Report on the

ESS Science Symposium

The Future of Soft Matter SANS:

Consequences for Sample Environment and Complementary Techniques

22 - 24 February 2012, Lund

Organizers: S.U. Egelhaaf (University Düsseldorf), P. Schurtenberger (Lund University)

Aim

During the last few years, the response of soft and biological matter to external stimuli has attracted increasing attention. This includes the relaxation pathways and kinetics after the application (or cessation) of an external stimulus as well as the steady-state that develops while an external field or potential is applied. The external stimuli range from concentration, temperature or pressure changes to electric, magnetic or flow (shear) fields and include complex combinations of stimuli, for example in microfluidic devices. The stimuli might be applied to the bulk of the sample, only locally or might show spatial and temporal variations. Currently various external control parameters are explored with their number and combinations continuously and very quickly increasing. This development has to be seen in the context of a current trend in soft matter research towards increasing complexity and out of equilibrium situations, and attempts to study industrially and technologically relevant materials under near-processing conditions.

Small-angle neutron scattering (SANS) is a very powerful tool to determine the structure of soft and biological matter. It is also successfully used to study and follow structural changes that occur in response to constant or time-dependent external stimuli, e.g. temperature, pressure, electric or magnetic fields and mechanical forces (shear). This requires dedicated sample environment. Furthermore, the increasing complexity of samples often needs complementary information and thus simultaneous in-situ measurements, such as light scattering, spectroscopy or rheology. Importantly, such sample equipment can be constructed, which still is almost transparent to neutrons, thus allowing for simultaneous neutron scattering experiments. This is only possible due to the specific interactions of neutrons with matter and thus offers a unique opportunity.

The aim of this Symposium was to gather ideas on future neutron experiments at the European Spallation Source (ESS). We particularly discussed scientifically interesting external control parameters and complementary in situ measurement techniques, as well as their consequences for the sample environment and possible constraints on neutron instruments, such as space requirements and mechanical or electrical interfaces. This issue concerns primarily sample environment, but has also important implications for the design of a SANS instrument. The instrument should provide the appropriate environment (e.g. enough space or mechanical and electrical interfaces) and avoid interference with the sample environment (e.g. in the case of magnetic fields).

Moreover, some of these experiments might require or significantly benefit from a specific instrument design, e.g. in terms of beam size or orientation as well as collimation. Ideally, the instrument and sample equipment should thus be designed together. This results in a large number of design features that need to be considered and thus a complex task. We hope that the results of this Symposium will feed into the design of the instruments at ESS, especially of the sample area but also, e.g., support labs. The points raised during the Symposium should be considered at an early stage such that the instrument design and the experiments performed at ESS in the future are driven by the best science rather than by the availability of instruments.

Structure and Programme

The Symposium was opened with presentations of the **ESS activities** in small-angle neutron scattering instrumentation (Andrew Jackson) and sample environment (Oliver Kirstein).

The main part of the Symposium consisted of **four sessions**, which reflect the above-mentioned aims of the Symposium.

- external fields
- space- and time-dependent fields
- complementary in-situ techniques
- consequences for the neutron instruments

Each of these topics was introduced by an invited speaker and its breadth illustrated by contributed talks. This was followed by an extended general discussion of the different suggestions as well as further aspects, which was lead by an invited discussion leader.

We were very lucky in attracting internationally-leading experts as **invited speakers** (45 min talks). The invited speakers covered the main topics of the Symposium and also presented industrial aspects reported on the experience from the related x-ray technique, SAXS.

