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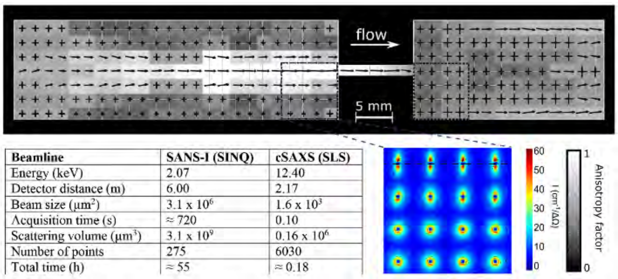
MAPPING OF FLOW-INDUCED NANOSTRUCTURES IN COMPLEX FLUIDS BY COMBINING MICROFLUIDICS AND SCANNING-SAXS

V. Lutz-Bueno[a], **M. Liebi**[b] **and P. Fischer**[a]
[a]ETH Zurich, IFNH, Schmelzbergstrasse 9, 8092 Zurich, Switzerland
[b] Paul Scherrer Institute, Swiss Light Source, 5232 Villigen, Switzerland

In situ measurements with high temporal and spatial resolution are necessary to understand the dynamics of macromolecules under flow. Variations in molecular shape and dimensions due to degradation/aggregation/self-assembly under shear, molecular alignment with flow and shear-banding are some examples of transitions under flow. By combining microfluidics and scanning-SAXS, the nanostructure of complex fluids like polymeric solutions, surfactants, proteins and biological fluids can be observed and quantified. Figure 1 shows the flow-map of wormlike micelles measured with SANS. The dependence of molecular alignment on shear and extension rates as a function of the volumetric flow rate was determined [1]. However, to gain in spatial resolution, the beam diameter had to be reduced, which increases the acquisition time of each pattern to about 10 minutes. On the other hand, the use of SAXS for flow-mapping allows measurements with higher spatial and temporal resolution. A newly developd microfluidic device (based on polyimide and glass) generated very low background scattering, resul-ting in strong signal from the samples, even in very thin channels (100 µm). The acquisition time was 0.1 s with a beam size of 40x40 µm, leading to much better resolution and data collection efficiency. Figure 2 shows as example: a wormlike micellar solution undergoing shear-banding at increasing volumetric flow rates. The color-code mapping of anisotropic scattering angle confirmed that the micelles align with flow in high shear/extension areas. Based on the evolution of the vortex formation (upstream), the influence of the fluid viscoelasticity can be determined as a function of confinement. The outlet region also has important information on the alignment of macromolecules in expansion flow.



Beamline	SANS-I (SINQ)	cSAXS (SLS)
Energy (keV)	2.07	12.40
Detector distance (m)	6.00	2.17
Beam size (µm^2)	3.1 x 10^6	1.6 x 10^3
Acquisition time (s)	≈ 720	0.10
Scattering volume (µm^3)	3.1 x 10^9	0.16 x 10^6
Number of points	275	6030
Total time (h)	≈ 55	≈ 0.18

Figure 1: SANS-mapping of wormlike micelles under flow. The gray scale is based on the anisotropy factor and the arrows indicate the direction. The table compares the parameters used for both experiments.

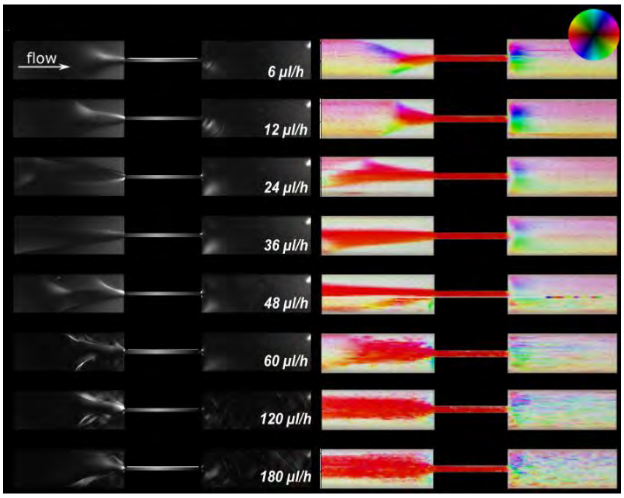


Figure 2: Wormlike micelles self-organizing under contraction flow. Left: visualization by polarized light. Right: SAXS-mapping of the preferential direction of macromolecule alignment under flow based on the anisotropy of the scattering patterns. The alignment angle is given by the color-coded circle. White areas represent isotropic scattering. The intensity is not represented.

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Submitting Author: viviane.lutz@hest.ethz.ch

SAXS AND SANS STUDIES OF THE STRUCTRE OF CONCENTRATED HARD SPHERE SUSPENSIONS

G. Bryant[a], **V. A. Martinez**[b], **A. B. Schofield**[b], **F. Zontone**[c] **and C. J. Garvey**[d]
[a]*Centre for Molecular and Nanoscale Physics, School of Applied Sciences, RMIT University, Melbourne, 3001, Australia*
[b]*SUPA, COSMIC and School of Physics and Astronomy, The University of Edinburgh, King's Buildings, Mayfield Road, Edinburgh EH9 3JZ, United Kingdom*
[c]*European Synchrotron Radiation Facility (ESRF), BP 220, F-38043 Grenoble Cedex, France*
[d]*Australian Nuclear Science and Technology Organisation, Lucas Heights, Australia.*

Colloidal suspensions of hard spheres are valuable experimental model systems for exploring phase behaviour and dynamics in condensed matter. Such colloids can form colloidal crystals at concentrations above the freezing volume fraction of 0.494, allowing the investigation of the kinetics and dynamics of crystallization. As colloidal particles are much bigger than atoms, processes are correspondingly slower, and metastable states can be studied in real-time using the well-established technique of dynamic light scattering (DLS), or the more recently developed technique of x-ray photon correlation spectroscopy (XPCS) [eg 1-2]. In this work we explore the use of modern Synchrotron Small Angle X-ray (SAXS) and Neutron (SANS) scattering for the study of structure in colloidal suspensions near the freezing volume fraction. In particular we explore their advantages and disadvantages relative to traditional light scattering techniques.

The advantages of SAXS are: it allows access to a much wider range of scattering vectors (see figure); the small beam diameter allows the probing of different parts of the sample to explore inhomogeneity; and the measurement time is short, allowing the study of fast kinetics. The chief disadvantages are potential beam damage, and the need for very thin samples (and therefore small sample volumes).

The advantages of SANS are: an expanded beam [3] can be used to obtain averaging over large volumes, so excellent statistics can be obtained - this is especially important when studying the early stages of crystallization [4]; and the ability to contrast match, particularly relevant to the study of binary systems [5]. Although contrast matching can be done with light scattering using very specialized particles [6], deuteration offers more flexibility in the types of particles that can be used. In this paper we will present the results of recent experiments at the ESRF and ANSTO designed to explore the possibilities and limitations of these techniques.

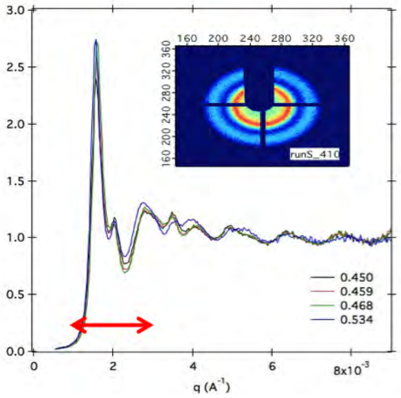

Figure 1: Static structure factors for hard spheres measured at a synchrotron SAXS beamline (ESRF). The arrow indicates the q range accessible using traditional light scattering techniques.

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Submitting Author: gary.bryant@rmit.edu.au

PROTEIN INCORPORATION INTO THE NANOSTRUCTURE OF BICONTINUOUS MICROEMULSIONS

<u>V.S. Urban</u>[a], **D.G. Hayes**[a,b], **R. Ye**[b], **R. Dunlap**[a,b], **S.V. Pingali**[a], **H.M. O'Neill**[a]
[a] *Biology & Soft Matter Division, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, Tennessee 37831, United States*
[b] *Department of Biosystems Engineering and Soil Science, University of Tennessee, Knoxville, Tennessee 37996-4531, United States*

We have used SANS to investigate the influence of incorporating proteins into the middle phase of 3-phase microemulsions [1]. These nanoscale sponge-like structures have high internal interface area, near-zero surfactant film curvature and intertwined water and oil filled channels that are separated by a surfactant layer. This self-organized molecular architecture bears resemblance to the functional sub-cellular structures (organelles) that are built from lipid membranes in the cells of living organisms. Bicontinuous microemulsions are therefore interesting model systems for studying the important questions of the physico-chemical interactions between proteins and membranes.

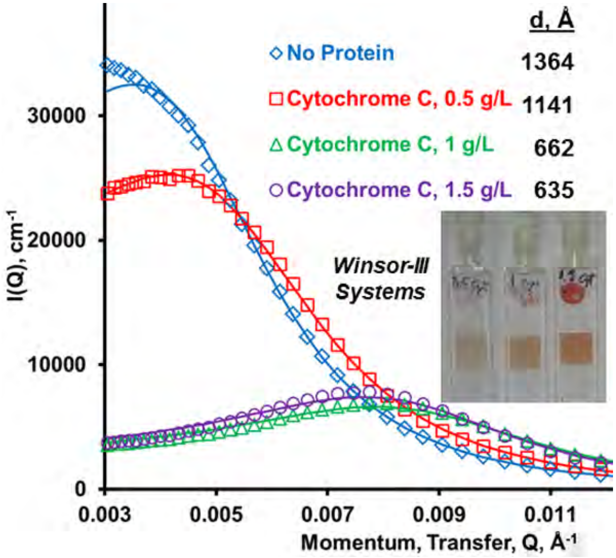

Figure 1: The reddish-brown protein cytochrome c shows high propensity for extraction into the middle phase of a Winsor-III system (inset picture) and strongly influences the quasi-periodic repeat distance, *d*, of the bicontinuous nanostructure.

Our Teubner–Strey analysis of Winsor-III systems formed from water, heptane and a mixed surfactant system composed of aerosol-OT and alkyl ethoxylate shows pronounced influence of proteins onto the nanostructure of the bicontinuous middle phase. The proteins cytochrome c, lysozyme, and α-chymotrypsin promote a decrease of the quasi-periodic repeat distance, *d*, of the bicontinuous nanostructure when incorporated near their respective solubility limit under high salinity conditions.

Our research demonstrates the central role of salinity or ionic strength for controlling the interactions between surfactant molecules and protein. Such details of these systems are of importance for potential applications of microemulsions and similar systems for example in drug delivery. They also begin to shed light onto physico-chemical interactions that may be imployed by living organisms for shaping their internal membranes into functional organelle architectures.

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Submitting Author: urbanvs@ornl.gov

TARGET NANOPARTICLES: SANS, ASAXS, DLS OF MODULAR DRUG CARRIERS

T. Nawroth[a], L. Krebs[a], P. Khoshakhlagh[a], R. Johnson[a], K. Buch[a], P. Langguth[a],
G. Goerigk[b], N. Szekely[c], P. Boesecke[d], A. Bravin[d], G. Le Duc[d], and R. Schweins[e]

[a]*Gutenberg University, Pharmacy and Biochemistry, Staudingerweg 5, 55099 Mainz, Germany*
[b]*HZB,* Soft Matter and Functional Materials, *Albert-Einstein-Str. 15, 14109 Berlin, Germany*
[c] JCSN-FRM-II outstation at MLZ, Lichtenbergstrasse 1, D-85747 Garching, *Germany*
[d]*ESRF, Avenue des Martyrs, F-38043 Grenoble, France*
[e]*ILL, LSS, Avenue des Martyrs, F-38042 Grenoble, France*

Target Nano-Pharmaceutics shall improve therapy and diagnosis of severe diseases, e.g. cancer, by individual targeting of drug-loaded nano-pharmaceuticals towards cancer cells, and drug uptake receptors in other diseases. Specific ligands, which are recognized by the diseased cells or by the drug uptake system, are bound to the nanoparticle surface, and thus capable of directing the drug carriers. In the current concept a ligand set is coupled by a fast assembly technique (click link) in the very last step of the formulation. The strategy has two branches: a) In the later clinical cancer therapy application the ligands set (2-5 different, membrane-linked) will be selected according to the biopsy analysis of the patient tissue e.g. from tumor.; b) in the oral drug delivery part the drug transport is enforced by excipients/detergents in combination with targeting materials for cellular receptors resulting in an induced uptake. Both targeting nanomaterials are characterized by a combination of SANS, DLS, SAXS and ASAXS in a feedback process during development.

We synthesize targeting modifiers of metal/ drug loaded nanoparticles which consist of four structure domains (fig.1). For cancer therapy the components are varied and optimized in a case specific manner. The nanoparticles, e.g. biodegradable polymer (PLGA), lipid particles as well as the anchor domain are hydrophobic. The linker binds the ligand in two steps: adsorption and a covalent bond formation as terminal step. The drug is included in hydrophilic domains or lumen for radiotherapy with heavy metals, but in the polymer and membranes in case of lipophilic drugs for oral administration (BCS class 2, 4) The structure of the modified nanoparticles is analyzed by dynamic light scattering DLS, neutron small angle scattering SANS and metal specific X-ray scattering ASAXS, while the effect of the drug is proven with kinetic cell cultures as tumor models. The multi-targeting modification (fig.) is applied for radiation therapy by lanthanide loaded polymer nanoparticles (PLGA) and liposomes as fast development system.

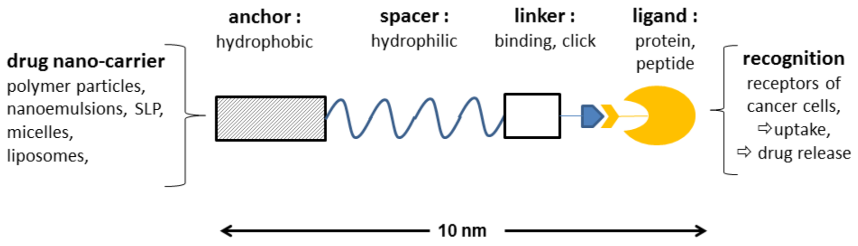

Fig.1: The targeting lipids and excipients (detergents) exhibit a modular structure of anchor, spacer, linker and a ligand (protein, cofactor), which induces the receptor recognition and uptake by the disease cells.

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Submitting Author: nawroth@mpsd.de ; nawroth@uni-mainz.de

SELF-ASSEMBLY OF PEPTIDE-POLYMER CONJUGATES IN SOLUTION: STRUCTURE & CHAIN CONFORMATIONS

R. Lund[a], **T. Xu**[b] **and H. Dong**[c]
[a]*Department of Chemistry, University of Oslo , 0315 Oslo, Norway*
[b] *Clarksson University, Potsdam, NY*
[c] *Department of Material Sciences and Engineering*
University of California, Berkeley

Hybrid biomaterials based on synthetic (polymer) and biological (proteins, peptides) building blocks, called protein-polymer conjugates, provide a wide range of opportunities for man-made materials to interface with biological system at the molecular level [1,2] For therapeutics, polymer functionalization, often by poly(ethylene glycol), PEG ("PEGylation"), is an effective method to improve the solubility, increase the life time and protect the proteins from the immune system[3]. However it is essential that the proteins maintain their structural integrity in solution- thus the role of the polymer and their interactions with proteins needs to be understood. Characterization methods capable of assessing the structural details in situ on the nanoscale are needed. In this work we show how small-angle X-ray scattering (SAXS) can be used as a powerful technique to characterize and separate detailed features in peptide-polymer conjugates in solution [4,5]. We specifically show that by applying geometrical modelling of the scattering data; very detailed structural features can be revealed, including the chain conformation of the polymers. In the presentation we will provide an overview of the methodology, specifically addressing model peptides that form either alpha-helical bundles [5,6] or beta-sheet structures [7,8] and relate their structure in solution to their crystallographic structure. Particular attention will be given to the effect of PEG and the modification of polymer conformation when attached to the peptides.

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Submitting Author: Reidar.lund@fz-juelich.de

TUNABLE PEPTIDE-PHOSPHOLIPID SYSTEMS SELF-ASSEMBLY INTO BILAYERS THAT STABILISES MEMBRANE PROTEINS

A. N. Larsen[a], K.K. Sørensen[b], A. Martel[c], K. J. Jensen[b], L. Arleth[a] and S.R. Midtgaard[a]
[a]*University of Copenhagen, Niels Bohr Institute, Universitetsparken 5, 2100 Cph., DK.*
[b]*University of Copenhagen, Department of Chemistry, Thorvaldsensvej 40, 1871 Frb., DK.*
[c]*Institut Laue-Langevin, Grenoble, France*

There is a great need for systems that can stabilise membrane proteins (MPs) better than traditional detergents. This can be achieved by generating a native-like lipid environment, is seen for the so-called Nanodisc system: a lipid bilayer surrounded by an amphipathic protein belt consisting of two membrane scaffold proteins (MSPs). However, using the Nanodisc system is laborious w.r.t. to purification and reconstitution of the MPs into the Nanodiscs. This was the main motivation for developing a new system similar to the Nanodisc system, but with the MSPs replaced by smaller and more flexible peptides. Previous work showed that the amphipathic and alpha-helical peptide 18A self-assembled easily with DMPC (dimyristoyl phosphatidylcholine) into slightly polydisperse disc-like particles with diameter about 10 nm[1], so called peptide nanodiscs. Furthermore, it was shown that these 18A peptide nanodiscs stabilised bacterio rhodopsin (bR) better than detergent octyl glucoside (OG).

In the present study we investigated peptide nanodiscs with three different dimers of the alpha-helical peptide 18A (see figure 1), and found that the interhelical linker in the peptides could be used to tune the structural and dynamic properties of the self-assembled particles. We used the name beltides for the novel belt peptides. Beltide 1 had no interhelical linker, beltide 2 had a single Pro, and beltide 3 had two Gly residues as interhelical linker. Beltide 1 was expected to be rigid, beltide 2 was known to induce a kink of 30° between the 18A helices[2] and beltide 3 was expected to induce flexibility to the dimer. The different linkers had significant effects on the self-assembly, dynamics and on the final structure of the peptide nanodiscs. Their structure was determined with combined SAXS and SANS and by fitting the scattering data with a geometrical model[1,3], structural details was revealed, such as overall size, number of peptides and pho pholipids per peptide nanodisc and details on the packing of the peptide belt. The peptide nanodiscs stabilised bR better than OG. Experimental results were compared with coarse grained molecular dynamics simulations, so details on the self-assembly process for the three systems could be described in detail.

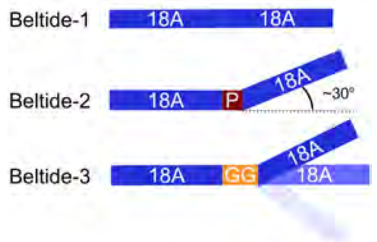

Figure 1: Three dimers of the amphipathic, alpha-helical peptide 18A, with respectively no interhelical linker, a Pro, inducing a 30° kink, and a flexible double Gly linker. The dimers self-assembled with DMPC into nano-scale membranes that can stabilise membrane proteins.

Besides constituting a new base for stabilization of membrane proteins, the peptide nanodisc also have potential as a dynamic drug-delivery system.

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Andreas Nørgård Larsen: anlarsen@nbi.ku.dk

CYTOCHROME C ADSORPTION ONTO CORE-SHELL MICROGELS ANALYSED BY ANOMALOUS SMALL-ANGLE X-RAY SCATTERING (ASAXS)

A. Petzold [a], M. Oberle [a], K. Lemke [a], M. Ballauff [a], G. Goerigk [a]
[a] Helmholtz-Zentrum Berlin GmbH, Albert-Einstein-Str. 15, 12489 Berlin, Germany

The understanding of protein adsorption onto polymer coated nanomaterials is of central importance in biotechnology, tissue engineering and nanomedicine. In particular cross-linked polymers attached to colloids (core-shell microgels) adsorb proteins reversibly and can be used to immobilize them. With a cooperative binding model the description of the thermodynamics of protein adsorption is possible [1], as well as the adsorption kinetics [2]. However the spatial distribution of the adsorbed proteins within the microgel is poorly understood. In this work anomalous small-angle X-ray scattering (ASAXS) is used to reveal the distribution of cytochrome C proteins in a core-shell microgel.

The core-shell microgels is composed of a polystyrene (PS) core which was covered by a shell of cross-linked NIPAM [3]. The hydrodynamic radii of the PS core as well as the complete microgel particle were determined by dynamic light scattering to be 13nm and 95nm, respectively.

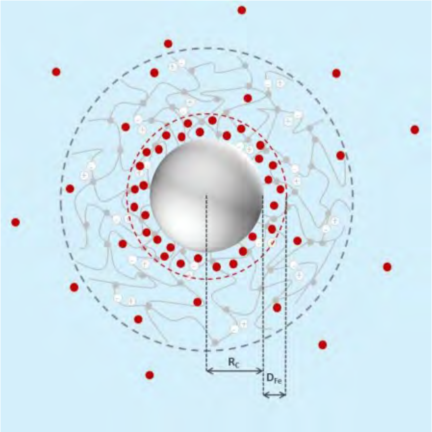

Figure 1: Structural model of the distribution of Fe ions inside the core shell microgel.

The adsorption behaviour of the Fe-containing protein onto the microgel is analysed in the energy range of the K adsorption edge of Fe. By use of the ASAXS technique we are able to discern the scattering contribution of the Fe complexes from the scattering contributions of the rest of the protein as well as the core-shell microgel [4,5]. From this (so-called) pure-resonant scattering contribution the spatial distribution of the Fe ions inside the microgel is determined (Figure 1). Moreover from the quantitative analysis a lower limit for the Fe-concentration can be deduced and complemented with the corresponding protein concentration. The results are compared to a model deduced from SASXS measurements on polymer brushes grafted onto PS colloids [6].

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Albrecht Petzold: albrecht.petzold@helmholtz-berlin.de

PROTEIN ADSORPTION ON NANOSTRUCTURED SURFACES: ACCESSING THE NANO-BIO INTERACTION BY SMALL ANGLE SCATTERING

Jens Meissner[a,b], **Bhuvnesh Bharti**[b] **and Gerhard H. Findenegg**[a]
[a]*Technische Universität Berlin, Stranski-Laboratorium for Physical and Theoretical Chemistry, Berlin, Germany*
[b]*North Carolina State University, Department of Chemical and Biomolecular Engineering, Raleigh, NC, USA*

During the last decade nanoscience has come of age and is spreading from the laboratory bench into a growing number of applications in our everyday life, reaching from the medical field to large-scale industrial applications. Nanotoxicity has therefore become an important issue which needs consideration whenever nanostructured material is released into the environment. In this context it is indispensable to develop a precise understanding of the interaction between nanomaterials and omnipresent biomolecules.

Much work has been done to understand the interaction of proteins with nanoparticles. We have previously studied the adsorption of lysozyme and cytochrome *c* on silica nanoparticles and the protein-induced aggregation of the silica particles over a wide pH and salinity range [1]. Small-angle x-ray scattering was employed to characterize the global structure of the hetero-aggregates and to estimate the effective attractive interaction among the silica particles. However, conformational changes of the adsorbed protein could not be investigated in this way.

Here we present a new approach for understanding the implications of adsorption on the morphology of globular proteins. We use small angle neutron scattering (SANS) as a primary technique to investigate the changes occurring in the shape and size of cytochrome *c* upon adsorption onto silica nanoparticles. Figure 1 shows experimental SANS profiles for silica nanoparticles loaded with increasing numbers of cytochrome *c* particles at pH 8.3 in D_2O. The scattering profiles were analyzed on the basis of a raspberry-like form factor model, in which the silica core is assumed to be decorated with a number of discrete protein molecules distributed at random on its surface [2]. A detailed analysis of the SANS profiles indicates significant deformations in the shape of cytochrome *c* upon adsorption, which we attribute to the electrostatic binding of the protein molecules to the silica surface.

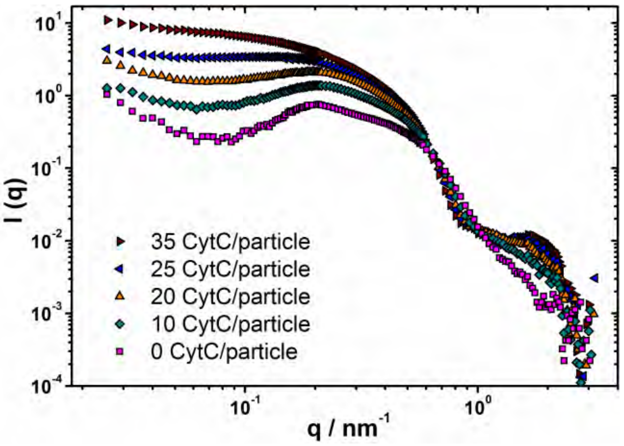

Figure 1: Experimental scattering profiles (SANS) of silica particles with increasing cytochrome *c* loading. The structure factor, visible in the low-q regime minimizes with higher loadings of protein while the form factor oscillation at the high-q region of the scattering curve signifies the appearance of an adsorbed protein layer on the particle.

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Submitting Author: jens.meissner@chem.tu-berlin.de

DIMENSIONAL METROLOGY OF NANOPATTERNS WITH SMALL ANGLE X-RAY SCATTERING FOR THE SEMICONDUCTOR INDUSTRY

D.F. Sunday,[a] D. Windover,[a] S. List,[b] J.S. Chawla,[b] and R.J. Kline[a]
[a]*National Institute of Standards & Technology, 100 Bureau Dr., Gaithersburg, MD 20899, USA*
[b]*Intel Corporation, Components Research Division, Hillsboro OR 97124 USA*

The semiconductor industry continues to shrink the feature sizes of their electronic devices. Currently mass produced devices have minimum feature sizes on order of 14 nm. Next generation devices under development have a 10 nm minimum feature size. In addition to shrinking the device dimensions, the industry has recently transitioned to a three-dimensional structure containing multiple materials. Characterization of the dimensions of the nanofabricated structures during the manufacturing is critical to maintaining high yields and low production costs. The semiconductor industry currently uses optical scatterometry (a variant of spectroscopic ellipsometry) for process control feedback on the dimensions. The method uses visible and ultraviolet light and is operated well beyond the diffraction limit. Next generation devices are so small that the index of refraction is now a function of the dimensions. The semiconductor industry is evaluating small angle X-ray scattering (SAXS) as a potential next generation dimensional metrology tool.[1] The method is called critical-dimension SAXS (CDSAXS). It is a variable-angle transmission SAXS measurement with a sub-100 µm spot size where the diffraction from a 1D or 2D grating is mapped like single crystal diffraction.[1,2] The shape of the grating is then solved using an inverse, iterative algorithm to match the diffraction calculated from a trial shape to the data. The semiconductor industry requires the measurement to be done in the fabrication facility and be rapid (~1 min) to provide timely process control feedback.

We report on evaluations of the CDSAXS method using sub-32 nm line gratings fabricated using a quadruple-patterning method that results in a 4x superlattice.[3] The key parameters are the shape of the grating profile, the pitch, and pitch errors within the superlattice. We demonstrate the ultimate resolution of CDSAXS using synchrotron radiation and then determine the reduction in resolution associated with the lower flux and worse signal-to-noise of laboratory sources. Figure 1 shows the fitted shape profile for the grating and example data.

