Elaine DiMasi, Masa Fukuto, Ben Ocko (BNL), Mark Schlossman (UIC)
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A group of 20 scientists and engineers met for the Liquid Interface X-ray Scattering breakout session associated with the NSLS-II Workshop of 17-18 July 2007, to discuss and plan future science and instrumentation. An overview of the field, provided by Peter Pershan of Harvard, made it clear that great strides have been made by this mature scientific community, whose interests span physics and physical chemistry, as well as biological and biomedical systems. Invited speakers addressing recent achievements were Mathias Lösche of Carnegie Mellon University, J. Kent Blasie of the University of Pennsylvania, and Ben Ocko of Brookhaven National Laboratory. The organizers presented additional research and technical topics.

At least ten synchrotron beamlines worldwide are equipped with instrumentation capable of structural measurements of systems involving liquid interfaces. The group assessed the current state of this resource base, identifying the most novel directions and the most important developments required. It was concluded that immediate development of both high and low energy instrumentation, augmented by advanced detectors and a variety of in-situ probes, would become a unique and valuable facility at NSLS-II.

Science

An enormous number of *static and slowly varying* interface structures have been described by the liquid interface community. The impact on the respective scientific areas has always been high, because the systems usually cannot be probed for equivalent information by other techniques. Liquid interfaces provide many advantages for studying fundamental aspects of self assembly since the surface energetics can be measured directly and since the substrate does not impose epitaxial order. Areas of interest have included structure and phase behavior of surfactant monolayers, liquid metal and alloy interfaces, polar and non-polar liquid-liquid interfaces, phospholipid-protein interactions in monolayers, membrane mimetic systems, ultrathin polymer films, interfaces undergoing mineralization, and, more recently, films of nanoparticles. Most of the interfaces studied have been *single-phase or homogeneous mixtures*. Discoveries from liquid interface scattering have inspired new ways of thinking about atomic forces and molecular assembly in all of these scientific areas.

Now, though, the keenest scientific interest lie in areas of greater complexity, including more realistic mimetic systems for interfacial biological processes, and in the description of dynamic interfacial assembly and reactions. These two aspects, which recurred in the context of all research areas mentioned, motivate our designs for the next generation of liquid interface scattering instrumentation.

Technical requirements

Requirement: x-ray energy tunability extending from 2 to 30 keV

Resonant measurements are expected to become more routine now that the techniques have matured. One unmet challenge is to extend liquid surface scattering measurements to x-ray energies below the current limit of ~6 keV down to ~2 keV to access light, biologically relevant elements such as P, S, K, Ca and others using resonant scattering techniques. Many liquid systems require sizable sample volumes and vapor rather than vacuum interface. The x-ray flux will be absorbed along the beam path, which will vary as the energy is tuned. Also at low energies, reflectivity must be carried out at quite wide scattering angles. In particular, the benefits of 2 keV capabilities for reflectivity must be carefully weighed against the extra instrumental complexity; for example, it may be preferable to establish 4 keV as a goal for reflectivity and 2 keV capabilities for grazing incidence diffraction and x-ray spectroscopies only. Overcoming the challenges of x-ray absorption and the mechanical design required for easy energy scanning in a liquid surface instrument, as well as refining the protocols to perform the low energy measurements, would engage the interest of many in the present community. In fact, this development need not wait for NSLS-II.

In addition to resonant reflectivity, a number of element-specific surface scattering techniques that rely on resonant absorption will be used. These techniques can be used to advantage in complex systems such as multi-component alloys and in molecular films where the local environments of particular atomic species provide insight into ordering and biological mechanisms.

On the higher energy side, the x-ray energy range of 15 keV to 30 keV allows for the study of certain buried interfaces. These include many liquid-liquid and solid-liquid interfaces. The workshop participants recognized that the U19 source does not provide high brightness above ~20 keV, and the U14 source that provides high brightness up to 30 keV may not be available. If U14 is not available, then U19 would be the preferred source and the ultimate range of this lower energy source would be 2–20 keV.

Requirement: high energy x-rays, 30-80 keV

The scattering of high energy x-rays from interfaces that are deeply buried within a bulk material is impeded by the x-ray absorption of the bulk. Bulk materials of interest to this community include water, oils, liquid metals, and solid materials such as silicon or minerals that are relevant for the study of solid-liquid interfaces. One example of interest to the study of complex biological interfaces is water, whose absorption length varies from ~0.1 cm at 8 keV to ~5 cm at 60 keV. Other considerations dictate the relatively large path length of x-rays through these samples, from about 2 cm for studies of the solid-liquid interface to 7 cm for studies of the liquid-liquid interfaces. Therefore, higher energy x-rays are a tremendous advantage to the study of these buried interfaces.

A new x-ray reflectometer using 71 keV photons has been developed at the ESRF by Harald Reichert and collaborators. This instrument employs bent Laue crystal optics along with compound lenses to focus the beam to micron size. By employing two different crystals to tilt the beam downward, this instrument is able to keep the sample height fixed while the incident angle is varied. This instrument has been used to investigate water, liquid metals and ionic liquids against a solid wall in addition to studies of liquid metal–vapor interfaces. With these deeply penetrating x-rays it is possible to carry out measurements that were previously in the neutron scattering domain, but with a much more extended q-range.

