BCA IG Small Angle Scattering SIG, Grenoble – Meeting Abstracts

Monday 2nd July 2007

09:00 Tour of ILL with *Charles Dewhurst, Isabelle Grillo and Ingeborg Te Groen*

The ILL, with more than 30 neutron beam instruments, is one of the most powerful neutron sources in the world. The ESRF is a 3rd generation 6 GeV synchrotron offering world-class intensities for more than fifty beam lines. The joint ILL-ESRF-EMBL site in Grenoble exemplify the complementarity of the scattering techniques. Neutrons are capable of probing magnetic matierials with ease, and especially sensitive to contrasts of hydrogen and deuterium, and minimal sample damage and great penetration allowing a wide range of sample environments. Some of these aspects too are matched with high energy X-rays; more important is their much higher intensities opening up fast kinetic measurements inaccesible to neutrons. Joint scientific activities are stimulated by the recent creation of the Partnership for Structural Biology, PSB, containing the ILL's Deuteration Laboratory, and there are current plans for similar Partnership in Soft Condensed Matter.

The SAS instruments at Grenoble are classic pin-hole cameras. At the ESRF the principal SAXS instrument is ID2, which also includes a novel ultra small angle and wide angle detector array which add to the versatility of this 10m instrument, The Dutch-Belgian Group, DUBBLE, at the ESRF operate a second SAXS instrument on BM26 with a maximum camera distance of 8m, also with WAXS, and energy ranges 5-18KeV.

At the ILL, D11, the original SANS instrument now has a maximum sample-detector distance of 36m, and usable neutron wavelengths between 4-20A. D22, with a larger detector, has a maximum length of 20m; with a higher flux at shorter wavelengths it can be used routinely for kinetic and stopped-flow measurements. A new instrument, D33, is at the detailed design stage.

In large-scale structure studies reflectometry is also of importance at the ILL for magnetic, interface and membrane studies. D17 is a dedicated, highly versatile, vertical plane reflectometer, and ADAM too is partly available for use, and a new instrument, FIGARO, is under construction.

Both ILL and ESRF have high intensity/high resolution diffractometers for powders and single crystals. These are exceptional in enabling a wide variety of measurements with samples in very demanding environments of pressure temperature and external fields.
PSB http://psb.esrf.fr/
ID2 http://www.esrf.eu/UsersAndScience/Experiments/SCMatter/ID02/
DUBBLE http://www.esrf.eu/exp_facilities/BM26/dubblemain.html
D11 http://www.ill.fr/YellowBook/D11/
D22 http://www.ill.fr/YellowBook/D22/
D17 http://www.ill.fr/YellowBook/D17/
ADAM http://www.ill.fr/YellowBook/ADAM/

11:00 An Introduction to SAXS and SANS.

***Peter Laggner**, Institute of Biophysics and Nanosystems Research Graz.*

Small-angle scattering of X-rays (SAXS) and neutrons (SANS) are powerful methods for nanostructure analysis with closely related, basic physical concepts and strong complementarities. The talk will first introduce the basic scattering theory and outline the conceptual approaches to the application for (a) dilute particle systems, (b) crowded particle systems, (c) porous or condensed heterophase systems, (d) low-dimensional ordered systems and liquid crystals, and (e) thin solid films (GISAXS) . In the second part, the talk will describe the complementary strengths and weaknesses of SAXS and SANS, respectively, with some representative examples from material research and biophysics. Finally, the pertinent principles of instrumentation: sources, optics, sample environment, detectors, and data analysis will be described.
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12:00 Smectic ordering in side-chain liquid crystal polymers (LCP's) and in LCP-silica nanocomposites. *Françoise Ehrburger-Dolle, Laboratoire de Spectrométrie Physique, CNRS-UJF, France.*

The mesophase behaviour of a side chain polyacrylate LCP grown by drying a solution has been investigated. This LPC characterised by a short spacer (4 carbon atoms) and a long tail (10 carbon atoms) displays, at increasing temperatures, SmC and SmA_d phases. The effect of the mean molecular weight *i.e.,* the mean number of side chains per polyacrylate main chain (18 and 51) on the lamellar width was studied. LCP-silica nanocomposites have been synthesised by a sol-gel process in presence of LCP in the solution, follows by subcritical drying. The mesophase behaviour of these nanocomposites was compared to that of the corresponding bulk LCP. The experimental methods were polarised optical microscopy, differential scanning calorimetry and synchrotron X-ray scattering.

