ESS workshop on Off-Specular Neutron Scattering

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Off-specular neutron scattering is concerned with the analysis of films and surfaces in order to obtain lateral structural information. Off-specular neutron scattering includes off-specular reflectometry as well as grazing incidence scattering, which can probe the two- and three-dimensional structure within a film. Off-specular neutron reflectometry measures the lateral structure of buried interfaces on the μm-scale, which makes it particularly powerful as a non-invasive tool to investigate film morphology. Grazing incidence neutron scattering additionally probes structures on the nm-scale, providing complementary information to optical techniques. A particular advantage of using grazing incidence neutron techniques is the ability to highlight specific parts or components of the structures using magnetic or isotopic contrast variation. The information gained is complementary to optical, electron and scanning microscopy techniques, as the average lateral structure and correlations can be measured in-situ without the need for invasive labelling, staining or drying.

Any form of off-specular neutron scattering suffers from weak signal compared to specular experiments. With the up-grade programs of the current major European neutron sources, from the ILL to the second target station at ISIS, and the optimisation of the instrumentation available, European scientists can start to fully explore this technique. It is clear that dedicated instrumentation (geometry, detectors, etc) is crucial. However despite these efforts, an increase in flux offered by the next generation spallation source (ESS) combined with next generation instrumentation and dedicated analysis tools, will be able to provide access to increased length scales and dynamical information on shorter time scales.

The ESS is very well-placed to integrate off-specular neutron scattering into its suite of capabilities, and a workshop is the ideal forum to bring together instrument scientists, the neutron user community, and scientists who would be interested in using dedicated instruments should they become available at the ESS.

The workshop was held at the Université Libre de Bruxelles on January 9 and 10 and consisted of 16 invited presentations and a panel discussion on the community's needs. These presentations reflected both science and instrumentation. Each day began with an ESS presentation from Markus Strobl and Hanna Wacklin on the ESS project and ESS reflectometry respectively.

Science

Professor Adrian Rennie from the University of Uppsala has the perspective of someone involved as an instrument scientist in the past, but also as a scientist with his own research goals and ambitions. In this talk titled "*Challenges and Advances in Scattering from Surfaces of Concentrated Colloidal Dispersions*" he described the needs to elucidate the two and three dimensional structure in concentrated colloidal systems where surface phenomena are distinctly different from those observed in the bulk, and require a grazing incidence solution. Neutron scattering methods have distinct advantages in elucidating multicomponent colloidal systems of societal relevance, such as those used in real life products.

Professor Kristiaan Temst of the Katholieke Universiteit Leuven discussed how magnetism research is benefiting from neutron scattering, and how off-specular techniques are crucial for an intimate understanding of disconnected magnetic nanostructures, in which traditional magnetometry measurements, such as SQUID are not applicable.. Given miniaturization

efforts in technology, such studies using polarised neutrons will become more important in future years.

Dr Johann de Silva of Trinity College, Dublin discussed in his talk "*Off-specular neutron reflectometry: exploring soft matter nanosctructures*" experimental data on the rupture of a buried polymer film and how the data might be analysed using periodic functions. His methodology was to simply convolve the structure of the polymer system with the experimental resolution, within the distorted wave Born approximation.

In his talk titled "*Characterisation of buried conjugated polymer interfaces by off-specular neutron reflectivity*", Dr Anthony Higgins from Swansea University presented a different approach to that of Dr de Silva where a rigorous application of the distorted wave Born approximation was applied to semiconducting polymers. The subject matter reflected the importance of performing reflectometry on buried interfaces. The nature of the interface in these conjugated systems can have implications for technology such as solar cells, so, like the magnetic nanostructures, there is a clear relevant modern technological aspect to the research.

Dr Emanuel Schneck from the University of Heidelberg presented a talk entitled ''Membrane-Bound Saccharides Studied by Specular and Off-Specular Neutron Scattering''. He showed how specular and off-specular neutron scattering is a powerful tool to study the mechanics of interacting membranes in situ. The surfaces of cell membranes are decorated with glycolipids, he studied the influence of these membrane-bound saccharides and their crosslinking on the mechanical properties of interacting membranes by using solid-supported membrane stacks and employing specular and off-specular neutron scattering. In such multilayer systems, the off-specular neutron scattering data can be in term of the Born Approximation, but if only the first Bragg reflection is available there is a need to go beyond this and use the Distorfed Wave Born Approximation.

