USER SCIENCE HORIZONS

2016 APS/CNM USERS MEETING

WORKSHOP AGENDAS AND ABSTRACTS

Tuesday, May 10

APS/CNM Workshop 2
Challenges in Integrating Data Science, Computational Modeling, and Advanced Characterization

Location: Bldg. 402, Room E1100/E1200

Organizers: Maria Chan (CNM), Doga Gursoy (CNM), Fatih Sen (CNM), Ross Harder (XSD), and Benjamin Blaiszik (CLS)

Integrating materials characterization data from multiple sources, including synchrotron x-ray and electron microscopy, with computational and theoretical methods is an integral aspect of materials design and development. Modern approaches in data analysis and recent advances in high performance computing opened up new ways to understand deep information from a wide variety of experimental methods such as x-ray spectroscopy and microscopy. These methods can provide knowledge about atomic positions, local chemical environments, electronic structures, phonon dynamics, as well as the evolution of these properties with time, temperature, chemical changes, and applied fields or forces. To reap the entire benefit from these large data and to extract information, effective computational and data mining methods need to be developed and implemented. Many mathematical and statistical analysis tools are available but very few are applied in photon sciences to advance our understanding of materials or to drive material discovery.

The revolutionized high-energy synchrotron facility proposed in the APS Upgrade project will increase brightness and coherence, leading to further increases in data rates, volumes and experiment complexity, creating further demands for advanced scientific computation. Many x-ray imaging techniques enabled by the APS Upgrade, including microscopy, coherence imaging, and time-dependent research will only realize their full potential with advances in analysis methods, materials informatics, data sciences and effective computing strategies.

The workshop aims to address the challenges, in theory, algorithms, hardware and software, in integrating data science techniques with materials modeling and characterization at APS and CNM. The goal is to identify and discuss synergistic efforts among beam line scientists, materials scientists, computational scientists, and computer scientists, who are involved.

Workshop topics:

☐ Hardware for data connection and transfer

☐ Data mining from large spectroscopy and image datasets

☐ Data platforms to support materials informatics

☐ Machine learning techniques for materials property prediction

☐ Integrating data analytics methods with different experimental techniques

☐ High-performance and high-throughput computing

☐ Information visualization from high-dimensional x-ray and electron datasets

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8:45–9:00	Introductory Remarks
9:00–9:40	Simon Billinge (Columbia University/Brookhaven National Laboratory) *Robust Prediction of Real Materials*
9:40–10:20	Brian Toby (Argonne National Laboratory) *Computational Science Challenges at the APS*
10:20–10:40	Break
10:40–11:20	Surya Kalidindi (Georgia Tech) *Data Analytics for Mining Process-structure-property Linkages for Hierarchical Materials*
11:20–12:00	Ben Blaiszik (University of Chicago) *The Materials Data Facility: Data Services to Advance Materials Science Research*

12:00–1:30	Lunch
1:30–2:10	David Skinner (Lawrence Berkeley National Laboratory) *Getting the Most Science from Your Data*
2:10–2:50	Nicola Ferrier (Argonne National Laboratory) *Multi-modal 3D Characterization*
2:50–3:10	Break
3:10–3:50	Rebecca Willet (University of Wisconsin) *Photon-limited Data Analysis in Material Structure Identification*
3:50–4:20	Ankit Agrawal (Northwestern University) *Data-driven Materials Science Enabling Large-scale Property Prediction and Optimization*
4:20–4:50	Konrad Kording (Northwestern University) *Challenges in Multimodal Data Integration for Neuroscience*
5:00	Adjourn

WK-2

Computational Science Challenges at the APS

Brian Toby
X-ray Science Division, Argonne National Laboratory,
Argonne, IL 60439

It has become increasingly clear that our ability to conduct beamline experiments and obtain scientific results is very much limited by available software. This will accelerate as x-ray detectors continue to improve and will become even more acute after the APS Upgrade.

This talk will review some of the information we have gathered about software that has been developed at the APS and what some of the present and future demands will be. As time permits, I will highlight some of our ongoing efforts.

WK-2

Data Analytics for Mining Process-Structure-Property Linkages for Hierarchical Materials

Surya R. Kalidindi
Georgia Institute of Technology, Atlanta, GA 30332

A majority of the materials employed in advanced technologies exhibit hierarchical internal structures with rich details at multiple length and/or structure scales (spanning from atomic to macroscale). Collectively, these features of the material internal structure are here simply referred to as the material structure or just structure, and constitute the central consideration in the development of new/improved hierarchical materials. Indeed, the existence of a causal relationship between the material structure and its properties is the central tenet in the field of materials science and engineering. It should be noted that the word structure is used very broadly in these statements to include and refer to any of the details of the material internal structure (spanning all relevant length or structure scales involved). Although the core connections between the material's structure, its evolution through various manufacturing processes, and its macroscale properties (or performance characteristics) in service are widely acknowledged to exist, establishing this fundamental knowledge base has proven effort-intensive, slow, and very expensive for most material systems being explored for advanced technology applications. It is anticipated that the multi-functional performance characteristics of a material are likely to be controlled by a relatively small number of salient features in its hierarchical internal structure. However, cost-effective validated protocols do not yet exist for fast identification of these salient features and establishment of the desired core knowledge needed for the accelerated design, manufacture and deployment of new materials in advanced technologies. The main impediment arises from lack of a broadly accepted framework for a rigorous quantification of the material's structure, and objective (automated) identification of the salient features that control the properties of interest. This presentation focuses on the development of data science algorithms and computationally efficient protocols capable of mining the essential linkages from large ensembles of materials datasets (both experimental and modeling), and building robust knowledge systems that can be readily accessed, searched, and shared by the broader community. The methods employed in this novel framework are based on digital representation of material's hierarchical internal structure, rigorous quantification of the material structure using n-point spatial correlations, objective (data-driven) dimensionality reduction of the material structure representation using data science approaches (e.g., principal component analyses), and formulation of reliable and robust process-structure-property linkages using various regression techniques. This new framework is illustrated through a number of case studies.

WK-2

The Materials Data Facility: Data Services to Advance Materials Science Research

Ben Blaiszik
Computation Institute, University of Chicago, Chicago, IL 60637

With increasingly strict data management requirements from funding agencies and institutions, expanding focus on the challenges of research replicability, increasingly complex challenges in multimodal analysis and data synthesis, and growing data sizes and heterogeneity, new data needs are emerging in the materials community. The Materials Data Facility (MDF) operates two cloud-hosted services, data publication and data discovery, to promote open data sharing, self-service data publication and curation, and encourage data reuse, layered with powerful data discovery tools. The data publication service simplifies the process of copying data to a secure storage location, assigning data a citable persistent identifier, and recording custom (e.g., material, technique, or instrument specific) and automatically-extracted metadata in a registry while the data discovery service will provide advanced search capabilities (e.g., faceting, free text range querying, and full text search) against the registered data and metadata. The MDF services empower individual researchers, research projects, and institutions to 1) publish research datasets, regardless of size, from local storage, institutional data stores, or cloud storage, without involvement of third-party publishers; 2) build, share, and enforce extensible domain-specific custom metadata schemas; 3) interact with published data and metadata via REST APIs to facilitate automation, analysis, and feedback; and 4) access a data discovery model that allows researchers to search, interrogate, and eventually build upon existing published data. We describe MDF design, current status, and future plans.

WK-2

Getting the Most Science from Your Data

David Skinner
Lawrence Berkeley National Laboratory, Berkeley, CA 94720

Powerful networks and HPC are shortening the delay between data collection and actionable insight. Composed interoperation of digital and experimental capabilities delivers not only faster data analysis but also allows us to ask different questions. Conversely workflow delays lead us to under-leverage the data we collect. This talk discusses modern challenges in integrating experimental methods and computational ones in the context of recent work at LBNL and SLAC. Drawing on case studies from x-ray science, genomic sequencing, and physics we review recent implementations of combined experimental and computational workflows. Cross-cutting these different science agendas are strategies for getting the most science from increasingly large data streams. Advances in detectors suggest we plan future implementations with scale in mind if data analysis is keep pace with data collection.

WK-2

Multi-modal 3D Characterization

Nicola Ferrier
Mathematics and Computer Science Division, Argonne National Laboratory, Argonne, IL 60439

Integrating data analysis (tomographic imaging, x-ray scattering) and molecular dynamics modeling can provide crucial insights into materials, and the processing parameters or methods that yield the desired properties. As an example system, we explored the 3D morphology of solvent annealed P2VP-*b*-PS-*b*-P2VP directed self-assembled films using scanning electron transmission microscopy (STEM) tomography, coarse-grained simulations and CD-SAXS scattering data. The combination of modeling and data analysis helped to understand defect origin. Our integrated approach leads to better understanding of the design and manufacture of nano materials.

WK-2

Photon-limited Data Analysis in Material Structure Identification

Rebecca Willett
University of Wisconsin-Madison, Madison, WI 53706

Accurate and experimentally validated atomic structures are foundational for materials science. They underlie theories of materials properties and performance and provide targets for efforts in materials synthesis. The structure of systems with a large number of positional and chemical degrees of freedom can be extremely difficult to obtain. The burgeoning quantity of experimental data has the potential to transform traditional simulation-based structure inference methods and data analysis methods which exploit low-dimensional models of material structure that can mitigate the challenges of the large number of extrinsic degrees of freedom. However, much of the experimental data available to materials scientists is necessarily photon or shot-noise limited. The inference task is particularly challenging since we often observe a non-trivial projection of the material structure. In this talk, I will describe novel algorithms and accuracy assessments when the underlying material exhibits low-dimensional structure. When the number of observed photons is very small, accurately extracting knowledge from this data requires the development of both new computational methods and novel theoretical analysis frameworks.

WK-2

Data-driven Materials Science Enabling Large-scale Property Prediction and Optimization

Ankit Agrawal
Department of Electrical Engineering and Computer Science,
Northwestern University, Evanston, IL 60208

In this age of “big data,” large-scale experimental and simulation data is increasingly becoming available in all fields of science, and materials science is no exception to it. Our ability to collect and store this data has greatly surpassed our capability to analyze it, underscoring the emergence of the fourth paradigm of science, which is data-driven discovery. The need for data informatics is also emphasized by the Materials Genome Initiative (MGI), further boosting the emerging field of materials informatics. In this talk, I will describe some of our recent works employing state-of-the-art data analytics for exploring processing-structure-property-performance (PSPP) linkages, both in terms of forward models (e.g., predicting property for a given material) and inverse models (e.g., discovering materials that possess a desired property). Such data-driven analytics can significantly accelerate the prediction/optimization process for materials design. With the ongoing research and development in data science and its growing popularity, it is expected to play a major role in the discovery, design, and deployment of next-generation materials.

WK-2

Challenges in Multimodal Data Integration for Neuroscience

Konrad Kording
Northwestern University, Evanston, IL 60208

Modern imaging technologies, not last of which x-ray tomography, promise to produce unprecedented amounts of data about brains. However, the questions we ask still come from the age of small datasets. So the field is often asking the same questions, just using bigger datasets. I will discuss current approaches and limitations. I will also sketch how ongoing research promises to allow us to ask entirely new classes of questions.

Tuesday, May 10

APS Workshop 3
Advances in *in situ* and Serial Biological Crystallography

Location: APCF Auditorium

Organizers: Craig Ogata (APS), David Kissick (APS), and Bob Fischetti (APS)

Recent developments in "*in situ*" crystallography open the possibility to solve structures from an expanding number of challenging biological systems in which material is severely limiting or the crystals are extremely fragile or small. The ability to record diffraction data from crystals in the original growth solution, i.e., *in situ*, will expand the range of problems that can be addressed with synchrotron radiation, especially the bright x-ray beams from the MBA-based 4th generation sources now under development. These new sources are well suited to the most challenging problems in macromolecular crystallography. As the APS user community prepares for APS-U, this is an ideal time to examine progress in methods to deliver sample to the beam, to minimize the effects of radiation damage while collecting data at non-cryogenic temperatures, and to assemble complete multi-crystal data sets.

8:30–8:45	Craig Ogata (Argonne National Laboratory) *Welcome and Introduction*
8:45–9:15	Jana Broeker (University of Toronto) *Development of a New* in situ *LCP Crystallization Format*
9:15–9:45	David Kissick (Argonne National Laboratory) *Development of Tools for* in situ *Data Collection at GM/CA*
9:45–10:15	Elizabeth Baxter (Stanford Synchrotron Radiation Lightsource) *Efficient Data Collection Using Multiple Crystals in High-density Grids*
10:15–10:45	Break
10:45–11:15	Karolina Michalska (Argonne National Laboratory) *Structural Biology Center Developments for* in situ *and* in cellulo *X-ray Data Collection*
11:15–11:45	Marc Allaire (Argonne National Laboratory) *Applications of Acoustic Methods in Macromolecular Crystallography*
11:45–12:15	Garrett Nelson (Arizona State University) *Serial Crystallography of Proteins Delivered by Viscous Media*
12:15–1:30	Lunch
1:30–2:00	Robin Owen (Diamond Light Source) *New Approaches for Microfocus Crystallography at Diamond and Beyond: From Smaller, Hotter Beams to Serial Delivery*
2:00–2:30	James Foadi (Diamond Light Source) *Assembling Data from Multiple Crystals with BLEND*
2:30–3:00	Sarah Perry (University of Massachusetts, Amherst) *Microfluidic Platforms for Time-resolved Serial Protein Crystallography*
3:00–3:30	Break
3:30–4:00	Sean McSweeney (Brookhaven National Laboratory) *New Beamlines at the Low-emittance NSLS-II*
4:00–4:30	Jeney Wierman (Cornell High Energy Synchrotron Source) *Recovering Protein Crystal Orientation from Sparse, "Unindexible" Data Frames*

4:30–5:00 Robert Fischetti (Argonne National Laboratory)
Future Applications at the APS-U

5:00 Adjourn

WK-3

Efficient Data Collection Using Multiple Crystals in High-density Grids

E.L. Baxter[1,2]
[1] Stanford Synchrotron Radiation Lightsource, Menlo Park, CA 94025
[2] Linac Coherent Light Source, SLAC National Accelerator Laboratory, Menlo Park, CA 94025

Higher throughput methods to mount and collect data from multiple small crystals are important to support challenging structural investigations using micro-focus synchrotron beamlines. Furthermore, efficient sample delivery methods are essential to carryout productive femto-second crystallography experiments at x-ray free electron lasers such as the Linac Coherent Light Source (LCLS). During these experiments often only a single still image may be collected from each crystal, and data from hundreds of crystals must be combined to produce a useful dataset. To address these needs, new methods will be described to efficiently deliver crystals on fixed targets including results from recent experiments at LCLS XPP. A high-density sample grid, useful for both *in situ* crystal growth and data collection, contains 75 mounting ports and fits inside a SSRL cassette or uni-puck for automated sample mounting onto the beamline goniometer. Grids may serve as a scaffold for crystal growth, and commercial liquid handling robots have been used to setup *in situ* crystallization experiments in grids. Methods to map multiple crystals in random orientations within grid ports and other high density sample holders for automated positioning for diffraction data collection have been developed. A new sample delivery device that uses a mesh to mount crystals directly from a vial of mother liquor will also be described. Initial experiments demonstrate the efficiency of this device for structure determination using delicate crystals at physiological temperatures.

WK-3

Structural Biology Center Developments for *in situ* and *in cellulo* X-ray Data Collection

Karolina Michalska, Gyorgy Babnigg, Kemin Tan, Changsoo Chang, Boguslaw Nocek, Hui Li, Catherine Hatzos-Skintges, Michael Molitsky, Randy Alkire, Youngchang Kim, and Andrzej Joachimiak
Structural Biology Center, Biosciences Division, Argonne National Laboratory, Argonne, IL 60439

To meet the demands of a growing interest in collecting x-ray diffraction data directly from the crystallization devices, methods for *in situ* and *in cellulo* data collection are being developed at Structural Biology Center at APS. These approaches reduce the amount of protein sample needed for structure determination and/or eliminate a step of crystal harvesting and handling. Specifically, we have developed a prototype of a 96-well plate scanner for *in situ* data collection. The system enables to evaluate crystal quality prior to any handling and to collect a complete data set suitable for anomalous phasing. In the future, the scanner will be integrated into the 19-ID end station and with automated controls will become available for remote access. Simultaneously, we are developing small-volume crystallization microfluidic devices that could be directly mounted on a goniostat. The third approach currently being explored, investigates the possibility of data collection from crystals grown inside the cell. Such method would completely eliminate protein purification step, but routine *in cellulo* diffraction experiment will require enhanced beamline capabilities.

This research has been funded in part by a grant from the National Institutes of Health GM094585, and by the U.S. Department of Energy, Office of Biological and Environmental Research, under Contract DE-AC02-06CH11357.

WK-3

Applications of Acoustic Methods in Macromolecular Crystallography

Marc Allaire
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Macromolecular crystallography (MX) continues to be the premier method to gain access to structural information and the understanding of biological function at a molecular level. It has become obvious that MX would benefit with better approaches in crystal preparations to take full advantage of high flux beam combined with fast detector. To address this challenge, we are exploiting the power of acoustic method to move nano-to-picoliter volume of samples. Applications of acoustic methods in MX cover a broad range of needs from crystallization to our recent development of an acoustic injector for drop-on-demand serial femtosecond crystallography.

