A SAXS/WAXS/GISAXS Beamline with Multilayer Monochromator

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Abstract. We discuss the construction of a new SAXS/WAXS beamline at the Advanced Light Source at Lawrence Berkeley Laboratory. The beamline is equipped with a multilayer monochromator in order to obtain a high X-ray flux. The detrimental effects that the increased bandwidth transmitted by this monochromator could have on the data quality of the SAXS and WAXS patterns is shown to be negligible for the experimental program intended to be operated on this beamline.

1. Introduction

Demand for synchrotron-based SAXS remains high, despite recent improvements in generator-based SAXS equipment. Several reasons for this can be given. Synchrotron beamlines still produce at least an order of magnitude more flux, have better collimation, and can more easily accommodate the larger sample handling equipment associated with time-resolved experiments. Similarly, these beamlines are better suited for combining SAXS with other experimental techniques, either X-ray based or spectroscopic (e.g., Raman spectroscopy).

The combination of SAXS and WAXS is an obvious example of such technique combinations since it provides structural information over a large length scale range. The pioneering work in this was done in Hamburg\textsuperscript{1}. After the first dedicated SAXS/WAXS beamline was constructed\textsuperscript{2} it has become common practice to design SAXS beamlines on which a material science program is conducted with WAXS options as well\textsuperscript{3}. 
In recent years the use of grazing incidence SAXS (GISAXS) has also gained in popularity. The reason for this is that the newer generation of synchrotron sources offers the X-ray beam stability that is required for this technique. At the same time, materials scientists are creating a wealth of new thin film molecular architectures with structural length scales that can be observed by SAXS methods. Since the experimental requirements for both SAXS and GISAXS are reasonably compatible we have implemented these techniques on the same beamline.

There are some minimum requirements regarding flux, beam size, low angle resolution etc. which have to be met in order for a beamline to be able to handle a competitive research program. Below we discuss some of these points with the understanding that it is possible to find exceptions to the general rules that are given.

The minimum X-ray flux required for a SAXS/WAXS beamline to be competitive is currently around \(10^{11}-10^{12}\) photons/second. The specific number that is required depends on several factors, but the foremost considerations are the speed at which one wishes to do time-resolved experiments, and the statistical data quality one wishes to obtain. For a large variety of time-resolved experiments one can safely say that the lower limit is 0.1 sec/frame. Obviously there are experiments that require a higher time resolution but for most commonly used sample environments it will be difficult to perturb the samples faster and still retain a homogeneous sample (e.g., with regard to temperature or chemical state) over the entire X-ray beam size. The statistical data quality is obviously not only a matter of the intensity of the direct beam but is also dependent on the scattering contrast and the efficiency of the detectors used. With the recent introduction of the Si pixel detectors\(^4\), which combine the high efficiency of CCD detectors with the single photon counting capacity of the traditional gas wire chambers, it is easier to obtain an acceptable data quality with less photons. It should be pointed out that the data quality issues are mainly limited to the wider angle region where one probes the matrix-particle interface and the scattered intensity is intrinsically low. In the lower scattering vector range the intensity is in general so high that even with old fashioned X-ray film one can still obtain decent results.

Another factor that should be considered is the beam size. There is a tendency to develop optics that minimize the beam size as much as possible but one should keep in mind that one still requires a certain number of photon-matter interactions in order to generate a scattering pattern. If all these interactions are taking place in a smaller volume there is an increased chance that the samples will suffer from radiation damage. This is less of an issue when one uses a micro sized beam for spatial scanning of a sample, but when one performs time-resolved experiments, and the sample is exposed to the beam for the entire period over which the sample evolution takes place, this can become a problem.

Although on some beamlines it is possible to observe \(q\)-values as low as \(q = 0.012\) nm\(^{-1}\) one should keep in mind that, when using the conventional photon energy range of 8-12 keV, the entire scattering range of \(0.01 < q < 0.06\) nm\(^{-1}\) will be mapped upon only a small number of pixels close to the shadow of the beam stop unless one uses unrealistic large sample-detector distances. It is questionable how high the information content of the data in this case is. However, to be able to observe a lower scattering angle limit of \(q = 0.06\) nm\(^{-1}\) is desirable.

At the Advanced Light Source (ALS) in Berkeley, which is primarily designed as a third generation soft X-ray source, it requires some ingenuity in the optical design in order to be able to satisfy the above described boundary conditions for a competitive SAXS/WAXS and GISAXS beamline. In the energy range of 8 -12 keV the superbend magnets produce sufficient flux but there is only a limited amount of X-ray ports available on these magnets. Still, the presence on the Berkeley Laboratory site
of both the National Center for Electron Microscopy and the Molecular Foundry creates strong local demand for a SAXS/WAXS/GIAXS beamline. The complimentarity between electron microscopy and SAXS is undisputed and there is a large synergy by having the option to locally characterize the nano structures created in the Molecular Foundry.

