ESS Science Symposium on Crystallography for Soft Matter

A satellite meeting to 16th International conference on Small Angle Scattering

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Institute for Macromolecular Chemistry

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Prague, Czech Republic

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Overview

The ESS Scence symposium on Soft Matter Crystallography and satellite meeting to the International Small Angle Scattering Conference in Berlin was attended by scientists from Germany, Sweden, the Czech Republic, Estonia, Denmark, the Netherlands, Australia and the United States. As well as a strong representation from instrument scientists from the ESS, other neutron facilities were represented: JCNS; HZB; ANSTO and ORNL. The researchers were from a diverse range of soft matter science fields, all interested in ordered forms of soft matter from fundamental soft matter physics, technological applications, structural biology and fundamental bioenergetic processes. The workshop successfully opened a dialogue with instrument designers at the ESS and will lead to awareness among the instrument designers at the ESS of the particular instrumental demands of this science and the opportunities and new scientific challenges that are possible with the developing instrumentation. It also was successful in that it identified a community of scientists working in a particular area of scattering, so further regular meetings are intended for the future. Neutron scattering and the ESS will be essential contributors to advances in this area.

Despite the overall broadness of scientific areas discussed, there were some overarching themes, which may be addressed by the development of instrumentation and facilities at the ESS to facilitate this science in a way not possible previously. These issues relate to the flexibility of instrumentation, and the development of sample environment and deuteration facilities. These developments aid promising approaches for investigations with neutrons in systems where the important issue is the structural characterization of mesoscopic order e.g. self-assembled soft materials. Among the examples discussed here were complex multiphase polyphiles, which offer huge potential for bio-compatible green materials, as well as outstanding potential for 100 Å-scale multiple chemical environments, akin to the exquisite micro-control of biochemical environments found within living cells [1,2]. A similar experimental approached would benefit structural elucidation of lipid based liquid crystalline drug delivery systems [3]; and oriented lamellar systems, which are relevant structural models for questions relevant to biophysics of cryobiology and solute/membrane interactions [4] and structural biology [5]. Technological important systems as clay platelets [6]; the templating [7,8] and alignment [9] of nanostructures from lyotropic liquid crystals also may exhibit high degrees of texture which can produce intriguing highly anisotropic transport properties such as selective membranes or barrier materials. Some engineering materials reveal the interesting issues are not precise structural characterization, for example, the role of texture and disorder on the anisotropic mechanical and hygro-expansive properties of wood [9] and transport in graphene based materials [10]. In the colloidal domain of interest are the fundamentals of condensed matter states [11, 12] and the controlled packing of particles through shape and interactions which may produce ordered materials with periodic spacings similar to those of light [13] as well as anisotropic disorder [14].]. Recent developments employ the particle shape [14-16] and magnetic interparticle interactions [17] to engineer self-assembled structures with novel symmetries at the submicron scale.

Science Challenges

Small angle scattering is the technique of choice for studying the low-resolution structure of objects in the size range of microns to nanometers, and this has driven the development of the modern fixed wavelength pin-hole SANS instruments. Such studies provide a unique window on the statistical 3-dimensional

structure in soft matter quite often under conditions which are very close to the actual functioning of the system or molecules of interest. These studies are generally applied in the dilute regime with the contrast variation technique playing an important role in improving the information content or narrowing the range of possible structural solutions to the scattering problem. Real space methods such as electron microscopy, with improved sample preparation and some technical advances in instrumentation and data analysis, provide a conceptually easier visualization of objects which is beginning to rival, in terms of the minimum length-scales, the view point of small angle scattering. Nevertheless the main drawback of real space imaging methods, the impracticalities of large sampling statistical deviations from defined structure (disorder) or non-destructively visualizing internal structure inside cells or soft matter in the presence of some external field or stimulus, represent a major barrier to practical implementation of this approach. Furthermore, for highly condensed systems where there is some degree of ordering of the internal structure, scattering provides a possibility for neutron diffraction in providing novel structural perspectives on soft matter non-destructively. These perspectives are the nature of the crystallographic unit cell and deviations from this unit cell (i.e. disorder).

