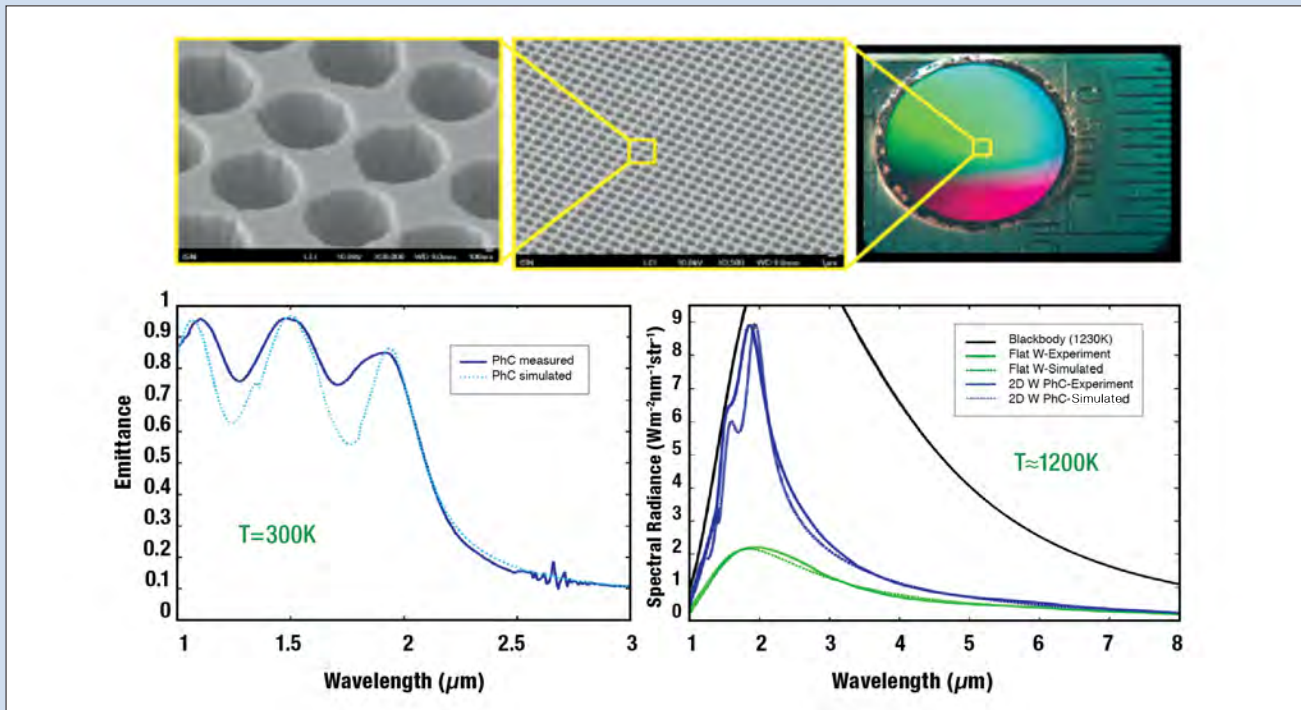
In mesophotonics, we explore artificially created materials (meta-materials) in which the structure is tailored at length scales smaller than the wavelength of light of interest. Because the substructure is smaller than the wavelength, light cannot really resolve the structure: it appears to the light as if it were propagating in a uniform medium, whose physical properties are substantially modified. By tailoring the mesostructure, we can tailor the laws of physics (as far as light is concerned) almost at will. This way, we can create artificial materials that display physical phenomena that do not exist in any naturally existing materials. For example, meta-materials have been used to demonstrate negative refraction, as well as to implement invisibility cloaks.

Photonic bandgap crystals (PhCs) are an example of this approach: they behave like "semiconductors for light": light of the frequencies within the bandgap is prohibited from propagation, while the frequencies outside of the bandgap are allowed to propagate. This way, by tailoring the mesostructure, one can tailor the photonic density of states almost at will, with good agreement between simulation and experiment. For example, within the photonic bandgap, the density of states is zero, while at some other frequencies, it can be dramatically enhanced. PhCs have been explored, for example, to implement some of the lowest power-threshold lasers. Moreover, since thermal emission of a hot body depends on the density of states, one can also tailor thermal emission (as well as absorption) of hot bodies almost at will. Source: Y.X. Yeng et al., *PNAS* **109**, 2280-2285 (2012).

Elucidating Non-equilibrium and Many-Body Physics of Electrons

Mesoscale architectures that confine electrons in semiconducting quantum dots, nanocrystals of metals, magnets and ferroelectrics, and novel materials such as carbon nanotubes and lithographically patterned graphene offer new horizons for discovery science and innovative technology.

Opportunity

Electrons occupy a special place in materials phenomena. Electrons are fast and agile compared to atoms, with a mass a thousand times lighter than the lightest atoms, and attosecond response times a million times faster than the picosecond times typical of atomic motion. Fast moving electrons give metals their high conductivity, excited electrons enable the absorption and emission of photons, and shared electrons create chemical bonds between atoms. Electrons mediate the interactions among atoms through their energy bands, chemical bonds, electrostatic and van der Waals forces, magnetic moments and exchange interactions, and hydrophilic/hydrophobic attractions or repulsions. Two of the five *Grand Challenges in Directing Matter and Energy: Five Challenges for Science and the Imagination* deal explicitly with electrons: How do we control materials processes at the level of electrons? How do remarkable properties of matter emerge from the complex correlations of atomic or electronic constituents?

With their light masses, electrons experience the mesoscale transition to quantized energy levels at much larger length scales than atoms (see sidebar "The Particle in a Box" on page 4), as large as 10, 100, or even 1000 nm. Confinement on such large length scales is relatively easily achieved in semiconducting quantum dots, small magnets, and nanocrystals. The wide range of phenomena mediated by electrons and the abundance of confining geometries make mesoscale electronic behavior a fertile field for discovering new phenomena, identifying organizing principles, and creating functionality by designing and imposing mesoscale structures. Confinement effects in semiconductor quantum dots have applications in transistors, solar cells, light-emitting diodes, diode lasers, medical imaging, and quantum computing. Metals, magnets, and superconductors show equally strong confinement effects, giving rise to surface enhanced electromagnetic fields, surface plasmon propagation, magnetic vortex dots, and enhanced superconducting critical fields.

Among electronic confinement effects, those involving strong electron correlation arising from the Coulomb repulsion of like charges or the magnetic interaction of electronic moments are rich in consequences and remain largely unexplored. Strong correlation is at the very forefront of materials challenges, spanning Kondo compensation, heavy electron behavior, and Mott-Hubbard localization leading to metal-insulator and superconducting-insulator transitions. Strongly correlated materials, such as the high

temperature superconductors and the manganese perovskites, have phase diagrams with many complementary and competing metallic, insulating, and magnetic phases, including novel pseudogap, charge ordered, and nematic electron phases where strong correlation plays a central role. These competing interactions give rise to intrinsic inhomogeneity and local structure on the mesoscale. The interaction of these intrinsic mesoscale structures with externally imposed mesoscale architectures has not been explored significantly. Confinement on strong correlation length scales is likely to dramatically change the observed behavior.

One strong correlation effect that has been explored in confined geometries is the Kondo effect, where a fixed local moment is partially or fully compensated by a cloud of itinerant electrons magnetically polarized in the opposite direction. In the last decade theory and experiments have examined the cloud of Kondo spin compensation surrounding a single impurity moment confined in quantum dots of ~100 nm dimensions, a tour de force of mesoscale science revealing the hidden details of the Kondo effect (see figure on next page). Similar mesoscale confinement experiments on other strong electron correlation phenomena remain to be explored and will be equally revealing.

Quantum information processing raises a host of mesoscale science challenges (see sidebar "Giant Magnetoresistance" on p. 35). Quantum computing relies on the quantum mechanical entanglement of

initial states of quantum bits ("qubits") to produce a final state representing a calculated result. The calculation is defined by the nature of the quantum interference among qubits; for certain calculations quantum computing is much faster than conventional computing. To be effective, the qubits must interact with each other strongly enough to reach the final state but interact with the environment only weakly to avoid disturbing the qubit interactions that define the calculation. The challenge is to control the interaction of multiple degrees of freedom: strong enough interaction among qubits to do the calculation, weak enough interaction with the environment to avoid noise that disturbs the calculation, and, after the final state is reached, a moderate interaction to read out the result without destroying it.

The requirement of quantum computing to minimize interaction with external degrees of freedom is counter to the usual goal of mesoscale science, which is to maximize the interactions among multiple degrees of freedom to promote emergent behavior. Although opposite in outcome, the two objectives rest on a common foundation: experimentally observing, theoretically understanding, and functionally controlling the interaction of disparate degrees of freedom. Whether the goal is to promote or inhibit, a firm observational base and predictive understanding of the interacting degrees of freedom are essential.

Meso Challenges

The meso challenges for strongly correlated electrons fall into theoretical and experimental components.
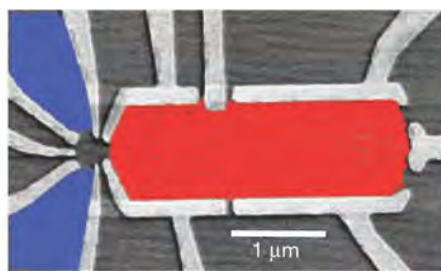
Quantum dot geometry for measuring the Kondo spin compensation cloud around a single magnetic moment. The small quantum dot on the left contains about 25 electrons and plays the role of a single magnetic moment. It communicates with the large quantum dot on the right (red), which provides a Kondo compensation cloud. The leads on the left (blue) allow the Kondo resistivity to be measured. Source: R.M. Potok et al., *Nature* **446**, 167-171 (2007).

On the theoretical side, the roles of charge correlation arising from the Coulomb interaction and spin correlation arising from magnetic interactions are fully intertwined by the coexistence of charge and spin on each electron—a spatial charge correlation implies a spatial spin correlation and vice versa, and a local magnetic field further splits spin correlations into up and down components. When all spins are itinerant, the spin compensation of the Kondo effect and the charge correlation of the Coulomb interaction reach their maximum complexity and subtlety. Electron density is a key feature of strong correlation affecting both the charge and spin compensation lengths; it differentiates correlation effects in metals and semiconductors. Mott-Hubbard localization introduces another fundamental variable: if electronic correlation becomes too strong, itinerant charges become localized, and they may further acquire a local magnetic moment that induces a new Kondo compensation cloud. Sorting out the roles and the interactions of charge

and spin compensation, localization, and local moment formation is a major challenge and opportunity for mesoscale science.

The experimental side of confining strongly correlated electron materials is equally challenging. Appropriate mesoscale boxes must be found to confine these materials on length scales that vary considerably depending on charge and spin densities. There is also a fundamental challenge to communicate the behavior of confined electronic phenomena to the macroscopic world. Electrical transport is a common probe of confined systems, attractive because it probes the quantized energy levels directly, and the transport voltage drop grows as the confinement becomes stronger. Many other probes based on thermodynamic, scattering, and spectroscopic measurements become weaker and less obvious as the size of the sample shrinks. Scanning tunneling spectroscopy is a good example of a revealing transport probe that can map local electronic behavior with atomic resolution over mesoscale fields of view.

In transport measurements electrons must be injected into and removed from the confined sample from meso- or macroscopic leads or tunneling tips, "boxes" that are much larger than the confined object, whose energy levels are continuous and whose electronic states are spread homogeneously over large dimensions. The essential elements of the confined state, quantized energy and spatial variation of electron density, are easily lost in the transition to the relatively featureless landscape of the leads (see figure on next page). Beyond the loss of

information on confinement, putting macroscopic leads on meso- or nanoscopic objects is a spatial contradiction: the small size advantage of a confined object is lost in the large leads or tunneling tips required to communicate with it. This challenge of communicating confined nanoscale behavior to the macroscopic world is a fully mesoscale challenge.
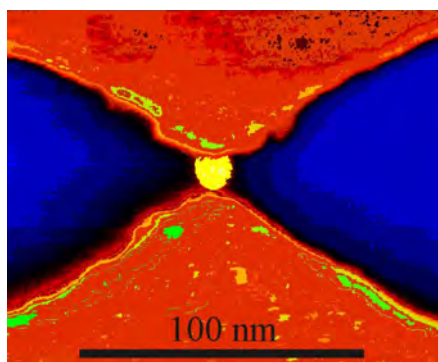
Metal nanoparticle (yellow) positioned between two leads (red) illustrating the size disparity between a confined nanoscale object and the much larger meso or macroscale electrodes that inject and remove electrons from the nano-object. The size disparity of the "boxes" representing the nanoparticle and the leads creates a dramatic mismatch in the quantized energy level structure and confined spatial variation of the electronic states in the nanoparticle and the continuous or nearly continuous energy level structure and extended spatial variation of the electronic states in the leads. The quantized electronic behavior of the nanoparticle can be lost as electrons transition to the more continuous electronic structure of the leads. Capturing the confined electronic behavior of the nanoparticle and communicating it to the larger meso or macroscopic world through transport measurements is a major mesoscale challenge. Image: Cees Dekker group at TU Delft, The Netherlands.

Research Directions

One route to exploring mesoscale confinement in strongly correlated electron materials follows the path taken by the spin compensation of the Kondo effect: shrink the size of the box. Theoretical predictions in the late 1990s showed the richness of the Kondo effect confined to a quantum dot, predicting the size of the Kondo spin compensation cloud to be of mesoscale dimensions (~100-1000 nm). This theoretical work stimulated a series of experiments looking for the Kondo compensation of the magnetic moment of a single impurity atom embedded in a semiconducting quantum dot. Transport experiments have observed confined Kondo effects in GaAs/AlGaAs quantum dots, silicon metal-oxide-semiconductor field-effect transistors (MOSFETs), carbon nanotubes, and single molecules. The success of these experiments has stimulated a host of suggestions for extensions of the confined Kondo effect by breaking the spin symmetry with a magnetic field or with polarized leads, connecting the dot to a resistive environment, imposing finite-size effects through the leads, embedding the dot in a mesoscopic ring to perform quantum interferometry, and connecting the dot to superconducting leads. These approaches are rich with new behavior and ideas embracing novel theory and experiment. The quantum dot approach can be adapted to explore other strong correlation effects such as electrostatic screening, heavy fermions, Mott-Hubbard localization, and local moment formation associated with localization. The long range of the Coulomb, dipole, and exchange interactions guarantees that these strong correlation phenomena are rich with unexplored mesoscale features.

Convenient systems for studying the mesoscale aspects of strong electron correlation are the high temperature superconducting copper oxide perovskites and the structurally similar magnetic manganese oxide perovskites. The copper oxides have a canonical phase diagram full of strongly correlated behavior (see figure on next page). The six distinct normal and superconducting phases are all strongly correlated, extending from the Mott-Hubbard antiferromagnetic insulator on the left to the Fermi liquid on the right. An additional feature of this phase diagram is the proposed quantum critical point under the superconducting dome, which would introduce an entirely different kind of mesoscale behavior as the coherence lengths of the two competing phases diverge.

Nanoparticle arrays are a second and strikingly different approach tfor bringing out the mesoscale aspects of electronic behavior (see second figure on next page). These arrays are an artificial mesoscale architecture consisting of confined nanoparticles, typically 1-20 nm, arranged in a periodic array in one, two, or three dimensions. The internal structure of the nanoparticles can be crystalline (in which case they are called "nanocrystals") or disordered. The nanoparticles are typically coated with ligands to keep the particles from agglomerating; the ligands also serve as linkers that connect the nanoparticles in the array, determine their spacing, and may provide a path for transmitting electrons or energy between neighbors.

Nanoparticle arrays provide one solution to the challenge of communicating confined behavior to the macroscopic world. Each nanoparticle communicates with its neighbors through tunneling or the linker ligands, maintaining the confined geometry and the quantized energy level structure on each side of the interaction. Contact with the external world is made by macroscopic leads at the edges of the array and covers many nanoparticles. The confined behavior is lost in those nanoparticles contacting the leads, but survives in the many more nanoparticles away from the contact area. The confined transport behavior in the pristine areas of the array dominates the transport properties and signals the confinement phenomena to the outside world.
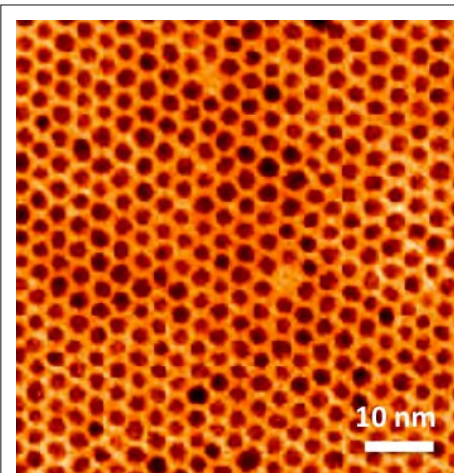
The architecture of nanoparticle arrays offers many knobs to probe and tune mesoscale behavior. Nanoparticle

Phase diagram for copper oxide high temperature superconductors (shown as a function of hole doping or oxygen content). There are at least six strongly correlated phases, one of which is superconducting. Correlation is strongest on the left, dominated by the antiferromagnetic Mott-Hubbard insulator, and decreases to the right. The mesoscale aspects of strong correlation are different in each phase and remain largely unexplored. The proposed quantum critical point (QCP) on the T = 0 line induces an entirely different kind of mesoscale behavior, as the coherence lengths associated with the competing phases diverge. Source: C.M. Varma, *Nature* **468**, 184-185 (2010).

size is a critical parameter, allowing the energy level spacing between quantized levels within the particle to be adjusted through the size of the confining box. The physical separation and the degree of communication between neighboring nanoparticles constitute a second knob, tunable by the length of the linker ligands connecting them. The composition of the nanoparticles introduces enormous flexibility, embracing metals with strong or weak electronic correlation and wide or narrow bands, semiconductors with low carrier density, magnets, ferroelectrics, and multiferroics. Composite nanoparticles, such as core-shell or Janus nanoparticles, add functionality to the individual elements of the array. Nanocrystals that display strong electronic correlation, such as the high temperature superconductors, allow exploring the effects of mesoscale conf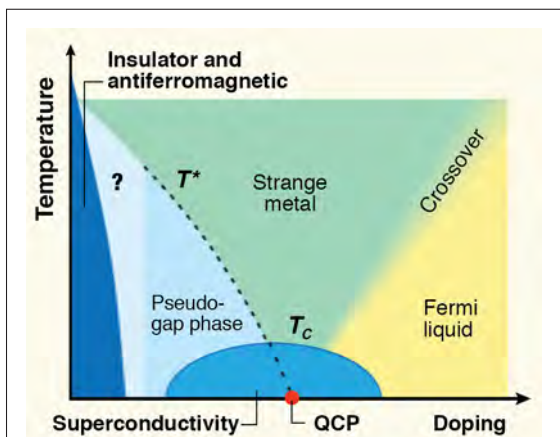inement on, for example, the doped Mott-Hubbard insulator, the pseudogap, the strange metal, or the superconductor. The shape of the nanocrystals introduces anisotropy, and arrays with two or more distinct kinds of nanocrystals (such as magnetic and metallic) in ordered or disordered configurations allow the interaction of distinct degrees of freedom. All of the hallmarks of mesoscale behavior—granularity, quantized energy level spacing, collective behavior, interacting degrees of freedom, defects and statistical variation, and heterogeneity—can be rationally designed and systematically tuned in nanoparticle arrays. The range of mesoscale behavior that can be explored is virtually unlimited. In principle, every phenomenon of ordinary atomic condensed

matter physics and chemistry can be recast in mesoscale terms via nanoparticle arrays, opening wide horizons of new or emergent behavior.

