Synchrotron Radiation News
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gsrn20

Opportunities with Synchrotron Radiation at the Mesoscale

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Published online: 25 Jul 2013.

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Participants in the SSRL Mesoscale Science Workshop, SSRL/LCLS Users Meeting, SLAC National Accelerator Laboratory, Menlo Park, CA, October 5–6, 2012.

What is mesoscale science? The modifier "meso" can mean different things to different communities. In many areas of science, "mesoscale" generally refers to a middle-ground domain of length, energy, or time where theories accurate at both lower and higher scales fail. In materials science, for example, mesoscale behavior often rises when quantum behavior begins to fade, collective effects become important, or statistical variation and defects appear, often at length scales larger than a few nm. However, for atmospheric scientists and ecologists, *mesoscale* means miles. For meterologists, *mesoscale* means hundreds to thousands of miles. The *mesoscale* arena for cosmologists is many light-years across.

To paraphrase from the September 2012 DOE-BES Mesoscale Science Report, "From Quanta to the Continuum: Opportunities for Mesoscale Science" (http://science.energy.gov/bes/news-and-resources/reports/basic-research-needs/), atoms and bulk materials are connected by a sequence of mesoscale architectures (e.g., chemical bonding, periodic lattices, or nanoparticle aggregation) and phenomena (e.g., fracture, reactive transport through mesoporous media). Mesoscale science entails the observation, understanding, and control of these intermediate-scale architectures and phenomena. It will ultimately lead to next-generation materials and technologies that provide innovative solutions to pervasive societal problems including energy security, environmental sustainability, climate change, and enduring economic growth. It will also lead to a more fundamental understanding of the natural world, where mesoscale processes govern the compositions and behavior of materials at the human scale, including natural waters, the atmosphere, and Earth's crust.

The DOE-BES Mesoscale Report also presents some of the knowledge gaps that must be filled in order to make accurate and robust predictions about materials and their properties in the mesoscale-size regime. One of the key gaps is ~~a~~ theory that bridges between nanomaterials, where quantum mechanics provides excellent insights to structure-property relationships, and micromaterials and larger, where continuum mechanics is generally successful in predicting properties. However, for many mesoscale phenomena, such as the fracturing of solids at the sub-micron scale, neither theory provides accurate predictions.

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.

To inform the user community about this exciting new research area, a workshop focusing on mesoscale scientific opportunities was held at the 2012 SSRL/LCLS joint Annual Users Meeting at the SLAC National Accelerator Laboratory (Menlo Park, CA). A brief synopsis of this workshop was described in a previous issue of *Synchrotron Radiation News* (*SRN* **26**(1), 43 (2013)). Here we present a comprehensive discussion of workshop results to illustrate mesoscale science concepts in different scientific problems, to discuss research opportunities, and to highlight roles of light sources in these developing research areas.

A unique perspective

As a group, the talks illustrated the point that "mesoscale" is not just a new way of grouping together existing research approaches. Rather, it provides a unique perspective that underscores new ways to manipulate nanoscale interactions and assemble nanoscale objects in new architectures to obtain new properties. In earth sciences, the mesoscale perspective provides a new way to understand how complex suites of chemical reactions combine with mesoscale properties to control the behavior of geological systems and the compositions of groundwater, lakes, oceans, and the atmosphere. The unique capabilities provided by X-ray light sources make them crucial to the development of this new research field. As outlined by George Crabtree (ANL/UIC), several hallmarks distinguish mesoscale materials and systems from the nanoscale world. These include: (1)

a diminishing impact of the exact location of an individual atom ("atomic granularity") on the properties of the system as size increases; (2) loss of quantized, well-separated energy levels as size and interaction with the external environment increase; (3) the development of identifiable collective behavior of an ensemble that is distinct from the behavior of the constituent components; (4) interaction or blending of disparate electronic, structural magnetic, and chemical responses to produce ever richer behavior that can be manipulated and controlled; (5) statistical fluctuations and imperfections within materials, which affect system properties; and (6) the presence of structural/compositional heterogeneities.