This work has been performed in collaboration with I. Morfin and F. Bley (CNRS-UJF, Saint Martin d'Hères) and N. Pesca da Sillveira, F. Vargas Pereira, A.A. Merlo, O.M. Ritter (UFRGS, Porto Alegre, Brazil) thanks to the CAPES-COFECUB project 411-03. The authors acknowledge ESRF, Grenoble, for access and the French CRG beamline D2AM and the help of its technical staff, J.F. Berar, N. Boudet, B. Caillot, S. Arnaud.

12:30 Small Angle X-Ray Scattering (SAXS) with NanoSTAR – Principles & Applications.
Richard Görgl *[1)], Lutz Brügemann [2)], Joachim Lange [2)]*

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Nanostructure investigation using small-angle x-ray scattering on a lab scale requires high standards for both the intensity and the divergence of the primary beam. The NanoSTAR system has always provided high-end technical solutions to this goal.

The first part gives an overview of the system including recent improvements (Incoatec micro-focus source (IμS) with integrated Montel optics, VÅNTEC-2000 detector).

Selected applications in the second part will include:

- Polymeric anorganic (Si & Zr) oxide composites (including data fittting and interpretation)
- Biological Macromolecule Urate Oxydase (including data fitting and interpretation)
- GISAXS measurements – comparison Lab-Synchrotron

14:00 SAXS studies of powder particle deformation during compaction.
Peter Laity *and Ruth Cameron, Dept. of Materials Science and Metallurgy, University of Cambridge*

Powder compaction is an important industrial process that is used for metal, ceramic and polymeric materials. Moreover, compacted tablets represent a widely used and very popular route for drug delivery. This has stimulated a considerable research effort into characterising compaction behaviour of the often complex mixtures of drugs and excipients used and the relationships with strength and swelling behaviour of the resulting tablets.

A number of mechanisms operate at the particle scale, during powder compaction. It is generally believed that particle rearrangements dominate at low pressures, while particle deformation and fracture become more important at higher relative densities, leading to greater interfacial contact and bonding between particles. However, very little direct evidence has been reported to demonstrate changes in the underlying mechanisms at different stages of compaction.

Small-angle X-ray scattering (SAXS) has been widely used to study polymer deformations, under various experimental conditions. Nevertheless, it does not appear to have been applied to powder compaction previously, even though it may be expected to provide a direct method for observing and

quantifying particle deformation. This presentation will describe some recent work at Cambridge, using SAXS to investigate the deformation of polymeric powders undergoing compaction.

14:30 D33 - A third Small Angle Neutron Scattering instrument at ILL.
***Charles. D. Dewhurst**, Institut Laue Langevin, Grenoble, France*

D33 will be a third Small-Angle Neutron Scattering (SANS) instrument at ILL, adding to and building upon the highly productive and world leading D11 and D22 instruments. Modern trends in materials science, physics and in particular nano-structured materials require that D33 should provide both high resolution and wide dynamic q-range. In 'monochromatic' mode a high-resolution velocity selector and flexible system of inter-collimation apertures will define the neutron beam. A double chopper system will enable a novel 'time-of-flight (TOF)' mode of operation (2Å to 20Å) allowing an enhanced dynamic q-range and flexible wavelength resolution. TOF on a reactor source has the distinct advantage that pulse frequency, bandwidth and resolution can be optimally matched to the neutron flight path without compromise.

Two large multitube detectors will allow a wide dynamic q-range ~ 15 and (a massive) ~150 in monochromatic and TOF modes respectively. Beam polarisation and 3He spin analysis will facilitate and expand studies of magnetism and allow a more quantitative analysis of spin incoherent samples. Enhancements such as focussing lenses will be available to allow the study of large samples without loss of resolution while refractive prisms will improve resolution at long wavelengths by cancelling gravitational effects.
The TOF chopper system will also allow time-resolved and kinetic studies (< 10's ms) using the 'TISANE' technique. The siting of D33 will be such as to allow high magnetic fields at the sample position. Low background sample environments are foreseen where possible incorporating windowless mating of common vacuum spaces. As a SANS instrument with full polarisation and analysis we ultimately have the ambitious intention to implement new and novel spin manipulation, 'bunching' and interference techniques which allow much higher resolution in either time or space.

15:00 In-situ studies of flowing samples with SAXS and SANS.
***Adrian R. Rennie,** Department of Physics, Uppsala University, Sweden*

Small-angle scattering is used to study a number of systems of practical interest such as dispersions of colloidal particles and polymers in solution. Many of these materials are synthesised or processed under conditions of flow. This talk will present some results from studies of synthesis using in-situ sampling with both small-angle X-ray and neutron scattering. Time resolved data that extends to the ultra small-angle scattering regime measured with double crystal instruments with both neutrons and X-rays gives new insights into synthesis. Some illustrations of templated synthesis of silica will be shown.