Diffraction is a standard technique to study crystal structure, alignment, texture and grain structure in hard matter. The important role of neutron diffraction in (hard) materials has been cemented by the penetrative and non-ionising nature of neutrons allowing non-destructive measurements in quite unusual sample environments, the sensitivity of neutrons to thermal motions, and the opportunities for isotopic studies. Similar issues arise in soft matter, where material properties (e.g. mechanical functioning, transport properties, internal surface, optical properties etc.) are highly influenced by analogues to these quantities formed by the arrangements of ensembles of molecules, often in a solvent, such as amphilipilic molecules or polymers rather than atoms. The structures formed consequentially occur at longer length-scales, and the role of thermal motions is rather different. While these concepts are quite usual for those studying hard matter, in a general sense the specific aims of this ESS Science Symposium was to define a new science area in terms of instrumentation which is not currently specifically considered in design constraints of the current neutron and x-ray scattering instrumentation. The materials focused on in this symposium exhibit varying degrees of order and may also have some degree of texture or alignment. Attendees at the meeting, including those non-presenting, were brought together by a knowledge of the limitations in current instrumentation, both for x-ray and neutron scattering studies, and the opportunities to interact with instrument scientists from the ESS and other facilities (Bragg Institute and JCNS) as well as those involved with SAXS at both laboratory and synchrotron sources.

The meeting was organized in general science areas with a further session on instrumentation chaired by Dr Garry McIntyre from ANSTO's Bragg Institute. Neutron scattering measurements were made on a range of instrumentation around the world, and overall the scientific challenges faced by a new facility in this area may be summarized simply in terms of the related issues of q/angular-resolution and solid angle coverage coupled to the limitations of (neutron) flux. The opportunities, and limitations, given by molecular deuteration in conjunction with neutron scattering, as well as various types of sample environment are natural discussions to have in this context.

Polymer and Materials Science

- "SANS/USANS determination of hierarchical structure of self-organised polymer microemulsions", Dr Petr Štepánek, Institute for Macromolecular Chemistry

- "Monolithic mesophase polymer membrane templated from ternary hexagonal lytropic liquid crystal system", Mr Guang Wang, Deakin University.
- "The ordered structure of block-copolymer systems studied by combined small-angle scattering and rheology", Professor Kell Mortensen, University of Copenhagen.
- "Instrumentation and analysis for characterization of new graphene-based soft materials", Ms Ashley Roberts, Monash University

In the area of soft materials science, a particular limitation of current instrumentation is the intermediate range of scattering vectors between classical diffractometers and SANS instrumentation. The importance of certain types of sample environments in some experiments was also discussed. Roberts (graphene based materials) and Guang (lyotropic liquid crystal molecular templates) discussed measurements in the region where both types of instrumentation were necessary. In the latter case it was not possible to resolve higher order reflections on SANS instrumentation, and in the former it was not possible to gain access to low enough values of scattering vector to include the first peaks on conventional thermal diffractometers. The overlap region between conventional SANS and thermal diffractometer is difficult to understand, and some effort has been expended to obtain a continuous curve. This is an important issue in developing technology based on graphene where the stacking of the graphene sheets and characterization of their disorder occurs in a region not covered well by SANS instruments and conventional thermal diffractometers.

Co-polymers have important abilities to self-organize on different length-scales and exhibit a large range of morphologies. This ability is used to provide materials with periodic structure on length-scales which have useful thermal and optical properties and also templates for other structures. Professor Mortensen gave a talk on the single crystal formed by shearing block co-polymers. General observations were made as to the difficulties in determination of the molecular organization of many soft-matter materials which is often limited by a correlation-length that is relatively short compared to the size of the unit cell and a molecular form factor that significantly reduces the scattering intensity at larger scattering angles. The talk represented an application of existing SANS instrumentation and a simple shear device, two parallel plates, to understand the ordering in a complex fluid. This science is enabled by resources devoted to sample environment since one of the real powers of neutron scattering is *in situ* structural characterization. Dr Štepánek's presentation was also focused on the organization of co-polymer systems, and the sensitivity of ultra-small angle scattering to the size of ordered domains (grains).

An important aspect of modern materials science are the structures which may be formed by organic or inorganic polymers around a template of self-assembled polymers/amphilles. Often the formation/polymerisation process leads to distortion of the template structure, so the properties of the template are not quite optimal. Examples of this may be structures which consist of isotropically oriented domains, grains, which are an impediment to materials where anisotropic properties are desirable. This is of technological relevance but also relates to the fundamental question of the nature of these grains as raised by de Gennes (18). Modern pinhole SANS instrumentation is not particularly suited for investigations of these issues.