Mineral-aqueous solution interfaces were highlighted as an important class of mesoscale geochemical systems (Figure 1). Chemical reactions at such interfaces control the rates of mineral dissolution and thus the composition of surrounding pore fluids. The atomic- to mesoscale spatial arrangements of ions and the presence of heterogeneities such as surface structural defects, impurities, and coatings, as well as the rates of individual reactions, control the system response. Heterogeneities impact reaction pathways and vice versa, resulting in complex systems that profoundly impact globally important processes such as CO_2 entrapment in geological repositories and geochemical isotope fractionation. Speakers also devoted attention to aquifers and rock-fluid systems. Mesoscale behavior in these systems arises from complex interactions between chemistry, diffusion-controlled rates, and hydrology at the scale of individual pores (microns), millimeters, and meters, where heterogeneities, such as impermeable layers in sediments and fractures, are the rule rather than the exception. The transport and fate of CO_2 in aquifers is strongly impacted by these mesoscale properties. All of the speakers highlighted the need for new approaches that can be used to image heterogeneities and characterize chemistry under *in-situ* conditions in mesocale systems. Synchrotron-based X-ray microscopy and spectroscopy techniques offer the capability to image mesoscale heterogeneities in materials over a range of length scales and to characterize chemistry in the time domain, and thus will play a major role in the development of this field.

The need for faster, higher-density data storage has led Hermann Durr and a team of researchers at SLAC to investigate nominally insulating novel materials that have the potential to be "switched" by light. FeCoGd alloys are a prototype material for all-optical data storage media. By modifying the mesoscale properties of the systems, particularly the dimensions and compositions of heterogeneities (phase boundaries) over nm-length scales (Figure 2), it is possible to temporarily (ps time intervals) induce these materials to act as metals, allowing atomic angular momentum to diffuse and encode the light pulse. Such materials offer the potential to minimize power consumption and device cost, which are crucial factors for the successful use of these novel materials. LCLS, SSRL, and similar light sources play crucial roles in this research because of their ability

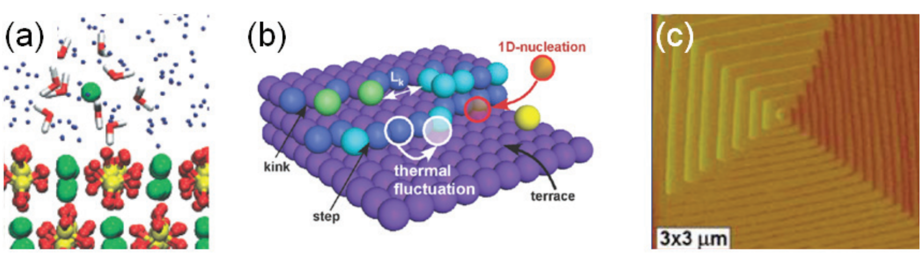

Figure 1: Mineral-water interfaces are mesoscale systems. (a) A Ba^{2+} ion begins to desolvate as it approaches the barite (001)-water interface [1]. Figure reproduced with permission from American Chemical Society, © 2006. (b) Schematic illustrating terrace, step, and kinks at crystal surfaces. (c) Spiral growth hillocks on the calcite (104). Reproduced from [2]. Figure reproduced with permission from American Chemical Society, © 2009. Crystal growth morphology and rates, and the composition of the growing crystal, are highly sensitive to interfacial chemistry.

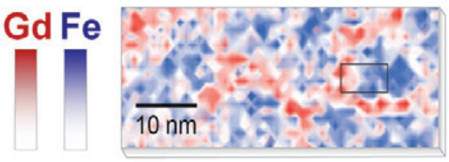

Figure 2: Scanning transmission electron microscopy image illustrating the nm-scale compositional heterogeneity of an FeCoGd alloy. Color scales denote deviation from the average (figure courtesy of Hermann Durr, SLAC).

to investigate spin mobilization dynamics on ps time scales. At the other end of length and temporal scales are structural materials used to fabricate aircraft engines, nuclear reactors, windmill turbines, and a host of similar energy technology products. The strength and durability of these materials, over micrometer to meter lengths and minute- to year-long intervals, are controlled by mesoscale material behavior. As described by Tony Rollett of Carnegie Mellon, the advent of synchrotron-based techniques such as High Energy Diffraction Microscopy (HEDM) to generate crystal orientation maps, combined with computed tomography to map out density variations, provides powerful new tools for investigating deformation and damage accumulation in materials. For fatigue cracks and ductile fracture in particular, these tools enable critical observations of damage nucleation in materials.

There is a pressing need to develop novel energy conversion devices to address the growing U.S. and global demand for energy. As discussed by Michael Chabynic of UCSB, organic solar cells can be fabricated at very low cost due to the ability to use high throughput printing technologies. The power conversion efficiencies of organic solar cells have now reached 10% in lab cells, but the fundamental mechanisms that lead to these values are still under investigation. The most efficient organic solar cells are bulk heterojunctions, which comprise a mesoscale assemblage of nanoscale phases that either donate or accept electrons (Figure 3). Synchrotron radiation is well suited to studying ordering at nanoscale dimensions in organic materials using both hard X-rays to reveal molecular order and soft X-rays to reveal longer length scale structures with molecular specificity. Research at SLAC has provided significant detail about the crystalline order in bulk heterojunction organic solar cells. This structural information feeds into models for charge transport that can reveal how the charge separation event leads to mesoscale charge extraction in thin films.