The synthesis of nanoparticle arrays presents major opportunities for mesoscale science that are just beginning to be explored. We are learning to

Array of nanometer-size gold nanocrystals connected by linker ligands. Source: R.P. Andres et al., *J. Vac. Sci. Technol.* **A 14**, 1178 (1996).

fabricate arrays by a variety of means, including slow evaporation of the solvent from a colloidal suspension of nanocrystals ("drop casting"), or directed assembly by DNA or polymer templates. Binary arrays with two distinct nanocrystal species and sizes have been made, as have arrays with quasicrystalline structure. The field is in its infancy. We are now learning to control the structural parameters of arrays including degree of order, number of nanoparticle species, and number of dimensions. As the fabrication challenges are conquered and synthesis of more complex architectures is mastered, the challenge of fabricating targeted functionalities will come to the fore. Solar cells sensitive to specific photon energies, memory bits as small as 1 nm, supercapacitors,

semiconductor lasers, advanced thermoelectrics, and biological and mechanical sensors are some of the potential functional applications.

Potential Impact

The confinement of electronic behavior in mesoscale architecture (such as semiconducting quantum dots; metallic, magnetic, and ferro-electric nanocrystals; carbon nano-tubes; and lithographically patterned graphene sheets) results in a host of new behavior that is just beginning to be explored. Confined electronic behavior described by quantized energy levels differs qualitatively and often dramatically from bulk macroscopic behavior governed by continuous energy distributions. The promise of mesoscale science is the opportunity to tune the degree of confinement to any arbitrary level, and to connect multiple confined electronic boxes expressing different charge, spin, and mechanical degrees of freedom to produce new behavior and ultimately new technology that performs faster, is cheaper, and boasts greater efficiency and durability. A host of applications to polymer-based nanocomposites, energy storage and conversion, environmental monitoring and remediation, biological diagnosis and therapy, quantum computing, and electronic and optoelectronic devices can be explored. The opportunities for innovation in mesoscale discovery science, identification of new orga-nizing principles, and creation of new technology are just beginning to emerge.

Giant Magnetoresistance: A Triumph of Mesoscale Science

Discovered in 1988 and generally considered to mark the birth of the field of spintronics, giant magnetoresistance exploits the mesoscale hall-marks of interacting degrees of freedom and heterogeneous structures to create new mesoscale phenomena and functionality and has perma-nently changed the landscape of computer memory.

Giant magnetoresistance controls the motion of the charge on an electron by manipulating its spin, exploiting the coupling between these disparate degrees of freedom. A typical configuration is shown in the figure. Ferromagnetic CoFe layers surround a non-magnetic MgO layer. As an electron crosses the sandwich, its spin magnetic moment is oriented by the first ferromagnetic layer and carried across the intermediate layer. The second ferro-magnetic layer blocks or passes the elec-tron if its spin is opposite or aligned with the polarization of the second layer. The magnetic polarization of the second layer is thus a switch for the electric current, capable of altering it by up to 200%. For memory applications, the size of the current reads whether the two ferromag-netic layers are set parallel or opposite.

Giant magnetoresistance embodies several hallmarks of mesoscale science. It exploits the coupling between charge and spin, two distinct degrees of freedom, to create a new phenomena, switching electric currents with a magnetic field. Its heterogeneous structure combines different functionalites in different compo-nents, magnetic layers for setting and filtering the electronic spin, and a non-magnetic layer for transmitting the electric current. It is also explicitly dynamic, trans-porting and processing charge and spin across the composite system.

Giant magnetoresistance spawned succeeding generations of concepts and devices, including spin valves and magnetic tunnel junctions, that enabled
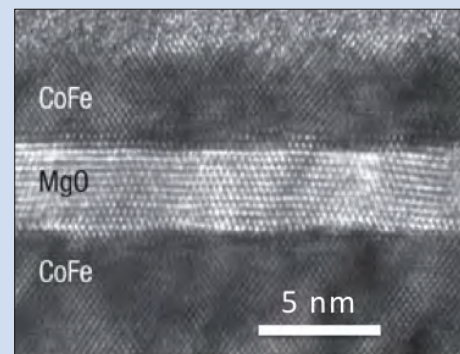
*Mesoscale trilayer sandwich consisting of ferromagnetic layers of CoFe enclosing a nonmagnetic layer of MgO. Switching the magnetic polarization in the ferromagnetic CoFe layers from parallel to antiparallel switches the electrical resistance by up to 200%. The interacting magnetic and electronic degrees of freedom create new mesoscale phenomena and functionality in a heterogeneous structure. Source: S. P. Parkin et al., Nature Materials **3**, 862-867 (2004).*

the era of high-density information storage that is now universally employed in digital electronics. The road from discovery to market was remarkably fast, only nine years before its introduction to commer-cial devices. In 2007, Peter Grunburg and Albert Fert were awarded the Nobel Prize for Physics for discovery of giant magneto-resistance. Giant magnetoresistance illus-trates many of the benefits of mesoscale science: discovery of new phenomena, creation of new technology, and manu-facturing at the mesoscale using minimal material and atomic level interconnects while producing high efficiency, low cost, long life, and high economic and societal impact.

Harnessing Fluctuations, Dynamics, and Degradation for Control of Metastable Mesoscale Systems

The inherent metastability of complex behaviors in mesoscale systems, including biological and human-made systems, is revealed not only on multiple length scales but also on *multiple time scales*. This metastability engenders near-equilibrium fluctuations and longer time dynamics. Ultimately, these conditions can be exploited to introduce real-time responses to environmental cues, mitigate materials degradation, and extend useful life.

Opportunity

At the mesoscale, control of complex systems whose behavior reflects properties across a wide range of length and time scales requires knowledge not only of the averages of pertinent observables as one usually assumes, but also statistical variances and time-dependent fluctuations around the time averages (see figure at right). Only with this knowledge can we reach the goal of controlling short-time and mesoscale dynamics with externally driven energy inputs or externally imposed structural modifications, with the ultimate aim of countering completely the degradation and failure that occurs over long time scales.

Human-made complex mesoscale inorganic- or bio-systems (such as those employed in long-lived photovoltaic technologies, biologically

inspired cargo delivery platforms, and environmentally responsive, self-assembly/disassembly processes) all require successful control of length and time scale evolution. In drug delivery platforms, for example, the targeted delivery time and location must be controlled by adapting inherently metastable features of the self-assembled drug vectors to induce them to disassemble and release their drugs on an external cue from outside the body. Controlling this kind of metastability and degradation occupies the center stage of many areas of mesoscale science.

Harnessing the metastability of mesoscale systems holds the promise of developing systems and processes that are self-organizing

and self-repairing (through *decreased metastability*), but at the same time also responsive to their local environments and amenable to external control (through *increased metastability*). The detailed manipulation of this fluctuation-enabled control would, for example, allow us to engineer the release time of cargo delivery platforms, control the assembly-disassembly kinetics of self-assembled macromolecular aggregates, and modify the lifecycles and extend the overall lifetimes of photovoltaic technology to improve its sustainability and reduce costs.

Meso Challenges

Metastable mesoscale systems exhibit fluctuations, correlations, and dynamics that lead to interesting
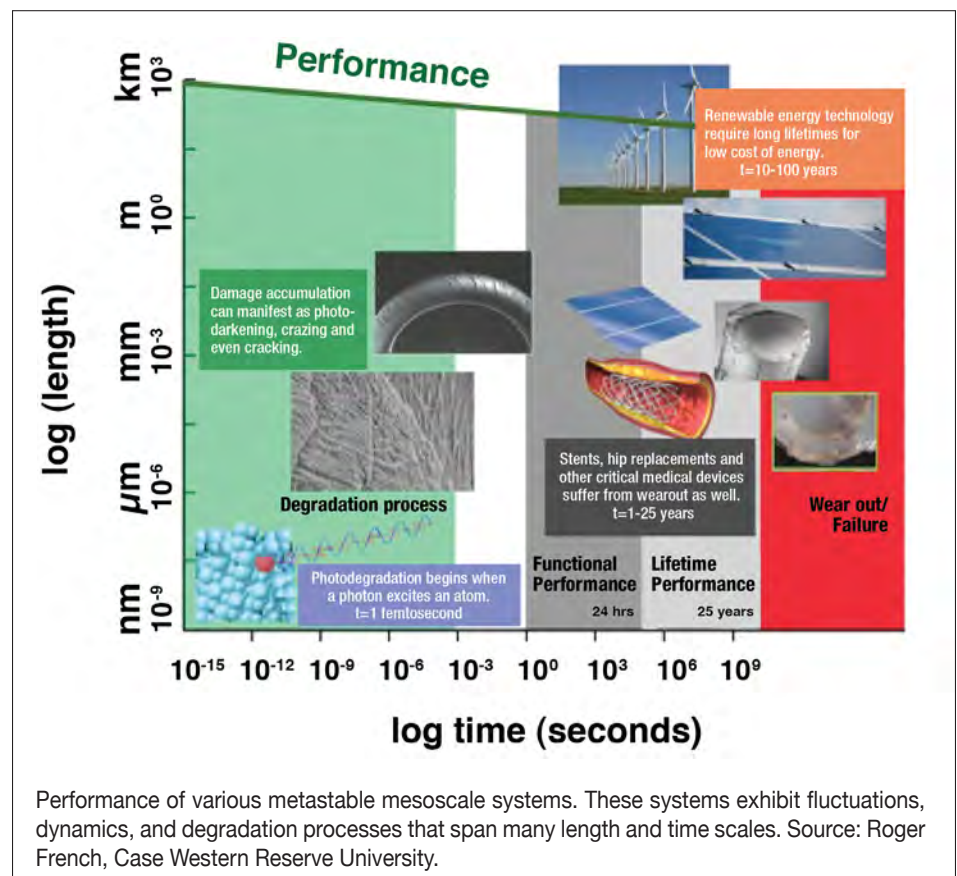
Performance of various metastable mesoscale systems. These systems exhibit fluctuations, dynamics, and degradation processes that span many length and time scales. Source: Roger French, Case Western Reserve University.

physical phenomena whose proper understanding requires fundamental physical insights on a wide range of length and time scales. For example, electromagnetic field fluctuations in dielectric media produce universal van der Waals–London dispersion interactions, electronic correlations in materials give rise to new electron and other quasi-particle states leading to complex optical properties, and atomistic correlations and fluctuations are essential to nucleation, phase transitions, and growth in inhomogeneous media.

The temporal behavior of mesoscale systems bridges a vast range of lifetimes from initial formation dynamics to time-dependent behavior of the pristine system, to individual particle degradation and defect generation, and all the way to aggregation of defects into more complex, larger units leading to eventual degradation and final disintegration of the system. The relevant evolution embraces length and time scales associated with formation and growth as well as degradation and disintegration. Current understanding of fluctuations and dynamics in driven systems, either close to or far away from equilibrium, is lacking in detail and depth due to the high degree of complexity ($>>10^7$ atoms) and the long span of length (10^{12}) and time ($>10^{24}$) scales. However, recently developed tools and insights from the computational, biological, physical, chemical, and materials sciences could pave the way for breakthroughs in harnessing the dynamics of these systems for time-responsive functionalities and for longer life without the need for unnecessary oversimplifications.

Lifetime and Degradation of Energy Technologies

In photovoltaic power applications, modules and their associated processes must have long lifetimes, 25 years or more, in order to make solar power a commercially viable energy technology. Current qualification standards are based on safety and initial performance; they do not serve as lifetime qualification tests, nor has the necessary lifetime and degradation science been developed to provide quantitative and mechanistic understanding. Advancing this reliability physics, or physics of failure, requires new metrology and metrics at the mesoscale for identifying and quantifying the degradation mechanisms and rates by using

a stress-and-response framework that extends from initial formation to complete functional degradation of the materials (see figure below).

Bio-inspired Rational Design of Cargo-Delivery Platforms Based on Plant Viruses

A central goal of nanotechnology is the fabrication of hybrid or cargo-loaded systems that programmably self-assemble at the atomic level. Biology has achieved this capability through evolution. We are now developing bio-inspired delivery platforms and hybrid systems that use plant-derived viral nanoparticles engineered to encapsulate cargos that are mineralized, metallized, or chemically engineered with ligands that enable site-specific

Power loss as a function of time for a photovoltaic (PV) module or power plant. Mitigating key degradation modes and lifetime penalties can increase a PV module's lifetime performance. The key degradation modes and rates are essential components of a practical reliability physics model and must account for the degradation of a module in real-world environmental conditions. L. S. Bruckman, R. H. French, unpublished.

delivery and deposition (see figure at bottom of page). Viral nanoparticles are dynamic structures that can be disassembled and reassembled into various configurations, depending on control signals from the environment. The challenge is to precisely control self-assembly and disassembly of components that encapsulate cargos and protect them during transport to the deposition site. Such a system could be used to assemble a semiconductor device. This can be accomplished only if the self-assembled viral nanoparticle states are sufficiently metastable that soft control of their environment precipitates the disassembled state that delivers their cargo to the targeted location at the targeted time.

Environmentally Responsive Long-range Interaction Driven Self-assembly/Disassembly

A rational design framework to control fluctuations on different time scales would enhance the design of nanotechnology processes. For example, for viral nanoparticles the rational design framework would be based on optimized assembly/disassembly parameters obtained from atomic-structure-based quantum chemical calculations, concurrent measurements of mesoscale properties of its components, and biophysical thermodynamic modeling and measurements of viral nanoparticle stability and assembly energetics related to cargo loading and release. These different approaches range over many orders of magnitude in time, starting at the high frequency of optical properties of materials out to the time scales that define equilibrium conditions. The new paradigm for a rational design framework based on a synergy of quantum chemistry, materials science, theoretical biophysics, and practical bioengineering would introduce a continuous feedback loop extending over multiple space and time scales, where the optimal parameters determined from the modeling framework would be provided directly to the experimental setup/pharmaceutical formulation, and would direct modification of the modeling scheme (see figure immediately below).
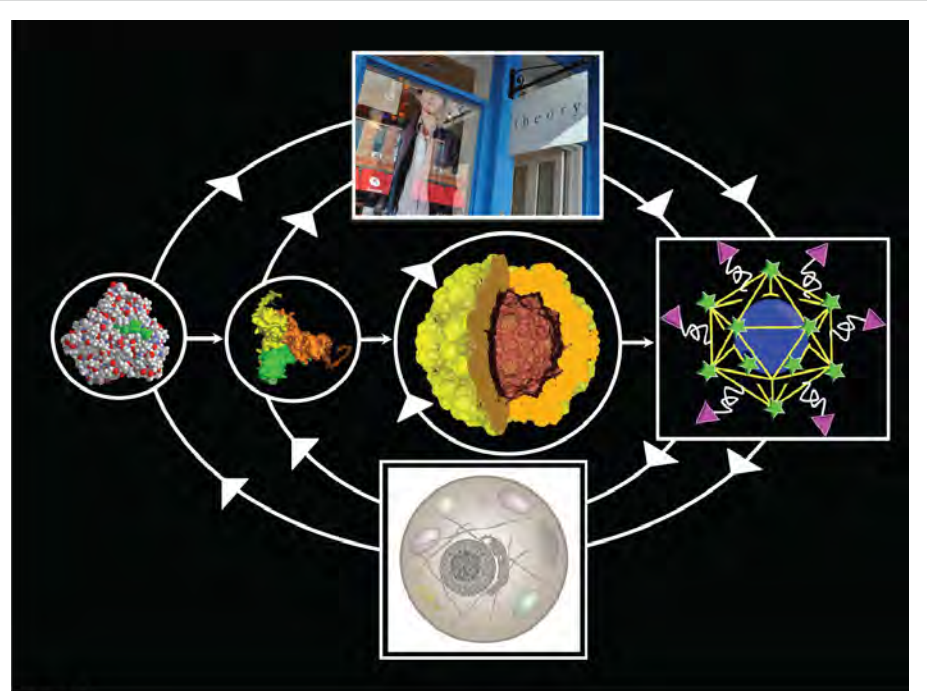
Mesoscale science feedback loop of measurement, learning, modeling, engineering, and application that informs the design, production, and lifecycle performance of viral nanoparticles loaded with cargos. Source: Rudolph Podgornik, University of Ljubljana, Slovenia.
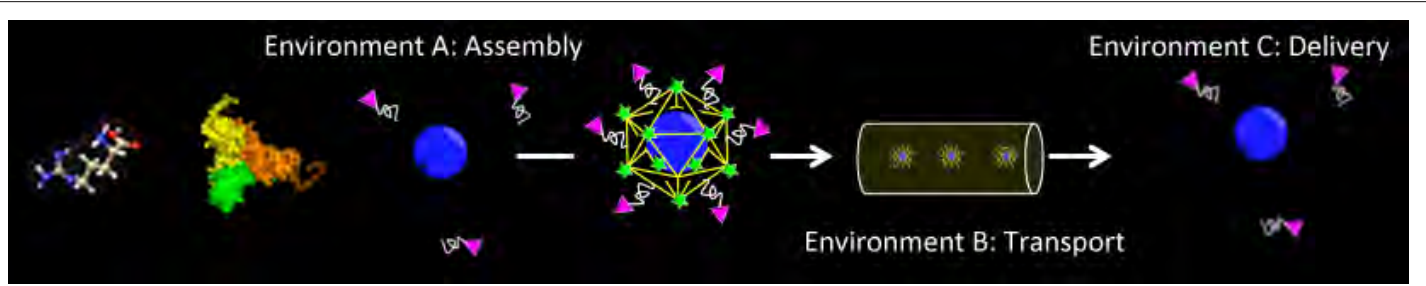
A mesoscale case study: lifecycle of a viral nanoparticle, from formation of amino acids and coated proteins to assembly of viral nanoparticle, then its transport and delivery and disassembly, followed by deposition of the cargo. Source: Nicole F. Steinmetz, Case Western Reserve University.

Research Directions

Metastable mesoscale systems encompass multiple space and time scales, including fluctuations, dynamics, degradation, and evolution in complex energy landscapes in response to varying external inputs. The research needed to control these complex interacting/evolving systems that span wide length and time scales can be subdivided into distinct regimes: equilibrium thermodynamics, close to equilibrium dynamics, far from equilibrium kinetics, and actively driven dynamics.

At equilibrium, complex mesoscale systems are controlled by short- and long-range interactions coupled to quantum mechanical and classical thermal fluctuations. In equilibrium with the environment, such systems can exhibit pronounced and controllable structural and functional changes in response to changes in environmental conditions (see figure below). The proteins and viruses in complex biological systems are examples of this kind of equilibrium response. This characteristic can be further harnessed in order to engineer specific dynamical response in various environmental conditions, as in targeted cargo delivery or in controlled self-assembly.

A second class of metastable systems and/or materials are those that are *not in equilibrium*, such as kinetically frozen or quenched systems (for example, atomic or molecular glasses) that are forced to reside in states that are often very far from equilibrium. Adding energy to the system from the environment can trigger an "annealing step" toward equilibrium, providing a mechanism to steer the system away from metastability toward a new quenched state with different structure, durability, or functionality.

A third metastable class is *driven systems*, such as biomolecular motors involved in viral DNA packaging and release, in which the addition of an energy source to the system (for example, from adenosine triphosphate) drives it away from equilibrium and toward metastability, as seen in mutant variants of partially filled or overfilled bacteriophages.

Across all of these heterogeneous equilibrium and nonequilibrium systems, fluctuations, dynamics, and degradation play a critical role. Exploiting fluctuations in various order parameters coupled via quantum and classical degrees of freedom creates opportunities for universal organizing pathways, avenues for environmental

Stabilization/destabilization of mesoscopic systems via thermal fluctuations of the van der Waals–London dispersion (vdW-Ld) interactions. The thermal fluctuations give rise to the Matsubara frequency terms, which are the classical contribution to the vdW-Ld interactions, while the zero frequency term is the quantum mechanical contribution. Source: V. Adrian Parsegian, University of Massachusetts, Amherst.

responsiveness, and scenarios for discovering improved lifetime and sustainability. As these metastable systems evolve in time, they exhibit dynamics over short time scales that can be used to perform designed tasks, and over longer time scales that control the life of the system. The metastable structure can be intentionally changed by response to environmental cues, leading to evolution through many time and length scales (see figure at right). These kinds of designed structural changes can lead to several salutary outcomes:

1. Reversible assembly/disassembly of soft matter and bio-systems whose structure is formed as a consequence of long-range interactions (as compared to the irreversible formation of covalent bonds), and that can be responsive to changes in environmental conditions and variables or moved to new environmental conditions, as in cargo delivery systems.