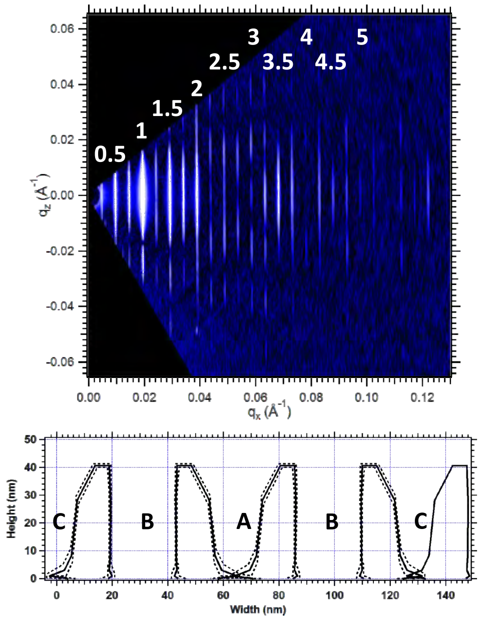

Fig. 1 – example reciprocal space map and fitted 2D shape profile of 32 nm pitch line grating

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Submitting Author: joe.kline@nist.gov

LIMITS OF SMALL ANGLE SCATTERING: CALCULATION OF SCATTERING PATTERN INCLUDING PHASE SHIFT BY PARTICLE AND PARTIAL COHERENT ILLUMINATION

U. Feye-Treimer[a,b] **and W. Treimer**[a,b]
[a]*Beuth Hochschule für Technik Berlin, Luxemburgerstr. 10, 13353 Berlin, Germany*
[b]*Helmholtz-Zentrum Berlin GmbH, Hahn-Meitner Platz 1, 14109 Berlin, Germany*

Small angle scattering of X-rays or neutrons neglects phase shifts because they are of the order of 10^{-4} - 10^{-2} rad for structures of size of 1nm – 100nm. However, if a structure is larger than few µm, phase shifts by the structure itself must be included in the calculation of the "SAS" pattern. This can be done using the Radon Transform R of the 2D (3D) scattering length density h(x,y), R{h(x,y)}, of the structure (slice), assuming a diluted system. The amplitude A(θ) in a scattering point is given by [1]

$$A(\theta)=\sum_t \cdot \exp\{-i\cdot k\cdot R\{h(x,y)\}\}\cdot \exp\{-i\cdot k\cdot t\cdot \sin(\theta_t)\}\cdot \mathrm{Gauss}(t)$$

. The first exponential function contains the 2D position-dependent phase shift of a sample slice, the second one represents the classical Fraunhofer-diffraction part. The scattered wave is scaled with a Gaussian function taking into account a finite wave packet with given a coherence length which is much larger than the structure. Note the difference in Fig.1 of the calculated scattering curve (numeric) from the one using the standard form factor formula for 50µm large spheres.

In the case that the lateral coherence width of the incident wave is (much) smaller then the structure, the incident wave w(x,z) must be scanned (2D) all over the structure, and for each wave the complete 2D scattering pattern calculated. The amplitude A in a point of a 2D scattering pattern is then given as [1], [2]

$$A(x',z')=\sum_j\sum_t e^{-ik\left\{(r_t(x',z')-t.\sin(\theta_t))+\int\limits_{\mathrm{path}} O(x,y,z_j)\cdot\delta(x,y,z_j)\cdot\delta_{\mathrm{Dirac}}(y\cdot\cos(\theta)+y\sin(\theta)-t)\cdot dx\cdot dy\right\}}\cdot \mathrm{Gauss}(t)$$

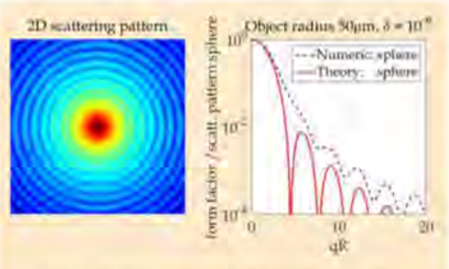

Fig.1 2D and 1D scattering pattern from a sphere

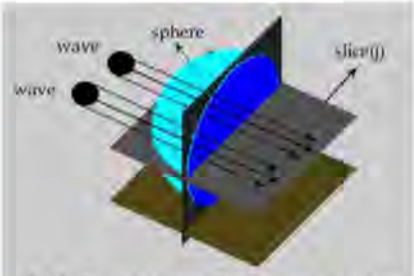

Fig.2 Partial coherent illumination of a sphere

and the corresponding intensity $I_{x',z'} = (A^*A)_{x',z'}$ must be added to all other intensities from other incident waves, the sum of all intensities yields the observed scattering pattern. With this procedure, USANS patterns from several Cu wires could be calculated with perfect agreement with experimental data.

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Submitting Author: treimer@helmholtz-berlin.de

Mon-L1: Dimensional Metrology by SAS 11:50

SCANNING SAXS IN THE CONTEXT OF OTHER IMAGING TECHNIQUES

O. Bunk

Paul Scherrer Institut, 5232 Villigen PSI, Switzerland

Small-angle X-ray scattering used in a 2D [1,2] or 3D [3,4] scanning mode images the density and orientation of nano-scale features spatially resolved over macroscopic areas of heterogeneous samples with lateral dimensions of typically several millimeters or even centimeters. It bridges the gap between high-resolution techniques with small field of view and low-resolution techniques with correspondingly larger field of view. The technique became mature and is used both at laboratory and at synchrotron radiation X-ray sources. At the latter millions of SAXS patterns can be recorded within less than a day, rendering scanning SAXS an imaging technique providing an abundance of information. The analysis needs to combine the extraction of qualitative and quantitative features from the data with an automated high-throughput treatment of data. The latter is especially relevant for a first online analysis during the measurement. An example is shown in Figure 1.

In this presentation the status of scanning SAXS as a method will be briefly reviewed. Then the complementarity to and overlap with other imaging techniques is described to illustrate the application fields. The other techniques are (1) scanning transmission X-ray microscopy with a pixelated detector for obtaining both absorption, differential phase and dark-field contrast, (2) high-resolution ptychographic coherent diffraction imaging, and (4) Talbot interferometry for determining absorption, differential phase and dark field contrast in full-field imaging. Application examples will be given with hierarchically structured materials from a number of areas of life and materials science.

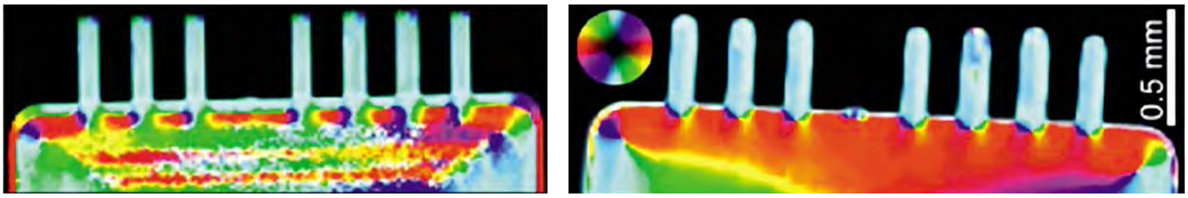

Figure 1: Orientation of polymer assemblies in injection-molded polymers: Left polypropylene, right polyvinylidenefluoride. Both samples consist of a thick support and approximately 35 μm thin cantilevers. The orientation derived from small-angle X-ray scattering at each position within the sample area is color-coded according to the inset disc. The selected momentum transfer corresponds to 8–18 nm feature size in direct space. For further details see Chimia **68,** 66-72 (2014) and J. Appl. Phys. **111**, 103530 (2012).

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Submitting Author: oliver.bunk@psi.ch

ORIENTATIONAL ORDER IN COLLOIDAL THIN FILMS AND CRYSTALS STUDIED BY X-RAY CROSS-CORRELATION ANALYSIS

M.A. Schroer[a,b], **F. Lehmkühler**[a,b], **F. Westermeier**[a,c], **B. Fischer**[a,d], **M. Sprung**[a], **C. Gutt**[e], **and G. Grübel**[a,b]
[a]DESY, 22607 Hamburg, Germany
[b]The Hamburg Centre for Ultrafast Imaging (CUI), 22761 Hamburg, Germany
[c]MPI Struktur und Dynamik der Materie, CFEL, 22761 Hamburg, Germany
[d]Institut für Physikalische Chemie, University of Hamburg, 20146 Hamburg, Germany
[e]Department of Physics, University of Siegen, 57072 Siegen, Germany

Ordered films and crystals made out of nanoparticles are interesting materials as they can exhibit exciting new optical properties and thus can be used e.g. as photonic crystals [1]. Crucial for the application of such systems is the degree of order of the nanoparticle arrays as well as their response to external stimuli, such as high pressure. In particular for colloidal films, special attention has to be paid to the local order within the nanoparticle arrays that depends on the underlying drying process. Investigating the structure and orientational order of both thin films and crystals under external perturbations can be perfectly done with the X-ray cross correlation analysis (XCCA) technique [2-4]. Two studies, a) on thin colloidal films and b) on colloidal crystal suspensions employing this method will be discussed.

First, we will present a scanning small angle X-ray scattering (SAXS) study using a nanometer size beam on dried nanoparticle films made out of a binary colloidal mixture of two particle species differing in size. Due to the small beam size only a finite number of particles give rise to the scattering signal. By scanning the sample, structure and composition of the films can be determined spatially resolved in terms of scattering intensity maps. The local type and degree of orientational order is revealed by studying the angular correlations of the scattering patterns via XCCA. Based on this X-ray cross correlation microscopy approach, spatial maps of the local degree of order are obtained that allow to identify specific differences in the local film structures formed by the two nanoparticle species [5].

In addition, we report on a recent SAXS and XCCA study on suspensions of colloidal crystals under high pressure. A complex pressure-dependence of the crystals is revealed, reflecting a delicate balance of water compression and changes of the electrostatic properties.

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Submitting Author: martin.schroer@desy.de

ULTRATHIN GOLD NANOWIRES: GROWTH MECHANISM AND SELF-ASSEMBLY

A. Loubat[a], M. Impéror-Clerc[b], L.-M. Lacroix[a], G. Viau[a]
[a]*LPCNO, Université de Toulouse, INSA-UPS-CNRS UMR 5215, F-31077 Toulouse, France*
[b]*LPS, Université Paris-Sud CNRS UMR 8502, Bat. 510, F-91405 Orsay, France*

Recently, ultrathin gold nanowires prepared by reduction of HAuCl4 in solution of oleylamine (OY) attracted a lot of attention [1]. They have a diameter of 2 nm with a very narrow distribution in size and are micron long (Figure 1). Their unique 1D feature confers them remarkable conductivity properties, such as quantum phenomena at room temperature [2]. Their growth mechanism is still under debate and the crucial role of the choice of oleylamine (OY) as ligand needs to be further understood [3]. Using synchrotron radiation at the French Source SOLEIL, we performed Small Angle X-ray Scattering experiments (SAXS) [4,5]. We obtained new insight on the growth mechanism of these 1D objects in solution. Our results are in favor of a 1D-micellar growth mechanism rather than an oriented attachment of small spherical seeds.

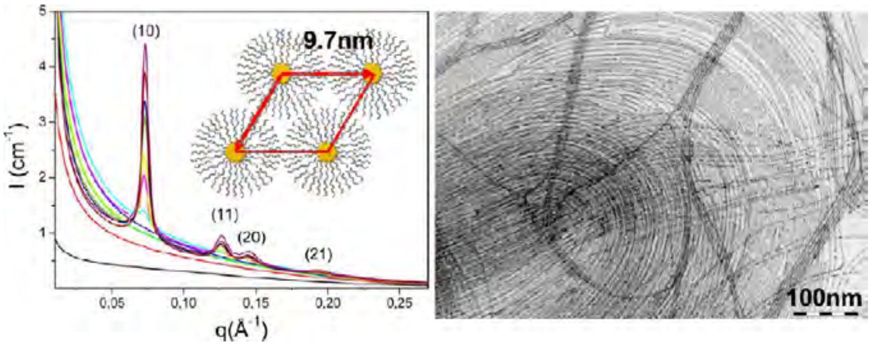

Figure 1: Self-assembly of ultrathin gold nanowires (TEM picture) into a hexagonal super lattice (SAXS).

Furthermore, we observed their self-assembly into a hexagonal super-lattice (Figure 1). Surprisingly, the value of 9.7 nm of the lattice parameter may be well explained by a ligand bilayer (mixture of OY Cl-/OY) at the surface of each nanowire, instead of a single layer as expected. Further investigations using Neutron scattering (SANS) are under way, in order to measure the ligand thickness at the surface of the nanowires.

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Submitting Author: marianne.imperor@u-psud.fr

SPAHE AND CONFORMATION DESIGN ON CORE-SHELL STRUCTURED NANOCRYSTALLITES: AN IN-SITU SMALL ANGLE X-RAY SCATTERING INSPECTION ON HETEROGENENEOUS NANOCRYSTAL GROWTH

T.-Y. Chen[a,b], **P. W. Yang**[a], **P. C. Huang**[b], **T. L. Lin**[a], **Y.-T. Liu**[c]
[a]*Department of Engineering and System Science, National Tsing Hua University, 30013 Hsinchu, Taiwan*
[b] *Institute of Nuclear Engineering and Science, National Tsing Hua University, Hsinchu 30013, Taiwan*
[c] *Department of Environmental Science and Engineering, Tunghai University, Taichung 40704, Taiwan*

Here we demonstrate that these intrinsic heterjunction can be manipulated in expected configurations by properly design the sequences of crystal growth at different components in particular at core-shell structured NCs. As elucidated by *in-situ* small angle X-ray scattering (Fig. 1), the core crystal is grown as nano-disk in shape. The subsequent shell crystal was grown atop radial and facet facets at different rates. Properly control the physiochemical heteroatomic exchange pathways at core-shell interface the initio crystal state confined the subsequent shell crystal growth mechanisms and thus the configurations. In the cases with low heteroatomic exchange (revealed by the interface milting zone), the shell crystal growth follows layer-plus-island (Stranski-Krastanov, SK) thin-film growth mechanism at the interfacet corner sites. In this case opened (low atomic packing density) facets at cylinder face possess the pseudo melting interface (region C in **Fig. 1**) for nuclear and crystal growth with larger extend of heteroatomic intermix comparing to the close packed facets at radial face. These phenomena further strengthen by doubling the shell to core atomic ratio. By increasing the exchange extent at initio state with prolonged chemical etching time and dose, the crystal was truncated into ellipsoid with isotropic shell thicknesses in different orientations. Taking together, the presented structure confinement approaches enables the facile control of the crystal structure with expected structure in varies energy applications.

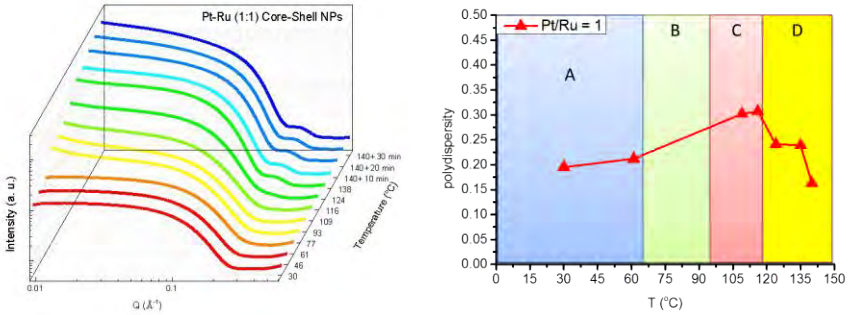

Figure 1: In-situ SAXS spectra of Ru_{core}-Pt_{shell} NCs upon crystal growth and the corresponding polydispersity as a function of reaction temperatures. Four regions are found in polydisperdsity curve which corresponding to (A) transmetallation nucleation of shell, (B) heterogeneous nuclei growth, (C) crystal growth on pseudo melting interface, and (D) heteroatomic segregation and solidification of interface.

References

NA.

Submitting Author: weissfuss@helmholtz-berlin.de

DOES A LOW-Q UPTURN IN ULTRA-SMALL-ANGLE SCATTERING REFLECT MATERIAL'S STRUCTURE?

Y. Shinohara and Y. Amemiya
Department of Advanced Materials Science, Graduate School of Frontier Sciences, The University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa Chiba, Japan

According to standard textbooks of small-angle scattering (SAS), scattering intensity profiles corresponds to the "fluctuation part" of scattering length density, while a forward scattering at $q = 0$, which is contributed in phase from all the scattering elements and is characterized by Dirac's delta function, is not explicitly considered, where q is the magnitude of scattering vector. This is because the forward scattering, which overlaps with the direct beam, is usually behind a beam stop and is never observed. Some textbooks describe that a finite beam size broadens the forward scattering but that it is still behind a beamstop due to the difference between the beam size and observed q-range. Recent advances in X-ray brilliance and X-ray optics make it possible to conduct scattering measurement at ultra small angles with a small beam size. We have found that the use of such small-beam and the measurement at low q lead to a significant contribution from the forward scattering on the measured scattering intensity profiles, which resembles a power-law-scattering intensity profiles depicted as Porod law of a large-scale structure. This fact indicates that a low-q upturn that is often observed for hierarchical system suffers from the forward scattering. In this presentation, we show how the scattering at $q = 0$ does affect the scattering intensity profiles and discuss perspectives on ultra-small-angle X-ray scattering and the use of nanobeam in SAS experiments.

Submitting Author: yuya@k.u-tokyo.ac.jp

SHAPE INDUCED PHASE TRANSITIONS IN CRYSTALS OF COLLOIDAL CUBES

Janne-Mieke Meijer, **Antara Pal, Henk N.W. Lekkerkerker, Albert P. Philipse and Andrei V. Petukhov**

Van 't Hoff Laboratory for Physical and Colloid Chemistry, Debye Institute for NanoMaterials Science, Utrecht University, The Netherlands

Self-organization of cubes with rounded corners into ordered single crystal lattices was experimentally investigated by sedimentation of micron-sized hollow silica cubes. Detailed translational and orientational order of the formed crystal structures were determined using small-angle X-ray scattering with microradian resolution. We observed two distinct features in the crystalline sediments. i) The formation of two different crystal structures, a plastic face centered cubic (FCC) crystal phase with translational order and rotational disorder and a rhombohedral crystal (C_1-lattice) phase with both translational and rotational order. ii) The formation of these crystal structures is dependent on the precise shape (i.e. extent of corner roundness) and size of the cubes that influence both the maximum packing density and osmotic pressure in the sediments. This work provides the first experimental proof for the formation of plastic FCC crystal phase and rhombohedral crystal phases by micron-sized colloidal cubes and agrees with recent simulation results of rounded cubes [1,2].

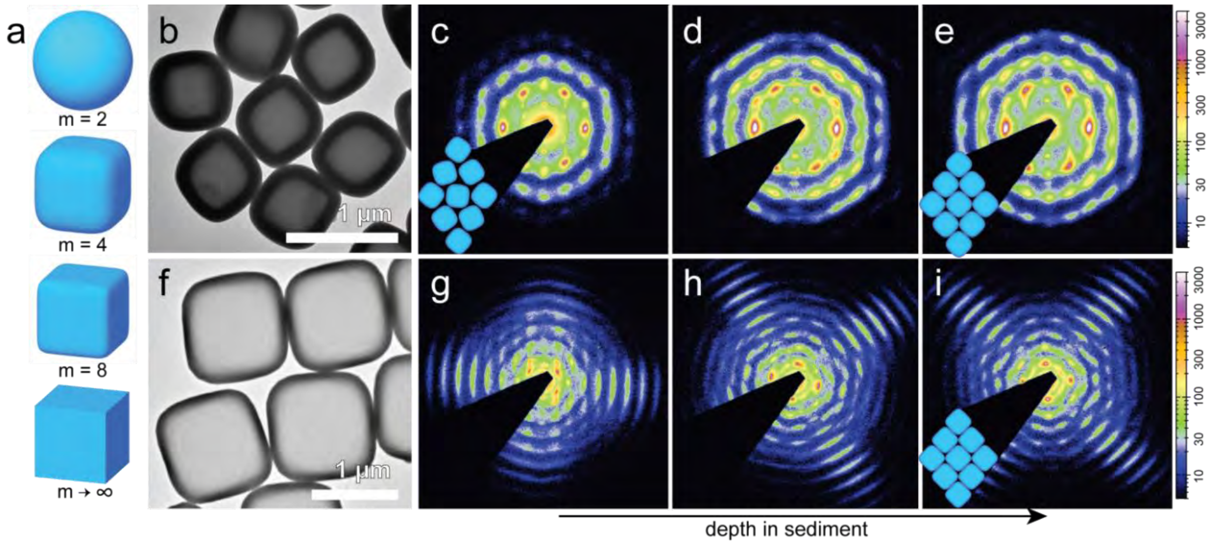

Figure 1. a) Schematic representation of the roundness of the cube corners expressed in shape parameter m, from a sphere, $m = 2$, to a perfect cube, $m \to \infty$. b, f) TEM images of two different colloidal hollow silica cubes.(c-e, g-i) SAXS patterns of the crystalline sediments at different depths of the two cubes showing the presence of FCC and rhombohedral crystal phases.

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Submitting Author: jannemieke.meijer@gmail.com

SAS STUDIES OF SELF-ASSEMBLING LIPOPEPTIDES

I. W. Hamley[a]
[a] *Dept of Chemistry, University of Reading, Whiteknights, Reading RG6 6AD, UK*

Self-assembling peptides and their conjugates offer exceptional potential in nanomedicine. I will present some of our recent work using SAXS and SANS to probe the self-assembly of peptide conjugates, focussing on bio-inspired and bio-derived lipopeptides [1, 2]. In one example, the mechanisms and dynamics of nanotube unwrapping into twisted tapes and helical ribbons observed for a lipopeptide C_{16}-KKFFVLK as probed by synchrotron SAXS and other techniques will be discussed.[3] This lipopeptide contains a hexadecyl lipid chain and a heptapeptide headgroup containing a key aggregating fragment KLVFF from the amyloid β peptide.[4] The dramatic change in self-assembled structure upon enzymatic degradation of this lipopeptide using α-chymotrypsin will also be discussed (this enzyme cleaves the peptide selectively at phenylalanine residues).[5] Examples from our recent work on other self-assembling lipopeptides will also be outlined, where the focus is to investigate potential relationships between self-assembly and bioactivity, in particular in the fields of regenerative medicine [6-10], antimicrobial systems [11, 12] and immune therapies [13].

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Submitting Author: I.W.Hamley@reading.ac.uk

CHARACTERIZING SELF-ASSEMBLED NANOPARTICLES EMPLOYED IN DURG DELIVERY: ADVANTAGE OF ANOMALOUS SAXS

K. Sakurai, Y. Sanada and I. Akiba
Department of Chemistry and Biochemistry, The University of Kitakyushu,
1-1 Hibikino, 808-0135 Kitakyushu, Japan.

Many therapeutic drug compounds need assist from delivering vehicles to accomplish their task. Self-assembled or supramolecular nanoparticles, including polymeric micelles, dedrimers, and vesicles, have been used as drug delivery system (DDS). In-situ characterization of the s DDS structures is essentially important for drug formulation. Among others, determining how the drug molecules are incorporated in the nano-particles is one of the most challenging issues.

This presentation reviews our recent studies on such an issue, focusing on polymeric micelles for anti-cancer delivery and dedrimers, mainly by use of anomalous small angle X-ray scattering (ASAXS). ASAXS enable us to extract the scattering from the particular elements such as Br from the overall scattering. We loaded a Br-bearing model drug into polymeric micelles or dedrimers and evaluated the spatial distribution of Br atoms inside of the drug particle.

For polymeric micelles, a core-corona spherical model was used to explain the shape of the micelles while the distribution of bromine atoms was explained with a hard-sphere model. The radius of the spherical region populated with bromine atoms was larger than the one of the sphere corresponding to the hydrophobic core of the micelle. This result suggests that the Br-bearing drug molecules infiltrate the PEG hydrophilic domain in the vicinity of the core/shell interface. The results of light scattering and SAXS indicate that the PEG chains at the shell region are densely packed and thus the PEG domain close to the interface has enough hydrophobicity to tolerate the presence of hydrophobic compounds.

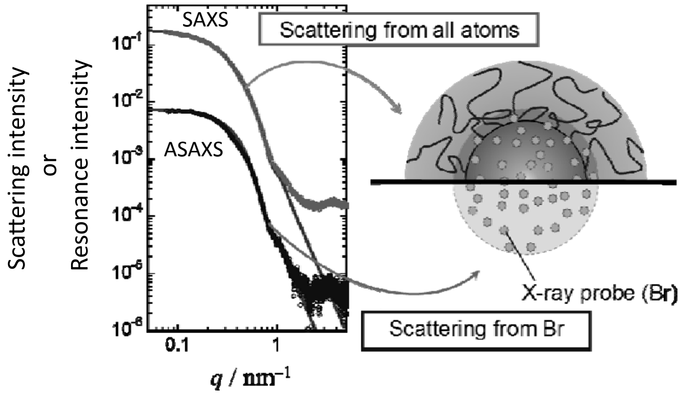

Figure 1: Hydrophobic molecules infiltrating into the PEG domain of the core/shell interface of a polymeric micelle: evidence obtained with anomalous SAXS.

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Submitting Author: sakurai@kitakyu-u.ac.jp

TOWARDS TRACEABLE SIZE DETERMINATION OF BIOLOGICAL NANOPARTICLES USING SAXS

Z. Varga[a], **C. Gollwitzer**[b], **R. Garcia-Diez**[b], **Y. Yuana**[c], **R. Nieuwland**[c] **and M. Krumrey**[b]
[a]Research Centre for Natural Sciences, Hungarian Academy of Sciences,
Magyar tudósok körútja 2, 1117 Budapest, Hungary
[b]Physikalisch-Technische Bundesanstalt (PTB), Abbestraße 2–12, 10587 Berlin, Germany
[c]Department of Clinical Chemistry, Academic Medical Centre of the University of Amsterdam,
Meibergdreef 9, 1105 AZ Amsterdam, The Netherlands

Characterization of biological nanoparticles (BNPs), such as extracellular vesicles (EVs) is challenging because of their small size (30 nm – 1 µm), low refractive index, and heterogeneity. Since vesicles are below the detection range of common methods, many new techniques have been developed, but have not yet been validated. Consequently, there is a need for traceable size determination of EVs.

In general, SAXS characterization of nanoparticles can be made traceable using the oscillations that occur in the Fourier regime of the scattering curve. However, biological nanoparticles usually show a complex inner structure and do not fulfill the requirements for monodispersity and shape uniformity, which are necessary for their traceable size determination.

In this work, the applicability of SAXS for the determination of the size distribution of BNPs is presented on the example of erythrocyte-derived EVs [1] and liposomes. Different data evaluation procedures for the interpretation of the scattering curves are presented (fitting of an analytical form factor and using the indirect Fourier-transformation approach), and the results are compared with those obtained by other methods, such as size exclusion chromatography coupled with dynamic light scattering, nanoparticle tracking analysis, resistive pulse sensing, and electron microscopy. These commonly used techniques provide slightly different size distributions that also depend on the settings and the detection limit of the given technique. From results of this comparison, there is a need for a biological reference material which mimics the chemical and optical properties of BNPs and possesses low polydispersity to validate the techniques for traceable size determination of EVs.

