APS Renewal Case - Soft Matter

Team Members
•Ken Shull (Northwestern)
•Gila Stein (NIST, U. Houston)
•Mark Schlossman (UIC)
•Jin Wang (APS)
•Brian Landes (Dow)
•Simon Mochrie (Yale)
•Derk Joester (Northwestern)

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1. Executive Summary

The Advanced Photon Source has played an important role in the soft materials area, and will continue to do so. Examples include the development of next-generation surface patterning technologies needed by the microelectronics industry, investigations of interfacial interactions in liquid systems, and development of advanced materials processing methods. The APS has played a leadership role in these areas, with scientific impacts in a range of fields that include energy research, environmental science and biomaterials development. The high energy x-rays offered by the APS are ideally suited for soft materials applications where beam damage needs to minimized and penetration depth needs to be maximized. Progress in these fields has been enabled by the availability of state of the art x-ray techniques, combined with an infrastructure that is particularly well-suited to meet the specific needs of outside users. Several illustrative examples are included in this report, which concludes with specific recommendations for facility enhancements that would further increase the scientific impact of the Advanced Photon Source.

2. Introduction

Applications of synchrotron-based x-ray probes to soft materials include investigations of traditional synthetic polymers, biological materials, and a wide range of hybrid materials. Uses include traditional reciprocal-space scattering techniques that probe length scales down to the Angstrom level, in addition to imaging modes able to probe length scales from tens of nanometers to millimeters. The spectrum of materials that fall into the 'soft materials' class discussed in this report are illustrated in Figure 1, which also includes a range of imaging techniques. The suite of synchrotron-based x-ray techniques that are most relevant to soft materials are listed below:

- Small angle x-ray scattering (SAXS): Traditional x-ray diffraction problems are not included in this class of methods, since the materials of interest are often (but not always) non-crystalline, and are characterized by longer length scales (nanometers or greater as opposed to Angstroms)
- Grazing incidence x-ray scattering (GIXS): This version of x-ray scattering is particularly well suited for investigations of molecular assemblies at surfaces. Both wide-angle and small-angle versions are utilized, depending on the length-scale of the surface features being investigated.
- x-ray standing waves (XSW): This technique is sensitive to the distributions of heavy atoms near interfaces.
- x-ray photon correlation spectroscopy (XPCS): This technique is able to probe the dynamics of electron density fluctuations at the wavelengths typically probed by scattering techniques, on time scales from $\sim 10^{-3}$ s to ~ 10 s.[1]
- Synchrotron x-ray fluorecence (SXRF) microscopy: Recent developments in this field enable the spectrocopic identification and localization of regions containing only tens of atoms[2]
- Transmission x-ray microscopy (TXM): This imaging technique has a resolution limit between those of light microscopy and electron microscopy, but is better suiteed than electron microscopy for the investigation of hydrated samples[3]□.

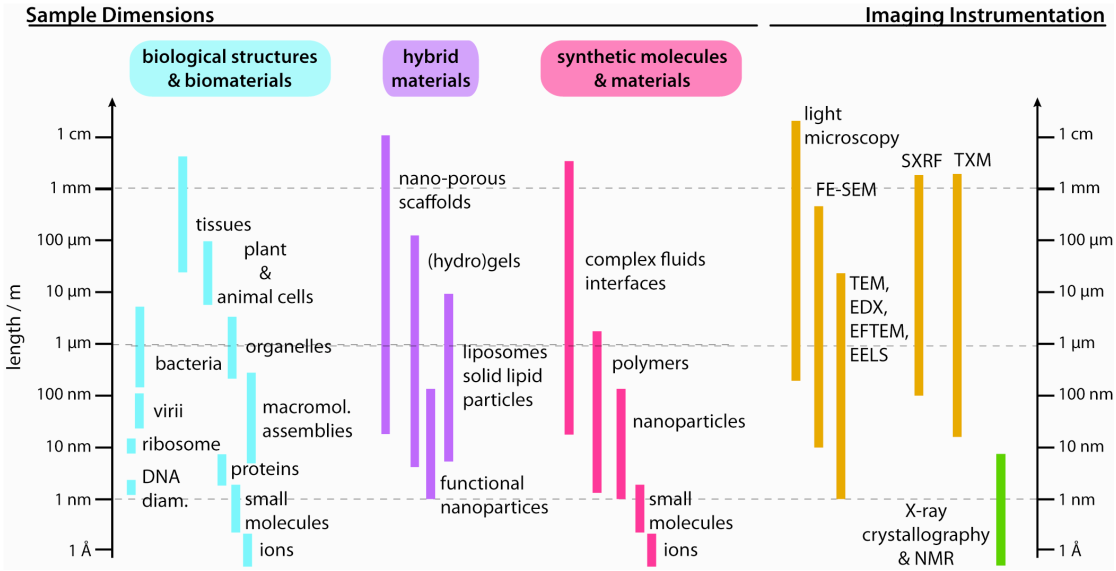

Figure 1: Scheme of the relevant length scales in synthetic, biological and hybrid soft matter samples and available instrumentation for imaging at these different length scales.