Colloid science

- "Self-assembly of anisotropic colloids: microradian diffraction", Dr Andrei V. Petukhov, Utrecht University.

- "Structure factor in hard sphere suspensions", Professor Gary Bryant, RMIT University

The instrumental challenges in this session were largely those associated with angular resolution and coverage of large solid angles applied to the self-organization of large colloidal scale particles. Bryant's talk on an aspect of fundamental soft condensed matter physics, examined the phase transitions in simple hard sphere suspensions with conventional pin-hole SANS. The possibilities of using contrast variation in mixtures of hard spheres to study specific structure factors in binary mixtures of hard spheres, provides a possibility for an insight into fundamental problems, in particular where complex interactions can be untangled using deuteration.

Dr Petukhov's work, using very low angle scattering from a synchrotron source, studied the self-organization of quite large particles (~ micron – Fig 1). The large size of the particles organized into highly textured/oriented materials, and the consequent very small angular resolution with a requirement for large solid angle coverage, provides very special challenges for measurement. Currently, x-ray scattering measurements with microradian resolution are performed at synchrotrons. However, similar concepts of proper beam focusing at the detector plane along with a possibility of using ultra-cold neutrons could provide comparable reciprocal-space resolution. This, in addition to contrast variation possibilities and sensitivity to the magnetic sublattice, can make neutron scattering an attractive tool for a broad community in colloid science and photonics.

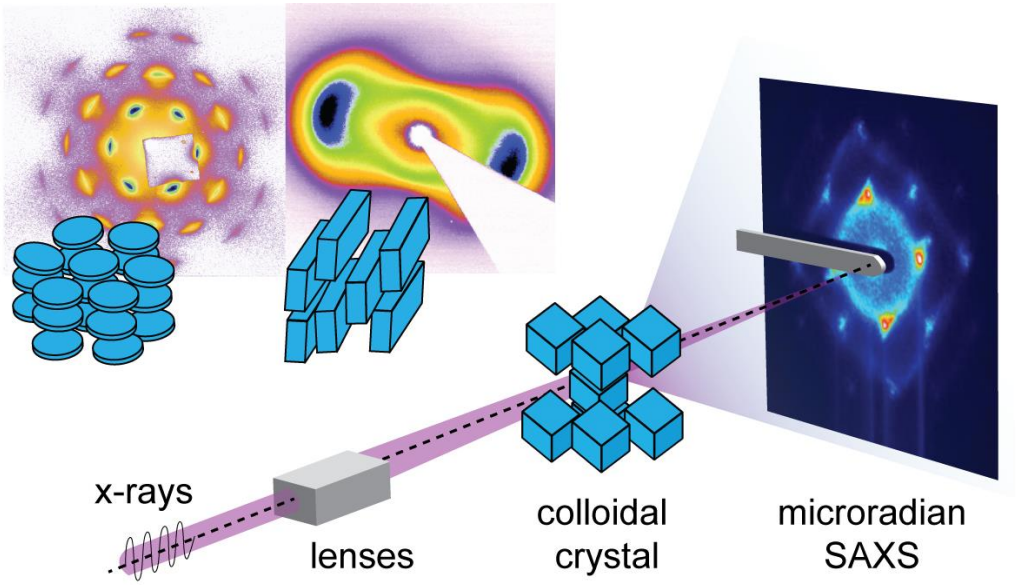

Fig. 1. *Examples of high-resolution x-ray diffraction studies of colloidal self-assembled crystals and liquid crystals. From left to right: columnar liquid crystals of colloidal discs (237 × 18 nm), biaxial nematic phase of colloidal boards (254 × 83 × 28 nm) and rhombic crystals of colloidal cubes (side length 652 nm). Microradian resolution is achieved by exploiting compound refractive lenses installed in front of the sample that focus the beam at the detector plane. From Ref. [16].*

Amphiphilic Self-Assembly

- "Heavy water effect on hydrated lipid systems in bicontinuous cubic phase" Professor Hiroshi Takahashi, University of Gunma

- "Hierarchical Ordering in Star Polyphiles" Dr Liliana de Campo, ANSTO
- "Large channels in cationic PEGylated cubosomes", Dr Borislav Angelov, Institute for Macromolecular Chemistry
- "Ordered amphilic systems at planar interfaces" Dr Henrich Frielinghaus, JCNS, Forschungszentrum Jülich.

