Science at the Hard X-ray Diffraction Limit (XDL2011)

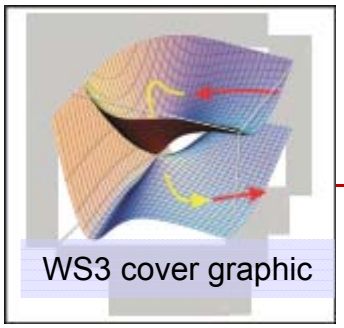
Don Bilderback* and Georg Hoffstaetter*, Cornell University

October 20, 2011

- Cornell hosted six, two-day international workshops in June of 2011 with 488 participants
- Focus was diffraction limited, high-repetition rate, hard x-ray sources, such as Energy Recovery Linacs (ERLs) and Ultimate Storage Rings (USRs).
- These source will provide high coherent flux and ultra-intense nanometer-scale x-ray probes.
- X-ray pulses occur at MHz to GHz repetition rates with durations of 50 fs to 10s of ps.

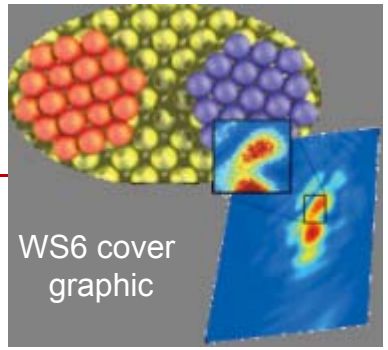
Participants in the 2nd workshop on Biomolecular Structure

- Organizers & Sponsors: Cornell, DESY, SLAC, KEK with additional US Federal support from NSF and DOE
- *for the organizers, speakers, and editors of XDL2011 workshops


WS3 cover graphic

Workshop Titles & Organizers

http://erl.chess.cornell.edu/gatherings/2011_Workshops/index.htm


WS6 cover graphic

WS1: Diffraction Microscopy, Holography and Ptychography using Coherent Beams
Organizers: Janos Kirz (Lawrence Berkeley National Lab), Qun Shen (National Synchrotron Light Source II), & Darren Dale (Cornell University)

WS2: Biomolecular Structure from Nanocrystals and Diffuse Scattering
Organizers: Ed Lattman (Hauptmann-Woodward Medical Research Inst.), Mavis Agbandje-McKenna (University of Florida), Keith Moffat (University of Chicago), & Sol Gruner (Cornell University)

WS3: Ultra-fast Science with "Tickle and Probe"
Organizers: Robert Schoenlein (Lawrence Berkeley National Laboratory), Brian Stephenson (Argonne National Laboratory), Eric Dufresne (Advanced Photon Source) & Joel Brock (Cornell University)

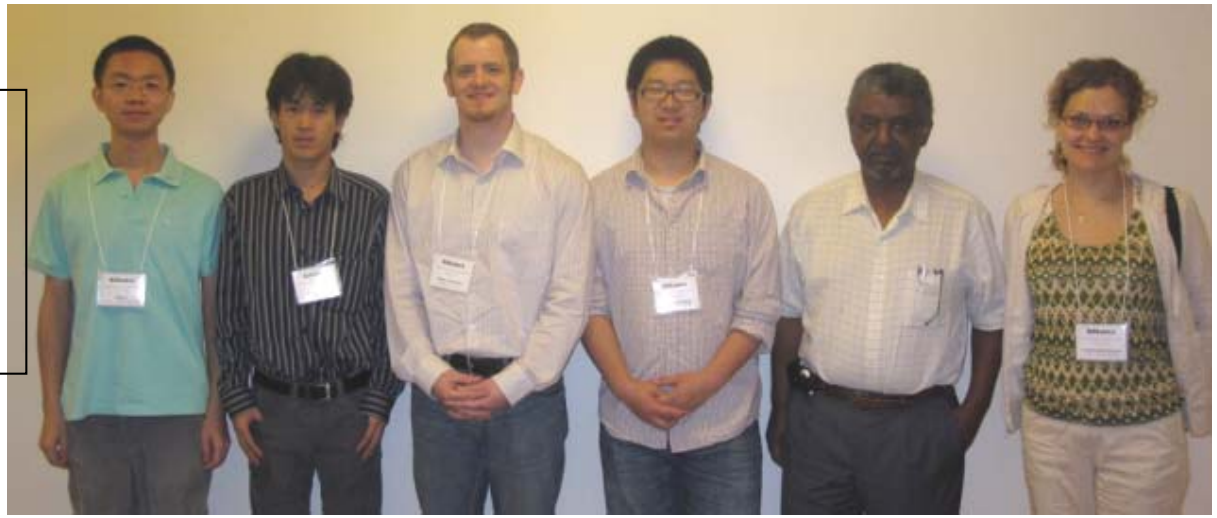
WS4: High-pressure Science at the Edge of Feasibility
Organizers: Russell J. Hemley (Carnegie Institution of Washington), Neil Ashcroft (Cornell University), Roald Hoffmann (Cornell University), John Parise (SUNY Stony Brook), & Zhongwu Wang (Cornell University)

WS5: Materials Science with Coherent Nanobeams at the Edge of Feasibility
Organizers: Christian Riekel (European Synchrotron Radiation Facility), Simon Billinge (Columbia University), Kenneth Evans-Lutterodt (Brookhaven National Laboratory), & Detlef Smilgies (Cornell University)

WS6: Frontier Science with X-ray Correlation Spectroscopies using Continuous Sources
Organizers: Mark Sutton (McGill University), Simon Mochrie (Yale University), & Arthur Woll (Cornell U.)

NSF Supported 20 Student Travel Awards

WS2: (L to R) Bing Li (Carnegie Institute), Junyue Wang (Argonne National Laboratory), Dane Tomasino (Washington State U), Dongzhuo Zhang (California Institute of Technology), Guebre Tessema (NSF), Svetlana Kharlamova (Carnegie Institute)

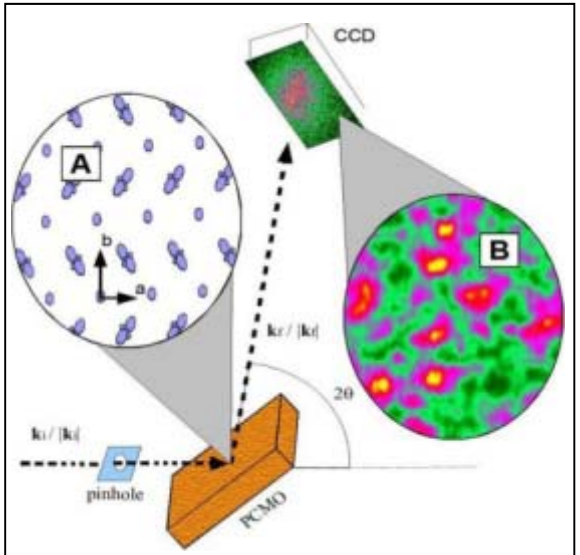


Some of the student participants

WS6: (L to R) Chenhui Zhu (Argonne National Laboratory), Dan Parks (University of Oregon), Gozde Erdem (Boston University), Jake Davis (Boston University)

Overview: Outstanding problems in materials

Simeon Billinge (Columbia), Paul Evans (U of Wisconsin)
& Reinhard Boehler (Carnegie Institution of Washington)



Coherent diffraction imaging of electronic textures in correlated materials. Information is available on nanometer spatial scale. Josh Turner et al., New J. Phys. 10 (2008) 053023.

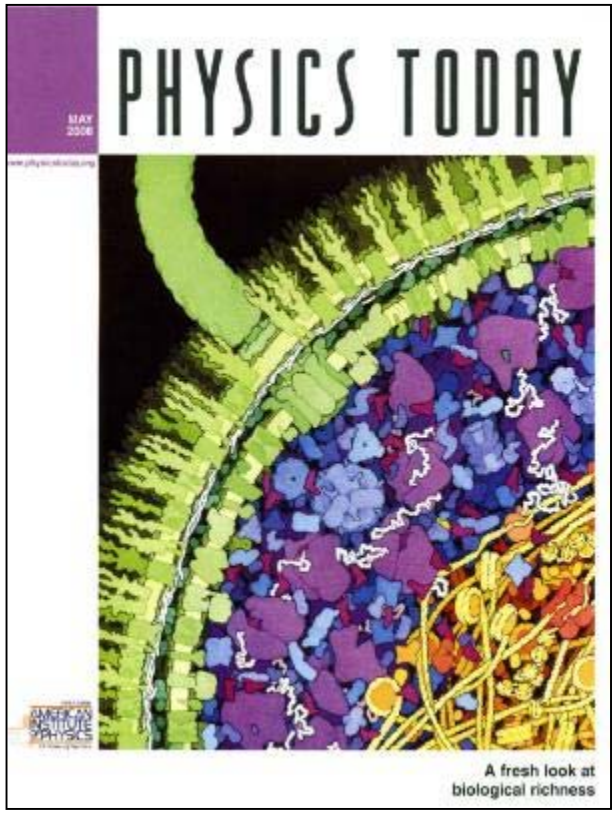
"Advances in materials science lie on the critical path of many technological solutions to mankind's most pressing problems, such as sustainable energy, environmental remediation and health. Increasingly we seek materials that have directed functionalities, in analogy with enzymes in biological systems, that can be built up into more complicated devices. This necessitates the study of materials of increasing complexity, for example, larger unit cells, more complicated compositions, heterostructures on the nanometer and micrometer length-scales, and structural modifications on the nanoscale. Nanostructured materials are at the heart of many of these proposed technologies.", Simeon Billinge

"These emerging hard x-ray sources can be focused to small spot sizes, at which they can provide high-resolution structural information via either diffractive imaging or scanning techniques. The fs to ps bunch duration of the electron bunches at these sources inherently allows such probes to provide time resolution simultaneously. Key examples of the scientific impact of these developments will arise in the study of both reversible and irreversible materials processes. The scientific needs for these probes arises in the study of fundamental excitations, GHz mechanics, dynamics in magnetic and spintronic devices, and dynamics and extreme conditions in complex oxides, etc.", Paul Evans

"Melting at high pressure is of fundamental interest and plays a key role in estimates on temperatures in planetary interiors and on the dynamics of dynamos creating magnetic fields and dynamics of motion in planetary mantels and plate tectonic. Melting temperatures of both metals and silicates/oxides measured statically in laser-heated diamond cells are in serious disagreement with those obtained from shock experiments for transition metals. Diffraction measurements on a millisecond resolved time sequence could resolve this issue to follow the structural evolution during the melting-freezing event." Reinhard Boehler

Overview: Outstanding problems in biological science

Ilme Schlichting (Max Planck Inst. Heidelberg) & Mavis Agbandje-McKenna (Univ. Florida)



The dream of the structural biologist is to visualize cellular components (e.g., macromolecules, complexes and organelles) at high, 3-D spatial and temporal resolution in defined functional states. This information is vital to understand function of cellular processes, and informs on cellular regulation, which helps the development of disease treatment strategies.