3. Key Science Drivers

While a wide variety of examples can be included in order to demonstrate the application of advanced x-ray techniques to problems of interest to the soft materials community, we have divided our examples into four general categories, each of which is discussed in more detail:

- Surface patterning
- Liquid systems
- Materials Processing
- Nanomaterials

Surface Patterning

<u>Molecular self-assembly at Interfaces</u>

The structure of organic thin films is of interest to multiple scientific communities, including those interested in soft matter physics,. applied microelectronics and energy research. Traditional x-ray scattering methods reveal the structure at molecular and bulk length scales, providing essential information to establish the origins of macroscopic function, but probing organic thin films is challenging due to weak contrast. As a result the demand for grazing-incidence x-ray scattering (GIXS) at synchrotron sources has greatly expanded in recent years. By operating near the condition for total external reflection, the grazing-incidence geometry is sensitive only to the near-surface region of the sample. GIXS is perfectly suited to evaluation of silicon-supported samples and permits depth-profiling (by varying the penetration depth of the x-rays) to distinguish the structure at the interfaces from the bulk.

Block copolymer films are ideal model systems for studying interfacial self-assembly because the bulk phase behavior is very well understood, and because the molecular parameters controlling structural and dynamic aspects of self-assembly can be exquisitely tuned. Thin block copolymer films self-assemble into periodic domains with size and periodicity on the order of 10 nanometers, offering a simple and inexpensive route for the generation of templates for nano-lithography. X-ray scattering has been integral to advances in this field. Some of the most demanding applications for block copolymer lithography require control over the positioning of domains with respect to features on or in the substrate, which is achieved with topographic or chemical registration features. An example of combined "top-down" and "bottom-up" self-assembly with topographic features is the lateral confinement of a single layer of block copolymer spheres in arrays of ~10 micrometer wide wells. Grazing incidence small-angle x-ray scattering (GISAXS) measurements have demonstrated that a single crystal can be assembled in every well, but that the positional correlation function of the domains decays algebraically, which is unacceptable for patterning addressable media[3]. These experiments offer general insight into the fundamental physics of ordering in low-dimensions, as well as specific guidelines to design better systems for patterning.

Structure-property correlations in organic electronics

Conjugated polymers that are solution processable are being investigated for fabrication of low-cost, large-area devices like thin film transistors and photovoltaic devices. The efficiency of charge transport is determined by both the molecular and macroscopic structure, such as the packing modes of adjacent polymer chains, the structure of the interface between active components, and the orientation of the conductive pathways with respect to the device. Out-of-plane x-ray diffraction measurements, rocking curve measurements, and in-plane grazing incidence x-ray diffraction experiments have demonstrated the importance of regio-regularity, molecular weight, and annealing conditions to achieve well-ordered crystallites of the conjugated polymers, which impacts the power conversion efficiency in photovoltaic materials and charge carrier mobility in thin film transitors[4], [5]. It has also been demonstrated that the substrate surface energy can be tuned to promote the desired crystal orientation, resulting in ten-fold performance enhancements[6].

Critical dimensions of resist structures

The resolution of the lithographic processes that define integrated circuits is rapidly approaching sub-100 nm dimensions, and new metrology techniques are required to quantify the critical dimensions of these nanostructures. Transmission small-angle x-ray scattering (SAXS) with high-energy x-rays has recently been proposed as a solution. The pitch, line width, height, and sidewall angle of resist lines are obtained with nanometer resolution by modeling the form factor oscillations[7], and the potential to measure line-edge/line-width roughness has been demonstrated[8]. Measuring the 3D shape of nanostructures with transmission SAXS requires rotation of the sample with respect to the incident beam over a range of approximately 50 degrees, which is time consuming in terms of executing both the experiment and the analysis. GISAXS is better suited to measuring depth-dependent structures, but the large beam footprint is not appropriate for patterns that only span small areas (~100 um^2). Constructing a GISAXS line with a micrometer sized beam is an attractive alternative, particularly if this were integrated with an AFM or optical microscope to facilitate alignment of the beam to the desired patterns on a chip. Resist relief structures scatter strongly and would not require additional flux to compensate for the reduced spot size.