- Prof. Nigel Clarke (University of Sheffield): external fields, especially the response to shear fields which was determined spatially resolved
- Prof. Lise Arleth (University of Copenhagen): space- and time-dependent fields, especially flow-through cells and microfluidics
- Prof. Bernard Cabane (ESPCI, Paris): space- and time-dependent fields, especially industrial applications
- Dr. Olwyn Byron (University of Glasgow): complementary in-situ techniques, especially analytical ultracentrifugation
- Dr. Wim Bras (DUBBLE, ESRF): consequences for the neutron instruments, especially lessons to be learned from SAXS

Everybody participating had the opportunity to present his/her ideas in a brief (15 min) oral presentation. There were 19 contributed talks. Five of the participants instead presented a poster. (Programme and list of participants are below.) The level and experience of the **speakers and poster presenters** was exceptionally high; by far the majority was either on a professorial level or instrument responsibles of key instruments at major neutron or x-ray centres. Their contributions nicely illustrated the different aspects of the four main issues and represented very interesting ideas for future science, suggestions for experiments to be done and the necessary equipment.

At the end of each of the four sessions there was an extended discussion (1.5 hours) of the different suggestions as well as additional aspects not covered in the talks. The discussion was stimulated and lead by **discussion leaders**, which were well-recognized experts in the field, most of them having considerable experience with instrumentation.

- Prof. Ulf Olsson (Lund University): external fields
- Dr. Theyencheri Narayanan (Beamline responsible ID02, ESRF, Grenoble): space- and time-dependent fields
- Prof. Adrian Rennie (Uppsala University): complementary in-situ techniques
- Dr. Joachim Kohlbrecher (Instrument responsible SANS I, PSI, Villigen): consequences for the neutron instruments

Wednesday, 22 February 2012 – external fields		
13:30	welcome	
13:45	Andrew Jackson	SANS at the ESS
14:15	Oliver Kirstein	Sample environment at the ESS
14:30	**Nigel Clarke**	SANS: Bridging the gap between polymer physics and polymer processing
15:15	COFFEE	
15:45	Pavlik Lettinga	Time-resolved SANS on wormlike micelles in shear flow
16:00	Karsten Vogtt	Casimir cell and RheoSANS: Sample environments for soft matter SANS at the HZB
16:15	Jerome Crassous	Probing magnetic particles in external magnetic fields with SAXS
16:30	Annie Brûlet	Structural changes in liquid crystal polymer vesicles induced by in situ temperature change, magnetic field or UV irradiation external stimuli
16:45	Peter Lindner	The project of a new SANS pressure cell at ILL
17:00	Julian Eastoe	High pressure SANS of CO_2 surfactant systems
17:15 - 18:45	**Ulf Olsson**	**discussion** external fields

Thursday, 23 February 2012 (am) – complementary techniques		
9:00	**Olwyn Byron**	GISANS … USANS … newSANS! Novel science from advanced sample environments and simultaneous complementary measurements
9:45	Ralf Schweins	Recent developments in sample environment for SANS at D11@ILL
10:00	Vasyl Haramus	The partitioning of emulsifiers in o/w emulsions: A comparative study of SANS, ultrafiltration and dialysis
10:15	Henrich Frielinghaus	Near surface characterization of microemulsions via GISANS
10:30	COFFEE	
11:00	Jacques Jestin	Polymer-particle nanocomposites: Influence of nanoparticles dispersion, of polymer chains conformation and of filler orientation on the macroscopic properties of the materials
11:15	Wim G. Bouwman	Combined SANS-SESANS: From 1 nm to 100 μm in one instrument
11:30	**Adrian Rennie**	**discussion** complementary (in-situ) techniques
13:00	LUNCH	

Thursday, 23 February 2012 (pm) – space- and time-dependent experiments		
14:00	**Lise Arleth**	Challenges and possibilities in relation to high through-put solution SANS with small sample volumes
14:45	Felix Roosen-Runge	Protein in aqueous and salty environment – protein interactions and phase behaviour
15:00	Sylvain Prévost	Non-equilibrium systems and packing parameters: Narrow-disperse micelles of block terpolymers
15:15	Jan Skov Pedersen	Increasing information content by labelling techniques in rapid mixing experiments on surfactant systems studied by SANS
15:30	COFFEE	
16:00	Bernard Cabane	SANS experiments for industry
16:45	Marianne Impéror-Clerc	Self-assembly in solution of silica-based hybrid materials: Contribution of in-situ SAS studies
17:00	Ezzeldin Metwalli	Thin film kinetics of soft materials under solvent vapor: Prospects for time-resolved GISANS study
17:15 -18:45	**Theyencheri Narayanan**	**discussion** space- and time-dependent experiments
19:30	SYMPOSIUM DINNER: Restaurant Kulturkrogen, Tegnersplatsen 4	