Instrumentation

Professor Jean Daillant, from the SOLEIL synchrotron, Paris discussed the needs from the viewpoint of someone strongly involved in x-ray scattering. His interests are in soft matter systems, particularly membranes and amphiphiles, and he highlighted where the need for neutrons lies, particularly due to the inapplicability of x-ray techniques, where beam damage and lack of contrast between components can be a problem. Spin-echo method was noted as being a particularly promising technique development, because of its ability to discriminate between specular and off-specular reflection.

Professor Sunil Sinha is based at the University of California in San Diego, but he has made seminal contributions to the development of neutron and x-ray scattering over 40 years. His talk entitled ''*Waveguided enhanced off-specular scattering for studying three dimensional structures of thin films*'' illustrated how by using standing waves generated by the interference of the scattered neutrons (or X-rays) from parallel surfaces of a thin film, the so-called waveguide effect, can be used to enhance or reduce the scatterings from certain depths of the film. This resonance effect provides depth sensitivity to extract information on buried structures in thin films, which are not readily accessible by most surface techniques. He illustrated this clearly with an example of a thin film of polymer and polymer/nanoparticle nanocomposites. The talk also illustrated a clear way to analyse the data by using the distorted wave Born approximation in a recursive wave similarly to the Parrat's formalism. He showed that by using this approach, information at the nanometre and sub-nanometre spatial resolution could be obtained in the depth profile of the buried interface, of course combined with the in-plane information. He also reported of an effort of the USA community to improve the availability of off-specular a d grazing incidence analysis programs for users to allow wider adoptation of these techniques.

Professor Boris P. Toperverg of the Ruhr-Universität-Bochum presented a talk entitled ''*Kinematics and dynamics of scattering at grazing incidence: General principles and optimization for long pulse TOF mode*''. The first part of the talk was to illustrate what can be learned by using neutron scattering at grazing incident (specular polarized neutron reflection, grazing incident polarized neutron off-specular scattering, inelastic grazing incident neutron off-specular scattering, time resolved and PNR scattering). He also illustrated typical PNR kinematics at the ILL, general scattering kinematics at grazing incident and the principle of analysis. This last point was developed in detail illustrating the formalism of the DWBA for PNR together with the general form of the specular PNR formalism. The scattering amplitude matrix in DWBA and examples of off-specular scattering map of uncorrelated and correlated domains were presented together with off-specular scattering of multilayered systems. The talk also illustrated the difference between the angular dispersive and the TOF reflectometry approach. The need of analysis programs, as well as the need to include the thermalisation of neutrons by water in modeling were fully discussed in the panel discussion session.

Professor Sean Langridge from the ISIS has been involved in the development of techniques at ISIS Target Station 2 as well as his own work on magnetic films. He, highlighted the spin-echo reflection measurements to probe in-plane structure (SERGIS) on the new OFFSPEC reflectometer at Target Station 2. This work illustrated the importance of a reflectometry mode of operation because of the ease of accessing buried interfaces, although grazing incidence is also possible on current SANS instrumentation at ISIS (the new SANS2d instrument). The relevance here is that ISIS are using two separate instruments to serve the community. It would came up again at the panel session that it is not a good idea to have one instrument attempting to satisfy both the grazing incidence and reflectometry needs.

Dr Roland Steitz of the Helmholtz Zentrum Berlin presented the BIOREF reflectometer at the Helmholtz Zentrum. Here, the primary applications are on biological systems, but soft matter in general was also discussed. In terms of biology, the need for off-specular work to consider biological membranes was highlighted, but real breakthroughs in understanding biological membranes are still some way off because of the difficulty in obtaining prior information; this is our view, rather than that expressed by the speaker. Nevertheless, real and practical examples of biomimetic systems were presented, for example through examples of protein stabilization on nanostructured surfaces. Dr Steitz recognized the magnitude of the subject and also reflected on the SERGIS arrangement, as well as grazing incidence needs. As by others before him the need to extend the accessible Q-range was highlighted. Clearly the problem of background is going to need to be addressed in future developments.

Dr Jochen Stahn of the Paul Scherrer Institut with his talk "*Concept for a reflectometer for the ESS with focusing in sample and scattering plane*" discussed his work on *Selene*, a remarkable instrument development which is supported by the ESS. Here the challenge is to create a smaller beam to focus on small structures. The key here is to replace slits, from which a divergent beam exits, with elliptically curved mirrors. The flexibility of such technology was highlighted (applicability to time-of-flight and spin echo for example) but the key point here was that a technology that would be compatible with some off-specular techniques would enable examinations of smaller area structures of a few mm in size.