WK-3

Serial Crystallography of Proteins Delivered by Viscous Media

Garrett Nelson
Department of Physics, Arizona State University, Tempe, AZ 85287

Within the last decade serial crystallography has become an exciting means of collecting high resolution room temperature diffraction data from protein crystals [1,2]. This "one-shot-per-crystal" technique uses diffraction snap-shots from random crystal orientations, with several thousands of snap-shots required for the 3D reconstruction of target species [3]. The crystal delivery mechanism must therefore place thousands of crystals into the beam at a rate that optimizes data collection efficiency. Highly specialized linear-flow systems have been developed to continuously inject crystals in their native medium across the beam [4-9]. With a tunable linear flow speed ranging from microns to centimeters/sec, the "LCP Injector" has become perhaps the most versatile workhorse injection systems used in serial crystallography [10]. Although initially developed for use in serial femtosecond crystallography at X-FEL sources, this viscous media injector has proven very favorable for serial crystallography at synchrotron sources as well [11]. In a recent series of pilot experiments performed at the GM/CA 23-ID-D beamline at APS, crystals ranging in size from 1 to 10 microns from lysozyme, thaumatin, PSII, phycocyanin, human adenosine A_{2A} receptor (A_{2A}AR) and beta-2 adrenergic receptor (β_2AR) were delivered to the beam in LCP and agarose. Diffraction patterns were collected in shutterless mode at a repetition rate of 10 Hz, photon energy of 12 keV, 10 micron beam size, using a Pilatus3 6M detector. Lysozyme, thaumatin and A_{2A}AR had hit rates of 38.1%, 15.1%, and 4.7%, respectively. Indexing rates ranged from 1.8% to 14%. The Lysozyme structure was solved to 2.5 Å resolution.

This work was supported by NSF STC award 1231306 and NIH award GM097463.

[1] Chapman, H.N., et al. "Femtosecond diffractive imaging with a soft-X-ray free-electron laser." *Nature Physics* **2**(12), 839–843 (2006).

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[7] Beyerlein, K.R., et al. "Ceramic micro-injection molded nozzles for serial femtosecond crystallography sample delivery." *Review of Scientific Instruments* **86**(12), 125104 (2015).

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WK-3

New Approaches for Microfocus Crystallography at Diamond and Beyond: From Smaller, Hotter Beams to Serial Delivery

Robin Owen, Darren Sherrell, and Danny Axford
Diamond Light Source Ltd., Harwell Science and Innovation Campus,
Didcot, Oxfordshire OX11 0DE, UK

Microfocus crystallography has had a considerable impact in recent years, with structure determination from crystals less than 10 microns in size now considered routine. This includes crystals held at room temperature in crystallisation trays. Ongoing developments mean that the beam focus at I24, Diamond Light Source, is now of order 3 × 5 μm^2 meaning that structure solution will become possible from even smaller crystals. With ever-smaller beams however, come new challenges. Routine aspects of the diffraction experiment from crystal mounting to data analysis become difficult, and new approaches are required for sample delivery and data collection.

Free Electron Lasers (FELs) offer an exciting new frontier in structural biology complementing data collected at synchrotron sources. Diffraction data are collected from femtosecond bursts of x-rays allowing the structure of extremely short-lived species to be studied, and changes in protein structure observed as a reaction occurs.

Despite the apparent contrast in experimental approach, many similarities exist between data collection at free electron lasers and microfocus synchrotron beamlines and I will describe the development of instrumentation for reliable delivery of many 1000's of crystals into the x-ray beam at both Diamond and FELs with examples of the data collected and results gained, in addition to changes to the I24 endstation facilitating serial, *in situ* and conventional crystallography of microcrystals.

WK-3

Assembling Data from Multiple Crystals with BLEND

James Foadi and Gwyndaf Evans
Diamond Light Source Ltd., Harwell Science and Innovation Campus, Didcot, Oxfordshire OX11 0DE, UK

In recent times, in macromolecular crystallography, it has become increasingly common at synchrotrons to obtain complete merged datasets using partial data wedges from multiple crystals. There are several reasons for the emergence of this recent trend, all pointing to the fact that completeness and redundancy can be improved when more crystals are used. A specific and particularly important case is represented by crystals not removed from their crystallization plates, the so-called *in situ* data collection. While the life span of fragile or small crystals in their mother liquor is longer compared to the case when they are removed from it and subject to cryo-cooling procedures, the intense beam radiation at room temperature allows only for relatively small wedges of data to be recorded before the crystals degrade. This means that many crystals are required to obtain complete spans of reciprocal space. Accordingly, users face two problems: isomorphism and the large number of possible datasets combinations. Both can be addressed using cluster analysis.

The program BLEND [1], developed at the Diamond Light Source synchrotron and available in CCP4 [2], makes use of cluster analysis and of the POINTLESS [3] and AIMLESS [4] programs to help users assembling useful and complete data from multiple crystals. BLEND acts by default in a semi-automated way, but it is most effective when used interactively in repeated sessions. BLEND has been employed successfully to assemble data for a variety of macromolecules, especially membrane proteins and protein complexes.

After a general introduction to the program's main aspects, this talk will focus on the way complete datasets can be assembled from multiple crystals. Details of a specific example of *in situ* data collection from crystals of a membrane protein [5] will help clarify the workings and potential of the program.

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WK-3

Microfluidic Platforms for Time-resolved Serial Protein Crystallography

Sarah L. Perry
Department of Chemical Engineering, University of Massachusetts Amherst, Amherst, MA 01003

Microfluidic chips for combinatorial analyses such as protein crystallization have advanced tremendously in recent years. These devices take advantage of miniscule sample volumes and parallel processing while creating an environment free of inertial or convective effects. This exquisite control over local conditions and gradients, and the subsequent ability to create highly reproducible microenvironments has proven to be a tremendous asset for improving the consistency and quality of protein crystals grown on-chip. By coupling these benefits with x-ray compatible device architectures, microfluidic technologies are poised to facilitate a wider range of structure-function studies than had previously been accessible. We utilize a microfluidic crystallization platform for serial crystallography, combining small quantities of data collected from a large pool of uniform crystals. This strategy takes advantage of integrated fluid handling and microfluidic geometries to enable the growth of a large number of high quality, isomorphous crystals, while eliminating the need for manual harvesting or manipulation of fragile crystals. We have demonstrated the efficacy of our approach for the *de novo* structure determination of a novel phosphonacetate hydrolase (PhnA) using single wavelength anomalous diffraction, and the time-resolved structural analysis of photoactive yellow protein (PYP) via Laue diffraction. However, our ultimate goal is to couple serial crystallography with the integrated fluid handling capabilities of combinatorial microfluidics to enable the use of chemical triggering (i.e., ligand addition) for time-resolved crystallography experiments. In addition to the fluid handling aspects of such experiments, it is critical that the diffusive timescale associated with the chemical triggering step occur at a faster rate than the biological reaction of interest. This can be achieved through the use of microcrystals, rather than the larger crystals typically associated with protein crystallography. To enable *in situ* time-resolved diffraction analysis of microcrystals, we have developed an ultra-thin microfluidic device architecture by incorporating single-layer graphene to facilitate on-chip x-ray diffraction analysis while creating a sample environment that is stable against significant water loss over several weeks. Building on this idea, it would also be possible to extend these types of studies to multivariable analyses to expand the scope and context of the resultant dynamic structural information.

WK-3

Recovering Protein Crystal Orientation from Sparse, "Unindexible" Data Frames

Jennifer L. Wierman[1,2], Ti-Yen Lan[3], Mark W. Tate[3], Hugh T. Philipp[3], Veit Elser[3], and Sol M. Gruner[2,3]

[1] Field of Biophysics, Cornell University, Ithaca, NY 14853
[2] Cornell High Energy Synchrotron Source (CHESS), Cornell University, Ithaca, NY 14853
[3] Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, NY 14853

In room temperature serial crystallography at storage rings, the number of diffracted x-rays falls with the crystal volume. When too few x-rays are collected per data frame to determine a crystal's orientation, we consider this to be a "sparse" frame. This sets a lower limit to the size of microcrystals that may be indexed with a given source fluence using traditional indexing methods. The EMC algorithm (Loh & Elser, 2009) has previously been applied to reconstruct structure from sparse noncrystalline data of objects with unknown orientations (Philipp et al., 2012; Ayyer et al., 2015). We conducted proof-of-principle experiments to show we can reconstruct the 3-dimensional diffraction intensity of a lysozyme crystal with as few as 200 photons per data frame, without prior knowledge of the orientation of the crystal in any data frame. This suggests that serial microcrystallography is not limited by the fluence of the x-ray source and collection of complete data sets from sparse data frames of microcrystals is feasible at, e.g., storage ring x-ray sources.

WK-3

Future Applications at the APS-U

Robert F. Fischetti

GM/CA and Advanced Photon Source, Argonne National Laboratory, Argonne, IL 60439

Microcrystallography capabilities on third-generation storage-ring based sources have enabled the determination of many important biological problems to atomic resolution. Some of the recent developments that have improved data quality, reduced primary radiation damage at liquid nitrogen temperatures, or improved user friendliness include: user-selectable micro-beams, raster mapping, vector data collection, shutter-less data collection, multiple crystal strategy and SONICC alignment of crystals. The Linac Coherent Light Source, an x-ray free-electron laser or XFEL, has also driven the development of new technologies and enabled "serial crystallography." These new technologies such as viscous jet sample injectors are now being implemented on storage-ring-source beamlines. In the near future, fourth-generation storage-ring sources based on multibend achromatic (MBA) lattices such as the APS-U will increase brightness by at least two orders of magnitude. In this talk, I will present the current state of microcrystallography and the potential game-changing future for structural biology enabled by the APS-MBA source, including pink beam, single crystal, single-bunch serial crystallography.

Tuesday, May 10

CNM Workshop 4

Frontiers in Superconducting Electronics: From Quantum Computing to Photon Detectors

Location: Bldg. 401, Room A5000

Organizers: Goran Karapetrov (Drexel, Argonne MSD) and Valentine Novosad (Argonne MSD)

Recently, the superconducting materials have enabled breakthroughs in such important areas as quantum computing and photon detectors. It is now clear that these advances will have direct impact on many areas of science as well as on the society. DOE user facilities and national laboratories play a crucial role both as enablers of this new superconducting technologies and as demanding end users of the product of this research.

Quantum computing could soon become a very serious player in supercomputing applications, especially in cases where fast solutions are sought for complex non-parallelizable tasks. Current superconducting electronics has large advantage over CMOS in speed and an even larger advantage in low power consumption, but few issues remain to be solved in order to make the quantum computing widely available to computer scientist. This part of the symposium will focus on the recent advances and remaining challenges in superconducting electronics for quantum computation and the role that national laboratories could play more active role as enabler and end user of the quantum computing technology.

Superconducting detectors span an unprecedented range of energies, from x-rays to terahertz and offer unsurpassed performance - high sensitivity, high energy resolution, high time resolution, and high speed. The application of superconducting detectors in everyday research encompasses wide range of disciplines from astrophysics, particle physics, synchrotron radiation studies through materials science and biophysics. In this symposium we want to spotlight the recent advances enabled by the breakthroughs in superconductor detector technology and project the immediate challenges for the next decade.

8:30–8:45	Goran Karapetrov (Drexel University) *Introductory Remarks*
8:45–9:25	Christopher Lobb (University of Maryland) *Superconducting Qubits: Disruptive Environments Challenge Disruptive Technology*
9:25–10:05	Sarah Sheldon (IBM T.J. Watson Research Center) *Challenges in Control of Superconducting Qubits for Universal Quantum Computing*
10:05–10:35	Break
10:35–11:15	Marc Manheimer (IARPA, Intelligence Advanced Research Projects Activity) *Progress in Superconducting Computing*
11:15–12:00	John Sadleir (NASA) *Understanding and Controlling the Superconducting Phase Transition in TES Microcalorimeters and Bolometers*
12:00–1:30	Lunch
1:30–2:10	Clarence Chang (Argonne National Laboratory-University of Chicago) *Superconducting Detectors and Studies of the Cosmic Microwave Background*
2:10–2:50	Raul Hennings (University of California, Berkeley) *Development of Low-Tc Transition Edge Sensors for Neutrino-less Double Beta Decay*
2:50–3:20	Break
3:20–4:00	Eric Shirokoff (University of Chicago) *Antenna-coupled Kinetic Inductance Detectors for mm-Wave Astronomy*
4:00–4:40	Thomas Cecil (Argonne National Laboratory) *Superconducting X-ray Detectors for Photon Science*

4:40–5:00	Closing Remarks
5:00	Adjourn

WK-4

Superconducting Qubits: Disruptive Environments Challenge Disruptive Technology

C.J. Lobb
Joint Quantum Institute and Center for Nanophysics and Advanced Materials, University of Maryland, College Park, MD 20742

In the past seventeen years, coherent state control in superconducting qubits has gone from laboratory *tour de force* to potential commercial technology. Progress has been made by balancing potentially conflicting requirements. The first requirement is the need to control and measure qubits through interaction with external signals and other qubits. The second requirement is to isolate against the fluctuations which cause decoherence. The conflict is that real devices are made from materials containing defects, and real measurement necessarily require some coupling to an electromagnetic environment; the material defects and electromagnetic environments cause decoherence. This talk will (hopefully) provide background for non-specialists to understand why these problems arise and how they are being dealt with.

WK-4

Challenges in Control of Superconducting Qubits for Universal Quantum Computing

Sarah Sheldon
IBM T.J. Watson Research Center, Yorktown Heights, NY 10598

Universal fault tolerant quantum computing requires error correction, which relies on the ability to extract information about the error. Stabilizer codes are an attractive solution to this problem in which the parity of the data qubits is measured with the aid of additional ancilla qubits. IBM is pursuing a quantum computing architecture built around using a particular stabilizer code known as the surface code for error correction. The surface code has relatively high error thresholds and requires connectivity only between nearest neighbor qubits on a lattice. After an overview of the quantum computing effort at IBM, this talk will focus on the current schemes for calibrating and characterizing one- and two-qubit gate operations on fixed-frequency transmon superconducting qubits. Current control techniques have allowed us to achieve gate fideilities better than 99.9% for single-qubit gates and 99% for two-qubit gates. Improved characterization schemes are now required for understanding the sources of both coherent and incoherent errors in the system, so we can further increase gate fideilites above the necessary thresholds.

WK-4

Progress in Superconducting Computing

Marc Manheimer
Intelligence Advanced Research Projects Activity (IARPA),
McLean, VA 22101

Since the 1950s, there have been several efforts to develop a computer based on superconducting logic. Each was abandoned due to technical limitations and to overwhelming competition from the semiconductor industry. The end of Moore's Law related improvements for CMOS coupled with the requirement to develop computers at the exascale has motivated the search for viable post-Moore technologies, suggesting another look at superconducting technology. This talk will discuss the IARPA Cryogenic Computing Technology program to develop a prototype superconducting computer and related developments around the world.

WK-4

Superconducting Detectors and Studies of the Cosmic Microwave Background

Clarence Chang
Argonne National Laboratory, Argonne, IL 60439
The University of Chicago, Chicago, IL 60637

Over the past decade, superconducting detectors have been instrumental in advancing the field of Cosmic Microwave Background (CMB) measurement. Measurements of the Cosmic Microwave Background and its polarization provide a unique window for studying cosmological neutrinos, Dark Energy and the physics of inflation. In this talk, I will discuss how superconducting photon detectors have led to breakthroughs in CMB measurements. I will also discuss their ongoing role in shaping the field of CMB experiments with particular attention on the enabling role of CNM in the SPT-3G and future CMB-S4 experiments.

WK-4

Development of Low-Tc Transition Edge Sensors for Neutrino-less Double Beta Decay

R. Hennings-Yeomans[6,1], J. Beeman[2], C.L. Chang[3,7], J. Ding[4], A. Drobizhev[6,1], B. Fujikawa[1], K. Han[6,8], S. Han[6], G. Karapetrov[9], Y. Kolomensky[6,1], V. Novosad[4], T. O'Donnell[6,1], J. Ouellet[6,10], J. Pearson[4], B. Sheff[6], V. Singh[6], S. Wagaarachchi[6,1], J. Wallig[5], G. Wang[3], and V.G. Yefremenko[3]

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Discovering the existence of the Neutrinoless Double Beta Decay (NLDBD) would imply that neutrinos are Majorana particles and that lepton number is not a conserved quantity in nature. The rate of this process is sensitive to the effective neutrino mass scale. Low critical temperature (Tc) Transition Edge Sensors (TES) maximize energy and time resolution, two key requirements that determine the sensitivity of the next-generation bolometric NLDBD experiments. We have developed Iridium-based bilayers that have a low Tc while keeping practical fabrication methods making large arrays possible. We will be presenting characterization of low-Tc Ir/Pt and Ir/Au bilayers as a function of Iridium deposition temperature and normal metal thickness in the context of a light detector fabrication R&D for CUPID (CUORE Upgrade with Particle Identification).

WK-4

Antenna-coupled Kinetic Inductance Detectors for mm-Wave Astronomy

Erik Shirokoff[1], Faustin Carter[2], Trupti Khaire[2], Ryan Mcgeehan[1], Valentine Novosad[2], Wei Quan[1], Ritoban Basu Thakur[1], and the SuperSpec Collaboration

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After decades of development, kinetic inductance detectors (KIDs) are today able to achieve the performance required for deployment in competitive scientific instruments. These devices offer robust, low-cost fabrication, natural multiplexing that allows thousands of detectors to be read out on a single microwave line, large dynamic range, and requires only off-the-shelf readout electronics. I'll discuss several ongoing projects that employ these detectors and related technologies, both for sub-mm-wavelength astronomy and for measurements of the cosmic microwave background, and the future prospects for large-scale focal planes and facility instruments based on this technology.

WK-4

Superconducting X-ray Detectors for Photon Science

Thomas Cecil

X-ray Science Division, Advanced Photon Source, Argonne National Laboratory, Argonne, IL 60439

Superconducting micro-calorimeters offer among the highest resolving power of any solid-state x-ray detector. With recent technological advances, these detectors are becoming increasingly attractive at synchrotron light sources for science applications such as fluorescence microscopy. In this talk I will discuss efforts within the XSD detector group to develop superconducting micro-calorimeters for use at modern light sources. The presentation will highlight several applications that could benefit from the capabilities these detectors offer. I will give an overview of the basic operation of these detectors along with requirements for use at a synchrotron facility. Additionally, I will address areas of potential collaboration between the numerous fields working with superconducting electronics.

Tuesday, May 10

APS Workshop 5
Overview of APS-U Beamline Proposals

Location: Bldg. 402, Lecture Hall

Organizer: Dean Haeffner (APS-U Project)

The APS-U Project beamline selection process is a multistage process, with the first step being the submission of a white paper. This full day workshop will consist of a series of short presentations by the proposers of white papers that have been selected to move to the full proposal stage. Time will be reserved after each presentation for discussion by audience members with proposers and information gathered in this discussion will feed back to APS/APS-U Project management for the final beamline scope determination.