In the following we describe the design of and results from a new X-ray scattering beamline constructed on a conventional bending port of the ALS. This beamline is equipped with a high flux multilayer monochromator and a toroidal focusing mirror. The optical engineering solutions that we have implemented can be usefully applied at other bending magnet beamlines.

2. Materials and methods

2.1. Optics

The Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory (LBNL) operates with a nominal energy of 1.9 GeV. In the recently introduced top-off mode the storage ring can operate with a constant beam current of 500 mA. One of the main benefits of this constant current are that the heat load on the optical elements is constant, which allows for stable operation of the beamlines.

The SAXS/WAXS beamline 7.3.3 receives the radiation from a bending magnet operated at 1.27 T, which means that the critical energy of the bend magnet is 3 keV. The source size is 0.1 x 0.01 mm² (H x V). The divergence of the beamline is 2.78 mrad. The beamline vacuum is separated from the storage ring vacuum by two 125 \( \mu \) m thick beryllium windows placed 13.7 m from the source. The beamline is designed to be operated at 10 keV, i.e. rather far above the critical energy and thus with a relatively low source intensity. In order to still retain a useful X-ray flux it was decided to utilize a multilayer monochromator built by RIGAKU. The monochromator consists of two multilayer mirrors of silicon <100> covered with 250 layers of alternating Mo and B\( _4 \)C. The d-spacing was kept constant at 2.0nm +/- 0.1nm. The bandwidth of the multilayer was calculated and measured to be around 97eV and at 10keV this results in an E/\( \Delta \)E ratio of 100. This monochromator has a roughly 10 times higher throughput compared to the often used Si(111) double crystal monochromator at the expense of transmitting a higher bandwidth (97 eV). For SANS applications this poses no serious problems\(^5\) and we will show later in the text that for WAXS applications the data quality remains similarly high.

To focus the beam we use a toroidal mirror (M1). The M1 mirror is located 2m downstream from the multilayer monochromator. The 500 A of Platinum coated toroid has a 1:1 focusing at 5.4 mrad incoming grazing angle with an rms roughness of 0.5 nm.
Figure 1. The schematic lay-out of the 7.3.3 SAXS/WAXS beamline.

The multilayer monochromator is placed at 14 m from the source point. The toroidal mirror is 16 m from the source. The sample position is at 32 m and the sample detector distance for the SAXS experiment can be varied between 1.3 m and 4.3 m. The beamline exit window material is a 100 µm thick muscovite mica.

At present the beamline is equipped with conventional knife edge slits but it is foreseen that newly designed scatter less slits will be installed in the near future\cite{6}. These will allow the beam size to be tailored to the desired size without introducing parasitic scatter.

2.2. Detectors

There are several detectors available that are suitable for different aspects of the experimental program operated on the beamline. At present the workhorse detectors that are being used in the SAXS/WAXS mode are two ADSC Quantum 4r CCD detectors. The main advantage of these detectors is their large active area (188 x 188 mm$^2$). The drawback of these detectors is their limited dynamic range and the relatively slow read out speeds, which makes them less useful for time-resolved experiments.

For faster experiments a Pilatus 100k detector is available\cite{4a}. This is a two dimensional single-photon counting detector with a high dynamics range of 20 bits and an active area of 83.8 x 33.5 mm$^2$. The Pilatus 100k is primarily installed for time resolved measurements due to its very fast readout time of 2.7 ms.

We have also ordered a Pilatus 1M detector, which will become available in the near future. This detector has a larger active area of 169 x 179 mm$^2$ and a maximum frame rate of 30Hz but for the rest has the same characteristics as the Pilatus 100k detector.

2.3. Controls and data acquisition software

The beamline control and data acquisition (DAQ) software has been written in LabVIEW. This allows for rapid integration of commercial off-the-shelf (COTS) devices and rapid development of user friendly Graphical User Interfaces (GUIs).

The beamline and experimental control is split between two PC’s. The first PC controls low-level beamline hardware such as optical components, sample positioning, detector positioning, and the X-ray safety shutter. It also reads experimental data from ion chambers, thermocouples, and other sensors. The beamline control software can operate in a standalone mode but it also contains a TCP
server so that the SAXS/WAXS DAQ software can communicate with it and retrieve the required experimental parameters.