This work was funded by the European Metrology Research Programme (EMRP) under the Joint Research Project HLT02 (METVES, www.metves.eu). The EMRP is jointly funded by the EMRP participating countries within EURAMET and the European Union.

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Zoltan Varga: varga.zoltan@ttk.mta.hu

VARIOUS NANOCELLULOSE CRYSTALS - A SHAPE AND STABILITY INVESTIGATION

M. Uhlig[a], **A. Fall**[b], **Gustav Nyström**[c], **Sylvain Prévost**[a,d], **Stefan Wellert**[a], **Lars Wargberg**[e] **and R. von Klitzing**[a]

[a]*TU Berlin, Institut für Chemie, Straße des 17. Juni 124, 10623 Berlin, Germany*
[b] *Stockholm University, Environmental and Material Chemistry Department, Svante Arrhenius väg 16 C, SE-106 91 Stockholm, Sweden*
[c]*ETH Zürich, Institute of Food, Nutrition and Health, Schmelzbergstrasse 9, 8092 Zürich, Switzerland*
[d] *ERSF, Avenue des Martyrs 71, 38043 Grenoble , France*
[e] *KTH Stockholm, School of Chemical Science and Engineering, Teknikringen 42, SE-100 44 Stockholm, Sweden*

Nanocellulose Crystals (NCC) extracted from native cellulose are a promising natural material. Due to their high stiffness, high aspect ratio, water solubility and low cost they are interesting for a lot of applications e.g. in nanocomposites [1]. The most commonly produced NCC is sulfuric acid hydrolyzed NCC-SO_3H. The repulsive interaction of the sulfate groups on the surface stabilize NCC-SO_3H in aqueous solution. However, salt addition can easily screen those repulsions and induce coagulation.

Modifying the NCC, e.g. by carboxylation [2] (NCC-COOH) or coating with polyethylene glycol amine (PEG-NH2)[3] overcomes the problem of aggregation at low ion concentrations.

This contribution focuses on the characterization of modified NCCs using Small Angle Neutron Scattering (SANS), Dynamic Light Scattering (DLS) and Transmission Electron Spectroscopy (TEM). DLS is used to investigate the increase in stability of modified NCC compared to unmodified one. SANS and TEM are used to investigate the change in shape and structure of modified NCC. Uncoated NCC both with sulfate groups and carboxylic groups were analyzed. Polymer coated NCC were prepared, either by electrostatic adsorption of polyethyleneimine (PEI) or chemically grafting of polyethylene glycol amine (PEG-NH2) to the NCC particles surface. Aqueous NCC dispersions where measured at various NCC and polymer concentrations and different polymer molecular weights. SANS data showed a structure peak at small q for (several) higher concentrated samples. Closer data analysis revealed a tendency of the rods to aggregate into 2D-stacks of several rods. The size parameters of these aggregates were extracted, using a 2-step fitting model.

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Submitting Author: martin.uhlig@tu-berlin.de

IN SITU SMALL ANGLE STUDIES OF ROLL-TO-ROLL COATED PEROVSKITE SOLAR CELLS

L. H. Rossander[a], **J. W. Andreasen**[a], **H. F. Dam**[a], **T. T. Larsen-Olsen**[a], **T. M. Schmidt**[a], **M. Corazza**[a], **I. Rajkovic**[b] and **F. C. Krebs**[a]
[a]*Department of Energy conservation and Storage, Technical University of Denmark, Frederiksborgvej 399, 4000 Roskilde, Denmark*
[b]*Paul Scherrer Institut, WLGA/131, CH - 5232 Villigen PSI, Switzerland*

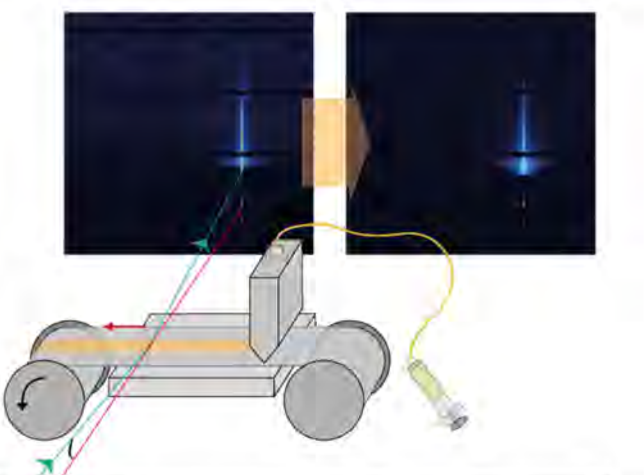

Figure 1: An schematic of the *in situ* setup with examples of small angle 2D images from the newly deposited(left) and dryed(right) film.

Printed solar cells represent a technological step forward which is important for the future of our societies. The technology has potential to reduce the cost per module significantly[1], which would make solar technology affordable for almost everyone. Lead-halide($CH_3NH_3PbI_{3-x}Cl_x$) perovskite is a new material that produces high efficiencies even when cast from solution[2].

We present studies of structural and morphological developments during formation of perovskite absorber layers for solar cells made by roll-to-roll (R2R) slot-die coating of a mixture of $PbCl_2$ and methylammoniumiodide (MAI). While adapting perovskites to R2R coating, we found that the morphology formation depends on the substrate, so using the setup in fig. 1 and both GIWAXS and GISAXS we investigated the formation *in situ* of a slot-die coated layer of perovskite on glass and PET substrates, in order to compare and possibly understand the structural differences.

We propose that the growth of the perovskite phase from the mixture is a flux reaction that critically depends on a sufficient excess of MAI during the growth phase but also relies on the evaporation of the flux during the growth and complete evaporation of excess MAI at the end of the growth. We support these findings with thermal studies of the mixture using differential scanning calorimetry (DSC) coupled with thermogravimetric analysis (TGA) with mass spectroscopic detection (MS). We finally observed that the perovskite layer was highly sensitive to X-rays and observed radiation damage at relatively low exposure doses.

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Submitting Author: lehro@dtu.dk

SANS: A POWERFUL AND UNIQUE TOOL TO PROVIDE STRUCTURAL INSIGHT INTO LARGE PROTEIN-PROTEIN AND PROTEIN-RNA COMPLEXES

F. Gabel[a,b]
[a]*Institut de Biologie Structurale, 71 avenue des Martyrs, 38044 Grenoble, France*
[b]*Institut Laue-Langevin, 71 avenue des Martyrs, 38042 Grenoble, France*

I will present an overview over recently published work on a number of large and challenging multi-subunit protein-protein and protein-RNA complexes. In all cases, small-angle neutron scattering (SANS) contributed crucial and unique information that complemented other structural biology techniques (crystallography and NMR) and/or biochemical results.

The examples presented will include the ternary protein-RNA complex Sxl-Unr-RNA (Fig. 1A) which is a key player in gene regulation and sexual development [1], the Box C/D complex (Fig. 1B) which regulates the function of ribosomes by chemically modifying ribosomal RNA [2], and the TET aminopeptidase which is major component in the destruction pathways of the ensemble of proteins (i.e. the proteome) biological cells [3].

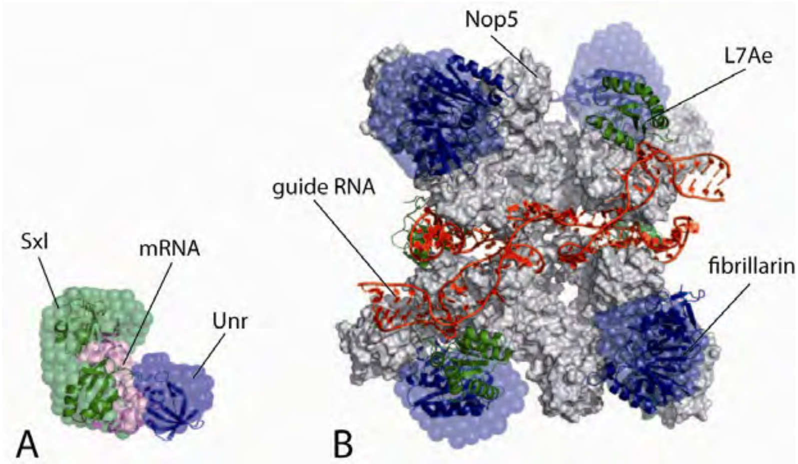

Figure 1: The Sxl-Unr-RNA and Box C/D complexes. Superposition of atomic models and low-resolution envelopes of the individual partners determined by SANS.

In all three cases, SANS was essential to determine the three-dimensional structures of the complexes by defining the respective positions of the individual protein (and RNA) partners within the complexes and by providing complementary structural restraints with respect to the other techniques used (crystallography, NMR and biochemistry).

In the light of these recent examples on important systems in structural molecular biology I will elaborate on the state-of-the-art of combining SANS (and SAXS) information with structural restraints from complementary biophysical and biochemical techniques.

Finally, I will discuss future perspectives of such hybrid approaches and requirements to apply them on a number of important and challenging molecular biology systems involved in genome and proteome regulation in biological systems of biomedical relevance.

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Submitting Author: frank.gabel@ibs.fr

STRUCTURAL, DYNAMICAL AND FUNCTIONAL STUDY OF THE PROTEASOME ACTIVATING COMPLEX (PAN)

Z. Ibrahim[1,2], **M. Colombo**[2], **G. Schoehn**[2], **S. Teixeira**[1], **M. Haertlein**[1], **B. Franzetti**[2], **F. Gabel**[2]

[1] *Institut Laue Langevin, EPN Campus, 71 avenue des Martyrs, 38000 Grenoble, France.*
[2] *Institut de Biologie Structurale, UMR5075 CNRS-CEA-UJF, EPN Campus, 71 avenue des Martyrs, 38000 Grenoble, France.*

The proteasome activating nucleotidase (PAN) complex is an archaeabacterial homologue to the AAA+ unfoldases involved in the regulation of the eukaryotic proteasome [1]. PAN is a molecular nano-machine that can be considered as an inverse chaperonin, aimed at preparing proteins to be degraded. The PAN subunits control and ensure the access of cytosolic proteins to the proteolytic heart in a multi-step ATP-dependent process [2]. The PAN system represents a good working model for the function of molecular machines of protein degradation (in particular the ATPases) in all kingdoms of life [3]. Its simplicity in terms of subunits with respect to the eukaryotic systems and its important thermal and structural stability represent major advantages for the study of the structure-function flexibility relationship with integrative structural biology approach combining cryo-electron microscopy (cryo-EM) with small angle x-ray (SAXS) and neutron (SANS) scattering. The ATP-driven protein unfolding mechanism processed by PAN remains unclear and the conformational changes of the PAN complex or its protein substrate during the unfolding process needs to be elucidated.

The aim of this project is to follow in real time at a molecular level the conformational changes of the PAN complex and its model protein substrate (GFP) needed for the unfolding process by using small angle neutron scattering (SANS) study with deuteration and contrast variation between the two partners. The PAN system has been intensively characterized biochemically and the PAN-GFP interaction has been studied by Surface Plasmon Resonance (SPR) prior to the SANS experiments. Preliminary SANS data were collected on the deuterated and hydrogenated proteins showing the technical feasibility of the real time experiment. The conformational changes of each partner in the PAN-GFP complex will be followed during the unfolding process. Many other biophysical techniques have been used for complete structural characterization of the PAN system, in particular cryo-electron microscopy and small angle x-ray scattering (SAXS). The accuracy of the cryo-EM models in different nucleotide states was checked by SAXS showing good agreement with the structural features of the complex in solution. Taken together, all these data show a unique and complete biochemical, functional, structural and dynamical study of the PAN activator.

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Submitting Author: ziad.ibrahim@ibs.fr

STRUCTURE AND DYNAMICS OF THE INTRINSICALLY DISORDERED MYELIN BASIC PROTEIN

A. Stadler[a], L. Stingaciu[b], A. Radulescu[c], O. Holderer[c], M. Monkenbusch[a], R. Biehl[a], and D. Richter[a]
[a]Forschungszentrum Jülich GmbH, ICS-1 & JCNS-1, Jülich, Germany;
[b]Forschungszentrum Jülich GmbH, Outstation at SNS, Oak Ridge, USA; [c]Forschungszentrum Jülich GmbH, Outstation at MLZ, Garching, Germany;

Intrinsically disordered proteins lack a well-defined folded structure and contain a high degree of structural freedom and conformational flexibility. In solution and in the lipid-free state myelin basic protein belongs to that class of proteins. Using small-angle scattering the protein was found to be structurally disordered similar to Gaussian chains. Modeling by a coarse-grained structural ensemble gave indications for a compact core with flexible ends, see figure 1. Neutron spin-echo spectroscopy (NSE) measurements revealed a large contribution of internal dynamics to the overall diffusion [1]. The NSE results showed a high flexibility of the structural ensemble. The observed dynamics represent nanosecond conformational fluctuations within the reconstructed coarse-grained structural ensemble allowing the exploration of a large configurational space. In an alternative approach, we investigated, if models from polymer theory are suitable for the interpretation of the observed motions. Within the framework of the Zimm model with internal friction (ZIF) a large offset of 81.6 ns is needed as an addition to all relaxation times due to intra-chain friction sources. The ZIF model, however, shows small but systematic deviations from the measured data. The large value of the internal friction leads to the breakdown of the Zimm model.

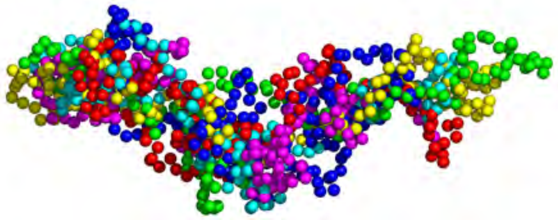

Figure 1: Representative Models of the Myelin Basic Protein Obtained from Small-Angle X-ray Scattering

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Submitting Author: a.stadler@fz-juelich.de

SMALL-ANGLE SCATTERING STUDIES OF LARGE LIPIDIC MOLECULAR MACHINES: THE A-ATPASE ASSEMBLY

H.D.T. Mertens[a], **E.M. Laming**[b], **R. Davies**[b], **A.G. Stewart**[b], **D. Stock**[b]
and D.I. Svergun[a]
[a]*European Molecular Biology Laboratory, Notkesstr. 85, 22607 Hamburg, Germany*
[b]*Victor Chang Cardiac Research Institute, 405 Liverpool Street, 2010 Sydney, NSW, Australia*

The cellular membrane provides an environment for the compartmentalisation of external and internal chemical reactions. Evolution has led to the development of membrane embedded amphiphilic assemblies of proteins that operate as machinery regulating the flow of essential molecules, in and out of the cell. One such example is the A-type ATP synthase, responsible for ATP driven H+ transport [1].

A hybrid approach has been employed to study this system, including x-ray crystallography, cryo-electron microscopy, mass spectrometry and small-angle X-ray and neutron scattering. Important insights into the mechanism of action of this large complex have been developed and guide future efforts to capture snapshots of the enzyme as it functions. Scattering data confirm in solution the arrangement of the A-ATPase structure as determined by microscopy, with both peripheral stalks associated with the complex, as is a corona of dDM detergent surrounding the transmembrane region of the membrane embedded A_o domain. Furthermore, monoclonal antibodies used to stabilise the structure during purification are also associated with the soluble A_1 domain in solution.

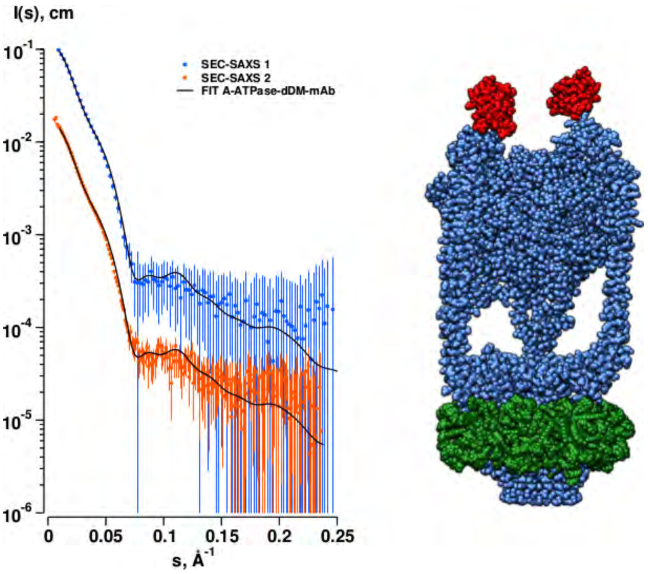

Figure 1. SAXS data for A-ATPase and hybrid model

Difficulties encountered with the data acquisition in a detergent environment will be presented and the practical implications of studying such multi-contrast systems discussed. The development of effective screening procedures for these increasingly important protein systems in lipidic environments, combined with accurate modelling procedures will be outlined for these challenging systems.

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Submitting Author: hmertens@embl-hamburg.de

INVESTIGATING MEMBRANE PROTEINS USING NOVEL MATCH-OUT DEUTERATED DETERGENTS AND SANS

S. R. Midtgaard[a], **T. Darwish**[b], **M. C. Pedersen**[a], **P. Huda**[a] **and L. Arleth**[a]
[a]*Structural Biophysics, Niels Bohr Institute, Copenhagen, Denmark*
[b]*National Deuteration Facility, Australian Nuclear Science and Technology Organisation, Lucas Heights, Australia*

Structural knowledge of membrane proteins is paramount to the understanding of a wide range of questions in life science. In recent years, a number of alternatives to traditional crystallization have emerged, among them the use of various lipid:protein particles (like the Nanodisc system) in connection with small angle scattering, SEC-SAXS of membrane proteins in detergents and also direct methods like Cryo-EM. Commonly for all of these methods is that the molecules or particles used to screen the hydrophobic membrane spanning region from the solvent are highly visible in the data and as such complicates the data analysis significantly.

Here, a new approach is presented using match-out deuterated analogues of commonly used membrane protein storage detergents in combination with SANS. Results on both the detergents and multiple different tested membrane proteins are presented. This method does not rely on the expensive and time-consuming approach of producing perdeuterated membrane proteins or deuterated lipids. Furthermore, as many membrane protein structures based on crystallography are of medium resolution at best, the resolution obtainable by using SANS can be very usefull.

In the future, this technique will be very applicable at facilities like ESS as the high flux can be utilized and thereby enabling a sample size well below 100ul.

Submitting Author: soromi@nbi.ku.dk

SAXS, GISAXS AND ASAXS IN THE TENDER X-RAY RANGE

M. Krumrey[a], C. Gollwitzer[a], A. Hoell[b], P. Müller[a], J. Wernecke[a]

[a]*Physikalisch-Technische Bundesanstalt (PTB), Abbestr. 2-12, 10587 Berlin, Germany*
[b]*Helmholtz-Zentrum Berlin (HZB), Hahn-Meitner-Platz 1, 14109 Berlin, Germany*

Small-angle X-ray scattering (SAXS) experiments and related techniques like GISAXS (grazing incidence) and anomalous scattering (ASAXS) are typically performed in the photon energy range between 8 keV and 25 keV. In recent years, the tender X-ray range between about 1.5 keV and 5 keV is of growing importance because it enables the access to the K absorption edges of technologically or biologically important elements like Si, P, S, Cl, K, Ca etc. At the four-crystal monochromator beamline of PTB at BESSY II, the photon energy range from 1.75 keV to 10 keV is accessible using Si and InSb monochromator crystals. A six axes UHV reflectometer allows to position any kind of sample. A dedicated in-vacuum hybrid pixel PILATUS 1M detector [1] can be used in the full energy range (Figure 1) to register the scattering pattern at a distance which can be continuously varied between about 2.5 m and 4.5 m by using the SAXS setup of the Helmholtz-Center Berlin. The entire beam path from the storage ring to the area detector is in vacuum.

In this contribution, the instrumentation is presented as well as selected examples like GISAXS on block-copolymers with contrast-matching at the Si K edge [2], ASAXS on CaF_2 nanoparticles in glasses at the Ca K edge [3], and SAXS on liquid samples containing extracellular vesicles in a dedicated sample holder utilizing silicon-nitride windows [4].

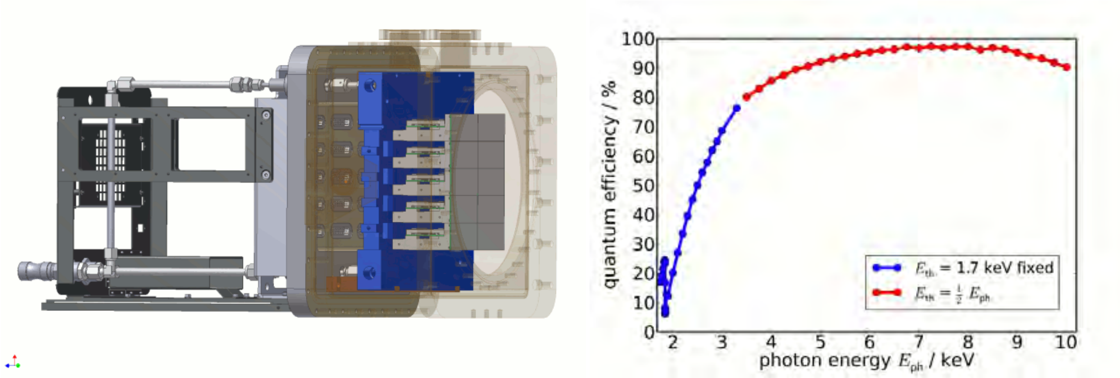

Figure 1: Sketch of the vacuum-compatible PILATUS 1M detector (left) and measured quantum efficiency (right)

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Submitting Author: Michael.Krumrey@ptb.de

OPPORTUNITIES AND CHALLENGES WITH HIGH-ENERGY COHERENT X-RAYS AT THE ESRF BEAMLINE ID10

F. Zontone[a], B. Ruta[a], C. Ponchut[a], M. Ruat[a], Y. Chushkin[a]
[a]European Synchrotron Radiation Facility, CS40220, 38043 Grenoble Cedex 9, France

High brilliance third generation synchrotron sources allowed the development of new scattering techniques exploiting coherent hard X-ray beams such as X-ray Photon Correlation Spectroscopy (XPCS) [1] and Coherent X-ray Diffractive Imaging (CXDI) [2]. XPCS has been applied to study dynamics in colloidal suspension [3, 4], liquid surface fluctuations [5], atomic motion in glasses [6] and alloys [7]… CXDI is progressively moving from demonstration experiments [2, 8] to imaging of relevant inorganic and biological specimens in 3D [9, 10]. Yet, many systems remain unexplored due to the radiation damage or strong absorption since most of these experiments are performed with an incident photon energy E below 10 keV. High energies open new possibilities for these techniques, in particular for XPCS. The E^{-2} loss of coherent flux can be in some cases compensated by larger sample volumes thanks to the E^{-3} dependence of the absorption, especially in small-angle geometry. In addition, the high penetration power of 20-30 keV X-rays allows the study of systems in bulky environments, e.g. at liquid-liquid or liquid-solid interfaces, at high pressure in diamond anvil cells, etc. The first demonstration of high energy XPCS [11] showed a great potential that was limited by the low coherent X-ray flux. With the progress in accelerator technology the future storage ring promises a 30 fold increase in brilliance. This will provide a coherent flux at 20-30 keV few times higher than the present values at 7-10 keV.

Here we show recent results with coherent high energy X-rays at the renewed ESRF beamline ID10. We compare XPCS measurements at 8 keV with 21 keV in small-angle and wide-angle geometries. To take full advantage of high energy, coherent X-rays efficient detectors are needed like the new MAXIPIX pixel detector with CdTe chips. We also show that CXDI can benefit from high energies only with the development of detectors with small pixel size.

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Submitting Author: zontone@esrf.fr

LABORATORY HI-RESOLUTION GISAXS APPARATUS FOR ADVANCED NANOSTRUCTURES

P. Siffalovic[a], **K. Vegso**[a], **M. Jergel**[a], **M. Hodas**[a], **M. Pelletta**[a], **Y. Halahovets**[a], **Z. Zaprazny**[b], **D. Korytar**[b] **and E. Majkova**[a]
[a]*Institue of Physics, Dubravska cesta 9, 84511 Bratislava, Slovakia*
[b]*Institute of Electrical Enginnering, Dubravska cesta 9, 84104 Bratislava, Slovakia*

The need for structural characterization of dedicated nanostructured thin films with desired functionalities is on the rise. Here, organic electronics is a typical example. Developments in polymer photovoltaic cells, organic light emitting diodes or organic transistors require access to structural correlations from Ångstroms up to hundreds of nanometers. Therefore, laboratory high-resolution GISAXS measurements, confined mainly to synchrotrons nowadays, are urgently needed.

Here, we introduce a high-performance GISAXS system based on the channel-cut diffractive optics with resolution of 500 nm in real space at the flux of 10^7 photons/s at the sample position. The X-ray source is liquid metal-jet generator (250W, Bruker AXS & Excillum) coupled to parabolic Montel optics (Incoatec). A dedicated Ge 220 channel-cut crystal (Integra TDS) based on a combination of symmetric and asymmetric diffractions is used for the 5-fold compression of the X-ray beam exiting Montel optics [1, 2]. The 200 m horizontal beam dimension is well matched to the point spread function of the PILATUS 300K detector for acquisition of GISAXS images, the horizontal divergence being less than 100 rad. The vertical beam size and divergence are restricted by a single crystal scatterless Ge pinhole and further limited by a small angular acceptance of the sample in the grazing-incidence geometry. A unique mutlifunctional setup based on two vacuum-compatible hexapods is shown in Figure 1. The first hexapod in the upside-down position is used for a fine alignment of the compressing channel-cut crystal. The second one is used for a precise sample adjustment with respect to the compressed X-ray beam leaving the channel-cut crystal. The imaging plate and MYTHEN 1K detector are at disposal for the ex-situ and in-situ GIWAXS studies, respectively. A flight tube with vertically adjustable offset and a movable PILATUS 300K detector provide high flexibility in mapping the reciprocal space in GISAXS configuration.

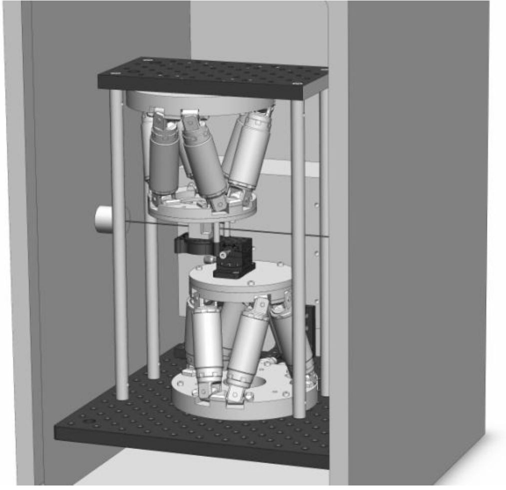
Figure 1: The experimental chamber.

As an example, we present a study of the patterned active layer of a polymer solar cell based on the P3HT:PCBM blend. The morphology of the spin-coated P3HT:PCBM layer was modified by pulsed UV laser annealing which induces periodic surface ripples with periods up to hundreds of nanometers depending on the laser power. The P3HT crystallinity, phase separation in the bulk heterojunction and surface ripples were all measured simultaneously in the single setup.