8:30–8:45	Dean Haeffner (APS-U) *Introductory Remarks*
8:45–9:10	Stefan Vogt (Argonne National Laboratory) *PtychoProbe*
9:10–9:35	Jorg Maser (Argonne National Laboratory) In situ *Nanoprobe Beamline*
9:35–10:00	Ross Harder (Argonne National Laboratory) *Atomic—A Beamline for Extremely High-resolution Coherent Imaging of Atomistic Structures*
10:00–10:20	Break
10:20–10:45	Alec Sandy (Argonne National Laboratory) *Wide-angle X-ray Photon Correlation Spectroscopy and Time-resolved Coherent X-ray Scattering Beamline*
10:45–11:10	Suresh Narayanan (Argonne National Laboratory) *Small-angle X-ray Photon Correlation Spectroscopy Beamline for Studying Dynamics in Soft Matter*
11:10–11:35	Jin Wang (Argonne National Laboratory) *Coherent Surface Scattering Imaging (CSSI) Beamline for Unraveling Mesoscopic Spatial-temporal Correlations*
11:35–12:00	Brian Stephenson (Argonne National Laboratory) *Coherent High-energy X-ray Sector for* in situ *Science (CHEX)*
12:00–1:30	Lunch
1:30–1:55	Sarvjit Shastri (Argonne National Laboratory) *A High-energy X-ray Microscope*
1:55–2:20	Jon Tischler (Argonne National Laboratory) *3D Micro-and Nano-diffraction*
2:20–2:45	Karena Chapman (Argonne National Laboratory) *Structural Sciences Beamline Suite: Pushing the Boundaries of Atomic Structure Analysis Across Multiple Time and Length Scales*
2:45–3:10	Xiaoyi Zhang (Argonne National Laboratory) *Dynamic Multiscale X-ray Microscopies: Scattering and Spectroscopy*
3:10–3:35	Break

3:35–4:00	Kamel Fezzaa (Argonne National Laboratory) *Multidimensional Full-field Real-time Imaging Facility*
4:00–4:25	Daniel Haskel (Argonne National Laboratory) *Polarization Modulation Spectroscopy—Electronic Matter: Inhomogeneity, Tunability, and Discovery at Extreme Conditions*
4:25–4:50	Zahir Islam (Argonne National Laboratory) *High Magnetic Field Facility*
4:50–5:00	Wrap-up
5:00	Adjourn

WK-5

PtychoProbe

Stefan Vogt
Argonne National Laboratory, Argonne, IL 60439

The goal of the PtychoProbe (Ptychography + Nanoprobe) beamline is to realize the highest possible spatial resolution x-ray microscopy both for structural and chemical information. The unprecedented brightness of the APS MBA lattice will be exploited to produce a nm-beam of focused hard x-rays to achieve the highest possible sensitivity to trace elements, and ptychography will be used to further improve the spatial resolution for structural components to its ultimate limit. The proposed beamline will enable high-resolution two- and three-dimensional imaging of thick objects and bridge the resolution gap between contemporary x-ray and electron microscopy. Pushing x-ray microscopy into the nanoscale is crucial for understanding complex hierarchical systems on length scales from atomic up to meso and macroscales, and time scales down to the microsecond level, and is applicable to scientific questions ranging from biology to earth and environmental materials science, to electrochemistry, catalysis and corrosion, and beyond.

WK-5

In situ Nanoprobe Beamline

Jörg Maser
Argonne National Laboratory, Argonne, IL 60439

The *in situ* Nanoprobe (ISN) will utilize the massive increase in coherent flux in the hard x-ray range enabled by the APS MBA Upgrade to provide transformative imaging and spectroscopy capabilities for *in situ* studies of complex hierarchical systems in varying environments, at very high spatial resolution, and with close to atomic sensitivity. This will enable entirely new microscopic studies of materials as diverse as batteries, catalysts, photovoltaic systems, nanoelectronics, earth and environmental systems, under a broad range of conditions, such as during synthesis and during operation. These systems have in common, heterogeneity at length scales from nanometers to macroscopic scales, complex compositional, chemical and structural features and functional units and sites, and high sensitivity to often multiple external environments such as temperature, gaseous environment, acidity and fields. The ISN will focus the coherent flux provided by the MBA lattice into a focal spot of 20 nm, enabling rapid, multidimensional imaging across many length scales, and combining x-ray fluorescence imaging and spectroscopy with coherent methods to achieve sub-10 nm spatial resolution and close to atomic sensitivity. The combination of brilliance increase and instrument design enables an increase in focused flux by 3 to more than 5 orders of magnitude compared to current nanofocusing capabilities, enabling very fast data acquisition across many length scales, and fast imaging of responses to changes in environmental parameters. Coupled with broad *in situ* capabilities, this enables qualitatively new understanding of functional materials and systems, and contributes to inspiring and conceiving new materials, materials systems and approaches required to address some of the current and future challenges in energy and sustainability.

WK-5

Atomic—A Beamline for Extremely High-resolution Coherent Imaging of Atomistic Structures

Ross Harder
Argonne National Laboratory, Argonne, IL 60439

In recent years coherent imaging has begun to reach down to length scales where atomic phenomena are ultimately responsible for the structural characteristics being seen. In fact, the very strength of Bragg coherent imaging is in its sensitivity to distortions of the crystalline lattice, which is inherently an atomistic feature. Here we intend to exploit the tremendous increase in coherent flux of the Advanced Photon Source Upgrade to push coherent imaging toward atomic resolution in both crystalline and amorphous materials. The instrumentation will also enable ultrahigh-resolution imaging of evolving structures both *in situ* and *operando*.

With a technical focus on extremely high resolution imaging of *operando* samples and structural evolution, the scientific fields impacted most will be energy transport and storage materials, structural materials, advanced electronics and magnetic material, and materials involved in catalytic and photocatalytic processes.

WK-5

Wide-angle X-ray Photon Correlation Spectroscopy and Time-resolved Coherent X-ray Scattering Beamline

Alec Sandy
Argonne National Laboratory, Argonne, IL 60439

X-ray photon correlation spectroscopy (XPCS) characterizes fluctuations in condensed matter at a combination of mesoscale length scales and timescales not otherwise accessible. Signal strengths depend on the x-ray beam coherence and minimum accessible time scales scale inversely with the square of the source brilliance so XPCS will benefit tremendously from APS-U. We propose to build a new beamline specialized in wide-angle (WA) XPCS. It will advance studies in a host of key areas in physics and materials science and engineering that include dynamic heterogeneity, structural dynamics in super-cooled liquids and fluctuations associated with competing mesoscale interactions in emergent materials. Features of the beamline include uniquely high time-averaged coherent flux, access to time delays as short as ~100 ns, access to higher coherent flux at energies up to ~20 keV for penetration into diverse samples and environments and extinction-free horizontal diffraction for increased set-up stability and flexibility.

WK-5

Small-angle X-ray Photon Correlation Spectroscopy Beamline for Studying Dynamics in Soft Matter

Suresh Narayanan
Argonne National Laboratory, Argonne, IL 60439

This white paper proposes an “in-place upgrade” of the X-ray Photon Correlation Spectroscopy (XPCS) beamline at 8-ID operating in the small-angle regime. The hallmark of APS-U is the dramatic increase in coherent flux, which will revolutionize XPCS, for example expanding its dynamic range by up to 6 orders of magnitude. The proposed beamline will be world leading in probing fluctuation dynamics in materials, over unprecedented length scales of 5 µm–1 nm and time scales of 10 nanoseconds–1000 seconds. As the science case below illustrates, this spatiotemporal range aligns well with key problems in soft matter. In addition, leveraging the APS-U, the beamline will have capabilities for sample environments, such as *in situ* rheometry, nanofluidic flow, and high pressure to access dynamics under conditions that are difficult or impossible to achieve today. The research enabled by the beamline will significantly impact key problems in soft matter and advance their potential applications in technologies across an array of sectors, from energy and transportation to health, agriculture, and national defense.

WK-5

Coherent Surface Scattering Imaging (CSSI) Beamline for Unraveling Mesoscopic Spatial-temporal Correlations

Jin Wang
Argonne National Laboratory, Argonne, IL 60439

At the center stage of scientific field of functional materials surface/interface phenomena are of great interest to scientists in a variety of fields ranging from energy production/storage to self-assembled hierarchical mesoscaled structures. The challenging topics include but not limited to evolution of biological membranes and supramolecules in aqueous environment, thin film and quantum dot growth at surfaces and interfaces, assembly of planner polymer nanocomposites, and structural analysis of three-dimensional (3D) nanoscaled additive manufacturing. Much progress has been made in the development of hard x-ray sources and tools such as storage-ring sources and x-ray free-electron-laser sources. Among all, grazing-incidence x-ray scattering and x-ray photon correlation spectroscopy exhibit unique advantages for exploring the surface/interface problems that are challenging to solve using other imaging and dynamics probes. A brightness increase of 100 to 1000 times has been proposed and such a high-brightness and high-coherence source is the cornerstone of the APS Upgrade (APS-U). The APS-U beams possess a large coherent fraction, well suited for measuring the spatiotemporal evolution of structures in complex systems with the highest precision, taking the full advantage. Coherent x-ray based surface imaging techniques provide ideal tools to directly observe surface/interface structures and their dynamics responding to external conditions. A new beamline for Coherent Surface Scattering Imaging, taking advantage of the drastically improved x-ray beam coherence, is proposed, for probing and understanding mesoscopic spatial-temporal correlations by integrating the coherence-based surface x-ray probe with state-of-the-art coherence-preserving optics, and advanced x-ray detectors.

WK-5

Coherent High-energy X-ray Sector for *in situ* Science (CHEX)

Brian Stephenson
Argonne National Laboratory, Argonne, IL 60439

The Coherent High Energy X-ray Sector for *in situ* Science will advance the frontier for *in situ*, real time studies of materials synthesis and chemical transformations in natural operating environments using the unprecedented coherence of the high-energy x-ray beams provided by the APS Upgrade. Coherent diffractive imaging and photon correlation spectroscopy will provide transformative insight into materials structure, its heterogeneity and disorder, chemical and long-range interactions, dynamics, and evolution under real-world conditions and time frames.

Beamlines will be optimized for coherent x-ray techniques at the high energies (15–60 keV) needed for *in situ* studies. Multiplexed, simultaneously operating beamlines will efficiently accommodate large, complex apparatus and amplify the beam time available for programs to address high-impact problems.

WK-5

A High-energy X-ray Microscope

Sarvjit Shastri
Argonne National Laboratory, Argonne, IL 60439

We propose construction of a high-energy x-ray microscope (HEXM) on a long beamline, which will provide unprecedented capabilities to investigate structure and its evolution within bulk materials. Current high-energy x-ray techniques will be refined, and combined with MBA-enabled coherence techniques, to provide multi-modal imaging spanning millimeters to angstroms in single experiments. HEXM requires the source characteristics unique to the MBA-upgraded APS: increased coherence and brilliance at high energies (35–120 keV) in order to provide non-destructive measurements at the highest spatial and temporal resolutions. New capabilities will benefit a wide suite of materials classes. An end-station external to the APS building will enhance the ability to study extreme material states, including *in situ* ion-irradiation and additive manufacturing. The coupling of this multi-scale information with modeling efforts promises to revolutionize our ability to accelerate material development.

WK-5

3D Micro- and Nano-diffraction

Jonathan Tischler
Argonne National Laboratory, Argonne, IL 60439

The 3D Micro- and Nano-diffraction beamline is designed to directly attack a wide range of spatially inhomogeneous materials problems at the mesoscopic length scale. These are problems in materials science, physics, geoscience, and most other fields of science where previous x-ray diffraction techniques are insufficient due to the short length scale of the inhomogeneities in the materials. This inhomogeneity is an important or intrinsic part of the material's properties, and so must be studied on its length scale; large perfect samples are either impossible to make or do not represent the real material. Due to the current extreme difficulty or impossibility of making these measurement we propose to use the bright MBA source to provide small intense x-ray spots (50–200 nm) to investigate the important spatial variations of strain and structure that define this wide range of scientifically and technologically important materials.

WK-5

Structural Sciences Beamline Suite: Pushing the Boundaries of Atomic Structure Analysis across Multiple Time and Length Scales

Karena Chapman
Argonne National Laboratory, Argonne, IL 60439

We propose an optimized suite of instruments that, together, meet the expanding needs of the Structural Sciences community for atomic-scale structural insights to answer challenging questions relevant to diverse scientific and technological areas. These instruments probe the atomic structure of a variety of sample forms using reciprocal-space and real-space methods, spanning pair distribution function, single crystal diffuse scattering, diffraction tomography, ultrafast scattering, and powder diffraction. The proposed implementation of these methods within the suite addresses the need for high-resolution measurements, extended-duration measurements, *in situ/operando* measurements, anomalous measurements and fast-time resolved measurements. The hard and high-energy x-rays that are a strength of the APS and APS-U are exploited by all instruments. This suite recognizes the growing need for more than one tool to completely characterize complex materials architectures, while balancing the need for access to different measurement modalities. To realize this beamline suite, new instruments will be constructed, and existing beamlines/instruments will undergo major upgrades to enhance current capabilities. By assembling a suite of distinct instruments with complementary capabilities we create a highly capable village to address the most complex characterization problems and the most important scientific questions, while avoiding the compromises and inefficiencies that often afflict general or multi-purpose instruments.

WK-5

Dynamic Multiscale X-ray Microscopies: Scattering and Spectroscopy

Xiaoyi Zhang
Argonne National Laboratory, Argonne, IL 60439

The extraordinarily high brightness per bunch of the APS-U offers singular opportunities for exploring complex, heterogeneous samples with unprecedented flexibility across multiple length and time scales. We propose a canted beamline which will provide critical insight into emergent problems in condensed matter physics, materials science, atomic and molecular physics, and chemical dynamics. One branch of the beamline will focus on dynamics of condensed-matter physics probed with high-coherence scattering experiments. The physics of condensed-matter systems are largely determined by the dynamic interactions of separated phases; domains with distinct structural, magnetic, and electronic properties; and defects within ordered states. By combining ptychography and full-field x-ray diffraction microscopy, we will capture the evolution of such features with 10 nm and 100 ps spatiotemporal resolution. The other branch will focus on electronic and structural dynamics underlying energy converting/conserving processes in chemistry and material sciences using *in situ/operando* high-flux x-ray spectroscopy in conjunction with small-angle scattering and pair-distribution function. This branch is directed to provide first-of-a-kind opportunities to investigate the important transient states with measurements of the full scale of inner- and outer-sphere atomic reorganization in a broad range of scientific disciplines, including solar energy conversion, catalysis, fuel cells, and electrochemical (battery) energy storage.

WK-5

Multidimensional Full-field Real-time Imaging Facility

Kamel Fezzaa, Tao Sun, Xianghui Xiao, Alan Kastengren, and Francesco De Carlo
X-ray Science Division, Argonne National laboratory. Argonne, IL 60439

Full-field imaging is an extremely versatile technique that is broadly applicable to almost all scientific and engineering disciplines. Its versatility is reflected by the fact that every major synchrotron facility in the world has a dedicated full-field imaging facility. In many cases, full-field imaging is the keystone linking a sample to other x-ray techniques such as ptychography, µXRF, µXANES, and µXRD.

The current APS source characteristics prevent the hierarchical characterization of dynamic systems and materials with spatial resolution below 1 µm, without a major sacrifice in time resolution.

Another existing limitation is the large difference in spatio-temporal resolution between full-field and scanning probe techniques, in practice preventing the integration of different modalities around full-field imaging for dynamic systems.

The new APS-U source, besides increasing sensitivity and resolution for parallel beam full-field imaging, will also enable a Kirkpatrick-Baez (KB) based Cone Beam projection x-ray Imaging (CBI) system to become the ideal choice for hierarchical characterization of dynamic systems at 50–1000 nm. The upgrade will thus bridge the existing resolution gap while preserving the single pulse (80 ps) time resolution that currently only parallel white beam imaging can afford.

The proposed new beamline will provide a unique multimodal characterization platform (imaging, diffraction, scattering and spectroscopy) all spanning a large range of spatial and temporal resolutions.

WK-5

Polarization Modulation Spectroscopy—Electronic Matter: Inhomogeneity, Tunability, and Discovery at Extreme Conditions

Daniel Haskel
Argonne National Laboratory, Argonne, IL 60439

Electronic inhomogeneity is a hallmark of correlated electron systems with competing interactions. These inhomogeneous quantum states underlie some of the most exciting phenomena of current interest in condensed matter physics including nematic charge/spin stripe order as a possible mediator of high Tc superconductivity in copper-oxide “cuprates,” and spin liquids where bond directional anisotropy or geometrical frustration leads to complex magnetic textures. We leverage two key properties of APS-U, namely, brilliant x-ray beams and round insertion device vacuum chambers to study mesoscale electronic/magnetic inhomogeneity in condensed matter physics and to tune/control these states with extreme high-pressures (Mbar range). A novel scheme for fast polarization switching (both linear and circular) using dual superconducting undulators coupled with ~100 nm beams results in x500 polarized flux gains and enables x-ray probes of electronic matter at extreme conditions to enter a new era of search and discovery.

WK-5

High Magnetic Field Facility

Zahir Islam
Argonne National Laboratory, Argonne, IL 60439

We propose a world-class beamline for x-ray scattering studies of novel states of electronic matter under an applied DC magnetic field reaching 25 T. The use of high-resolution diffraction, resonant scattering, and enhanced capabilities of coherent techniques due to the MBA upgrade, on materials subject to high DC fields will vastly expand our knowledge of many problems in contemporary condensed matter physics. Although they are limited in scope due to short dwell time in high field, we have glimpsed of such discoveries in some favorable systems using recent pulsed-magnet x-ray experiments, which demonstrated the symmetry-breaking role of nematic order in pnictides, shed light on the magneto-elastics of a spin liquid, and revealed charge-density waves in a high-temperature superconductor. These pioneering studies only expose the tip of new physics, but to properly study it, a DC magnet is required. With its year-round availability this facility, long recommended by National Research Council, is essential to BES Grand Challenge Sciences, including superconductivity and extreme conditions.