Liquid Systems

Assembly at liquid/liquid and liquid/vapor interfaces

Self-assembly and ordering of ions and molecules at interfaces in soft materials underlies many processes of industrial and scientific importance. For example, biological membranes exist at aqueous-aqueous interfaces and provide a structural and dynamical platform for important cell processes. Phase transfer catalysis, pharmaceutical drug delivery, many electrochemical processes, nanoparticle synthesis and numerous chemical reactions take place at the interface between two immiscible liquids. Important environmental processes that rely upon interactions at interfaces include tertiary oil recovery, solvent extraction of radionuclides from nuclear waste, and liquid membranes used for the cleanup of heavy metals in the environment. Industrial applications include the use of self-assembled surfactants in many domestic products, ion selective electrodes, paints and coatings, among many others.

Recent x-ray scattering studies of buried liquid/liquid interfaces have probed the distribution of ions at soft interfaces. These distributions underlie processes as diverse as electron and ion transfer at biomembranes and redox processes at mineral-solution interfaces, and also influence many practical applications in analytical chemistry and electrochemistry. The classic Gouy-Chapman theory of ion distributions ignores the liquid structure, *i.e.*, it ignores the sizes and shapes of solvents and ions, as well as any correlations between them. Studies performed at the APS have addressed the limitations in the Gouy-Chapman theory by demonstrating that x-ray reflectivity data from the interface between two immiscible electrolyte solutions can be described by a Poisson-Boltzmann theory that includes a potential of mean force for the individual ions, as well as an electrostatic term[9]. Such studies lay the groundwork for the investigation of electrostatically controlled interfacial processes.

One important application that can take advantage of knowledge recently gained from x-ray scattering from liquid interfaces is extractant-mediated transfer of metal ions from an aqueous to an immiscible organic phase[10]. This process is complex and dynamic, depending on the diffusion of the ionic species in the two phases, the interfacial transport, and chemical reactions taking place in the system. In spite of a large body of research on this solvent extraction process, no consensus exists on the fundamental mechanism that controls the kinetics. The most important component of any solvent extraction process is the extractant, *i.e.*, a surfactant with a functional group capable of chemical interactions with the target ion. Permeation liquid membranes that contain long chain azacrown ethers and fatty acid surfactants selectively extract transition metal ions such as Cu(II), Pb(II), and Cd(II), which are common environmental toxins[11]. Understanding of these extraction processes requires further investigations of ionic distributions and surfactant ordering at liquid interfaces. X-ray interface scattering provides critical information about these processes that is unavailable from other techniques.

Biological Processes

Many biochemical processes and reactions occur at surfaces and interfaces. These include interactions between cells and the extracellular matrix, protein interactions at cell and organelle membranes, gas transfer at the lung tissue-air interface, and drug intake by cell membranes. Synchrotron x-ray surface scattering techniques are used to determine structure on the sub-nanometer length scale at soft, hydrated interfaces of biological interest. These studies are complementary to macromolecular crystallography because many bio-interfacial processes rely upon the interaction of biomolecules within disordered interfacial structures that cannot be crystallized. Recent studies of lipid-protein and lipid-peptide interactions illustrate the power of these techniques. For example, studies of cytosolic phospholipase A_2-C2 domain binding to an SOPC monolayer supported on water showed that analysis of x-ray reflectivity yields detailed information on the bound structure of this protein[12]. This structure indicated that the binding mechanism depends upon non-specific electrostatic calculations, hydrophobic interactions, and entropic effects due to water molecules that hydrate the lipid head groups. Future studies of bio-interfacial processes will explore the role of chemical heterogeneity in membrane processes and the structural basis for the kinetics of important cell processes such as cell signaling and trafficking.

Structure, dynamics of emulsified heterogeneous fuels

One of the current grand challenges faced by the world at large is the depletion of nonrenewable fossil energy resources, including coal, oil, and natural gas. Efficient, environmentally friendly extraction of the remaining resources is of increasing importance. Bitumen-based fuels represent an example where enhanced understanding of interfacial issues is needed. Bitumin is a stable liquid, multiphase fuel made of very fine oil droplets dispersed in water, originating from heavy hydrocarbon feedstock such as refinery residue. Bitumen-based fuels represent a potentially important source of secured energy for the United States. Extraction and utilization of these fuels in an economically viable way is very challenging, however. X-ray techniques can provide a better understanding of the extraction process and the structural and combustion properties of the fuel. Fundamental research on combustion of bitumen-based fuels to fully understand the fuel extraction and combustion processes are of vital importance.