2. Systems near or far away from equilibrium that evolve driven by an instantaneous energy shock in the direction of a preset form and structure, far removed from that dictated by equilibrium thermodynamics alone. Examples of this condition are quenched disorder of many types in kinetically frozen systems and their evolution over short or very long time scales.

3. Mesoscale metastable systems which are explicitly driven by a continuous energy input, such as biological motors and contractile tissues with an abundant energy source (see figure above). These systems are far from equilibrium while energy input continues,

Biological systems display metastable mesoscale behavior, including self-organization across scales. Upper image: Length scale for proteins self-organizing into living materials. Lower image: Self-organization of treadmilling polymers that utilize chemical energy to do mechanical work. Source: Margaret Gardel, University of Chicago.
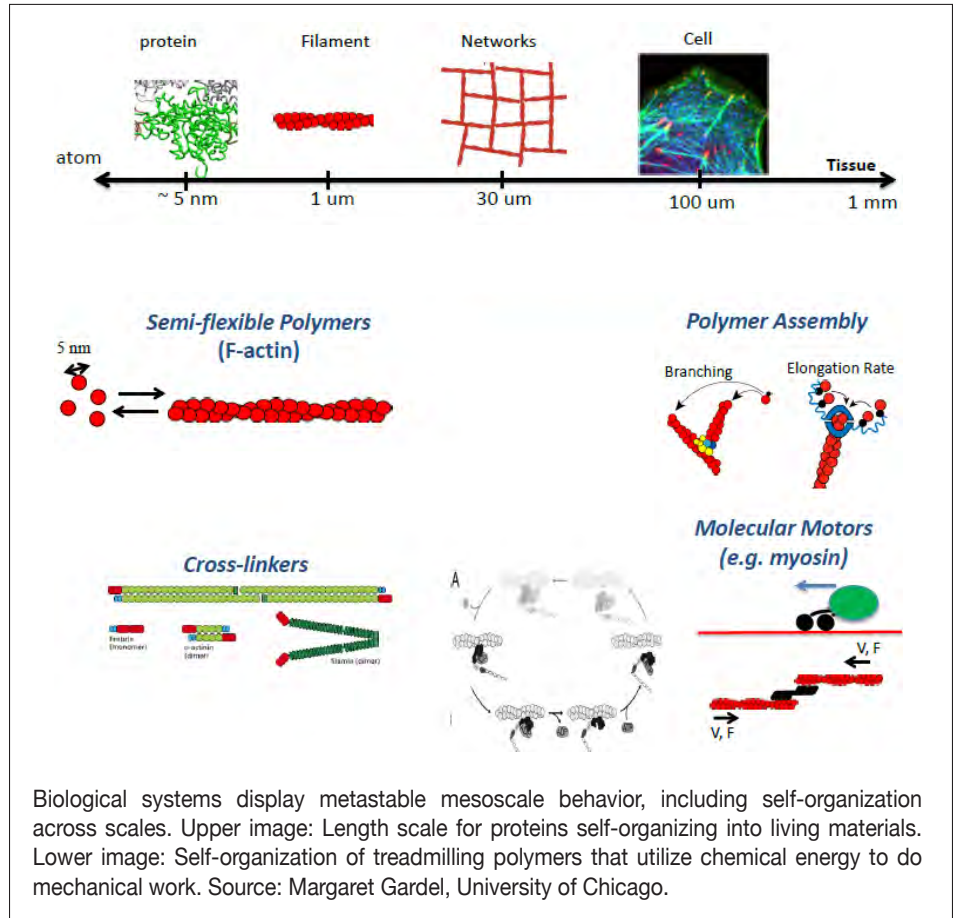
and resulting work is performed as an outcome of energy degradation. Once the energy source is removed, they revert to their quiescent equilibrium structure.

Potential Impact

The potential impact of harnessing fluctuations, dynamics, and degradation in order to control metastable mesoscale systems is significant, both for bio-inspired and inorganic systems (see sidebar "Opportunities to Enlist Bacteria as an Energy Workforce" on page 42).

In the bio-inspired rational design of cargo delivery platforms based on plant viruses, the goal is to fabricate a delivery platform that first

self-assembles and later disassembles or disintegrates with programmability, a property biology has naturally achieved through evolutionary processes. This requires simultaneous control of the properties of the system on multiple length and time scales. The mesoscale component is crucial here because our control of these systems is neither wholly microscopic, though we are dealing with nanostructures, nor is it wholly macroscopic, because we need not steer a macroscopic number of cargo-carrying virus-like nanoparticles. Frequently it suffices to control properly only a small number of effectively targeted molecular vehicles. By harnessing inherent fluctuations and metastability of the self-assembled

molecular carriers, researchers will be able to drive them by design down well-defined dynamical paths that eventually lead to the place and the time where they are needed.

Mesoscale system performance over a lifetime is a significant challenge. Typically, the focus has been only on initial performance and the initiation of degradation, a far easier task. Lifetime correlates closely with the nature of change from a robust initial structure to a degraded condition through damage accumulation. Mesoscale properties and behavior deviate from those set by initial values due to real-world interactions and exposures, leading to either catastrophic failure or continuous degradation in performance to a level without utility. The lifetime and degradation of complex mesoscale systems, such as photovoltaic cells, are intrinsically metastable and dominated by large numbers of defects, interactions, and competing degrees of freedom. For example, the degradation of a photovoltaic module over its lifetime presents a significant challenge to forecasting the cost of solar technologies and their levelized cost of electricity and net present value. Understanding the degradation modes, mechanisms, and rates of decay of photovoltaic modules in a vast array of real-world conditions would give insights into ensuring high performance of future generations of solar technologies.

For energy systems and medical devices and technologies, lifetime requirements of greater than 20 or 40 years correspond to dynamical processes spanning the range from 10^{-18} or 10^{-15} seconds to 10^9 seconds. This suggests that a fundamental challenge is studying the time evolution of metastable systems over 27 orders of magnitude. Typically, we have been unable to span 6 or 9 orders of magnitude in time without being overwhelmed by the limitations of our assumptions, approximations, and methodologies. Advances in mesoscale theory and computation have the potential to significantly expand this range with corresponding impact.

Enlisting Bacteria as an Energy Workforce

Cell signaling enables large colonies of cells to coordinate their functions and work in concert, presenting mesoscale opportunities to disarm pathogens and reprogram function to produce energy.

Biological systems involve vast numbers of living cells whose interconnected networks define function. Protein synthesis, translocation, and modification, for example, present a complex network at the nanoscale that is guided by a diversity of cues. The interactions between cells that determine phenotype are also guided by signaling events, wherein cells respond to cues of various forms—from structurally distinguishing small molecules and charge-specific ions produced by nearby cells to mechanical forces imposed by neighboring tissues. Then, populations of cells, including consortia of bacteria or tissue composed of differentiated cell types, guide complex physiological systems such as the gastrointestinal tract. Identifying and re-programming the machinery that enables bacterial colonies to communicate present a major opportunity for them to, for example, generate energy. These opportunities include:

- **Cell signaling.** Unraveling the language of cell signaling is both a scientific grand challenge and a major mesoscale frontier—involving large numbers of cells, multiple cell types, length scales from small molecules on the nanoscale to larger cells and tissues on the microscale, and time frames ranging from small molecule binding, enzyme reactions and diffusion for signaling entities to evolution of cell groups and tissues among species. The implications for society are profound if research can unravel nature's complex network of nano- and mesoscale cell-signaling processes.

- **Bacteria in human health.** Bacterial cells substantially outnumber human cells in our bodies, particularly in the digestive tract, and they are essential to health. The importance of bacteria and their contribution to our metabolic well-being is becoming increasingly apparent. In the last decade, the "microbiome" has received significant attention, particularly as a target of next-generation sequencing technologies racing to identify commensal species as well as the emergence of pathogens. Dangerous bacterial attacks have become commonplace and routinely newsworthy—tainted spinach, methicillin resistant Staphylococcus aureus and anticipated "superbugs", infections initiated by catheters in hospitals, and others. Signaling between these patho-
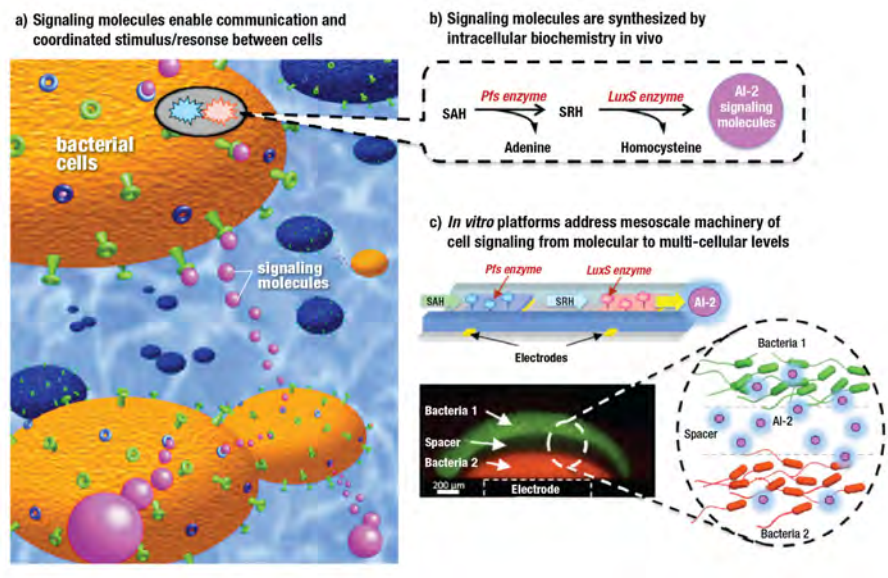
Cell Signaling. *(a) Small signaling molecules are made and sensed by cells, enabling coordinated behavior among bacterial colonies and stimuli/responsive behavior between different cell and tissue types. (b) Signaling molecules are manufactured by metabolic pathways within cells, e.g., the autoinducer-2 family involved in bacterial attack. (c) In vitro microfluidic platforms present one approach to diagnosing and modulating these cell signaling processes. Sources: K.K. Carter et al., Metabolic Eng.* **14** *(2012) 281-288 (2012); X. L. Luo et al., Lab on a Chip* **8**, *420-430 (2008); Y. Cheng et al., Adv. Func. Mater.* **22**, *519-528 (2012).*

genic bacteria is what enables their mischief, but research to understand, detect, and re-engineer their communication and behavior is in its infancy.

- **Re-programming bacterial behavior.** Identifying and re-programming the machinery that enables bacterial colonies to communicate presents a major opportunity with implications from biomedicine to energy. In medicine, traditional antibiotics to control pathogenic bacteria work by killing them and all nearby healthy bacteria, forcing the remaining cells to mutate, evolve, and do more damage. Accordingly physicians, concerned about their increasing inefficacy, are more reluctant to administer antibiotics. New mechanisms to redirect/re-engineer bacterial activity offer promise, e.g., by interfering with the networks by which signaling molecules are made, relayed, and transduced, and thereby altering the collective behavior of extended bacterial populations. This is an inherently mesoscale challenge.

- **Bacteria as an energy workforce.** A parallel opportunity exists at the mesoscale in understanding and directing ubiquitous bacterial colonies to generate energy, either as biofuels (e.g., from cellulose) or as electricity (e.g., from microbial fuel cells). The efficiency of these sources depends on how well we can understand and re-engineer bacterial behavior from biomolecular processes to signaling between cells and longer range interactions with various tissue types. Microbial fuel cells also require efficient interfacing of cell populations to electrical wiring that maintains connections as well as cell health. Thus, enlisting bacteria for energy production will likely require that we modify the biochemical machinery at the subcellular level, assemble robust architectures for evolving bacterial colonies, and control the signaling cues which determine this evolution—challenges centered at the mesoscale.

Directing Assembly of Hierarchical Functional Materials

The integration of disparate materials classes by "top-down" and "bottom-up" approaches, now quite distinct and representing different operating principles and spatial scales, is an underpinning focus of directed meso-scale assembly.
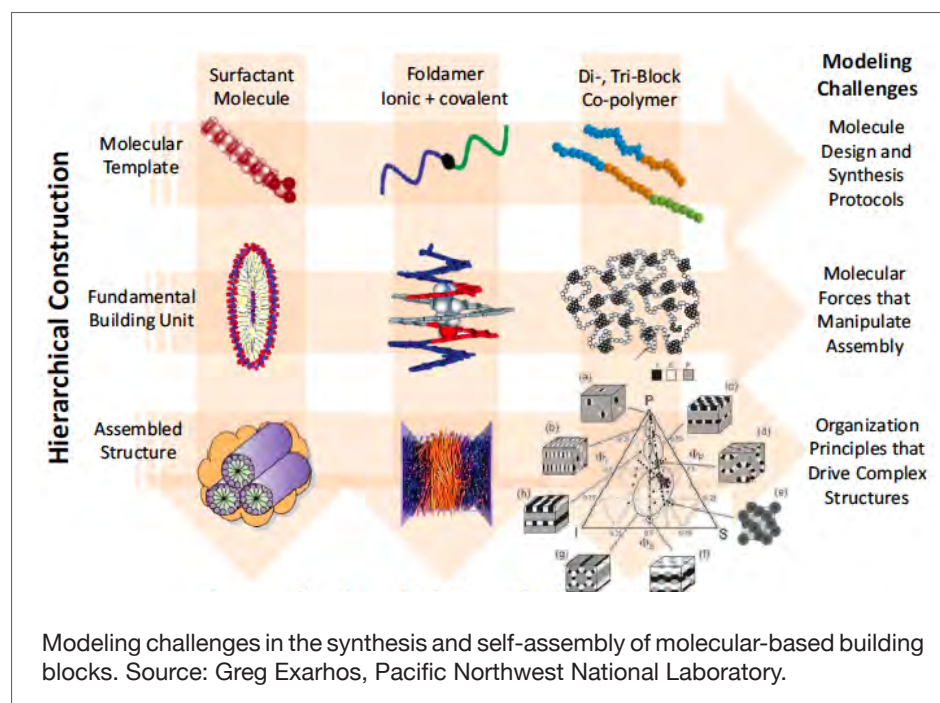
Opportunity

A grand challenge in materials science is to create multiscale functional structures that encode information; adaptively respond to their environment; and capture, transport, and utilize energy. The ability to design and realize the complex and composite materials that we envisage will require significant advances in how we synthesize materials, how we process and assemble them, and how we control their composition and architecture. The parameter space available to us is simply enormous, thereby necessitating a concerted experimental and theoretical approach, particularly considering that both equilibrium and nonequilibrium states of matter are of interest. The emphasis in mesoscale synthesis and assembly is on integration of disparate materials classes by "top-down" and "bottom-up" approaches. Bridging the gap and allowing these two powerful approaches to influence, complement, and reinforce each other are a major challenge and opportunity of mesoscale science.

Meso Challenges

Synthesis and Self-assembly of Programmable Building Blocks

Molecular-Based Building Blocks. The rational design and synthesis of structure-directing, molecular building blocks (surfactants, foldamers, amphiphilic peptides, charged electrostatic complex formers, multi-block polymers, etc.) are required to guide the hierarchical self-assembly of desired architectures over large distances (see figure below). Toward this objective, a fundamental understanding and ability to precisely manipulate the intra- and inter-molecular forces that enable and guide self-assembly are needed. The full range of non-covalent forces (van der Waals, π-stacking, metal-ion coordination, hydrogen-bonding, electrostatic, hydro- and solvo-phobic, steric, and packing) will be deployed in more extensive, creative fashions to achieve the goals of mesoscale materials science. Beyond this, molecular architectures will become more intricate and complex. Through the intermediary of block copolymers, with increasing numbers, chemical types, and various architectural connectivities of blocks, the science of synthetic macromolecules will progress toward the realm of protein folding and self-assembly. At the same time, through the tools of synthetic biology, genetically programmed synthesis of amino acid polymers, comprising natural and unnatural amino acids, polypeptides and their analogs (e.g., polypeptoids) may increasingly develop new materials based on their mesoscale structure. Exploiting the self-assembly possibilities with polymers containing charged blocks that can complex with oppositely charged segments makes the analogy to proteins even stronger.

Modeling challenges in the synthesis and self-assembly of molecular-based building blocks. Source: Greg Exarhos, Pacific Northwest National Laboratory.

Particle-Based Building Blocks. Toward this objective, a fundamental understanding is needed of the often subtle and competing consequences of anisotropic repulsive and attractive forces (typically strong and spatially short ranged) and coupled translational-orientational Brownian dynamics over a wide range of length and time scales, problems that have no counterpart in traditional materials science based on atoms or homogeneous spherical particles. As a result, supracolloidal assemblies in both isotropic and anisotropic configurations can be produced that possess widely varying connectivity, porosity, and properties (see figure below at left).
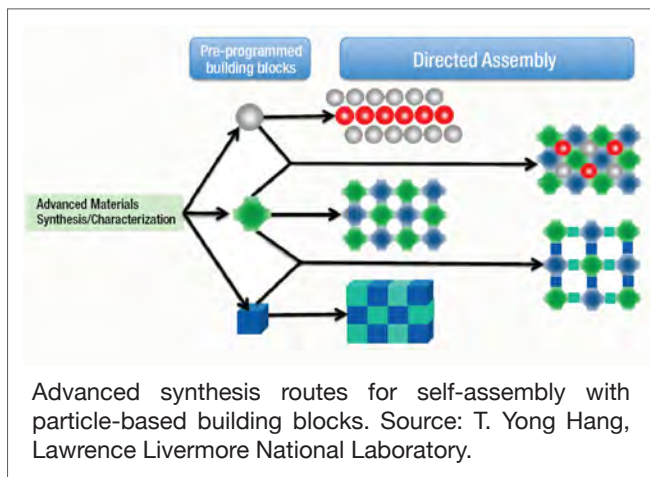
aspects due to building block shape and rigidity. The size and shape of the self-assembled clusters are highly sensitive to both interparticle interactions (e.g., charge, hydrophobicity) and "Janus balance." Intentional variation of this latter parameter, defined by α, can be achieved by scalable synthetic methods.

To date, only a limited range of programmable building blocks has been realized, yet by tailoring both particle shape and chemical heterogeneity, programmable surface forces acting in concert with the nonadditive consequences of steric p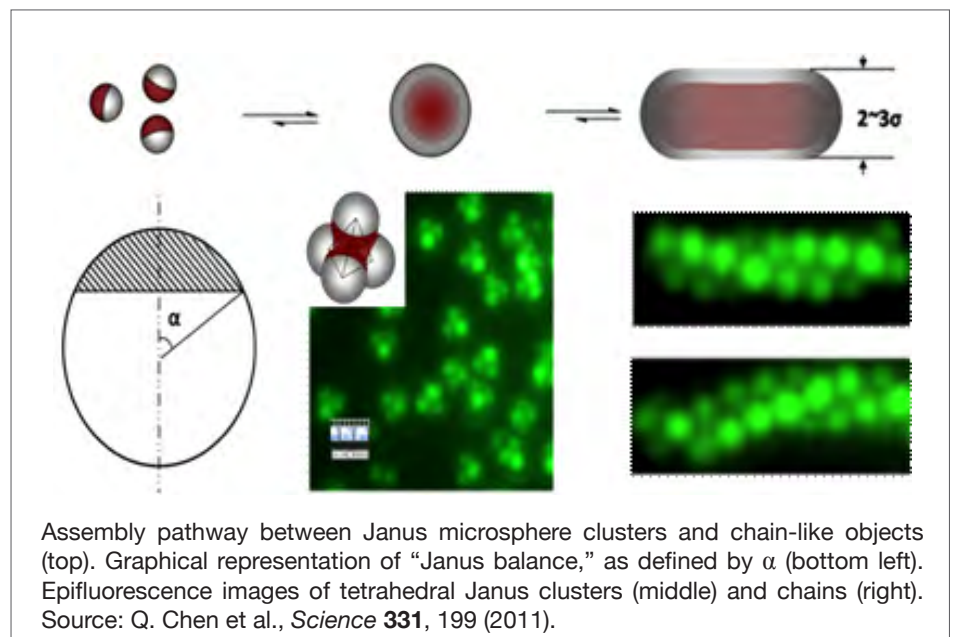acking constraints will enable new assemblies and dynamical behavior to be realized. Computationally, more insight into structural possibilities has been gained from simulation of dense particle systems, where shape or "patchiness" (beyond Janus) confers on particles

some of the character of atoms and molecules that arise from the symmetries of atomic and molecular electronic orbitals. Translation of these nanoscale particle symmetries into materials structures at the mesoscale is a current experimental challenge.