Molecular self-assembly of surfactant molecules provides a route to nanoscale arrangements for drug delivery, templating of polymeric and silica structures and the physical basis for the selectively models for bio membranes. The traditional approach to characterization of self-assembled cubic structures with SAXS and Cryo-TEM real space techniques and novel applications was discussed by Angelov. He noticed the interplay between the form and structure factor in liquid crystalline nanoparticles (cubosomes). More speculatively the impact of grain size (Fig 2), the size of ordered domains, on the kinetics of drug delivery were discussed (19). Particular strengths of neutron scattering measurements are the ability to use contrast variation to improve the information content of the scattering experiment and resolve detailed structural reconstructions. These issues were discussed by de Campo, with an emphasis on the resolution of peaks which are close together (Δq) and these may be addressed to a degree with the superior resolution that choppers and the time of flight technique may impose. Reservations in using D_2O as a simple replacement for light water were expressed by Professor Takahashi in the context of bicontinuous phases. This was discussed in the wider context of sample deuteration. While there is some general feeling that there are subtle differences between deuterated and hydrogenated species clearly the application of molecular deuteration is highly successful a critical evaluation of the limitations of the technique would be beneficial.

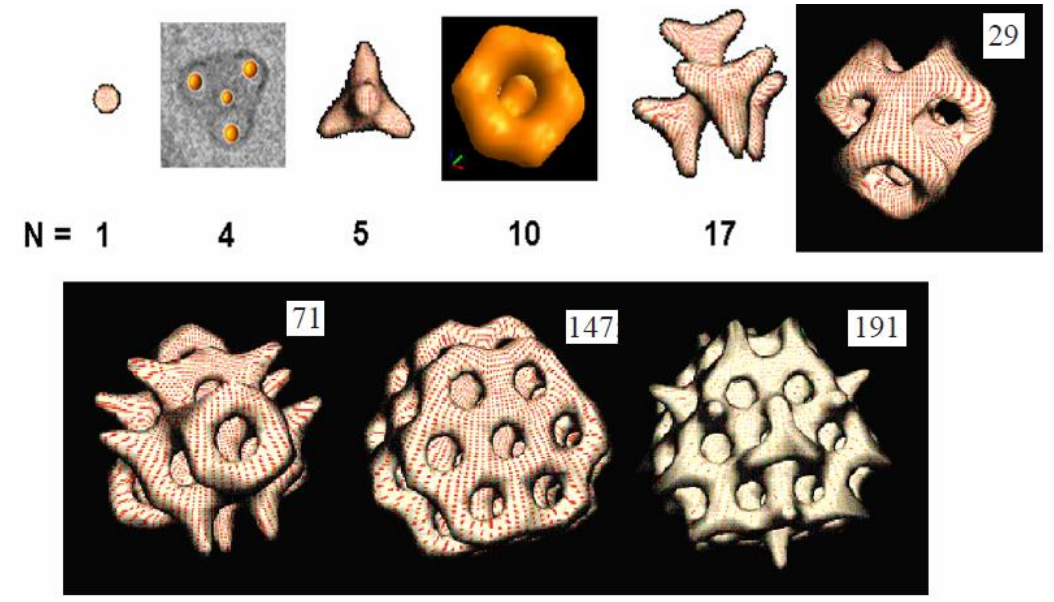

Fig. 2. *Angelov et al. have built up a highly constrained model for growth of the diamond type bilayer arrangement in a grain where N is the number of repeat units in each particle. Adapted from Ref [19].*

The grazing incidence technique is sensitive to in-plane organization in a manner complementary to specular reflectivity and may be used to probe organization and dynamics with respect to a rigid interface. These issues are important because of the important role of interfaces in ordering particularly in the presence of a shear field. Frielinghaus reported the application of this measurement geometry to neutron

spin echo spectroscopy of micro emulsions and lamellar systems. The grazing incidence geometry is ideal for the study of complex ordered fluids, for example at shearing interfaces as previously discussed by Mortensen. These issues are related to the interaction between the neutron beam and the sample, and require a flexibility greater than that found with most SANS instrumentation. Variable slit systems are commonly implemented on reflectometers.