Behavior o f high-speed liquid jets

High-speed liquid jets, with Weber number exceeding 10^3 and Reynolds number above 10^5 are very important in a range of applications in agriculture, energy, medicine, materials processing, and combustion. These jets remain poorly understood, largely because scattering prevents visualization of the internal structure by visible light. Techniques recently developed at the APS have enabled the imaging of ultrafast phenomena with a time resolution of 100 ps. With this time resolution it is possible to image moving liquid jets traveling at velocities of 10,000 m/s with a motion blur of only 1 μm . With this capability it is now possible to address long-standing and fundamental issues of droplet stability in high-speed liquid jets. Related processes of interest include droplet nucleation from a rapidly expanding supercritical fluid mixture.

X-ray photon correlation spectroscopy studies of dynamics

In x-ray photon correlation spectroscopy (XPCS), characterization of the time correlations in the coherent scattering intensity is used to obtain dynamical information about the sample under investigation. Access to dynamics at small length scales and long time scales makes XPCS valuable for studies of model glassy materials, such as colloidal gels and glasses, where microscopic dynamics become exceedingly slow as the materials approach structural arrest. The approach to glassy states is typically associated not only with a slowing of dynamics but more precisely with a growing separation of microscopic time scales. Certain localized motions, known as "beta" relaxations, remain relatively fast while the terminal structural relaxation becomes exceedingly slow. These beta processes, whose nature is intimately associated with the approach to the glassy states, have eluded XPCS studies so-far. However, the faster time scales accessible with a renewed APS will enable XPCS studies that capture this dynamic.

A wide variety of complex fluids show structures with characteristic length scales that are in the few-tens-of-nanometers range and characteristic dynamics in the microsecond to millisecond range. Enhanced capability to probe dynamics in this range of length and times will enable new opportunities to investigate such materials. Significant examples of such nanostructured complex fluids include nanocolloidal suspensions, mesophases of block copolymers, and membrane-based phases of oil and water mixtures that are stabilized by amphiphilic surfactants, such as the sponge and bicontinuous microemulsion phases. In recent years, these phases have been the subject of intense interest, including detailed theoretical work focusing on their dynamics. However, this dynamical behavior has largely eluded experimental investigation because the key length scales are too small for light scattering and the time scales are too long for neutron spin echo.

Materials processing

The continual drive for faster interconnects in integrated circuits requires the development of new interlayer dielectric materials with dielectric constants less than 2.2. Porous polymer based semiconductor dielectric resins have been developed to achieve this low dielectric constant by introducing nanometer-sized pores into the polymer matrix. The development of metrology to characterize the pores in porous films was critical for successful adoption of the material in the industry, both to ensure that the film attains the desired dielectric properties and to monitor pore characteristics that may impact the integration process. Due to the complex nature of the porous structure, on-wafer characterization methods needed to be developed to quantify the porosity in porous films of SiLK (a silicon-based low-dielectric constant material produced by Dow Chemical). The use of small angle x-ray scattering (SAXS) to measure void fraction, pore size and size distribution, pore morphology, and their uniformity across porous dielectric films was made possible by technology developed at the APS. The SAXS technique provided critical metrics of the porosity of porous SiLK films, and enabled a successful adoption of the material by the semiconductor industry. In addition the SAXS methodology developed at the APS was used as both the basis for commercial metrology technology demanded by the semiconductor industry.

Nanomaterials

The impact of nanotechnology on materials research is hard to overestimate. As applications, especially in imaging and bionanotechnology, are starting to be commercialized fundamental research into making "smart" nano-materials by sophisticated design strategies is becoming increasingly important. Very frequently, the resulting materials are hybrids of inorganic, organic, and/or biological molecules. Examples for such hybrids are oligonucleotide-functionalized TiO2 nanoparticles[2] PA carbon nanotube assemblies, inorganic or Au@Si@Au multilayered nanoshells[13]. Nanoparticles are usually characterized by light scattering techniques, by spectroscopy in case of fluorescent particles, by dry TEM/SEM, or dry/wet SPM. Especially in the case of complex assemblies, liposomes, and hybrid materials it is crucial that the particles remain pristine in their aqueous environment away from the distorting influence of overpowering interfacial forces that they are exposed to in conventional SPM imaging. APS instrumentation, specifically synchrotron x-ray fluorescence and transmission electron microscopy are ideally positioned to aid in the development of high-resolution imaging applications utilizing next-generation hybrid and transiently stabilized amorphous nanoparticles.

4. Significance of APS

The APS has already played a leading role in the development and use of many of the techniques that have been described above. Notable examples include the imaging capabilities utilized for liquid jets and for heavy metal atom distributions.