Dynamic Synthesis via Biomimetic Architectures

While the synthesis of functional materials as static or even responsive entities remains a challenging frontier area of research, a higher level of sophistication—the *dynamic synthesis* of functional materials—remains virtually unexplored. Dynamic synthesis would enable on-demand growth, re-configurability, and restoration, characteristics that are mostly unachievable in today's materials or rudimentary in concept. To meet the requirements of mass and energy transport for dynamic materials synthesis, as well as the regulatory capabilities needed for control, new mesoscale materials and associated science and technology are needed in the area of artificial circulatory systems. This understanding will enable the design of vascularized

Advanced synthesis routes for self-assembly with particle-based building blocks. Source: T. Yong Hang, Lawrence Livermore National Laboratory.

The power of this concept is shown in the illustrative example (see figure at right) in which amphiphilic Janus microspheres self-assemble into a variety of motifs, including stable Janus clusters, whose composition and shape can be *uniquely specified* (as opposed to polydisperse collections) as well as long chiral semiflexible chains. The chemical heterogeneity that drives cluster formation is akin to the polar/ nonpolar balance in molecular and polymeric surfactants, but with qualitatively new geometric

Assembly pathway between Janus microsphere clusters and chain-like objects (top). Graphical representation of "Janus balance," as defined by α (bottom left). Epifluorescence images of tetrahedral Janus clusters (middle) and chains (right). Source: Q. Chen et al., *Science* **331**, 199 (2011).

solids and functional fluids flowing through the channels. The challenges of dynamic materials synthesis will require, for example, fluids capable of delivering reagents, catalysts, and synthetic precursors with spatial and temporal gradients in concentration appropriate to achieve the desired synthetic target. In one embodiment, we envision the guided delivery of suspended carrier particles in flowing vascular streams. The size, interfacial chemistry, and mechanical characteristics of the particles will govern their partitioning between channel wall and fluid stream, thereby enabling complex transport mechanisms, such as rolling, as a possible means to facilitate surface-guided particle delivery (see figure below). Interfacial interactions between particles will also allow particles to communicate, thereby controlling the stoichiometry and concentration of synthetic precursors delivered to the active zone. Finally, we imagine the need for particles to be equipped with triggering mechanisms for stimuli-initiated deployment of their payloads.

Directed Assembly of Hierarchical Functional Architectures

Directed assembly is a powerful approach for integrating top-down and bottom-up assembly strategies. The ability to deterministically assemble functional objects into planar and three-dimensional configurations would enable significant advances in the design and performance of materials for light capture and utilization, battery electrodes, and lightweight structures. Achieving this mastery requires a deep integration of expertise in the design, synthesis, assembly, and modeling of a broad class of materials in myriad shapes, including nanoparticles, microwires, monocrystalline semiconductor platelets, and so on.

Massively parallel assembly of micro/nanostructured materials represents a capability that is critically enabling for a wide array of energy-relevant devices. Starting from the fluid state, particles and nanowires suspended as individual elements or assembled clusters can be used as inks to form

functional structures by fluid printing strategies. In the solid state, methods that control fracture at soft material interfaces enable a different form of printing, with complementary capabilities for producing hierarchical assemblies of materials and devices in a highly deterministic mode (see figure below at right). These fundamental
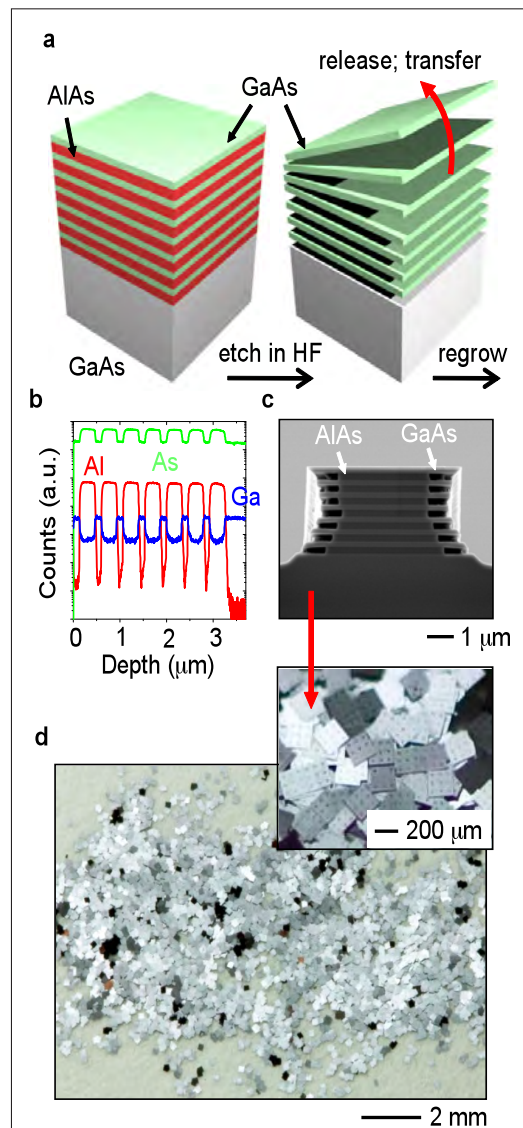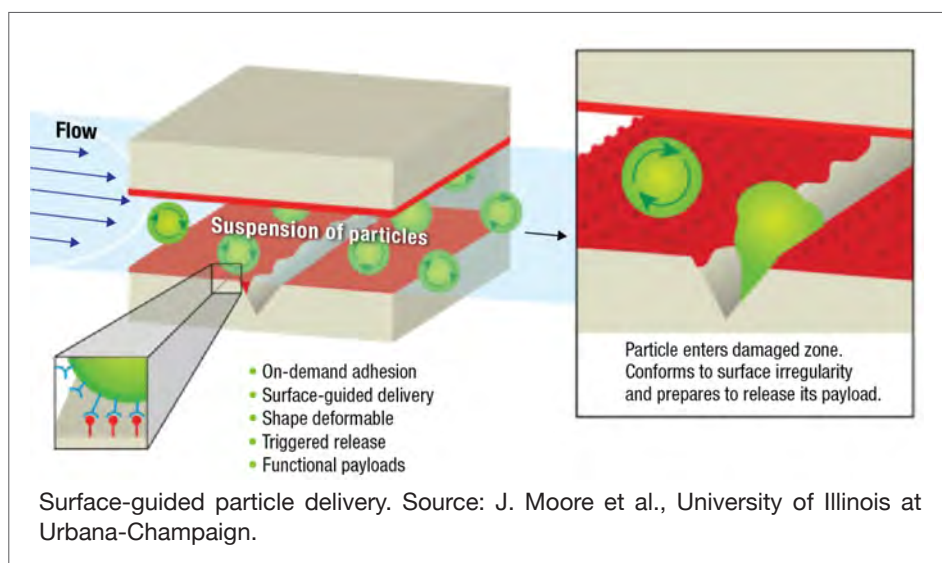
An epitaxial multilayer approach to bulk quantities of semiconductor building blocks. (a) Schematic illustration of a multilayer of GaAs/AlAs before and after release by etching of AlAs. (b) Corresponding profile. (c) Cross-sectional image after partial etching of AlAs. (d) A large collection of GaAs plates derived from complete etching. Source: J. Yoon et al., Nature **465**, 329-333 (2010).

Surface-guided particle delivery. Source: J. Moore et al., University of Illinois at Urbana-Champaign.

advances lead to compelling options in engineering due to their ability to capture certain characteristics that are prominent in biological systems, including (1) the combined use of hard and soft components in hybrid structures for unusual mechanical and geometrical forms (e.g., flexible "skin-like" architectures); (2) heterogeneously integrated collections of dissimilar materials in wide ranging sizes and shapes for increased levels of functionality; and (3) dynamic tunability in structure and conformation for responsive designs. The specific systems of interest are important, because they offer a combination of unique features and levels of performance that would be difficult or impossible to achieve by other routes.

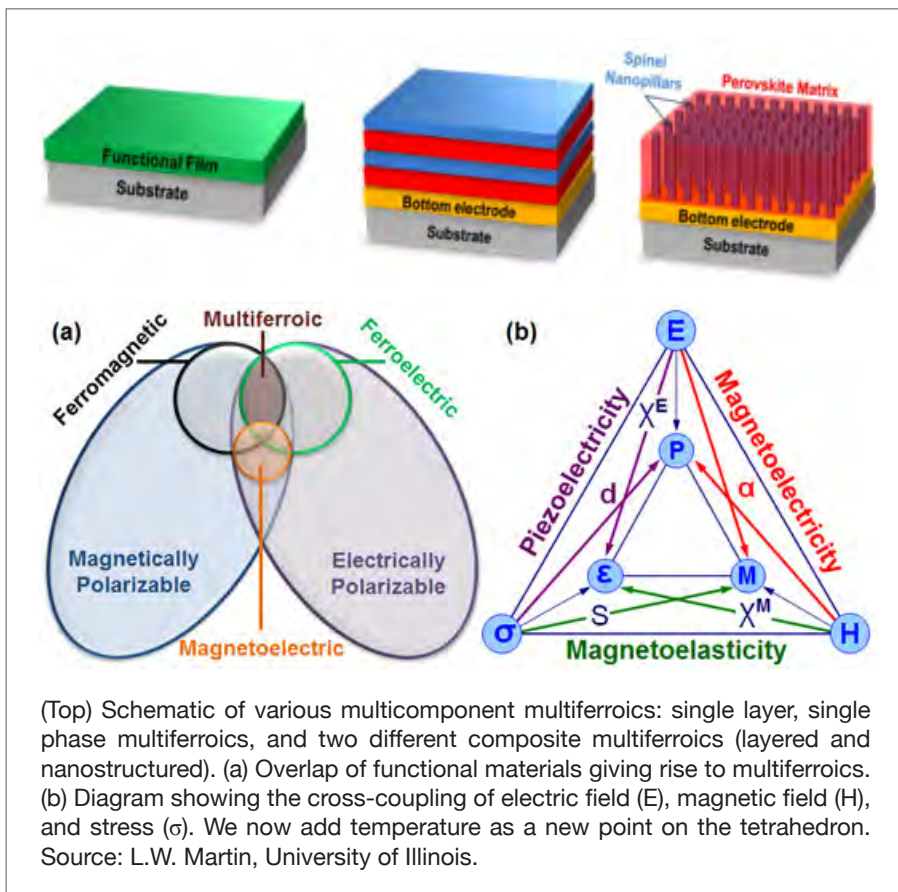**Flexible "Skin-Like" Architectures for Light Capture and Utilization.** It is expensive to grow large, high-quality wafers of III-V semiconductors and intimately integrate them on silicon or amorphous substrates such as glass or plastic, thereby restricting their use. Solid "inks" composed of thick, multilayer epitaxial assemblies can be created in a single deposition sequence on a growth wafer, then distributed over large areas by transfer printing, in a step-and-repeat mode. This innovative approach has been used for creating flexible "skin-like" architectures for high-speed electronics, efficient photovoltaic modules, and inorganic light-emitting diode arrays for solid-state lighting. This approach has been adopted by Semprius to make/manufacture concentrator photovoltaic cells with world-record efficiency. One can readily imagine extending these concepts to other energy-harvesting devices, such as those composed of

piezoelectric platelets. The power of this approach lies in the sophistication in both device architecture and materials heterogeneity realized when top-down and bottom-up approaches are truly integrated.

Functional Complex Oxide Heterostructures. Complex oxides, such as multiferroic and magnetoelectric materials, that simultaneously possess two or more order parameters—ferroelectricity, ferromagnetism, or ferroelasticity—have garnered considerable attention. Magnetoelectricity refers to a linear magnetoelectric effect or the induction of magnetization by an electric field or polarization by a magnetic field. Researchers have been driven by the promise of coupling magnetic and electronic order parameters and the potential to manipulate one with the other. Such materials come in the

form of single-phase and composite nanostructures.

An exciting opportunity for mesoscale science is to advance these materials beyond the realm of electric-field control of magnetism to include a new property—temperature (or heat). The coupling between electric field, ferroelectricity, and magnetism in these materials generates a collective mesoscale effect where multiple degrees of freedom work together to enhance response by generating the maximum field-induced entropy changes possible via so-called magneto-electro-caloric and pyro-electric-magnetic effects (see figure below). These systems could potentially be used for waste heat energy conversion (complementary to thermoelectrics); low-power, refrigerant-free solid-state cooling; advanced

(Top) Schematic of various multicomponent multiferroics: single layer, single phase multiferroics, and two different composite multiferroics (layered and nanostructured). (a) Overlap of functional materials giving rise to multiferroics. (b) Diagram showing the cross-coupling of electric field (E), magnetic field (H), and stress (σ). We now add temperature as a new point on the tetrahedron. Source: L.W. Martin, University of Illinois.

electron emitters; and thermal imaging.

To meet this challenging objective, a multi-faceted approach is required that combines directed assembly of heterogeneous materials; advanced multi-modal experiments that bring together electric field, magnetic field, and temperature (as well as the corresponding material susceptibilities); and multi-scale models from atomistic first-principle studies of new materials and effects to large-scale, device-level models of efficiency and loss.

Three-Dimensional Hierarchical Architectures. Recent efforts have focused considerable attention on the design and directed assembly of three-dimensional hierarchical architectures composed of diverse classes of functional materials. There are many potential applications—lightweight structural materials, battery electrodes, metamaterials, and well beyond—that would benefit from the unparalleled properties and performance realizable through advances in mesoscale engineering.
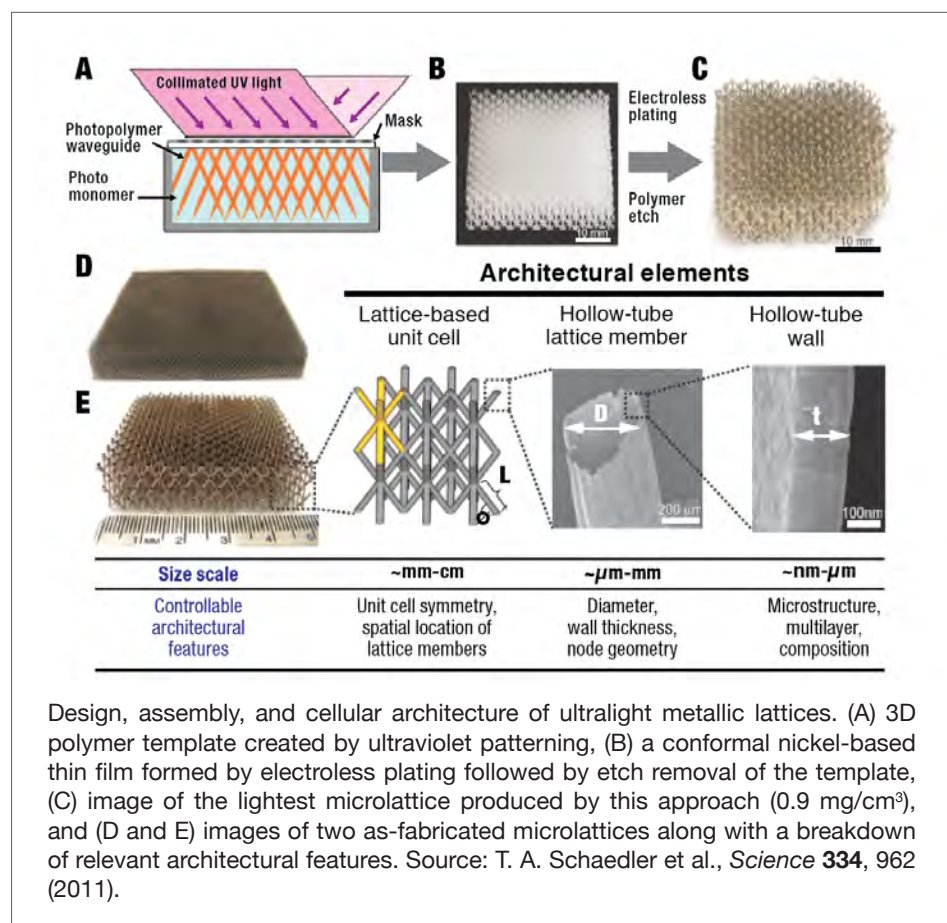
Material properties are governed by the chemical composition and spatial arrangement of constituent elements at multiple length scales. This condition fundamentally limits material properties with respect to each other, creating trade-offs when selecting materials for a specific application. Decoupling these property relationships could result in previously unobtainable performance. For example, new lightweight structural materials are needed that exhibit low density, yet high stiffness. The design challenge is to find solutions to multi-variable and multi-scale problems in order to decouple various structural and functional properties. The fabrication challenge is to build these architectures, which often are multi-dimensional, multi-scale, and multi-material. Toward this grand challenge, advanced microstructural design, using flexure and screw theory as well as topology optimization, could be combined with new directed assembly techniques to create novel material systems and architectures with previously unachievable property combinations. Much of this enhanced performance can be realized by tailoring material architecture at the nano-to-millimeter scale. One powerful example of this approach is the ultralight metallic lattice (see figure below), which is created by coating a three-dimensional polymer template with nickel metal followed by template removal.

New methods for scalable directed assembly are needed to reliably produce three-dimensional multiscale architectures that are composed of multiple materials for both structural (e.g., strength, stiffness, thermal expansion, and Poisson ratio) and functional (e.g., electronic, optical, magnetic, and energy) applications.

Another recent example is the meso-structuring of electrodes for electro-chemical energy storage (batteries), which offers potential to concurrently optimize electrical and ionic connectivity, and to maximize the active-material volume fraction. Minimization of strain-induced damage—in particular, in emerging high-energy density

Design, assembly, and cellular architecture of ultralight metallic lattices. (A) 3D polymer template created by ultraviolet patterning, (B) a conformal nickel-based thin film formed by electroless plating followed by etch removal of the template, (C) image of the lightest microlattice produced by this approach (0.9 mg/cm³), and (D and E) images of two as-fabricated microlattices along with a breakdown of relevant architectural features. Source: T. A. Schaedler et al., *Science* **334**, 962 (2011).

materials—is a unique opportunity for mesostructured systems. The challenge is to identify the architectures and materials, which might be quite different from those in use today, that take full advantage of meso-scale phenomena and functionalities, and to develop scalable methods to self- or deterministically manufacture these systems.

Electrode mesostructuring can come in many forms, including colloidal self-assembly, direct ink writing, and holographic methods. Understanding building block interactions, coupled with synthesis of building blocks with unique structures and chemistries, will enable realization of advanced electrode designs. Sacrificial templates that are later removed enable structuring of broad classes of materials. As one illustrative example of this approach, colloidal crystal templating has been exploited to create a new class of bicontinuous cathodes composed of three interpenetrating networks that provide highly efficient electron and ion transport pathways due to their high surface area and short diffusion paths (see figure below). Future efforts on mesoscale

battery electrodes promise to lead to the discovery of new phenomena and functionalities from both current and emerging energy storage materials with high performance and low cost that will transform the energy storage landscape.

Templated self-assembly of block copolymers is a demonstrated means of spanning the nanoscale (domain structure in ordered block copolymers) to mesoscale (functional patterns for applications ranging from integrated circuit manufacture to biomaterials development). The extension of this directed self-assembly capability into three dimensions is just being explored.

Research Directions

All elements of directed assembly described thus far, from the building blocks to the strategies of process assembly, rely on guidance provided by multiscale and mesoscale models to design new materials, to devise new processing strategies, and to assist in the interpretation of experimental data.