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Submitting Author: peter.siffalovic@savba.sk

HIGH-FLUX SAXS INSTRUMENT WITH LIQUID METAL JET SOURCE WITH AUTOMATED SAMPLE HANDLER AND STOPPED-FLOW APPARATUS

J.S. Pedersen[a], J. Lyngsø[a], E. Konusch[b], and L. Bruegemann[b]
[a] *Interdisciplinary Nanoscience Center (iNANO) and Department of Chemistry, Aarhus University, 8000 Aarhus C, Denmark*
[b] *Bruker AXS, Östliche Rheinbrückenstr. 49, 76187 Karlsruhe, Germany*

During the last 10-20 years great progress has been made in instrumentation for laboratory based pinhole SAXS. The combination of optimized geometry [1], curved multilayer optics, powerful new micro x-ray sources [2] and, more recently, the liquid metal jet source from Excillum [3] has provided the basis for this. Another important development has been the introduction of 'scatterless' slits [4], in which the edges are made of single crystals of Ge or Si, to reduce the parasitic scattering and reflection from the edges. The use of these has meant that the traditional three-pinhole collimation, where two pinholes collimate the beam and a third one in front of the sample removes parasitic scattering, can be replaced by a two-pinhole setup with larger beam and larger divergence, and thus larger flux.

A new SAXS NanoSTAR with a liquid metal Ga jet source has recently been installed at Aarhus University. The instrument employs a long high-quality parabolic Montel multilayer optics from Incoatec [5] and a compact scatterless pinhole slit with Ge edges built at Aarhus University. The combination of the powerful source and the optimized geometry gives an integrated X-ray intensity close to 10^9 photons/s for a standard range of scattering vector moduli, $q = 0.01–0.35$ Å^{-1}, where $q = (4\pi \sin\theta)/\lambda$, where λ is the Ga Kα wavelength of 1.34 Å.

The high intensity of the instrument means that even dilute samples of less than 1wt% of protein or surfactants can be measured in a few minutes. Therefore, in order to get an efficient use of the instrument a flow-through cell (built at Aarhus University) in combination with an automated sample handler has been installed at the instrument. The sample handler is based on the commercial Gilson GX-271 Injection system (delivered by Biolab, Risskov, Denmark [6]), which also allows the samples to be stored under thermostated conditions. The sample handler inserts and removes samples, as well as cleans the cell between measurements. The minimum volume of the flow-through capillary is about 25 μL.

The high intensity also allows time-resolved measurements to be performed. For this purpose a stopped-flow apparatus, SFM-3000 from Bio-Logic [7], was connected to the flow-through measuring cell by HPLC tubing. This solution was chosen as it allows the vacuum around the sample cell and thus a low background. The only drawback of the longer distance to the sample cell is that it increases the deadtime when injecting a new sample, however, this is unimportant for the time resolution of some seconds, which can achieved for the setup.

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Submitting Author: jsp@chem.au.dk

NEW OPPORTUNITIES FOR TIME-RESOLVED ULTRA SMALL-ANGLE X-RAY SCATTERING AT THE ESRF

T. Narayanan, J. Leonardon, P. Van Vaerenbergh, M. Sztucki, P. Boesecke, J. Gorini,
L. Claustre, F. Sever and J. Morse
ESRF-The European Synchrotron, 71, Avenue des Martyrs, Grenoble, France

This presentation will give an overview of new possibilities offered by the upgraded ID02 beamline for Time-Resolved (TR) and Ultra Small-Angle X-ray Scattering (USAXS) studies of soft matter and related systems. The new beamline (TRUSAXS) combines SAXS, WAXS and USAXS to one unique instrument, covering a wide scattering vector (q) range of 10^{-3} nm^{-1} q 50 nm^{-1} using 1 Å X-ray wavelength. The main component of this instrument is an evacuated (5x10^{-3} mbar) stainless steel detector tube of length 34 m and diameter 2 m. Three different detectors, Rayonix MX170, Pilatus 300K and FReLoN 4M are housed inside a motorized wagon which travels along a rail system with high precision. The detector tube scheme facilitates automated change of the sample-to-detector distance from 1 m to 31 m and selection of the desired detector for a particular q range. A wide angle detector (Rayonix LX170) is appended to the entrance cone of the tube for optional WAXS measurements. A novel beamstop system enables monitoring of the transmitted X-ray beam intensity and automated insertion of selected masks behind the primary beamstop when required.

The variation of sample-to-detector distance over the full range is facilitated by means of a novel focusing scheme that preserves the source brightness. The required collimation is achieved by a combination of primary and secondary slits or by two pseudo channel-cut crystals. The focusing optics and slit collimation scheme permit to cover a scattering vector (q) range of 0.002 nm^{-1} q 50 nm^{-1} with one unique setting using 1 Å wavelength for moderate flux (5x10^{12} photons/sec). However, for high flux (6x10^{13} photons/sec), minimum q (q_{Min}) is of the order of 0.01 nm^{-1}. For unprecedented resolution ($\Delta q \approx 0.0004$ nm^{-1}) and $q_{Min} < 0.001$ nm^{-1}, either slit collimation or pseudo channel-cut crystal setup could be employed but at the expense of flux (≈5x10^{10} photons/sec). The reduction of flux is not an issue due to typically high scattering level in the USAXS range. For a sample-to-detector distance of 31 m and 1 Å wavelength, two dimensional USAXS patterns can be recorded down to $q \approx 0.001$ nm^{-1} with much superior quality than the one dimensional profile obtained with a Bonse-Hart instrument. An added feature is the high degree of coherence that is illustrated by speckles in the scattering patterns.

The new beamline offers time-resolved capabilities down to the millisecond range. Using a tandem shutter scheme, stroboscopic experiments down to 100 µs can be performed. Using 31 m sample-detector distance, anisotropic scattering patterns can be recorded down to $q \approx 0.001$ nm^{-1}. The broad q-range and time resolution facilitates in-situ studies of many hierarchically ordered systems. For example, with a muscle fiber both the sarcomere (unit cell) reflections (≈2.2 µm), and actin and myosin based reflections (tens of nm) can be acquired in the same preparation. Typical scattering patterns recorded with the highest resolution display speckles which open the possibility for probing the equilibrium dynamics by X-ray Photon Correlation Spectroscopy in the USAXS range. Access to simultaneous static and dynamic information in the micrometer scale is useful in the investigation of complex systems such as active matter.

Although the flux is optimized for X-ray energy of 12.5 keV, the incident energy is tunable over a range of 8-20 keV for anomalous SAXS experiments. In summary, the upgraded ID02 beamline offers unprecedented potential for USAXS studies of soft matter and allied systems.

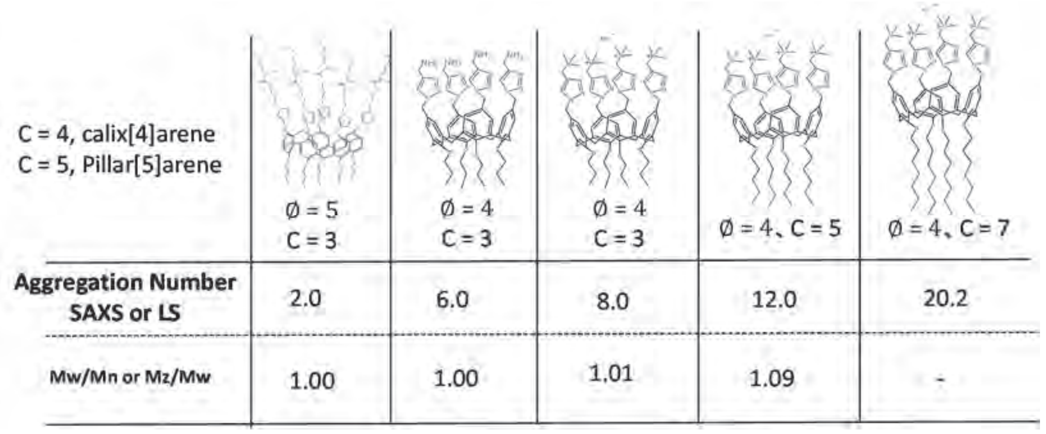
Submitting Author: narayan@esrf.fr

SHAPE PERSISTENCE MICELLES HAVING THE SAME AGGREGATIONS WITH THE PLATONIC SOLIDS

Kazuo Sakurai
Department of Chemistry and Biochemistry, University of Kitakyushu,
Hibikino, Kitakyushu 808-0135, Japan

A series of calix[4]arene-based lipids with alkyl chains of varying length were newly synthesized and found that some of them form spherical micelles with a defined aggregation number. These aggregation numbers are 6, 8, 12, and 20, interestingly coinciding the numbers of the Platonic solids. Synchrotron small-angle X-ray scattering (SAXS) patterns exhibited a sharp intensity minimum, indicating high symmetry and shape monodispersity. The size monodispersity of the micelles was confirmed with analytical ultracentrifugation and asymmetric filed flow fractionation. The present results indicate that a suitable combination of tail length, head volume, and rigidity of the building block is necessary to attain the shape persistency. With a shape determination program of Dummy and molecular dynamics calculation, the micellar architecture was determined and an atomic scale model to reproduce SAXS profile was constructed.

We have a hypothesis that can rationalize why the aggregation numbers are taking such a discreet manner and chosen from the numbers of the Platonic solids; the aggregation number is determined by the J. J. Thomson's theorem to determine the minimum electrostatic potential energy configuration of N electrons on the sphere surface that repel each other. We suppose this can be extended to the other spherical micelles when the aggregation numbers are small enough.



C = 4, calix[4]arene C = 5, Pillar[5]arene	Ø = 5 C = 3	Ø = 4 C = 3	Ø = 4 C = 3	Ø = 4、C = 5	Ø = 4、C = 7
Aggregation Number SAXS or LS	2.0	6.0	8.0	12.0	20.2
Mw/Mn or Mz/Mw	1.00	1.00	1.01	1.09	-

Table 1. Chemical structures of calixarene lipids and their aggregation numbers.

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Submitting Author: sakurai@kitakyu-u.ac.jp

COEXISTING CRYSTAL AND MELT STRUCTURES IN COLLOIDAL BINARY MIXTURES

A. R. Rennie[a], **M. S. Hellsing**[a], **S. E. Rogers**[b] **and R. K. Heenan**[b]
[a]*Department of Physics and Astronomy, Uppsala University. Box 516, SE-75120 Uppsala.*
[b]*ISIS Facility, Rutherford Appleton Laboratory, Didcot, OX11 0QX, United Kingdom.*

Charged colloidal particles can order as dispersions in deionised water and are well-known to form crystal structures that have a low yield stress and flow readily while exhibiting long-range three dimensional order (see e.g. [1]). Use of normal hydrogenous and deuterated latex particles in combination with small-angle neutron scattering and H_2O/D_2O contrast variation allows the partial structure factors for each component in a mixture to be determined. Results for a number of concentrations and compositions of particles in deionised water will be presented. These will be contrasted with earlier studies that have investigated dispersions with added electrolyte so as to resemble binary liquid mixtures.

Mixtures of strongly interacting (repulsive potential) particles with two different sizes display interesting behaviour in that small particles can be inserted in the gaps between large particles. We have observed that for systems where each component would on its own form crystals, the crystalline order of the large particles in a mixture is destroyed whereas the small particles retain sharp Bragg diffraction peaks. Small particles thus act as macroions that screen interactions as well as cluster within interstices between large particles.

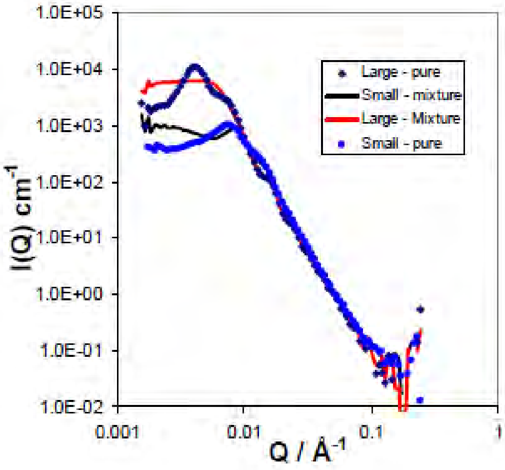

Figure 1: Small-angle neutron scattering results for dispersions of particles alone and in binary mixtures at the same concentration.

Example data is shown in Figure 1. These result for a mixture of large deuterated (R = 330 Å) and small hydrogenous (R = 130 Å) particles are measured in corresponding matching solvents of low ionic strength. Both latices had interaction potentials of about 35 mV. On their own, each species show clearly diffraction from ordered structures. In the mixture, the regular structure of the large particles is destroyed as seen by a single broad peak. The upturn at small Q is interpreted as clustering. Data for a range of compositions and particle sizes will be presented with model fits.

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Submitting Author: Adrian.Rennie@physics.uu.se

BULK NANOSTRUCTURE OF THE SOLVATE IONIC LIQUID [Li(G_4)]TFSI AND CONFORMATION OF DISSOLVED POLYETHYLENE OXIDE

Rob Atkin[a],* **Thomas Murphy,**[a] **Zhengfei Chen, Greg Warr**[b]
[a] *The University of Newcastle, Newcastle, Australia*
[b] *The University of Sydney, Sydney, Australia*

Equimolar mixtures of glymes (oligoethers of the form $CH_3(OCH_2CH_2)_nOCH_3$, abbreviated G_n) with Li metal salts can form solvate ionic liquids (SILs) via partial donation of lone pair electrons from the glyme molecule to the alkali metal ion. This leads to the formation of a complex cation, with the anion coming from the lithium salt. The resultant SIL, [Li(glyme)]X, has physicochemical properties that are typical of ionic liquids including high thermal stability, wide electrochemical potential window, high ionic conductivity, and high Li^+ transfer number. This makes SILs appealing for electrochemical devices such as capacitors and lithium ion batteries.[1] Polymers such as polyethylene oxide (PEO) are frequently added to the electrolyte in these devices as they can suppress dendrite growth during the cycling of lithium metal.

Neutron diffraction with empirical potential structure refinement fits (ESPR) reveal the structure of pure tetraglyme bis(trifluoromethanesulfonyl)amide [Li(G_4)][TFSA] (c.f Figure 1*left*) while small angle neutron scattering (SANS) elucidates the morphology of PEO dissolved in [Li(G_4)][TFSA] from the dilute to concentrated regimes (Figure 1 *middle* and *right*). At high PEO concentrations, the zero average contrast condition is employed by mixing deuterated and hydrogenated PEO at a certain ratio. The radius of gyration, R_g, decreases slightly with concentration in the dilute regime but more strongly in the semidilute regime, and is approximately constant in the concentrated regime. The changes in R_g with concentration allow C* and C** to be identified (13 and 48 mg/mL) and Zimm plots reveal that [Li(G4)][TFSA] is a intermediate to good solvent for PEO.

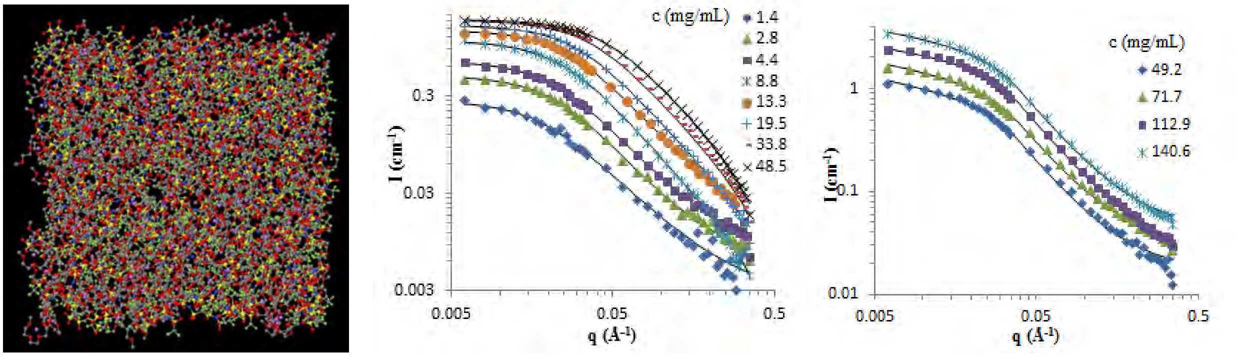

Figure 1. (left) Front face of the EPSR fit simulation box to neutron diffraction data for [Li(G_4)][TFSA]. **(middle)** SANS intensity for d-PEO-[Li(G_4)][TFSA] solutions with background ubtracted. Lines are Polymer Excluded Volume model fits to the data. **(right)** SANS intensity for PEO-[Li(G_4)][TFSA] solutions at zero average neutron contrast with background subtracted. Lines are Guinier Porod model fits to the data.

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Submitting Author: rob.atkin@newcastle.ed.au

NEUTRON SCATTERING STUDIES OF SELF-ASSEMBLY IN AMPHIPHILIC IONIC LIQUIDS

G.G. Warr[a], **R. Atkin**[b], **H. Jiang**[a], **M. Araos**[a], **A. Dolan**[a], **T. Murphy**[b] **and S. Imberti**[c]
[a]*School of Chemistry, The University of Sydney, NSW 2006 Australia*
[b]*The University of Newcastle, Newcastle, Australia*
[c]*STFC, Rutherford Appleton Laboratory, Didcot, United Kingdom*

Ionic liquids, and particularly protic ionic liquids (PILs), have been extensively examined over the past decade due to their ability to promote solvophobic self-assembly by surfactants and amphiphilic polymers.[1-3] This has been attributed to their high cohesive energy density resulting from a combination of electrostatic and H-bonding interactions. More recently it has been shown by neutron diffraction that many PILs are themselves nanostructured, forming a bicontinuous network of polar, H-bonding and non-polar domains.[4-6] Whereas in aqueous solution the length scales of solvent and self-assembly structure are well-separated, in PILs this is not the case.

Using a combination of SAXS/WAXS, SANS and wide angle neutron diffraction with contrast variation by multiple isotopic substitutions, we have examined the self-assembly of conventional poly(oxyethylene) n-alkyl ether nonionic and cationic ammonium salts amphiphiles into micelles, as well as the unconventional self-assembly of aliphatic alcohols in PILs.

Neutron diffraction, analysed using empirical potential structure refinement (EPSR), yields a detailed high-resolution picture of the liquid structure. This includes the H-bond network and amphiphilic nanostructure of the PILs ethylammonium and propylammonium nitrate (EAN and PAN) themselves, and also how they solvate various solute functional groups such as -OH, -CH_2CH_2O- and (C_2-C_{12}) alkyl chains both as molecular solutions and in micelles. This is complemented by SAXS and SANS studies, in which the structure of functional groups -$(CH_2CH_2O)_nOH$, -$N(CH_3)_mH_{3-m}$, -C_nH_{2n+1} and counterion type in the amphiphiles is systematically varied. PIL structure is similarly varied.

We find that polar domain structure of PILs is critical in determining the behaviour of solvophilic, polar groups on solutes, but that the hydrophobic alkyl chains are sensitive only to the average solvent environment. This effect depends strongly on the ratio of solute to PIL alkyl chain length: for solutes with alkyl chains longer than twice that of the PIL, the solute cannot be accommodated within the existing solvent nanostructure. This prompts self-assembly into micelles and lyotropic mesophases. The amphiphilicity of PIL cations is also found to be critical in stabilising micelle and microemulsion-like self-assembly of primary aliphatic alsohols.

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Submitting Author: gregory.warr@sydney.edu.au

PHASE BEHAVIOR OF DENSE LYSOZYME SOLUTIONS

J.Schulze[a], **J. Möller**[b] , **M. Paulus**[a] , **J. Nase**[a] , **M. Tolan**[a] **and R. Winter**[c]
[a]*Fakultät Physik/Delta, Technische Universität Dortmund,44221 Dortmund ,Germany*
[b]*ESRF- The European Synchrotron, 38043 Grenoble, France*
[c] *Fakultät Chemie und Chemische Biologie, Technische Universität Dortmund, 44221 Dortmund, Germany*

The influence of thermodynamic properties or salt concentration on protein stability, aggregation propensity, intermolecular interaction as well as crystallization and phase behavior of dense protein solutions has been in the focus of protein science in recent years. As small-angle X-ray scattering (SAXS) is an ideal tool for the investigation of proteins and their interactions, it was used in previous studies to determine the intermolecular interaction potential of proteins in aqueous solution under the influence of varying conditions such as hydrostatic pressure, temperature or ionic strength. A non-monotonous correlation between the strength $J(p)$ of the attractive part of the protein-protein interaction and the hydrostatic pressure was found with a minimum at about 2 kbar, which is probably related to changes in the water structure at elevated pressures [1,2]. Adding 500 mM NaCl led to a linear increase of the attractive part of the interaction potential, besides the well-known screening effect of the Coulomb repulsion [3,4].

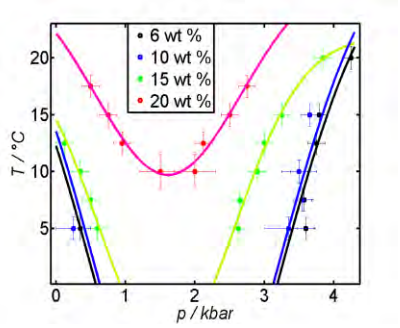

Fig 1: Phase boundaries for four different lysozyme concentrations in presence of 500 mM NaCl at selected pressures and temperatures. Below the curves, the system is always in LLPS, above in homogenous phase.

In this contribution, we will discuss the phase behavior of lysozyme solutions as a function of concentration, pressure and temperature in the presence of 500 mM NaCl. If the short range interactions become too attractive (*e.g.* at high lysozyme concentrations or low temperatures), a phase transition into the so-called LLPS (Liquid-Liquid Phase Separation) phase can be observed. In this phase, two liquid phases, which differ in their protein concentration, coexist. At elevated hydrostatic pressure however, this phase separation is suppressed. Due to the non-monotony of $J(p)$, a further pressure increase leads to a re-entrant LLPS phase. Hence, the phase diagram reflects the non-monotonous pressure dependence of the protein-protein interactions (see Fig 1; [5]). In this contribution the unusual phase behavior of lysozyme over a wide range in concentration and temperature will be discussed.

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Submitting Author: julian.schulze@tu-dortmund.de

SAXS STUDY OF PEPTIDE SELF-ASSEMBLY IN SOLUTION

Valeria Castelletto, Ashkan Dehsorki and Ian W. Hamley
School of Chemistry, University of Reading, RG6 6AD, Reading, U.K.

A large number of water soluble peptides self-assemble into organized structures that can be used for different applications. In this work we present several SAXS studies of peptide self-assembly motifs in solution.

We studied the self-assembly of a peptide amphiphile, namely C_{16}-G_3-RGDS (R: arginine, G: Glysine, D: Aspartic acid, S: Serine), which represents a promising material for designing new cell adhesion substrates [1]. SAXS was used to show that this peptide self-assembles into nanotapes with an internal bilayer structure. C_{16} chains were highly interdigitated within the nanotape cores, while the peptide blocks formed water-exposed β-sheets.

We also performed a SAXS study of the interaction of C_{16}-G_3-RGDS with the lipid-free apoliprotein, Apo-AI, to get an insight into the formation of lipopetide/Apo-AI discs [2]. These discs are analogous to those reported for lipids, but containing peptide-functionalised lipopeptide molecules wrapped with the Apo-AI. SAXS data for Apo-AI could be fitted using a published crystal structure of the Apo-AI dimer, while the SAXS data for the lipopeptide/Apo-AI mixtures indicated a fraction of nanodiscs, although these coexist with fibrillar structures from the lipopeptide self-assembly process.

In a separate work, SAXS is used to determine that a designed peptide amphiphile C_{16}-KKFFVLK (K: Lysine, F: Phenylalanine, V: Valine, L: Lysine) self-assembles into nanotubes and helical ribbons in aqueous solution at room temperature [3]. A remarkable unwinding transition, leading to twisted tapes, is studied by SAXS on heating. Nanotubes and ribbons re-form on cooling.

Finally, the self-assembly of the alanine-rich amphiphilic peptide KA_6E (A: Alanine, E: Glutamic acid) was studied by SAXS [4]. This peptide contains the A_6 sequence, designed to serve as substrates for the enzyme elastase. The enzymatic degradation of KA_6E hydrogels upon addition of elastase was investigated by SAXS. Results show that KA_6E hydrogels may serve as model substrates for elastase and this could ultimately lead to applications in biomedicine and regenerative medicine.

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Submitting Author: v.castelletto@reading.ac.uk

SMALL ANGLE X-RAY SCATTERING AS A VERSATILE TOOL TO EXPLORE MINERALIZATION PATTERNS IN HEALTHY AND DISEASED BONE

W. Wagermaier[a], I. Schmidt[a], R. Hoerth[a], N. Fratzl-Zelman[b], P. Roschger[b], K. Klaushofer[b], B.M. Willie[c], G.N. Duda[c] and P. Fratzl[a]
[a]Max Planck Institute of Colloids and Interfaces,
Department of Biomaterials, Research Campus Golm, 14424 Potsdam, Germany
[b]Ludwig Boltzmann Institute of Osteology at Hanusch Hospital of WGKK and AUVA Trauma Centre Meidling, 1st Med. Dept. Hanusch Hospital, Vienna, Austria
[c]Julius Wolff Institute & Center for Musculoskeletal Surgery, Charité - Universitätsmedizin Berlin, Campus - Virchow Klinikum, 13353 Berlin, Germany

Bone is a biological material made from organic collagen and inorganic hydroxyapatite platelets at the nanometer scale. These nanoscale building blocks are universal in different types of bone, but size and orientation of the mineral platelets changes during bone formation as well as during bone diseases. The mineral platelets and the organic matrix form a two-phase system with two different electron densities, which enables a quantitative analysis of mineralization patterns in bone by small angle X-ray scattering (SAXS). By applying high resolution scanning synchrotron SAXS we are able to determine mineralization patterns in bone and relate these findings to the dynamic biological processes in diseased and healthy bones. During bone fracture healing, tissue reconstitution mainly occurs via the initial formation of soft tissues that stabilize the fracture gap. These soft tissues are eventually replaced by a bony callus formation that happens in a two-wave process, where poorly ordered woven bone is initially deposited and later replaced by highly ordered lamellar bone. Small angle X-ray scattering enabled us to study mineral particle dimensions and mineral particle arrangement in small animal models and to reveal changes within the nanostructure during the bone healing processes [1].

Osteogenesis imperfecta (OI) is a genetic disorder characterized by an increase in bone fragility on the macroscopic scale. The disease is generally caused by autosomal dominant defects in the genes encoding type I collagen. An abnormally high bone matrix mineralization has been observed in all OI cases investigated so far. To better understand the effects of OI on the properties of human bone, we studied several transiliac bone biopsy samples from affected children and healthy controls [2]. We used synchrotron SAXS, which allows the determination of mineral particle at the same positions where the matrix mineralization density was previously determined by using quantitative backscattered electron imaging (qBEI). We found that mineral particles are not larger in OI than in controls and thus conclude that the high mineral density in human OI is not due to increased particle size but rather to increased particle packing density.

In conclusion, we were able to characterize the properties of mineral particles in bone in different systems and described anomalous behavior or successive changes the nanostructure undergoes during healing or in diseases. We found that in both studied cases not only the meso or macro scale of the hierarchical material bone showed different properties, but also the nanoscopic scale and therefore the basic building block of bone displayed crucial differences compared to healthy and mature bone tissue.

