

UPBL9a: Time-resolved ultra small angle X-ray scattering	
Current designated sector:	Facility goes to:
ID02	ID02

1.1 SUMMARY

Applications of high brilliance small-angle X-ray scattering (SAXS) and allied techniques in soft matter and related areas of biology have steadily advanced over the past decade. A unique feature of SAXS is that it offers nanometric spatial and millisecond range time resolution. The main motivation for the upgrade is to push the applicability of SAXS to relatively unexplored non-equilibrium dynamical systems of fundamental and practical interests. Examples range from colloidal plasma state to highly self assembled biomimetic systems to complexities of flocking motions of microorganisms. To make SAXS amenable to such systems and complex processes, the present limits in angular resolution, wave vector range, signal detection, and time-resolution need to be improved by several orders of magnitude. While maintaining the possibility for conventional SAXS experiments, the upgraded beamline will provide certain unique features not readily available elsewhere. These instrument developments together with adaptive sample environments and advanced modelling methods could dramatically change the outlook of SAXS.

1.2 PROJECT HISTORY

This project is an evolution of the ID02 beamline presented as the SAXS CDR in the Purple Book. Following the Upgrade meeting in October 2007, it was proposed to be merged with the TRD CDR which is an evolution of the ID09 time-resolved beamline. The combined project is termed as UPBL9. However, a detailed technical scrutiny revealed that this merger imposes severe compromises on both projects and technically not feasible to implement them within a reasonable budget. In addition, both ID02 and ID09TR are heavily oversubscribed and it is not reasonable to share 50% of beamtime on a single straight section. Whilst the SAXS and TRD projects have different requirements in terms of source and optics, there is strong overlap in areas such as detectors, sample environments, data modelling, and most importantly in terms of the experimental protocols and data acquisition strategies. Both techniques require very high detection capability of weak signals, absolute intensity scale, high stability of measurement, etc. As a result, it is proposed that the combined UPBL9 project be located on two straight sections adjacent to each other. This will allow a very effective sharing of expertises, sample environments, support laboratories, data analysis platforms and to some extent the manpower.

UPBL9a will be specialised in SAXS and high resolution ultra-SAXS with sub-millisecond time resolution capability, whilst UPBL9b will be focused on time-resolved wide-angle X-ray scattering (WAXS) and diffraction in the millisecond to sub-nanosecond range. The complementarity of these two instruments will be maintained by having sufficient overlap in the intermediate SAXS/WAXS region and in the millisecond time range. For UPBL9a, the ultimate angular resolution is limited to a microradian by the size of the coherent patches in the synchrotron beam and therefore the term sub-microradian has been dropped from the specification.

The issue of the synergy between the UPBL9a and UPBL9b sub-projects was discussed extensively during the brainstorming meeting held in December 2008. Participants overwhelmingly supported the proposal which led to the conclusion that there is a strong potential for new scientific applications emerging from this unique combination. Many solution phase sub-millisecond and microsecond time-resolved SAXS experiments will be flux limited at UPBL9a. This class of experiments could be moved to UPBL9b. This will be more cost effective than developing the pink beam or multilayer option at UPBL9a. The complementarity of SAXS option and sample environments at UPBL9a and b would give the beamtime review panel enough flexibility to exchange many life science related proposals between these two instruments depending upon their scientific merit and the oversubscription factor in each proposal round. In addition, the high energy SAXS option at UPBL9b would be an advantage for sub-millisecond pressure-jump experiments. Sample environments such as laser temperature-jump, pressure-jump, stopped-flow and microfluidic continuous flow devices, detectors, and sample preparation lab will be shared between the (a) and (b) branches.

1.3 SCIENTIFIC CASE

Soft matter and many biological materials possess a microstructure which responds to even weak external deformations or stimuli [1]. Scattering techniques are ideally suited for probing these structures which often extend to multiple levels. Developments over the last decade have promoted applications of SAXS and related techniques such as WAXS and USAXS in soft matter and noncrystalline structural biology [2]. Scattering experiments are often combined with a variety of thermophysical and rheological techniques. As a result, not only equilibrium structures are revealed but also non-equilibrium dynamics and kinetics down to the millisecond range can be probed [3]. Quantitative scattering experiments have allowed to study rapid growth kinetics in very dilute samples (volume fraction $<10^{-7}$) [4,5], counterion distribution in polyelectrolytes [6,7], etc.