Tuesday, May 10

APS Workshop 6
Illuminating Current and Future Geochemistry and Geomicrobiology Research at APS

Location: Bldg. 401, Room A1100

Organizers: Sang Soo Lee (Argonne National Laboratory) and Joanne Stubbs (GSECARS, University of Chicago)

Studies of molecular-scale phenomena are essential to truly mechanistic understanding of geochemical and geomicrobiological processes occurring in natural environments.

Synchrotron-based x-ray scattering and spectroscopic techniques have expanded our knowledge by enabling visualization and quantification of both structural and physicochemical properties of the reactants and products during these processes. Our capabilities will be vastly enhanced upon the emergence of new x-ray sources with higher brilliance that will be brought by the APS Upgrade. This workshop will focus on novel experimental results from molecular-scale geochemical and microbiological processes, highlight advances in experimental synchrotron techniques for these studies, and discuss new opportunities that the APS Upgrade can bring to the geochemical community in the future.

8:55–9:00	Introductory Remarks
9:00–9:30	Bhoopesh Mishra (College of Science, Illinois Institute of Technology) *Biogeochemical Controls on Contaminant and Nutrient Cycling*
9:30–10:00	David A. Fike (Washington University in St. Louis) *Mapping the Spatial Distribution and Chemical Speciation of Sulfur Phases in Sedimentary Carbonates*
10:00–10:30	Evert Elzinga (Rutgers University) *Using XAFS Spectroscopy to Examine the Geochemistry of Fe(II) in Riparian Soils*
10:30–10:45	Break
10:45–11:15	Anastasia G. Ilgen (Sandia National Laboratory) *Reactivity of Fe(III) in the Octahedral Sheet of Natural and Synthetic Fe Phyllosilicates*
11:15–11:45	Jeffrey G. Catalano (Washington University in St. Louis) *Surface X-ray Scattering Studies of Ion Adsorption, Redox Reactions, and Water Structure at Mineral-fluid Interfaces: Recent Observations and New Possibilities with the APS Upgrade*
11:45–12:15	F. Marc Michel (Department of Geosciences, Virginia Tech) *Real-time Scattering Studies of Mineral Growth by Nanoparticle Aggregation*
12:15–12:20	Concluding Remarks
12:20	Adjourn

WK-6

Biogeochemical Controls on Contaminant and Nutrient Cycling

Bhoopesh Mishra[1,2]

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Bulk x-ray spectroscopy is a powerful tool for understanding oxidation state, speciation and coordination environment of elements under probe. X-ray microscopy, on the other hand, provides unparalleled information regarding the distribution and localization of the key species driving the reaction dynamics. Integration of the two results in what is often called x-ray spectromicroscopy, which embodies the strengths of both x-ray spectroscopy and microscopy techniques. Similarly, x-ray Raman embodies the advantages of hard x-rays for obtaining information in soft-x-ray regime.

Taking advantage of some of these recent developments at APS, our research combines x-ray microscopy, x-ray spectroscopy, and x-ray scattering techniques to understand the mechanisms of coupled (biological and inorganic) reaction pathways, and their reaction kinetics in order to integrate molecular constraints with modeling efforts. Lack of molecular-level insight hinders the development of accurate reaction networks in models, which in turn limits the predictive ability of the global elemental cycles.

Using mercury (Hg) and carbon (C) as examples of contaminant and nutrient, this presentation aims to demonstrate that an in-depth understanding of molecular-scale processes affecting elemental speciation is a critical research need for modeling the global cycling of elements in order to advance fundamental understanding of coupled reaction processes in complex natural environments and enable system-level environmental prediction and decision support.

WK-6

Mapping the Spatial Distribution and Chemical Speciation of Sulfur Phases in Sedimentary Carbonates

David A. Fike[1], Catherine V. Rose[2], Jocelyn Richardson[1], Jeffrey G. Catalano[1], Matthew Newville[3], Antonio Lanzirotti[3], and Samuel Webb[4]

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The sulfur biogeochemical cycle integrates the metabolic activity of multiple microbial pathways along with abiotic reactions and geological processes that cycle sulfur through various reservoirs. Over geological timescales, cycling of sulfur is closely tied to the redox state of Earth's surface through the burial of oxidized (sulfate) and reduced (sulfide) sulfur species in marine sediments and is coupled to the global carbon cycle and climate through the remineralization of organic carbon. The stable isotopic measurements ($\delta^{34}S$) of sulfate and sulfide phases preserved in sedimenatary carbonates document secular changes in the sulfur cycle and help shape our understanding of the redox evolution of Earth's surface over geologic time. However, as traditional bulk-rock proxies, these $\delta^{34}S$ signals can consist of multiple origins of sulfate and sulfide within carbonate minerals. Deciphering these phases is critical in order to extract meaningful information about the depositional and diagenetic environment in which the samples formed.

Here, we use x-ray spectromicroscopy to map the distribution of primary and secondary S-bearing sedimentary phases at the micron-scale in a well-characterized suite of Ordovician-aged (~444 million years ago) carbonate strata from Anticosti Island, Quebec. The high-resolution maps of sulfate variability show major differences between clasts and various stages of calcite cement, as well as subtle variation in sulfate concentrations between fossils of different biological affinities. Further, we can distinguish the sulfate content of different stages of calcite cement, helping to constrain the diagenetic history and relate specific cements with the chemistry of the waters from which they formed. In conjunction with secondary ion mass spectrometry (SIMS) $\delta^{34}S$ measurements, this new analytical approach can distinguish isotopic signatures between primary and diagenetic phases, enhancing our ability to interpret $\delta^{34}S$ isotopic signatures and reconstruct biogeochemical sulfur cycling over Earth history.

WK-6

Using XAFS Spectroscopy to Examine the Geochemistry of Fe(II) in Riparian Soils

Evert Elzinga

Department of Earth and Environmental Sciences, Rutgers University, Newark, NJ 07102

The work discussed here addresses the complex question of Fe(II) geochemistry in riparian areas, the dynamic transition zones between aquatic and terrestrial ecosystems. These areas undergo cycles of reduction and oxidation that induce major changes in the solubility and speciation of both major and trace elements. A key element is iron, which is present predominantly as insoluble Fe(III)-oxides under oxic conditions, but undergoes reductive dissolution to aqueous Fe(II) under anoxic conditions. The fate of dissolved Fe(II) in the reducing environments is not particularly well understood, which is at least in part due to the fact that experimental work with Fe(II) is challenging due to its high sensitivity to oxidation. In our recent studies, we have used EXAFS spectroscopy in conjunction with wet-chemical laboratory studies to determine how common soil minerals may influence the fate of dissolved Fe(II) through sorptive interactions. This work has demonstrated the importance of Fe(II) precipitation as a potentially major pathway of Fe(II) retention in riparian soils. We observe rapid and extensive precipitation of layered Fe(II)-hydroxides during Fe(II) sorption onto common soil minerals (Al-oxides and clays) under conditions typical of submerged soils. These secondary Fe(II) minerals control Fe(II) solubility and are highly reactive towards trace metals in our laboratory experiments, indicating that they likely play a major role in the biogeochemical cycling of Fe and trace metals in reducing environments. This talk will discuss recent work addressing the geochemical controls on these precipitation reaction and the resulting Fe(II) mineral products, and future studies intended to extrapolate these recent laboratory findings to natural riparian systems. The critical role of synchrotron work in these studies will be highlighted.

WK-6

Reactivity of Fe(III) in the Octahedral Sheet of Natural and Synthetic Fe-phyllosilicates

Anastasia Ilgen
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The mobility and bioavailability of redox sensitive nutrients and contaminants are controlled by the heterogeneous redox reactions in soils and aquatic systems. Clay minerals are abundant, and contain iron from trace amounts to up to 30 wt.%. This pool of iron residing in clay mineral structure is reactive and can catalyze or directly participate in electron transfer reactions. The estimated redox potential for the Fe(II)/Fe(III) couple in smectite clay mineral nontronite is 0.710 V, while the standard redox potential of the As(III)/As(V) couple is 0.56 V, therefore, nontronite is expected to oxidize As(III) to As(V); however, the oxidation is not observed under ambient conditions.

In our previous work we have demonstrated that converting a minor portion of Fe(III) to Fe(II) in the octahedral sheet of Fe-rich clay mineral (nontronite) effectively activates its surface, making it redox-active, as evidenced by the oxidation of As(III) to As(V) under both oxic (catalytic pathway) and anoxic (direct oxidation) conditions. We proposed that the octahedral corner-sharing Fe(III)-Fe(II)-Fe(III) in the octahedral sheet of nontronite is the reactive moiety. We observed analogous activation of the synthetic phyllosilicate (SIP), synthesized and characterized in our laboratory. This synthetic substrate becomes redox-active following partial reduction treatment, and similarly to natural nontronite—oxidizes As(III) to As(V) under both oxic and anoxic conditions. For both substrates, the degree of As(III) oxidation is higher under oxic conditions, indicating that only a limited number of the reactive moieties on the phyllosilicate surface is accessible for the As(III) oxidation reaction. To validate whether this synthetic iron-phyllosilicate is an appropriate analog for natural nontronite, we compared the solid phase speciation of arsenic (adsorbed), as well as iron (resides in the mineral structure) in these two substrates using X-ray Absorption Spectroscopy (XAS).

This material is based upon work supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences. Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

WK-6

Surface X-ray Scattering Studies of Ion Adsorption, Redox Reactions, and Water Structure at Mineral-fluid Interfaces: Recent Observations and New Possibilities with the APS Upgrade

Jeffrey G. Catalano
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The APS is the leading facility for conducting *in situ* surface x-ray scattering measurements of geochemical reactions occurring at mineral-fluid interfaces. Our recent observations, made possible by APS x-ray scattering facilities, reveal new insight into fundamental processes that affect contaminant fate and biogeochemical cycles in aquatic systems. Arsenic adsorption to mineral surfaces is more complex than predicted by long-standing models, with both inner- and outer-sphere species coexisting on oxide mineral surfaces. The reaction of dissolved Fe(II) with iron oxide surfaces produces structural changes associated interfacial redox reactions. Different surfaces of the same mineral may show distinct ordering of interfacial water, and this ordering may be substantially perturbed by adsorbates. The planned future upgrades to the APS will make possible new applications of surface x-ray scattering that probe the dynamics of mineral-fluid interface reactions under a wide-array of *in situ* conditions.

WK-6

Real-time Scattering Studies of Mineral Growth by Nanoparticle Aggregation

F. Marc Michel[1], Rui Serra Maia[1], Alexandria Hoeher[1], J. Donald Rimstidt[1], and Chang Lu[2]

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Crystallization by particle attachment (CPA) is the non-classical process whereby solids grow by stepwise addition and attachment of particles ranging from multi-ion complexes to nanoparticles [1]. Developing a comprehensive, quantitative understanding of CPA will deepen our understanding of many low-temperature mineral-forming processes, as well as provide insights into novel synthesis methods for technological applications. However, this potential cannot be fully realized without new information on the specific steps involved in CPA, as well as how those steps are connected. Current knowledge gaps are due to the lack of experimental methodologies for making direct, real-time observations of CPA processes in solution. Furthermore, much research is still based on samples synthesized at randomly chosen (ad hoc) conditions, which are often not representative of that found in nature. Few studies have taken a fully systematic approach to characterizing the structure and composition of both the precursors (monomers, multi-ion complexes and nanoparticles) and final solids as a function of synthesis (formation) conditions. Furthermore, it is not clear how the aggregation of particles that leads to CPA is affected by hydrodynamic conditions, and how this fits into existing theoretical models of particle-particle interactions and aggregation behavior used extensively in applications such as water treatment technologies.

To gain fundamental understanding of mineral growth by CPA, we are conducting real-time crystallization experiments in custom fabricated milli- and microfluidics devices designed explicitly for use with synchrotron total scattering methods. These *in situ* devices are essential to CPA research because they provide us the ability to: 1) initiate chemical reactions that synthesize different minerals, 2) precisely control mixing behavior and formation of turbulent, laminar and static fluid conditions, and 3) conduct real-time monitoring of atomic structural, chemical and physical characteristics of the solids, as well as solution chemistry (e.g., pH) in order to determine extent of reaction and kinetics. An example of our current work using pair distribution function (PDF) analysis to understand formation of a ferric hydroxysulfate nanomineral will be discussed. We expect the new models of mineral growth that are developed from real-time experiments will not only lead to a more thorough understanding of the biogeochemical cycling of nutrients/metals, but will also help develop better strategies for environmental remediation.

F.M.M. gratefully acknowledges financial support provided by the National Science Foundation, Geobiology and Low-Temperature Geochemistry Program (NSF Award #EAR-1451996) and the Virginia Tech Institute for Critical Technology and Applied Science (ICTAS). We also thank the Advanced Photon Source, Argonne National Laboratory.

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Wednesday, May 11

CNM Workshop 7

Revealing Hidden Structures and Properties: 3D Characterization of Nanoscale Materials

Location: Bldg. 401, Room A1100

Organizers: Tamar Segal-Peretz (MSD), Amanda Petford Long (MSD), and Charudatta Phatak (MSD)

Nanoscale materials, both organic and inorganic, have strong correlation between their three- dimensional structure and their functionality and performance. Therefore, in recent years, there has been a tremendous progress in utilizing 3D characterization techniques such as x-ray tomography, FIB-SEM tomography, and TEM tomography, to probe and understand the 3D and 4D properties of a range of nanostructured materials over multiple length scales, including batteries, magnetic materials, catalysts, and polymers. The progress in characterization tools together with progress in image analysis, data manipulation, and visualization has created new opportunities such as correlative tomography using multiple modalities to answer both fundamental and applied questions in material science through 3D characterization.

This workshop will focus on two areas: firstly, recent advances in experimental and computational techniques that enable quantitative characterization of the spatial structure and properties of nanoscale materials. The workshop will examine state-of-the-art and current challenges in sample preparation, experiments and data workflow including data acquisition as a function of external environment and time, algorithms for data analysis, and new tools for visualization. Secondly, applications of the new methods to materials science as well as biological science will be discussed.

8:30–8:40	Tamar Segal-Peretz (Argonne National Laboratory) *Opening Remarks*
8:40–9:20	Wen Jiang (Purdue University) *Cryo-EM 3-D Reconstruction of Viruses at Sub-3 Angstrom Resolutions*
9:20–10:00	Mark Ellisman (University of California, San Diego) *Multiscale Microscopy of the Brain: Where's the Dark Matter?*
10:00–10:20	Break
10:20–10:40	Nestor Zaluzec (Argonne National Laboratory) *Challenges in Hyper-spectral Imaging and Analysis in the Analytical Electron Microscope*
10:40–11:20	Rafal E. Dunin-Borkowski (Research Centre Jülich) *Towards Inverse Modeling of Magnetization and Charge Density in Nanoscale Materials Using Electron Microscopy*
11:20–12:00	Jonathan Winterstein (National Institute of Standards and Technology) *How Quantitative is TEM Tomography?*
12:00–1:30	Lunch
1:30–2:10	Hongqian Wang (Northwestern University) *3D Tomographic Measurements of Solid Oxide Fuel Cell and Li-Ion Battery Electrodes*
2:10–2:50	Robert Winarski (Argonne National Laboratory) *Nanoscale X-ray Imaging Using Novel Contrast Mechanisms*
2:50–3:10	Break
3:10–3:50	Daniel Pelt (Centrum Wiskunde & Informatica, Amsterdam) *Using Neural Networks to Improve the Reconstruction and Analysis of Nanoscale Tomography Data*
3:50–4:30	Xiaogang Yang (Argonne National Laboratory) *Mathematical Methods for Multimodal Imaging*
4:30–5:00	Charudatta Phatak and Amanda Petford Long (Argonne National Laboratory) *Closing Remarks*

WK-7

Cryo-EM 3-D Reconstruction of Viruses at Sub-3 Angstrom Resolutions

Guimei Yu, Kunpeng Li, and Wen Jiang

Markey Center for Structural Biology, Department of Biological Sciences, Purdue University, West Lafayette, IN 47907

Single particle cryo-EM is revolutionizing structural biology. It has been used to determine many structures of viruses and protein complexes to 3–5 Å resolutions and a few cases at sub-3 Å resolutions in recent years. To allow routine achievement of sub-3 Å resolution 3-D reconstructions, we have been developing methods to improve all relevant steps for cryo-EM projects from sample preparation, data collection, to image processing algorithms. In this presentation I will present an overview of single particle cryo-EM and two of our recent technique advances that allowed us to obtain several virus structures at sub-3 Å resolutions. The first is computational determination and correction of elliptical magnifications that distort the images. Our method is formulated as a generalized 2-D alignment problem that is performed during image refinement instead of relying on pre-calibrations using poly-crystalline samples. This formulation discovers the correction parameters from the data and automatically adaptive to potential variations of the distortions. The second advance is optimization of antibody-based affinity grid sample preparation method to capture low-yield/low concentration particles on grid substrate and at the same time without introducing excessive background noises. We showed that affinity grid method is capable of achieving near-atomic resolution 3-D reconstruction.

WK-7

Challenges in Hyper-Spectral Imaging and Analysis in the Analytical Electron Microscope

Nestor J. Zaluzec

Electron Microscopy Center, Center for Nanoscale Materials, Argonne National Laboratory, Argonne, IL 60439

Microanalysis in the Analytical Electron Microscope (AEM) has become a routine tool for characterization of solid materials down to the sub-nanometer scale. Recent developments in hardware and software have allowed the integration of Hyper-Spectral Imaging (HSI) during *in situ* and tomographic studies in the AEM. This work will outline the recent advances, current limitations and future prospects for the application of HSI to materials research problems.

This work is supported by the U.S. Department of Energy, Office of Basic Energy Sciences under Contract No. DE-AC02-06CH11357 at the Electron Microscopy Center in the Center for Nanoscale Materials of Argonne National Laboratory.