The DAQ software controls the beamline control software in a master-slave configuration. It therefore effectively controls and coordinates the motors and sample environments. It also communicates with the independent control PC that is required for the different detectors. The interface that is available to the users is a GUI that presents a limited but flexible set of options. The user can take an image, find sample positions, or set sample temperatures with the push of a button. In addition, the user can graphically create extended command sequences, so as to automate more complex experimental protocols. These automated sequences are useful, for example, if one wishes to control temperature-annealing protocols or take SAXS/WAXS images at specified intervals. These sequences can be saved as a file and retrieved or modified for later use.

At each stage, the GUI provides feedback to the user. As images are taken, progress bars show their status and estimate the total time to complete all imaging. Temperature changes are displayed in real time. When automated sequences are run, the GUI displays them as a sequential queue in which the current step is highlighted.

The data reduction is performed using the NIKA and IRENA software(7) which has been adapted to be able to read the different proprietary data formats that are generated by the different detectors in use on the beamline. In order to correct for detector sensitivity we are using the flat-field correction provided by ADSC. Upstream of the sample as well as downstream we have ion chambers to correct for sample transmission. Typical samples for q-range calibrations are Silver behenate for the small-angle and Aluminum for the wide-angle range.

2.4. Sample handling

In the design of the beamline great care has been taken to provide as much flexibility and space around the sample position. This was done in order to be able to accommodate as large a variety of sample environments as possible. For a multi-user facility this, and the availability of additional experimental infrastructure, is a crucial requirement. A motorized 200 mm Newport translation stage as well as a motorized 76 mm Siskiyou vertical stage form the base of the sample setup.

Several dedicated sample cells have been developed, including a sample cell for solution scattering for proteins and a sample cell for high-throughput imaging of large numbers of capillary tubes. A conventional Linkam DSC(8) has been incorporated in the beamline and in the experimental control software. In addition a next generation heat stage is being developed to handle multiple samples with different annealing schedules.

For GISAXS experiments a Huber 5203.10 goniometer is used together with a Newport URS100PP rotational stage. An annealing stage for the GISAXS setup is currently under development.

3. Results

In this section we will show some representative results that have been obtained on beamline 7.3.3 in the different configurations that are available. It should be mentioned that the beamline is in full operation and that numerous publications have appeared(9)
The flux that is measured at the sample position is $1.3 \times 10^{12}$ photon/sec at 10 keV photon energy. The lowest angle resolution that so far has been reached is $\mathbf{q} = 2\pi/d = 0.002 \text{ Å}^{-1}$. It is expected that this number will decrease to even lower Q values when the new scatterless guard slits are installed.

3.1. Wide Angle spatial resolution

The 2D WAXS detector is suspended on a gantry, which allows the placement of the detector in an arbitrary orientation and sample-detector distance. The q-vector range is in general calibrated using the (200) and (111) of an Aluminum foil. Figure 2 shows a cropped WAXS image of the (111) at 2.69 Å$^{-1}$ and the (111) Aluminum (200) 3.1 Å$^{-1}$ peak.

![Figure 2. WAXS of rolled Aluminum foil. The (200) peak shows a clear broadening as a result of anisotropic grain orientation intrinsic to rolled Aluminum. The blue line on the left hand side is an instrumentation effect due to the gap between the CCD modules.](image)

The Al (200) shows a clear peak broadening characteristic of Aluminum foil. The rolling of the foil during production creates texture and hence the peak broadening. It proves that the instrumental resolution is adequate to detect features such as line broadening in the WAXS regime and that the increased wavelength bandwidth does not pose a problem for the experiments for which the beamline is designed.

3.2. Simultaneous SAXS/WAXS experiments

Block copolymers (BCP) are composed of two or more monomer units covalently bound together. The variety in monomer units as well as length of the units creates a rich and diverse phase diagram with correspondingly diverse properties. In order to maximize the efficiency of such materials, complete control of the morphology has to be achieved. Here we show a rod-coil polymer system poly-(2,5-di(2'-ethylhexyloxy)-1,4-phenylenevinylene) (DEH-PPV) as a model system for materials with a potential use as organic electronics. Questions regarding the morphology of this system, for example if the rods align perpendicular to the lamellae formed by the BCP or at a slight angle, can be answered with a combined SAXS/WAXS experiment. The question could be answered by aligning the entire sample in a magnetic B field and the expected scattering pattern for the case that the rods are perpendicular to the lamellae direction is shown in figure Figure 3. The lamellar spacing is around 20 nm, which is in the SAXS regime. The rod-rod distance is around 1Å and in the WAXS regime.
In the case that the angle between the rods and the lamellae would deviate from being perpendicular one would expect the WAXS 110 peak to split up into two peaks on either side of the equator.