Despite the significant progress over the last decade, scattering methods are somewhat overshadowed by the parallel advancements in real space and manipulation techniques. Most notably confocal microscopy together with optical tweezers has emerged as one of the most attractive technique in soft matter [8]. The success of these techniques can be partly attributed to the ability to design appropriate model systems and data analysis based upon advanced computer simulation methods [8]. Moreover, the system size sampled by the real space techniques is comparable to the box size used in computer simulations. However, real space methods are susceptible to various artefacts and have limitations when quantitative structural or kinetic information is desired. As a result, scattering techniques remain essential for quantitative studies. On one hand, the most

powerful approach is to combine scattering and real space methods in a complementary fashion. On the other hand, scattering experiments need to be pushed in a direction where imaging techniques cannot effectively compete.

The new beamline not only enhances the performance of conventional techniques such as small-angle X-ray scattering (SAXS), wide-angle X-ray scattering (WAXS) and ultra small-angle X-ray scattering (USAXS), but also introduces non-traditional scattering and imaging methods. The emphasis will be on quantitative scattering experiments which together with advanced sample environments and data analysis methods could open new avenues in soft matter, active matter, noncrystalline structural biology, materials and environmental sciences.

In order to make scattering methods more attractive, not only are instrumental developments required but greater emphasis on designing model systems, advanced data analysis methods based on analytical theories and computer simulations are also required. The latter aspects necessitate much broader and interactive collaboration between the user community and large facilities which will be facilitated with the Partnership for Soft Condensed Matter.

In the following, representative scientific disciplines driving the development of scattering techniques are listed. The list is certainly not exhaustive.

Soft matter: self-assembly, microstructure and non-equilibrium dynamics

Self-assembly is primordial to many fascinating features of soft matter systems. One of the less understood questions is how the self-assembly brings unique structural and dynamic features which are different from their building blocks. Soft matter self-assembly is also relevant to many nano/biotechnological applications. Although the equilibrium structure of a large variety of self-assembled systems has been widely investigated, the kinetic pathways of self-assembly remain largely unexplored [9]. Examples include surfactants, block copolymers, and phospholipid-biopolyelectrolytes (e.g. DNA, actin, etc.) complexes [10]. Such studies require very high time and q (magnitude of scattering vector) resolution. The relationship of microscopic structure and dynamics to macroscopic rheology is reasonably well understood in homopolymer and spherical colloidal systems [11]. However, self-assembled block copolymer and amphiphilic systems and anisotropic colloids impose fresh questions which can be readily addressed using combined flow and scattering experiments. Soft matter microstructure in complex flows (e.g. in a microfluidic environment) has only been a little explored so far.

Even with relatively simple fluids, thermally driven non-equilibrium fluctuations are not well understood (e.g. the transition to turbulence, crossover region from inertial to viscous dissipation) [12]. Access to an enormously large q range could provide new insights in such studies. Unusual dynamic arrest (jamming) in systems dominated by competing repulsive and attractive interactions [13] is another topic of contemporary interest where scattering methods together with appropriate theoretical modelling can shed new insight on out-of-equilibrium states such as gels, attractive glasses, cluster phases, etc.

Noncrystalline structural biology: structure-function relationship

The key advantage of SAXS for studying biological systems is that it can provide physiologically relevant structural information. The widely studied system is muscle where a molecular level understanding of the structure and mechanical function has been reached [14,15]. Further studies will involve control over not only the mechanical state but also the biochemical environment [15]. This will help to understand how the chemical energy is converted to mechanical force. Similar investigations are being extended to excitable membranes (e.g. axonal membranes in nerve) and many other soft tissues where again chemical potential is associated with electrical or mechanical action. The success of these studies critically depends on the improvement in scattering detection with sub-millisecond time resolution since the structural changes are rapid and at the same time samples are even more susceptible to radiation damage [14]. Other topics include dynamic and interfacial processes such as adsorption of proteins at interfaces [16], self-assembly of natively unfolded proteins, the early stages of protein refolding, e.g. the hydrophobic chain collapse and formation of secondary structures (α helices and β sheets), etc. where scattering methods could provide direct structural information. Protein interactions including the condition for crystallisation and the behaviour under extreme conditions still remain active topics of research.