WK-7

Towards Inverse Modeling of Magnetization and Charge Density in Nanoscale Materials Using Electron Microscopy

Rafal E. Dunin-Borkowski[1], Jan Caron[1], Patrick Diehle[1], András Kovács[1], Zi-An Li[2], Jörn Ungermann[3], Martin Riese[3], Vadim Migunov[1], and Giulio Pozzi[1,4]

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[4] Department of Physics and Astronomy, University of Bologna, Bologna 40127, Italy

Off-axis electron holography is a powerful technique for recording the phase shift of a high-energy electron wave that has passed through an electron-transparent specimen in the transmission electron microscope (TEM). The phase shift is, in turn, sensitive to the magnetic induction and electrostatic potential within and around the specimen. Recent developments in the technique have included the use of advanced specimen holders with multiple electrical contacts to study nanoscale working devices, the use of ultra-stable transmission electron microscopes to achieve improved phase sensitivity and the use of direct electron detectors to improve temporal resolution.

We are currently working on both model-independent and model-based approaches that can be used to reconstruct projected or three-dimensional distributions of magnetization and charge density from phase images recorded using off-axis electron holography. For three-dimensional measurements of magnetization or charge density, we apply iterative model-based algorithms to tilt series of recorded two-dimensional phase images. Such iterative approaches avoid many of the artifacts that result from using backprojection-based tomographic techniques, as well as allowing additional constraints and known physical laws to be incorporated. Examples will be presented from studies of sub-100-nm magnetite nanoparticles, magnetic skyrmions and electrically-biased atom probe tomography needles.

We are grateful to Michael Farle, Marco Beleggia, and Tom Kelly for valuable contributions to this work and to the European Research Council for an Advanced Grant.

WK-7

How Quantitative is TEM Tomography?

J.P. Winterstein

National Institute of Standards and Technology,
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The ability to obtain 3D information with nanometer resolution in the TEM has become a valuable imaging method applied to variety of materials science problems. However, TEM tomography is often used only for qualitative assessments of 3D microstructure while reliable 3D metrology could significantly impact research in catalysis and semiconductor manufacturing among other fields. Although quantification of 3D data is occasionally attempted, there is a lack of clarity regarding determination of measurement uncertainties. In this talk I will review the current status of descriptions of measurement uncertainties and reliable methods of quantification. I will also describe ongoing attempts at NIST to use standard samples of facetted nanoparticles or fabricated multilayer films with known *a priori* dimensions for determination of measurement accuracy in tomography. These measurements are an attempt to introduce an analog to physical phantoms widely used in medical x-ray tomography to the TEM tomography community. Based on experiments with these samples, the influence of various experimental parameters on the accuracy of reconstructions will be described. Finally, possible improvements in reconstruction algorithms and acquisition methods will be suggested.

WK-7

3D Tomographic Measurements of Solid Oxide Fuel Cell and Li-Ion Battery Electrodes

Hongqian Wang
Northwestern University, Evanston, IL 60208

Fuel cell and battery electrodes have complex multi-phase morphologies. Quantitative analysis of this electrode microstructure is a key element in connecting materials processing and electrochemical performance, as well as understanding degradation mechanisms. Here we will describe three-dimensional (3D) electrode tomography measurements and results from the use of this data—including in 3D simulation models of electrochemical processes and correlation of measured microstructural evolution with degradation of electrochemical properties. 3D measurements and electrochemical simulations of solid oxide fuel cell (SOFC) electrodes, including Ni-Y-stabilized Zirconia (Ni-YSZ), (La,Sr)MnO_3-YSZ, and (La,Sr)(Fe,Co)O_3, as well as of Li-ion battery positive electrodes (e.g., $LiFePO_4$ and $LiCoO_2$), will be discussed. Experimental and simulation results on the structural evolution of Ni-YSZ electrodes, and how the changing microstructure impacts electrochemical performance, will be described.

WK-7

Nanoscale X-ray Imaging Using Novel Contrast Mechanisms

Robert P. Winarski
Nanoscience and Technology Division, Argonne National Laboratory, Argonne, IL 60439

X-ray imaging techniques are being developed to visualize *in situ* and *in operando* behavior of materials. These new capabilities allow us to visualize changes in systems in real time using the brightness provided by the Hard X-ray Nanoprobe Beamline, with image resolutions better than thirty nanometers [1,2]. We have developed techniques to image structural and elemental changes in a wide variety of materials including battery electrodes, advanced cement composites, and electronic junctions [3–5]. In this presentation, I will be discussing the techniques that we have developed for exploring system dynamics, and some of the new knowledge that we have gained from being able to see what is really happening inside these evolving materials.

The Hard X-ray Nanoprobe Beamline has the advantage of combining a variety of measurement techniques for understanding the nature of samples. The Hard X-ray Nanoprobe instrument is a combination scanning probe and full-field imaging microscope that incorporates scanning fluorescence imaging, nanodiffraction, and transmission imaging.

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WK-7

Using Neural Networks to Improve the Reconstruction and Analysis of Nanoscale Tomography Data

Daniël Pelt
Centrum Wiskunde & Informatica, Amsterdam 1098 XG, Netherlands

In many advanced tomographic experiments, the acquired projections are either noisy or limited in number. In these cases, standard tomographic reconstruction algorithms often produce results that are not sufficiently accurate for further analysis. Advanced iterative algorithms can produce more accurate results, but typically have computational requirements that are too high to be useful in practice. In this talk, a new reconstruction algorithm is presented that uses neural networks to improve reconstruction accuracy for limited-data problems. The algorithm is computationally efficient, making it applicable to large datasets.

During a separate training phase, the algorithm learns how to exploit scanner and object characteristics to maximize reconstruction quality. In the training phase, the algorithm can also be optimized for the type of analysis that will be performed after reconstruction. The talk will consist of a detailed explanation of the algorithm, along with examples of its use and results for different types of tomographic data. Furthermore, an application of the method to HAADF-STEM microscopy data of gold nanoparticles will be presented as well. In this case, the number of acquired projections could be reduced from 151 to only 10 without suffering a significant loss of both qualitative and quantitative accuracy.

WK-7

Mathematical Methods of Multimodal Imaging

Xiaogang Yang
Advanced Photon Source, X-ray Science Division, Argonne National Laboratory, Argonne, IL 60439

Advanced imaging techniques based on x-ray, electron or magnetic field are the import tools for modern scientific research. All the techniques have their advantages and limits in consideration of the spatial resolution, temporal resolution, measurement accuracy, measurement field, etc. Measuring a single object with multiple techniques, which is so-called multimodal imaging, becomes popular in recent year. The data processing for multimodal imaging is a crucial problem because complicated data sets are obtained from different techniques. Simple combination or comparison are not valid for most of the cases. We will review the general mathematical methods such as, image registration and image fusion, for multimodal imaging. We will also present an imaging study of a Li-ion battery particle agglomerate with combination of Transmission X-ray Microscopy (TXM) and Scanning Transmission Electron Microscopy (STEM). In this case, we use the cross-correlation based method to search the matching part of the 3D images from TXM and STEM. We also use a dictionary learning method to improve the TXM image quality from STEM data.

Wednesday, May 11

APS Workshop 8
Fundamentals and Emergent Applications of Ionic Soft Matters

Location: Bldg. 401, Room A5000

Organizers: Prof. Matthew Tirrell (IME, UChicago/ANL), Dr. Wei Chen (IME/MSD, ANL), and Dr. Hua Zhou (APS, ANL)

Ionic soft matter is a class of conventional condensed soft matter with prevailing contribution from electrostatics and, therefore, can be subject to possible long-range correlations among the components of the material and in many cases crucially affecting its physical properties. Among the most popular representatives of such a class of materials are natural and synthetic saline environments, like aqueous and non-aqueous electrolyte solutions and molten salts as well as a variety of polyelectrolytes, ionic liquids, and colloidal suspensions. All these systems are examples of soft matter strongly influenced, if not dominated, by long-range electrostatic forces (e.g., ionic interactions).

This workshop will discuss some fundamental challenges of ionic soft matter physics as well as some emerging functionalities and applications of ionic media in the electronic, energy, environmental and biological processes that are governed by electrostatic forces. The topics will focus on fundamental phenomena like association, adsorption, solvation, double-layering, criticality, screening, thin film stability, collective dynamics and transport through membranes, the behavior of ions at the surfaces/interfaces that is a fundamental process encountered in a wide range of biological and energy systems, as well as applied aspects, such as highly charged macroions, polyelectrolyte chains and ionic surfactant complexes that are important for a wide range of applications ranging from drug formulations to coating materials. Moreover, the crosscutting of ionic soft matter with strongly correlated systems (i.e., ionic liquid electrochemical gating driven emergent phenomena and exotic phase transitions in complex oxides) will be specially attended.

The workshop will combine the recent advances in the understanding of ionic soft matter systems by covering various aspects from applied research to basic science (including endeavors and contributions from the APS and CNM) and bring together a group of experts from different research sectors that include chemists, physicists, materials scientists, biologists and engineers.

8:30–8:40	Matthew Tirrell (University of Chicago/Argonne National Laboratory) *Introductory Remarks*
8:40–9:10	Nicholas Abbott (University of Wisconsin) *Modulation of the Strength of Hydrophobic Interactions by Proximally Immobilized Ions*
9:10–9:40	Igor Aronson (Argonne National Laboratory) *Living Liquid Crystals*
9:40–10:10	Kenneth R. Shull (Northwestern University) *Structure Development in Ion-containing Block Copolymer Membranes for Water Purification*
10:10–10:30	Break
10:30–11:00	Michael Bedzyk (Northwestern University) *Electrolyte-mediated Assembly of Charged Nanoparticles*
11:00–11:30	Ahmet Uysal (Argonne National Laboratory) *Room Temperature Ionic Liquid Structure and Dynamics at Charged Graphene Interface*
11:30–12:00	Jeremy E. Come (Oak Ridge National Laboratory) *Elucidating the Interfacial Structure at the Ionic Liquid-solid Interface Using Atomic Force Microscopy and Molecular Dynamics*
12:00–1:30	Lunch
1:30–2:00	Shriram Ramanathan (Purdue University) *Complex Oxides and Brain Science*

2:00–2:30	Sarah Perry (University of Massachusetts-Amherst) *Molecular Engineering Polyelectrolyte Complex Materials*
2:30–3:00	Jian Qin (Stanford University) *A Simple Model of Polyelectrolyte Complex*
3:00–3:20	Break
3:20–3:50	Jodie Lutkenhaus (Texas A&M University) *Water's Importance in Polyelectrolyte Multilayers and Complexes*
3:50–4:20	Daniel Hallinan (Florida State University) *An Electrochemical Approach to Measuring Oxidative Stability of Solid Polymer Electrolytes for Lithium Batteries*
4:20–4:50	Wenjie Wang (Ames Laboratory) *Ion Induced 2D Self-assembly of Gold Nano-particles at Vapor/liquid Interfaces*
4:50–5:00	Closing Remarks
5:00	Adjourn

WK-8

Modulation of the Strength of Hydrophobic Interactions by Proximally Immobilized Ions

Nicholas L. Abbott

Department of Chemical and Biological Engineering, University of Wisconsin-Madison, Madison, WI 53706

The structuring of water near non-polar molecular fragments or surfaces mediates cohesive interactions (so-called hydrophobic interactions) that underlie a broad range of interfacial, colloidal and biophysical phenomena. Substantial progress has been made during the past decade towards understanding hydrophobic interactions in simple model systems, but in most biological and technological contexts, non-polar domains are found in close proximity to polar and charged functional groups. Theories and simulations hint that the effects of nanometer-scale chemical heterogeneity on hydrophobic interactions may be important, but these ideas have not been tested experimentally. In this presentation, I will show that ions immobilized adjacent to non-polar domains can substantially increase or decrease the strength of hydrophobic interactions, with the effect strongly dependent on the specific ion type. By using chemical force microscopy and surfaces presenting alkyl and amine/ammonium (Am) units, we have found that protonation of amines can double the strength of hydrophobic interactions. In contrast, guanidine/guanidinium (Gdm) groups, when co-immobilized with alkyl groups, are found to eliminate measurable hydrophobic interactions. These divergent effects of proximally immobilized cations were confirmed by single-molecule measurements with a biologically-inspired system comprised of conformationally-stable β-amino acid oligomers (β-peptides) that generate precise nanopatterns of non-polar and either Am- or Gdm-bearing subunits (β^3-homolysine and β^3-homoarginine residues, respectively). These results demonstrate that the "hydrophobicity" of non-polar domains is not a property of the species that constitute the domain but rather is strongly modulated by functional groups located as far away as 1 nm. This understanding provides a fresh starting point for optimizing molecular recognition processes as well as the self-assembly of synthetic amphiphiles, colloids, or macromolecules by judiciously placing charged groups near non-polar domains to tune hydrophobic driving forces.

WK-8

Living Liquid Crystals

Igor Aronson

Materials Science Division, Argonne National Laboratory, Argonne, IL 60439

Bacteria are among the oldest and most abundant living species on Earth, and their activity influences the planet's environmental dynamics in multiple ways. Bacteria often migrate *en masse* over large distances, moving in dense groups in a highly organized, collective fashion known as "swarming motility." The flow dynamics of dense bacterial colonies can be very complex and, because of the interaction between the bacteria and the fluid, remarkably different from those predicted by conventional fluid models. In particular, turbulent swimming patterns often emerge, characterized by chaotic motions and the formation of vortices, even in situations where liquids should exhibit laminar flow. But these complex phenomena are difficult to characterize experimentally, and a predictive model that describes them has not emerged to date. Additional complications arise when the suspending medium is anisotropic exemplified by lyotropic liquid crystals. In my talk I will survey the most recent progress in experimental and theoretical studies of manipulation of bacterial swimming trajectories in liquid crystals [1,2]. We also demonstrated that shear flow created by rotating magnetic particle leads to surprisingly rapid depletion of bacterial concentration near the particle [3]. Our observation highlights that the expulsion of bacteria is not caused by the centrifugal forces but rather a non-trivial interplay between shear induced alignment and locomotion of bacteria.

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WK-8

Structure Development in Ion-containing Block Copolymer Membranes for Water Purification

Kenneth R. Shull

Department of Materials Science and Engineering, Northwestern University, Evanston, IL 60208

Pentablock copolymers with a polyelectrolyte midblock have been developed previously for nanofiltration applications. The transport properties and the mechanical strength of these materials are determined by the internal nanodomain morphology, which is strongly influenced by processing conditions. In this work we use grazing incidence small-angle x-ray scattering to investigate the effect of solvent and copolymer composition on the internal structure of the membranes, which is then correlated with the creep resistance of the membranes in an aqueous environment.

WK-8

Electrolyte-mediated Assembly of Charged Nanoparticles

S. Kewalramani, G.I. Guerrero-García, L.M. Moreau, J.W. Zwanikken, C.A. Mirkin, M. Olvera de la Cruz, and M.J. Bedzyk

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Colloidal crystallization is crucial in synthesizing a wide range of materials: from photonic, to magnetic, to biological. Therefore, understanding and controlling the crystallization of colloids, has been a long-term scientific goal. Our recent *in situ* small angle x-ray scattering (SAXS) studies reveal that electrolyte-mediated like-charge attractions can induce ordered assembly of highly charged nanoparticles in aqueous solutions. As a model system, we analyze spherical Au nanoparticles coated with noncomplementary DNA designed to prevent interparticle assembly via specific short range interactions (Watson-Crick hybridization). SAXS shows that these highly negatively charged nanoparticles undergo “gas-like” to face-centered cubic (FCC) to “glass-like” transitions with increasing NaCl or $CaCl_2$ concentration [1]. Corresponding MD simulations show that crystallization is concomitant with the interparticle interactions changing from purely repulsive to a long-ranged attractive potential well condition. The range and magnitude of the attraction is determined by the positional correlations between the electrolyte ions and the distribution of ions surrounding the nanoparticles. In the “gas-like” dilute system we also demonstrated the use of heavy ion replacement SAXS (HIRSAXS) in extracting the distribution of counterions surrounding these nanoparticles with extremely electron-dense cores [2]. Specifically, small differences in the SAXS intensity profiles from DNA-coated AuNPs dispersed in a series of solutions containing different monovalent ions (Na^+, K^+, Rb^+, or Cs^+) were analyzed to determine the radial distribution of the monovalent cations surrounding the DNA-coated AuNPs. Overall, SAXS proves to be a powerful tool in deciphering the structural signals of electrostatic interactions between the charged nanoparticles and between the charged nanoparticles and the electrolyte ions.

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WK-8

Room Temperature Ionic Liquid Structure and Dynamics at Charged Graphene Interface

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Supercapacitors with room temperature ionic liquid (RTIL) electrolytes and graphene-based electrodes are promising candidates for small electronic devices, especially flexible and wearable ones. The theoretical upper limit for the electric double layer (EDL) capacitance of graphene is the highest in all carbon materials. Also, graphene-based electrodes open up novel designs that are free of binders and inert conductive additives [1]. Furthermore, RTILs stand out as safe, non-volatile electrolytes with a wide potential window. However, our knowledge of these highly dense ionic plasmas at electrified interfaces is still at its infancy due to the lack of *in situ* experimental data about their potential-dependent EDL structures and dynamics [2].

Here, we use *in situ* real-time x-ray reflectivity integrated with fully atomistic molecular dynamics (MD) simulations to elucidate the interfacial ionic liquid structure and dynamics at epitaxial graphene electrode during cyclic voltammetry and potential steps [3]. Our results suggest that the graphene-RTIL interfacial structure is bistable in which the EDL structure at any intermediate potential can be described by the combination of two extreme-potential structures whose proportions vary depending on the polarity and magnitude of the applied potential. This picture is supported by the EDL structures obtained by MD simulations at various static potentials [4]. The potential-driven transition between the two structures is characterized by an energy barrier (~0.15 eV) that is independent of temperature. The model nicely explains the coexistence of distinct anion and cation adsorbed structures and provides further insights to ultra-slow response of the interfacial structure to potential steps.