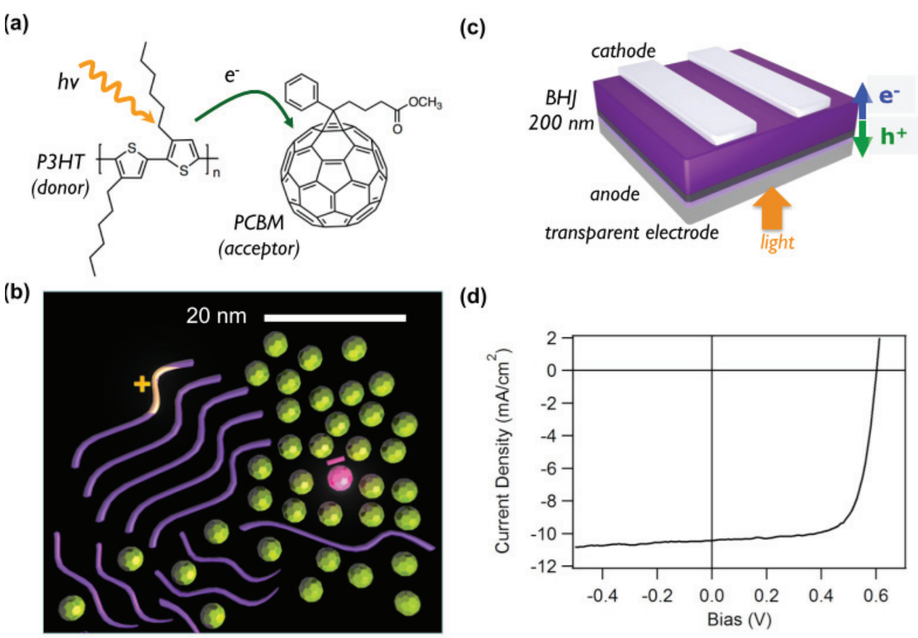

Figure 3: *(a) Molecular charge transfer leads to charge generation in an organic solar cell between materials such as poly(3-hexylthiophene) (P3HT) and PCBM, a fullerene derivative. (b) Bulk heterojunction (BHJ) solar cells have nanoscale phase separated structures comprising polymer-rich, fullerene-rich, and mixed domains. (c) A schematic of the typical device structure of a bulk heterojunction organic solar cell where the molecular-generated charge travels over ~100–200 nm to the electrodes. (d) Current-voltage characteristic of a lab-scale (~0.1 cm^2 area) P3HT:PCBM solar cell with 4.5% solar power conversion efficiency (figure courtesy of Michael Chabynic, UCSB).*

Cross-cutting themes

Several themes ran throughout all of the mesoscale studies. The importance and centrality of imaging (i.e., the ability to visualize and quantify compositional and physical heterogeneities), such as spin domain boundaries, heterojunctions, microcracks, pore throats, surface coatings, and organelles, was repeated throughout the workshop lectures. This point was forcefully illustrated by Carolyn Larabell (LBNL), who described research to develop synchrotron-based soft X-ray tomography and cryogenic light microscopy to study sub-cellular architecture and organization in eukaryotic cells. Living cells are the ultimate mesoscale systems; an abundance of nm-scale components (organelles) are connected by highly functional heterogeneities (interfaces) (Figure 4). The organelles and interfaces act together in a highly regulated manner to function as a single system.

Heterogeneities were concluded to be of central importance to mesoscale systems. In particular, heterogeneity size, composition, and distributions result in the unique mesoscale behavior of materials and systems and are of intense interest in materials design. Interactions between juxtaposed mesoscale domains and between heterogeneities and the system matrix (e.g., between microcracks and solid material, or between groundwater and reactive coatings on sediment particles) were found to be universally important controls of mesoscale system properties and performance. Another common theme was the need for both upscaling (constructionist) and downscaling (reductionist) approaches. For example, in porous geologi-