Biomimetic and bio-inspired systems: structure, self-assembly and kinetics

This is an interdisciplinary area between soft matter and biology and involves extremely complex systems. Time-resolved scattering together with the corresponding biochemical and mechanical protocols would allow one to learn about the recipes optimised by Nature over millions of years [17]. The underlying problems (e.g. biomineralisation) involve multiple length and time scales [18]. A combination of USAXS, SAXS and WAXS techniques reveals a wealth of structural information in biomimetic systems. These studies can then address questions such as how the kinetic competition in the self-assembly process leads to structures with unique mechanical properties (e.g. biological tissues, bones, etc.) [18]. A related issue is also how biological systems inhibit large scale mineralisation by forming mineral-protein complexes.

Environmental sciences: nucleation and growth

New material synthesis largely depends on novel synthetic routes which are often constrained by increased environmental concerns. A way to overcome this issue is to perform chemical reactions in miniature volumes (e.g. microfluidic devices) [19]. Scattering techniques offer interesting possibilities in green chemistry, particularly to monitor reactions at the nanoscale, thereby allowing the conditions to be optimised. In environmental sciences, control of aerosol growth resulting from the combustion of fossil fuels is a major issue. Recently, synchrotron scattering experiments have been used to elucidate the mechanism of soot formation and their multiscale structure in flames and at the exhaust of a diesel engine [20]. These systems can be classified as open non-equilibrium systems with complex self-organisation and intermittent behaviour. Another example is the in situ spray pyrolysis used for the synthesis of nanomaterials [2,4]. In all these cases, a combination of SAXS and USAXS provide insight to intermittent structural development from a few nanometres (nucleation) to micron scale (aggregates and agglomerates). Similar studies can be extended to dusty plasmas to directly probe

charged nanoparticles and their long-range correlations [5]. However, the systems mentioned above are in a highly non-equilibrium state and to probe the transient processes at large length scales a long pinhole type USAXS instrument is required. Access to a very wide range of structural levels from molecular to microscopic scales has potential applications in smart materials vigorously pursued for addressing the grand challenges in energy research [21].

Active matter: non-equilibrium dynamics and complexities

Much of the soft matter research so far is based on passive particles and macromolecules. In recent years, interest has bifurcated to so-called active matter, where the individual constituents possess a chemical motor [22]. Such self-driven systems display many fascinating features and directly relate the mesoscopic processes to the macroscopic world. The rich variety of non-equilibrium dynamics of active matter (e.g. flocking or coherent motions) is only beginning to be explored [22]. These systems tend to violate certain conventional wisdom in statistical mechanics (e.g. the central limit theorem). One of the interests is to have experiments in the thermodynamic limit (the number density tends to infinity) [22]. Unlike model colloids or polymers, such active particles cannot be synthesised chemically at present. Therefore, microorganisms such as bacteria are used as model systems. Therefore, to access the relevant length scales conventional SAXS is inadequate and high resolution USAXS is required. Note that light scattering is influenced by multiple scattering. Developments in USAXS and related scattering methods could be valuable for unravelling the physics of complexities of active matter.

1.4 TECHNICAL CONSIDERATIONS

Source

The limiting source property for the proposed upgrade is the large horizontal emittance. A reduction in the horizontal source size and divergence would have been a significant advantage. The undulators and the vacuum chamber have been recently upgraded to the requirement of the proposed beamline. Two of the new U21 undulators with a minimum gap of 11 mm are optimised for a working energy of 12.4 keV (fundamental) with tunability up to 15 keV. The new U35 undulator is suitable for variable energy operation over the range 8 to 24 keV. With the availability of 6 m straight section, it is desirable to have a fourth undulator optimised for high energy operation in the range of 20 keV. The front-end was only upgraded two years ago and it will be adequate for the upgrade beamline.