15:30 Creating 3D-Networks and Hydrogels from Self-Assembling Peptides.
***Alberto Saiani,** School of Materials, The University of Manchester, Grosvenor Street, Manchester M1 7HS, UK*
Molecular self-assembly is a powerful tool for the preparation of molecular materials with a wide variety of properties. This is illustrated by the abundance of self-assembled proteins and polysaccharides encountered in Nature. Peptides are particularly promising as building blocks for a number of reasons. The natural amino acid pool consists of 20 members with different physical properties including polar, non-polar, acid, basic and aromatic groups. In addition, an infinitenumber of unnatural amino acids can be designed in the laboratory. Amino acids can be combined in endless different ways leading to a vast number of building blocks with different physical properties. However, the understanding of the molecular interactions and self-assembly rules in these materials is still limited, consequently, the

fundamental link between building block structure, mesoscopic structure and material properties has not yet been elucidated.
In our work we decided to undertake a systematic investigation of the self-assembly and gelation properties of a series of octa-peptides. Small angle neutron scattering (SANS) was used to investigate the structures formed. In addition to SANS, atomic force microscopy (AFM), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR) and micro differential scanning calorimetry (-DSC) were used to characterise our systems.
In our presentation we will show how the amino acid nature and sequence affect the selfassembly and gelation ability of these peptides. By manipulating the peptides chemical architecture we were able to obtain non self-assembling peptides, self-assembling peptides that do not formhydrogels and self-assembling peptides that form hydrogels with different type of network topologies and therefore mechanical properties. The number of structures and morphologiesobtained show how versatile peptide self-assembly can be and how a fundamental understanding ofthe self-assembly and gelation rules could lead to the creation of new materials with properties tailored to specific applications.

16:30 Use of Small-Angle Scattering for the characterisation of precipitates in metallic alloys.
Alexis Deschamps, *SIMAP, (Science et Ingénierie des Matériaux et Procédés), France.*

Small-Angle Scattering is one of the oldest techniques for characterising nanometre-scale precipitates in metallic alloys. However, the increasing access to high flux and high resolution synchrotron X-ray sources has considerably widened the possibilities of this technique. The present contribution will summarize some of the recent progress we have achieved on metallic alloys:

1. Understanding non-isothermal precipitation using in-situ measurements during fast temperature changes. The competition between precipitate dissolution and transformation of metastable to stable precipitates during continuous heating of AlZnMg alloys will be presented, and compared to modelling results.

2. Characterisation of the precipitation state in weld heat affected zones by microstructure mapping. The effect of initial microstructure and welding parameters on the 2-D distribution of precipitate microstructures will be shown in the case of Friction Stir Welding of aluminium alloys. It will be shown that this microstructure distribution enables to understand the weld mechanical behaviour.

3. Determination of the heterogeneous chemical structure of precipitates in AlZrSc alloys using high sensitivity measurements. It is now well accepted that in the AlZrSc system precipitates consist of a Sc-rich core and a Zr-rich shell. It will be shown that SAXS enables to quantitatively determine the parameters of this peculiar structure (thickness, composition, .) and that these parameters can thus be followed in-situ during a variety of heat treatments. The unusual precipitation kinetics of this system will be discussed.

4. Perspectives on the evolution of precipitation under the combination of stress/strain and temperature will be given, through preliminary results obtained using a specific stage developed in our laboratory.

17:00 Microwave heating in materials science and biology: is it all just hype and hypochondria?

*Gaetan Giriat**, Andrew Harrison***†**, *Gareth Oakley, Philip Kay, Marcela Pina-Sandoval, Graeme Robb, Gavin Whittaker, Douglas Youngson. School of Chemistry and EastChem, The University of Edinburgh, West Mains Rd., Edinburgh, EH9 3JJ, UK*

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Microwave heating is becoming increasingly important as a method of driving chemical synthesis and materials processes, both in solution, and in the solid state. There are also increasing concerns about the possible harmful effect that such radiation – as used in mobile 'phones - may have on biological tissue, over and above what might be expected from consideration of the likely heating effects at low exposure level. However, both aspects of this field are served by almost no direct experimental measurements of the nature of such effects and in many respects the microwave oven is treated merely as a 'black box'. We have developed several different types of microwave reactor that enable us to study how the structure and composition of materials change during microwave irradiation by in situ X-ray or neutron scattering measurements on powders, single crystals, colloidal and liquid crystal systems. We are also able to measure temperature accurately and precisely throughout such processes. This equipment has been used follow materials synthesis in solution and in the solid-state, revealing phase-selective temperatures and phase changes during microwave irradiation. It has also been used to probe the possible effect of microwave radiation on the structure of proteins and biological membranes through in situ small angle neutron scattering measurements.