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Submitting Author: wolfgang.wagermaier@mpikg.mpg.de

QUANTIFYING TIE-CHAIN CONTENT IN SEMICRYSTALLINE POLYOLEFINS WITH VAPOR-FLOW SMALL-ANGLE NEUTRON SCATTERING

A. G. McDermott[a,b], **C. R. Snyder**[a], **P. J. DesLauriers**[c] **and R. L. Jones**[a,b]
[a]*National Institute of Standards and Technology, Materials Science and Engineering Division, Gaithersburg, MD, USA*
[b]*National Institute of Standards and Technology, nSoft Consortium, Gaithersburg, MD, USA*
[c]*Chevron Phillips Chemical Company, Bartlesville, OH, USA*

Tie molecules bridging adjacent crystalline lamellae in semicrystalline polymers strongly impact mechanical properties, but they remain difficult to characterize. We demonstrate a new method of measuring tie-chain content: applying equilibrium swelling theory [1] to small-angle neutron scattering patterns from semicrystalline polyethylene films whose interlamellar amorphous regions are swollen with deuterated organic solvent in a vapor-flow sample environment [2] (Figure 1). To aid in validating the measurement, measured tie-chain content is compared with a primary structural parameter (PSP2) that is calculated from molecular architecture and correlates with slow crack growth behavior [3]. Agreement is favorable for a linear polyethylene and a series of ethylene-hexene copolymers. Recent applications of the technique are also discussed.

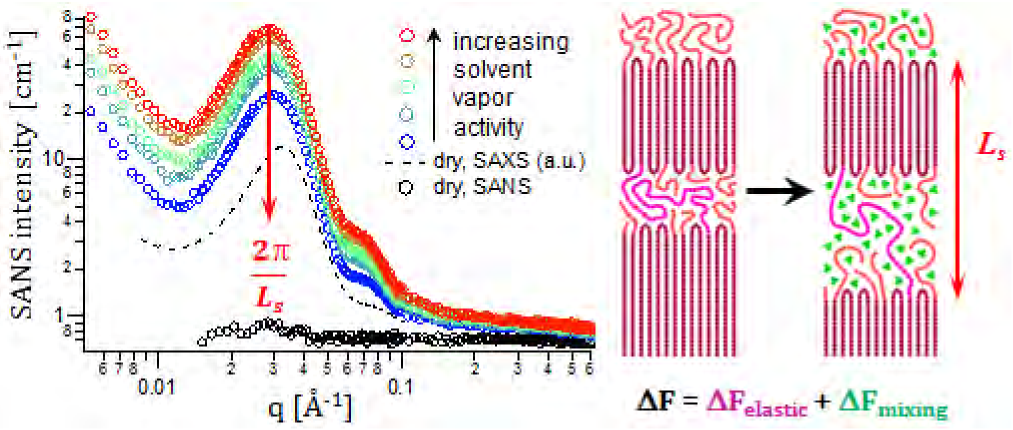

Figure 1: As the interlamellar amorphous layer in polyethylene is swollen with a deuterated solvent, the peak associated with the long period *L* shifts to lower wavevectors, and the SANS intensity increases as the amorphous-crystalline contrast increases. While the free energy of mixing drives solvent absorption, the entropic cost of tie-molecule stretching restricts swelling. Parameters derived from modeling SANS patterns are used in thermodynamic analysis to quantify the tie-chain content.

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Submitting Author: amanda.mcdermott@nist.gov

CONONSOLVENCY OF WATER/METHANOL MIXTURES FOR PNIPAM AND PS-*b*-PNIPAM: PATHWAY OF AGGREGATE FORMATION INVESTIGATED USING TIME-RESOLVED SANS

K. Kyriakos[a], A.V. Berezkin[a], M. Philipp[a], P. Müller-Buschbaum[a], A. Miasnikova[b], A. Laschewsky[b,c], I. Grillo[d], and C.M. Papadakis[a]
[a]*Technische Universität München, Physik-Department, James-Franck-Str. 1,*
85748 Garching, Germany
[b]*Universität Potsdam, Institut für Chemie, Karl-Liebknecht-Str. 24-25,*
14476 Potsdam-Golm, Germany
[c]*Fraunhofer Institut für Angewandte Polymerforschung, Geiselbergstr. 69,*
14476 Potsdam-Golm, Germany
[d]*Institut Laue-Langevin, Large Scale Structures Group, 6, rue Jules Horowitz,*
38042 Grenoble, France

Diblock copolymers consisting of a short hydrophobic polystyrene (PS) and a long thermoresponsive poly(N-isopropylacrylamide) (PNIPAM) block form core-shell micelles in aqueous solution. PNIPAM displays lower critical solution temperature behavior, i.e. the chains collapse and form large aggregates when the aqueous solution is heated through the cloud point. Moreover, PNIPAM features cononsolvency, i.e. addition of a cosolvent results in a depression of the cloud point. We have investigated the effect of the cosolvent methanol on aqueous solutions of PS-*b*-PNIPAM diblock copolymers and, as a reference, PNIPAM homopolymers of similar molar mass [1].

Using a stopped-flow instrument, fully deuterated methanol (*d*-MeOD) was added to a solution of PS-*b*-PNIPAM or PNIPAM in D_2O at mixing ratios between 5 and 20 vol.-% (Figure 1). The structural changes on mesoscopic length scales were followed by time-resolved small-angle neutron scattering (TR-SANS) with a time resolution of 0.1 s. In the PNIPAM solution, very large aggregates (> 150 nm) are formed within few milliseconds. In contrast, the growth of the aggregates in the PS-*b*-PNIPAM system features several regimes with a final aggregate size of ~50 nm, thus much smaller than for the homopolymer. For the diblock copolymer, the time-dependence of the aggregate radius can be described by two models: In the initial stage, the diffusion-limited coalescence model describes the data well; however, the resulting coalescence time is unreasonably high. In the late stage, a model including an energy barrier which is proportional to the aggregate radius is successfully applied.

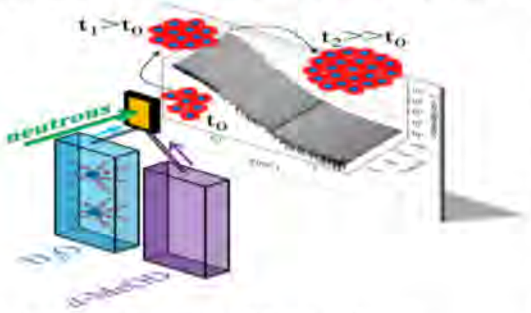

Figure 1: Schematics of the experiment.

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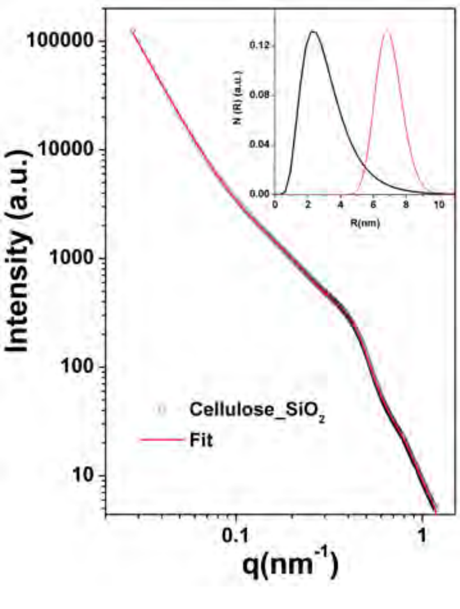
Christine M. Papadakis: papadakis@tum.de

SAXS STUDY ON THE HIERARCHICALLY STRUCTURED NANOPARTICLES-CELLULOSE COMPOSITES: STRUCTURE AND INTERACTIONS

U. Garusinghe[a], V.S.Raghuwanshi[a], C. J. Garvey[b], G. Garnier[a]
[a]*Monash University, Department of Chemical Engineering, Clayton, Victoria,3800, Australia*
[b] *ANSTO, Lucas Heights NSW 2234, Australia*

Nowadays,extensive work has been focused on developing sustainable and environmentally friendly materials. Cellulose nanofibres are an emerging organic material due to its unique mechanical, optical properties and renewable attributes. Cellulose is the most abundant polymer on earth, mostly occurring in plant based materials, making it an excellent source of raw material for biocompatible and eco-friendly products[1-3]. Cellulose nanofibre sheets have exciting prospects as materials for liquid and air separation. However, the nanofibre sheets produced have shown a limited range of porosity and surface area properties for a given source of nanofibres. A hypothesis is raised that the preparation of nanoparticle-nanofibrenano-composites can control both porosity and surface area to engineer hierarchically structured materials of unique properties. Polymers such as nanocellulose take the role of a semi-continuous or connecting phase to bridge and link nanoparticles (NPs) to provide a new structure with voids, in which the change in porosity and pore structure relies on NPs. Here, samples with different loading of SiO_2 and TiO_2NPs of variable diameters in the cellulose matrix are used for SAXS investigations. Cationic polyelectrolyte was used for surface coverage of SiO_2 or TiO_2 to give maximum coagulation rate. Polyelectrolytes helps NPs to be retained in the nanofibre network. Figure shows the SAXS curve of 8 nm (diameter) SiO_2 nanoparticles loaded in cellulose matrix. The curve fitted with the bimodal sphere model. Inset shows the evaluated size distribution obtained after curve fitting. SAXS data analysis show average spheres diameter of about 8 nm and 15 nm. Further data analysis allow to systematically quantifying the effect of the NPs on the composite structure and properties, studying how different NPs interact with the cellulose matrix, determine nanofibre structure and binding, NP size selection and binding/agglomeration, self-assembly and void fraction. Outcome of the investigations give a superior view on how NPs cellulose nanofibres interactions affect different properties. The experimental results allow tailoring different properties of nanocellulose-NP composites for specific functional applications. Novel materials for packaging applications and degradation of organic matter via photocatalysis will also be benefited from this study.



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Submitting Author: vikram.raghuwanshi@monash.edu

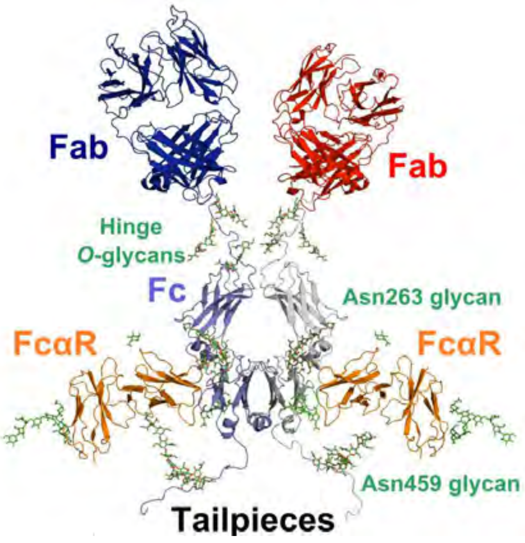
THE ASYMMETRIC SOLUTION STRUCTURES OF NATIVE AND PATIENT MONOMERIC HUMAN IGA1 REVEAL NEW INSIGHTS ON IGA NEPHROPATHY

David W. Wright[a*], **Gar Kay Hui**[a*]. **Owen L. Vennard**[b*], **Lucy E. Rayner**[a], **Melisa Pang**[a], **See Cheng Yeo**[b], **Jayesh Gor**[a], **Karen Molyneux**[b], **Jonathan Barratt**[b] **and Stephen J. Perkins**[a] * These three authors contributed equally to this work.

[a]*Department of Structural and Molecular Biology, Division of Biosciences, Darwin Building,*
University College London,Gower Street, London WC1E 6BT, U.K.
[b]*Department of Infection, Immunity and Inflammation, Maurice Shock Medical Sciences*
Building, University of Leicester, University Road, Leicester, LE1 9HN, U.K.

IgA nephropathy (IgAN) is a leading cause of chronic kidney disease in developed countries. In IgAN, immune complexes containing the IgA1 antibody subclass are deposited in the mesangium to result in glomerular damage. Native IgA1 contains an O-glycosylated 23-residue hinge region that joins its Fab and Fc regions, while IgA1 in IgAN have undergalactosylated hinges.

Here, we have determined the solution structures of IgA1 from the plasma of a healthy control and three patients with reduced or elevated *O*-linked GalNAc levels in their hinges. Analytical ultracentrifugation showed that all four IgA1 glycoproteins were monomeric with similar sedimentation coefficients $s^{0}_{20,w}$ of 6.2-6.4 S. X-ray scattering showed that the radius of gyration R_G significantly increased with IgA1 concentration, but two peaks *M1* and *M2* seen in their distance distribution curves *P(r)* were unchanged with concentration. Neutron scattering in heavy water also indicated an unchanged solution structure, however IgA1 was prone to non-specific aggregation.



An atomistic mIgA1 model was created. From this, Monte Carlo and molecular dynamics simulations were used to create a conformationally varied ensemble of candidate structures using CCP-SAS software. Comparisons of 127,000 and 177,000 conformationally-randomised IgA1 structures with the experimental scattering curves extrapolated to zero concentration revealed similar extended Y-shaped asymmetric IgA1 solution structures. An example is shown in the figure. This modelling suggested that the N-glycans at Asn263 were folded back against the Fc surface, while its C-terminal tailpieces conformations could not be defined. The Fab and Fc regions of full-length IgA1 were positioned asymmetrically to allow ample space for the binding of two FcαR receptors to the Fc region.

Even though only monomeric IgA1 was studied here, these similar outcomes for the four samples suggest that hinge galactosylation is linked with the onset of IgAN through the different exposure, flexibility or aggregation tendency of the extended O-galactosylated hinge structures in the four different IgA1 samples.

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Presenter: dave.wright@ucl.ac.uk ; submitting author: s.perkins@ucl.ac.uk

Decoding the unfolding intermediates of Bovine Serum Albumin using scanning HPLC/SAXS/UV-vis system

Yi-Qi Yeh[a], Kuei-Fen Liao[a], Wei-Ru Wu[a], Chun-Jen Su[a], Po-Chang Lin[a],
Ying-Jen Shiu[a], Meng-Ciao Ho[b], and U-Ser Jeng[a,c,*]
[a]*National Synchrotron Radiation Research Center, Hsinchu 30076, Taiwan*
[b]*Institute of Biological Chemistry, Academia Sinica, Taipei 115, Taiwan*
[c]*Department of Chemical Engineering, National Tsing Hua University, Hsinchu 30013, Taiwan*

Serum albumin, the most abundant protein in vertebrate blood plasma, has a good binding capacity for fatty acids, hormones, commonly used grug, water, and essential metal ions. Bovine serum albumin (BSA, 583 amino acids, MW 66.5kDa), a serum albumin protein derived from cows, has long been widely used in immunodiagnostics. The BSA crystal structure is resolved, however, only very recently. Nevertheless, correlations of the solution structures with functions of the protein are still difficult to be elucidated, owing to the complicate and coexisting polymorphic states of monomers, dimers, and oligomers.

In this study, we have developed an on-line high-performanc liquid chrotomography (HPLC) system at 23A small- and wide-angle X-ray scattering (SAXS/WAXS) endstaiton of the National Synchrotron Radiation Research Center (NSRRC), Taiwan [1]. Further incorporated with an UV-vis absorption spectrometer at the sample area, the HPLC/SAXS/UV-vis system allows separating the coexisting BSA monomer, dimers, and oligomers along the elute sample flow path for simultaneous SAXS/UV-vis mesaurements, under a thermodsated sample temperature range of 288-337K and sample solution pH values between 2.1 to 7.2. The SAXS results reveal that the folding-unfolding behaviors of BSA monomers exhibit multistep unfolding process, with at least three intermediate structures. The intermediate structures are extracted from the SAXS data, using GASBOR protocol provided by the EMBO group [2]. The intermediate structures are correlated to the protein crystal structure for a possible unfolding sequence of BSA. Implication of the intermediate unfolding steps is further addressed in terms of the thermodynamic parameters extracted from the SAXS data based on a modified Ising model for the unfolding free energy of each local unfolding group of BSA. Since albumin undergoes reversible conformational modification in pH 2-7 [3], the pH selectively control on BSA may help undersatnding in ligand/druo release and distribution mechanism.

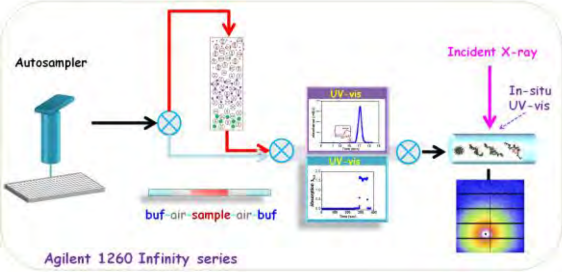

Figure 1. The on-line HPLC/SAXS/UV-vis system at 23A SAXS/WAXS endstation of NSRRC. The system provides by-pass or HPLC mode, with thermostated sample temperature and dry air flow.

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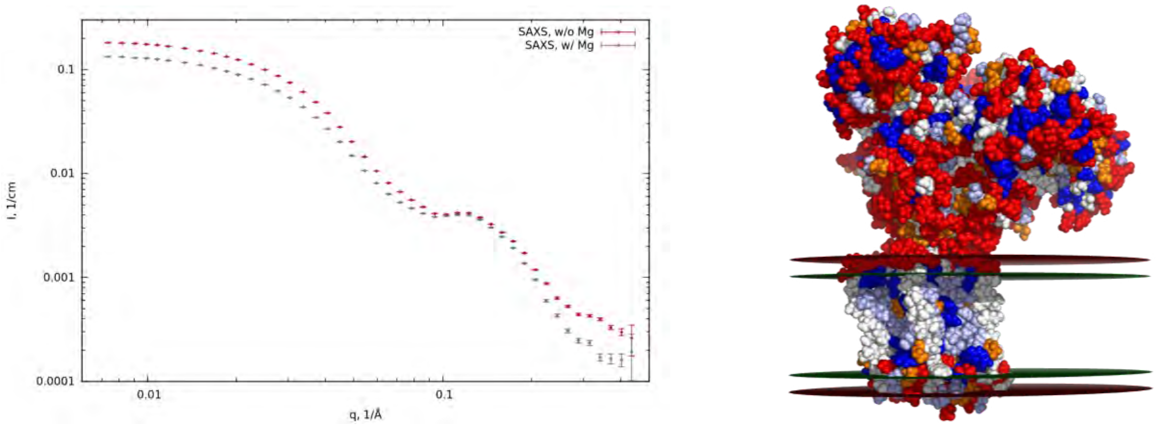
Yeh, Yi-Qi: yeh.yq@nsrrc.org.tw

Structural characterization of magnesium transporter CorA by small-angle X-ray scattering using the nanodisc as sample holder

Pie Huda[1], Martin Cramer Pedersen[1], Mikaela Rapp[2] and Lise Arleth[1]
[1]Structural Biophysics, Niels Bohr Institute, University of Copenhagen, Denmark
[2]Department of Medical Biochemistry and Biophysics, Karolinska Institutet, Stockholm, Sweden

Magnesium is the most abundant divalent cation in cells and assists in stabilizing the ribosomes and cellular membranes among many other functions (1). The transmembrane homopentameric magnesium transporter CorA serves as the primary magnesium uptake system in prokaryotes. CorA has been successfully crystallized in its Mg bound state; however, crystallizing its ligand-free state has not been possible (2). Several speculations on its ligand free form have been suggested, including a very interesting MD simulation structure (3). Using solution small-angle scattering, we have been able to record X-ray data of CorA from T. maritima in its ligand bound and unbound state, showing a significant structural difference beween the two. This was made possible using Membrane Scaffold Protein (MSP) based phospholipid bilayer nanodiscs (4) as molecular sample holders for CorA, thereby keeping the protein in a defined environment in solution. As well as by building on our previous development of a strategy for small-angle scattering analysis, which allows low-resolution structures of membrane proteins to be obtained (5). While several publications report studies of membrane proteins utilizing the nanodisc as sample holder, the large majority of these studies are on functionality. Obtaining the high quality samples that are crucial for structural studies such as small-angle scattering (6) has proven not to be a trivial matter. For the first time, we have been able to propose a low-resolution structure of a very complicated membrane protein using the combined nanodisc and small-angle scattering approach. Our data from the Mg-free state strongly supports the suggested MD simulation, while the data from the Mg bound state indicates that the crystal structure of the Mg bound CorA does not provide a complete description.



Left: Small-angle X-ray scattering data of CorA reconstituted in nanodiscs in the presence and absence of magnesium. Right: Modeled structure of CorA in a nanodisc in its unbound state based on the shown scattering data and MD simulation obtained from (3). The nanodisc is described as a simple geometric model combined with a bead model describing CorA

THE COUNTERION DISTRIBUTION AROUND DNA STUDIED BY ASAXS

G. Lotze[a], **J. Hub**[b], **F. Roosen-Runge**[c,] **M. Sztucki**[a], **T. Narayanan**[a]
[a]*ESRF – The European Synchrotron, 71 Avenue des Martyrs, 38000 Grenoble, France*
[b]*Georg-August University Göttingen, Department of Molecular Structural Biology, Justus von Liebig Weg 11, 37077 Göttingen, Germany*
[c]*Institut Laue-Langevin, 71 Avenue des Martyrs, 38000 Grenoble Cedex 9, France*

In the soft matter field highly charged sample systems appear as polyelectrolytes, ionic micelles, membranes, and nucleic acids such as DNA or RNA [1,2]. The common ground between all these systems is a highly charged macroion being surrounded by its counterions determining its physical properties. DNA represents one of the most highly charged systems on its surface with $1e^-$ per 1.7 Å arising from the negative charges due to the ionisation of the phosphate groups along its backbone [3]. In aqueous solutions DNA is always surrounded by an atmosphere of positively charged counterions, which govern certain functionality of the DNA. E.g. they are involved in the formation of secondary and tertiary structures of the DNA. Moreover, they facilitate interactions between the DNA and other molecules. Overall, counterions play an important role in charged soft matter systems [4].

Anomalous Small-Angle X-ray Scattering (ASAXS) allows to probe the spatial distribution of certain counterions around the DNA [3]. By varying the energy of the incident X-ray photons around the adsorption edge of the counterions, it is possible to extract quantitative information on the spatial distribution of counterions. Near the absorption edge, the decomposition of the energy dependent scattered intensity yields three terms [4]. The dominant term is the non-resonant term that is equivalent to the conventional SAXS intensity away from the absorption edge. The second term involves the scattering amplitudes of the macroion and the counterion usually referred to as the cross-term [2]. The third term is a weak contribution solely due to the counterions that contains information about the spatial information of the counterions [2,4]. This self-term is unique to elucidate the correlation between the counterions and their macroions as well as the inter-ionic correlation for counterions. In addition, it provides evidence for the existence of non-random counterion fluctuations [2].

Here we will present ASAXS measurements on a 25 base-pair DNA surrounded by rubidium and strontium ions. The decomposition of the ASAXS intensities allowed to obtain the cross-term as well as the self-term of the counterions. These results are compared with two different models, the Poisson-Boltzmann approach and an atomistic approach based on molecular dynamics simulations.

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Gudrun Lotze: gudrun.lotze@esrf.fr

AMBIGUITY ASSESSMENT OF SMALL-ANGLE SCATTERING CURVES FROM MONODISPERSE SYSTEMS

M.V. Petoukhov[a] **and D.I. Svergun**[a]

[a] *European Molecular Biology Laboratory, Hamburg Outstation. EMBL c/o DESY, Notkestr. 85, 22607 Hamburg, Germany*

A novel approach [1] is presented for an *a priori* assessment of the ambiguity associated with a spherically averaged single particle scattering. The approach allows for a rapid and model independent assessment of inherent non-uniqueness of three-dimensional shape reconstruction from scattering experiments on solutions of biological macromolecules. One-dimensional scattering curves recorded from monodisperse systems are nowadays routinely utilized to generate low resolution particle shapes but potential ambiguity of such reconstruction remains a major issue. The (non-)uniqueness of the reconstruction is typically assessed by *a posteriori* comparison and averaging of repetitive Monte-Carlo based shape determination runs [2, 3]. The new *a priori* ambiguity measure is based on the number of distinct shape categories compatible with a given data set. For this purpose, a comprehensive library of over 14,000 shape topologies has been generated containing up to seven beads closely packed on a hexagonal grid. The computed scattering curves rescaled to keep only the shape topology rather than the overall size information provide a “scattering map” of this set of shapes. For a given scattering data set one rapidly obtains the number of neighbors in the map and the associated shape topologies such that in addition to providing a quantitative ambiguity measure the algorithm may serve also as an alternative and rapid shape analysis tool. The approach has been validated in model calculations on geometrical bodies and its usefulness is further demonstrated on a number of the experimental X-ray scattering data sets from proteins in solution. A quantitative ambiguity score (*a-score*) is introduced to provide an immediate and convenient guidance to the user on the uniqueness of the *ab initio* shape reconstruction from the given data set.

The authors acknowledge support by the European Commission, BioStruct-X project (contract number 283570).

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Submitting Author: petoukhov@embl-hamburg.de

COMBINING SCANNING SAXS WITH TENSOR TOMOGRAPHY: ORIENTATION ANALYSIS OF NANOSTRUCTURES IN 3D

M. Liebi[a], **M. Georgiadis**[b], **A. Menzel**[a], **O. Bunk**[a] **and M. Guizar-Sicairos**[a]
[a]*Swiss Light Source, Paul Scherrer Institut, 5232 Villigen, Switzerland*
[b]*Insitute for Biomechanics, ETH Zurich, Wolfgang-Pauli-Str. 14 8093 Zurich, Switzerland*

We present a new method, which combines scanning small-angle X-ray scattering (SAXS) with computed tomography (CT) to assess the three-dimensional ultrastructural orientation with 3D spatial resolution.

In 2D scanning SAXS the sample is moved continuously through a focused X-ray beam while 2D SAXS patterns (see Figure 1a) are recorded using a single-photon counter. In a defined *q*-range (indicated as white circles in Figure 1a), the main scattering direction can be determined for each scanned point [1]. This allows the investigation of structures in nanoscale (in reciprocal space) over areas extending many square millimeters (in real space). Figure 1b shows the result from such a 2D scanning SAXS measurement, using a color code where the hue value represents the main scattering orientation (as indicated with the color wheel), the saturation the degree of orientation and the value being brighter for high density of isotropic scattering structures. The pixel marked in white corresponds to the SAXS pattern in Figure 1a.

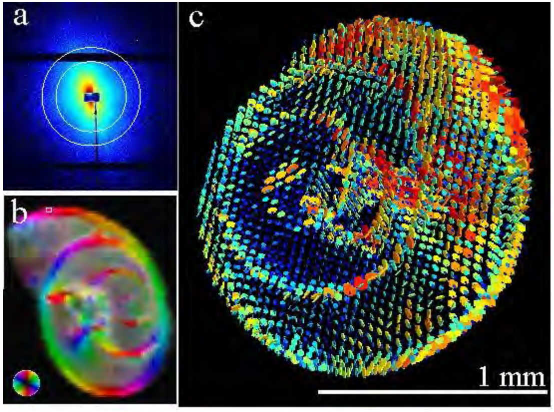

Figure 1: One representative SAXS pattern (a) obtained from the shell of a dwarf snail (*Punctum pygmaeum*) used to obtain the preferential scattering orientation for a 2D projection (b). Measuring 2D projections with different rotations in respect to the X-ray beam allows the reconstruction of the 3D ultrastructure orientation of the 3D object (c).

It has been shown that 3D anisotropic scattering from oriented nanostructures can be retrieved with measurements at different rotations of the 2D sections relative to the X-ray beam [2,3].