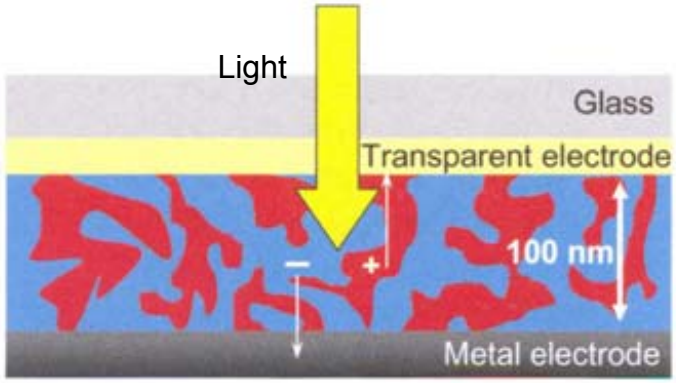
Many cellular components have poorly understood structures, including weakly bound complexes, membrane proteins, transient intermediates (including catalysis and folding), chromatin, the nuclear pore complex, the Golgi apparatus, membrane fusion pores, many viruses – the list goes on.

Conventional x-ray methods are limited by the need for large crystals, exposure times that are longer than the process being studied, and radiation damage. **The intense, temporally short, coherent nanobeams from ERLs and USRs open vast new areas for study**: Nanobeams enable structural determination from crystals that are only practically available in the submicron range. Nanobeams also enable time-resolved solution scattering studies of transient structures in fluid jets. Coherent diffraction methods yield structural information on non-periodic cellular systems on nanometer length scales. Intense subpicosecond pulses provide time-resolved snapshots of triggerable proteins. The high brilliance enables rapid 3-D ptychographical methods on hierarchical materials (e.g., bone, teeth, shells).

Determine 3D Nanomorphology for Improving Organic Solar Cells

Harald Ade, North Carolina State University

From XDL2011 WS1: Diffraction Microscopy, Holography and Ptychography using Coherent Beams

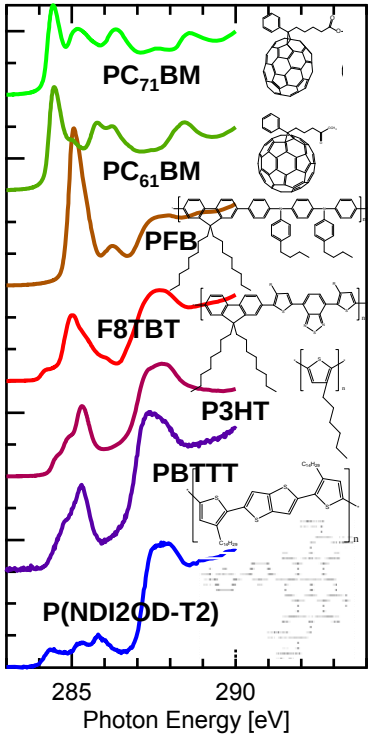


Solution-processed organic solar cells are attractive as low-cost photovoltaic technology. They can be spin-coated or printed like a newspaper or ink-jet coated onto flexible substrates of plastic or glass. Currently most designs are based on bulk heterojunction (BHJ) structures of 100 to 200 nm thickness. Even a two-phase description is idealistic. A complex morphology of at least three phases might have to be considered. To be efficient, the inter-digitated electrodes must be only separated by 10 to 30 nm.

To establish full control, one needs to control the average domain size, domain size distribution, domain purity and domain interface widths. For each of these novel materials systems, the miscibility, morphology and domain purity, connectivity of domains, crystallinity, phase and interface properties need to be measured in order to understand device performance deeply and rationally seek processing and materials improvements.

Characterization of 3D structure of organic blends with ~10 nm resolution poses a key technical challenge. High-resolution hard x-ray scattering, electron tomography and TEM have only limited electron density contrast for these polymer/polymer blends, limiting the use of conventional tools for these materials. **A new suite of analysis tools such as 3D resonant ptychography or holography with compositional sensitivity are required**.

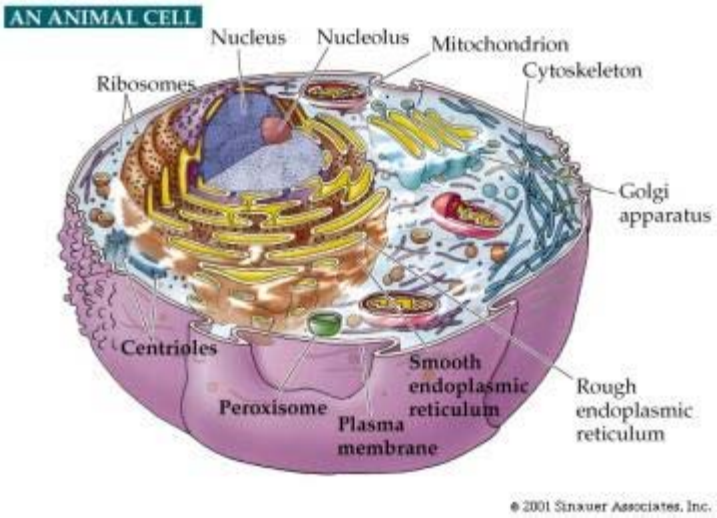
These forms of coherent imaging require bright sources and would be well matched to an **Energy Recovery Linac.** Ideally, multiple energies near the carbon K 1s absorption edge (i.e. 260-320 eV) are utilized to provide maximum compositional sensitivity. **Thus, advanced imaging tools enabled by an ERL would be able to make tremendous contributions to improving Organic Solar Cells.**



Structures of biological cells with < 10 nm resolution in 3D

Chae Un Kim, Cornell University

From XDS2011 WS1: Diffraction Microscopy, Holography and Ptychography using Coherent Beams



Visualization of sub-cellular components in 3D at high resolution is essential to understanding how cells function. However, the currently existing microscopic techniques have limitations for this purpose. Optical microscopy cannot provide high enough resolution (typically worse than 200 nm) and electron microscopy is poorly suited for thick cellular samples, requiring >1,000 sections.

X-ray diffraction microscopy (XDM) is a lensless microscopic technique and uses the high penetration power of X-rays to image biological cell (of a few microns in size) at high resolution in 3D. **XDM offers potential to image whole cancer cells or the structure and connectivity of the sub-cellular organelles in 3D at 5-10 nm resolution.**

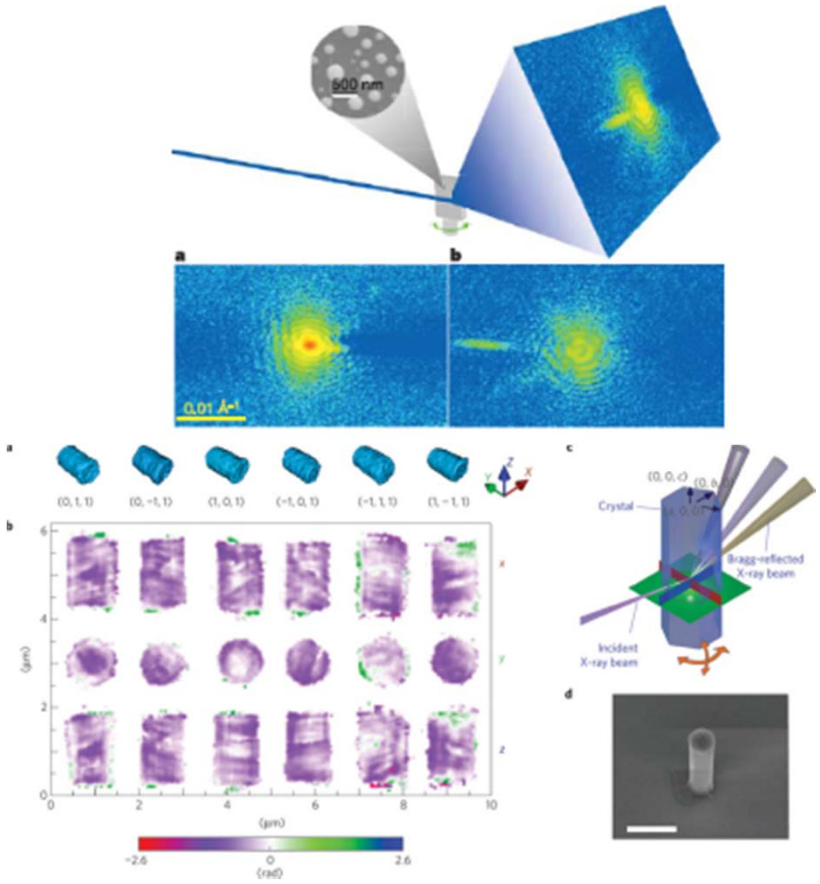
The fundamental image resolution of XDM for biological samples is set by radiation damage. A variety of cryopreservation methods have been developed, including ambient plunge-freezing and high-pressure cryocooling techniques. The cryopreservation of hydrated samples replaces water with either low-density amorphous (LDA) or high-density amorphous (HDA) ice. Both LDA and HDA ice exhibit density fluctuations, whose structure and origins are presently poorly understood, which limit the use of cryopreservation for XDM.

Probing local structures of HDA/LDA ice requires highly brilliant/coherent nano-focused X-ray beams. The X-ray sources such as ERLs/USRs provide an ideal X-ray probe for this types of study. After better accounting for these density fluctuations, we anticipate that **the highly brilliant and coherent X-ray beams from ERLs/USRs will allow, for the first time, study of cellular structures in 3D with 5 to 7 nm spatial resolution. Other applications are the imaging of chromosomes and origins of crack formation in solid state materials.**

Materials Processing

Ross Harder, Argonne National Lab

Workshop 1: Diffraction Microscopy, Holography and Ptychography using Coherent Beams



*Top: Coherent Bragg diffraction from a nanocrystal [Pfeifer, Nature, **442**, 63]. Bottom: Reconstructed amplitude and phase of a single ZnO nanorod for six Bragg reflections [Newton, Nature Materials, **9**, 120]*

Since the mid 1950's researchers have only been able to speculate on the microscopic mechanisms of the most fundamental aspects of grain nucleation and defect formation. Annealing twins, which play a critical role in the mechanical strength of FCC metals, are seen to emanate from grain boundaries during growth. Yet very little is known about the mechanisms through which they form at specific locations on grain boundaries.

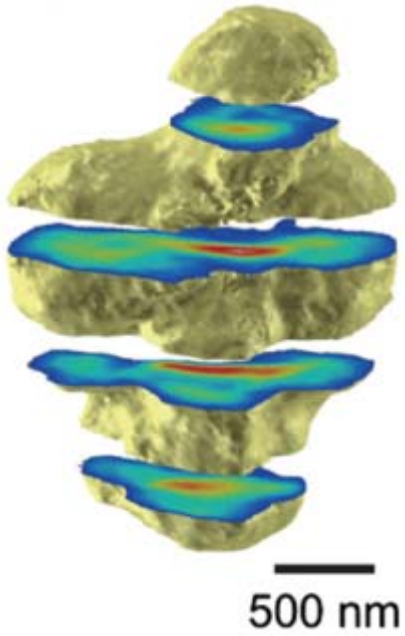
Coherent diffraction imaging in the Bragg geometry offers a unique capability to study the mechanisms of grain growth on the nanoscale. **Unique to Bragg CDI is an ability to study a single crystalline domain, buried in a thick polycrystalline sample, with nanometer spatial resolution**. Because the method exploits the coherent scattering in the vicinity of Bragg peaks to obtain images of the sample, it can also be used to **map strain in the crystalline lattice, which can be caused by defects and dislocations**.