The central premise of bottom-up multi-scale modeling approaches is to use electronic structure methods and state-of-the-art molecular dynamics and Monte Carlo sampling techniques to calculate the fundamental interactions that arise between distinct components of a material. These interactions are subsequently fed into mesoscale-level simulations, which seek to predict the emergent interactions or contributions to the free energy that arise in pure and composite systems as a result of enthalpic and entropic forces. A particularly important challenge for mesoscale modeling efforts is to describe the structure and dynamics of complex materials over multiple length and time scales, thereby enabling prediction of hitherto unknown nonequilibrium states of matter. As alluded to throughout the previous sections, the assembly processes envisaged in emerging mesoscale-based technologies are inherently nonequilibrium, requiring the use of flow, voltage, or surface fields to attain desirable metastable states of matter and trap the proposed materials in such states.

In the context of particle assembly, new models are now capable of describing structure at a molecular level, while treating fluctuating hydrodynamic interactions in multiparticle systems and in the presence of surfaces and interfaces. Such models permit prediction of the assembly that occurs as a function of particle
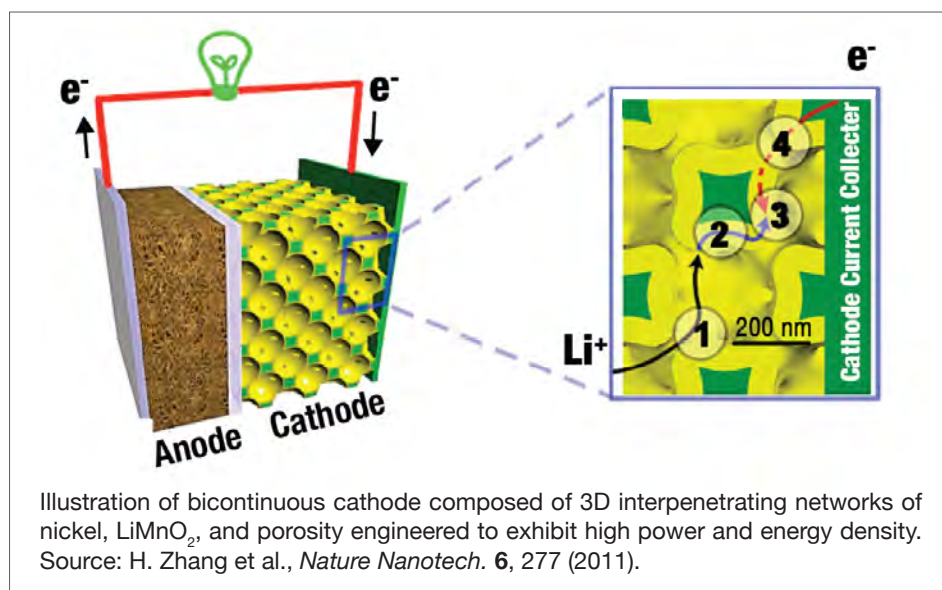

Illustration of bicontinuous cathode composed of 3D interpenetrating networks of nickel, LiMnO$_2$, and porosity engineered to exhibit high power and energy density. Source: H. Zhang et al., *Nature Nanotech.* **6**, 277 (2011).

structure and applied fields and are essential, for example, in the context of dynamic synthesis with biomimetic architectures. In the context of nanostructured polymeric materials, recent approaches have been shown to be capable of describing entanglements, microphase and macrophase separation, and confinement or free interfaces in composite systems in a concurrent manner. Such approaches enable prediction of the dynamics of morphology formation in hierarchical materials, and provide the means to design out-of-equilibrium processes that lead to controlled, specific outcomes.

Potential Impact

The overarching goal of directed assembly is to establish the scientific basis and assembly pathways required to enable the formation of "designer" materials and architectures. Of specific interest is the establishment of the fundamental knowledge required for assembly and disassembly of information-encoded building blocks with spatial and temporal control. This effort hinges on the ability to model, synthesize, and assemble building blocks whose exotic motifs embed information from the nanometer to the microscale via anisotropies in their chemical makeup, shape, and/or softness. Importantly, achievement of this goal requires a deep integration of expertise in assembly, characterization, and computational/theoretical modeling of building blocks, clusters, and mixtures thereof. With this knowledge, one can create novel forms of matter in a rational manner via directed assembly and disassembly—whose spatial organization and connectivity are dynamically tunable over multiple length scales ranging from those over which intermolecular and/or interparticle forces act to progressively longer scales associated with the individual building blocks, clusters, and supra-cluster assemblies.

Mesoscale Manufacturing

Manufacturing entirely at the mesoscale using bottom-up self-assembly of functional components connected directly at the mesoscale without macroscopic wires, mechanical linkages, or fluid channels enables faster, cheaper, more efficient, and longer lasting products.

Manufacturing at the mesoscale is a dramatically new and compelling outcome of mesoscale science. Its building blocks will be mesoscale units displaying the hallmarks of mesoscale behavior such as collective response, interacting degrees of freedom, heterogeneity, and densely spaced energy levels (see Introduction: "The Hallmarks of Mesoscale Behavior" on page 3). These building blocks will be assembled at the mesoscale with nano- or mesoscale interconnects.

Mesoscale manufacturing differs fundamentally from the miniaturization techniques of manufacturing that have been so successful in advancing digital electronics. Moore's Law reflects the long success of semiconductor electronics: the number of transistors on a chip doubles approximately every 18 months. Moore's Law is robust because inventors have followed a top-down process, finding ways to make macroscopic components smaller, faster, and cheaper by miniaturization. Mesoscale manufacturing starts from a different premise: that the innovations of the future will exploit new phenomena firmly rooted in mesoscale behavior, occupying the transition region between nano and macro. One can imagine sequential catalytic reactions for producing alternative biofuels, or self-assembly on massive scales of membranes that purify water, or mesoscale structuring of battery electrodes that coordinate the electronic, ionic, and mechanical degrees of freedom needed to convert electricity into chemical bonds and vice versa. These processes naturally occur on the mesoscale; manufacturing and assembling them exclusively on the mesoscale without recourse to the macroscale techniques and interconnects that we now routinely employ is a major operational and strategic opportunity.

The benefits of manufacturing on the mesoscale are dramatic and legion. Employing bottom-up self-assembly incorporates all the starting materials into the final device, with little or none remaining as waste. Connections between mesoscale functional units will be made at the mesoscale through interfaces designed and implemented at the atomic and molecular level. Because these direct "atom to atom" interconnects avoid extraneous wires, mechanical linkages, and flow channels, efficiency will rise and the risk of failure will fall. The simpler design and construction of mesoscale devices mean longer lifetime and lower cost.

Arrays of single crystals of order 1-15 nm in diameter are a promising route to mesoscale manufacturing. Nanocrystal arrays display a wide range of mesoscale behavior that is different from both bulk materials of the same composition and individual isolated nanocrystals. The behavior of arrays can be tuned by many techniques: the size, shape, composition, and structure of the nanocrystals; the chemical linkers binding them; and their physical proximity. The arrays themselves can be mono- or polydisperse, and be assembled in one-, two-, or three-dimensional configurations. The diver-
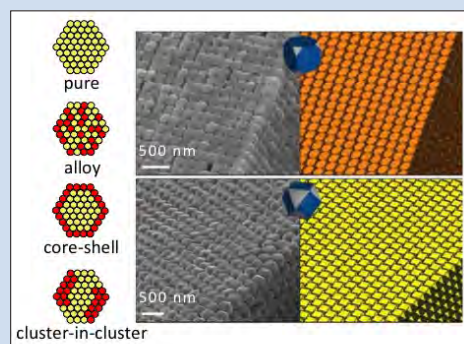

*Mesoscale arrays can be self-assembled from nanocrystals that have pure, alloyed, core-shell or cluster-in-cluster internal structures, and arranged in a variety of one, two and three dimensional lattice configurations. The properties of the arrays are tunable by a host of techniques (see text) and are fundamentally different from those of the individual nanocrystals or bulk materials of the same composition. Source: J. Henzie et al., Nature Materials **11**, 131 (2012).*

sity of programmable behavior in these arrays is enormous, and the opportunity for applications in biological diagnosis and therapy, polymer-based nanocomposites, energy storage and conversion, environmental monitoring and remediation, and electronic and optoeletronic devices is virtually limitless. The capability of synthesis and characterization of nanocrystal arrays is in its infancy, with far more phenomena remaining to be discovered than have yet been found. Incorporating these arrays into mesoscale devices without using macroscopic techniques and interconnects is a primary challenge for mesoscale science.

Tuning Bottom-up Self-Assembled Energy Converters with Mesoscience

*Mesoscale features dramatically alter the photovoltaic performance of nanocrystal assemblies.*

The energy conversion performance of composite mesostructures, such as nanocrystal arrays linked with organic molecules, can be tuned over wide ranges by adjusting their interfacial behavior. The behavior of electrons excited by light or electrical potential in nano-crystal arrays is dictated by the organic linking ligands, and organic molecules are an infinitely diverse toolbox by which we can tune the interfacial chemistry of the individual nanoparticles. In turn, assembling nanocrystal arrays into multilayer "sandwich" structures yields materials with exceptionally high flux of charge and energy across the layer interfaces, and a set of "knobs" to chemically control these fluxes. The result is a collection of high-efficiency mesoscale energy converters. The power of this approach is illustrated with the self-assembly and photovoltaic performance of nanocrystal arrays.
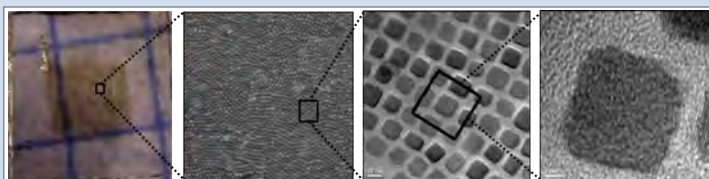
Lead sulfide nanocrystals (~10 nm size) connected with oleate linkers (~2 nm separation) are self-assembled into a nanocrystal array. The size and shape of the nanocrystals and their separation are governed by the organic linkers connecting them. The mesoscale features of these arrays are intermediate between atomic and macroscopic dimensions; they govern the macroscopic photovoltaic performance of the array.
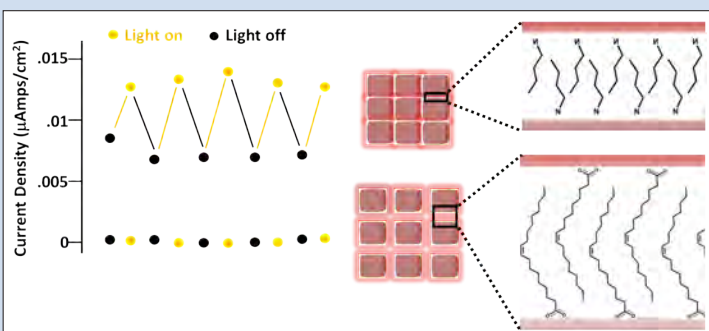
The photovoltaic properties of lead sulfide nanocrystal arrays depend critically on the organic linkers connecting the nanocrystals. Nanocrystals separated by oleate (length ~2 nm) have negligible dark (light off) and photocurrent (light on) densities (bottom left), both less than one pico-ampere per square centimeter. Nanocrystal arrays in which the oleate ligands have been exchanged for butylamine (length ~0.3 nm) have large dark and photocurrent densities approximately 10 nano-amperes per square centimeter (top left). The organic linkers in nanocrystal arrays are a powerful knob to adjust the performance of next generation photocells.
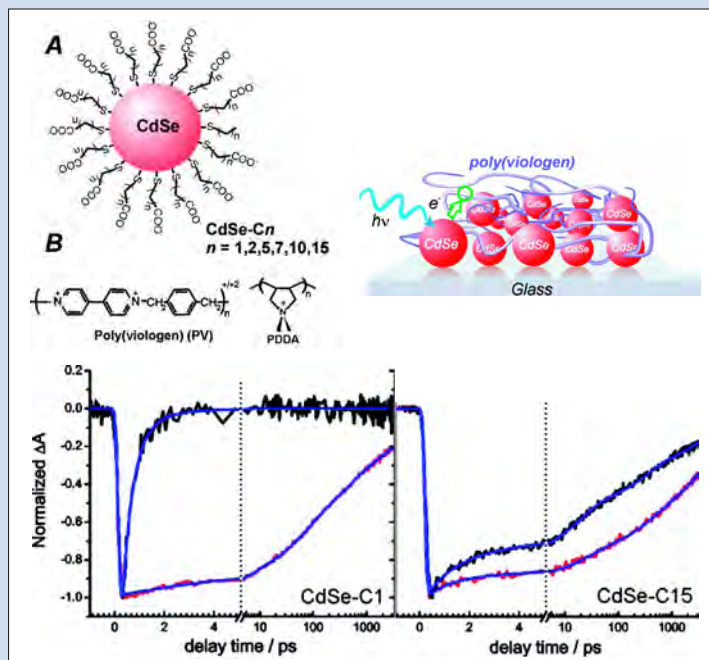
*Like the lead sulfide nanocrystal arrays at the left, the photoelectron transfer rate of cadmium selenide nanocrystals arrays depends criti-cally on the length and composition of the organic ligands linking the nanocrystals. Cadmium selenide nanocrystal arrays are prepared with mercapto-alkylcarboxylate linkers whose length varies with the number of alkyl units from n=1 to n=15 (top left). Layers of the redox-active polymer poly(viologen) (middle left) are alternated with the nanocrystal arrays to form a multilayer "sandwich" (top right). Photoexcitation of the stack transfers electrons from the cadmium selenide nanocrystal array to the poly(viologen). The rate of electron transfer, however, depends critically on the number of alkyl groups (and thus the length) of the organic ligands linking the nanocrystals. The upper curves in the lower figure show the dramatic change, where the longer linker ligands (CdSe-C15) maintain lower values for the normalized absorption for much longer times than do the short linker ligands (CdSe-C1). This strong dependence of electron transfer rate on nanocrystal array configuration provides a control "knob" for tuning phenomena and creating new functionality in solar cells for producing electricity and for driving photochemical reactions. Source: M. Tagliazucchi et al., ACS Nano **5**, 9907-9917 (2011).*

Capability Gaps for Mesoscale Science

Realizing the meso opportunity requires advances not only in our knowledge but also in our ability to observe, characterize, simulate, and ultimately control matter. The areas of knowledge that are poised for breakthroughs have been discussed in the preceding priority research directions. In this section gaps in our capabilities to make, measure, and model materials on the mesoscale are highlighted. Of at least equal importance as the research infrastructure is the human capital required to explore the frontiers of mesoscale science. This section also discusses workforce considerations for mesoscale science.

First and foremost among the capability gaps for realizing the meso opportunity are advances in our ability to integrate theory, modeling, and simulation seamlessly with synthesis and characterization. The inherent complexity of mesoscale phenomena, often including several nanoscale structural or functional units, requires theory and simulation spanning multiple space and time scales. New organizing principles that describe emergent mesoscale phenomena arising from many coupled and competing degrees of freedom wait to be discovered and exploited at the mesoscale. An integrated and coupled approach in which measurement directly influences theory-guided synthesis will accelerate the discovery of new mesoscale phenomena and architectures.

Measurements that are dynamic, *in situ*, and multimodal must replace static characterization. The mesoscale is an inherently dynamic regime, where energy and information captured at the nanoscale are processed and transformed to create new outcomes. Given the complexity and dynamism of mesoscale phenomena, multiple measurements of transient phenomena are key. Spatially diverse measurements in three dimensions capturing coupled transformations in different parts of the mesoscale assembly are critical. Complex mesoscale ensembles are not identical and inevitably display a range of behaviors; effective measurements must capture the range of possible outcomes and not just characterize a "representative" sample.

Finally, the ability to design and realize the complex and composite materials we imagine will require qualitative advances in how we synthesize materials, both in moving from serendipitous to directed discovery and in advancing our ability to assemble and control materials systems and architectures from smaller structural and functional units. The integration of "top down" and "bottom up" approaches, now quite distinct and representing different operating principles and spatial scales, is key to mesoscale synthesis.

Synthesis Capabilities

Creating the materials, structures, and architectures that access the benefits of mesoscale phenomena requires advances in at least three broad categories of synthesis capabilities:

- Directed synthesis to create complex materials, controlled interfaces, and patterned structures;

- Assembly processes and patterning strategies for fabricating heterogeneous, spatially defined structures; and

- Computational tools that simulate these synthesis and assembly steps to facilitate formation of the desired structures and estimation of their resulting properties and behavior.

More generally, significantly enhanced capability and capacity for materials synthesis, fabrication, and processing are needed to fully explore known and discover unknown mesoscale phenomena and architectures in pursuit of controlled functionality.

Directed Synthesis

Dimensional Control. For new phenomena on the mesoscale to emerge and be exploited, materials synthesis must be highly controlled—in composition, microstructure, characteristic length scale, and reproducibility. The challenge of understanding collective behavior often arises from multilayer heterostructures whose attributes depend on synchronization of material layers at mesoscale dimensions or from the matching of length scales arising from distinct and competing degrees of freedom. Optical and plasmonic structures are an example:

dimensions of material layers (e.g., thicknesses) must achieve explicit relationships to optical wavelengths, which are themselves defined at the mesoscale. Because the interplay between collective behavior and defects is critical to mesoscale phenomena, capability for highly controlled synthesis conditions offers the possibility to intentionally introduce defects (e.g., impurities) from which correlations can be developed between defect populations and mesoscale phenomena. One must also remain open to serendipitous discovery of new phenomena and new architectures through exploratory synthesis. Characterization techniques to identify defects and their properties and behavior, ideally *in situ* during synthesis, are of course required.

Interface Control. Control of interfaces accompanies this requirement, because surface and interface properties can strongly influence the materials synthesized on them. Interface control plays an important role from complex oxides to soft materials, influencing properties such as the quality of epitaxial alignment in the former and soft material properties (e.g., polymerization products and kinetics) in the latter.

Patterning. Directed synthesis may require or benefit from patterning of material configurations to mesoscale dimensions in order to understand collective phenomena (e.g., multiferroic behavior) arising at the mesoscale. This patterning or templating can arise in three dimensions, including in the direction of growth. It may be accomplished

through conventional lithographic approaches, which are more difficult and expensive in the submicron regime. Soft lithography (e.g., molding and transfer printing) offers other options. Spatially selective material deposition, employing either selectivity of a chemical process or focused beam deposition, is a more challenging method.

Self-assembled Structures. New methods for directed synthesis are needed to create structures on the mesoscale. Examples range from synthesis of mesoscale structures such as carbon microtubes (100-1000 nm in diameter) to electrocatalytic features formed by galvanic displacement reactions. Surface area considerations make meso- and nanoscale structures both credible candidates for energy applications, yet much less attention has been devoted to synthesis of mesoscale features.

Assembly Processes

Multistep Synthesis of Heterogeneous Structures. Assembly of mesoscale systems often requires heterogeneous structures, which are formed through a sequence of synthesis and patterning steps. Various synthesis processes and corresponding equipment are already known and available. They are based on physical, chemical, and electrochemical phenomena in both vapor and liquid phase. However, directed synthesis to reproducibly elicit mesoscale phenomena imposes new requirements, such as *in-situ* thickness measurement and control, or self-limiting process mechanisms

(e.g., atomic layer deposition). Surface and interface control may require *in-situ* processing equipment that enables successive steps without exposure to air and other chemical contaminants.

Nanostructure Assemblies. Important mesoscale phenomena also arise from nanostructure assemblies covering mesoscale dimensions. As an example, nanowire battery structures packed close together with high aspect ratio are promising pathways to future storage technology. However, their spatial proximity, driven by high aggregation at the mesoscale, raises important new questions of transport limitations and coupled electrochemical phenomena that would limit performance. Thus, tools are needed not simply to make the nanostructures, but to synthesize high-aspect-ratio nanostructures in well-controlled high-density arrays extending to the mesoscale. These can then be patterned to form functional connections (e.g., contacts) to the arrays.

Combinatorial Strategies for Mesoscale Phenomena. Synthesis of functional nanostructure arrays begins with self-assembly of aperiodic scaffolds (e.g., porous gels) or ordered templates (e.g., anodic alumina and colloidal particle arrays), followed by wet or dry deposition techniques that emphasize thickness control and uniformity/conformality over formation of complex 3-D nanostructure shapes. Such synthesis can be facilitated by self-assembly, self-limiting processes, and self-aligned structures. However, the challenge

for mesoscale research is to develop efficient synthesis and experimentation protocols as combinatorial strategies for varying nanostructure array configurations to reveal the parameters and mechanisms controlling new mesoscale phenomena.