Optics

In order to handle the high heat load of the recently installed undulators, a new liquid nitrogen cooled Si-111 channel-cut monochromator is being designed and it will be installed during the winter shutdown 2009/2010. This design will meet the heat load requirement with all three undulators closed to their minimum gaps. In addition, the primary slits will also be replaced by the high power version. As result, there is no further upgrade of the monochromator and primary slits required in the immediate future.

The focusing optics requires a complete upgrade to reach the ideal source properties in terms of size and divergence in 1:1 configuration. Therefore, high mechanical stability and low figure errors will be of utmost importance. In addition, the parasitic background scattering from the optics need to be maintained very low. The optimum choices for focusing optics and collimation are described below.

Combined SAXS and WAXS

Figure 1 schematically depicts the existing beamline (ID02) with two end-stations for SAXS/WAXS and Bonse-Hart USAXS. Typically, photon flux of the order of 5×10^{13} photons/sec/100 mA is obtained at the sample position when two U21 undulators are closed to their optimum gaps for 12.4 keV (with $\Delta E/E \approx 0.015\%$). In the SAXS range, the present detection limit is of the order of 0.1% of water scattering (10^{-6} mm^{-1}). One of the aims of the upgrade is to improve the SAXS detection levels to unprecedented levels. An improvement by several orders of magnitude would allow more quantitative investigations of dilute and radiation sensitive samples, increase the time resolution in kinetic studies and recording of weak scattering features of low contrast samples. These improvements would also benefit anomalous scattering methods applied to soft matter systems.

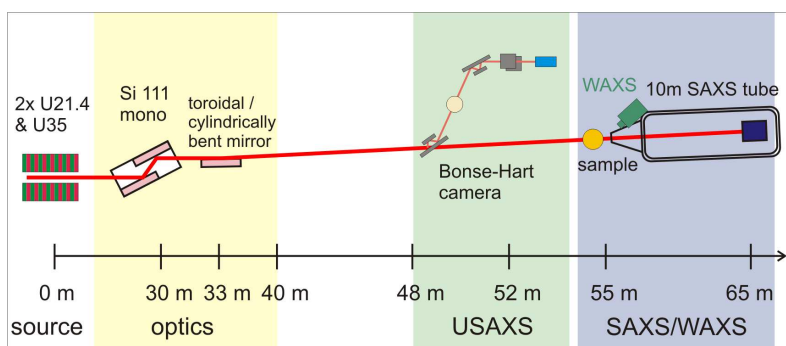


Figure 1. Schematic layout of the existing beamline displaying SAXS/WAXS and Bonse-Hart USAXS stations.

Figure 2 (upper panel) shows the proposed beamline configuration when it will be used for SAXS/WAXS experiments. This scheme will use 1:1 focusing with lowest possible figure errors (cylindrically bent mirrors) and exploit the increased length of the beamline to 115 m in curtailing the parasitic background. Owing to the limited height available for hutch construction at the inner periphery of the new experiment hall, the beam will have to be reflected downwards. This configuration could be useful for studying liquid-vapour interfaces at grazing incidence. In addition, the long beamline provides the critical space required for installing large and complex sample environments. Advanced data analysis methods will be crucial for exploiting these technical developments and there will be space to have an attached computing environment.

SAXS/WAXS detectors will be the most important component eventually determining the ultimate performance of these techniques. As a result, it is foreseen to install different detectors depending up on the particular application. For high resolution SAXS, a large CCD based high sensitivity (with average single photon level well above the noise floor) detector (FReLoN) will be developed. For time-

resolved experiments in the millisecond range and below, a large area pixel detector (PILATUS) will be required. In this case, the q resolution is compromised for higher time resolution. For WAXS, a hypothetical detector with a central hole will be pursued. Technologically, it has become possible to realise such a detector using overlaying CCD arrays. Such detectors are under development for XFEL applications.