This effort was supported as part of the Fluid Interface Reactions, Structures and Transport (FIRST) Center, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences. The research described here was done in collaboration with S.S. Lee, H. Zhou, P. Fenter (Argonne National Laboratory), G. Feng, S. Li, P. Cummings (Vanderbilt University), P. Fulvio, P. Zhang, S. Dai (Oak Ridge National Laboratory), J. McDonough, Y. Gogotsi (Drexel University).

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WK-8

Elucidating the Interfacial Structure at the Ionic Liquid-solid Interface Using Atomic Force Microscopy and Molecular Dynamics

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The structure and properties of ionic liquids (ILs) at the solid-liquid interface will govern their performance in all applications including energy storage and catalysis. Although it is well known that the interfacial structure of ionic liquids is very different to that of classical dilute electrolytes, a comprehensive understanding of the ion structure within the electrical double layer for this class of electrolytes is still lacking. Therefore it is necessary to have experimental methods to elucidate the interfacial ion structure which can be related to electrochemical performance. Atomic force microscopy (AFM) force spectroscopy is capable of probing the layered ion structure formed at the interface, and offers advantages over other techniques (e.g., x-ray and neutron reflectivity, surface force apparatus) due to its high spatial resolution allowing for the ion structure to be examined in a spatially resolved manner. Although there are several studies demonstrating the impressive ability of AFM to probe the interfacial ion structure in ionic liquids, several questions remain regarding the measured AFM response. (e.g., What is the role of the AFM probe?, Do we measure cations or anions?, Can we tune ion selectivity?)

In this work we examine the AFM force profiles of various ionic liquids at different substrates to examine how the substrate and ionic liquid properties affect the interfacial ion structure. We also use a series of different AFM probes of different geometry and chemistry to determine the effect on the measured force profiles. Our experimental results are compared directly with molecular dynamics simulations, and through a combination of experimental and theoretical approaches we are able to develop a better understanding of the measured force response and factors determining the interfacial structure at the ionic liquid-solid interface.

The experimental and modeling efforts of J.C., J.B., G.F., Y.Z., P.Z., S.D., and P.T.C. were supported by the Fluid Interface Reactions, Structures and Transport (FIRST), an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences. Additional personal support was provided by the

U.S. Department of Energy, Basic Energy Sciences, Materials Sciences and Engineering Division through the Office of Science Early Career Research Program (NB) and the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility. (M.B.O. and S.V.K.). We thank the computational resource from the National Energy Research Scientific Computing Center, which is supported by the Office of Science of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. G.F. also acknowledges the funding from the Hubei Provincial 100-Talent Program.

WK-8
Complex Oxides and Brain Science

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Frontiers of materials physics are ever expanding. New semiconductors that can adapt to the environment and learn from experience (such as voltage/external stimuli) are particularly interesting to explore in the context of simulating neural circuits and improving our understanding of animal learning behaviors. I will introduce the class of correlated oxides and their interfaces with soft systems like gels and liquids that allow bio-mimicry. These studies suggest a new opportunity to exploit orbital non-degeneracy in ionic lattices in evolutionary biology.

WK-8
Molecular Engineering Polyelectrolyte Complex Materials

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Polyelectrolyte complexation can be used in the self-assembly of a wide range of responsive soft materials ranging from dehydrated thin film and bulk solids to dense, polymer-rich liquid complex coacervates, and more complex hierarchical structures such as micelles and hydrogels. This responsiveness can include swelling, dissolution, and liquid-to-solid transitions. These behaviors can be harnessed to facilitate encapsulation and the subsequent fabrication of functional materials. However, little is known about the molecular-level factors that drive these various responses. We utilize precisely controlled synthetic polymer chemistry in tandem with detailed rheological studies to understand the mechanistic nature of the various material transitions present in polyelectrolyte complex materials. Moving beyond simple homopolymers, we are further interested in understanding how the patterning or presentation of charges and other chemical functionalities can be used to modulate the responsiveness and corresponding material properties of polyelectrolyte complex materials. We explore these effects using polypeptides and polypeptide derivatives as a model polymer system to study the effects of branching, chirality, sequence, and patterning effects on materials self-assembly. This experimental effort is supported by the parallel development of computational approaches for modeling and predicting the phase behavior of patterned polymeric materials. The goal of this systematic investigation is the elucidation of molecular engineering design rules to facilitate the tailored creation of materials based on polyelectrolyte complexation with defined properties for a wide range of applications.

WK-8
A Simple Model of Polyelectrolyte Complex

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Mixing solutions of polycations and polyanions under favorable salinity and pH condition results in the coexistence of two liquid-like phases. One such phase contains 20 to 30 percent of polymers and is highly viscous. The other, the supernatant phase, is nearly depleted of polymers. This coexistence behavior is conventionally treated as a type of macroscopic phase separation, and analyzed by using the Voorn-Overbeek model proposed in 1957. The essence of the model is a free energy expression that includes the mixing entropy terms and a term representing the Debye-Hückel correlation free energy for disconnected charges. We show that the model works for some weakly associating polyelectrolyte pairs, extend the model by deriving transparent expressions for the interfacial tension between the two phases, and comment on the various deficiencies of the model, the major ones being the missing of charge connectivity and dielectric heterogeneity. Our current view regarding the modeling of such system is also provided.

WK-8
Water's Importance in Polyelectrolyte Multilayers and Complexes

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In the last decade, evidence for an intriguing glass-transition-like phase transition has emerged in hydrated polyelectrolyte complex precipitates and polyelectrolyte multilayers. Without hydration, the transition disappears. Thus, it is important to understand how water drives the transition and how it affects the structure of the complex or multilayer. Although the transition is weak, it stimulates large-scale macroscopic phenomena such as shrinking, swelling, and rearrangement. To date, there is not a clear consensus on what causes this transition, although a growing body of evidence indicates that salt and water are key parameters. Recent simulations of hydrated polyelectrolyte complexes show that water molecules form a stabilizing hydrogen-bonded network and that this network is disrupted by dehydration of the polyanion at the thermal transition, leading to segmental relaxation of polymer chains [1]. If true, this would explain the transition's dependence on water and extrinsic compensation as well as its glass transition-like character. This talk will focus upon water's role in the transition, in which a strong dependence on hydration is observed. Quartz crystal microbalance with dissipation (QCM-D) and modulated differential scanning calorimetry (MDSC) are used to track the transition in polyelectrolytes complexes as a function of hydration. More broadly, a stronger understanding of water-polyelectrolyte interactions is needed to fully understand the internal structure of polyelectrolyte multilayer and complexes.

This work is supported in part by National Science Foundation Award Nos. 1049706 and 1312676.

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WK-8

An Electrochemical Approach to Measuring Oxidative Stability of Solid Polymer Electrolytes for Lithium Batteries

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Polymer electrolytes are an interesting class of electrolytes that hold promise for safer, flexible, high-energy batteries. Their unique properties stem from being a solid-state ion conductor. This benefit is a challenge for electrochemical investigations, since most electrochemical experiments have been designed for liquid electrolyte. In order to quantitatively evaluate polymer electrolyte stability, an electrochemical approach especially designed for solid electrolytes is presented. This approach uses a set of linear sweep voltammograms from different, large overpotentials to open circuit voltage, which the authors term variable reverse linear sweep voltammetry. By allowing the cell to relax between each polarization, the first data points of each voltammogram are not mass transfer limited. This yields current versus overpotential data that can be analyzed with a kinetic model, such as the Butler-Volmer model. Oxidative stability of poly(ethylene oxide) and polystyrene-*b*-poly(ethylene oxide) with lithium bis-trifluoromethanesulfonimide salt has been investigated on several electrode materials. The block copolymer electrolyte has been found to be quite stable to electrochemical oxidation, up to 5 V at 40°C. The degradation reaction has been found to be slow with large thermal activation energy.

WK-8

Ion Induced 2D Self-assembly of Gold Nano-particles at Vapor/liquid Interfaces

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One of the main goals of the nanotechnology is the mastery of the controllable construction of the desirable, hierarchical structures formed by building units such as nanoparticles (NPs). Owing to the nice physical and chemical properties of gold (Au), the AuNPs have been most thoroughly studied in the past decades in attempts to form meso- and macro-scale orderly structures. Bottom-up, self-assembly approaches have been established to form three-dimensional (3D) colloidal crystalline structures mediated through DNA-capped AuNPs in aqueous solutions, pioneered by Mirkin and Alivisatos et al. [1,2]. In parallel to the persistent pursuit of the 3D formation of superlattice of AuNPs, efforts on forming two-dimensional (2D) super-lattice of the AuNPs have emerged recently [3–6], where the air-liquid interfaces become naturally the platform where the formed structures reside. Up to date, two approaches to construct a 2D surface assembly of AuNP have been studied. One is through the surface charged templates that attract oppositely charged DNA-AuNPs [3,4], mimicking the interactions between a Langmuir monolayer and counter-ions. The other is the spontaneous surface adsorption and densification of DNA-AuNPs, an analog to the Gibbs monolayer formation [5,6]. Many experimental conditions, such as subphase contents, pH, surface charge density, are playing crucial roles in forming orderly surface structures. To correlate the multi-parameter space to the surface structures of AuNPs, we employed liquid surface scattering and spectroscopy techniques to characterize 2D assembly of AuNPs in both Langmuir monolayer and Gibbs monolayer scenarios. In all cases, the ionic content in the fluid phases are crucial in regulating the interfacial assembly. For instance, divalent ions Mg^{2+} and Ca^{2+} efficiently promote the formation of 2D super-lattice for DNA-capped nanoparticle at an air/water interface, in contrast to other monovalent and trivalent ions at the same ionic strength. The grazing incidence x-ray reflectivity (XR) and small-angle scattering (GISAXS) provide the information on in-depth and in-plane structures of the AuNPs. Moreover, the grazing incidence fluorescence spectroscopy provides direct evidence of the surface AuNPs aggregation mediated with divalent ions (i.e., Ca^{2+}). Our study extends beyond DNA-capped AuNPs systems and we have successfully assembled 2D ordered structure of polymer-capped AuNPs.

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Wednesday, May 11

APS Workshop 9
The Dynamic Compression Sector: Real-time Investigations of Dynamically Compressed Materials at Multiple Length Scales

Location: Bldg. 402, Room E1100/E1200

Organizers: Yogendra M. Gupta and Paulo Rigg (Washington State University)

2015 was an important year in the development of the Dynamic Compression Sector (DCS): Experimental stations were completed, beamline x-ray optics were installed and tested, and a variety og time-resolved commissioning experiments were performed to demonstrate the DCS capabilities. In preparation for general user operations in 2016, this workshop will introduce the APS User community to the DCS technical capabilities, including a tour, and the exciting new scientific opportunities at this first-of-a-kind user facility.

Understanding the atomistic level response of condensed matter under extreme conditions is of central importance to the fundamental science frontiers in numerous disciplines and to the development of many advanced technologies. In particular, dynamic compression experiments are both unique and versatile in their ability to produce and probe a broad range of extreme conditions on very short time scales. The DCS represents a new paradigm to examine and understand the dynamic response of materials at multiple length scales. A key scientific feature of the DCS experiments—because of the coupling to tunable, temporally separated, high-energy x-ray pulses—is the ability to afford time-resolved, *in situ*, atomistic-scale investigations of condensed matter phenomena “on-the-fly” or as they occur in single event experiments. The DCS capabilities address long-standing scientific challenges with the potential for unprecedented scientific payoff in the areas of structural changes, deformation and fracture, and chemical reactions. Representing an exciting and visionary capability, the DCS offers an opportunity to pursue fundamental science not possible previously at any synchrotron radiation facility to date. The DCS Workshop will provide participants with a broad overview of dynamic compression science opportunities provided by the DCS experimental capabilities.

The DCS, a DOE/NNSA sponsored user facility, was developed as a partnership between WSU and the APS, with significant participation by the NNSA and DoD Laboratories, and the academic community. The DCS at APS is operated by Washington State University (WSU) through a DOE/NNSA Cooperative Agreement. The commissioning experiments were carried out by teams from WSU, LANL, LLNL, and ARL/JHU.

8:30–8:40	Yogendra M. Gupta (Washington State University) *Welcome, Introductions, and Workshop Objectives*
8:40–9:00	Yogendra M. Gupta (Washington State University) *Dynamic Compression of Condensed Matter: Continuum-to-atomistic Scale Understanding*
9:00–9:40	Paulo Rigg and John Sethian (Washington State University) *Dynamic Compresssion Sector (DCS): Overview and Experimental Capabilities*
9:40–10:20	Tour of the DCS
10:20–10:40	Break
10:40–11:20	Stefan Turneaure (Washington State University) *Temporal Evolution of Structural Transformations and Microstructural Changes under Shock Compression*
11:20–12:00	Brian Jensen (Los Alamos National Laboratory) *Using X-ray Phase Contrast Imaging to Examine the Dynamic Compression of Materials*
12:00–1:30	Lunch
1:30–2:10	Thomas Duffy (Princeton University) *Geological and Planetary Materials under Dynamic Compression*

2:10–2:50	Trevor Willey (Lawrence Livermore National Laboratory) *Measurements of Carbon Condensates during High Explosive Detonation Using Time-resolved Small-angle X-ray Scattering*
2:50–3:20	Break
3:20–4:00	Todd Hufnagel (Johns Hopkins University) *Dynamic Deformation of Structural Metals: Twinning and Phase Transformations*
4:00–4:40	Jon Eggert (Lawrence Livermore National Laboratory) *Laser-driven Dynamic Compression Experiments—the Promise of DCS*
4:40–5:00	Group Discussion *Opportunities and Future Direction*
5:00	Adjourn

WK-9

Dynamic Compression of Condensed Matter: Continuum-to-atomistic Scale Understanding

Yogendra M. Gupta
Washington State University, Pullman, WA 99164

Dynamic compression experiments are both unique and versatile in their ability to produce and probe a broad range of extreme thermo-physical conditions (very large compressions, high temperatures, and large deformations) on very short time-scales (ps to µs). By linking state-of-the-art dynamic compression platforms to appropriate time-resolved measurement capabilities, significant insights can be gained into time-dependent, physical and chemical changes as they occur under well-defined, extreme dynamic loading. This talk will outline the scientific potential of the Dynamic Compression Sector (DCS) at the APS, a first-of-its-kind national user facility, and set the stage for the subsequent talks in this Workshop.

WK-9

Dynamic Compression Sector (DCS): Overview and Experimental Capabilities

Paulo Rigg and John Sethian
Washington State University, Pullman, WA 99164

The Dynamic Compression Sector (DCS) at the APS represents a new paradigm to examine and understand the dynamic response of materials at multiple length scales. A key scientific feature of the DCS experiments—because of the coupling to tunable, temporally separated, high energy x-ray pulses—is the ability to afford time-resolved, *in situ*, atomistic-scale investigations of condensed matter phenomena “on-the-fly” or as they occur in single event experiments. DCS has a unique suite of drivers that can be used to dynamically compress materials. This unique facility will enable studies of the dynamic response of materials over a broad range of time scales and shock wave amplitudes. This talk will provide an overview of the DCS and will introduce the APS user community to the DCS experimental capabilities.

WK-9

Temporal Evolution of Structural Transformations and Microstructural Changes under Shock Compression

Stefan J. Turneaure and Y.M. Gupta
Washington State University, Pullman, WA 99164

Shock compression of solids can drive structural changes and cause inelastic deformation on nanosecond timescales. A fundamental understanding of these shock-induced processes requires real-time lattice level measurements during the shock-compression event. The Dynamic Compression Sector (DCS) at the Advanced Photon Source (APS) is a unique facility for examining the temporal evolution of structural transformations and microstructural changes during single-event shock compression experiments; plate impact loading is used to shock-compress solids for durations of hundreds of nanoseconds and pulsed, hard, synchrotron x-rays (153.4 ns period or smaller, ~100 ps duration) are used to examine the time-evolution of the shocked material via x-ray diffraction (XRD). Two examples of XRD data obtained on shock-compressed solids at the DCS will be presented. First, XRD was used to identify the high-pressure structure of polycrystalline and single crystal silicon samples shock-compressed to 19 GPa. The XRD patterns from the shocked single crystal silicon samples exhibited features indicating a high-degree of preferred orientation for the high-pressure structure. Analysis of these diffraction patterns provided the orientation relations between the ambient cubic diamond and high-pressure structures. The experimental method and associated analysis used to determine the orientation relations between silicon polymorphs represent a new approach for understanding structural transformation mechanisms. Second, XRD results on polycrystalline Al shock-compressed to 12 GPa will be presented which provide insight into shock-induced microstructure. The results demonstrate the formation of sub-grains due to plastic deformation, but no significant changes in texture.

WK-9

Using X-ray Phase Contrast Imaging to Examine the Dynamic Compression of Materials

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Recent advances in coupling synchrotron x-ray diagnostics to dynamic compression experiments are providing new *in situ* formation about the response of materials at extremes conditions. For example, propagation based x-ray Phase Contrast Imaging (PCI) which is sensitive to differences in density (or index of refraction) has been successfully used to study a wide range of phenomena including jet-formation in metals, crack nucleation and propagation, and detonator dynamics. These experimental results have relied, in part, on the development of a robust, optically multiplexed detector system that captures single x-ray bunch images with micrometer spatial resolution on the nanosecond time scale. In this work, the multi-frame PCI (MPCI) system is described along with experiment highlights that include the compression of an idealized system of spheres subjected to impact loading. Experimental results, implications, and future work will be discussed.

WK-9

Geological and Planetary Materials under Dynamic Compression

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Dynamic compression studies have wide-ranging applications to problems in Earth and planetary science ranging from the effects of impacts and explosions to the synthesis of new phases and materials. Shock wave studies are fundamental to understanding planetary formation, shock metamorphism, and the nature of high-pressure phases otherwise only found in the inaccessible deep interior. The transient loading of rocks and minerals during impact events produces unique deformation features and phases that are characteristic of such events and have been studied intensively in samples from terrestrial craters and meteorites. In addition, laboratory shock wave experiments using gas guns have provided a wealth of detailed information regarding the response of geological material to high strain rate loading. However, traditional experimental approaches that involve either continuum measurements (e.g., wave profiles) or *ex situ* sample recovery have limitations that often lead to ambiguous interpretation of the material changes occurring during loading. The new Dynamic Compression Sector at the Advanced Photon Source promises to revolutionize laboratory study of impact phenomena in geological materials. In particular, the capability to obtain *in situ*, time-resolved, lattice-level structural information by x-ray diffraction and imaging will address long-standing questions about the structural state of geological materials under dynamic loading. Here I will provide a summary of the current state of knowledge regarding structural phase transitions in silicates and other minerals under shock loading and outline how the capabilities of DCS can be applied to advance our understanding of these systems.