Friday, 24 February 2012 – consequences for instruments		
9:00	**Wim Bras**	Sample environments and technique combinations for SAS beamlines
9:45	Aurel Radulescu	The small-angle neutron diffractometer KWS-2 for high inteisty / wide Q-range studies in soft-matter and biology
10:00	Richard Heenen	Sample environment and the user experience on SANS2d at ISIS
10:15	COFFEE	
10:45	**Joachim Kohlbrecher**	**discussion** consequences for the instruments
12:15	closing remarks	

Posters		
	François Boué	SANS under deformation: towards understanding stress in model and industrial nanocomposites
	Peggy Heunemann	Vorticity and velocity banding in shear thickening solutions of wormlike micelles: Time-resolved SANS measurements
	Julien Schmitt	Self-assembly in solution of silica-based hybrid materials – Modeling of in-situ SAS: From SBA-15 towards new systems
	Grethe Vestergaard Jensen	Time-resolved synchrotron SAXS study of micelle formation
	Dirk Wallacher	Soft Matter SANS Sample Environment at the Helmholtz-Zentrum Berlin

The abstract booklet, which was distributed to the participants, is attached.

Participants

We aimed at 28 participants to give all participants the possibility to present their ideas and suggestions as well as keeping the group small enough that a discussion is possible. However, we were overwhelmed by the response of scientists interested in participating in the Symposium, among them excellent scientists with a dedicated expertise on neutron scattering as well as very experienced and innovative neutron or x-ray instrument scientists. To limit the number of rejections, we increased the number of participants to 40, the maximum number the venue could hold. Despite this large number, all requests for oral contribution and posters could be satisfied. Furthermore, the discussions during the Symposium were very lively and did not suffer from the increased number of participants. A very large fraction of the participants very actively participated in the discussions following the talks as well as the general discussions.

Almost half of the participants were instrument scientists from neutron (ESS, ILL, ISIS, JCNS / FRM-II, HZB, LLB, PSI, Delft) as well as x-ray (ESRF, MAXlab) centres and the other half were scientists working at universities and science centres, by far the majority on professorial level. Most of them are very experienced neutron and x-ray users, but also early-stage scientists with a lot of enthusiasm for neutrons were present. This produced a very nice mix of very innovative and original science- as well as instrument-driven ideas. At the same time, the participants represented an enormous experience in instrument design and building, which was important in view of experience at other facilities, technical possibilities, feasibility and thus acted as a very healthy technical ‘reality check’.

List of participants:

Lise Arleth, University of Copenhagen
Manja A. Behrens, Lund University
François Boué, LLB, Saclay
Wim G. Bouwman, Delft University
Wim Bras, DUBBLE, ESRF
Annie Brûlet, LLB, Saclay
Olwyn Byron, University of Glasgow
Bernard Cabane, ESPCI, Paris
Nigel Clarke, University of Sheffield
Jérôme J. Crassous, Lund University
Julian Eastoe, University of Bristol
Stefan U. Egelhaaf, University Düsseldorf
Henrich Frielinghaus, JCNS, München
Vasyl Haramus, HZG, Geesthacht