Computational Synthesis/Assembly

Materials and Process Modeling. Experimental synthesis is expensive in time and cost; major advances are needed in modeling and simulation of synthetic approaches to guide experiment. A rich portfolio of approaches is currently available to predict outcomes of processes, sequences, and consequences for material and structure properties. It includes information on surface chemistry during deposition/etching, 3-D profile evolution, materials properties derived from *ab initio* density functional theory, and continuum mechanics and multiphysics behavior of structures, all enhanced by high-performance computing infrastructure.

Mesoscale Context. Unique phenomena at the mesoscale present new opportunities for computational and theoretical research. Collective behavior underscores the need to develop and implement into modeling frameworks and codes a coupling between statistical mechanics of mesoscale assemblies and material properties that leads to emergent phenomena. Multistep, multicomponent synthesis involving multiple length and time scales demands new means for bridging synthesis steps and scales (e.g., system reduction, sampling, filtering, and projection techniques).

New Design Modalities. A particularly exciting notion is the possibility that mesoscale designs could decouple structure and function, based on additive manufacturing of micron to millimeter features. While use of materials configurations to accomplish particular behavior is constrained by structure-function coupling, assembling different structures from mesoscale components offers a pathway to decoupling. The structures of micro-electro-mechanical systems (MEMS) offer examples of the effective separation of structure and function, albeit targeted more at applications in which new phenomena do not emerge at the mesoscale.

Availability of Synthesis Infrastructure

Distributed Synthesis Facilities. Experimental facilities needed for synthesis span a broad spectrum of equipment types and associated infrastructure (chemicals, materials, etc.). Multistep fabrication of multicomponent mesoscale structures requires even more individualized facilities. This situation places value on synthesis resources widely distributed and widely available to serve the specific needs of meso research groups, rather than a reliance on a few major national facilities. To be sure, some synthesis capabilities at national facilities, following the successful example of the Nanoscience Research Centers, as well as at end stations at existing characterization (electron, neutron, and photon) facilities designed to foster *in situ* measurement, are very desirable for research at the mesoscale, but they cannot replace the need for widely distributed capabilities.

Cultivation of Synthesis Expertise.
An even more compelling case for distributed synthesis facilities may be the alignment of mesoscale research with broad-based technologies and advanced manufacturing. In fields from energy research to new materials to biomedical devices, it is the ability to synthesize, fabricate, and assemble materials and structures at the mesoscale that translates into an economic and social benefit through technology-based products. The competitive posture of the U.S. workplace can be the direct beneficiary of educating scientists and engineers at all levels in the skills represented in mesoscale synthesis and related research areas. The relevance and quality of their experience are notably enhanced by the availability of state-of-art equipment and computational infrastructure throughout their daily routine.

Characterization Capabilities

The Office of Basic Energy Sciences (BES) is the principal steward of large-scale characterization facilities in the U.S., and recent investments have significantly increased the suite of available tools. Currently available and emerging capabilities at large-scale facilities such as the Spallation Neutron Source (SNS) at Oak Ridge National Laboratory (ORNL), Linac Coherent Light Source (LCLS) at the SLAC National Accelerator Laboratory (see figure at top right), and National Synchrotron Light Source (NSLS) II at Brookhaven National Laboratory (BNL) (see figure at bottom right), as well as advances in laboratory-scale measurement tools, position the community well to address mesoscale
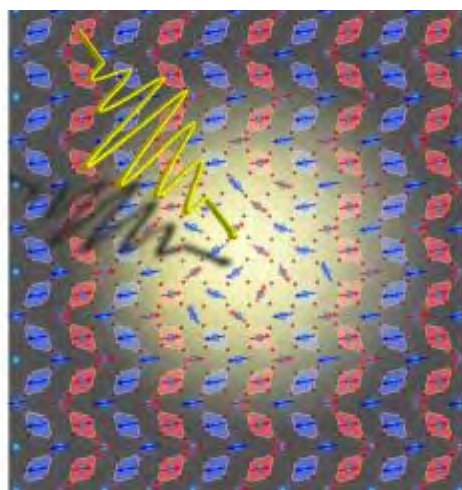
Graphic depiction of an ultrashort pulse of terahertz light (yellow arrow) distorting a manganite crystal lattice. The induced rearrangement of magnetic moments on Mn atoms (red and blue arrows) and atomic displacement patterns (suggested by the red and blue diamonds) are probed with short x-ray laser pulses. Changes in the ordering are probed with a time resolution of 250 fs. Experiment performed at the LCLS. Source: M. Först et al., *Phys. Rev. B* **84**, 241104(R) (2011).
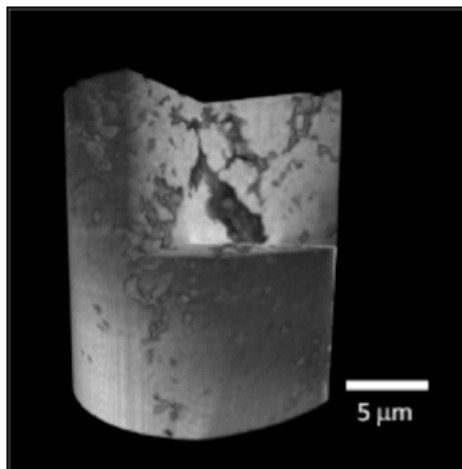
A 3D reconstruction of a 20-µm lithium-ion battery electrode obtained with a transmission hard x-ray microscope at the NSLS, with resolution of 25 nm. Measurement of 1,441 2D images required 4 hours, with a speed increase of 1,000 expected when applied at NSLS II. Source: J. Wang et al., *Appl. Phys. Lett.* **100**, 143107 (2012).

challenges. Nevertheless, gaps exist in our characterization capabilities for fully exploring mesoscale opportunities. Needs include capabilities for

- Time-dependent spatial and functional characterization of materials and structures with mesoscale resolution in four dimensions (space and time);

- *In situ, operando* measurement to explore the dynamics of mesoscale phenomena in the environment in which they are active, including synthesis environments; and

- Sustained measurements over the lifetime of a component, including long-duration measurement tools and the means to artificially age materials through accelerated testing.

Implicit in these characterization capabilities is the challenge of very large data sets and the need to separate on the fly the signal from the noise or risk a massive data storage challenge. Further, significant needs exist for additional end stations and instruments, including those capable of producing relevant sample environments, as well as advanced detectors in order to take maximal advantage of the newly available sources.

Current State

Ideally, one would like to have a universal tool, something like a "scientific Swiss army knife," with the following capabilities:

- Map structure in three spatial dimensions and as a function of time, including for nonperiodic molecules.

- Cover length scales from 10^{-10} to 10^{-3} m and time scales from 10^{-15} to 10^9 s.

- Have sensitivity to chemical elements and to magnetic moments and electric moments simultaneously with structural resolution.

- Detect vibrational, electronic, and magnetic excitations with energies from 10^{-9} to 10^1 eV and their associated excited state dynamics.

- Measure as a function of applied electric field, magnetic field, pressure, or chemical environment as well as extremes of temperature.

While such a universal tool may be beyond our reach, we do possess several different toolboxes, each containing a range of sophisticated instruments that provide complementary capabilities. These toolboxes are exemplified by the BES user facilities that have been constructed with past investments. They can be distinguished by the types of particles that are used to probe materials: photons, neutrons, and electrons. Each has its own advantages and limitations, and all are needed to provide the desired range of capabilities and approach the vision of a universal tool. Importantly, these large-scale tools are complemented by a widely distributed array of characterization capabilities. Where possible, combining these probes with each other simultaneously to enable multi-modal measurements is a mesoscale opportunity.

Synchrotron light sources, including the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory (LBNL), the Advanced Photon Source (APS) at Argonne National Laboratory (ANL), the NSLS (and soon to arrive NSLS-II) at BNL, and the Stanford Synchrotron Radiation Lightsource (SSRL) at SLAC, provide high intensity beams of photons from infrared light to x-rays. The scattering of infrared light from a sample can provide sensitivity to chemical bonds (through their vibrational energies) and the ability to carry electrical currents (through the electronic conductivity). Ultraviolet light is commonly used to probe the electronic structure of materials through photoemission spectroscopy. X-rays can probe crystal structure via diffraction or absorption spectroscopy, and new imaging modes have recently been developed to provide both *in-situ* zone-plate imaging under controlled environments and lensless imaging for hard x-rays at high resolution. One can obtain elemental and chemical sensitivity by tuning the x-ray energy to an atomic transition. With some atomic transitions, it is also possible to obtain information on the local magnetization.

With all of these techniques the beam can be rastered across the sample (or the sample through the beam) to spatially map characteristics. In this mode, the spatial resolution is limited by the size of the beam spot focused on the sample, which can be in the range of 10^{-7} to 10^{-6} m. Depth sensitivity varies. A technique such as photoemission is surface sensitive (an advantage for some applications) but cannot sample the bulk of a specimen. Hard x-rays can penetrate 10^{-6} to 10^{-3} m, but with the tradeoff that the more penetrating x-rays do not provide elemental sensitivity. One application of x-rays is tomography, in which one can map the density of materials by assembling a series of images just as is done for people (humans) with CT scans. A new approach, which can provide fine spatial resolution, involves "lensless" imaging. Rather than making the beam spot smaller and imaging one point at a time, this approach uses a large spot size and collects coherent diffraction measurements with small displacements of the spot position on the sample. The spatial image of the sample is reconstructed from the data via computer. The time required for measurements can vary widely. An individual "snapshot" might take 10^{-3} s, while high-resolution 3D imaging can take minutes to hours.

Inelastic x-ray scattering provides information on how atoms and electrons fluctuate within materials. To obtain the necessary energy resolution, one must throw away most of the beam intensity, resulting in relatively low rates of data collection. As a consequence, inelastic instruments have not yet focused on spatial resolution or time-dependent studies.

The LCLS at SLAC is an x-ray free electron laser that provides very short pulses of light (10^{-14} s) with remarkable flux. Beam lines provide capabilities for soft and hard x-rays. A typical application is to excite a sample with an impulse, usually from an optical laser, and then follow the evolution of the sample with time using x-ray pulses. Delay times between the initial impulse and the probe can be resolved on the scale of 10^{-13} s. The time between x-ray pulses is 10^{-2} s, so the pump and probe measurements must be repeated many times to map the time evolution of the sample. One challenge is that the energy of individual x-ray pulses can be sufficient to damage

the sample; clever schemes are used to move samples in the beam so that each pulse probes pristine material (information travels at the speed of light, and damage at the speed of sound, enabling use of "probe before destroy" measurement methodologies). It is clear that the full potential of x-ray free electron lasers has yet to be realized, and various concepts are being developed to tap this potential, including at the mesoscale.

Neutron sources include the SNS and the High Flux Isotope Reactor (HFIR) at ORNL and the Lujan Neutron Scattering Center at Los Alamos National Laboratory (LANL). Whereas x-rays and electrons scatter from the electron density in a sample, neutrons scatter from atomic nuclei and magnetic moments. As a result, neutrons can probe the entire volume of samples with thicknesses greater than 10^{-2} m. Real-space imaging is done with spatial resolution of 10^{-4} m, with particular sensitivity to hydrogen-containing compounds. Variations in crystal structure can be mapped in 3D with a resolution of 10^{-9} m^3 (1 mm x 1 mm x 1 mm). Frequently, one is interested in the statistical distribution of particle, pore, or domain sizes, and this can be determined with small-angle neutron scattering (see figure at top right). The structures of polymer films or magnetic multilayers can be determined by neutron reflectivity with spatial resolution of 10^{-9} m (see figure at bottom right). With diffraction and more-generalized scattering instruments, it is straightforward to measure spatial correlations among atomic magnetic moments, including the excitations of such systems. Atomic vibrations and molecular motions are probed with inelastic
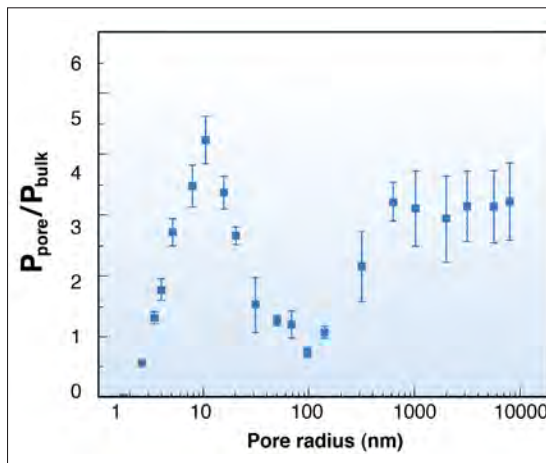
Variation of the density of CO_2 in pores of coal relative to bulk liquid density as a function of pore size. Data obtained from small-angle neutron scattering measurements performed at ORNL High Flux Isotope Reactor and the Center for Neutron Research of the National Institute of Standards and Technology. Results are relevant to the challenge of carbon sequestration. Source: A. P. Radlinski et al., *Langmuir* **25**, 2385 (2008).
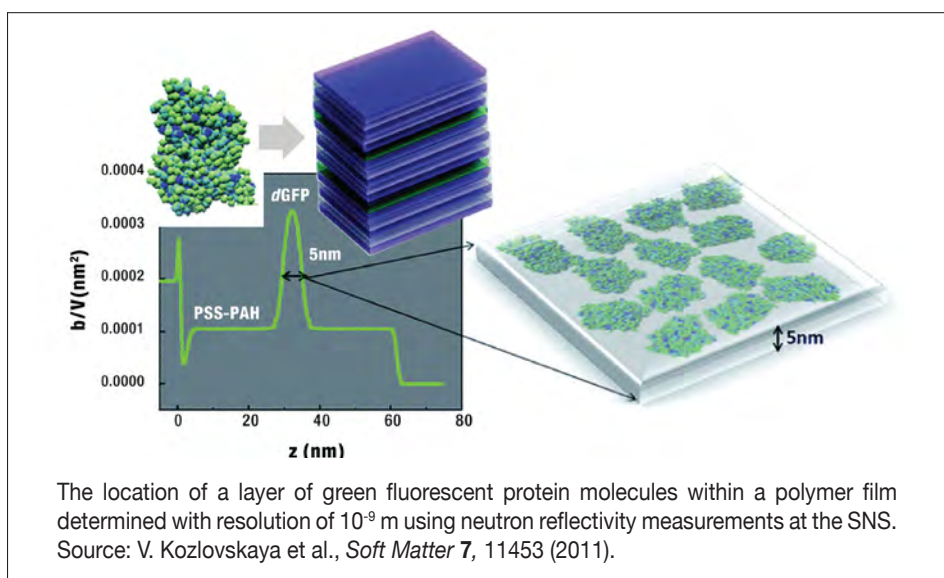
The location of a layer of green fluorescent protein molecules within a polymer film determined with resolution of 10^{-9} m using neutron reflectivity measurements at the SNS. Source: V. Kozlovskaya et al., *Soft Matter* **7**, 11453 (2011).

scattering instruments having energy resolutions ranging from 10^{-6} to 1 eV. In applications to chemical spectroscopy, one can fingerprint molecular bonds by their vibrational frequencies. Neutron capabilities are not as ubiquitous as photon sources, and measurements can require more time and greater expert knowledge by the user. Nevertheless, neutron capabilities are particularly well suited to a number of mesoscale science challenges.

Electron beam microcharacterization centers are located at ANL, LBNL, and ORNL, with further capabilities

available through BES's Nanoscience Research Centers (and various university-based nanocenters). Transmission electron microscopy (TEM) allows atomic-scale imaging of thin samples. Beyond determining positions of atoms, the types of atoms can be resolved with electron-energy-loss spectroscopy. TEM is ideal for characterizing grain boundaries and interfaces between distinct materials. A particular opportunity for electronic scattering is to extend their exquisite spatial resolution into the time domain (i.e., dynamic electron microscopy) and into a greater suite of environmental conditions; initial efforts are

underway in these regards. A strength of the Nanoscience Research Centers is their physical co-location with photon and neutron sources. This proximity is yielding positive results in the coupling of synthesis and theory with characterization as well as the acquisition of a suite of multi-modal, *in situ* measurements of relevance to mesoscale science.

Characterization Needs

As indicated in the above section, an important step toward realizing the meso opportunity is to continue to explore and stretch the limits of the capabilities of newly available large-scale facilities. While the sources of probe beams are relatively well in hand, significant advances in probe optics, detectors, sample environments, and data handling/processing are needed. Particular challenges identified in the priority research directions include:

- New methods to find and watch structural and functional defects evolve in 3D and sub-surface systems are prerequisite to mastering defect mesostructure and evolution. Defect evolution, i.e., an explicit focus on dynamic phenomena, must acquire the importance already attributed to static structural defects, since defects in materials systems evolve in time and directly translate to performance and reliability in physical systems. To effectively direct assembly of mesoscale architectures, one must observe these processes during the assembly events.

- *In situ, in operando* measurements including defect decoration techniques, employing selective chemistry or other phenomena to enable the real-time tracking of active sites, can be crucial in finding and watching functional defects while they perform in their local mesoscale architecture and at heterogeneous reactive sites during chemical processes.

- Long-duration measurements and accelerated testing in new modalities, based on advanced mesoscale characterization methods, promise major advances in prediction and controlled evolution of functional defects and also enable the harnessing of fluctuations and the inhibition of degradation for intrinsically metastable systems.

- Data mining strategies, as developed for applications from security to marketing, must become an essential component of data-rich materials science instrumentation (e.g., computed tomography and orientation mapping) now available, particularly at advanced user facilities, to answer questions such as: How do we find features in large 3D CT images? How do we correlate data from disparate sources such as images and acoustic emission? This is particularly acute when the data challenge is at least five dimensions: three spatial dimensions, temporal resolution, and the environmental state in which the measurement is taking place.

To efficiently take advantage of new characterization capabilities, a researcher often requires a high level of experimental expertise in a single technique. This demand can

be an obstacle to effective mesoscale research, where it is often desirable to use multiple techniques to probe multiple length and time scales (simultaneously, if possible). This barrier can be reduced by suitable investment in instrument staff and software development at facilities to allow efficient collaboration and data processing on the research projects of outside users. Similarly, before a user takes a sample to a facility, the quality of the sample needs to be characterized in the laboratory in which the sample was synthesized. Much needed is an appropriate scale of support for such mid-scale characterization instrumentation as a complement to the large-scale facilities.

Theory and Simulation Capabilities

An essential element of the mesoscale challenge is to discover the underlying theoretical principles that give rise to emergent phenomena as the system size increases from atomistic to macroscopic. Theoretical tools and approaches do not exist today to bridge these processes across scales in space, time, and energy. Currently, multiscale phenomena are treated in isolation or coupled only through *ad hoc* scale separation and parameter passing. *A major theoretical challenge is to develop a seamless and unified theoretical framework that describes physicochemical phenomena across multiple spatiotemporal scales*, especially in the presence of mesoscale defects and interfaces that cause the mesoscale to be a unique scale in the evolution from atomistic to continuum. Further, there are unknown unknowns that arise at the mesoscale and give rise to unanticipated phenomena through coupled and competing interactions. *The complementary theoretical*

challenge is to develop reliable many-body quantum models to incorporate emergent meso phenomena to yield first principles design of materials with targeted functionality. Finally, these models must be operational at a level that can guide characterization methods in extracting relevant observables and direct synthesis in tailoring mesoscale architectures to yield the controlled functionality we seek. *Thus, the third element of the challenge is to realize these advanced multi-scale and many-body models in a broadly available and well-documented form (e.g., widely distributed community codes) in order to empower and motivate a broad suite of synthesis and characterization efforts.*

Recent advances in computational power and software development have enabled partial success in this pursuit, including development of reliable, quantum-based models of atomic-scale structure and reactivity, and large-scale continuum simulations (e.g., adaptive grid methods to solve partial differential equations) of complex structures and transport in materials in three dimensions with low symmetry. The advent of "exascale computation" holds further promise for mesoscale science breakthroughs.