An additional factor of significance is the nature of the partnership between the users and staff scientists at the APS. The development of the nanoporous dielectric materials is a good example of this type of partnership. The scattering intensity from these relatively thin, nanoporous films is quite low, and the background radiation obtained from parasitic scattering needed to be reduced considerably in order for these experiments to be successful. The resulting design, development, and application of ultra low background on-wafer transmission SAXS represented a true breakthrough technology and provided the semiconductor industry with a fast, quantitative screening tool for commercial scale processes. This development was made possible only by the ability offered by the APS to optimize both a beamline and an experimental configuration for a specific application. Once a successful experimental protocol was fully defined, the key attributes were transferred for development on both laboratory and commercial scale devices. These advances led to development of commercial technology by equipment vendors for use in both laboratory and production environments. As a result it is now possible to rapidly and accurately quantify the average pore size and pore size distributions for nanoporous SiLK™ coatings. This approach has been adopted by a variety of industrial partners, customers, and instrument vendors, as the primary tool for porous media characterization. The technology has provided significant understanding on the effects of chemistry, formulation, and process on the development and retention of porous structures in SiLK™ films. In addition, this technology is now ready to provide information on the effects of the previously listed variables on both incipient pore formation and on the kinetics of pore development during cure. Future development is focusing on high throughput methods for both data acquisition and data reduction / analysis.

5. Scientific Community

The examples given in the previous sections illustrate ways in which the soft materials community benefits from APS capabilities. Some of the broad thematic areas that the APS is able to address are further delineated below.

Environmental Research

Metals, radionuclides and potentially also metal and semiconductor nano-particles are major anthropogenic contaminants in a wide range of environmental settings. Sadly, war and terror are increasingly adding to already significant industrial pollution of this kind. In order to better understand the fate of these elements in natural systems, we need to gather more information on the occurrence of these metals in amorphous and crystalline mineral phases, colloidal particles, and on the mechanisms that control their release and migration in the surface environment (e.g. the sequestration of nanoparticles by agarose fibers). In addition, to probe their (radio)-toxicity we need to understand how they interact with microbes on a cellular and organismic level. APS imaging capabilities play an important role in this work.

Biomaterials Research

Examples include biologists who are interested in studying physiological processes, biophysicists interested in the underlying mechanisms of such processes, and materials scientists who are interested in using these processes to synthesize new materials. Imaging applications based on the use of functional nanoparticles as contrast agents are an additional area of relevance.

Energy research

Example include processing issues related to polymer-based, affordable solar cell, fuel extraction from bitumen, and jet stability and droplet nucleation in fuel sprays.

6. Requirements and Capabilities

The following capabilities are needed in order to build on existing work, and to accomplish some of the broader goals mentioned in previous sections.

Extended Energy Range

Development of a liquid interface instrument that is optimized for use at high energies (30 keV to 80 keV, or possibly higher) would be useful for the study of buried interfaces, including liquid-liquid, liquid-solid, and solid-solid interfaces. Use of higher energies would minimize absorption effects, valence changes in ions, and allow access to certain resonances in heavy metals.

Detector resolution

As top-down/bottom-up assembly techniques move closer to perfection, the resolution limits of the two-dimensional detectors will prevent analysis of the diffraction line shape. This is just one area where enhanced detector resolution would be helpful.

Beam focusing, time resolution

The development of x-ray scattering from liquid interfaces has been closely tied to advances in synchrotron sources and instrumentation. These experiments usually require a very brilliant x-ray beam. Flat, buried interfaces, such as liquid/liquid interfaces or bilayer lipid membranes supported at the solid/water interface, can be studied with the high energy x-rays currently available. Needed advances include focusing techniques that are optimized for the study of liquid interfaces that are heterogeneous, small in lateral extent or highly curved. Also, new time-resolved instruments are required to meet the need for studying kinetic and dynamic interfacial processes at interfaces. Development of a time-resolved dispersive reflectometer will address the need for studying kinetic and dynamic interfacial processes, as well as the need for fast measurements of fragile biological materials.

Cryogenic Capabilities

With much enhanced resolution in imaging, the demands on sample preparation have increased dramatically. Previously practiced “gold standard” procedures are now rapidly becoming obsolete: Random crosslinking by chemical fixation, structural distortions by drying, elemental contamination, relocation and removal of mobile/soluble species by staining and washing can no longer be tolerated. Even more important is the realization that many soft matter samples contain structural water or maintain their structure only in the presence of a solvent. This has lead to a renaissance of cryogenic imaging in electron microscopy, and similar developments are needed in the x-ray community. It is thus imperative that synchrotron based X-ray imaging instrumentation be adapted such that routine work at cryogenic temperatures becomes possible in the next 5 years.

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