Richard K. Heenan, ISIS, Didcot
Peggy Heunemann, ETH Zürich
Marianne Impéror-Clerc, Univ. Paris-Sud
Andrew Jackson, ESS, Lund
Grethe V. Jensen, Aarhus University
Jacques Jestin, LLB, Saclay
Oliver Kirstein, ESS, Lund
Joachim Kohlbrecher, PSI, Villigen
Pavlik Lettinga, FZ Jülich
Peter Lindner, ILL, Grenoble
Ezzeldin Metwalli, Tech. Univ. München
Theyencheri Narayanan, ESRF, Grenoble
Ulf Olsson, Lund University
Jan Skov Pedersen, Aarhus University
Tomás S. Plivelic, MAXlab, Lund
Sylvain Prévost, Tech. University Berlin
Aurel Radulescu, JCNS, München
Adrian Rennie, Uppsala University
Felix Roosen-Runge, University Tübingen
Julien Schmitt, Université Paris-Sud
Peter Schurtenberger, Lund University
Ralf Schweins, ILL, Grenoble
Markus Strobl, ESS, Lund (part time)
Karsten Vogtt, HZB, Berlin
Dirk Wallacher, HZB, Berlin

Location

We initially planned to hold the meeting in the ESS premises to get the participants as close as possible to ESS. This would have allowed them to experience that ESS is really existing and thriving, and would have reduced the cost. However, due to the move of ESS to the new facilities at about the same time, this was not possible. Instead the Symposium was held at a conference facility of Lund University in the centre of the city, Palaestra (room 105), shown on the front cover.

Main Discussion Points

The main results of the Symposium are summarized according to the four sessions of the Symposium, although a number of ideas and suggestions are beyond these topics or cover several topics. Furthermore, details of individual external fields or complementary techniques are avoided in favour of more general comments and concerns, which is considered more helpful at the present stage of ESS.

1. External fields

There is a significant trend to study soft matter in more complex situations, which typically include external fields. This is not only very interesting and timely from a scientific perspective, but often approaches situations encountered in industry (conditions during processing and, e.g., in running engines) or biology (ranging from hot springs and deep sea conditions to the sensing of magnetic fields) and biotechnology (e.g. catalysts, composite biomaterials). Thus it also has significant impact on technology and neighbouring disciplines, mainly chemistry, biology and engineering. Note that this was also reflected in the backgrounds of the participants, which included industry as well as biology, chemistry and other areas.

A number of external fields were discussed, in particular temperature, pressure, vapour pressure, humidity, gravitational field (especially centrifugation), magnetic fields, electric fields, fluid flow and shear fields (with different geometries, namely Couette, plate-plate, cone-plate, cross-slot, deformation, contraction, extension, stretching, extrusion).

The fields need to be well-defined (typically homogeneous, but not always), reproducible, reliable, can ideally be combined and are tuneable within a large range of magnitudes, in some cases reaching extreme conditions. Some of the external fields, e.g. magnetic or electric fields and shear, introduce a directionality. It is thus important how these fields are oriented with respect to the neutron beam and with respect to gravity. This also implies that the direction of the neutron beam relative to gravity becomes important. Their relative orientation is also crucial because many samples are liquid and thus their interface is susceptible to gravity and cannot be freely oriented. (The same reason why horizontal reflectometers are needed in addition to vertical reflectometers.)

Furthermore, the orientation of the sample (relative to the beam and gravity) and, for extended samples and/or fields, the position of the observed volume is important and thus rapid, precise, reproducible and reliable positioning (translational and rotational) is considered crucial. This extends to (multiple) sample changers, which allow the user to simultaneously keep samples at different conditions, mainly temperatures, and to tumble or mix the samples. Large series of samples, e.g. contrast variation series, might also be measured with the help of robots (as they exist at SAXS beamlines) thus efficiently covering a large parameter space. Also automated liquid handling and flow-through cells will allow users to efficiently measure large series. There are also attempts to develop 'intelligent' microfluidic devices to prepare samples using a feedback loop, i.e. samples are prepared in response to previously measured and automatically analyzed samples. This sample preparation 'on demand' provides high throughput, reproducibility and flexibility. It thus optimizes the use of resources, i.e. neutrons and sample material. Furthermore, external fields (e.g. UV irradiation or pressure) can not only induce a physical transition (e.g. change the conformation and/or interaction of polymers, lead to microphase separation or protein unfolding), but can cause reversible or irreversible changes in molecules that are intrinsically susceptible to external stimuli (e.g. breaking of chemical bonds or initiating trans-cis isomerisations).