Professor Beate Klosgen of the University of the South Denmark highlighted the need to use specular and off-specular neutron scattering to probe specific membrane issues otherwise inaccessible. Results obtained from studies on an active membrane model system that consists of a photoswitchable variety of cholesterol (modified by an azobenzene group) in a POPC host membrane were illustrated. While some results were obtained with X-ray reflection, the talk illustrated the need for higher flux neutron scattering (both off-specular and specular) to probe clearly the 3D structure of the very thin membrane during externally

controlled switching of the mechanical state. Moreover, Prof. Klosgen also discussed the need for the dynamic experiments to probe changes in the elastic properties of the membrane upon switching.

Dr Fabrice Cousin of the Laboratoire Léon Brillouin (LLB) discussed how this laboratory could contribute to grazing incidence techniques even though with a 14 MW reactor, it could not compete on intensity with more modern technologies. He showed how GISANS was used for in-plane structural characterization of magnetic dots and magnetic stripes and on a solid/liquid interface of a system of nanospheres grafted on a surface in contact with the same nanospheres in bulk solution. The low signal-to-noise ratio owing to the poor neutron flux however inhibited a quantitative study. He highlighted work at the LLB on the development of GISANS collimation on a new SANS instrument, which will be operational in 2014. He also illustrated the off-specular measurements performed to characterize multilamellar tubes of fatty acids with a diameter of the order of the micrometer adsorbed at the air/liquid interface. The talk discussed some crucial aspects (data reduction, modeling, etc.) which are important to make off-specular neutron scattering techniques attractive for a large soft matter community that includes chemists and biologists.

Dr Robert Barker from the ILL presented a talk on ''Future perspective in membrane research: Can neutron reflectometry help?''. He illustrated the importance of neutron scattering to probe membranes by illustrating three topics: membrane fluctuations, protein interaction/pore formation and rafting in biology. He discussed the need of a multi-technique approach and dedicated sample environment for neutron scattering. The talk clearly illustrates that, when moving towards more complex systems, there is a need to increase selective deuteration to understand in-plane ordering.

Panel discussion

The purpose of the panel discussion was heralded as the community's opportunity to discuss the future instrumentation at the ESS and what it wanted from the ESS. Different possibilities were explored but it became quickly apparent from the discussion that the community did not want compromise. A grazing incidence machine should not be designed in conjunction with utility as an off-specular reflectometer. Furthermore, the community felt very clearly that both of these instruments were necessary. It was readily apparent from local (ESS) contributions that grazing incidence is seen as a key theme related to small angle scattering. It was also noted that reflectometry is at the heart of what the ESS wished to do. Hanna Wacklin and Markus Strobl from ESS were both clear in the point that, although the ESS would start with only seven instruments, this does not mean that other instrumentation could not appear reasonably quickly. Large-scale structures would have at least five instruments (eventually) in all, which should satisfy the community. This perspective has also to be seen in the light that the long pulse nature of the ESS source is in contrast to short pulse sources especially suited for large scale structure investigations such as performed with reflectometers and SANS instruments. This is especially the case given the recommendation of Sean Langridge that SANS will be in huge demand, and grazing incidence might end up being marginalized if it is merely a bolt-on to another SANS instrument. The group were also concerned that instruments be designed that used the advantages of the ESS. While advantages for reflectometry was clear (high flux pulsed beams for TOF experiments, matched for time-resolution requirements, low background), the long pulse resolution would be something of a problem for many experiments (limit on the dynamic wavelength band, the changing resolution with wavelength) and so this should be factored into instrument design. (However the low background inherent on long instrument should be of benefit to off-specular neutron reflectometry in particular.)

As with the grazing incidence scattering, where a machine could get inundated with demand by SANS users, it is also a problem that a machine optimised for reflectometry would be heavily used for specular reflectometry, and because of this it is not necessarily the case that a machine optimised for specular reflectometry would be the most appropriate for off-specular data. This is particularly important even if a spin-echo technique is being used. Nevertheless, if off-specular data were obtained simultaneously, it would increase the user base. Whether a machine like Selene designed for very small samples should be used for this purpose is not presently clear.

The group also made the point that we require good analysis tools. It was clear from the presentations that many groups are making useful contributions to this, but whether these can be translated to other research areas and other research groups remains to be seen.

Recommendations

There is a broad community ready to take an interest in off-specular techniques. The concept of obtaining three-dimensional information is inherently appealing, especially given that current technology being developed for the ESS will be designed with new users in mind. As such the ESS should develop:

- *More than one SANS instrument including one the primary purpose of which is grazing incidence scattering*
- *A dedicated reflectometer capable of performing both specular and off-specular reflectometry probably using a SERGIS-type design taking advantage of the pulsed ToF set-up rather than limit to a single wavelength as is usually performed.*
- *Instrument design should prioritise small samples with (initially at least) a specular reflectometry experiment using e.g. the Selene geometry.*