The workshop participants recognized that further discussion would be required to determine if this high energy beamline would require optics that allows the energy to be tuned, or if a fixed energy endstation would be appropriate. We anticipate that a wiggler source would be required for this work.

Requirement: time resolution (microfocus and detector R&D)

Currently reflectivity curves, which provide snapshots of the surface-normal electron density profile, require 30-60 minutes or more of scanning. Grazing-incidence diffraction scans using linear detectors, which give information on in-plane molecular ordering, take minutes to tens of minutes. However, these systems undergo dynamic processes on times scales on the order of milliseconds to minutes. It would be desirable to take advantage of area detectors, but liquid surface scattering poses special challenges.

In a reflectivity measurement from liquid surfaces, a range of incident angles must be applied and the liquid surface cannot be tilted. Therefore, a range of *q*-vectors can be measured quickly only by fast-scanning incident optics or by an energy-dispersive measurement using a broad energy spectrum incident beam. In the latter, an effective area detector must be spectroscopic [e.g., 300 eV energy resolution over an energy bandpass of 7–30 keV provides a resolution in q_z of 0.003 Å^{-1} that is more than adequate] and be able to read out and shift pixel strips on Hz time scales or faster. Energy dispersive schemes might include fast monochromator sweeps (as used for quick-EXAFS), or combinations of mirror and large-bandpass diffractive incident optics, which would need to be developed. Whereas the fast scanning might be possible using a conventional design with an undulator source, an energy-dispersive instrument might require a white beam source.

In a grazing-incidence diffraction measurement, significant scattering from the bulk makes it difficult to use an area detector unless the beam is of micron height. A larger beam spreads over a footprint of 10–100 mm length on the sample surface, and wide angle scattering obtained along this line is overwhelmed by isotropic bulk diffuse scattering. Also, lateral wave-vector resolution suffers if detected rays originate from a long footprint. This is why the present setups typically use Soller slit collimation before a linear detector for wide-angle grazing-incidence diffraction. Microbeam focus is required to enable more efficient diffraction experiments. Again it is best if the detector is fast, and covers a wide angular range.

Implied Requirements

Based on the scientific drivers we require wide x-ray energy access and vastly improved time resolution. Implied and secondary requirements include:

1. optics for microbeam focus
2. beam positional and angular stability better than 1 micron, 50 microradians
3. advanced detectors
4. computing infrastructure: data server, possible onsite analysis, other
5. wet preparation laboratory

Community

We have identified a core of ~20 PI's who carry out experiments that require 10 day runs at existing endstations. This implies beamtime consumption of 200 days in a year if each group runs only once. Therefore, we are confident that we will be building a valuable resource at NSLS-II, especially since the shutdown of NSLS-I will remove the only full-time liquid reflectometer station in the US (X22B) and another half-time station (X19C). The three stations at the APS run no more than 1/3 of available operations each.

The above discussion has mainly encompassed liquid interface reflectivity and wide angle grazing incident scattering. We also identified common interests with other communities, which will broaden the user base.

1. GISAXS and SAXS. Grazing-incidence small angle scattering is as useful at liquid interfaces as at other types of surfaces and bulk compounds. GISAXS capability will be

built into the new Liquids station, and the instrumentation will be made available to the broader community.

2. Surface scattering from solid films and interfaces, in particular the solid-liquid interface. In many applications the Liquids instrumentation may have advantages, such as six-circle reciprocal space access, microbeam, and detector modes, useful for solid-liquid interfaces. Outreach to the catalysis and mineral-liquid interface communities is planned.
3. Neutron scattering and reflectometry from liquid interfaces. Neutron and x-ray surface scattering from liquid interfaces provide complementary information. Our current accounting of potential users does not include those who have carried out strictly neutron studies. We plan to invite this community to a future workshop to interest them in the use of the proposed liquid interface instruments at NSLS-II. These users will benefit from complementary x-ray scattering studies because of the larger *q* range accessible with x-rays.

Plan

The assembled group agreed provisionally that the community still requires a "standard" steering-crystal-based liquid surface reflectometer. We plan to begin discussion of a reflectometer capable of handling Langmuir troughs and large vacuum chambers, updating the design and extending the lowest accessible energy, with a goal of 2 keV. The type of insertion device will need to be determined. The Liquids community plans a second station dedicated to high energy operation on a wiggler line. Several quite different optics and spectrometer designs are under consideration.

Concurrently with the x-ray instrumentation the team plans to consider ancillary in-situ measurements, such as optical microscopy, Brewster angle microscopy, ellipsometry, interferometry, UV-Vis spectroscopy, and others. Due to the heterogeneous nature of many interfaces, these complementary techniques can be necessary to understand the interfacial structure. Simultaneous or consecutive measurements on the same sample with different techniques are desireable. We want to distinguish the new Liquids stations by designing these other probes in tandem with the scattering instrumentation. An appealing model for contributing partners is to provide ancillary equipment and maintain it for general users. Such practice would benefit a broader community than, as is typical now, simply having each group do its own engineering for these probes.

Working group members have been identified from among the workshop participants, to focus respectively on low-energy, high-energy, and ancillary instrumentation. A future two-day workshop is the next important step in the design of Liquids instrumentation at NSLS-II.