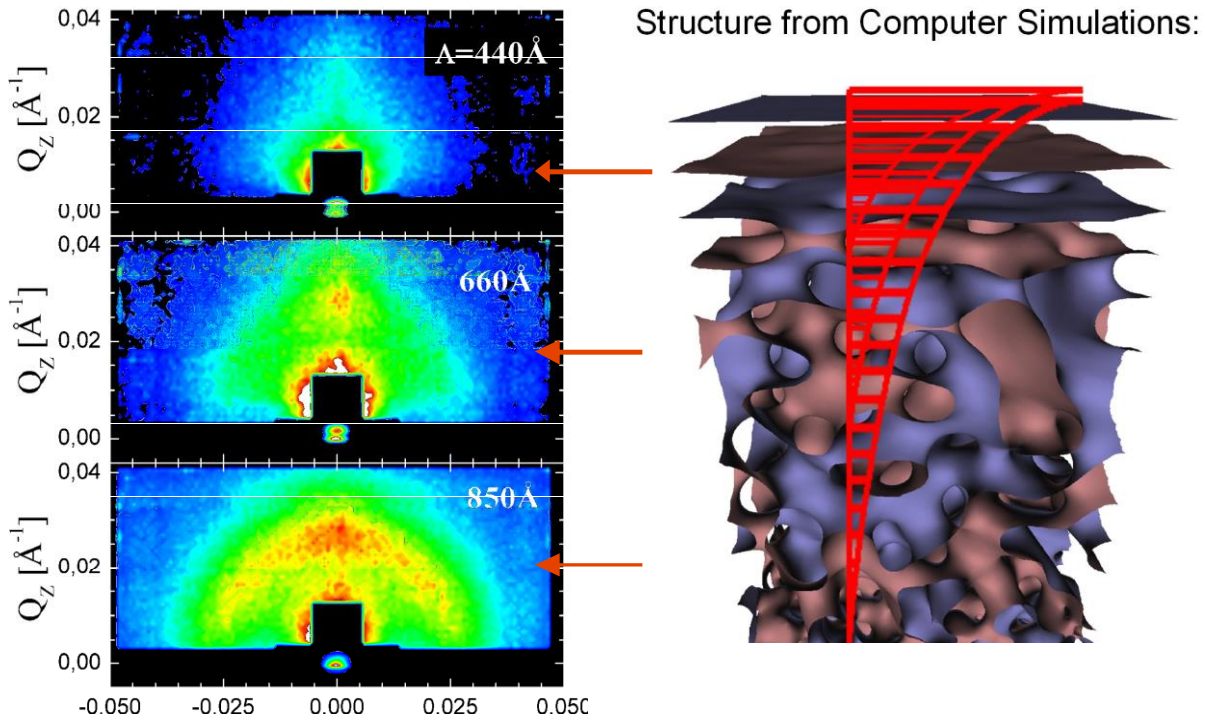

Fig. 3. *The grazing incidence geometry allows neutron scattering to probe order as a function depth from a slip boundary at the top(Frielinghaus et al.).*

Biology

- "Application of membrane diffraction and small angle scattering in photosynthesis research" Professor Jörg Pieper, University of Tartu
- "Challenges in mapping structural uniformity and texture of the cubic phases in butterfly and beetle wing scales with synchrotron pin-hole ultra-small angle x-ray scattering", Dr Christopher J. Garvey, ANSTO.
- "Neutron scattering from photosynthetic membrane in living bacteria" Dr Robert Corkery, KTH Royal Institute of Technology
- "Small-Angle neutron diffraction from biological membrane systems", Dr Volker Urban, Oakridge National Laboratory
- Structural and functional characterization of three closely related intrinsically disordered LEA proteins from *Arabidopsis thaliana*", Mrs Anne Bremer, Max Plank Institute for Molecular Plant Physiology.

- "Probing lipid-disaccaride interaction with neutron membrane diffraction", Dr Ben Kent, Helmholtz Zentrum Berlin.