Using the two to three orders of magnitude greater coherent hard x-ray flux afforded by an ERL or USR source, we will be able to **image the evolution of such materials properties on time scales of minutes at sub ten nanometer resolution**.

Microscopic imaging of single chromosomes

Yoshinori Nishino, Hokkaido University

Workshop 1: Diffraction Microscopy, Holography and Ptychography using Coherent Beams



Human Chromosome
Nishino, et al., PRL **102,** 018101 (2009), from 38 images from -70 to +60 degrees, estimated resolution of 120 nm, SPring-8 data.

The chromosome is the package of DNA and proteins and its structure is of utmost biological significance in understanding the mechanism of faithful transmission of the genomic information from one generation to the next. However, **the structure of the chromosome is not well understood** despite a long history of research, because there has been no adequate microscopy to visualize them. For example, **conventional light microscopy does not have enough resolution, and transmission electron microscopy falls short of the penetration power to observe sub-cellular organelles intact**.

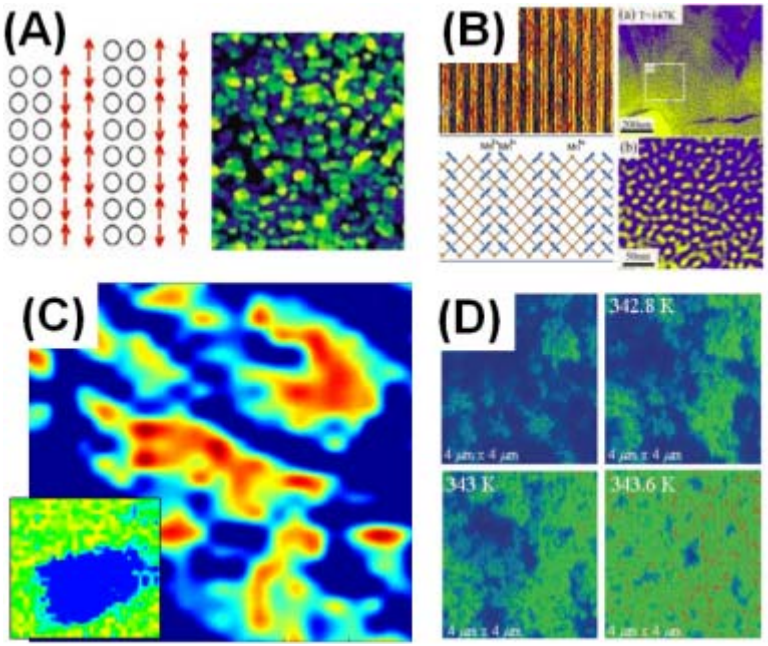
X-ray diffraction microcopy (XDM) recently provided a new opportunity to visualize thick organelles, such as chromosomes, in three dimensions with high image contrast. X-ray fluorescence technique also provides a unique way to map a specific element in sub-cellular organelles. For chromosomes, mapping phosphorus is especially valuable as it provides how DNA backbones are internally folded.

By carefully controlling the radiation dose and employing cryopreservation, **the high brilliance of an ERL or USR** will enable to effectively **visualize organelles in 3D at 10 nm resolution.**

Nanoscale Phase Separation in Correlated Oxides

Oleg Shpyrko, University of California at San Diego

Workshop 1: Diffraction Microscopy, Holography and Ptychography using Coherent Beams



Examples of nanoscale inhomogeneities in a variety of strongly correlated systems: ***(A)*** *Scanning Tunneling Spectroscopy of the inhomogeneous superconducting gap distribution as well as stripe (or checkerboard) patterns in underdoped high-T_c superconductors [Tranquada, Nature,* ***429****, 534; Dagatto, Science,* ***271****, 618]* ***(B)*** *Phase separation in Colossal Magnetoresistive (CMR) Manganites [Mori, Nature,* ***392****, 473; Mathur, Physics Today, Jan 2003, p26]* ***(C)*** *Charge-Density Wave [Shpyrko, Nature,* ***447****, 68] and Spin-Density Wave (inset) [Evans, Science,* ***295****, 1042] domains in Chromium;* ***(D)*** *Coexistence of Conducting and Insulating domains in VO_2 at the onset of the Metal-Insulator Transition [Qazilbash, Science,* ***318****, 1750]*

Strongly correlated systems often feature **competing spin, charge, orbital and lattice degrees of freedom**, which result in spontaneous emergence of **nanoscale inhomogeneities**, which **can strongly influence material properties**. These domains typically occur as a result of competition between phase separation and strong correlations. However, it is not yet clear whether domain structure arises primarily from these interactions, or if crystalline imperfections – such as lattice strain, defects or inhomogeneous distribution of dopants – may strongly influence formation of textured domain patterns.

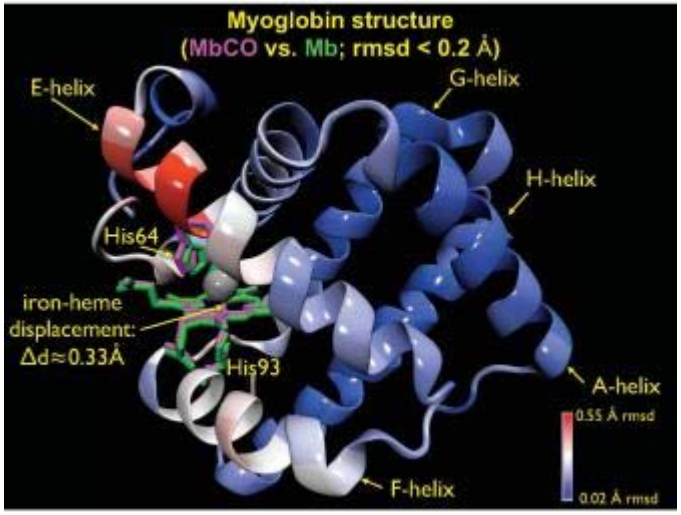
Resonant microdiffraction and lens-less imaging can be used **to study spin, charge, lattice and orbital degrees of freedom in correlated electron systems, as well as strain and defects, with nanometer-scale resolution**. These types of microscopy studies will answer many fundamental questions about how electronic correlations emerge, what role crystalline disorder plays in their formation, and the interplay between these degrees of freedom, which results in complex competition and coexistence between various ground states.

The high coherent flux produced by an USR/ERL will make it possible to study the dynamics of this competition at timescales 100 to even 10,000 times faster than at third-generation sources. Imaging structures will be 100 times faster than at third generation sources, such that nanoscale resolution could become routinely accessible.

New opportunities in time-resolved solution scattering of proteins

Phillip Anfinrud, NIH

From XDL2011 WS2: Biomolecular Structure from Nanocrystals and Diffuse Scattering



Structural changes in myoglobin upon laser flash photolysis of bound CO, as a proxy for O_2 binding, have been determined using Laue methods. The duration of the storage ring pulse limited the time resolution to ~100 ps.

(from Cho et al., PNAS 2010 **107**,7281)

The ability to observe **structural changes in biomolecules while they function** has been a goal of cellular biology for many decades. **NMR is limited** to tens of microseconds, the need for large quantities of (often) isotopically-labelled material, lengthy scan times, and difficulties of reaction initiation in the NMR machine.

Time-resolved SAXS (Small Angle X-ray Scattering) & WAXS (Wide-Angle X-ray Scattering) are valuable complements to time-resolved Laue crystallography, time-resolved laser spectroscopy, and computational modeling - and increasingly useful in studies of protein structure, function, and dynamics. **Time-resolved solution SAXS patterns are exquisitely sensitive** to protein volume changes and mass transport into and out of the protein. **Time-resolved WAXS fingerprints contain a wealth of structural information down to 2.5 Å**, and provide **stringent constraints** for models of conformational states and structural transitions between them.

In practice, x-ray pulses are directed through a flow of specimen solution to mitigate radiation damage. The minimum time resolution achievable using x-rays from storage rings is limited by the x-ray pulse width to ~100 ps. ERLs improve the time resolution of SAXS/WAXS to **~100 fs, orders of magnitude better** than with present day storage rings.

Micro x-ray beams and microfluidics to crystallize and solve protein structure

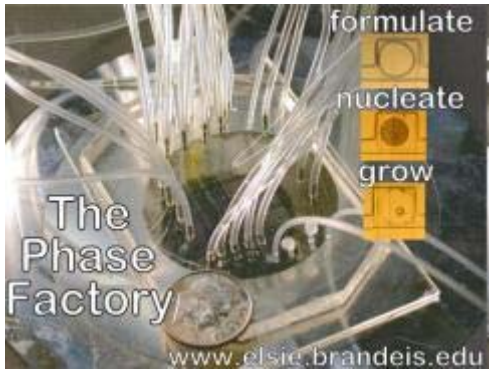
Seth Fraden, Brandeis University

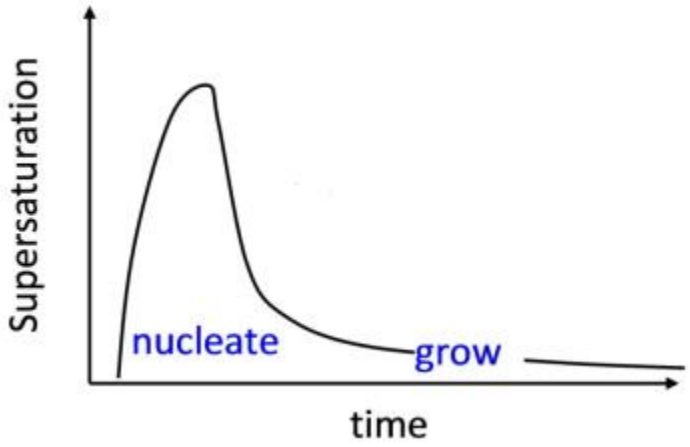
Workshop 2: Biomolecular Structure from Nanocrystals and Diffuse Scattering

Crystallization is the major bottleneck in the crystallographic determination of biomolecular structure. **Membrane proteins** and **macromolecular complexes** are particularly reticent to crystallize.

The key to optimizing crystallization is the separation of nucleation and growth, and to obviate the need to grow large crystals. To nucleate a crystal on a short enough time scale to be practical requires a large supersaturation, which often leads to rapid crystal growth and resulting in crystals which have defects and diffract poorly. **Microfluidic devices** are being devised to temporarily bring the protein solution into deep supersaturation where the nucleation rate is high and then, after a single crystal has nucleated, decrease the supersaturation of the solution. This is done either by lowering the protein or precipitant concentrations, or by raising temperature in order to suppress further crystal nucleation and to establish conditions where slow, defect free crystal growth occurs.