In order to assess the 3D orientation within a 3D specimen, this has to be combined with computer tomography. Compared to e.g. absorption-based tomography, for which a single rotation axis is sufficient, for scanning SAXS tensor tomography as presented here multiple tilt angles of the tomographic rotation axis are needed. Here for each voxel we reconstruct a scalar representing the isotropic scattering, the degree of orientation, and the main orientation direction (two spherical angles). The reconstruction uses an optimization algorithm, where for each voxel, and for a radially integrated q-range, the X-ray scattering in 3D is modeled using spherical harmonics.

The technique is demonstrated here on the shell of a dwarf snail (*Punctum pygmaeum*). The result obtained from scanning SAXS tensor tomography is shown in Figure 1c, where in each voxel the orientation and the degree of orientation are represented by the direction and diameter of platelets, respectively, whereas the isotropic scattering is represented by the color.

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Submitting Author: marianne.liebi@psi.ch

ESRF ID01: A NEW BEAMLINE FOR NANOSTRUCTURE RESEARCH

P. Boesecke[a], G. Bussone[a], G. Chahine[a], H. Djazouli[a], M. Elzo[a],
S. Fernandez[a], R. Grifone[a], J. Hilhorst[a], R. Homs[a], S. Leake[a], L. Petit[a],
M.I. Richard[a], P. Van Vaerenbergh[a], T.U. Schülli[a],
[a]*ESRF-The European Synchrotron, 71, Avenue des Martyrs, 38000 Grenoble, France*

In the scope of the ESRF Upgrade phase I the ID01 beamline was entirely rebuilt. Originally focusing on anomalous scattering and diffuse scattering [1] the new beamline aims for investigations of structure-function relationships in the sub-micrometer and nanometer range of polymorphous materials. Possible experiments comprise diffraction mapping techniques [2], imaging techniques [3, 4], anomalous small angle and grazing incidence scattering techniques [5, 6]. This contribution will present the beamline giving emphasis to small-angle scattering experiments.

The optical beamline layout has been chosen with the very strong intention of delivering a stable beam suitable for focusing to spot sizes down to 100 nm in a large, contiguous energy range (5 keV to 40 keV), with preferred working energies around 10 keV and 20 keV. At 10 keV the typical FWHM photon source size is 100 um x 25 um and the typical FWHM photon source divergence 200 urad x 17 urad (horizontal x vertical, assuming a single U27 undulator). For reducing the heat load on the monochromator a white beam double mirror is used. By using a horizontal reflection geometry for the optics, including the monochromator, the high vertical brilliance of the beam can be conserved effectively. By doubling the distance between source and experiment from originally 60 m to now 120 m a focusing ratio of 1:250 becomes feasible. Compact refractive lenses at 55 m and a bender for the second surface of the white beam double mirror allow flexible prefocusing to the sample position (120 m) or the virtual source (100 m).

The new end station houses a high-precision nano-goniometer for diffraction experiments and a 5 m long evacuated flight tube with a movable detector wagon for small angle scattering and full field imaging experiments. Coherent scattering and imaging experiments in forward direction (cSAXS) and at Bragg condition (CDI) will be possible as well as (anomalous) small (ASAXS) and wide angle scattering experiments. For diffraction experiments the flight tube can be rotated horizontally. This system is currently under commissioning.

Until now, an ESRF MAXIPIX 2x2 pixel detector is used for most experiments. A high-resolution CCD-detector for full-field imaging and an ESRF integrated PSI pixel detector system for fast time-resolved experiments in conjunction with a high band-pass monochromator will become available.

The SAXS data acquisition and processing software will be aligned to the ID02 system [7].

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Submitting Author: boesecke@esrf.eu

SAXS AND FREE JET MICROMIXER TO STUDY THE SUB MILLISECOND/MILLISECOND INTERACTION OF SILICA NANOPARTICLES WITH PROTEINS

B. Marmiroli[a], **B. Sartori**[a], **J. Meissner**[b], **G. Grenci**[c], **M. Girod**[d] , **G. H. Findenegg**[b], **and H. Amenitsch**[a]

[a]*Graz University of Technology, Institute of inorganic chemistry, NAWI, Stremayrgasse 9/IV, 8010 Graz, Austria*

[b] *Technische Universität Berlin, Institut für Chemie, Strasse des 17. Juni 124, D-10623 Berlin, Germany*

[c] *National University of Singapore, Mechanobiology Institute (MBI), T-Lab 5A Engineering Drive 1, Singapore*

[d] *Elettra-Sincrotrone Trieste, SS 14 km 163.5, 34149Basovizza (Trieste), Italy*

Understanding the interaction of proteins with nanoscale materials is of fundamental importance both in modern biotechnology and in the biomedical field. Up to now, poor attention has been paid to protein-induced clustering of nanoparticles, although the potentially bioadverse consequences of such particle aggregation processes are well recognized [1]. Recently, the adsorption of a protein like lysozime at silica nanoparticles causing heteroaggregation and flocculation within a wide pH range has been described [2].

In situ SAXS measurements using the stop flow apparatus have already been performed at the Austrian SAXS beamline at Elettra to study the kinetics of silica nanoparticles and proteins by changing the pH of the solution. The results have shown that after 10 ms the reaction has already occurred. There is therefore the need to reach a different time scale.

Recently, we have combined synchrotron SAXS technique, rapid mixing by means of microfluidics, and a free liquid microjet in air to push the limits of time resolved measurements of fast chemical reactions below the millisecond time range [3]. We have designed, fabricated and tested a microfluidic device based on hydrodynamic focusing and a free-jet optimized for synchrotron SAXS time resolved measurements (scheme in figure 1) [4].

In this communication we present the first results of the early stage studies of the interaction of silica nanoparticles with lysozyme by using a free jet micromixer in combination with SAXS, describing the measurement issues (i.e. the determination of the liquid jet behavior [5]), and demonstrating the suitability of the technique for this kind of studies.

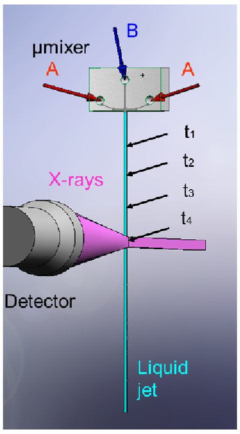

Figure 1: Scheme of the SAXS measurement of the free jet. Measuring at increasing distance from the mixer exit corresponds to measuring at increasing time from the beginning of mixing.

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Benedetta Marmiroli: benedetta.marmiroli@tugraz.at

OBSERVATION OF TWINNING IN GOLD NANO-PARTICLES USING CORRELATED X-RAY SCATTERING (CXS)

Derek Mendez[a], Jason Platt[b], Herschel Watkins[c],
Thomas Joseph Lane[d], Daniel Ratner[e], and Sebastian Doniach[a,b,c]
Departments of [a]Applied Physics, [b]Physics, [d]Chemistry Stanford University, Stanford CA, USA ,[c]Geballe Lab for Advanced Materials, Stanford University, [e]SLAC National Accelerator Center, Menlo Park, CA, USA

The availability of high intensity X-ray sources including X-ray free electron lasers (xFELs) and micro-focus beamlines makes possible the measurement of angular correlations of azimuthal deviations from the angular-averaged scattering as a function of scattering vector. Correlated X-ray Scattering (CXS) is an emerging field which involves recording many snapshot exposures of an ensemble of randomly oriented, mono-disperse molecules or particles and employing photon intensity correlation analysis in order to recover a function dependent only on the average internal structure of the objects in the random ensemble. We have previously reported observation of internal FCC structure for silver nano-particles (NPs) [1].

Here we report more detailed studies made at the SACLA xFEL at SPRING8, Osaka, Japan. By averaging over the correlators for 10,000 X-ray shots of 60 nm gold NPs injected into the X-ray beam as a suspension in olefin, the measured angular correlations showed clear evidence of twinned domains. The measurements were distinguishable from a hypothetical strained FCC model that could only occur in the absence of dislocations or other defects. These experiments demonstrated that CXS observed with high-intensity X-ray beams could yield information, not available from traditional SAXS/WAXS measurements, about the internal order of scattering particles for ensembles of particles that are rotationally disordered.

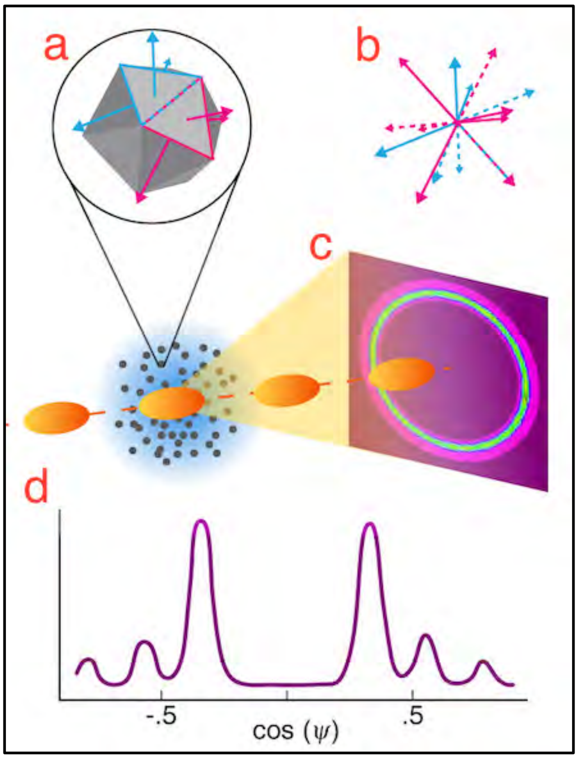

Figure 1 ***a***: Icosahedral twinned FCC particle. Highlighted are two nearest-neighbor tetrahedral regions (twins) ***b***: The Bragg vectors arising from these neighboring tetrahedral regions. ***c,d***: Simulation of the {111} scattering and autocorrelator, respectively. In *d*, cos(ψ) is the angle between {111} Bragg vectors. The smaller peaks arise from inter-twin correlations.

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Submitting Author: Derek Mendez, dermen@stanford.edu

POLARIZATION ANALYSIS IN NEUTRON SMALL ANGLE SCATTERING WITH A NOVEL TRIPLET DNP SPIN FILTER

N. Niketic, B. van den Brandt, W.Th. Wenckebach, J. Kohlbrecher, P. Hautle
Paul Scherrer Institute, CH - 5232 Villigen PSI, Switzerland

We have developed a novel neutron spin filter based on the strong spin dependence of the neutron scattering on protons. The filter is small (5x5x5 mm3) needs little cryogenics (25 K) and works also in inhomogeneous and weak magnetic fields (down to 0.01 T). The protons in the naphthalene spin filter crystal are polarized with a recent method of dynamic nuclear polarization (DNP) using photo-excited triplet states, which allows the design of a compact apparatus that can be placed at a short distance (30 mm) from the sample under investigation. With the present prototype system a flipping ratio of 4.5 at an overall transmission of above 30 % is typically achieved for cold neutrons.

We will shortly introduce the novel method and then discuss the first demonstration experiment: its application as polarization analyzer in a magnetic small-angle neutron scattering experiment where a ^{3}He filter can only be operated with a proper magnetic shielding. The performance of the analyzer has been demonstrated by measuring the spin dependent scattering signals of a CuFeNi alloy that has a pronounced textured structure factor of ferromagnetic precipitates in a paramagnetic matrix. The data can be understood using simulations based on a model of superparamagnetic particles which are ordered in a simple cubic paracrystalline lattice.

Submitting Author: Joachim.kohlbrecher@psi.ch

STRUCTURE OF AMPHIPHILIC CO-NETWORK GELS

M. Shibayama[a], **T. Hiroi**[ab] , **S. Kondo**[c], **and T. Sakai**[c]
[a]*The Institute for Solid State Physics, The University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8581, Japan*
[b]*Department of Chemistry, School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan*
[c]*Department of Bioengineering, School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan*

Amphiphilic networks, which are composed of hydrophilic units and hydrophobic units, are unique materials because of their affinity to both polar solvents and non-polar solvents. Such kinds of materials are developed for various applications, e.g., substrates of catalysts, carriers of drug delivery system. However, it is difficult to determine quantitatively their structures because of inhomogeneities of the networks. Recently we developed inhomogeneity-free amphiphilic polymer gels by end-crosslinking of tetra-arm polyethyleneglycol (PEG) and linear polydimethylsiloxane (PDMS). We report the structural analysis of this network measured by small-angle scattering technique.

The gels were prepared by mixing of active ester-terminated tetra-arm PEG [1], amine-terminated linear PEG and amine-terminated linear PDMS (Figure 1). These units react with each other in toluene and become gels. Figure 2 shows SANS and SAXS profiles of these PEG-PDMS gels. By changing the proportion of PDMS among the linear amine terminated components, *r*, we are able to quantitatively control the PDMS fraction in the resultant gels. Interestingly, SANS and SAXS profiles show totally different appearance. One of the major reasons for this is interference between scattered wave from PEG and that from PDMS. We will show fitting results by using appropriate form / structure factors such as core-shell model and paracrystal theory.

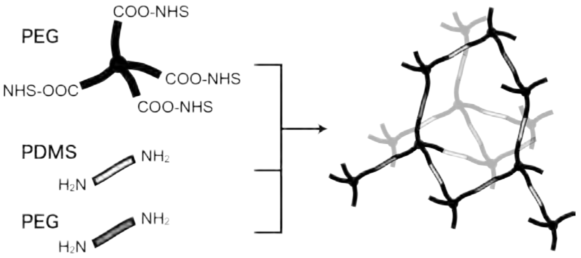

Figure 1: Preparation of PEG-PDMS gels.

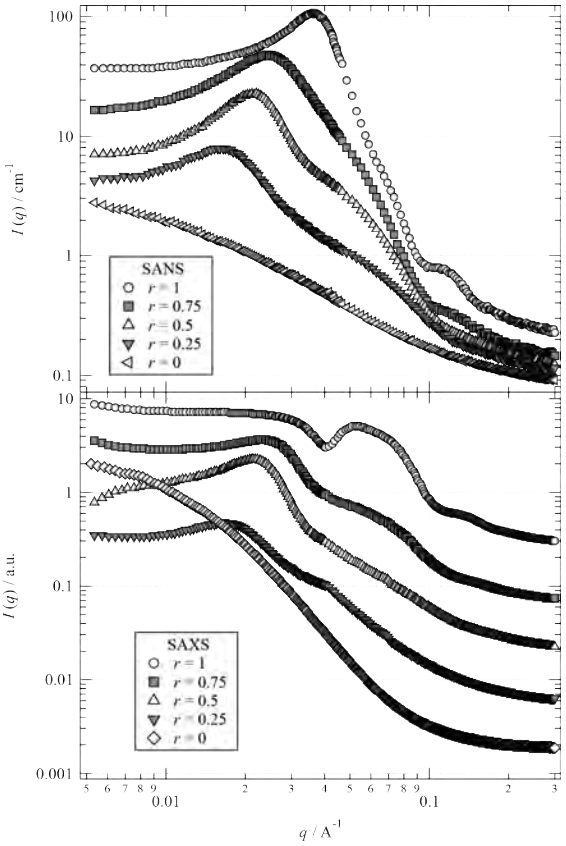

Figure 2: SANS/SAXS profiles of PEG-PDMS gels.

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Submitting Author: sibayama@issp.u-tokyo.ac.jp

FDDD PHASE IN DIBLOCK COPOLYMER MELTS

M.Takenaka[a,b], **Y.Wang**[a], **M.I.Kim**[a], **T.Wakada**[a], **S.Akasaka**[a], **S.Nishitsuji**[a]
T.Hikima[b], **K.Ito**[b], **M.Takata**[b], **K.Saijo**[a] **and H.Hasegawa**[a]
[a]*Department of Polymer Chemistry, Graduate School of Engineering*
Kyoto University, Kyoto, 615-8510, Japan
[b] *Structural Materials Science Laboratory*
SPring-8 Center, RIKEN Harima Institute Research
1-1-1, Kouto, Sayo-cho, Sayo-gun, Hyogo 679-5148, Japan

Block copolymers are composed of two or more kinds of chemically different polymers connected by a covalent bond. the phase behaviors of Diblock copolymer A-*b*-B can be represented in terms of χN and f, where N is the polymerization, f is the volume fraction of A component in A-*b*-B, and χ is the Flory-Huggins interaction per monomer parameter between A and B, which is usually proportional to inverse of temperature. The theoretical and experimental studies on the phase diagram of diblock copolymer melts have explored the phase behavior including lamellae (L), gyroid (G), hexagonally packed cylinder (C), and sphere in the body-centered lattice (S). Howver, inaddition to the morpologies, we firstly found *Fddd* structure exists as an equilibrium phase in diblock copolymer melts of polystyrene-*block*-polyisoprene (SI)[1]. We sythesized 13 samples of SI, investigated the temperature depndencies of the morphologies in the samples with small-angle X-ray scattering (SAXS) and transmission electron microscopy (TEM) and determiend the phase boundary of *Fddd* phase in SI.

Figure 1 shows the phase boundary of the *Fddd* phase. Compared to the *Fddd* region in polyisoprene (PI)-rich region or $0.5 < f_{PI}$, the *Fddd* region in polystyrene (PS)-rich region ($0.5 > f_{PI}$) is much narrower than that in PI-rich region in the parameter space of χN on f_{PI}, where f_{PI} is the volume fraction of polyisoprene in SI. In the case of PI-rich region, the *Fddd* phase extends to $0.629 \leq f_{PI} \leq 0.649$ and $25.6 < \chi N < 29.8$. On the other hand, the *Fddd* phase in PS-rich region appears at $0.37 \leq f_{PI} \leq 0.373$ and $19.5 < \chi N < 21.1$. Besides, the location of the *Fddd* phase in PS-rich region is not symmetric to that in PI-rich region in terms of χN and f_{PI}. The asymmetry of the *Fddd* phase in PS-rich rich regions agrees with the phase diagram calculated with self-consistent field theory including the effects of conformational asymmetry by Matsen, indicating that the conformational asymmetry causes the asymmetry of the *Fddd* phase in the phase diagram of SI diblock copolymers.

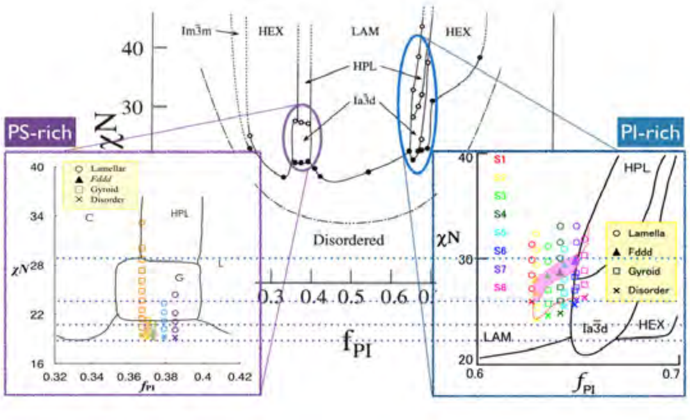

Figure 8 The phase boundary of the *Fddd* phase in SI.

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Submitting Author: takenaka@alloy.polym.kyoto-u.ac.jp

HAND-CAST AND MACHINE-PROCESSED THERMOPLASTIC POLYURETHANES. MORPHOLOGY EVOLUTION MECHANISMS UNDER STRAIN

A. Stribeck[a], X. Li[a], F. Jokari[a], B. Eling[b], E. Pöselt[b], S. Funari[c], G. Santoro[c], A. Hoell[d]
[a]*Universität Hamburg, Dept. Chemie, Bundesstr. 45, 20146 Hamburg, Germany*
[b]*BASF Polyurethanes GmbH, Elastogranstr. 60, 49448 Lemförde, Germany*
[c]*HASYLAB at DESY, Notkestr. 85, 22607 Hamburg, Germany*
[d]*Helmholtz-Zentrum Berlin GmbH, Albert-Einstein-Str. 15, 12489 Berlin, Germany*

Preparation and composition of thermoplastic polyurethanes (TPU) are varied systematically. The samples are strained and monitored by SAXS. The analysis comprises longitudinal projections [1], and in real space the chord distribution function (CDF) [2] and the IDF. We aim to identify straining mechanisms and to retrieve characteristic parameters for the modeling to design customized TPU materials. Part of the work is presently being published [3-5].

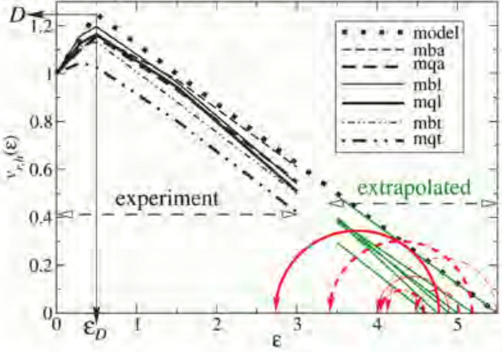

Figure 1: Variation of the relative volume fraction of hard domains from an IDF analysis of SAXS projections appears related to the strain at break for different TPU composition

Hand-cast materials show a washed-out morphology. IDFs from their longitudinal projections can be fitted by stacking statistics. Figure 1 shows the resulting variation of hard domain volume as a function of strain for materials based on MDI hard-segments (m), differing chain extenders (b=BD, q=HQEE) and varying soft segments (a=adipic ester, l=PCL, t=PTHF). A model is obvious. Extrapolation yields the strain at break. The abbreviations for the components are common to chemists.

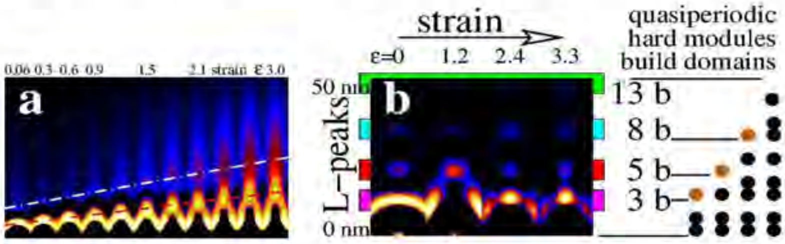

Figure 2: Nanostructure evolution as a function of strain viewed in meridional long period regions cut from CDFs. a) a handcast TPU. b) a machine-processed TPU c) sketch of hard module arrangement (module: MDI + BD).

The morphology of machine-processed material is more uniform. In the strained state the CDFs exhibit a short-range quasiperiodic arrangement of the hard modules (MDI+BD) with a basic length of 4 nm in agreement with crystallography. Figure 2 depicts differences between hand-cast and machine-processed materials. Only the hand-cast material shows long-period distributions that move and expand with the strain.

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ENTANGLED POLYMER MELTS IN EXTENSIONAL FLOW RHEOLOGY AND SMALL-ANGLE NEUTRON SCATTERING

Kell Mortensen[a], **Jacob JK Kirkensgaard**[a], **Ole Hassager** [b], **Ludovica Hengeller** [b], **Qian Huang**[b], **Kristoffer Almdal**[c] **and Andriy Dorokhin**[c],
[a]*Niels Bohr Institute, University of Copenhagen, Denmark,*
[b]*Chem. Engineering. Technical University of Denmark, Lyngby, Denmark*
[c]*Nanotech, Technical University of Denmark, Lyngby, Denmark*

Liquid bridges occur in a variety of situations in nature - yet our understanding of the dynamics and stability is very limited. Examples of liquid bridges are the process used by spiders to form draglines and the process used by cats lapping milk. We have an extended program aiming to provide generic knowledge about the process in which macromolecular fluid filaments are extended and stretched and show how the extensional properties are related to the properties on individual molecules. We combine structural and rheological studies of a series of model polymers with different composition and architectures. The project entails synthesizing model polymer systems of precisely known molecular architecture, subjecting these materials to controlled extensional flows and to measure the molecular deformation under controlled flow situation by SANS. Neutron contrast is obtained using specific deuterium labeled molecules.

Figure 1: Samples as available after being exposed to different extensional flow rates.

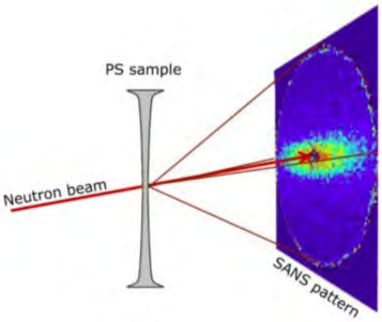

Figure 2: Schematic illustration of the molecules to be studies and the SANS experiment.

We have targeted different systems: first a “simple” sample of homogeneous high-molar mass polymers, where only the central part of a fraction of the polymers were D-labelled with the aim to highlight the polymer deformation and avoid influence of fast relaxation near the polymer ends [1]. Another example is a bimodal mixture of linear polymer chains with respectively high and low molar mass, and we have studied samples with more complex geometry, including POM-POM architecture. The 2D-SANS data have typically Lozenge shaped contour which is analyzed using the Read- McLeish-model of stretched polymer network [2]. The structure and rheology are measured both as a function of stain flow velocity, final Hencky strain ratio and during the relaxation after cessation of extensional flow.

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Submitting Author: kell@nbi.dk

CHAIN SIGNAL IN NANOLATEX BASED NANOCOMPOSITES

A. Banc[a], **A-C. Genix**[a], **C. Dupas**[a], **R. Schweins**[b], **M-S Appavou**[c] **and J. Oberdisse**[a]
[a] *Laboratoire Charles Coulomb, UMR5221 CNRS-Université, F34095 Montpellier, F-France*
[b] *Institut Laue-Langevin, 6 rue Jules Horowitz, F38042 Grenoble, F-France*
[c] *Forschungszentrum Jülich GmbH, Jülich Centre for Neutron Science JCNS, 85747 Garching, Germany*

The mechanical properties of nanocomposite materials are controlled to a large extent by the filler-filler interactions. Nevertheless, another important contribution - less well understood - is due to the polymer chain-filler interactions. Experimentally, the radius of gyration (R_g) of polymer chains in nanocomposites can be measured by SANS using the zero average contrast conditions (mixing hydrogenated (H) and deuterated (D) chains) in order to match the filler signal and measure the chain form factor. However, many studies display an unexplained polluted SANS signal in the low-q range.

In this talk, we will discuss the measurement of polymer chain signal in nanocomposites prepared from the drying of a colloidal dispersion of silica and polymer particles. In such samples, the mixture of H and D chains results from the dissolution of H and D latex beads. This dissolution was followed by SANS in the low q range, as function of thermal annealing (figure 1) and filler content using an original model [1]. Experimental results demonstrate that the dissolution dynamics of polymer chains is significantly slowed down by the presence of silica nanoparticles [1].

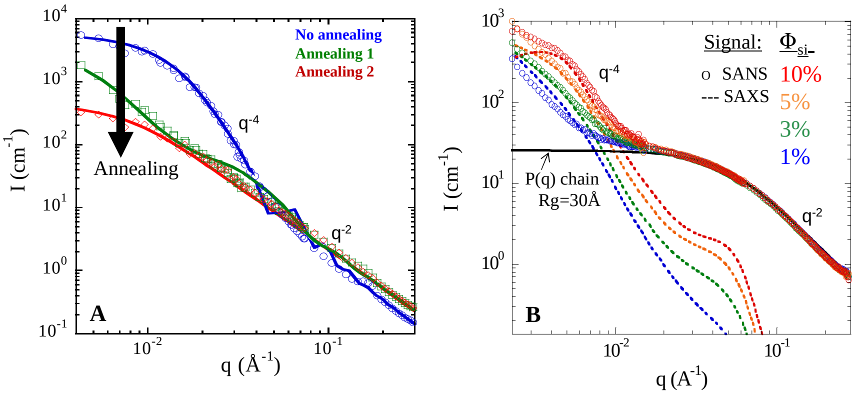

Figure 1: (A) SANS signal of latex based matrix as function of annealing fitted with our model. (B) SAXS and SANS signals of nanocomposites filled with small silica nanoparticles.