The lamellar diffraction technique, particularly when applied to oriented stacks of lipid bilayers and certain cell membranes has long been used to study the orientation of membrane bound structures, in particular proteins and peptides. The technique combined with deuteration and molecular dynamics simulations has also provided very fundamental knowledge on the behavior of lipid chains and other hydrophobically solubilized molecules that have shaped the modern structural and dynamic view of cell membranes. In this session there were two very novel applications of the technique to study the locus of an important cryoprotectant sugar (Kent) and a small protein in the aqueous layer (Bremer). Cold diffraction instruments, which are also important in magnetism experiments, have modest needs, but provide a flexible instrument with solid angle coverage and q resolution intermediate between SANS instrumentation and conventional diffractometers. The problems with using a conventional SANS instrument (BIOSANS at ORNL) to study these problems was discussed (Urban). The major problems being that background and q_{max} limits the number of higher order reflections and thus the truncation of Fourier terms becomes a major limitation of structural precision of the measurement.

The group at ORNL have also explored the use of the SANS instrument to study periodic membrane stacking in photosynthetic organisms. At one level these organisms' ability to convert photons into electrochemical potential (photosynthesis) may be simple considered the most essential source of energy in the biosphere. The degree of interest in these system is reflected in the number of presentations discussing the use of SANS as a structural probe of membrane spacing in living metabolizing cells (Pieper, Urban and Corkery). Photosynthetic system are characterized by high degrees of membrane order (Fig. 4) and changes in these structures may be related to physiological functioning (20).

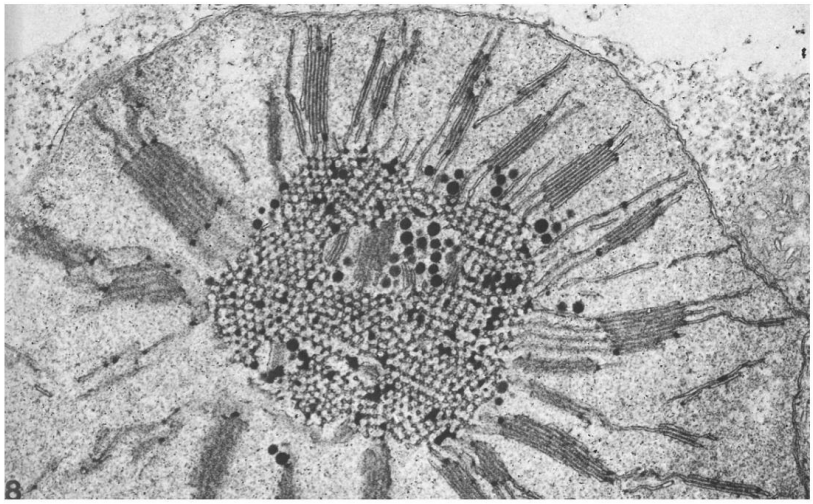

Fig. 4. *Cryo-TEM of prolamellar body showing the highly organized nature of membrane within the organelle. Upon exposure to light the membranes reorganize to form thylakoids and grana – the photosynthetic machinery (image courtesy of Kirkensgaard and Jakubauskas).*

The ESS: Instrumentation, Sample Environment

- "NMX – A Macromolecular Diffractometer at the European Spallation Source", Dr Esko Oksanen, ESS

- "Opportunities for soft matter diffraction experiments on ESS reflectometers and SANS instruments" Dr Hanna Wacklin, ESS
- "Status of ESS and instrumentation", Dr Markus Strobl, ESS

As discussed above the demands for data acquisition for these classes of experiments are quite different for conventional SANS instrument. Conventional diffractometers match the requirements for resolution but lower angles become limited by flux, and eventually at some point the quest for lower angles is abandoned. Currently there is one dedicated (cold) diffractometer operating in a user program, D16 (ILL), for the medium q regime with high enough resolution for many of the types of science discussed here. While optimal instrumentation may be designed in the science challenges discussed above there is a demand for timely data acquisition to optimize the acquisition time within the largely competitive constraint of q-resolution, in the simplest case to resolve the angular position of diffraction peaks. Furthermore, in many cases there is a deficit in the available q-range, particularly in the case of those analysis which use the Fourier reconstruction of the unit cell, where each resolved peak leads to an additional Fourier term in the unit cell and enhancement of the spatial resolution of the analysis. In this case the analysis of the peak intensity and position makes few assumptions about the basis of the peak shape, however for the analysis of different kinds of disorder the peak shape as well as the intensity is of interest. This requires a good understanding of the effect of the instrument (the instrumental convolution) on the shape of diffraction peaks. The discussions around the questions resolved with synchrotron x-ray scattering measurements, where effectively there no practical limitations to flux, provides an interesting contrast to neutron scattering measurements, and perhaps a window to science challenges of the future.