The result is a stream of microdrops, each containing a tiny single crystal. These are conveyed sequentially at kHz rates into an intense ERL/USR microbeam for a single diffraction pattern before radiation damage destroys the crystal. Complete data sets are then obtained by merging many diffraction patterns. **Since the crystals are tiny and the x-ray patterns are weak, x-ray source brilliance is essential to provide sufficient flux density at the sample** to obtain data sets in reasonable time.



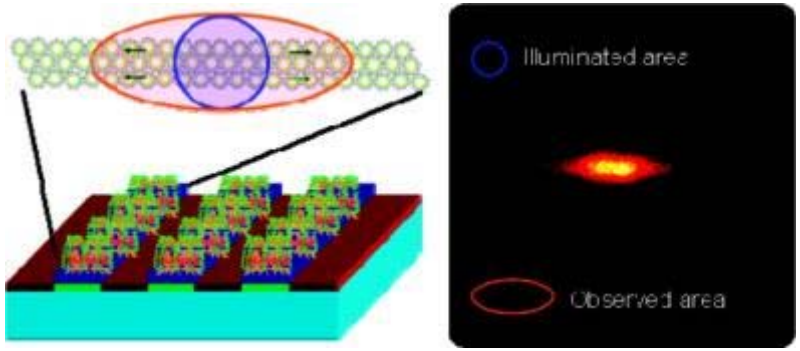


XOp microfluidic chip optimizes crystal growth by varying the degree of supersaturation versus time. See www.elsie,brandeis.edu; Shim et al., JACS **127** (2007) 8825.

Tracking energy flow in light-harvesting antenna-proteins

Ed Castner, Rutgers

From XDL2011 WS3: Ultrafast Science with "Tickle and Probe"



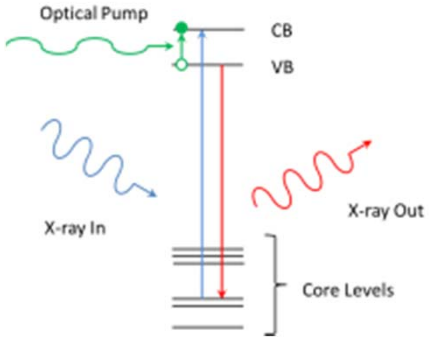
[We] report the first observation of long-range transport of excitation energy within a biomimetic molecular nanoarray constructed from LH2 antenna complexes from Rhodobacter sphaeroides.

Escalante, et al., *Nano Letters, 2010.* **10**(4): p. 1450-1457

Biomimetic researchers copy or incorporate biological processes or components into engineered materials, processes, or devices. For example, light-harvesting antenna-proteins collect solar energy and efficiently transport the resulting electron-hole pair to a photosynthetic reaction center where chemical synthesis occurs. The ability of light harvesting molecules to efficiently guide energy makes them intriguing candidates for components in nanofabricated photonic devices.

The electronic excitations travel up to 50nm and are believed to last for 100's of ps in an individual protein. In the example on the left, an nanofabricated array of antenna-proteins transports the excitation over microns.

Resonant Inelastic X-ray Scattering (RIXS) measurements provide access to the unoccupied electronic structure information present in XAS and correlate it with the occupied electronic structure information present in XES measurements, producing a complete description of valence excitations.



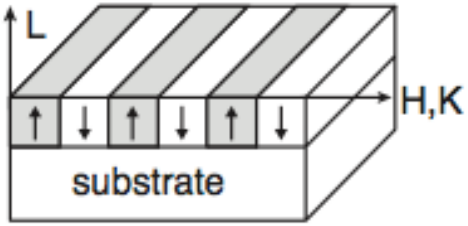
Temporally (ps) and spatially (10 nm) resolved RIXS could **map the migration of the electronic excitation following (optical) photoexcitation.** The energy tunability, high spectral brightness, few nm x-ray spot sizes, and high repetition rate, sub-ps pulses of the ERL/USR enable this type of measurement.

Speed Limits for Ferroelectric/Multiferroic Switching

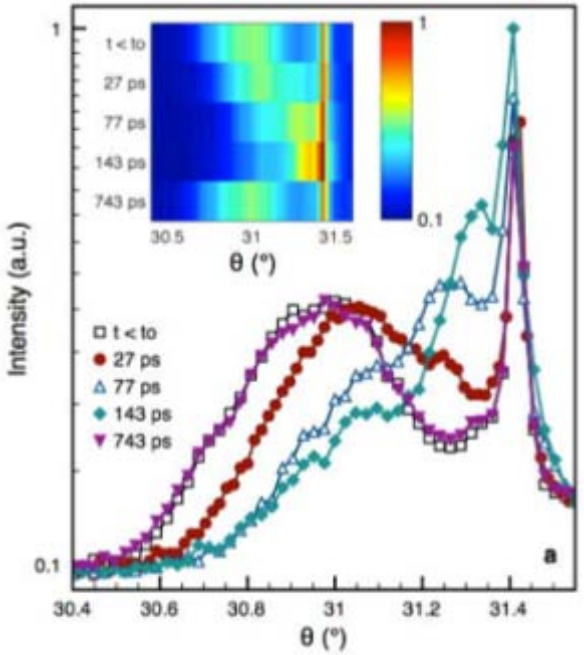
Aaron M. Lindenberg, SLAC National Accelerator Laboratory

From XDL2011 WS3: Ultrafast Science with "Tickle and Probe"

Complex-oxide multiferroic materials are promising candidates for advanced technological applications. A high-repetition-rate, ultrafast, hard x-ray source will provide the capability to study the speed limits to switching in these materials.



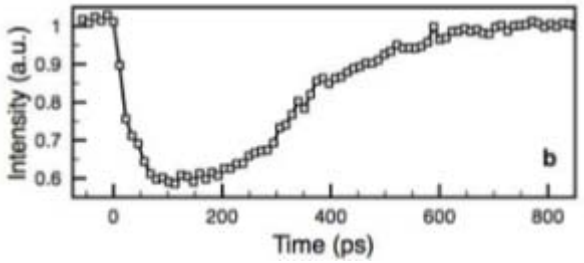
Similar to ferromagnets, ferroelectrics minimize their energy by breaking into antiphase domains, frequently with a characteristic length scale. Short range ordering of these domains produces diffuse x-ray scattering features in addition to the sharp Bragg peaks from the lattice.



The ferroelectric stripe phase of $PbTiO_3$ can by destroyed or enhanced by an ultrafast optical pulse with rapid relaxation on few nanosecond time-scales, enabling high-rep-rate experiments of ultrafast switching and nucleation dynamics.

T=430C ferroelectric phase ($PbTiO_3$ on $DyScO_3$)

- Reversible optically - induced switching from ferroelectric to paraelectric phase at fluences <100 μJ/cm^2
- Recovers on few hundred picosecond time-- - scale

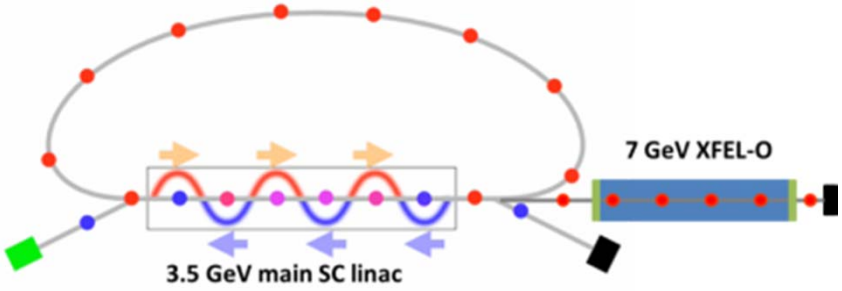


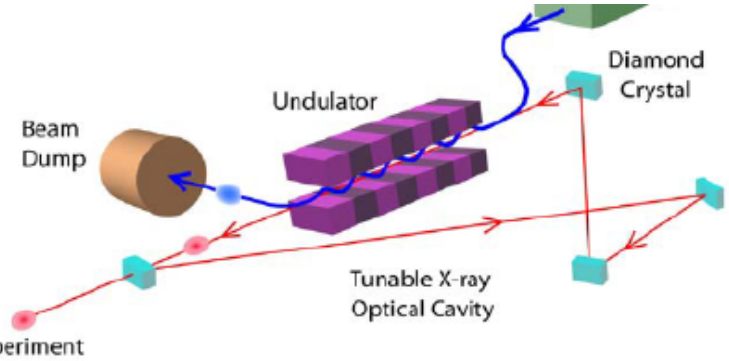
The flux of the ERL/USR will enable ultrafast, high-repetition rate, pump-probe studies with much less intense pump pulses. One expects flux increases of 10^4 relative to existing slicing and low-alpha sources

Towards Fourier-limited X-ray Science

Shin-ichi Adachi, Photon Factory, KEK & PREST, JST

From XDL2011 WS3: Ultrafast Science with "Tickle and Probe"

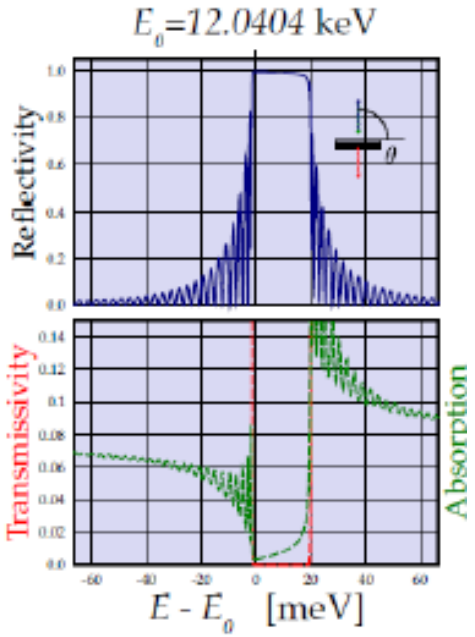




K.-J. Kim

A continuous sequence of ultralow emittance multi-GeV electron bunches and a low-loss optical cavity constructed from high-reflectivity Bragg crystals can create an X-ray FEL Oscillator (XFELO). The x-ray beam from an XFELO would be Fourier transform limited, have tunable wavelength, and the peak power would be small enough to not adiabatically damage samples. The beam will have an average **spectral brightness 10^3-10^5 x greater** than available on existing or planned sources.

X-ray Beam Properties	
Photons/pulse	10^9
Rep rate	1-100 MHz
dE/E	10^{-6}
τ	1 ps
K.-J. Kim, et al., Phys. Rev. Lett. **100** (24) (2008).	



Y. Shvyd'ko

The X-ray beams produced by an XFELO would be fully Fourier-limited, upgrading existing techniques or enabling novel ones such as nonlinear X-ray optics, inelastic scattering, two-photon correlation spectroscopy, and transient grating spectroscopy. For example, the meV energy resolution would enable inelastic scattering studies of thermally generated excitations in small samples.