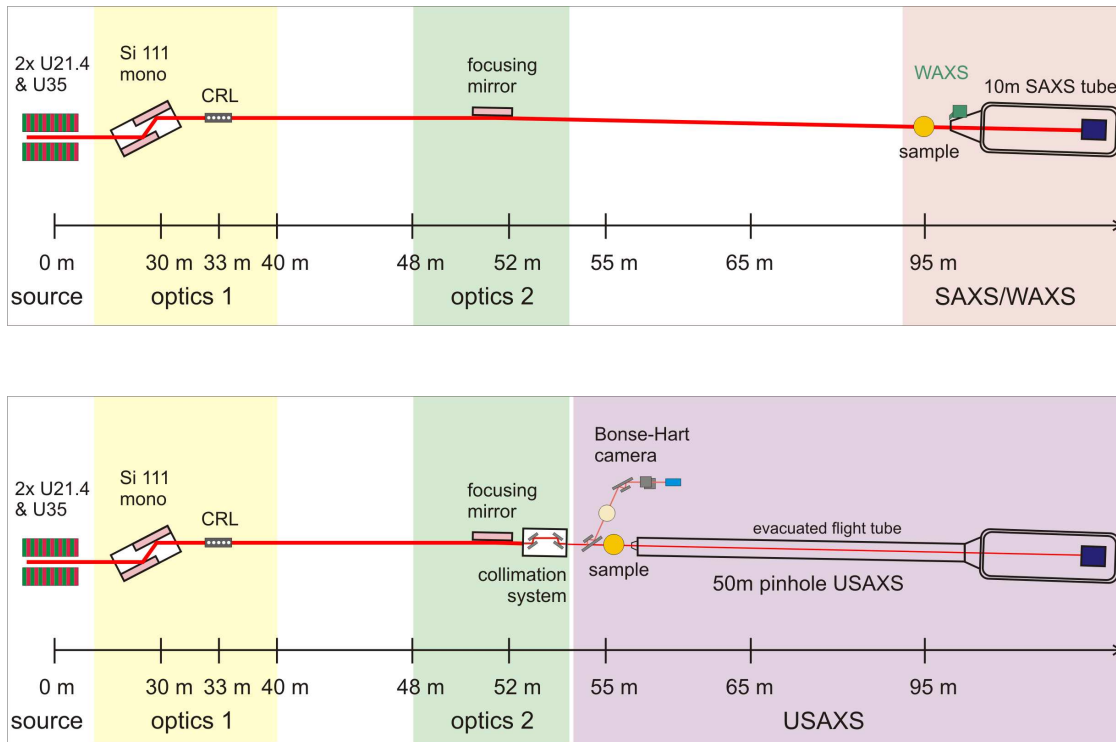


Figure 2. Schematic layout of the two different configurations of UPBL9a. The upper panel shows the standard time-resolved SAXS/WAXS setup. The lower panel displays the transformation to 50 m pinhole USAXS configuration. The Borss-Hart USAXS option is still maintained.

USAXS

Borss-Hart USAXS has now emerged as a mature technique providing high intensity dynamic range ($>10^8$), low background, absolute intensity scale and high q resolution ($\Delta q \sim 10^{-3} \text{ nm}^{-1}$). It is important to maintain this technique as complimentary to SAXS and light scattering. However, this is a scanning method which provides only one dimensional scattering profile. Therefore, it is desirable to have a long pinhole USAXS instrument with similar q resolution and intensity dynamic range of a Borss-Hart camera. This instrument will be suitable for investigating self-organised growth kinetics in non-equilibrium systems (e.g. spray pyrolysis, dusty plasmas) [4,5], radiation sensitive biological specimens (e.g. protein complexes, tissues, etc.) [24], and ordered samples with lattice spacing in the micron range (e.g. photonic crystals) [25]. In addition, combination of USAXS and imaging will be a powerful approach to study hierarchically ordered systems in medical applications [26].

The parasitic background of the instrument needs special consideration. In the existing pinhole instrumentation for a sample-detector distance of 10 m, the best

performance corresponds to $\Delta q \sim 3 \times 10^{-3} \text{ nm}^{-1}$ and $q_{Min} \sim 6 \times 10^{-3} \text{ nm}^{-1}$. To make significant improvement with the given source size and divergence, and reasonable detector resolution ($\sim 25 \text{ }\mu\text{m}$), the sample-detector distance has to be increased to 50 metres and the collimation needs to be improved by a factor 10. Therefore, it is proposed to use a hybrid configuration of Bonse-Hart and pinhole instruments. Figure 2 (lower panel) illustrates this scheme. The crossed channel-cut crystals condition the beam impinging on the sample to the desired divergence and curtail the parasitic background from the upstream optics. The scattered intensity will be recorded by the high resolution detector placed in the evacuated flight tube at 50 m from the sample. In order to make significant cost savings, the detector section of the long pinhole instrument will be the same as in the regular SAXS/WAXS instrument.