An outline of the overall instrumental capabilities was provided by Strobl. More specific detail on the planned SANS instruments and reflectometer were given by Wacklin and a particularly detailed view on the SKADI spectrometer by Frielinghaus. In general, the time of flight technique and the flexibility in Δq resolution versus acquisition time provided by the design of chopper systems give a potentially great advantage to the instrumentation at a spallation source (Fig 4). This is a general feature of all proposed diffractometers at the ESS, both SANS and more conventional diffraction instrumentation - they all are planned to have a greater accessible range of scattering vectors than is possible on existing instrumentation, addressing many of the problems of measurement discussed at the symposium. Traditional challenges with the TOF technique particularly on the effects of the wavelength dependence of the incoherent background may be limited in part by molecular deuteration. Non-conventional geometry measurements could be investigated for grazing incidence measurements.

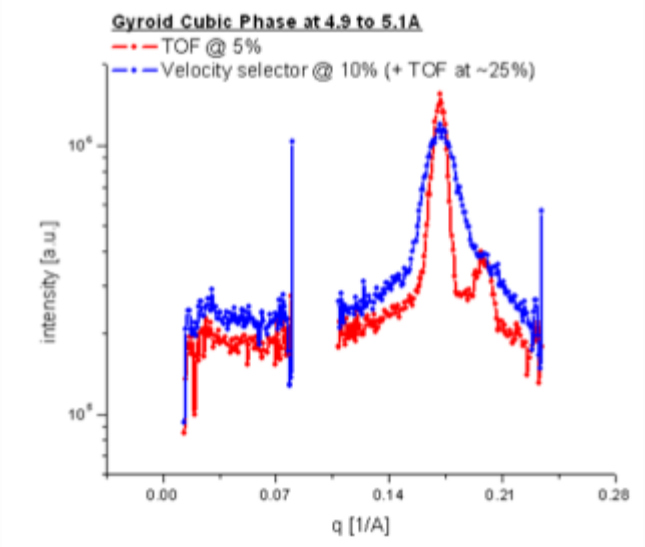

Fig. 5. *Effects of chopper resolution on the clarity of diffraction from gyroid cubic phase (Bilby SANS instrument, courtesy de Campo and Sokolova).*

Molecular deuteration is an important tool to enhance the capabilities of the neutron scattering instrumentation. Facilities have established for the production of deuterated biomass for subsequent fractionation and chemically deuterated molecules along with neutron scattering laboratories. There have been great advances in the chemical deuteration of molecules, and support for such facilities is vital for future neutron scattering studies of soft matter.

Conclusions

The symposium demonstrated growing demand and interest facing neutron instrumentation which is in many ways not ideally suited for specific investigations requiring the corresponding (adjustable) resolution in a small to wide angular ranges with preferably long wavelengths. The scientific problems discussed were remarkable in their parallels to those issues facing hard matter scientists. Limitations in many existent neutron diffractometers and the dominant x-ray scattering techniques were discussed. The aims of the meeting were: to bring together a community working in this science field; and engage this community in using neutrons to solve major questions where neutrons are the best choice of a probe. Thus we defined the scope of the field and the general science case and consequently defined specific requirements for neutron instruments to enable such research. This does not necessarily mean to define a dedicated or single instrument specialized for such science case, but to take care and identify requirements that existing and in particular planned new instruments in particular at ESS should meet in order to enable such promising and invaluable research.

It is therefore important with a view on ESS instrumentation efforts and the stage of its development to impact some design choices and scope on instruments potentially well suited and world leading in the future for such applications and science case. Instruments like NMX, SANS, neutron teflectometers or diffractometers able to approach long wavelengths and small angles like e.g. Heimdal are of specific interest for investigating the needs of this science concerning the yet shapeable potential of

accommodating such investigations. The time seems quite right currently when the scope of instruments is to be set and technical pre-design is to be on its way.

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