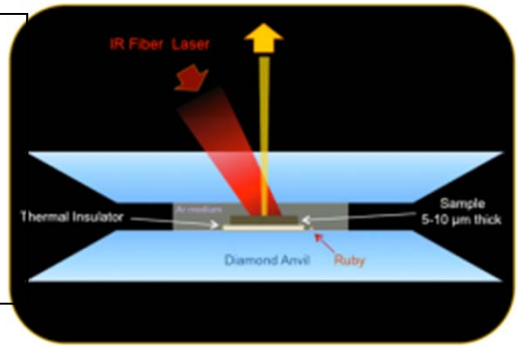
Static and Dynamic heating of Materials

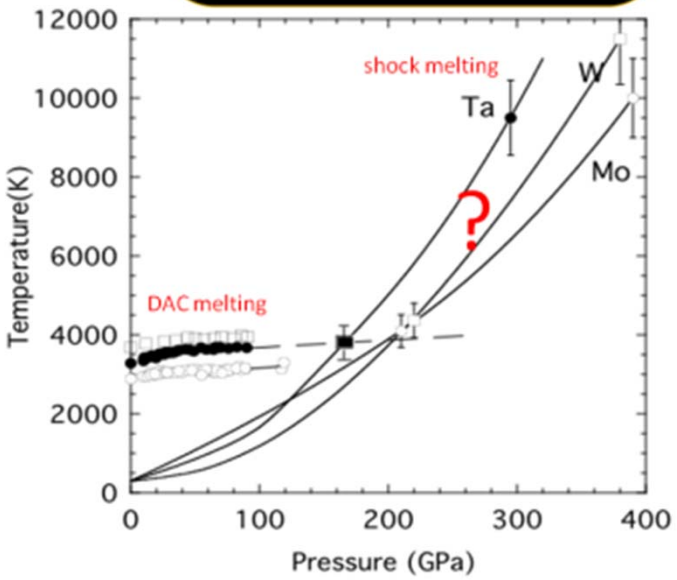
Reinhard Boehler, Carnegie Institute of Washington

XDL Workshop 4: High Pressure Science at the Edge of Feasibility

An understanding of melting phenomena at high pressure is of fundamental interest, critical for estimating planetary interior temperature, understanding magnetic fields and material transport within planetary mantels and tectonic plates. Yet serious disagreement exists (as indicated in the lower figure) when comparing the melting phase diagram, of metals & silicate oxides, measured in a laser-heated DAC and by shock driven methods. Systematic melting measurements, at extreme temperature & pressure have not been possible to do using synchrotron radiation, but recent SEM studies indicate that experimental problems can be circumvented in millisecond x-ray measurements. This would be accomplished if msec. pulse-laser heating of samples inside the DAC were monitored, in time, by sequential, microsecond x-ray diffraction study. The flux available in ERL pulses would help address the possible existence of a plastic-like state before melting of bcc metals like Ta, W & Mo. Through focusing of extremely bright ERL beams one could measure local stress-strain behavior across the pulse-laser heated sample. This would help provide estimates of sound velocity that will lead to better understanding of the Earth's core…

Diamond cell pulsed laser heating & below melting curves from DAC & shock experiments.





Understanding Planetary Interiors with an ERL

J.M. Jackson & D. Zhang / Caltech

From XDL2011 WS4: High Pressure Science at the Edge of Feasibility

An understanding of the dynamics & composition of planetary interiors will lead to new insights about the solar system and better interpretation of seismic data collected here on earth. This depends on knowledge of material characteristics such as melt viscosity, elastic constants, sound velocity and thermodynamic parameters of liquid-iron alloys and other earth materials, at pressures in excess of 100GPa and temperatures greater than 1000K.

The ERL will deliver 100 times the flux/unit energy/square micron of existing storage rings or those under construction, in the energy range of interest here. This will enable new classes of experiments, like momentum-resolved inelastic scattering (IXS) on individual grains within assemblages inside diamond anvil cells (DAC)….

X-ray stimulated nuclear resonance measurement of acoustic vibrations yield sound speed, IXS reveals anisotropy & phonon dispersion, melting & structural phases are identified by diffraction, and emission & absorption spectroscopies provide chemical information. The ERL will enable delivery of unprecedented sub 100nm focused beams for: selection and imaging of individual grains, measuring diffusion constants at microsecond time scales, and revealing liquid dynamics in the pico- to nano-second range….

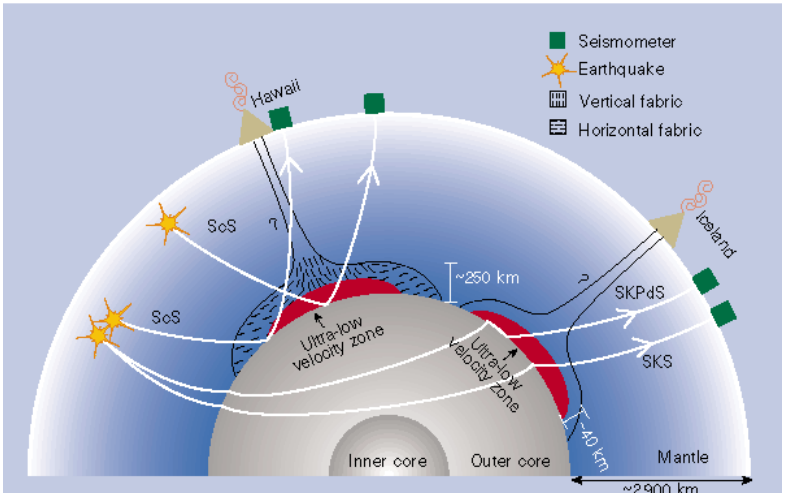


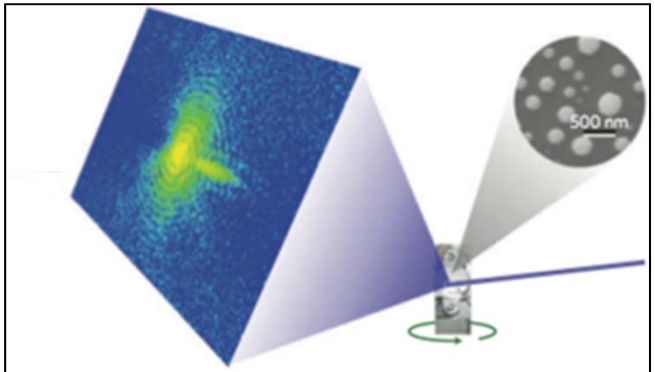
Figure illustrates why knowledge of p-,s-wave sound speed and material properties through the core, mantle and interface region is essential for seismic interpretation.

Synchrotron techniques: x-ray tomography and imaging through diamond anvil cells

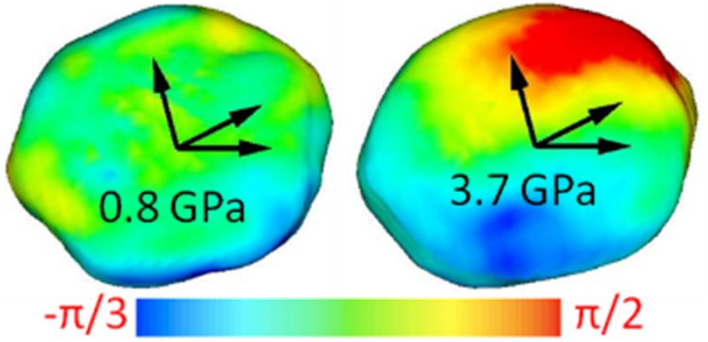
Wenge Yang -- HPSynC & Geophysical Laboratory of Carnegie Institution of Washington

Workshop 4: High Pressure Science at the Edge of Feasibility

Nanofocused x-ray beams are being used to: understand phase & grain boundary evolution, measure density in-situ, study structure of confined liquids & non-crystalline solids, and monitor strain as a function of pressure.



CDI near (111) reflection of 200nm gold particle
M.A. Pfeifer,et.al. Nature (2006). Lattice



CDI reconstruction yields lattice strain map of gold under pressure W.Yang, (early results).

Coherent diffraction imaging (CDI) of nanoscale strain has wide application for understanding nanomaterials under extreme pressure & temperature, and during deformation or chemical processing. X-ray methods are especially suited for in-situ measurement for example inside a diamond anvil cell (DAC).

Nanoscale materials often exhibit unusual strength so it is important to examine them under stresses that lead to breakdown. X-ray CDI can also be used to study pattern formation in materials synthesis, for example to understand growth limitations associated with self-assembly in the presence of surfactants.

ERL beams will have unprecedented transverse coherence and flux up to 60KeV, and the small round source is ideal for nanometer focusing and for matching horizontal & vertical coherence lengths.

Upper left illustration: CDI experiment and representative data. Lower left: Phase retrieval methods can produce 3-dimensional strain maps - color represents atomic scale lattice strain along specific directions resulting from pressures & surface truncation.

nanoXRF and nanoXANES in Art Conservation

Jennifer Mass, U Delaware and Winterthur Museum

Workshop 5: Materials Science with Coherent Nanobeams at the Edge of Feasibility

Color alteration in a Seurat painting,
as seen in the cross section of a paint chip

Preserving the cultural heritage of mankind has become a major challenge in art conservation. This shall be illustrated by color alterations in Impressionist and Early Modern Art masterpieces. Degradation of pigments by either oxidation or reduction has led to fading and color shifts all the way to catastrophic failure in the works of van Gogh, Matisse, Manet, Seurat, and Picasso.

Photo-induced degradation is a surface phenomenon, often occurring in only the **top 1-5 microns of the paint layer**, and the photo-degradation products are often minor phases within this alteration layer. The preservation of the icons of early modern art hinges on the spatially-resolved atomic and molecular characterization of these minute heterogeneous alteration layers, an analytical challenge requiring **non-destructive chemical imaging with at least nanogram sensitivity**. New rapid, high resolution, and highly sensitive chemical imaging tools for the inorganic and organic components of the disfiguring degradation layers are needed.