Owing to their small particle size and large surface areas most nano- and mesoscale structures are inherently far from equilibrium and intrinsically metastable (see figure at right). *We need to develop theoretical/simulation tools to elucidate how a system evolves to achieve a state of persistent metastability.* This requires understanding how systems organize by characterizing the nature of the attendant collective motions, elucidating the energy landscape, and identifying

As represented by the trajectory (red) of a system between two stable states (blue circles), evolution of complex systems involves rapid local fluctuations and rare, frustrated, large-amplitude transitions between basins of stability/metastability. Source: G.K. Schenter, Pacific Northwest National Laboratory.
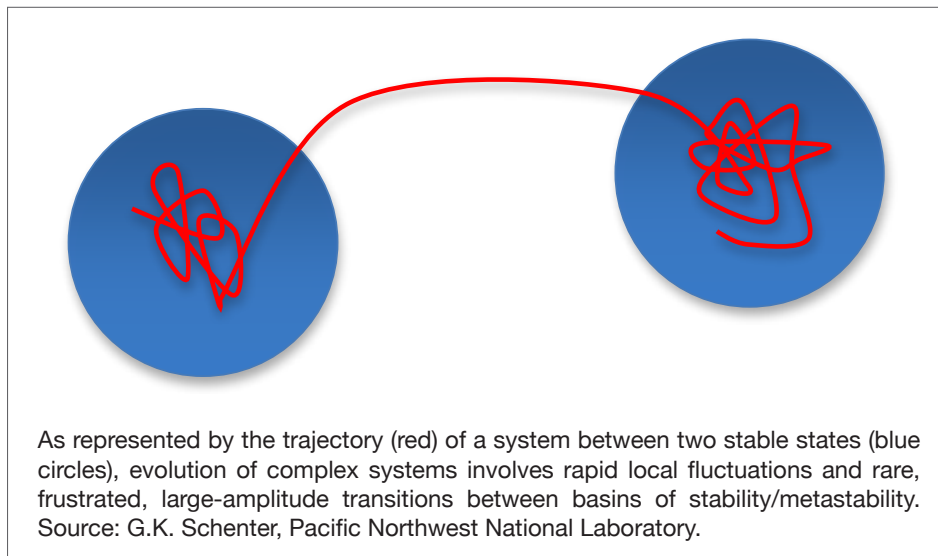
domains of local equilibria and their associated fluctuations. In metastable systems such domains are frequently connected through a complex network. New tools are needed to identify the large-amplitude, rare, frustrated, and fluctuation-driven motions that underlie this connectivity.

At the core of this scientific investigation is an effort to develop "mesoscale principles" that couple simulation techniques and theoretical frameworks at different length and time scales (see figure on next page). At each scale, techniques exist to describe transport, flow, diffusion, transformation, equilibrium, fluctuations, and transient response to external stimuli. The fact that the appropriate order parameters, coordinates, or field variables that are used to characterize the state of a system are *not universal* is at the heart of the scientific challenge in realizing a unified mesoscale model. Finding the formal relation between scales is required for the multiscale simulation to be accurate and predictive. Furthermore, it is essential to the efficiency of simulation techniques to

find the optimal and most economical connection between scales to avoid unnecessary simulation or the need to track dynamics of irrelevant fluctuations or flows.
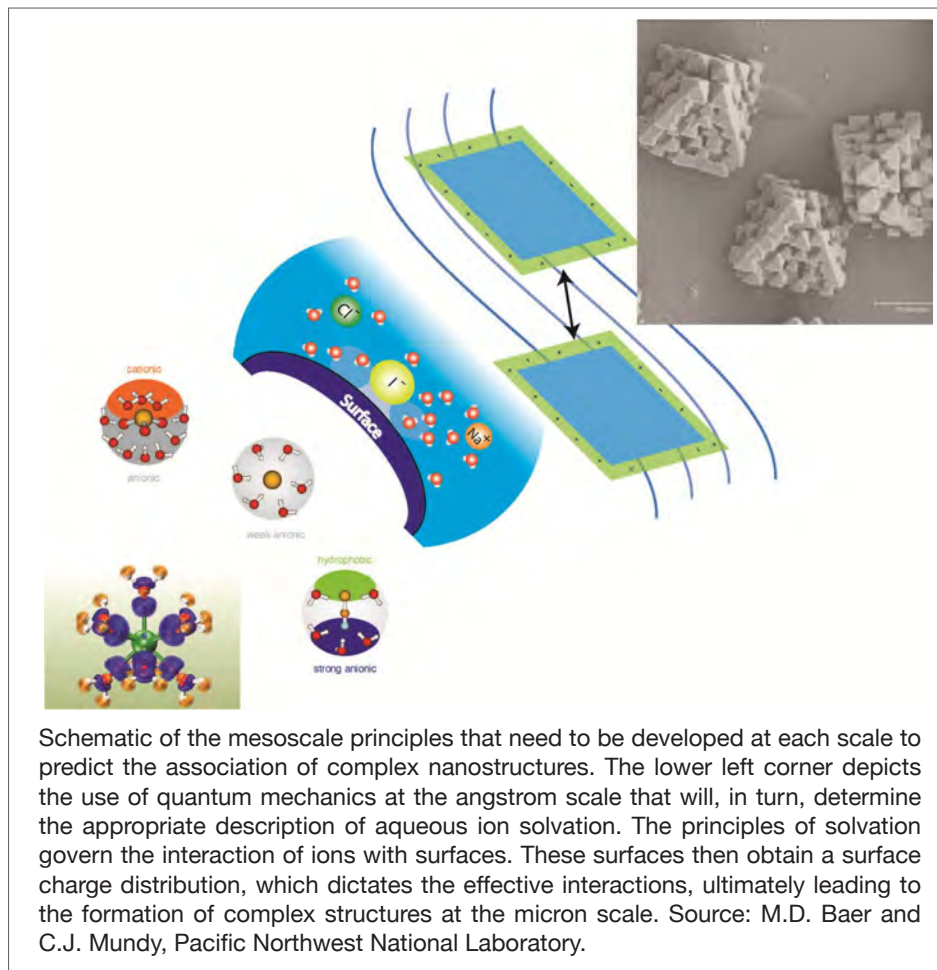
Across scales, the simulation tools that need to be employed and enhanced can be partitioned into four classes: (1) models of molecular interaction, (2) sampling techniques, (3) exploration of essential collective variables and order parameters, and (4) projection and coarse graining methods.

Models of molecular interaction include fully correlated electronic structure calculations, which allow characterization of excited states. Reduced (mean field) levels of electronic structure include density functional theory and semi-empirical methods either based on approximations to Hartree-Fock or methods based on the tight-binding Hamiltonian. The use of efficient and accurate electronic structure methods will be imperative to ascertain reduced levels of description, where the relevant short-range/fast degrees of freedom can be accurately

folded into a mean field description at large scales that will contain the relevant aspects of important correlation effects. The rigorous determination of this reduction will enable one to define the important principles to extract from one scale to another.

The importance of sampling the relevant fluctuations, especially temporally, is significant at every scale. The sampling methods are, in principle, independent of the complexity of the interaction potentials. Statistical sampling methods will be all important in defining collective variables or order parameters to provide input into a reduced description of the relevant interactions. Important examples of methods that allow the elucidation of complex collective variables are meta-dynamics and its extensions, as well as parallel tempering. Even for reduced forms of the interaction potential, these methods will require modern computational resources to ensure their effectiveness. Additional methods such as transition path sampling and other path sampling techniques will become important in identifying basins of stability/metastability. In principle, one could use a reduced form of the interaction potential to provide a rough estimate of the free energy landscape by using the aforementioned methods. The free energetics and the concomitant kinetics could be refined with higher levels of theory to obtain more accurate estimates of the rates and thermodynamics, which could then be passed to another scale for further analysis.

Challenges at the molecular scale are borne out when electrostatics

Schematic of the mesoscale principles that need to be developed at each scale to predict the association of complex nanostructures. The lower left corner depicts the use of quantum mechanics at the angstrom scale that will, in turn, determine the appropriate description of aqueous ion solvation. The principles of solvation govern the interaction of ions with surfaces. These surfaces then obtain a surface charge distribution, which dictates the effective interactions, ultimately leading to the formation of complex structures at the micron scale. Source: M.D. Baer and C.J. Mundy, Pacific Northwest National Laboratory.

become dominant or important. Many coarse-grained simulations use interaction potentials derived from potentials of mean force. When ions that are contained in a solvent or electrolyte interact significantly with nanoparticles, other approaches must be formulated to obtain a reduced description of the interaction. Such electrostatic effects can play a dominant role and are currently underrepresented in simulations of colloidal suspensions and continuum simulations of porous media. Many simulations of suspended particles leave out interactions between charged colloidal particles with dissolved counter ions that, in turn, determine

properties such as stability. Novel theoretical methods of reduction must be developed that go well beyond the mean field approaches, such as Poisson-Boltzmann, to derive effective dielectric continuum theories that contain correlations imported from molecular simulation.

In the extension of theoretical representations to larger scales, explicit molecular-level detail describing the ensemble must be replaced by an appropriate set of reduced field variables that propagate in space and time. Traditionally, these fields consist of conserved quantities such as number, momentum, and energy

density. The focus on the larger scale will be to relate the results of detailed molecular simulations to field descriptions of transport and material properties. Partitioning the system into relevant volumes that can be described by using molecular-level detail or the appropriate field description of fluid dynamics, dielectric behavior, elastic properties, fixed impenetrable volume, etc., will be the challenge. The rigorous coupling of molecular detail described by quantum mechanics or Newton's equations of motion to fluid descriptions of the system described by Navier-Stokes equations or elastic solid descriptions of the system described by linear or nonlinear solid mechanics will require new mathematical formulations of numerically efficient projection techniques. As mentioned before, electrostatics needs to be efficiently introduced by extending dielectric continuum theories, where a more accurate mean-field ionic approximation is achieved through inclusion of a correlation from the molecular scale.

Ultimately, the appropriate mesoscale principles can be used to develop improved field-based representations of reaction, flow, and transport at scales ranging from nanometers to microns. Such representations are relevant for understanding how many systems behave in practical settings, both in the natural environment and in industrial applications.

These new field-based descriptions can still be quite complicated. Explicitly incorporating information from microscopic properties will require extending the usual continuum description of flow and transport in bulk fluid to include multiple surface species, 2D transport along surfaces, nonuniform properties on the surface, and appropriate couplings between surface fields and fields defined in the bulk fluid. Additional complexity arises if the surfaces are moving or deformable, as is the case in fluid-fluid interfaces and surface deposition/dissolution. In addition to correctly formulating these equations, substantial computational challenges are associated with solving them numerically for realistic geometries. Understanding the utility and extensions of smooth particle hydrodynamics, dissipative particle dynamics, the diffusion equation, the Langevin equation, and kinetic Monte Carlo and lattice Boltzmann descriptions of motion will be required. A significant component will be the solution of the relevant partial differential equations using unstructured 2D and 3D meshes. The coupling of 2D and 3D fields via complex boundary conditions presents unique challenges for developing the mathematical and simulation foundation necessary for elucidating organizational principles at the mesoscale.

Workforce Considerations

Research in materials science, condensed matter physics and chemistry, especially at the nanoscale, provides a strong base for the development of mesoscience, including the capabilities discussed above. Understanding and controlling emergent phenomena at the mesoscale requires new modalities of research and training that cross boundaries separating not only traditional disciplines such as chemistry, physics, materials science and the engineering disciplines, but also specialized areas within disciplines such as organic and inorganic chemistry, atomic, molecular and optical physics, and biomolecular materials. Traditional disciplines reflect the history of reductionist science that divides phenomena into component parts, each with a rich and deep foundation to be elaborated. Nanoscience shows us that the boundaries between traditional disciplines become fuzzy and tend to disappear at small length scales. Mesoscience takes this a step further, requiring active cross-disciplinary research to explore new architectures and phenomena arising from interactions among nanoscale degrees of freedom and mesoscale collective responses, defect configurations, fluctuations and heterogeneity. A new emphasis on creating an interdisciplinary workforce led by established scientists at the research frontier and extending to the training of students, postdocs and early career scientists is needed to embrace the potential of mesoscience.

Certain areas of interdisciplinary science stand out as especially important for mesoscience. Self-assembly is a ripe opportunity for the new cross-specialization area of computational materials synthesis. Predicting complex self-assembled architectures on the basis of starting components and assembly conditions is a rich and mostly unexplored opportunity. The current state of the art of self-assembly targets controlling the formation of complex structures; the coming high-payoff opportunity is targeting not only structure but also previously unachievable functionality and performance. Developing a workforce proficient in next-generation self-assembly requires fluency in materials chemistry, condensed matter, layer-by-layer growth, and the new area of computational synthesis.

Understanding mesoscale phenomena requires an emphasis on relating collective properties and dynamics to the generation and evolution of lower-dimensional defect structures. An enhanced focus on defects intentionally introduced into controlled, low-defect synthesis processes may be an important enabler. Experimental efforts can be profoundly assisted by combinatorial approaches for experimental design and by development of a portfolio of modeling and simulation tools, especially when coupled to *in situ* characterization. A further need from computational infrastructure is for means to couple the statistical mechanics of mesoscale assemblies to materials properties and hierarchical modeling frameworks that bridge both synthesis processes and length/time scales. Such advances present the possibility of powerful mesoscale designs that enhance functionality by decoupling structure and function.

Theory, modeling, characterization and synthesis are traditional areas of specialization within materials and chemical sciences that must be much more intimately merged to pursue the opportunities of mesoscience. The complexity of mesoscience, and the sheer number of components, parameters, phenomena and functionalities it comprises cannot be embraced without strong mutual interaction. Computation must rise to the challenge of describing and ultimately predicting more complex materials behavior; and characterization must include computation and modeling to integrate and organize the wealth of information it will produce by the new generation of multi-modal, *in situ*, space- and time-resolved coordinated measurements. Data management and mining strategies must be developed; new theoretical formulations that describe mesoscale emergent behavior must

be devised. The workforce that easily crosses the theory, modeling, characterization and synthesis worlds does not yet exist. Building such a workforce requires bringing these specialized communities together in innovative ways that remain to be designed and implemented.

The need for interdisciplinary and cross-specialization cooperation creates a second challenge. The breadth of knowledge required for mesoscience is much wider than for traditional reductionist science. Highly cooperative research teams strategically chosen to develop specific opportunities are needed. Such teams are emerging in centers such as the Energy Frontier Research Centers and the Energy Innovation Hubs. These models should be embraced and exploited, identifying best practices and lessons learned and extending their reach to the specific disciplines and specializations needed to achieve the potential of mesoscience. The organizational principles, operating modes, and reward systems for interdisciplinary and cross-specialized research teams must be developed and implemented.

To realize the mesoscience opportunity in a timely manner, the mesoscale workforce of the future must be nurtured aggressively. The next generation of mesoscientists must be trained in cross-disciplinary and cross-specialization science. They are best trained by hands-on experience working directly in the integrated frontier research teams. They must see and experience the new inclusive paradigm during their formative years to fully embrace, deploy and extend its power. Their first hand familiarity with the full range of cross-boundary research including its intellectual, technical and human dimensions is the fastest and most direct approach to realizing its benefits.

New modalities of training are needed to implement the constructionist principles of mesoscience. The traditional single mentor/advisor mode of training graduate students can be extended to include dual or triple mentorship, with close communication and advising by two or more mentors from different fields or specializations. Two advisors, for example, can implement training in computational synthesis, one expert in each field, mentoring one or more students in a cooperative effort. Every boundary that needs to be bridged, such as multi-modal characterization spanning spectroscopy, structure and dynamics by x-rays, neutrons and electrons, can be approached in the same way. Incentives for dual or triple mentoring and advising can be implemented, such as research funding, fellowships and student or faculty awards that require cross-boundary training.

The Office of Science's Early Career Research Program is an exciting opportunity for fostering the mesoscale workforce. Compelling opportunities exist for students and post-docs to acquire skills in both experiment and theory, as well as to gain hands-on synthesis experience through joint mentoring arrangements. The need is particularly acute for instrument scientists to exploit newly available characterization sources to impact mesoscale science through multi-modal measurements in collaboration with users. Importantly, these researchers will not only define the future of mesoscale science but also represent an opportunity for developing a diverse technology and manufacturing workforce well suited to the industries and products arising from materials and nanotechnology development.

Realizing the Meso Opportunity

The promise of mesoscale science is discovering and managing the connections among phenomena, degrees of freedom, and functional units to create materials with new behavior, higher performance, longer life, and lower cost, advancing the science of rational design of materials with targeted functionality. The mesoscience approach to materials is qualitatively different from conventional macroscale approaches that rely on serendipitous discovery followed by top-down reductionist analysis of the new macroscopic phenomena to identify their nanoscale origins. Instead, the constructionist meso approach emphasizes bringing disparate nanoscale phenomena and degrees of freedom together to discover or direct new emergent behavior at the mesoscale. Bottom-up synthesis streamlines the innovation process, eliminating the distraction of pre-existing and fully formed macroscopic behavior that competes with alternate innovative or emergent outcomes, and simplifying the building blocks to their most basic atomic, molecular, or nanoscale level. The promise and vision of mesoscience are to make mesoscale emergence a predictive theoretical enterprise steeped in numerical modeling and implemented through mesoscale synthesis and characterization.

Realizing the meso opportunity requires developing new approaches to observation, characterization, synthesis, fundamental theory, phenomenology, and numerical modeling. Beyond the technical means of realizing mesoscience, there is a strong cultural component that must be fostered. The next generation of mesoscientists must not only be fully comfortable with synthesis, characterization, and analytical theory/numerical modeling, but also actively pursue all three of these basic activities in her/his mesoscience research. This requires establishing early training with multiple mentors and team research as the mesoscience standard to cover the broad range of required expertise.

The prior section outlined needed technical directions in synthesis, characterization, and theory/modeling required for effective mesoscience, and the cultural

shifts in approach, integration, and team-oriented research that will bring the mesoscience opportunity to fruition. The Mesoscale Science Subcommittee has distilled these six specific actions that will significantly advance mesoscale science:

1. Increase investment in small- and intermediate-scale lab instrumentation for mesoscale science;

2. Develop detectors, sample environments, instruments, and end stations for mesoscale research that fully capitalize on the large-scale sources available at national user facilities;

3. Grow the cohort of beam line and facility scientists defining the frontiers of increasingly sophisticated mesoscale measurements at user facilities;

4. Attract and retain the best and brightest graduate students and postdoctoral researchers to be the mesoscale energy scientists of the future; and establish dual or triple mentorship/advisor paradigms to train them in cross-boundary mesoscience; and

5. Stimulate the formation of multi-disciplinary research groups that include theorists and experimentalists and span from discovery science to use-inspired research.

Conclusion

The mesoscale opens a new frontier of scientific opportunity. Mesoscale science builds on the remarkable nanoscience insights that the research community is now producing. The reductionist drive to understand bulk materials and phenomena from the top down has revealed the central role of atomic, molecular, and nanoscale structure in shaping bulk behavior. We are now ready to explore the opposite direction, a bottom-up journey from atomic, molecular, and nano structures and phenomena to the broader horizons and more complex behavior of the mesoscale. The mesoscale brings profound changes, replacing the atomic granularity of matter and the quantization of energy with continuous matter and energy, and enabling the onset of collective behavior of ensembles of particles, the interaction of coupled and competing degrees of freedom, the appearance of defects and fluctuations that profoundly alter the behavior of perfect structures, and the formation of heterogeneous composite systems whose parts work cooperatively to transform energy, charge, and mass. Building on knowledge from the nanoscale, these emergent mesoscale features can be manifested in innovative architectures to create targeted new materials phenomena and functionalities, and, ultimately, disruptive technologies with the potential to outperform existing technologies and dominate the competitive market. Seizing the opportunity to develop mesoscale science and to dominate the innovation opportunities it spawns brings an enduring competitive advantage for future economic growth.