Besides, the effect of the filler size on the chain signal in the nanocomposites was studied by a combination of SAXS and SANS measurements and reveal that the filler contribute to the SANS signal in nanocomposites filled with small silica nanoparticles (compared to the latex beads) contrarily to nanocomposites filled with bigger silica particles. We rationalize this observation considering an attractive interaction between polymers and silica particles leading to an inhibited interdiffusion of latex particles in the vicinity of silica particles, and a statistical local assymmetry due to the small number of latex beads defining the environment of small silica particles. Finally, no evolution of the polymer R_g was found in our samples.

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Submitting Author: amelie.banc@univ-montp2.fr

CONTROLLING THE SELF-ASSEMBLY OF DENDRIMERS AND DYES: THE ROLE OF THERMODYNAMICS

G. Mariani[a,b], R. Schweins[a] and F. Gröhn[b]
[a] *Institut Laue – Langevin, DS / LSS, 71 Avenue des Martyrs, 38000 Grenoble, France*
[b] *Friedrich-Alexander Universität Erlangen-Nürnberg, Department of Chemistry and Pharmacy & Interdisciplinary Center for Molecular Materials (ICMM), Egerlandstr. 3, 91058 Erlangen, Germany*

The rational design of supramolecular nanoparticles produced by self-assembly is motivated by the wide field of applications and the possibility of control through external triggers such as pH or light. Understanding the shape-determining factors is the key for tailoring nanoparticles with desired structural properties. We show how the thermodynamics of the interaction controls the shape of the nanoparticles (cf. Figure 1). Moreover, we highlight the connection between the molecular structure of the building blocks and the interaction strength allowing for an a priori shape determination.

As a model system, we have investigated electrostatically self-assembled nanoparticles of polyamidoamine (PAMAM) dendrimers and oppositely charged azo dyes relying on the combination of electrostatic and π-π interactions. The structure of the aggregates was investigated as a function of pH, the azo dye molecular structure, the dendrimer generation (from 2 to 8) and of the component ratio. These parameters permit the modification of interaction strength, flexibility of the particles, geometrical constraints and charge compensation providing insights into the assembly process.

The nanoparticles have been characterized using atomic force microscopy, static light scattering, small angle neutron scattering and UV-Vis spectroscopy. We show that the isotropy of the nanoassemblies is related to the dye valency (cf. Figure 1). Isothermal titration calorimetry has been used to investigate both dye-dye and dye-dendrimer interaction. A threshold value in entropy and enthalpy exchange for both dye-dye and dye-dendrimer interaction separating isotropic and anisotropic shapes has been found.

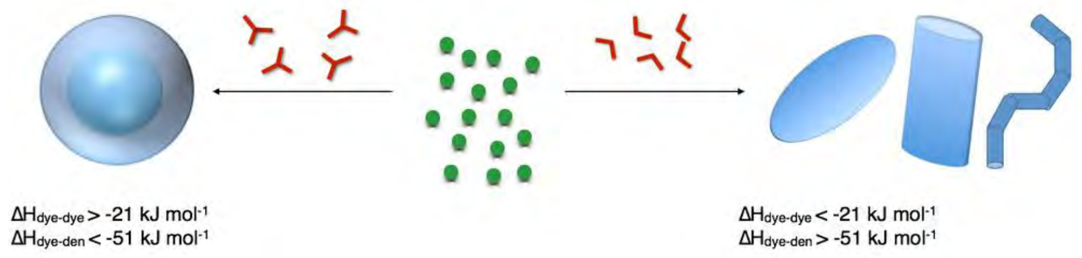

Figure 1: Schematic representation of the self-assembly process, showing in the middle in green the dendrimer and in red different dyes, forming nanoparticles when being mixed which are on the one hand isotropically and on the other hand anisotropically in shape.

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Submitting Author: schweins@ill.eu

BIO-INSPIRED MINERALIZATION OF MAGNETITE NANOPARTICLES IN GELATIN HYDROGEL: A SMALL ANGLE SCATTERING INVESTIGATION

B. Wu[a,b], M. Helminger[b], D. Schwahn[c], H. Cölfen[b], V. Pipich[a]
[a] *Jülich Centre for Neutron Science JCNS, 85747 Garching, Germany*
[b] *Universität Konstanz, 78457 Konstanz, Germany*
[c] *Technische Universität München, Forschungs-Neutronenquelle Heinz Maier-Leibnitz (FRM II),85747 Garching, Germany.*

We have recently reported an *in-situ* mineralization protocol designed for the preparation of magnetic hydrogels consisting of biodegradable polymer gelatin and magnetic iron oxide nanoparticles [1]. The gelatin hydrogels have a spatial confined cavities structure so that magnetite particles were placed in the meshes homogeneously distributed throughout the gel matrix. We explore the roles of gelatin hydrogels on the bio-inspired magnetite mineralization mechanisms by using Small (SANS) and very-small (VSANS) angle neutron scattering in conjunction with SAXS/TEM/AFM/XRD measurements.

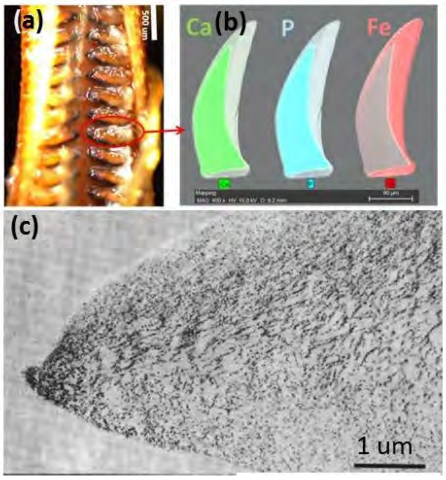

Figure 1: (a) A microscopy image of Chiton radula teeth, (b) SEM EDX of Chiton tooth (cross section) (c) TEM of nano magnetite in the Chiton tooth.

The studies focus on the nucleation and growth of the magnetite in gelatin gel, which are bio-inspired hybrid materials from natural bio-minerals. The contrast variation method was used by exchange of solvent in order to analyze the individual components of the structure. These results are expected to provide structural information in-situ for understanding the mechanisms of magnetite mineralization. Several hypotheses have been introduced to explain how organic matrix function in magnetite biomineralization. These structural and mineralization mechanism are compared with the biological samples (Chiton teeth). We aim to provide novel insights for establishing a direct relation between the gelatin matrices of spacing confinement and gelatin molecular controlling on the mineralization mechanism in order to eventually produce highly sophisticated materials with optimal properties.

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Submitting Author: v.pipich@fz-juelich.de

PTYCHOGRAPHY AND SCANNING SAXS WITH MICRO- AND NANO-BEAMS ON BONE SECTIONS

B. Weinhausen[a], **M. Verezhak**[b], **A. Gourrier**[b] **and M. Burghammer**[a]
[a]*ESRF – The European Synchrotron, 71, Avenue des Martyrs, 38000 Grenoble, France*
[b]*Laboratoire Interdisciplinaire de Physique, UMR 5588 CNRS, Université Joseph Fourier Grenoble I, 140, Avenue de la Physique, 38402 Saint Martin d'Heres, France*

Bone is a biological composite material exhibiting a complex hierarchical organization. At the nano-scale, bone tissue is composed of two principal components: collagen fibrils of ~100 nm in diameter and platelet-shaped calcium phosphate mineral nanocrystals with dimensions of ~5×50×100 nm. Previous studies using scanning SAXS with synchrotron micro-beams have shown that the size, shape and organization as well as the crystal structure of the nanoparticles vary throughout bone tissue and can be strongly altered in pathological cases [1,2]. In order to adapt to external mechanical loads during the lifetime of an individual, bone is continuously renewed by different cellular processes. The most abundant cells in the adult skeleton are osteocytes, which compose over 90-95% of all bone cells and are thought to be the major bone cell responsible for sensing mechanical strain and orchestrating signals of resorption and formation. Recent studies suggest that the perilacunar matrix surrounding the osteocyte is distinct in terms of its elastic modulus and that the osteocyte can modify its microenvironment in response to environmental factors like mechanical strain [3].

The combination of focused monochromatic X-rays with scanning SAXS offers a powerful technique to study the multi-scale organization of bone, by simultaneously providing information in real space and in reciprocal space. The individual scattering patterns provide information about the local molecular to mesoscale structure and lateral variations can be resolved. Here, the lateral resolution in direct space is mainly limited by the focal spot size ranging from a few microns down to less than 100 nm. In addition, coherent diffractive X-ray imaging using ptychographic phase retrieval algorithms allows us to reconstruct the projected electron density of the sample with a real space resolution better than 100 nm. In this contribution, we will present results from the ongoing research at ID13 beamline concerning the nano-scale architecture of the perilacunar bone matrix. Using both scanning SAXS and ptychography, the lacunae and the canalicular network were imaged and structural variations on length scales of ~100 nm or less could be identified.

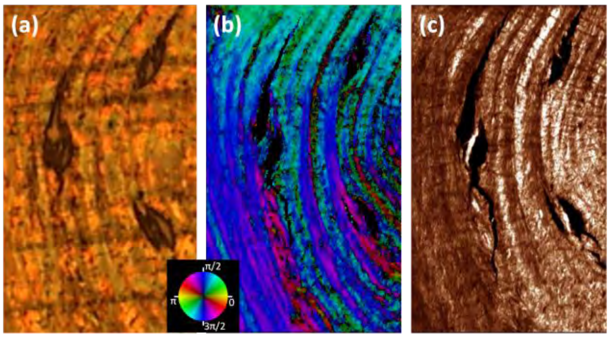

Fig. 1 Scanning SAXS with a nano-beam on bone thin sections. (a) Transmission microscopy image of a 1 µm thin section of bovine bone. (b) Orientation (color) and degree of orientation (brightness) of the mineral platelets and (c) integrated SAXS intensity. Scan parameters: 50×84 µm² scan area, 200 nm step size.

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Submitting Author: britta.weinhausen@esrf.fr

OUTSET OF THE MORPHOLOGY OF NANOSTRUCTURED SILICA PARTICLES DURING NUCLEATION FOLLOWED BY ULTRA SMALL ANGLE X-RAY SCATTERING

Julien Schmitt(1), **Tomas Kjellman**(2), **Pawel Kwasniewski**(3), **Florian Meneau**(4), **Jan Skov Pedersen**(5), **Karen Edler**(6), **Adrian Rennie**(7), **Viveka Alfredsson**(2) **and Marianne Impéror-Clerc**(1)

(1) *Laboratoire de Physique de Solides, UMR 8502, Bât. 510, Université Paris-Sud, F-91405 Orsay, France*
(2) *Physical Chemistry, Lund University, P.O. Box 124, SE-221 00 Lund, Sweden*
(3) *ID2 beamline, ESRF, 6 rue Jules Horowitz, F-38000 Grenoble, France*
(4) *SWING beamline, Synchrotron Soleil, BP 48, F-91192 Gif-sur-Yvette, France*
(5) *Department of Chemistry and iNANO Interdisciplinary Nanoscience Center, Århus University, DK-8000 Århus, Denmark*
(6) *University of Bath, Department of Chemistry, Bath BA2 7AY, Avon, England*
(7) *Department of Physics and Materials Science, Angström Laboratory, Uppsala University, P.O. Box 530, SE-751 21 Uppsala, Sweden*

Mesoporous silica materials, with a porosity controlled by use of a surfactant, are systems extensively studied those past 15 years. Their formation, by sol-gel process, is due to the self-assembly properties of amphiphilic molecules in solution. Along the numerous existing materials, SBA-15 prepared mixing a Pluronic as surfactant (P104 or P123) and a silica precursor (TMOS or TEOS) is one of the most studied.

By the so-called precipitation method, it is possible to form the SBA-15 mesoporous material under the shape of (sub)micrometer grains. By controlling two important parameters (the synthesis temperature and the stirring in the solution), one can also control the morphology of the final grains.

Thanks to SAXS in situ measurements, not only it is possible to follow the kinetic of synthesis of such materials and the self-assembly mechanisms between micelles of surfactant and silica species allowing the formation of a hybrid organic/inorganic mesophase, but also via USAXS measurements made at ID02 (ESRF) we were able for the first time to study the formation of the material grains up to 1 µm.

Specifically, three main syntheses were studied, with three well-defined morphologies: platelets (obtained with P104+TMOS at 56°C under constant stirring), donuts (P123+TEOS at 56°C without stirring) and long rods (P123+TEOS at 50°C without stirring). USAXS curves demonstrate that primary particles with a defined shape are present very early in solution, right after a very fast nucleation step. Characteristic form factors (platelet, donut and rod) of the different morphologies are indeed detected. The effect of aggregation between the objects was also evidenced.

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Submitting Author: julien.schmitt@fkem1.lu.se

TIME RESOLVED SANS STUDY OF WOOD DISINTEGRATION IN IONIC LIQUID

N. Szekely[a], **H. Frielinghaus**[a], **C. Hövelmann**[a], **J. Viell**[b], **D. Richter**[a]
[a]*Forschungszentrum Jülich GmbH, Jülich Centre for Neutron Science JCNS Outstation at MLZ, Lichtenbergstraße 1, 85747 Garching, Germany*
[b]*RWTH Aachen University, Aachener Verfahrenstechnik, 52056 Aachen, Germany*

To reduce the dependence on fossil fuels, there is a growing interest for the use of lignocellulosic biomass. Until now, wood is mainly used for the production of paper from cellulose, and most of the other components of wood are simply incinerated to produce energy. More effective conversion technologies are required. Therefore there are increasing efforts in developing efficient, environmentally friendly and cost effective ways of converting wood in bioenergy and bio-based products. Treatment of wood with ionic liquids is one promising new conversion technology since ionic liquids improve enzymatic hydrolysis with regard to yield and time [1]. While early studies focused on the dissolution of wood [2], the pretreatment first involves ultrastructural changes in the wood which have not been understood so far. [2-4]

The pretreatment in ionic liquids (IL) proved to be efficient because the IL swells the fibers effectively and the wood starts to disintegrate. The aim of the study was to monitor the structural changes occurring on a nanometer scale in real time in order to better elucidate the complicated mechanisms of disintegration during pretreatment. In situ time-resolved SANS measurements were performed on beech wood in the IL 1-ethyl-3-methylimidazolium acetate at 100°C covering a wide Q-range (Figure 1). In order to obtain a better contrast, deuterated IL was synthesized within our group, and used for the SANS experiments.

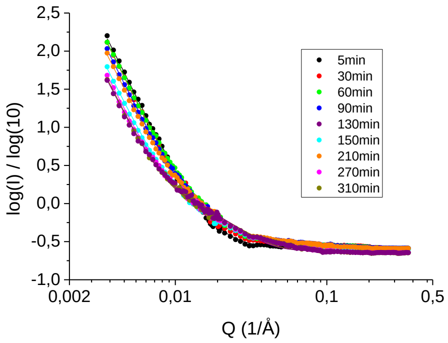

Figure 1: SANS scattering curves obtained from beech wood in ionic liquid at 100^{o}C for several different time steps.

Following the data analysis presented on SANS results of switchgrass [5], as a first approach for threating our data we also applied a multi-scale fractal model (Beaucage). This revealed structural changes over time on different length scales for these highly complicated systems. This analysis leads us to our current hypothesis that we are observing the filling of the voids in wood by IL followed by the swelling of the cellulose microfibrils eventually resulting in the disintegration of the cell walls. The elaboration of a model, which describes more accurately the processes, is ongoing. The SANS results will be compared to existing results of WAXS, Infrared and Raman Spectroscopy and from real time microscopy.

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Submitting Author: n.szekely@fz-juelich.de

MAGNETIC SMALL–ANGLE NEUTRON SCATTERING OF SOFT-MAGNETIC NANOCOMPOSITES

D. Honecker[a], **C.D. Dewhurst**[a], **K. Suzuki**[b] **and A. Michels**[c]
[a]*Institut Laue-Langevin, 71 Avenue des Martyrs, 38000 Grenoble, France*
[b]*Department of Materials Science and Engineering, Monash University, Clayton Campus, Clayton, Victoria 3800, Australia*
[c]*Physics and Material Science Research Unit, University of Luxembourg, 162A Avenue de la Faiencerie, 1511 Luxembourg, Grand Duchy of Luxembourg*

Small-angle neutron scattering (SANS) is a powerful method to resolve the magnetic microstructure in the bulk and on length scales between about 1 – 100 nm. In this contribution, we present results on the magnetic SANS of Fe-based two-phase nanocrystalline alloys. In the investigated soft magnetic heterogeneous nanocomposites, the jump of the magnetization at the phase boundary between particles and matrix gives rise to a dipolar stray field, which represents a non-negligible source of spin disorder.

The magnetic-field-dependent SANS data of such particle-matrix-type ferromagnets can be interpreted with the help of a recently developed, analytical micromagnetic theory for the SANS cross section [1]. It can be shown that the magnetic anisotropy and magnetostatic field decisively determine the properties of the magnetic SANS cross section, such as the asymptotic power-law behaviour, the range of spin-misalignment correlations and angular anisotropies. In particular, the presented micromagnetic SANS description explains the 'clover-leaf'-shaped angular anisotropy (left panels of Figure 1), which was observed for several nanostructured magnetic materials and which can be attributed to jumps of the magnetization at internal interfaces. Moreover, the micromagnetic aproach allows one to specify the field behaviour of the magnetic SANS and to quantitatively assess substantial features of the spin structure, for instance, the average exchange-stiffness constant as well as the magnetic anisotropy and magnetostatic fields [2].

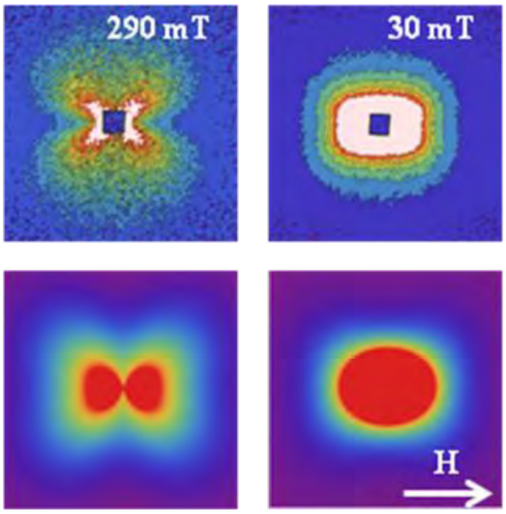

Figure 1: Comparison between experimental (upper row) magnetic 2D-SANS cross sections $d\Sigma_M/d\Omega$ of $Fe_{89}Zr_7B_3Cu$ and prediction by the micromagnetic theory (lower row) at selected applied magnetic fields. $d\Sigma_M/d\Omega$ is obtained by subtracting the scattering at a saturating field. The applied magnetic field **H** is horizontal. The corner of the detector corresponds to a momentum transfer $q = 0.45$ nm^{-1}.

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Submitting Author: honecker@ill.eu

STRUCTURAL DEFECTS IN COLLOIDAL GOLD NANOPARTICLES

B. Fleury[a], **R. Cortes-Huerto**[a], **O. Taché**[a], **C. Canbek**[a], **N. Menguy**[b], **F. Testard**[a] **and O. Spalla**[a]

[a]*UMR3685 NIMBE/LIONS, CEA Saclay 91191 Gif-sur-Yvette CEDEX, France*
[b]*IMPMC Université Pierre et Marie Curie 4 Place Jussieu 75005 Paris, France*

Metallic nanoparticles are commonly synthetized in aqueous or organic solutions to be used mainly in plasmonics, in biomedicine and for catalysis. It is known that their properties and/or efficiency are strongly linked to their shape, their size and their structure [1]. Although their shape and size can be estimated using TEM and SAXS, complete structural characterization of the nanoparticles is rarely done. Here we present a methodology to get a deeper analysis of colloidal gold nanoparticles, including defects.

Model gold particles are synthetized in organic solution using mild conditions [2]. The obtained material is a mixture of monocrystalline and defected particles, as several stable structures exist (Figure 1) [3]. Then, X-ray total scattering diagrams (SAXS/WAXS/XRD) are taken.

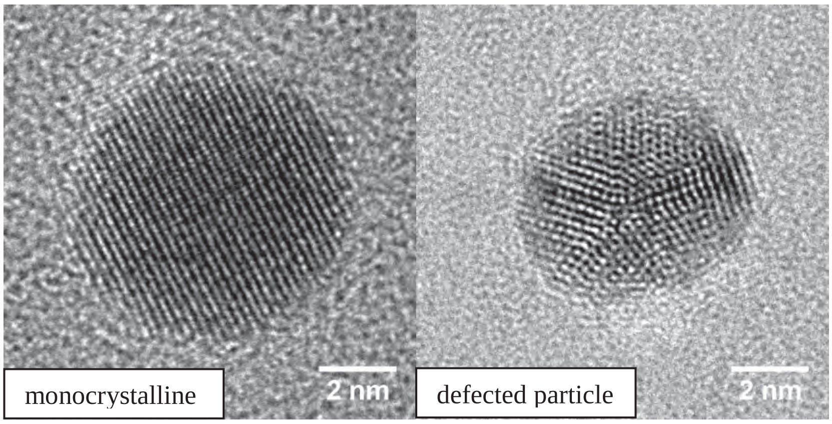

Figure 1 : TEM on monocrystalline (left) and defected (right) gold seeds.

Using molecular dynamics [4], monocrystalline, pentatwinned and icosahedra particles are quenched. The output structures are then used to calculate their scattering cross-sections (Debye equation), allowing to count the number of twinned and monocrystalline particles in the sample. Our samples are found to be mainly defected. Precisely, icosahedra particle concentration is ~3-4 times higher than decahedra particle's. A similar measurement can be obtained in direct space, using Pair Distribution Functions (PDF). Depending on the particle and our knowledge on their defects, one or another technique would rather be used.

This methodology is not limited to metallic nanoparticles and could be applied as well to oxides, alloys and hybrid particles.

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Submitting Author: blaise.fleury@cea.fr

ANISOTROPIC MAGNETIC CORRELATIONS IN NANOCOMPOSITES

S. Erokhin[a], **D. Berkov**[a] **and A. Michels**[b]
[a]*General Numerics Research Lab, An der Leite 3B, D-07749 Jena, Germany*
[b]*Physics and Materials Science Research Unit, University of Luxembourg, 162A Avenue de la Faiencerie, L-1511 Luxembourg, Grand Duchy of Luxembourg*

We present the results of numerical studies of the magnetization state in a bulk magnetic nanocomposite material. A relatively large simulation volume has been sampled due to our recent achievements in micromagnetic modeling of nanocomposites [1,2,3]. Magnetic SANS cross-sections obtained from our simulations agree very well with experimental SANS data.

The main object of our study is a magnetic nanocomposite with typical structural length scales of a few tens of nanometers. A vivid example of such kind of materials is a nanocomposite of the Nanoperm type, consisting of iron-based crystallites embedded in an amorphous magnetically soft matrix. Our results underline the decisive role of the internal magneto-dipolar field arising around hard inclusions via the formation of an unusual angular anisotropy of the experimental SANS cross-section.

For the example of a porous ferromagnet, where the magnetic inhomogeneity reaches its maximum, we show explicitly the anisotropic nature of the magnetic correlations in this type of nanocomposite. This investigation employs numerical studies of spatial correlation functions of the magnetization distribution.

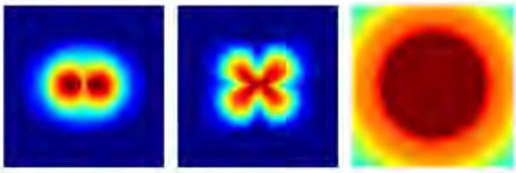

Figure 1: Numerically computed Fourier transformations of the individual Cartesian components (x,y,z - from left to right) of the spatial magnetization distribution in nanoporous iron. The magnetic field is applied horizontally along the z-direction.

Figure 1 demonstrates the possibility to 'decrypt' the total magnetic SANS cross-section by extracting the individual contributions of each magnetization component (its spatial Fourier transformation). Thus, our methodology allows one to analyze these individual contributions instead of the complicated weighted combination of all magnetization components decorated by the interaction of neutrons with the magnetodipolar stray field of magnetic moments. This approach opens up new possibilities to obtain fundamental insights into the magnetic neutron scattering of bulk magnetic media.

This research was supported by the DFG Project BE 2464/10-3.

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Submitting Author: s.erokhin@general-numerics-rl.de

DIRECTING THE ORIENTATIONAL ALIGNMENT OF ANISOTROPIC MAGNETIC NANOPARTICLES USING DYNAMIC MAGNETIC FIELDS

S. Disch[a] **and P. Bender**[b]
[a]*Department Chemie, Universität zu Köln, 50939 Köln, Germany*
[b]*Experimentalphysik, Universität des Saarlandes, 66041 Saarbrücken, Germany*

The response of magnetic nanoparticles to applied static and dynamic magnetic fields is the subject of intense research in view of its fundamental technological importance, *e.g.* for medical applications such as imaging and magnetic hyperthermia [1], or sensor applications [2]. The field-assisted self-assembly of shape-anisotropic nanoparticles in dispersions is particularly desired for liquid crystalline or optically anisotropic materials [3] and as a prerequisite for self-organization into long range ordered arrangements with anisotropic physical properties [4].

Whereas magnetic nanorods commonly align their long axis parallel to the inducing magnetic field, weakly ferromagnetic hematite spindles bear a magnetic easy axis in their crystallographic basal plane and are thus known to orient with their principal axis perpendicular to an applied magnetic field [5,6]. We have recently determined the frequency-dependence of their orientation distribution in alternating and rotating magnetic fields using time-resolved SAXS. In addition to the particle orientation distribution obtained by static SAXS, the time-resolution of our stroboscopic SAXS experiment provides information on the dynamic particle orientation for a given state of an applied alternating or rotating magnetic field. The dynamic reorientation behavior was further exploited towards self-organization of these elongated nanoparticles. Using a dynamic field-induced self-assembly process, we developed nanoparticle arrangements with parallel and perpendicular orientation towards the substrate that exhibit directionally anisotropic magnetic properties [7].

In this contribution, we will demonstrate the dynamic, field-induced reorientation behavior of elongated magnetic nanoparticles in dynamic magnetic fields using time-resolved SAXS. We will further report on the consequent influence of the applied magnetic field on the particle alignment obtained in oriented assemblies.