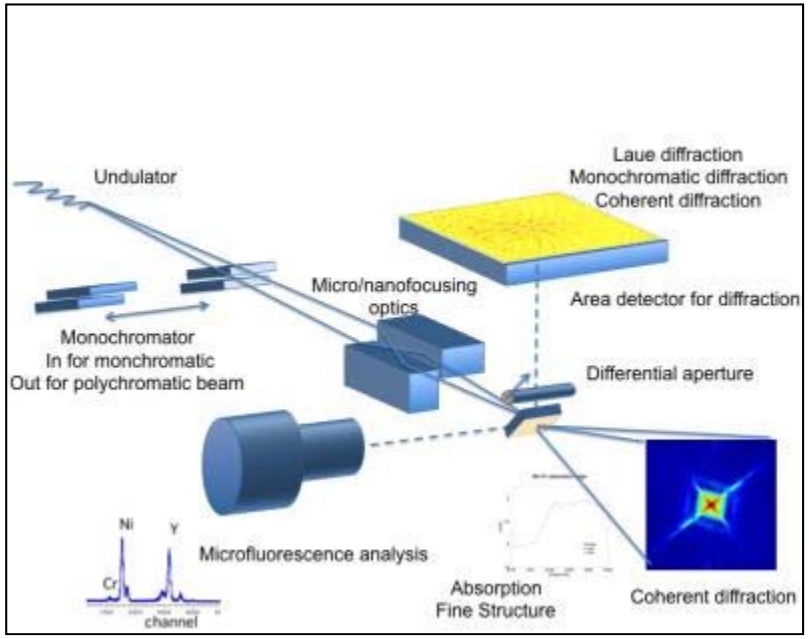
From merely analyzing the damage mechanisms, efforts in art conservation aim to detect damage in its early stages and prevent further degradation. Analyzing the surface pigment layers requires **confocal XRF and XANES microscopy with nanoscale resolution**. In order to keep up with the large amount of endangered artifacts, **fast scanning and analysis methods** will be mandatory.

An ERL will have major impact on **x-ray confocal microscopy**. So far achieved 3D resolution ranges from 1 micron to several microns, i.e. pigments could only be imaged as a whole or as an ensemble. Only the **unprecedented average brilliance of an ERL** will make such an highly efficient chemical nanoprobe feasible.

3-D Nanodiffraction to Improve Polycrystalline Materials

Gene Ice, Oak Ridge National Laboratory

Workshop 5: Materials Science with Coherent Nanobeams at the Edge of Feasibility



Schematic multi-probe 3-D nanoprobe station (Courtesy of G. Ice)

Improving polycrystalline materials, such as metals and ceramics, is a fundamental goal of materials science. Materials behavior is dominated by defects and heterogeneities on micron and submicron length scales, information that is hard to extract from ensemble averages. X-ray methods are particularly important because they can nondestructively interrogate local strain, structure and texture of imbedded volumes to follow how real materials respond to loads and processing variables. This information has simply not been available.

Two important, recently developed x-ray approaches to diffraction mapping are **differential aperture microscopy, and 3-D diffraction microscopy**. These techniques are **severely limited by scan times** at existing x-ray sources.

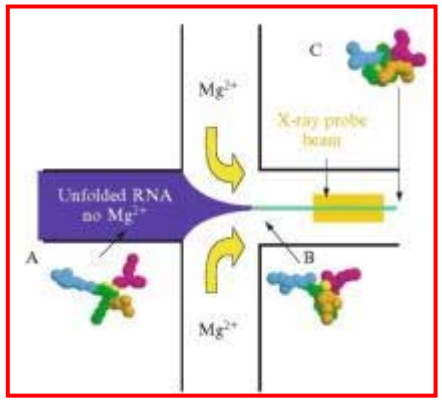
ERLs/USRs will have two huge impacts on differential aperture microscopy: (1) The high focused beam intensity will allow rapid measurements, and (2) the small beam size will allow for advanced achromatic optics with diffraction limited beam sizes and useful working distances. For example, with fly-scan methods and feasible detectors, it will be possible to map volumes with 2×10^6 volume elements/ hour. This will **enable unprecedented visualization of materials structure and behavior in minutes, instead of days.**

Beyond existing methods, the instrumentation developed for differential aperture microscopy has implications for coherent imaging of important materials. Already coherent imaging has achieved spatial resolution of 2 nm. Given the proposed brilliance of ERLs and USRs, it will be possible to extend the differential-aperture microscopy into the coherent regime to gain spatial resolution **at far smaller length scales than possible today**.

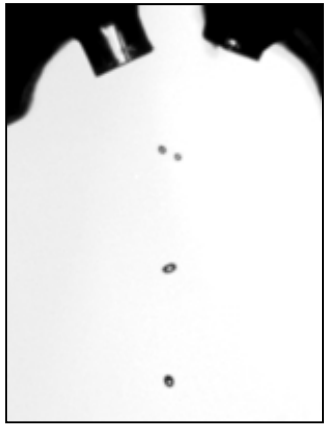
Time-resolved structure of macromolecular folding

Christian Riekel (ESRF), and Lois Pollack (Cornell Univ.)

From XDL2011 WS5: Materials science with coherent nanobeams at the edge of feasibility



Lithographically fabricated lamellar flow micromixer used to study macromolecular folding. See Russell et al., PNAS, 99 (2002) 4266.



Merging inkjet microdrops. Rita Graceffa, *PhD thesis*, Grenoble (2010)

Most cellular chemistry occurs in solution, and often involves dramatic and rapid changes in structure. Phenomena that are not understood, but central to cellular function include **folding of proteins and RNA, multimeric complex association and disassociation upon ligand binding, and alteration in macromolecular structure upon changes in the surrounding solution chemistry.**

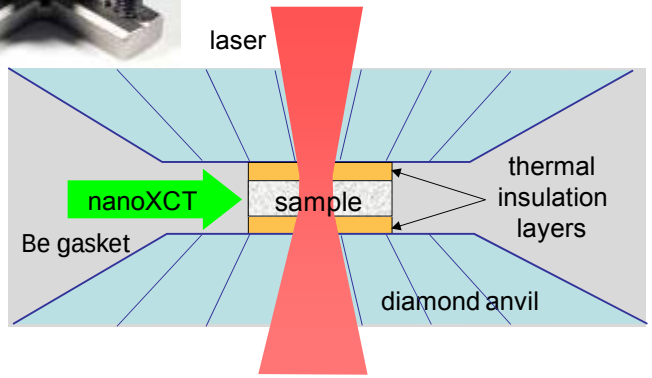
Spectroscopy is of limited use in determining global structure. But small and Wide Angle X-ray Scattering (SAXS/WAXS) can provide this information when coupled with methods to rapidly initiate reactions and acquire x-ray data. The recent development of **lamellar flow mixers** and **inkjet drop mixers** enable rapid **reaction initiation** by solution mixing down to **tens of microseconds**.

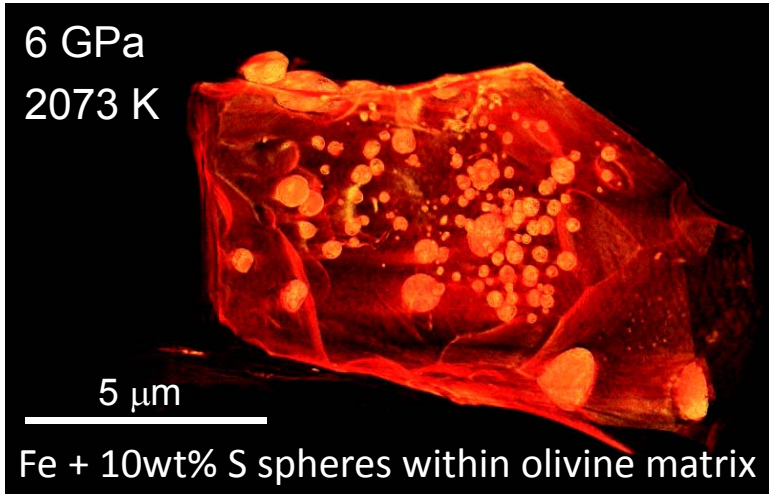
The experiments are challenging because of the micron-sized widths of sample involved and the need to gather the scattering data in very short periods of time. In the case of **lamellar flow mixers, reduction of background** from the surrounding fluid requires a beam that is on the order of the jet width, which is microns for the fastest time scales. In the case **of the inkjet mixers, data must be acquired on time scales that are fast compared to the movement of the droplet**. Both considerations **require the intense microbeams possible with ERLs and USRs.**

Nanotomography for Materials under Extreme Conditions

Wendy Mao, Stanford University

From XDL2011 WS5: Materials Science with Coherent Nanobeams at the Edge of Feasibility





High pressure research is a rapidly changing and expanding field, both with regards to materials of interest as well as x-ray techniques. The latter development is driven by the emergence of very high brilliance x-ray sources. Of particular interest is **combining nanobeam x-ray computed tomography** (nanoXCT) with diamond anvil cell technology (upper left figure). This enables the study of **multi-component materials under high pressure and at high temperature**, as shown in the lower left figure. nanoXCT contrast mechanisms include absorption, scattering, and element-specific fluorescence, but also **inelastic scattering** and **x-ray Raman scattering** are of high interest to be able to distinguish between different phases and their **shape and volume changes under extreme conditions**.

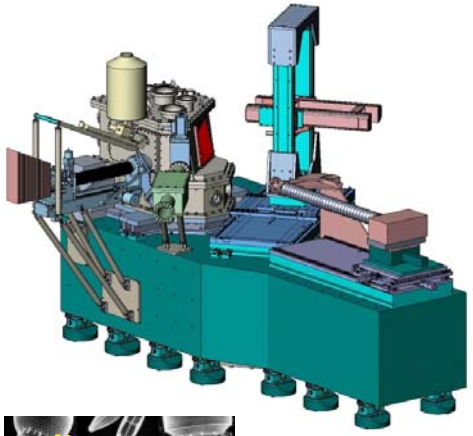
Tomography facilitates characterization of **texture and shape** of multi-phase assemblages, the precise determination of the volume of amorphous materials, density of light-element phases and the morphology of nanomaterials. In addition the multiprobe approach will make it possible to study **chemical reactions, defects**, and **diffusion** of materials under high pressure and at high temperature.

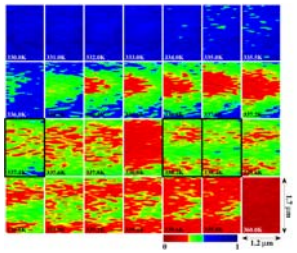
An ERL or USR will **enable high-flux nanobeams at high-energy,** enabling high-resolution 3D imaging on a **fast timescale** that will enable **diffusion and deformation** processes to be studied in real time. With the newly acquired capability of studying **complex materials under extreme conditions** as well as the advent of new high-brilliance x-ray sources, high-pressure research is poised to write a new chapter.