To reach microradian angular resolution, the Si-999 reflection will be required. The collimation setup should then have the required mechanical and thermal stability. For experiments requiring lower angular resolution, lower order reflections will be used. To suppress the surface parasitic scattering by the crystals, a pseudo channel-cut configuration will be constructed using highly optimised individual crystals [27]. For a reasonable beam stop size of $\sim 2 \text{ mm}$ a q_{Min} of $\sim 5 \times 10^{-4} \text{ nm}^{-1}$ will be possible with this setup. The ultimate q resolution will be determined by the spatial coherence of the X-ray beam, but the target is $\Delta q \sim 1.0 \times 10^{-4} \text{ nm}^{-1}$. A high intensity dynamic range ($>10^5$) two-dimensional detector will be essential for covering a wide q range. In addition, the beam centre should be stable to within 0.025 mm at the beam stop position.

The classical Bonse-Hart option will be still maintained for very high dynamic range USAXS measurements and as an ultimate calibration standard (see the lower panel in Figure 2). In normal operation, the Bonse-Hart conditioning crystals will be out of the way of direct beam. The section of the pinhole USAXS instrument from 55 to 65 m would also provide adequate space for conceptual experiments involving scattering or imaging. One of them is the near-field X-ray scattering (NFXS) [28] as opposed to the far field techniques such as SAXS and USAXS. NFXS is based on the analysis of heterodyne speckle formed by the mixing of strong transmitted and scattered beams [28]. The scattered intensity is given by the power spectrum of the fluctuating component of the recorded signal. A detector with high spatial resolution ($\sim 0.2 \text{ }\mu\text{m}$) and dynamic range ($>10^5$) will be essential since the size of the speckle corresponds to size of the scattering objects and fluctuating signal level lying over the strong transmitted beam need to be recorded. To preserve high degree of coherence, NFXS experiments will have to be performed with least number of optical elements. Other possibilities include microradian diffraction setup using compound refractive lenses (CRL) [25], USAXS imaging [26], etc.

Figure 3 shows the typical space and time scales that will become accessible with the extended SAXS, WAXS and USAXS techniques at UPBL9a. The time resolution for real-time experiments will be limited by the scattering power of the sample as well as the detector readout electronics. Therefore, provision for stroboscopic experiments using special shuttering scheme is foreseen for the sub-millisecond range. A new tandem shutter arrangement with $10 \text{ }\mu\text{s}$ time window is under development.

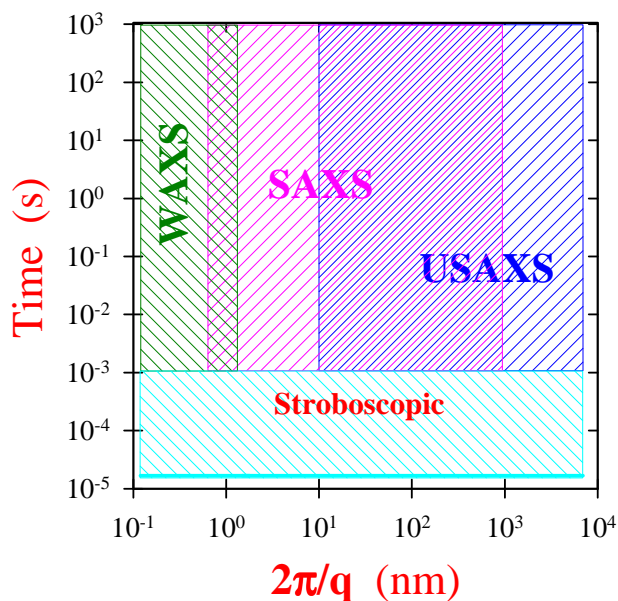


Figure 3. Expected space and time scales accessible for real time SAXS/WAXS and USAXS techniques after the Upgrade. Sub-millisecond experiments will be limited to stroboscopic measurements.

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