WK-9

Measurements of Carbon Condensates during High Explosive Detonation Using Time-resolved Small-angle X-ray Scattering

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Most commercial nanodiamond originates from detonation of high explosives, particularly from RDX/TNT mixtures. Models suggest that the phase, crystallinity, and morphology of carbon is strongly dependent on the type of high explosive used and the exact evolution of temperature and pressure conditions during detonation; however, experimental probes of carbon condensation under the extreme conditions present at 100 ns timescales has been technically challenging. A new time-resolved small-angle x-ray scattering (SAXS) end-station was developed at LLNL and deployed at the Advanced Photon Source. This end-station at the Dynamic Compression Sector is capable of synchronously initiating detonation, and acquiring SAXS patterns from discrete 80 ps x-ray pulses, which arrive every 153.4 ns. We interleave three shots to provide ~51 ns time steps beginning immediately post-detonation. Here, we present a comparative survey of early time carbon condensation from three CHNO high explosives: HNS, Comp B (60% RDX, 40% TNT), and DNTF. Models predict that this array of explosives should provide graphitic, nanodiamond, and liquid carbon phases, respectively, at early times; the nanoparticle morphologies indicated by the time resolved SAXS is remarkably consistent with these computational predictions.

This work performed under the auspices of the U.S. DOE by LLNL under Contract DE-AC52-07NA27344, and primarily funded by LLNL-LDRD-14-ERD-018.

WK-9

Dynamic Deformation of Structural Metals: Twinning and Phase Transformations

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There are many applications of structural metals that involve deformation at high rates. Examples include steels used as structural components in automobiles (where high-rate loading can occur during a crash) and armor (due to impact of projectiles). Developing new materials with enhanced properties requires an understanding of how the underlying physical mechanisms of deformation change with strain rate.

In this talk, I will briefly review the basic mechanisms of plastic deformation of metals, discuss how they may be influenced by loading rate, and describe *in situ* techniques for investigating them. Examples will be drawn from recent work in my group, including *in situ* studies of deformation twinning in magnesium and transformation-induced plasticity in steels. I will conclude with some comments on the promise for future work in this area.

WK-9

Laser-driven Dynamic Compression Experiments—the Promise of DCS

Jon Eggert

Lawrence Livermore National Laboratory, Livermore, CA 94550

Over the past 20 years laser-driven compression experiments have improved from very exciting (but high uncertainty) stress-density equation of state (EOS) experiments to highly-accurate shock and ramp-compressed measurements. I will briefly review a range of high-energy density (HED) EOS measurements now possible on large lasers including Hugoniot measurements above 50 (even 500 Mbar) and recent nearly-isentropic absolute EOS measurements to 5–50 Mbar with ~1% accuracy. Improvements in laser-pulse shaping has allowed us to supplement traditional HED measurements of stress-density with shock temperature, sound speed, Gruneisen parameter, and specific heat, as well as reflectivity, phase transitions, and even crystal structure on shocked, multi-shocked, and ramp-compressed materials.

Unfortunately, the availability of the laser drivers necessary to perform these experiments is very limited; primarily accessible only to National Laboratory employees in several countries, and their collaborators. With the commissioning of the DCS-laser hutch-C this summer that situation is about to change. The availability of a permanent, dedicated, pulse-shaped, 100 J blue laser at a synchrotron source will open the field of laser-driven compression experiments to all qualified researchers. It is likely that measurements of the kinetics (dynamics) of phase transitions, the radial-distribution function of shocked liquids, short and long range order of both solids and liquids, accurate determination of the temperature of materials under ramp compression, and the detailed time-evolving spatial structure of shock fronts and shocked materials, will all come to pass within the next few years at hutch-C DCS. I will discuss the experimental design and diagnostic requirements necessary to obtain the high-quality, accurate results that will make laser-driven compression a field attractive and open to the broad scientific community. The upcoming inauguration of hutch-C at DCS marks the beginning of an extraordinarily exciting new direction for HED experiments.

Wednesday, May 11

CNM Workshop 10
2D Materials Beyond Graphene: Exploring the Heterostructures

Location: APCF Auditorium

Organizers: Irma Kuljanishvili (Saint Louis University), Saptarshi Das (Penn State),
and Subramanian Sankaranarayanan (CNM)

This workshop aims to facilitate and strengthen the synergestic approach to experimental and theoretical works of experts from academia, national labs and industries to discuss the latest developments in the synthesis, characterization, and application of nanostructured 2D materials and device architectures with the emphasis on exploring their unique potential as surface sensitive and substrate responsive systems. The properties of these layered 2D materials can be tuned by lateral confinement and vertical multi-layer z-stacking. This offers opportunity for development of the next generation of multi-functional and energy efficient devices whose properties can be engineered or designed to specific performance. The materials of interest include graphene and TMDC heterostructures. Recent advances in the development of 2D materials and understanding of their electronic, optical, thermal, chemical and mechanical properties have demonstrated vast potentials in these systems.

The Center for Nanoscale Materials at Argonne has expertise and state-of-the-art facilities in the synthesis, functionalization and characterization of 2D materials, and has a strong research program focused around the fundamental studies on physical properties across different length scales. The workshop will include topics covering intriguing fundamental physical aspects of 2D materials and heterostructures, their growth, characterization and applications. Device architectures across different length scales will be discussed. Computational modeling offers the opportunity for computational experimentation and testing of physical and chemical interactions with the substrate with emphases on tuning interfaces of these layered materials by geometrical designs and surface chemistry. We will also aim to facilitate discussions that explore routes for scalable device applications.

This workshop is expected to provide an opportunity for academics, R&D scientists at industry, and students to exchange ideas, think creatively about new avenues for collaborations with user facilities at Argonne and to work on expanding knowledge of nanoscience into development and implementation of new frontiers in nanotechnology.

Workshop topics:

- Advances in growth processes and characterization of Graphene/TMDCs interfaces and heterostructures with emphasis on understanding and controlling synthesis and their scalability for commercialization.
- Computational studies and interface designs: Computational approach for understanding the role of the substrate with emphases on interface engineering.
- Novel energy efficient device ideas with emphasis on Tunneling Transistors and Optoelectronic switches.
- Heterostructures on Flexible Substrates.

8:00–8:10	Introductory Remarks
8:10–8:50	Mildred Dresselhaus (Massachusetts Institute of Technology) *Stacking and Stitching Heterostructures for Functionality*
8:50–9:30	Phillip Kim (Harvard University) *Electronic and Optoelectronic Physics in the van der Waals Heterojunctions*
9:30–9:45	Break
9:45–10:25	Sanjay Banerjee (University of Texas) *Electronics and Spintronics in Flatland*
10:25–11:05	Joerg Appenzeller (Purdue University) *Electronic Properties of Transition Metal Dichalcogenide and Black Phosphorous Field-effect Transistors*

11:05–11:20	Break
11:20–11:50	Morning Panel Discussion Mildred Dresselhaus, Phillip Kim, Sanjay Banerjee, and Joerg Appenzeller *Designing Electronic Architectures with Novel 2D Materials: Device Fabrication and Metrology*
11:50–1:20	Lunch and Poster Session
1:20–2:00	Peter Littlewood (Argonne National Laboratory) *2D Materials for Energy and Sustainability*
2:00–2:40	Li Yang (Washington University in St. Louis) *Black Phosphorous and Beyond*
2:40–2:55	Break
2:55–3:3	Ganesh Kamath (Interx, Inc.) In silico *Predictions of Ionic Liquid Assisted Exfoliation and Dispersion of 2D Nanosheets*
3:35–4:15	Mark Hersam (Northwestern University) *Fundamentals and Applications of Two-dimensional Nanoelectronic Heterostructures*
4:15–4:30	Break
4:30–5:00	Afternoon Panel Discussion Peter Littlewood, Li Yang, Ganesh Kamath, and Mark Hersam *Growth and Characterization of 2D Materials and Heterostructures: Challenges and Prospectives*
5:00–5:15	Closing Remarks
5:15	Adjourn

WK-10

Stacking and Stitching Heterostructures for Functionality

Mildred S. Dresselhaus
Massachusetts Institute of Technology, Cambridge, MA 02139

Research on the use of layer stacking and the in-plane joining of nanostructures at interfaces increases the possibilities for combining layered materials to achieve new functionality. Particular attention is given to advances in both materials synthesis and modeling capabilities, and particular interest has been the constructive interaction between these two research directions. The special contribution of national laboratories to the constructive interaction is also highlighted.

WK-10

Electronic and Optoelectronic Physics in the van der Waals Heterojunctions

Phillip Kim
Harvard University, Cambridge, MA 02138

Recent advances of van der Waals (vdW) materials and their heterostructures provide a new opportunity to realize atomically sharp interfaces in the ultimate quantum limit. By assembling atomic layers of vdW materials, such as hexa boronitride, transition metal chalcogenide and graphene, we can construct novel quantum structures. Unlike conventional semiconductor heterostructures, charge transport of the devices is found to critically depend on the interlayer charge transport, electron-hole recombination process mediated by tunneling across the interface. We demonstrate the enhanced electronic optoelectronic performances in the vdW heterostructures, tuned by applying gate voltages, suggesting that these a few atom thick interfaces may provide a fundamental platform to realize novel physical phenomena, such as hydrodynamic charge flows, cross-Andreev reflection across the quantum Hall edges states, and interlayer exciton formation and manipulations.

WK-10

Electronics and Spintronics in Flatland

H. Movva, A. Rai, S. Kang, A. Sanne, R. Ghosh,
A. Roy, B. Ghosh, S. Majumder, E. Tutuc, L.F. Register,
and S.K. Banerjee
Microelectronics Research Center, University of Texas at Austin,
Austin, TX 78712

Transition metal dichalcogenides (TMD) have opened up avenues in beyond-CMOS logic and memory device concepts involving single/many-particle 2D-2D tunneling showing negative differential resistance, and topological insulators (TI) show promise for spintronics. We will discuss

CVD and MBE growth of TMDs such as MoS_2, WSe_2, $MoTe_2$ and ReS_2, and schemes for doping and ohmic contact formation to these materials. Novel low power logic and memory devices possible in 2D materials will be discussed. MBE of TIs such as Bi_2Se_3 which show spin-helical locking will be discussed for novel logic and non-volatile memory applications.

WK-10

Electronic Properties of Transition Metal Dichalcogenide and Black Phosphorus Field-effect Transistors

Joerg Appenzeller
Electrical and Computer Engineering, Purdue University,
West Lafayette, IN 47907

Over the last years, two-dimensional (2D) materials are attracting an increasing amount of interest for various electronic applications owing in particular to the ideal electrostatics conditions that can be enabled in a three-terminal field-effect transistor (FET) geometry. Transition metal dichalcogenides (TMDs) as MoS_2, WSe_2, or WS_2, to just name a few, or black phosphorus (BP) offer sizable bandgaps at mobilities that cannot be achieved in three-dimensional, bulk type materials that are scaled down to similar dimensions. The key is the absence of dangling bonds at the 2D semiconductor to substrate or gate dielectric interface that allows for highly conductive channels with sub-nm body thicknesses. In my presentation I will discuss the benefits of an ultra-thin body structure for scaled device applications. I will also elucidate the critical impact of Schottky barrier (SB) contacts in the context of TMD and BP devices and will present an analytical approach that allows extracting materials and device information as the SB height and bandgap of single- and multi-layer FET structures.

WK-10

2D Materials for Energy and Sustainability

Peter Littlewood
Argonne National Laboratory, Argonne, IL 60439

Efficient and low-cost materials technologies are needed to support our transition to a sustainable planet. At the forefront will be progress in energy capture, storage, transmission, and use, as well as water management, distributed sensing, and energy-efficient information technology. If our experience of the last century is any guide, evolving technologies will spawn new scientific questions and likely, whole new directions of enquiry.

2D materials offer a new materials platform in a variety of areas. I will discuss a few science directions:

- Bandstructure engineering and defect design in 2D materials
- The opportunities for optoelectronic strong coupling in 2D materials and ultra-thin films
- Interface engineering in oxides

Work performed with Alejandor Lopez-Bezanilla (Material Science Division, Argonne National Laboratory), Wushi Dong (Department of Physics, University of Chicago), and Alex Edelman (University of Chicago).

WK-10

Black Phosphorus and Beyond

Li Yang
Department of Physics, Washington University in St Louis,
St. Louis, MO 63130

I will present our theoretical studies on a new family of two-dimensional (2D) materials: black phosphorus and its corresponding group IV-VI isoelectronic materials. For black phosphorus, these results include its intrinsic, fundamental properties such as quasiparticle band gaps, excitons, and anisotropic thermal conductance, and further engineered properties such as strain-tunable anisotropic electrical conductance and realizing Dirac cones and graphene electronics. Beyond black phosphorus, we find that the group IV-VI isoelectronic materials (monolayer GeS, GeSe, SnS, and SnSe) may exhibit dramatically enhanced piezoelectric effects; their characteristic piezoelectric coefficients are about two orders of magnitude larger than those of monolayer transition metal dichalcogenides (TMDCs) and conventional bulk piezoelectric materials. Most of our theoretical predictions have been confirmed by subsequent experiments and may ignite further research on fundamental science and applications.

WK-10

In Silico Predictions of Ionic Liquid Assisted Exfoliation and Dispersion of 2D Nanosheets

Ganesh Kamath
InterX Inc., Berkeley, CA 94704

Research on 2-D materials is proceeding at a relentless pace as scientists of both experimental and theoretical bents seek to explore and exploit their superlative attributes including large intrinsic charge mobility, and thermal conductivity, stiffness, and strength. Of course, fully exploiting the remarkable properties of such low dimensional materials requires reliable, large-scale production methods which are non-oxidative and introduce few defects, criteria not fully satisfied by any known approach. A major advance in this direction was the recent discovery that ionic liquid-assisted exfoliation of graphite leads to isolation of few- and single-layer graphene sheets with yields two orders of magnitude higher than with earlier approaches using surface energy-matched solvents like Nmethyl-pyrrolidone. The overarching goal of this talk is to develop a molecular-level view of a representative IL/graphene model interface to elucidate and better control key chemical interactions responsible for efficient exfoliation. Free energies for graphene exfoliation from bilayer graphene using ionic liquids based on various cations paired with the bis(trifluoromethylsulfonyl) *a priori* screening tool for performance based rank order prediction of novel ionic liquids for the dispersion and exfoliation of various nanocarbons and inorganic graphene analogues. Various other examples are presented in this talk about using these potential of mean force simulations for evaluation of free energies of other 2-D materials such as hexagonal-boron-nitride (*h*-BN) and metal dichalcogenides such as MoS_2. These calculations should tantalize experimentalists and open up avenues for exploring the IL exfoliation and dispersion of Inorganic Graphene analogs. We further probe into the various interactions responsible for dispersion and exfoliation of 2D nanosheets using quantum chemistry and try to correlate the degree of interaction to the amount of charge transfer and various other electronic properties. A further endeavor includes tuning of the optoelectronic of 2D nanosheets via defect engineering and non-covalent functionalization where again we provide trends and electronic structure insights, thus paving the way for fabrication of graphene-based devices and supercapacitors.

WK-10

Fundamentals and Applications of Two-dimensional Nanoelectronic Heterostructures

Mark C. Hersam
Department of Materials Science and Engineering, Northwestern University, Evanston, IL 60208

Two-dimensional materials have emerged as promising candidates for next-generation electronic and optoelectronic applications. As is common for new materials, much of the early work has focused on measuring and optimizing intrinsic properties on small samples (e.g., micromechanically exfoliated flakes) under idealized conditions (e.g., vacuum and/or cryogenic temperature environments). However, real-world devices and systems inevitably require large-area samples that are integrated with dielectrics, contacts, and other semiconductors at standard temperature and pressure conditions. These requirements are particularly challenging to realize for two-dimensional materials since their properties are highly sensitive to surface chemistry, defects, and the surrounding environment. This talk will thus explore methods for improving the uniformity of solution-processed two-dimensional materials with an eye toward realizing scalable processing of large-area thin-films. For example, density gradient ultracentrifugation allows the solution-based isolation of transition metal dichalcogenides (e.g., MoS_2, WS_2, $MoSe_2$, and, WSe_2) and boron nitride with homogeneous thickness down to the single-layer level. Similarly, two-dimensional black phosphorus is isolated in solution with the resulting flakes showing field-effect transistor mobilities and on/off ratios that are comparable to micromechanically exfoliated flakes. In addition to solution processing, this talk will also report on the integration of two-dimensional materials with dielectrics and other semiconductors. In particular, atomic layer deposition of dielectrics on two-dimensional black phosphorus suppresses ambient degradation, thereby preserving electronic properties in field-effect transistors at atmospheric pressure conditions. Finally, gate-tunable p-n heterojunction diodes with Type I and Type II band alignments are demonstrated by integrating n-type single-layer MoS_2 with p-type semiconducting single-walled carbon nanotubes and pentacene, respectively.

Tuesday, May 10 and Wednesday, May 11

APS Workshop 11
In situ Studies of Materials Transformations Using Coherent X-rays

Locations: Tuesday session in Bldg. 401, Room A1100
Wednesday session in Bldg. 402, Lecture Hall

Organizers: Ross Harder, Hawoong Hong, Barry Lai, Jörg Maser, and Brian Stephenson

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Development and synthesis of advanced materials require understanding of structure, composition, defects and inhomogeneities during both fabrication and operation. For example, flow of ions during battery charging and discharging may lead to strain and phase changes in the battery electrodes, and reduce both capacity and lifetime of the battery. Structural or compositional defects introduced during materials synthesis may negatively impact device performance, or may offer opportunities for defect engineering that benefits the performance of materials and devices. In catalysts, strain induced in catalytically active areas of nanocrystals may reduce the energy barrier of desirable chemical reactions, or may help pinpoint position and properties of catalytically active sites, thus helping understanding and engineering of catalysts. In all of these classes of materials, hard x-rays provide good penetration through gases and environments, and very high sensitivity to structure, strain, elemental, and chemical inhomogeneities.