Hard X-ray Nanoprobes

Jörg Maser & Stefan Vogt, Advanced Photon Source

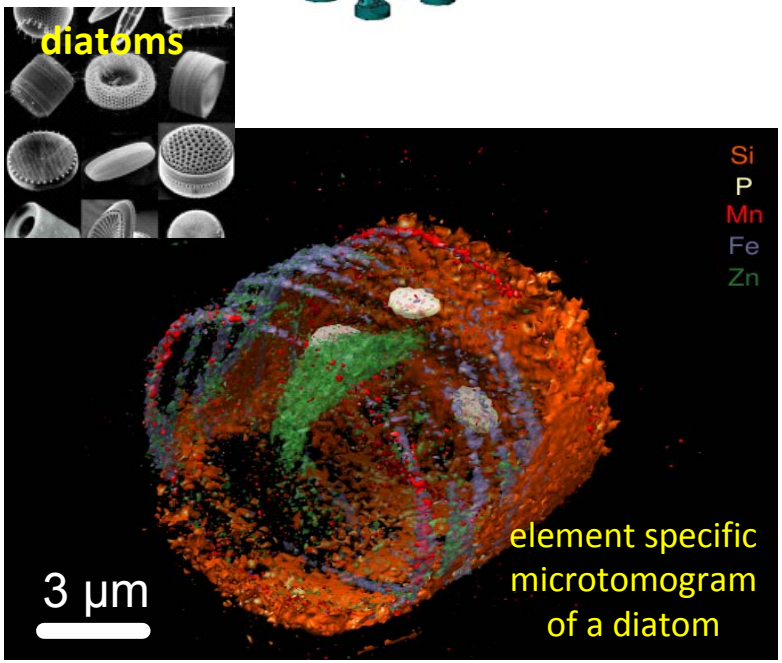
Workshop 5: Materials Science with Coherent Nanobeams at the Edge of Feasibility





Structural phase transition in VO_2

The study of **complex materials on the nanoscale** makes **a multi-probe approach** mandatory, in which multiple properties of such multicomponent materials can be studied at the same time. The CNM/APS nanoprobe combines a hard x-ray nanobeam of 40 – 50 nm with high precision sample positioning. The microscope can run in scanning mode and in full-field mode using an additional condensor and x-ray imaging lens. Scanning images based on x-ray fluorescence and scattering contrast can be combined with nanoXRF mapping, and is used for strain mapping, studies of phase transition, and elemental analysis. Moreover, nanobeam tomography yields 3D images in absorption and phase contrast, with a 2D resolution of currently 30 nm.



Another nanoprobe community is forming in the **biological, medical, and environmental sciences**. A second dedicated instrument was delivered recently. As an example, the microtomogram shows the 3D elemental distribution in a sweet water diatom [de Jonge et al, PNAS, 107 (2010) 15676]. Diatoms are a major part of the phytoplankton and play an important role in **carbon sequestration** in the oceans. Anther important application area are 3D element distributions in **tissue samples in medical studies**, in particular for **cancer research**.

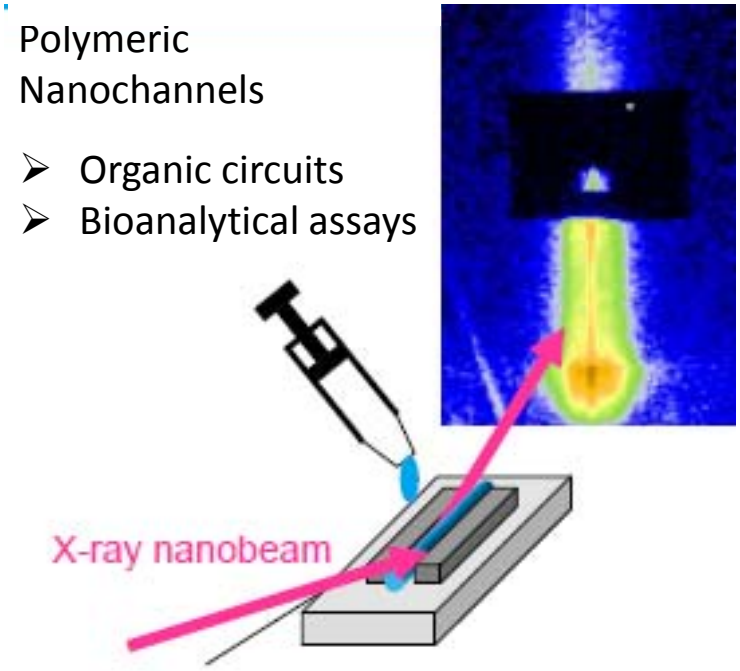
An ERL or USR with its **high coherent flux** will enable **ptychographic Bragg coherent diffraction with curved wavefronts**, which has the potential to study structure and strain of both isolated and continuous crystalline nanoscale regions in 3D, in complex matrices and in situ. The approach was demonstrated by Hruszkewycz et al. [Optics Letters 36 (2011) 2227]. At an ERL or USR such measurements could be performed in a **time-resolved** fashion.

XDL 2011 · PF Photon Factory · CHESS · SSRL · DESY

Probing Organic Microstructures with Spatially Resolved NanoGISAXS

Stephan V. Roth, DESY

Workshop 5: Materials Science with Coherent Nanobeams at the Edge of Feasibility



P. Müller-Buschbaum et al.
APL **88**, 083114 (2006)

As **nanotechnology and organic electronics** move towards **device applications and production**, the new objects of study are small organic deposits on a substrate as microdrops (inkjet printing, offset printing) or microwires (organic circuits). The new challenge is to study the effects of **new boundary conditions** such as **curved interfaces** as well as **drying and processing kinetics**. This requires probing such structures **on a submicron scale in-situ and in real-time**. While first nanoGISAXS has been demonstrated [Roth et al., Appl. Phys. Lett. 91 (2007) 091915], much development remains to be done. **Fast scanning nanoGISAXS for real-time studies** helps to stay **one step ahead of the radiation damage**.

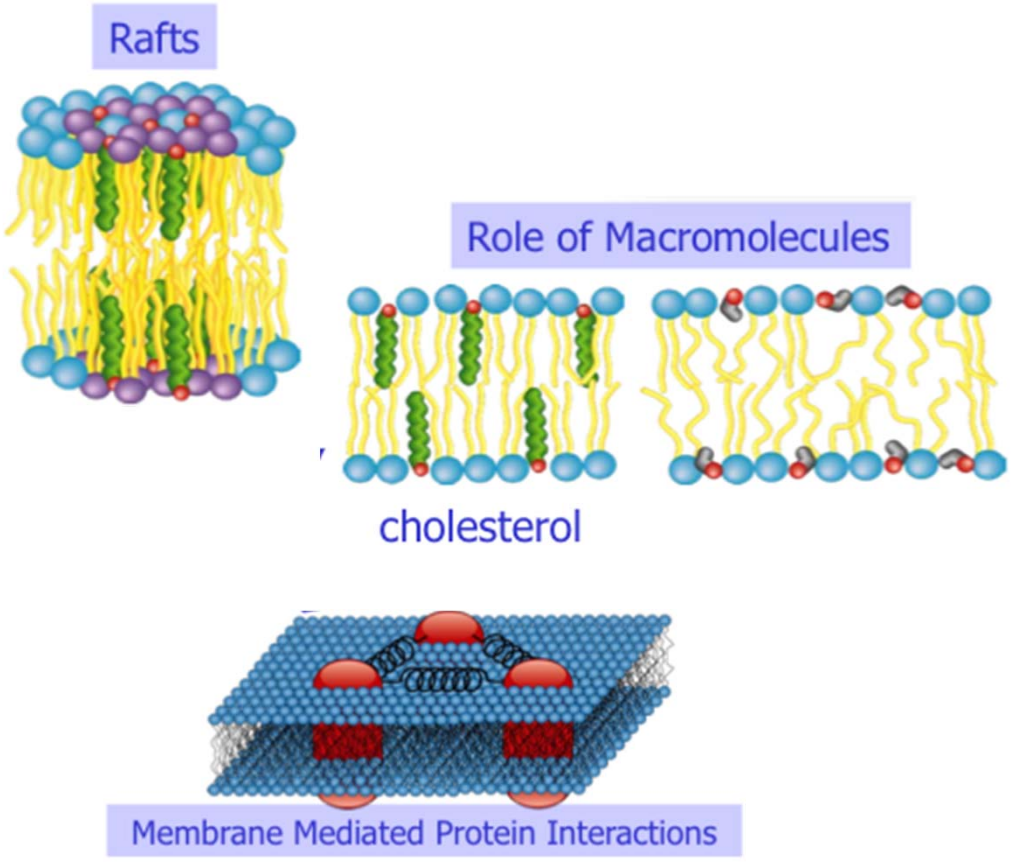
These goals require a **multiprobe approach** combining various x-ray detectors (area detectors, fluorescence detectors) and ancillary probes such as optical microscopy, ellipsometry, or AFM. An imaging ellipsometer was recently commissioned at MiNaX beamline of the Petra III facility [Roth et al., J. Phys.: Condens. Matter 23 (2011) 254208]. nanoGISAXS can be combined with other methods such as **microtomography**, using either the absorption or the scattering signal [Kuhlmann et al, Langmuir 25 (2009) 7241.], to retrieve 3D information.

The highly coherent nanobeams at an ERL or USR will facilitate a **reconstruction of the real space electron density via coherent diffraction imaging,** as demonstrated in first test experiments [Yefanov et al, Appl. Phys. Lett. 94 (2009) 123104]. An ERL or USR will provide the coherent flux for fast real-time studies. With the advent of new brilliant sources, **GISAXS with micro- and nanobeams** is looking into a bright future.

Biomembrane Dynamics

M. Rheinstadter[1], A. Fluerasu[2], L. Lurio[3], S. Mochrie[4]

From XDL2011 WS5: X-ray Correlation Spectroscopy using continuous beams



Increasing evidence suggests the presence and importance of **nanodomains**, such as rafts, In membrane function, **yet such domains have not yet been directly observed in a cell.** Membrane properties may also be strongly affected by interactions and collective dynamics between **membrane-embedded proteins.**

In both cases, the key interactions are likely to occur at length scales of 1-100 nm, and over time scales of 10^{-6}-10^{-2} seconds.

XPCS, *with the 2-3 orders of magnitude increase in brilliance provided by* an ERL or USR, may reveal direct signatures of such domains through their fluctuations, which are beyond the reach of other techniques.

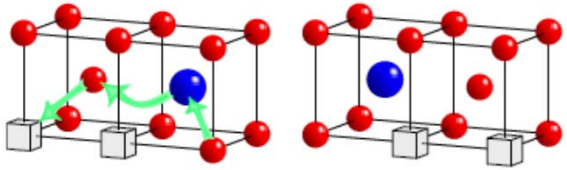
[1]Laboratory for Membrane and Protein Dynamics, McMaster University and Canadian Neutron Beam Centre, NRC

[2]NSLS-II, Brookhaven National Laboratory
[3]Department of Physics, Northern Illinois University
[4]Department of Physics, Yale University

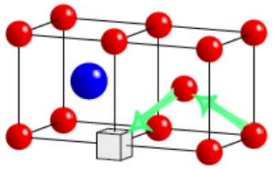
Atomic Diffusion

Bogdon Sepiol, *Department of Condensed Systems, University of Vienna*

XDL2011 WS6: X-ray Correlation Spectroscopy using continuous beams



Different jump mechanisms



Diffuse Scattering from a bulk crystal

Atomic diffusion is critical to materials synthesis and stability, and thus dictates the behavior of much of the material world. Yet, it is difficult to measure directly, and imperfectly characterized in most systems of interest.

XPCS provides direction-specific sensitivity to atomic diffusion in bulk materials, but requires measurement of fluctuations in *weak, diffuse* scattering between Bragg Peaks.