In Figure 4 the SAXS pattern is shown on the left and the corresponding WAXS pattern on the right. The SAXS pattern shows the peak of the BCP lamellae at 20nm. Simultaneously we measured the WAXS pattern and the 110 peak of the tetragonal unit cell of the rods. The angle between the lamellae peak and the rod-rod peak was measured to virtually 90°, which proves that the rods are aligned perpendicular to the lamellae.

The X-ray beam was focused at 2.75m to a spot size of 250µm x 125 µm. The data quality in both the SAXS as well as the WAXS pattern is of high quality, and thus we can conclude that the over/under-focus, i.e. the depth of field, on both detectors does not cause a severe loss of resolution. This is not completely self evident when using a broad bandpass monochromator like the one used for this work.

3.3. Grazing incidence X-ray Scattering
Grazing Incidence X-ray Scattering (GISAXS) has become a vital tool to study surfaces and thin films. In particular in the field of polymer thin film GISAXS has received interest in the last few years.\[9c, 9h, 11\]

Thin block copolymer films show great potential in a wide variety of fields. Their potential applications include inexpensive printable photovoltaics, organic light emitting diodes, organic fuel cell membranes, and next generation hard drives. These new technologies are based on polymer self-assembly processes that happen on the nanometer length scale in films 10s to 100s of nanometers thick. These films are too thin to be measured in transmission geometry but can be studied by grazing incidence methods.

Figure 5 (a) shows a scanning force micrograph of the top surface of a thin poly(styrene)-poly(ethylene oxide) (M\textsubscript{w} = 32k-11k) block copolymer (BCP) film.\[9h\] The BCP is spincast on the surface of a faceted sapphire substrate and solvent-annealed with THF and water. Figure 3 (b) shows the corresponding GISAXS data. The horizontal axis corresponds to the in-plane vector \(q_x\) and the vertical axis to the out-of-plane momentum transfer vector \(q_z\). In Figure 5 (b) we show the scattering pattern where the X-ray beam was aligned to coincide with the (10) plane of the hexagonally arranged standing up cylinders.

The observed peaks along the \(q_x\) direction correspond to the (10), (20) and the (30) plane. No other peaks are observed, which confirms that the standing up cylinders exhibit a single crystal orientation over the entire probed area as shown in ref 9h. Along the \(q_z\) direction streaks are observed corresponding to the form factor of the standing up cylinders.

3.4. Beamline operation

The stability of a beamline can be influenced by many factors, including the radiation source itself. Also the behavior of the X-ray optics under the thermal load of the white X-ray beam and the stability of the detector systems over an extended period is of importance. With the recent introduction of top-off mode at the ALS (cf. introduction) and the use of a Pilatus pixel detector we have been able to follow the development of density fluctuations in a temperature quenched glass that was annealed at elevated temperatures\[12\] (Figure 6).
Density fluctuations in glass are in general very difficult to detect, since they can easily be swamped by only the smallest variations in beamline behavior. In fact, before the top-off operation mode of the ALS was introduced, after every machine refill there was a period of around 30 minutes in which the optics had to recover from the change in thermal load, and as a consequence the acquisition of this kind of data would not have been possible. The fact that we were able to follow the development for periods up to 24 hours is rather striking.

At present the time-resolution that can be achieved in combined SAXS/WAXS experiments is limited by the read out time of the CCD detectors and not by the available X-ray flux. The present limit is 10 sec/frame. The introduction of the new generation of pixel detectors, which have a read out time of only 0.03 seconds, will allow faster experiments to be carried out and will also improve the duty cycle (read out time vs. real data acquisition time). This is useful in materials science experiments where time resolutions of 0.1 sec/frame or longer are desired. However, it is also foreseen that time-resolved protein solution scattering experiments can be performed.

4. Conclusions

In combined SAXS/WAXS synchrotron radiation based experiments where independent detectors are used to collect the SAXS and WAXS patterns these detectors are often placed at considerable distance from each other. In theory this can be detrimental to the data quality since optimum data quality can only be achieved when the X-ray beam is focused onto a detector. When using a multilayer monochromator, with a transmission bandwidth that is larger than the commonly used Si-based monochromators, one aggravates this situation. However, we have shown that with the small X-ray beam divergence of the ALS and a sensible limit on the separation distance between the SAXS and WAXS detectors it is feasible to construct a beamline that has more than adequate operational performance in terms of X-ray flux, angle resolution, and diffraction resolution, even when using a multilayer monochromator.

The introduction of the ALS top-off mode and the use of a new generation of pixel detectors in combination with stable multilayer optics has allowed us to create a extremely versatile multi-user facility at which an extended materials science and biological research program can be carried out.
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