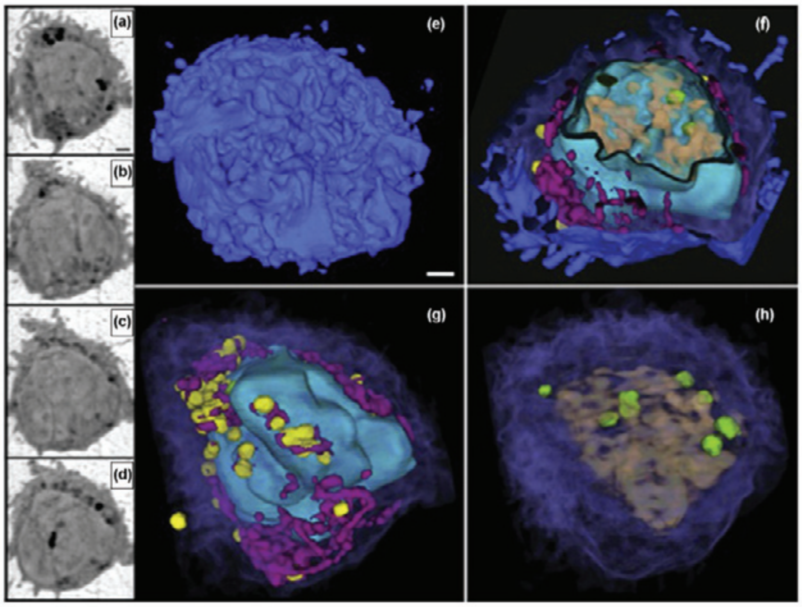

Figure 4: *X-ray tomography of a lymphocyte (T-cell). (a–d) Orthoslices from the tomographic reconstruction of a cryo-fixed T-cell imaged in a capillary. (e–h) Segmented volumes. (e) Cell surface with numerous filopodial extensions. (f–h) Cut-away views showing the typical, highly folded large nucleus (cyan) surrounded by a small rim of cytoplasm (purple). Multiple highly absorbing vesicles (yellow) surround the nucleus (cyan), along with less absorbing structures, including mitochondria (magenta) in the cytoplasm. Chromosomes (salmon) and nuclear bodies (green) are seen in the nucleus. The diameter of the cell is 8 mm. The scale bar represents 1 mm. Reproduced from [3]. Figure reproduced with permission from Elsevier.*

cal media, reductionist approaches are required to describe chemical reactions and flow characteristics occurring within regions of a host aquifer. However, accurate prediction of these processes at the mesoscale requires scaling of rate laws derived at the submicron pore scale to matrices at the meter and kilometer scales. The development of novel material for higher density data storage provides an excellent example of tailoring materials from the nanoscale to create new properties at the mesoscale. In comparison, understanding the mesoscopic behavior of structural materials will benefit from constructionist approaches that predict micrometer- to meter-scale behavior based on submicron characteristics. The importance of using multiple characterization techniques to investigate systems and materials at multiple length scales was recognized by workshop participants as a major need in relating nano- and mesoscale observations to real material properties and chemical reactivity. This finding was true for both inorganic and organic systems, including biological cells.

Opportunities and challenges for X-ray light sources in mesoscale science

The ability of synchrotron and FEL X-rays to image the internal structures of objects from millimeter to molecular scales and to provide information on bonding and chemical dynamics provides the experimentalist with many tools required to interrogate key properties of mesoscale systems. Going forward, there are tremendous opportunities for the DOE to leverage its light sources to expand and energize mesoscale science. In order to do this, however, both DOE and the light sources will need to recognize and embrace important characteristics of mesoscale science research. These include:

- Access for scientists who have relatively little experience with synchrotrons and FELs, but who need to use multiple techniques in their mesoscale science research. This is a "human interface" problem that requires a focus on both training and collaboration. It is likely to require significant staff resources, more than are presently available at light sources such as SSRL.
- Access to "suites of techniques," including surface-, nano-, meso-, and molecular-scale capabilities, as opposed to focusing on single-technique approaches common at light sources. This will require integration of disparate techniques at the user administration level.
- Increased access to X-ray imaging techniques.
- High sample throughput capabilities.
- Energy filtering to image variations in chemical composition in materials.
- *In-situ* and real-time operation of a large range of techniques (XAS, XES, PES, scattering-based methods, XAS imaging/microscopy/tomography) to characterize evolution in microstructure (biological and materials specimens, for example).
- Advanced data analysis capabilities that can empower novice and advanced experimenters.
- Integration of synchrotron and non-synchrotron tools (e.g., TEM, MS, FT-IR).
- Integration of numerical simulation and prediction with experimental characterization, to describe increasingly complex and often counter-intuitive mesoscale behavior.

With attention to these needs, synchrotron and FEL light sources can catalyze growth in mesoscale science for a brighter future. ■

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