A precise measurement of the applied field is required and should routinely be recorded during the neutron measurements. In this context it has to be noted that some of the fields might affect the (neutron) measurements, e.g. sapphire windows show a strain-induced, i.e. pressure-dependent, anisotropy.

2. Space- and time-dependent fields

Not only samples in a steady-state, which has been induced by an external field (as discussed above), but also the kinetics and pathways during or after changes in external parameters attract increasing scientific interest. This requires to follow the changes in the sample by (possibly repeated) real-time monitoring. Also these situations are closer to industrial or biological processes, which all occur under non-equilibrium conditions.

Changes in all the above-mentioned external fields can be applied to start processes in samples, including changes in the magnitude, orientation or combination of the fields. In addition, changes in the sample concentration or composition (including its pH) can be induced, e.g. using a stopped-flow apparatus, and the system's response to these changes studied as they occur. Furthermore, chemical reactions can be followed after adding the educts to a (stirred) reaction vessel which is monitored or which is connected to a pump-driven circuit, part of which is monitored. In addition, changes in the chemical composition of the sample can be induced by external fields, e.g. by flash photolysis or the pump-probe technique. Similar applies to physical processes, such as industrial polymer processing (e.g. film formation, solvent casting, extrusion, mixing)

While the main requirements for the external fields have been described above, they now have to be changed, typically quickly. This is often more difficult or even impossible for large sample volumes, which thus calls for small sample volumes (see point 4). Furthermore, changes in the external fields might induce (temporary or stationary) inhomogeneities in the sample, which also require to restrict the observation volume and, possibly, to scan the sample to determine the spatial and temporal evolution of the sample. This renders a combination with neutron imaging desirable (see point 3).

3. Complementary in-situ techniques

With an increasing complexity of the conditions and the samples, a thorough and comprehensive characterization of the sample is crucial. The complex conditions often also require to perform the measurements simultaneously. Complementary measurement techniques must thus not only be available in the home laboratory and the support laboratories of the neutron facilities, but also at the instruments to allow for simultaneous in-situ measurements. In some cases, it might also be advantageous to perform the complementary measurements off-line but close to the sample position, possibly in the sample area but not in the neutron beam, with an automated transfer of the sample into the neutron beam (with the same cell or into another cell). The advantages of simultaneous in-situ measurements always have to be balanced with possible disadvantages or constraints on the neutron measurements, which sometimes cannot be avoided.

The range of complementary techniques is large and steadily increasing. There are techniques that have already proven to be particularly powerful when combined with SANS, such as (multi-angle) static and dynamic light scattering, diffusing wave spectroscopy, rheology, UV-vis spectroscopy. Many others techniques are very promising, e.g. further optical spectroscopies (IR, AT-IR, CD etc.), SAXS and WAXS, calorimetry, refractive index and viscosity measurements, analytical ultracentrifugation and microscopy. Furthermore, a combination of SANS with other neutron techniques, in particular neutron imaging, WANS, SESANS, MIEZE, TISANE, GISANS and QENS, would open very interesting opportunities.

Combinations with separation methods permit to reduce the complexity of the samples, such as their polydispersity in size and shape, but also to remove aggregates or precipitates. This can be done by dialysis, ultrafiltration or chromatography (HPLC, GPC). Analytical ultracentrifugation, although difficult to implement, is particularly promising in biological applications of SANS because it allows to separate different components which nevertheless stay in equilibrium with each other. This provides a means to deal with, e.g., particle interactions, aggregate formation and multi-component samples like mixtures of protein-containing and empty vesicles.

In addition, synthesis facilities are required to provide, in particular, deuterated molecules or other isotope-substituted chemicals. More powerful measurement facilities and more complex samples also require more precise, e.g. monodisperse or isotope-pure, ingredients.

4. Consequences for the neutron instruments

The above-mentioned sample environments and complementary techniques require attention in different areas: the design of the instruments, in particular, but not only, of the sample area; the support labs; the organization and general procedures at ESS.