Demonstration experiments at ESRF employed count rates of

1 count per 10 minutes per pixel!

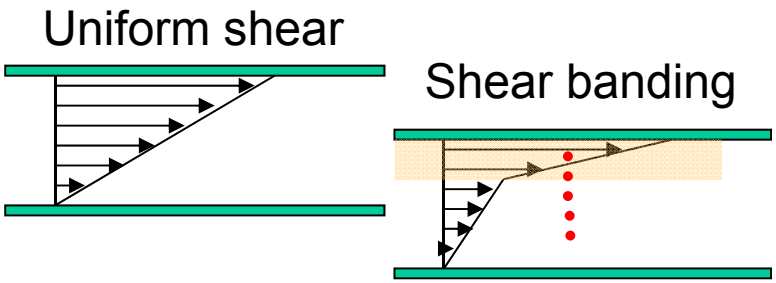
ERL/USRs would increase count rates by upwards of 3 orders of magnitude, rendering such measurements routine, and allow different jump mechanisms to be distinguished.

Dynamics of soft matter & complex fluids

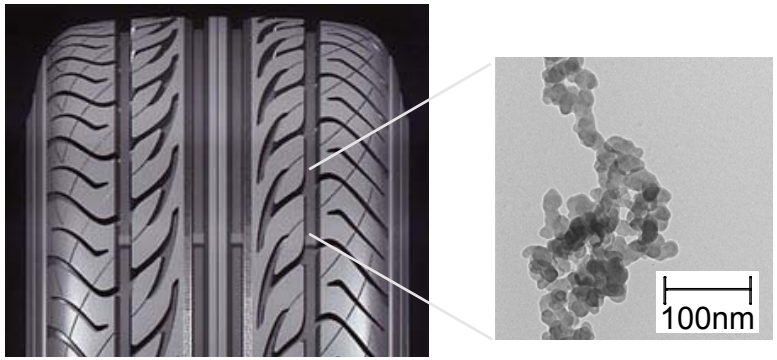
Y. Shinohara[1], W. Burghardt[2], A. Fluerasu[3], S. Mochrie[4] , L. Lurio[5]

From XDL2011 WS6: X-ray Correlation Spectroscopy using continuous beams

Nonlinear viscoelasticity



Colloidal aggregates in soft-matter



Many engineered and biological soft materials, such as polymers, colloids, emulsions, gels, etc., exhibit important but poorly understood behavior in non-equilibrium conditions, such as non-linear viscosity during flow (left). For example, although colloidal particles are often added to rubber to manipulate performance, the affect of such additives on elasticity and viscosity is difficult to predict.

The origins of such behavior involve molecular-scale fluctuations on length scales of 10-1000 nm and 10^{-6}-10^{-2} second time scales.

XPCS can directly measure these fluctuations, but such length and time scales require 2-3 orders more coherence flux. ERL/USR sources should make such measurements routine, with potential impacts in many areas of application, such as improved tire performance.

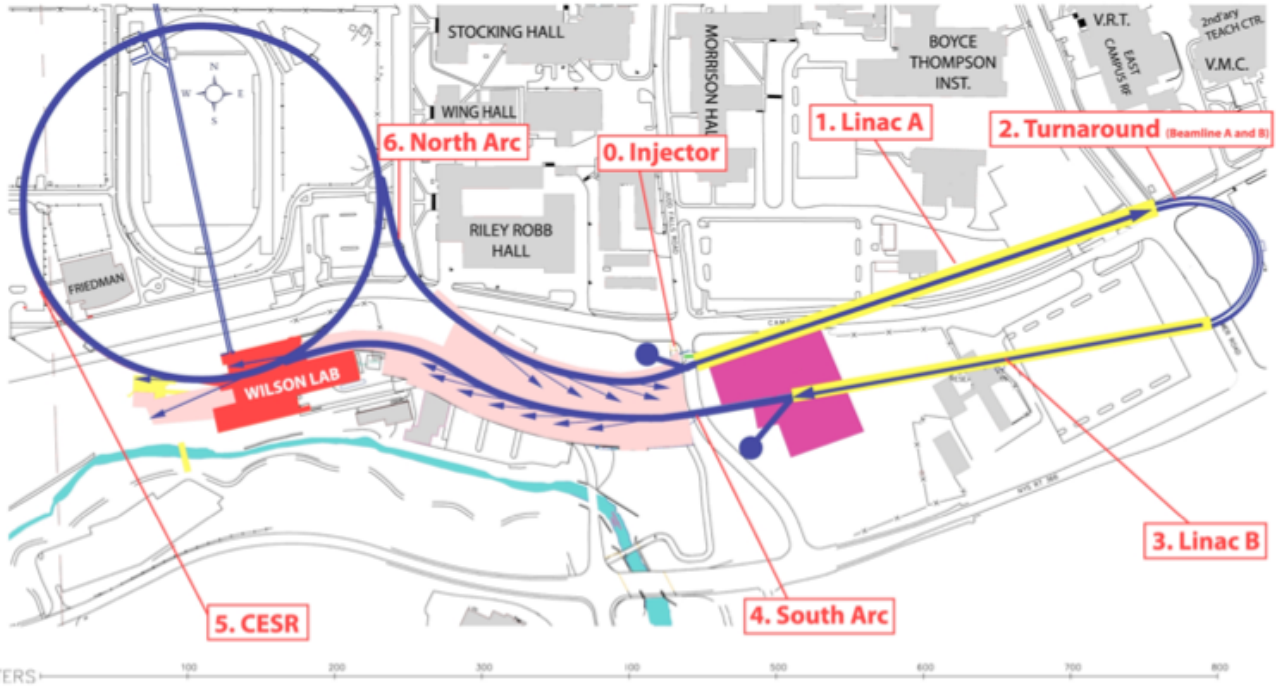
[1]Department of Advanced Materials Science, University of Tokyo
[2]Department of Chemical and Biological Engineering, Northwestern University
[3]NSLS-II, Brookhaven National Laboratory
[4]Department of Physics, Yale University
[5]Department of Physics, Northern Illinois University

XDL2011 will be used for the science case of Cornell's ELR Project Design Definition Report

Editors: Georg Hoffstaetter, Sol Gruner, Maury Tigner

Contributors: I. V. Bazarov, S. A. Belomestnykh, D. H. Bilderback, M. G. Billing, J. D. Brock, B. W. Buckley, S. S. Chapman, E. P. Chojnacki, Z. A. Conway, J. A. Crittenden, D. Dale, J. A. Dobbins, B. M. Dunham, R. D. Ehrlich, M. P. Ehrlichman, K. D. Finkelstein, E. Fontes, M. J. Forster, S. W. Gray, S. Greenwald, S. M. Gruner, C. Gulliford, D. L. Hartill, R. G. Helmke, G. H. Hoffstaetter, A. Kazimirov, R. P. Kaplan, S. S. Karkare, V. O. Kostroun, F. A. Laham, Y. H. Lau, Y. Li, X. Liu, M. U. Liepe, F. Loehl, L. Cultrera, T. Miyajima, C. E. Mayes, J. M. Maxson, A. Meseck, A. A. Mikhailichenko, D. Ouzounov, H. S. Padamsee, S. B. Peck, M. A. Pfeifer, S. E. Posen, P. G. Quigley, P. Revesz, D. H. Rice, U. Sae-Ueng, D. C. Sagan, J. O. Sears, V. D. Shemelin, C. K. Sinclair, D. M. Smilgies, E. N. Smith, K. W. Smolenski, Ch. Spethmann, C. Song, T. Tanabe, A. B. Temnykh, M. Tigner, N. R. A. Valles, V. G. Veshcherevich, Z. Wang, A. R. Woll, Y. Xie, Z. Zhao

Special Thanks: Chris Mayes is acknowledged for tireless editorial help and layout organization, and Sherrie Negrea for language editing.



Out for comments by selected advisors.

530 pages between conceptual design and engineering design.

Getting ready for suitably timed submission to the NSF.

Supporting documents of the PDDR

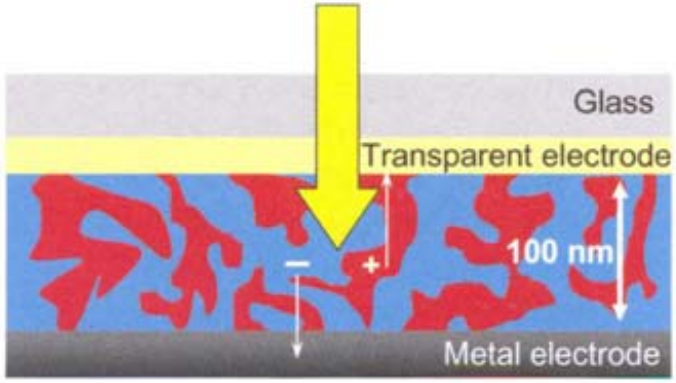
The **science case** for a hard-X-ray ERL, supported by ideas and finding from **XDL2011,**
Together with the **technical description**, distributed for comments,
Together with completed accompanying **engineering and impact studies,**
Will be the documentation to attract funding.

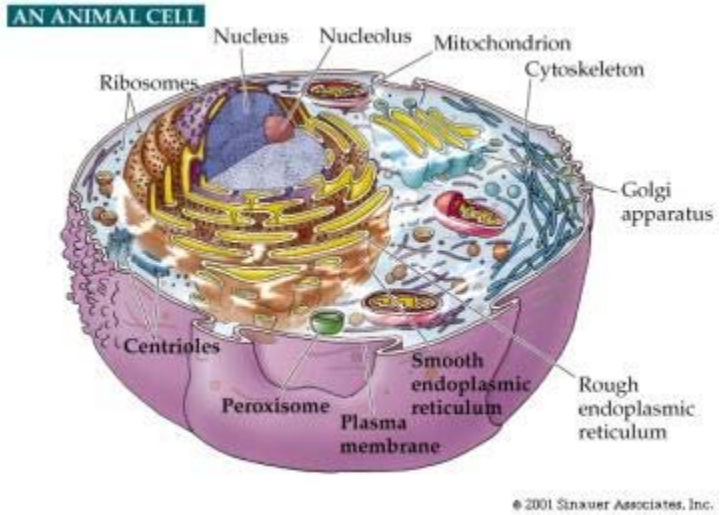
Studies for ERL Phase 2 (hard x-ray source construction)

a) Design decisions: Geometry, accelerator components layout, technical choices, beam dynamics analysis, radiation protection.
b) Proposal for electron-beamline construction
c) Proposal for large cryogenic plant
d) X-ray science building design
e) Tunnel design and construction study
f) Underground Technology advisory panel report
g) Environmental impact study

All these are to some extend reflected in the PDDR.

The END


Glass
Transparent electrode
100 nm
Metal electrode


AN ANIMAL CELL
Nucleus
Nucleolus
Mitochondrion
Cytoskeleton
Ribosomes
Golgi apparatus
Centrioles
Smooth endoplasmic reticulum
Rough endoplasmic reticulum
Peroxisome
Plasma membrane
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