The promise of mesoscale science is rich. Manipulating mesoscale architectures assembled from nanoscale building blocks enables virtually endless possibilities to discover, design, and enhance complex phenomena and functionalities. Directed assembly offers unprecedented opportunity to create complex structures and functionalities, inspired in part by biology. Light can be manipulated in photonic crystals, metamaterials, and surface plasmon polaritons to promote chemical reactions, harvest energy from sunlight, and enhance the performance of light-emitting diodes. New generations of electrodes for batteries and fuel cells can be designed to promote the coordinated motion of electrons, ions, and gases and to maximize efficiency and energy density. Mesoporous membranes with defined charge and chemical profiles lining the pores can be designed to separate carbon dioxide, purify water, and catalyze chemical reactions.

There are new organizing principles for mesoscale behavior to be discovered. We understand quantum mechanics for atomic, molecular, and nanoscale phenomena, and classical mechanics for macroscale behavior, but we do not know the organizing principles governing the mesoscale. What principles govern

self-assembly, for example, or the appearance of new behavior from the interaction of competing degrees of freedom? New phenomena will emerge as mesoscale architectures are tuned to promote collective behavior or the interaction of targeted degrees of freedom. As mesoscale systems grow in size, defects, interfaces, and fluctuations appear and can be manipulated to program the thermal, electronic, and mechanical response of the bulk. Mesoscale science thus represents a discovery laboratory for finding new phenomena, a self-assembly foundry for creating new functional systems, and a design engine for new technologies.

This report describes the richness and scope of the mesoscale frontier in six priority research directions:

- Mastering Defect Mesostructure and its Evolution
- Regulating Coupled Reactions and Pathway-Dependent Chemical Processes
- Optimizing Transport and Response Properties by Design and Control of Mesoscale Structure
- Elucidating Non-equilibrium and Many-Body Physics of Electrons
- Harnessing Fluctuations, Dynamics and Degradation for Control of Metastable Mesoscale Systems
- Directing Assembly of Hierarchical Functional Materials

Realizing mesoscale science opportunities requires advances not only in our knowledge but also in our ability to observe, characterize, simulate, and ultimately control matter. A key need is the seamless integration of theory, modeling, and simulation with synthesis and characterization. Treating the complexity of mesoscale phenomena, often including several nanoscale degrees of freedom and structural or functional units, requires theory and simulation spanning space and time scales over many orders of magnitude. Analytical theory is needed to find and formulate new organizing principles that describe emergent mesoscale phenomena arising from many coupled and competing degrees of freedom. Computational advances are required to extend nanoscale simulations to the mesoscale and beyond. Theory and simulation have an unprecedented opportunity to guide the complex multistep synthesis and directed assembly of mesoscale architectures.

Mesoscale measurements that are dynamic, *in situ*, and multi-modal must replace the static single-property character-ization now common in macro and nano regimes. The mesoscale is an inherently dynamic regime, where energy and information captured at the nanoscale are processed and transformed to create new macroscale outcomes. Given the complexity and dynamism of mesoscale phenomena, multiple, simultaneous measurements of transient phenomena are essential. Spatially diverse measurements capturing coupled transformations in different parts of the mesoscale assembly are critical. Because complex mesoscale ensembles are large enough to have defects, fluctuations and statistical varia-tion, they inevitably display a range of behaviors that requires many measurements to capture the distribution of possible outcomes and not just a single measurement of a "representative" sample.

Finally, the ability to design and realize the complex and composite materials of the mesoscale will require qualitative advances in how we synthesize materials, both in moving from serendipitous to directed discovery and in gaining the ability to assemble and control materials systems and architectures from smaller structural and functional units. The inte-gration of top-down and bottom-up approaches, now quite distinct and representing different operating principles and spatial scales, is key to mesoscale synthesis. Bridging the gap and allowing these two powerful approaches to influence, complement, and reinforce each other represent major synthesis challenges and opportunities of mesoscale science.

While the challenge of controlling mesoscale phenomena is enormous, the potential benefits are significant and far-reaching. Success will enable transformational outcomes for society. Mesoscale science has the potential to re-energize innovation, deliver high-performance, low-cost technologies, and provide a competitive foundation for enduring economic growth. Transformational mesoscale outcomes include

- The ability to manufacture at the mesoscale: that is, the directed assembly of mesoscale structures that possess unique functionality that yields faster, cheaper, higher performing, and longer lasting products, as well as products that have functionality that we have not yet imagined.

- The realization of biologically inspired complexity and functionality with inorganic earth-abundant materials to transform energy conversion, transmission, and storage.

- The transformation from top-down design of materials and systems with macroscopic building blocks to bottom-up design with nanoscale functional units producing next-generation technological innovation.

It is both the magnitude of the challenge in bridging quanta to the continuum and the potential dividend in controlling the mesoscale that have energized the research community and motivated this report.

Appendix: Community Input to the BESAC Meso Subcommittee Process

To foster engagement with the broader scientific community and to collect input on the frontiers of mesoscale science, the Meso Subcommittee organized town hall meetings at the American Physical Society meeting in Boston (February 2012), the American Chemical Society meeting in San Diego (March 2012), the Materials Research Society in San Francisco (April 2012), and in Chicago in May 2012. It also hosted an American Chemical Society webinar in April 2012. More than 1000 researchers participated in one or more of these outreach activities. These efforts led to more than 100 contributed quad charts that are listed by title and contributor below. They can also be found at www.meso2012.com.

Mesoscale Science of Damage Accumulation in Long-Lived Systems, R. French (Case Western Reserve University)

Role of Microscopic Quenched Disorder in Macroscopic Stability, R. Podgornik (University of Massachusetts)

Failure Mechanism in Materials and Meso-Scale Structures, W. Ching (University of Missouri, Kansas City)

Time- and Length-Scales of Radiation Damage Processes, S. Kucheyev (Lawrence Livermore National Laboratory)

Self-organization by Irradiation and Plastic Deformation, Pascal Bellon (University of Illinois at Urbana-Champaign)

Plasticity of Crystal Interfaces, S. Mesarovic (Washington State University)

Mesoscale Structural Changes from Atomic Scale Radiation Damage, D. K. Shuh (Lawrence Berkeley National Laboratory)

Optimizing Flow Stress of a BCC Metal at $T/T_m<0.1$, Anthony Bryhan

Damage Accumulation in, and Lifetimes of Materials, Tony Rollet (Carnegie Mellon University)

Microstructure Based Heterogeneity Evolution Leading to Phase Transformation and Damage/Failure Events, C. A. Bronkhorst (Los Alamos National Laboratory)

Harnessing Non-linear Effects for Mesoscale Devices, D. Lopez (Argonne National Laboratory)

Fluctuation De/stabilization of Mesoscale Structures, V. A. Parsegian (University of Massachusetts)

Magnetization Dynamics: The Inherently Mesoscale Problem, A. Hoffman (Argonne National Laboratory)

Lithium Batteries: Composite Electrode Materials by Design, J. Flake (Louisiana State University)

Wetting and Fluid Transport Phenomena under Mesoscale Confinement, A. Checco (Brookhaven National Laboratory)

Making Better Foams, R. Chau (Lawrence Livermore National Laboratory)

The Role of Defects in Phase Transitions and Kinetics, M. Akin (Lawrence Livermore National Laboratory)

Chemistry at Extremes, M. Akin (Lawrence Livermore National Laboratory)

Thermal Conductivity of Thin Films at High Temperature (> 4000 K) and Pressure (> 100 GPa), D. Fratanduono (Lawrence Livermore National Laboratory)

Mesoscale Phases: Control of Global Structural and Physical Properties, R. Jin (Louisiana State University)

Nanoscale Materials Engineering for Mesoscopic Functionality, W. Plummer (Louisiana State University)

Electrocatalysts: Active Sites and Interfaces of Clusters, J. Flake (Louisiana State University)

Dynamic Tomography: Polymers, Batteries, and H_2 Storage, Les Butler (Louisiana State University)

3D Mesostructured Battery Electrodes, Paul Braun (University of Illinois, Urbana-Champaign)

Functional Metal-Organics for Gas Storage, J. Spence (Arizona State University)

Self-adaptive Electrodes for Energy Applications, T. Rajh (Argonne National Laboratory)

Multifunctional Metal-Organic Frameworks, V. Zapf (Los Alamos National Laboratory)

Multistep Multiscale Control and Delivery, Mark Jensen (Argonne National Laboratory)

Mesoscale Functionality from Interface-Dominated Oxides, Brandon Chung (Lawrence Livermore National Laboratory)

Rational Design of Electrode/Electrolyte/Membrane Interfaces for Energy Storage, Michel Dupuis (Pacific Northwest National Laboratory)

Ionomer and Solvent Structure Interactions in Electrodes, R. Borup (Lawrence Berkeley National Laboratory)

Mesoscopic Perspectives in Separations Science, Ross Ellis (Argonne National Laboratory)

Interfacial Durability of Meso-scale Systems, Debbie Myers (Argonne National Laboratory)

Thin Boundary Layer Heat Transfer, Charles Agosta (Clark University)

Functional Mesoscale Systems, Gary Rubloff (University of Maryland)

Meso Challenge: Multi-Valent Interactions in Poly-electrolytes, Matt Tirrell (University of Chicago)

Meso-photonics for Energy Applications, Marin Soljacic (Massachusetts Institute of Technology)

Controlling Optical Properties of Functional Mesoscale Systems via Multi-Scale Interfacial Interactions, Stephen K. Doorn (Los Alamos National Laboratory)

"Upscaling" Nanoscale Thermoelectrics: The Mesoscale Design Challenge for Real-World Energy Needs, Jennifer Hollingsworth and Andrei Piryatinski (Los Alamos National Laboratory)

Design and Control of Interfaces in Soft Materials, Sergei Tretiak (Los Alamos National Laboratory)

Heteroatom-Doped Graphene-Sheet Structures in High-Performance Li-Ion Battery Anode, Gang Wu and Piotr Zelenay (Los Alamos National Laboratory)

Role of Fluctuations in Formulating Organizing Principles in Meso-scale Systems, Roger French (Case Western Reserve University)

Controlling Coupled Ferroic Domains at Meso-scopic Length Scale, Stephen K. Doorn (Los Alamos National Laboratory)

Emergent States in Oxide Interfaces, Alexander Balatsky (Los Alamos National Laboratory)

Cooperative Phenomena in Excitonic-Plasmonic Systems: Plasmon-Enhanced Quantum-Dot Devices, Victor I. Klimov and Jeffrey M. Pietryga (Los Alamos National Laboratory)

Emerging Mesoscale Conduction Mechanisms: Charge Transport in Nanoscale Assemblies and across Complex Interfaces, Victor I. Klimov and Istvan Robel (Los Alamos National Laboratory)

Shuffling Materials Chemistry: Controlling Emergent Phenomena in Layered Materials, Michael Janicke and Mark McCleskey (Los Alamos National Laboratory)

Meso Magnets: Understanding the Quantum to Classical Transition, I. K. Schuller and L. J. Sham (University of California, San Diego)

Quantum Design of Materials with New Functionalities, Valerii Vinokur (Argonne National Laboratory)

Alternate Explosives Signatures for Detection, David S. Moore (Los Alamos National Laboratory)

Functional Materials in Extreme Subsurface Conditions, Amr Abdel-Fattah (Argonne National Laboratory)

Next-Generation Theory and Modeling Approach for Multiphase Flow in Porous Media, H. H. Liu (Lawrence Berkeley National Laboratory)

How Is Electronic Structure Correlated with Morphology and Mesoscopic Structural Stability? J. Biener (Lawrence Livermore National Laboratory)

Hierarchically Structured Porous Electrodes for Energy Storage, M. Tang (Lawrence Livermore National Laboratory)

Integrating Mesoporosity into Nanoporous Materials, J. Biener (Lawrence Livermore National Laboratory)

Elastic Properties for Mesoporous Structures under Extreme Conditions, N. Butch (Lawrence Livermore National Laboratory)

Fluid, Mass, and Energy Transport in Porous and Quasi-porous Media, A. Tompson (Lawrence Livermore National Laboratory)

Emergent Transport Phenomena in Natural Systems, Mei Ding (Los Alamos National Laboratory)

Gas Transport in Mesoporous Inorganic-Organic Hybrids, Jeff Urban (Lawrence Berkeley National Laboratory)

Reactive Transport through Mesoporous Media, Gordon Brown (Stanford University)

Multi-physicochemical Transport/Interfacial Processes in Permeable Media, Qinjun Kang and Piotr Zelenay (Los Alamos National Laboratory)

Visualization and Control of Transport and Flow through Mesoporous and Crowded Environments, Juan G. Duque, Jared J. Crochet, and Stephen K. Doorn (Los Alamos National Laboratory)

Gas Flow in Mesoporous Media, Qinjun Kang (Los Alamos National Laboratory)

Confinement in Meso Pores-Macromolecular Crystals and Sensors, I. K. Schuller (University of California, San Diego)

Role of Solvent Meso-structures in Catalysis, R. Williams, J. Gordon, and D. Thorn (Los Alamos National Laboratory)

Self-assembled Heterostructures for Energy, S. Darling (Argonne National Laboratory)

Optically Directed Assembly of Mesoscale Hybrid Structures, S. Sankaranarayanan (Argonne National Laboratory)

Self-assembly and Dis-assembly of VNPs with Cargos, N. Steinmetz (Case Western Reserve University)

Directed Assembly of Pre-programmed Building Blocks at the Mesoscale, T. Han (Lawrence Livermore National Laboratory)

Proteins Self-organize into Living Materials, M. Gardel (University of Chicago)

Self-assembled Peptide Amphiphiles to Control Cellular Response, G. Schatz (Northwestern University)

Understanding and Controlling Self-assembly of Inorganic Nanoparticles through Mass-Selected Ion Deposition, Julia Laskin (Pacific Northwest National Laboratory)

Designing Solution Self-assembly Routes to Meso-scale Materials, Greg Exarhos (Pacific Northwest National Laboratory)

Design of Mesoscale Catalytic Processes, Roger Rousseau (Pacific Northwest National Laboratory)

Self-organization of Materials under Irradiation, Igor Veryovkin (Argonne National Laboratory)

Hierarchical Assembly of Confined Nanomaterials into Multifunctional Mesoscale Arrays, Igor I. Slowing (Iowa State University)

Self-assembly of Inorganic Nanoparticles, George Crabtree (Argonne National Laboratory)

Self and Guided Assembly in Biology, Douglas Tobias (University of California, Irvine)

Programmable Polymer Membrane Composite Meso-materials, Gabriel A. Montano (Los Alamos National Laboratory)

Ultrasonically Guided Assembly of 3D Periodic Structures, Dipen Sinha (Los Alamos National Laboratory)

Artificial Leaves: Integrated Soft, Biological & Composite Mesoscale Systems for Enhanced Bioenergy Production, Amr Abdel-Fattah (Los Alamos National Laboratory)

Nanomaterial-Based Complex Architectures for Structural and Functional Heterogeneity, H. Zbib (Washington State University)

Driving Structural Phase Transitions in Periodic Mesostructures, J. Crowhurst (Lawrence Livermore National Laboratory)

Taming Complexity from Atoms to the Mesoscale: NP/Organic Hybrids, P. Duxbury (Michigan State University)

Hierarchically Structured Porous Electrodes for Energy Storage, M. Tang (Lawrence Livermore National Laboratory)

Microcatalyst Engineering, C. Chang (National Renewable Energy Laboratory)

Interfacial Control of Polymer Properties, Frances Houle (Lawrence Berkeley National Laboratory)

A Novel Substrate-Free Synthesis of Carbon Microtubes, Hoon T. Chung and Piotr Zelenay (Los Alamos National Laboratory)

Advanced Characterization of Mesoscopic Materials, C. Fadley (Lawrence Berkeley National Laboratory)

Rapid Evolution of Mesoscale Material Structure by DTEM, B. Reed (Lawrence Livermore National Laboratory)

Connecting Mesoscale Structure to Macroscopic Material Performance, J. Bernier (Lawrence Livermore National Laboratory)

High Energy Diffraction Microscopy: Enabling Higher-Order Characterization of Polycrystalline Microstructures, J. Bernier (Lawrence Livermore National Laboratory)

Supra-grain Correlations and Materials DNA, M. Kumar (Lawrence Livermore National Laboratory)

Microcatalyst Engineering, C. Chang (National Renewable Energy Laboratory)

Ionic Liquid at Interfaces and under Confinement, B. Ocko (Brookhaven National Laboratory)

Strongly Nonlinear Waves at the Mesoscale: Design of Metamaterials, E. Herbold (Lawrence Livermore National Laboratory)

Isotopic Probes of Ionic Diffusion and Solid Surfaces, D. J. DePaolo (Lawrence Berkeley National Laboratory)

Multi-dimensional Soft X-ray Microscopy of Mesoscale Behavior, Peter Fischer (Center for X-Ray Optics/Lawrence Berkeley National Laboratory)

4D Imaging of Mesoscale Structures, Wah-Keat Lee (Brookhaven National Laboratory)

Dynamic 3D Imaging, Dula Parkinson (Lawrence Berkeley National Laboratory)

Mesoscale Plasticity by Synchrotron X-Laue Micro-diffraction and Reverse Modeling Simulation, Nobumichi Tamura (Lawrence Berkeley National Laboratory)

X-Ray Studies of Meso Materials, Dennis Mills (Argonne National Laboratory)

The Potential of High Energy X-ray Diffraction and Microtomography for the Study of UO_2 under Processing and Operating Conditions, Don Brown and Mark Bourke (Los Alamos National Laboratory)

3D Imaging of Mesoscale Architectures with Nanoscale Resolution, John Spence (Arizona State University)

In-situ Monitoring of Dynamic Phenomena during Phase Transformations, Amy Clarke and Jason Cooley (Los Alamos National Laboratory)

Integrating Mesoporosity into Nanoporous Materials, J. Biener (Lawrence Livermore National Laboratory)

Computational Design and Additive Manufacturing of Mesoscale Architectures for High Performance Materials, C. Spadaccini (Lawrence Livermore National Laboratory)

Predicting Mesoscale Material Kinetics with Atomistically-based Computation, R. Rudd (Lawrence Livermore National Laboratory)

Meso-scale Investigation of Particle Transport in Porous Media, Y. Kanarska (Lawrence Livermore National Laboratory)

Meso-scale Investigation of Mechanically and Thermally Induced Reactions in Reactive Solid Mixtures and Structures, I. Lomov (Lawrence Livermore National Laboratory)

Application of Mesoscale Simulations toward the Development of Predictive Models for Deformation and Failure of Heterogeneous Granular Materials, T. Antoun (Lawrence Livermore National Laboratory)
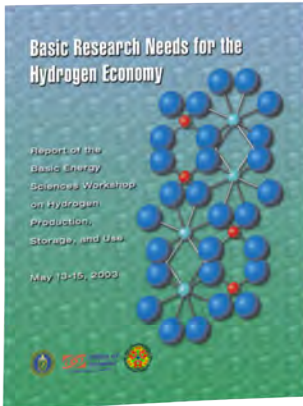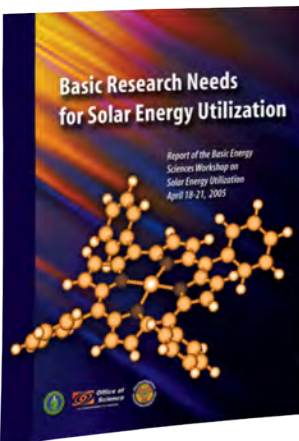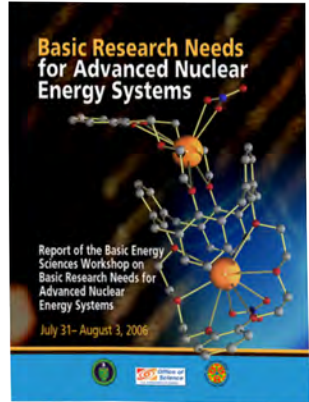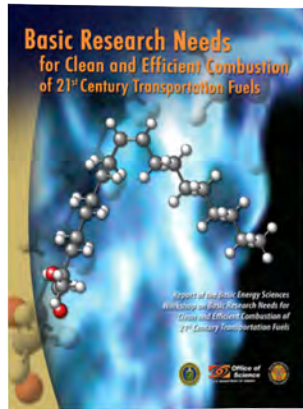
Theory & Computation for Self-assembly, Chris Mundy (Pacific Northwest National Laboratory)

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