17:30 I22 - A non-crystalline diffraction beamline for the physical and life sciences

Jennifer. Hiller, *M. Malfois, A. Marshall, J. Rawle, S. Rogers, K. Wilkinson, N.J. Terrill*

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The UK has an active community that is at the forefront of developments in Non Crystalline Diffraction. Their interests encompass the fields of medicine, biology, environment and materials. They include: studies of supramolecular organization in biological systems, the structure and function of muscle filaments, corneal transparency, biological membranes, polymer processing, self assembly of mesoscopic metal particles, colloids, inorganic aggregates, liquid crystals and devices. The work is supported by the BBSRC, EPSRC, MRC and NERC. NCD is one of the truly synergistic interdisciplinary sectors within UK science and the wider international arena.

The requirements to meet the scientific and technological challenges of the next decade are for a high resolution, high brightness beamline which can only be provided by an undulator insertion device on a third generation synchrotron radiation light source.

The new beamline at Diamond, I22, will use an in vacuum undulator source to deliver a high photon flux into a focused 75 x 300 μm spot (approx. 1 x 1 μm with microfocusing) in the energy range 4-20keV. The experimental station, with associated linear and area detectors for static and time resolved measurements, will be capable of recording the scattered radiation from samples contained in purpose

designed specialized environmental cells. Its modular arrangement will allow a choice between small angle scattering for large fibrous structures or microfocus illumination, each with a wide angle scattering option for materials studies.

I22 will play an important role in progressing our knowledge of macromolecular structure into function and into advancing the industrial development of biomaterials, biosensors and other devices. X-ray rheology experiments will improve the understanding of food gels and lead to the manufacture of better designed polymers and a more efficient production technology.

Tuesday 3rd July 2007

09:00 Ultra low k Dielectrics for Microelectronics.

Jean-Paul. Simon. *SIMPAP, CNRS-UJF-INPGrenoble, BP75, 38402 Saint Martin d'Heres, France (jean-paul.simon@ltpcm.inpg.fr)*

The increase of the integration density and of the operation speed in ultra large scaled integrated microelectronics requires to reduce the dielectric constant for high frequency insulation between the copper connections of some tenth-of-micrometer thickness. The quality of the dielectric is defined by its dielectric constant k (> 1) relative to the unpolarized vacuum (k = 1). Bulk low k will never reach k lowed than 3 and the only way to achieve further k decrease is to introduce nanopores dielectric films compatible with required mechanical behaviour.

For deposited layers much thicker (~300nm) than the size of the scattering objects (<10nm), GISAXS analysis of the corrected data is the same as the one of SAXS in transmission. GISAXS allows to measure layers deposited on opaque buffers and, due to the grazing angle (above the critical angle, in order that the beam penetrates into the layer), increases the signal in 1/sin(ai), ai being the grazing angle, i.e. of ~300. The drawbacks are: i) the measure needs a synchrotron beam (in the present case the anomalous scattering/diffraction beamline, D2AM, at ESRF, ii) due to the shadow oof the sample for ai in the range 0.1-0.5 degree at 8keV, we are unable to measure scattering object sizes large then ~10nm in the direction perpendicular to the layer. Comparative (or absolute) intensities can only be extracted if the beam monitoring do correspond to the beam impinging the sample: thanks to our 70mm long samples and our 0.1mm beam heigth, all the beam is intercepted by the sample and a correction of the intensities in 1/sin(ai) give a superimposition of the SAXS patterns for different ai. We compare the merits and the structure determined of different growth processes, porogen approach, self assembled and PECVD. All of them are baked in order to cure the amorphous SiwOxCyHz "skeleton" (SiOCH). Depending on the process used, the poremorphologies are very different: they range from well-defined pores of 4-5 nm of diameter, with occasionally a strong anisotropy of the pattern, to sub nanometric ill-defined pores which may be described as density fluctuations. The sizes and volume fraction fv can be compared to two othertechniques: elipsometry-porosimetry and X-ray Reflectivity. Finally, it appears that the curing process is a key problem, which up to now has been difficult to characterize by GISAXS.

Acknowledgements: The presented exemples are taken from the long term collaboration with V. Jousseaume and G. Rolland from the LETI/CEA-Grenoble. Thanks also to the D2AM team Drs Bérar, Boudet and Caillot.