Coherent x-ray methods such as diffraction-limited focusing, coherent diffraction imaging, and photon correlation spectroscopy provide a unique window into processes during synthesis of materials and operation of devices. For example, nanofocusing optics allow studies with very high spatial resolution and very high sensitivity to composition and chemical state. Coherent diffraction methods provide very high sensitivity to atomic arrangements, strain, and dynamics, with a spatial resolution of well below 10 nm. All of these can be performed under electric and magnetic fields, at variable temperature, and under flow of gases and fluids. The Upgrade of the APS will massively increase the coherent photon flux at hard x-ray energies, and thereby significantly improve resolution and throughput even of existing experiments. New APS beamlines are anticipated to uniquely take advantage of the new source capabilities for hitherto non-feasible experiments. An outcome of the workshop will be a description of the scientific opportunities in this area, as well as the nature of beamline facilities and related research infrastructure needed to make rapid progress.

May 10, 2016

1:30–2:10	Ross Harder (Argonne National Laboratory) *Workshop Introduction and Goals*
2:10–2:50	Steven Leake (European Synchrotron Radiation Facility) *The Upgraded ID01 Beamline in Light of the Extremely Brilliant ESRF*
2:50–3:30	Nenad Markovic (Argonne National Laboratory) *APS Facilities and Future of Electrochemistry*
3:30–4:00	Break
4:00–4:40	Michael Pierce (Rochester Institute of Technology) *Coherent X-ray Scattering of Surfaces: From High-Z Systems in Vacuum to Real-world Environments at Interfaces*
4:40–5:20	Matthew Cherukara (Argonne National Laboratory) *Characterizing Evolving Processes through Coupled CDI and Molecular Dynamics Studies*
5:20	Adjourn

May 11, 2016

8:50–9:30	Andrew Ulvestad (Argonne National Laboratory) *Bragg Coherent Diffractive Imaging of Catalytically Active Nanoparticles during Ascorbic Acid Decomposition and CO_2 Reduction to CO*
9:30–10:10	Karl Ludwig (Boston University) *Co-GISAXS as a Tool to Investigate Surface Growth Dynamics*
10:10–10:40	Break
10:40–11:20	Divine Kumah (North Carolina State University) *Controlling the Functional Properties at Polar Oxide Interfaces*
11:20–12:00	Steve May (Drexel University) *Topotactic Transformations of Oxide Thin Films*
12:00–1:30	Lunch
1:30–2:10	Gyula Eres (Oak Ridge National Laboratory) *Dynamics of Materials Synthesis on the Elementary Building Block Level*
2:10–2:50	Christian Lavoie (IBM T.J. Watson Research Center) *Contacts in Advanced CMOS: History and Emerging Challenges*
2:50–3:20	Break
3:20–4:00	Mariana Bertoni (Arizona State University) *Understanding Polycrystalline Solar Absorbers:* In situ *X-ray Characterization of CIGS*
4:00–4:40	Paul Evans (University of Wisconsin) *Coherent X-ray Methods Enabling Control of Interfaces in Electronic Materials*
4:40–6:00	All participants, chaired by Brian Stephenson (Argonne National Laboratory) *Discussion of APS Upgrade Facilities Needed*
6:00	Adjourn

WK-11

The Upgraded ID01 Beamline in Light of the Extremely Brilliant ESRF

Steven J. Leake, Peter Boesecke, Gilbert A. Chahine, Hamid Djazouli, Jan Hilhorst, Marie-Ingrid Richard, and Tobias U. Schulli
ESRF–The European Synchrotron, Grenoble 38043, France

With the completion of the first phase of upgrade of the European Synchrotron (ESRF), the ID01 beamline has returned successfully to user operation. We offer; scanning diffraction microscopy at 100Hz with 100 nm focused x-ray beams [1], full field x-ray diffraction microscopy using compound refractive lenses [2] and focused coherent x-ray beams for coherent diffractive imaging applications [3]. The implementation of the future upgrade of the storage ring [4] and beamline will amplify data rates by a factor of 100 or more and provide opportunity for new experiments.

An overview of the type of experiments available now and the strategy towards the next upgrade of the facility will be provided with an emphasis on coherent beams. The need for a generic set of inter-synchrotron compatible tools will be addressed given such a data deluge in order to make such techniques routinely available to non-expert users. The emphasis from ID01 is to collaborate to generate a framework of such tools to avoid continuously reinventing the wheel.

[1] G.A. Chahine et al., *Applied Physics Letters* **106**, 071902 (2015).

[2] J. Hilhorst et al., *J. Appl. Cryst.* **47**, 1882–1888. (2014).

[3] S. Labat, et al., *ACS Nano* **9**(9), 9210–6 (2015).

[4] ESRF: Phase II - white paper (http://www.esrf.eu/files/live/sites/www/files/about/upgrade/documentation/whitepaper-upgrade-phaseII.pdf).

WK-11

Coherent X-ray Scattering of Surfaces: From High-Z Systems in Vacuum to Real-world Environments at Interfaces

Michael S. Pierce
Rochester Institute of Technology, Rochester, NY 14623

X-ray photon correlation spectroscopy (XPCS) can be used to measure both equilibrium and non-equilibrium q-dependent dynamics, at an atomic scale, from surfaces and interfaces. Recently such work has been extended to high-Z metals in vacuum as well as model electrochemical and gas-phase environments. Such measurements have revealed information about temperature and potential dependent behavior of surface reconstructions, and atomic terraces and islands. However, to this point complete extension of the technique has been limited due to coherent flux as well as x-ray energy. In particular there are many open questions for lower Z elements in real-world conditions. Higher energy coherent flux should provide several opportunities for this technique to be extended and find significantly wider application for the study of surface phenomena.

WK-11

Characterizing Evolving Processes through Coupled CDI and Molecular Dynamics Studies

Mathew J. Cherukara[1], Kiran Sasikumar[2], Jesse N. Clark[3], Badri Narayanan[2], Wonsuk Cha[4], Dongjin Kim[5], Hyunjung Kim[5], Subramanian Sankaranarayanan[2], and Ross J. Harder[1]

[1] X-ray Sciences Division, Argonne National Laboratory, Argonne, IL 60439
[2] Center for Nanoscale Materials, Argonne National Laboratory, Argonne, IL 60439
[3] Stitch Fix
[4] Materials Sciences Division, Argonne National Laboratory, Argonne, IL 60439
[5] Department of Physics, Sogang University, Mapo-gu, Seoul, South Korea

Coherent x-ray diffraction imaging (CDI) is a powerful technique for *operando* characterization with the ability to provide evolving snapshots of defect structure, lattice dynamics and structural evolution. It is however, limited to ~10 nm in spatial resolution, and can only image crystalline structures. Molecular dynamics (MD) simulations provide a complete atomic picture of dynamically evolving processes for system sizes that perfectly complement CDI experiments. We present case studies from recent joint experimental and modeling studies of slowly evolving, catalytic processes as well as ultra-fast lattice dynamics following laser excitation. Finally we look at the potential to extend the effective resolution provided by CDI by coupling molecular statics (MS) simulations to experimental data through machine learning approaches.

WK-11

Bragg Coherent Diffractive Imaging of Catalytically Active Nanoparticles during CO_2 Reduction to CO

Andrew Ulvestad[1], Yihua Liu[1], Wonsuk Cha[1], Stephan Hruszkewycz[1], Hoydoo You[1], Allison Yau[2], Xiaofeng Feng[2], Matt Kanan[2], and Brian Stephenson[1]

[1] Materials Science Division, Argonne National Laboratory, Argonne, IL 60439
[2] Department of Chemistry, Stanford University, Stanford, CA 94305

Efficient electrochemical conversion of CO_2 and H_2O to fuels such as CH_4 and H_2 is an integral part of meeting grand challenges. However, highly active catalysts for selective CO_2 reduction are rare. Recently, it was demonstrated that a new type of metal nanoparticle catalyst, known as an “oxide derived” catalyst, is selectively active for CO_2 reduction due to large numbers of grain boundaries [1]. However, direct observation of GB activity *in situ* and under *operando* electrochemical conditions has remained elusive. Here I will discuss BCDI studies of gold nanoparticles during CO_2 reduction using a recently built *in situ* 3-electrode electrochemical cell. I will also touch on BCDI studies of grains in a gold thin film. The ability to visualize both dislocations [2,3] and catalytic activity using BCDI will pave the way for potential advances in rational catalyst design.

This research used resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357. W.C., Y.L., M.J.H., H.Y., P.Z., S.H., and G.B.S. were supported by the DOE Office of Science, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering. We thank the staff at Argonne National Laboratory and the Advanced Photon Source for their support.

[1] Li, C.W., Ciston, J., and Kanan, M.W., “Electroreduction of carbon monoxide to liquid fuel on oxide-derived nanocrystalline copper.” *Nature* **508**, 504–7 (2014).

[2] Ulvestad, A., Singer, A., Clark, J.N., Cho, H.M., Kim, J.W., Harder, R., Maser, J., Meng, Y.S., and Shpyrko, O.G., “Topological defect dynamics in *operando* battery nanoparticles.” *Science* **348**, 1344–7 (2015).

[3] Clark, J.N., Ihli, J., Schenk, A.S., Kim, Y., Kulak, A.N., Campbell, M., Nisbit, G., Meldrum, F.C., and Robinson, I.K., “Three-dimensional imaging of dislocation dynamics during crystal growth and dissolution.” *Nat. Mater.* 1–6 (2015).

WK-11

Co-GISAXS as a Tool to Investigate Surface Growth Dynamics

Karl Ludwig

Department of Physics and Division of Materials Science and Engineering, Boston University, Boston, MA 02215

We have used x-ray photon correlation spectroscopy (XPCS) in a grazing-incidence small-angle x-ray scattering (GISAXS) geometry to investigate the fundamental dynamics of kinetic roughening during amorphous thin film growth of Si and WSi_2 by sputter deposition. In the late stage, surface roughening reaches a dynamic steady state in which the intensity autocorrelation function $g_2(q,t)$ becomes stationary. The $g_2(q,t)$ functions exhibit compressed exponential behavior at all wavenumbers studied. The overall dynamics are complex, but the most surface sensitive sections of the structure factor and correlation time exhibit power law behaviors consistent with dynamical scaling. We also observe a continuously variable mixing of surface and bulk scattering signals by controlling the x-ray penetration and escape depths. Under conditions where the x-ray signal comes from both the growth surface and the thin film bulk, oscillations in temporal correlations arise from coherent interference between scattering from stationary bulk features and from the advancing surface.

WK-11

Controlling the Functional Properties at Polar Oxide Interfaces

Divine Kumah

Department of Physics, North Carolina State University, Raleigh, NC 27606

The structural, electronic and magnetic response at interfaces between complex oxide materials has led to the discovery of a wide range of unique electronic, orbital and magnetic. The ability to form heterostructures comprising of atomic layers of different oxide materials with differing properties using molecular beam expitaxy has led to the realization of emergent interfacial phenomena including multiferroicity, high mobility two dimensional electron gases and superconductivity which are not found in the constituent materials. A key research question relates to understanding the origin of these interface-induced phenomena. Using high-resolution synchrotron diffraction to image the interfacial structures of oxide heterostructures, we show that structural distortions driven by interfacial polar distortions significantly affect their electronic, orbital and magnetic properties. This talk will focus on rare-earth nickelate and manganite thin films where observed structural distortions affecting the transition metal-oxygen bond lead to metal-insulator and magnetic transitions and the role of *in situ* synchrotron x-ray scattering in understanding and manipulating these transitions.

WK-11

Topotactic Transformations of Oxide Thin Films

Steven J. May

Department of Materials Science and Engineering, Drexel University, Philadelphia, PA 19104

Advances in thin film deposition techniques have enabled the synthesis of ABO_3 perovskite films and superlattices with monolayer precision and abrupt interfaces between dissimilar compounds. Despite these great strides made in oxide film processing, limitations remain, including the restricted range of anion chemistries and difficulties in stabilizing cations in unfavored oxidation states. In this talk, I will describe the use of topotactic post-growth reactions to alter the composition of complex oxide films while retaining the epitaxial crystalline framework. Examples will include low-temperature reversible oxidation and reduction of epitaxial oxides and fluorination reactions to realize oxyfluoride perovskite films. Fundamental open questions regarding these reactions will be discussed, highlighting the need for *in situ* x-ray characterization to obtain a better understanding of how the topotactic transformations occur across various length scales.

WK-11

Dynamics of Materials Synthesis on the Elementary Building Block Level

Gyula Eres

Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831

In this talk I discuss a couple of examples of unexpected behavior in thin film growth kinetics of $SrTiO_3$ by pulsed laser deposition (PLD) observed with real-time surface x-ray diffraction (SXRD) measurements. In addition to being instrumental in advancing the understanding of condensed matter physics phenomena at complex oxide interfaces, PLD is an important method for studying fundamental film growth physics because it naturally incorporates multiple time scales and multiple length scales. Perhaps more than any other materials synthesis method PLD would tremendously benefit from the new generation of *in situ* probes made possible by the improved coherence and increased brightness of the APS upgrade. The unexpected behavior in PLD relates to appearance of cooperativity in the time-dependent coverage data and quasi step flow growth mode. The presence of these phenomena is indicative of self-assembly and self-organization in film growth that go beyond the simplistic models of crystal growth by surface diffusion and random nucleation. It is an intriguing question whether the self-assembly process occurs and is possible to control on length scales different from atoms. And if so, what would the building blocks (BB) be in such a process. X-rays are ideally suited for covering multiple length scales and x-ray photon correlation spectroscopy (XPCS) would provide an unprecedented picture of the self-assembly from such BBs. Synthesis of new materials can be envisioned by combining different type building blocks associated with specific functionality. The most intriguing aspect of PLD for XPCS is the quasi step flow growth mode. The island size distributions obey scaling and two distinct regimes of island growth, diffusion and attachment limited kinetics. A crossover from diffusion limited to attachment limited regime, which occurs in a narrow island size range, indicates a change in fundamental surface transport processes from diffusive to ballistic transport. Direct measurements in the quasi step flow regime reveal that PLD self-organizes island growth on a length scale consistent with temperature and PLD conditions. This scale independent step flow is made possible by ballistic interlayer transport. In the limiting case, ordinary step flow is the asymptotic limit of quasi step flow for infinite size islands.

Research sponsored by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division.

WK-11

Contacts in Advanced CMOS: History and Emerging Challenges

Christian Lavoie
IBM T.J. Watson Research Center, Yorktown Heights, NY 10598

With the continued evolution of CMOS technologies, which included recent changes in both device geometries and contact schemes, the contact length of advanced devices is now reaching below 20 nm. At these dimensions, material microstructure (grain size) becomes similar to contact size, interface quality becomes critical to device performance and mechanisms that cause defects (such as stress driven diffusion or segregation) become prevalent in certain situations.

In this presentation, we will describe the evolution of materials used for contacts through the scaling of CMOS technologies, putting emphasis on where high-throughput synchrotron measurements have direct impact on technology development. With the expected reduction in size for contacts and metal lines, and the complications associated with non-planar devices, the criteria for material selection are now broadening so that monitoring and understanding reactions at interfaces within nanostructures is becoming even more critical. In the near future, the fabrication of new arrays of nanostructures in manufacturing facilities combined with the availability of x-ray beams with enhanced characteristics will certainly expand our understanding of such interfacial reactions at these dimensions.

WK-11

Understanding Polycrystalline Solar Absorbers: *In situ* X-ray Characterization of CIGS

Mariana Bertoni
Arizona State University, Tempe, AZ 85281

The performance of many materials is regulated by inhomogeneously distributed nanoscale defects. These defects can take the form of impurities, stoichiometric variations, microstructural misalignments, and secondary phases - the majority of which are created during growth or processing. For the particular case of polycrystalline solar absorbers the compositional inhomogeneities inherent of these systems combined with the recombination characteristics of grain boundaries (GB) play a crucial role that depending on the material system could be benign or detrimental to the overall solar-cell efficiency.

In this work we will present our results using *in operando* and *in situ* x-ray microscopy (XRM) techniques to address the correlation of composition, structure and electrical performance for thin film absorber layers of industrial relevance.

Our studies allow for the one to one correlation of electrical properties and compositional variations at high resolution, which show with unprecedented statistical meaningfulness the impact of elemental the elemental distribution on the electrical properties of these films.

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Coherent X-ray Methods Enabling Control of Interfaces in Electronic Materials

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Coherent x-ray scattering and diffraction methods present a series of new opportunities in the characterization and design of electronic materials. We will focus in particular on two examples: the creation of buried interfaces within semiconductor heterostructures and the control of the growth of two-dimensional electronic materials. With respect to semiconductor heterostructures created by epitaxial growth techniques, a variety of interface structural effects emerge as a result of growth phenomena including plastic relaxation and step dynamics, which create features within the electronically relevant layers of the heterostructure [1]. Other nanoscale structural features can result from the formation of metal-semiconductor interfaces during device formation [2]. X-ray nanobeam methods presently provide for the *ex situ* evaluation of these devices and materials using coherent diffraction [1,2]. *In situ* coherent scattering methods promise to allow surfaces and interfaces to be probed during synthesis. Doing this would allow the creation of materials with favorable structural features, for example step distributions with favorable electronic properties.

In two-dimensional materials, tremendous opportunities in the design and development of materials for electronic and optical applications would be enabled by controlling of the strain, interface structure, lateral size, edge structure, and similar parameters. Synthesis methods, including chemical vapor deposition are beginning to allow control over these parameters, including the potential to create narrow graphene nanowires [3]. These methods, however, involve a complex series of structural phenomena including surface faceting [4] that are only beginning to be understood. *In situ* coherent x-ray methods will enable important questions in the synthesis of 2D materials to be answered, using a combination of imaging, scattering, and spectroscopic techniques.

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