For space-resolved measurements, instruments which are optimized for small sample volumes (not necessarily small samples) are advantageous. Small sample volumes are also favourable

for scanning applications. A flexible and efficient scanning needs a reproducible and fast movement of the sample and/or beam, with the former applicable for small samples and small sample equipment, the latter required for heavy and bulky samples or sample equipment. On the other hand, time-resolved experiments need high efficiency, namely high count rate over a large q range, which requires not only a high neutron flux, but also a high detector efficiency and a small background as well as a large q range accessible in a single setting (as obtained by TOF and large detectors). For fast changes of control parameters a small sample volume is advantageous, often inevitable. A balance between both requirements, small sample volume and high efficiency, has to be found and/or specialized instruments optimized for the different situations need to be designed and built. The best compromise has to take into account the neutron pulse structure, which sets the time resolution beyond which the flux is considerably compromised. (In addition, to accumulate reasonable statistics, the experiments might have to be repeated for which histogramming and synchronization possibilities are required.) For very fast kinetics it might be advantageous to reduce the q resolution in favour of an increased flux. Thus, an optimum compromise (or in the case of several instruments complementary compromises) between the size of the sample volume, incoming and detected flux, q range and q resolution have to be found. Ideally, the instruments' flexibility allows the users to optimize these parameters for their experiments. Note that the (fluctuating) neutron flux has to be monitored with the same time-resolution (and wavelength resolution) as the scattered neutrons.

In the instrument design a combination with other neutron techniques should be considered, for example using imaging or polarization techniques (which require the instrument built from non-magnetic materials). This might extend the q range (USANS and focusing optics/lenses, WANS), provide complementary real space information (neutron imaging, SESANS), add sensitivity to interfaces (GISANS) or supply inelastic data (QENS, MIEZE/MISANS). Imaging, i.e. a spatially (and wavelength) resolved transmission, is particularly interesting in combination with scanning applications, which require this information for a quantitative data analysis.

As mentioned above, some external fields (e.g. electric, magnetic and shear fields) are not isotropic (as, e.g, temperature or pressure is). This introduces a further direction to the directions of the neutrons and gravity. While the direction of the external field can usually be chosen, the direction of the neutron beam relative to gravity should be considered. For some applications, such as rheology and centrifugation, a vertical neutron beam would be advantageous. Since soft matter samples, almost by definition, have a low viscosity, they are very susceptible to gravity (e.g. a liquid interface always stays horizontal). Thus for some soft matter experiments a vertical beam, i.e. a beam direction parallel to gravity, would provide new possibilities.

For the application of external fields as well as complementary techniques, enough space has to be provided in the sample area. (This might be particularly difficult for a compact SANS.) There should also be an optical access to the neutron beam direction to allow for complementary measurements, e.g. light scattering or optical imaging, to be performed in the same direction as the neutron measurements. The hardware, such as the amount of space, the neutron beam height, or the fixtures, should be standardized and have a modular concept. This will also best allow for future developments and implementations, which, despite all current efforts, will and should occur. The standard should include the interface to the instrument control electronics and software as well as data input (e.g. data acquisition through the sample environments and complementary techniques) and data output (e.g. control of the equipment and trigger signals for synchronisation). The software should provide preliminary fast in-line data reduction (in event mode), analysis and visualization as well as quality control. It

furthermore might contain general auto-settings and adjustment capabilities. It should be user-friendly also for occasional and non-expert users. For tests without neutrons, a mock instrument might be provided which, given a standard, can simulate all available neutron instruments. A general standard requires that all sample environments and complementary techniques are designed, constructed, operated and maintained by the same sample environment department. It will be difficult, if not impossible, to have in-house expertise for all complementary techniques. This could be obtained through partnerships, links to Lund University and other Universities, and MAXlab.

Close to the instruments, support labs with chemical and biological preparation, storage and characterization equipment should be available. Furthermore, a facility for isotope-labelling, especially deuteration, should be available, not necessarily on-site.