09:30 SAXS with micrometer-sized synchrotron radiation beams.
Christian Riekel *European Synchrotron Radiation Facility, B.P. 220, F-38043 Grenoble Cedex France*
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The talk will introduce small- and wide-angle X-ray scattering (SAXS/WAXS) techniques using micron- and submicron-sized synchrotron radiation beams. I will show selected scanning SAXS/WAXS experiments for synthetic polymers and biopolymers, which allow the generation of "diffraction images" based on the extraction of specific parameters such as long period, local orientation, or crystallinity from a series of diffraction patterns. Microbeams are also very convenient for in-vivo studies of biological processes like silk extrusion, for studying protein aggregation in microfluidic environments or for grazing-incidence scattering (GISAXS) studies on small sample areas.

10:00 Structural Hierarchies in biological macromolecules.
Tim Wess, *Cardiff University*

The emergent properties of many biological tissues collagen- cellulose – elastic assemblies- depend on the modulation of molecular properties and interface contacts over a range of lengthscales, SAXS is an optimal tool to define structural parameters at a variety of levels such as intermolecular distances, fibrillar size, interface properties and interfibrillar interference. The changes in these properties can also be observed in dynamic mechanical testing, and modulation by effects such as heat and chemical treatment. I will show how we have used SAXS on solid state ex planted samples of biomaterials to understand the interaction within intact tissues. We have also used solution SAXS to determine molecular shapes of molecular components of assemblies. Highlighted are studies go toward explaining
1) the molecular topology and structural hierarchies of collagen
2) the structural hierarchies of fibrillin a ubiquitous elastic protein of animals.

11:00 SAXS experiments within conventional XRD instrument.
Vladimir Kogan, *DANNALAB & PANalytical BV, The Netherlands.*

Advances of modern x-ray diffractometry are mostly related to accuracy, modularity, new x-ray optics and x-ray sources. The combination of these factors makes it possible to conduct good quality small angle x-ray scatteringexperiments competing with dedicated SAXS setups.
We will present the results of SAXS evaluation on nano-particles, polymers and biological macromolecules conducted on the conventional X'Pert MRD diffractometer equipped with dedicated collimation system*, optics and source.

** patent pending*

11:30 The joys of SAXS and other toys.
Wim Bras, *ESRF*

The information content of an average SAXS pattern is in practice rather low. However, the combination with information derived from other techniques can turn SAXS into a very powerful tool especially when dealing with time-resolved data-sets.

The DUBBLE beam lines have specifically been designed to make such technique combinations possible. The obvious partner of SAXS is WAXS and these two techniques are routinely combined in a single experiment. However, also the combination of SAXS/WAXS and EXAFS has been implemented.

In the presentation I will show how combined SAXS/WAXS data sets in combination with neutron

scattering and electron microscopy can unravel the story of crystallisation in a glass ceramic in full detail. The glass used is cordierite which is a low expansion, high shock resistance material used in car exhaust and electronic chip packaging. Even though this is a technologically relevant material the emphasis will be on the benefits of the technique combination for which cordierite is a textbook example.

The second part will deal with the combination of scattering and spectroscopic techniques on a catalytically important material. Here it will be discussed that no change still can mean a lot even outside the context of a political party program.

12:00 SAXS of Surfactant Meso-phases (including a general Q&A session to end the meeting).
Richard Morris, *Morris Analytical X-ray.*

Structured surfactant systems are used in a huge variety of applications (household, industrial & institutional, personal care, agrochemicals…)
A structured system is a pourable composition comprising water, surfactant and (usually) a structurant, which form a three-dimensional, lyotropic liquid-crystal matrix (properties change with changes in concentration).
The system has an internal yield stress, which is large enough to suspend solid particles, but is low enough to allow the system to flow as a normal liquid.

Surfactants are amphiphilic molecules, which can form lyotropic liquid crystals under controlled conditions. Amphiphilic molecules are composed of two different parts:
A non-polar, or hydrophobic, hydrocarbon tail that is insoluble in water, and a polar or hydrophilic head that tends to dissolve in water.

Some other amphiphilic molecules that form lyotropic liquid crystals are bile salts and phospholipids.

When these compounds are dissolved in water, they can form spherical aggregates such as micelles or vesicles (spherulites) or structures such as a bilayer.

<u>What can SAXS tell us?</u>

The phase or “crystal lattice” of the surfactant.
The size of the bilayer spacing.
We can use it to “tune” surfactant formulations.
The thermal stability of the system can easily be determined (in this case, over the temperature range 0-70°C).
The data can be incorporated into patents.

A brief description of this laboratory-based analysis will be given during the presentation, together with corresponding polarised light and SEM micrographs.

Question and Answer session concludes the meeting.