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Submitting Author: sabrina.disch@uni-koeln.de

CHARACTERISATION OF ION TRACKS USING SAS

P. Kluth[a], **D. Schauries**[a], **P. Mota**[a], **A. Nadzri**[a], **M. Proft**[a], **N. Kirby**[b], **E. Gilbert**[c], **M. Lang**[d], **K. Nordlund**[e], **C. Trautmann**[f]
[a]*Research School of Physics and Engineering, Australian National University, Mills Road, Canberra ACT 2601, Australia*
[b]*Australian Synchrotron, 800 Blackburn Rd, Clayton, VIC 3168, Australia*
[c]*Australian Nuclear Science and Technology Organisation, Kirrawee DC, NSW 2232, Australia*
[d]*Department of Nuclear Engineering, University of Tennessee, Knoxville, 37996, USA*
[e]*Department of Physics, Helsinki Institute of Physics, University of Helsinki, Helsinki, Finland*
[f]*GSI Helmholtz Centre for Heavy Ion Research/Technische Universität Darmstadt, Germany*

When penetrating a solid, ions with MeV to GeV energies interact predominately through inelastic interactions with the target electrons. The resulting intense electronic excitation can produce narrow trails of permanent damage along the ion paths, so called ‘ion tracks’. Ion tracks are generally between 5-10 nm in diameter and can be tens of micrometers long. They have been observed in many materials and have numerous important applications across a variety of scientific areas such as materials science and engineering, nanotechnology, geology, archaeology, nuclear physics, and interplanetary science.

If generated in an accelerator, an ensemble of ion tracks comprises parallel, (almost) identical nano-sized objects with negligible overlap. Due to their high monodispersity, small angle scattering, albeit measuring typically ~10^7 ion tracks, can yield information about the individual track structure averaging out fluctuations on an atomic level. Only formfactor scattering needs to be considered due to the stochastic distribution and parallel alignment of the ion tracks. Monte Carlo calculations enable analysis using complex track shapes.

This presentation will give an overview of our recent advances in characterising ion tracks using both small angle x-ray and neutron scattering experiments. *In situ* annealing experiments of ion tracks in quartz were used to study the complex elastic behaviour of the tracks, which provide a model system for nanoscale cylindrical inclusions in a matrix [1]. Ion tracks in amorphous materials are inherently difficult to characterise, yet using SAXS we were able to observe a fine structure in ion tracks in amorphous SiO_2 [2], amorphous Ge [3], and amorphous Si [4]. Ion track formation at elevated temperatures in apatite and quartz shows an increase in the track radii by approximately 1 Å/100°C as a consequence of an increased local temperature leading to a larger melting radius in the thermal spikes generated by the ions [5]. Using *in situ* annealing combined with SAXS measurements of samples in diamond anvil cells, the damage annealing of ion tracks in apatite, which is important for the determination of the thermal history of geological material, was found to be enhanced at elevated pressures such as those present in the earths’ crust. Ion tracks in polycarbonate were characterised using SAXS and SANS. The combination of both techniques enables to estimate the stoichiometry in the ion track region.

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Submitting Author: patrick.kluth@anu.edu.au

THE FIRST EXPERIMENT OF SPIN CONTRAST VARIATION AT J-PARC BL15 TAIKAN

Y. Noda[a], **D. Yamaguchi**[a], **S. Shamoto**[a], **T. Hashimoto**[a], **T. Kumada**[a], **S. Takata**[b], **S. Koizumi**[c], **K. Ohishi**[d], **J. Suzuki**[d], **T. Masui**[e], **R. Mashita**[e], **and H. Kishimoto**[e]
[a]*Quantum Beam Science Center, Japan Atomic Energy Agency, Ibaraki 319-1195, Japan*
[b]*J-PARC Center, Japan Atomic Energy Agency, Ibaraki 319-1195, Japan*
[c]*College of Engineering, Ibaraki University, Ibaraki 319-8511, Japan*
[d]*Comprehensive Research Organization for Science and Society, Ibaraki 319-1106, Japan*
[e]*Sumitomo Rubber Industries, Ltd., Kobe 651-0072, Japan*

Neutron scattering length of a proton (b_H) is largely dependent on the proton spin polarization (P) as $b_H = (-0.374 + 1.456P) \times 10^{-12}$ cm, when neutron beam is fully polarized. This effect can be utilized for contrast variation study in small angle neutron scattering (SANS). For high P, dynamic nuclear polarization (DNP) technique is usually used, in which unpaired electrons should be introduced into a sample, and the large spin polarization of unpaired electrons should be transferred to that of proton spin by microwave irradiation. As a source of unpaired electrons, (2,2,6,6-tetramethylpiperidine-1-yl)oxy (TEMPO) radical can be used. At ambient temperatures, TEMPO vaporizes and spontaneously permeates a fluid phase of polymer or rubber samples. We believe that polymer or rubber sample, into which it is difficult to introduce deuteron, is an effective application target of spin contrast variation technique.

Our early studies on spin contrast variation were conducted at SANS-J-II in JRR-3 [1,2]. Later, in November 2014, we conducted the first experiment of spin contrast variation SANS at J-PARC BL15 TAIKAN, equipped with a neutron polarizer. Prior to multi-component system studies, we should confirm the performance of contrast variation at the spallation neutron source instrument by using block polymer and particle-filled rubber samples with well-known structures.

Figure 1 shows the observed SANS profiles for silica-filled SBR rubber. We can clearly see fringes due to sphere's form factor, since the employed silica particles have quite small radius dispersion. With increasing P, the SANS intensity first reduced, then turned up from P = +36% to +44%. The observed intensity variation was well explained by the contrast between silica and SBR rubber phases. For the first time to us, the high P beyond the matching point between silica and SBR rubber (P = +30%) was achieved, thanks to our recent upgrade of the DNP instrument and the sample preparation process.

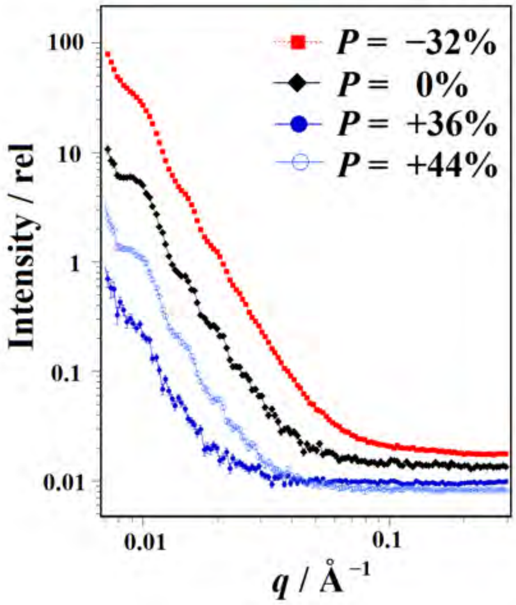

Figure 1: SANS profile variation as a function of proton spin polarization, P, for silica-filled SBR rubber. Into the sample, silica particles with a radius of about 600Å were introduced by 10%vol.

This work was supported by Grant-in-aid for Young Scientists (A) by JSPS (25706033).

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Submitting Author: yoheinoda@gmail.com

LOKI - A SANS INSTRUMENT FOR SOFT MATTER, MATERIALS AND LIFE SCIENCE AT THE ESS

A. Jackson[a], K. Kanaki[a], C. Lopez[a], C. Zendler[a], E. Nilsson[a], G. Nagy[b], N. Cherkashyna[a], A. Sandström[a], T. Nielsen[a], A. Pettersson[a], P. Bentley[a], T. Gahl[a], R. Hall-Wilton[a], I. Sutton[a] and K. Anderson[a]

[a]*European Spallation Source, PO Box 176, Lund 221 00, Sweden*

[b]*Laboratory for Neutron Scattering and Imaging, Paul Scherrer Institute, 5232 Villigen PSI, Switzerland*

The European Spallation Source (ESS) will be a long pulse 5MW spallation neutron source built in Lund, Sweden. It is expected that 7 out of a final suite of 22 instruments will enter commissioning in 2019/2020, with the remainder coming online by 2025.

Since SANS instruments can operate with a somewhat relaxed resolution, there should be a large benefit from the ability to make use of most, if not all, of the long pulse and the significant flux gain over existing sources that this implies.

LoKI is a beamline designed primarily with the needs of the soft matter, biophysics and materials science communities in mind. The trend in all of these fields is towards complexity and heterogeneity. These factors are manifested both spatially and temporally and so high flux, small beam sizes and a wide simultaneous Q range are required.

We are thus constructing a 10 m + 10 m SANS instrument with the sample position 22m from the source. This provides a wavelength band of 7 Å at 14 Hz or 17.5 Å at 7 Hz whilst maintaining reasonable resolution. The resolution can be enhanced with an optional series of additional choppers. Combining this with multiple banks of detectors covering a large solid angle, maximal use is made of the flux available from the ESS source and measurements with over 3 orders of magnitude in simultaneous Q range are possible.

Submitting Author: andrew.jackson@esss.se

FIRST APPLICATION OF SIMULTANEOUS SANS AND DIFFERENTIAL SCANNING CALORIMETRY: MICROPHASE SEPARATED ALKANE BLENDS

S A Pullen[a], N Booth[a], S R Olsen[a], B Day[a], F Franceschini[a], D Mannicke[a]
and E P Gilbert[a]
[a]*Australian Nuclear Science and Technology Organisation (ANSTO), Locked Bag 2001,*
Kirrawee DC NSW 2232, Australia
[b]*Hobsons Instruments Services, 1/6 Sherbourne St, Essendon Vic 3042, Australia*

For almost 30 years, it has been possible at synchrotron facilities to perform small-angle x-ray scattering experiments whilst simultaneously measuring phase transitions using differential scanning calorimetry (DSC). However, a range of challenges exist to enable the collection of simultaneous small-angle neutron scattering (SANS) and DSC data associated not only with intrinsic flux limitations but also scattering geometry and thermal control. The development of a DSC (temperature range ca. −150 C to 500 C) suitable for SANS is detailed here which, to our knowledge, is the first and only one of its kind. An example study is presented from the 40 m SANS instrument, QUOKKA, at the OPAL reactor at ANSTO (Figure 1), concerned with phase transitions in a binary blend of normal alkanes in which one component has been deuterium labelled[1]. The ability to conduct simultaneous DSC and neutron scattering studies allows investigators to use these two complementary techniques to provide insight into structural and thermal changes and opens up the opportunity for SANS to make significant new contributions to a range of systems in which either scattering contrast is insufficient for SAXS studies or where neutron scattering is essential or inherently desirable (e.g. isotope effects).

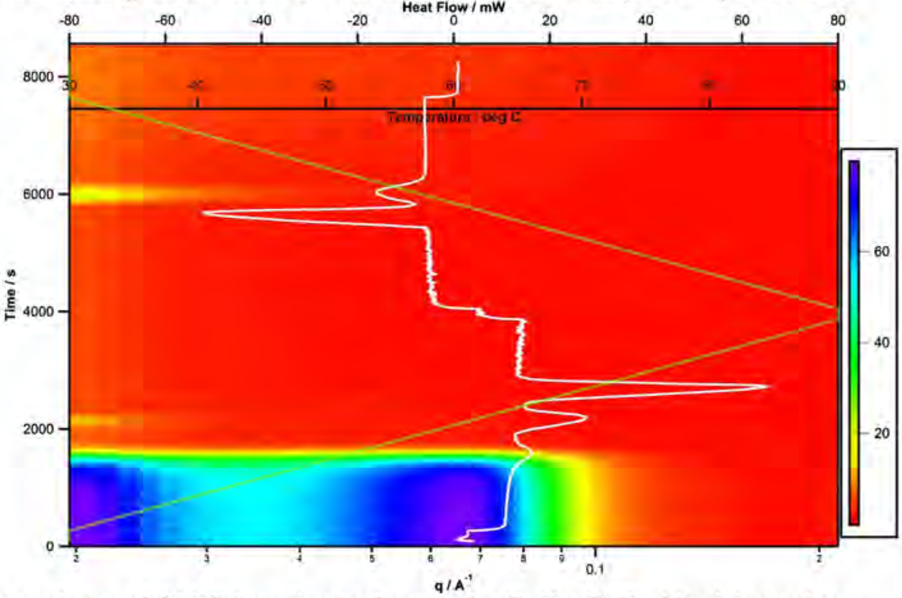

Figure 1 - Time-evolution of SANS from demixed equimolar $C_{30}H_{62}$:$C_{36}D_{74}$ blend during heating and cooling at 1 K min^{-1}; DSC data, collected simultaneously, are superimposed. Intensity is shown on a linear colour map (right). DSC data are shown as a solid curve and the temperature profile of the DSC experiment is shown as a dotted line.

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Submitting Author: elliot.gilbert@ansto.gov.au

SKADI – SMALL-K ADVANCED DIFFRACTOMETER

Sebastian Jaksch[a], Henrich Frielinghaus[a], Jacques Jestin[b], Sylvain Désert[b]
[a]*Forschungszentrum Jülich GmbH, JCNS at Heinz Maier-Leibnitz Zentrum,*
Lichtenbergstrasse 1, D-85747 Garching
[b]*Laboratoire Léon Brillouin CEA/CNRS, CEA Saclay, 91191 Gif/Yvette Cedex, France*

The Small-K Advanced DIffractometer SKADI is a versatile SANS instrument, proposed for the European Spallation Source, which enables scientists to perform a wide range of investigations on topics requiring small Q-values to access long length scales [1]. The scientific areas targeted by SKADI include investigations of smart materials, biological and medical research, magnetic materials and materials for energy storage, as well as experiments on nanomaterials and nanocomposites or colloidal systems. To maximize the applicability of these studies SKADI is designed to accommodate in-situ measurements with custom made sample environments to provide "real-world" conditions.

To achieve all these goals SKADI will feature the following general design properties:

- Flexibility (sample area is approx. 3x3 m2, and versatile collimation)
- Very small Q accessible through VSANS (using focusing collimation elements)
- Polarization for magnetic samples and incoherent background subtraction
- Good wavelength resolution, being the longest SANS instrument
- High dynamic Q-range (using two detectors)

With a flux at about 25 times higher than at the D22, an accessible size regime between the Anstrom and micrometer scale and the high dynamic Q range for fast data acquisition with a high resolution both in Q and time, this instrument will open the ESS for a wide scientific community.

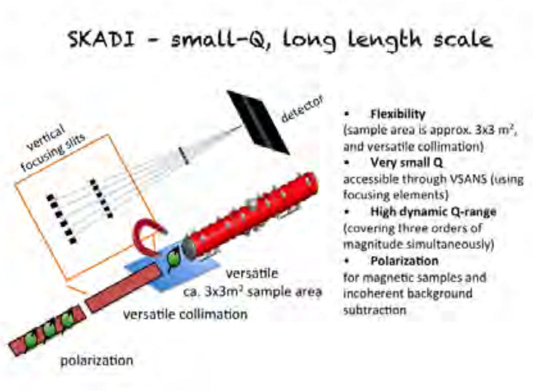

Fig. 1. Sketch of the setup of SKADI.

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Submitting Author: s.jaksch@fz-juelich.de

SPIN-ECHO MODULATED SMALL ANGLE NEUTRON SCATTERING IN TIME-OF-FLIGHT MODE

M. Strobl[c], **M. Sales**[a,b], **J. Plomp**[d], **W.G. Bouwman**[d], **A.S. Tremsin**[e], **K. Habicht**[b] **and C. Pappas**[d]
[a]*Univ Copenhagen, Niels Bohr Inst, Nanosci Ctr, DK-2100 Copenhagen, Denmark*
[b]*Helmholtz Zentrum Berlin Mat & Energie GmbH, D-14109 Berlin, Germany*
[c]*European Spallat Source ESS AB, Div Sci, SE-22100 Lund, Sweden*
[-]*Delft Univ Technol, Fac Appl Sci, NL-2629 JB Delft, Netherlands*
[e]*Univ Calif Berkeley, Space Sci Lab, Berkeley, CA 94720 USA*

Spin-Echo Modulated Small Angle Neutron Scattering (SEMSANS) utilises the manipulation of the spins of polarised neutrons by the use of magnetic fields with inclined surfaces to map a small angle scattering signal from a sample into a dampening of the amplitude of a spatially intensity modulated neutron beam. Our work involves the characterization and use of such an instrument in Time-of-Flight (ToF) mode where a white pulsed neutron beam is used to probe a set-up of multiple samples simultaneously[1]. Such an instrument would be able to excel at pulsed neutron sources such as the European Spallation Source (ESS) currently under construction. Our method enables straightforward quantitative dark-field neutron imaging, i.e. quantitative microstructural characterization combined with spatial image resolution. For the first time quantitative microstructural reciprocal space information from small angle scattering can be combined with the macroscopic image information creating the potential to cover several orders of magnitude in structure sizes simultaneously.

Figure 1: Multi-sample set-up. Shim image. Normalized amplitude image. Example of modulation. Normalized amplitude vs spin-echo length, SEMSANS. Comparison with SESANS data and theoretical curves for random two phase media.

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Submitting Author: markus.strobl@esss.se

STRUCTURAL STUDY ON SYNDIOTACTIC POLYSTYRENE COCRYSTALS BY A SIMULTANEOUS TIME-RESOLVED SANS/FTIR MEASURING SYSTEM

F. Kaneko[a], **N. Seto**[a], **S. Sato**[a], **A. Radulescu**[b], **M. M. Schiavone**[c], **J. Allgaier**[c] **and K. Ute**[d]
[a]Graduate School of Science, Osaka University, Toyonaka, Osaka, 560-0043, Japan,
[b]JCNS, Outstation at MLZ, Lichtenbergstraße 1, 85747, Garching, Germany,
[c] JCNS and ICS, Forshungszentrum Jülich GmbH, 52425 Jülich, Germany,
[d]Dep. of Chem. Sci. and Tech., The University of Tokushima, Tokushima 770-8506, Japan.

Small angle neutron scattering (SANS) is a powerful and convenient method to investigate the higher order structure of static polymer systems. SANS has increased its presence even in the research concerning time-dependent structural evolution. However, if a system of interest is a multi-component system, the interpretation of the time-dependent changes in SANS profile is not an easy job. It is desirable to obtain two or more different kinds of structural information simultaneously from the same sample.

Infrared spectroscopy has been employed as a complementary tool of X-ray scattering. We have expected that the combination of SANS with Fourier Infrared spectroscopy (FTIR) would also produce a fruitful methodology and developed a novel method for the simultaneous SANS/FTIR measurement[1], which was realized by building a device consisting of a portable FTIR spectrometer and an optical system that allows both a neutron beam and an infrared beam pass through a sample coaxially, as shown in Figure 1. The device was installed on a small angle neutron diffractometer, KWS2 at MLZ in Germany. To check the performance of this system, the structural changes in cocrystals of deuterated syndiotactic polystyrene (d-sPS) with polyethylene glycol dimethyl ethers (PEGDMEs) during the course of heating were followed.

Fig. 2(top) reproduces the changes in SANS 2D image for d-sPS/PEGDME(m.w.178) cocrystal. The intensity of the two lamellar reflections gradually decreased as the temperature increased and then increased slowly above 100℃. Fig. 2(bottom) shows the temperature dependence of IR spectra measured in parallel with SANS images. As the temperature increases, the bands due to PEGDME significantly decreased in intensity, whereas the bands due to d-sPS kept their intensities. The IR spectral changes suggest that the SANS profile changes are mainly caused by the migration of PEGDME from the crystalline region to the amorphous region and the subsequent evaporation from the film, since the distribution of PEGDME is a main factor to determine the scattering length density profile of the d-sPS/PEG cocrystal film.

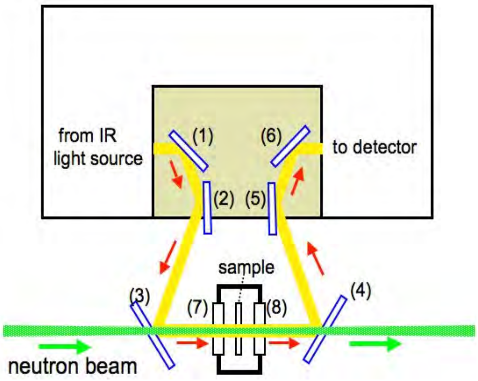

Figure 1. Schematic representation of the simultaneous measurement system.

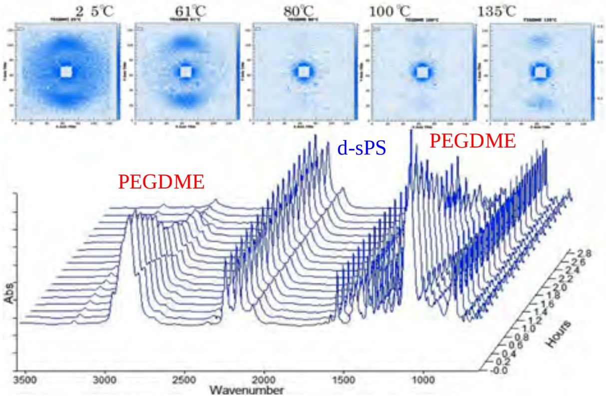

Figure 2. Temperature dependence of SANS 2D images (top) and FTIR spectra (bottom).

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Submitting Author: toshi@chem.sci.osaka-u.ac.jp

TOPOGRAPHIC MEASUREMENTS OF BURIED THIN FILM INTERFACES BY GRAZING INCIDENCE SOFT X-RAY SCATTERING

E. Gann[1], C.R. McNeill[1], J. Cochran[2], M. Chabinyc[2], C. Wang[3], J. Seok[4], A. Watson[5], J. R. Tumbleston[5], H. Yan[5], H. Ade[5]

[1] *Materials Engineering, Monash University, Clayton VIC 3800, Australia*
[2] *Materials Department University of California, Santa Barbara, CA 93106 USA*
[3] *Advanced Light Source, LBNL, Berkeley, CA 94795 USA*
[4] *Department of Materials Science and Engineering, NCSU, Raleigh, NC 27695 USA.*
[5] *Department of Physics, NCSU, Raleigh, NC 27695 USA*

The internal structures of thin films, particularly interfaces between different materials, are critical to system properties and performance across many disciplines, but characterization of buried interface topography is often unfeasible. In this work, we demonstrate that Grazing Resonant Soft X-ray Scattering (GRSoXS), a technique using diffusely scattered soft X-rays in grazing incidence geometry, can reveal the statistical topography of buried thin film interfaces. By controlling and predicting the X-ray electric field intensity throughout the depth of the film and simultaneously the scattering contrast between materials, we are able to unambiguously identify the microstructure at different interfaces of a model polymer bilayer system. We additionally demonstrate the use of GRSoXS to selectively measure the topography of the surface and buried polymer-polymer interface in organic thin film transistors. In such systems, where only indirect control of interface topography is possible, accurate measurement of the structure of interfaces for feedback is critically important. We demonstrate the method using polymeric materials, but also show that the technique is readily extendable to any thin film system with elemental or chemical contrasts exploitable at absorption edges.

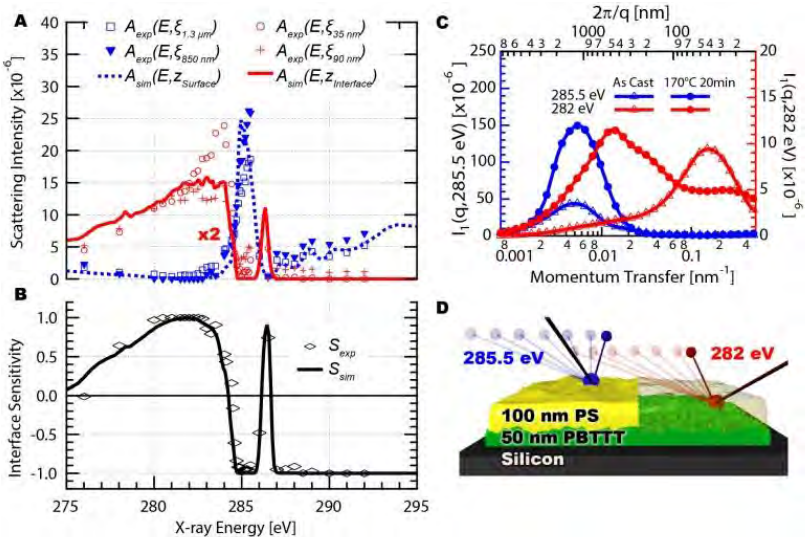

Figure.1. A) Experimental and simulated scattering intensities for an OTFT sample. B) experimental and simulated interface sensitivities for the OTFT sample. C) Scattering intensity at the index-matched energies for the surface and internal interface before and after annealing. D) A schematic of the system illustrating the surface sensitivity at 285.5 eV nm and interface sensitivity at 282 eV.

Submitting Author: eliot,gann@monash.edu

Out-of-equilibrium studies using simultaneous SAXS/WAXS investigation

P. Panine[a], **S. Tencé-Girault**[b] **and F. Bargain**[b,c]
[a]*Xenocs SA, 19, rue François Blumet, Sassenage, France*
[b]*Matière Molle et Chimie, UMR 7167 ESPCI ParisTech, 10 rue Vauquelin 75005 Paris, France*
[c] *Arkema- Piezotech CRRA, rue Henri Moissan 69493 Pierre-Benite Cedex, France*

Polymer transformation from raw material towards finalized product involves several processing steps from precipitate of original powder up to the film formation. At each step, the macromolecular chain may undergo a phase transformation, with its own history and/or phase transformation and potentially trapping macromolecular chains in a metastable state. Finally, the ultimate performance of such polymer are most of the time related to the phase present as well as to the level of crystallinity. Most of time, when intermediate states are encountered, complete thermal path from synthesis up to final step has to be taken into consideration. As a reason, processing departments determine empirical routes, usually by the mean of annealing protocols prior delivering the final material toward end user. Such an annealing step is time and energy consuming but often necessary in the attempt to erase any prior thermal history or to provides specific properties to the samples. These protocols are usually predefined using standard thermal tool i.e. differential calorimetry (DSC) but do not evidence precisely the phase content or phase distribution. The existence of interdependence of a structure present at the atomic scale (crystalline phase) and at the mesoscale (i.e. lamellar…) is usually suspected but the related signature in the DSC remains imprecise with this respect. It is therefore of particular interest to perform a simultaneous investigation of the structures present, both at the atomic and mesoscopic scale. Simultaneous data collection is here of particular interest since both scales will be probed in the course of the thermal treatment, enabling to reveal crystalline phase, morphology and kinetic interdependencies without ambiguity.

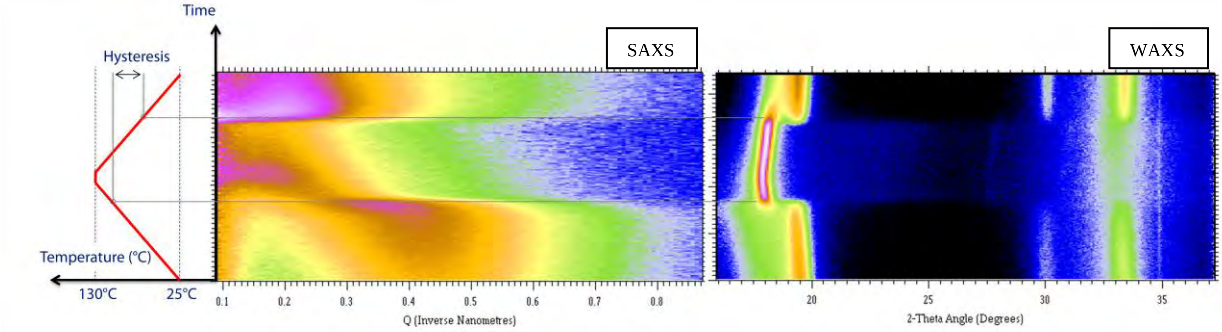

Figure 1: Temperature ramp up then down between 25 °C and 130 °C at 1 °/min of a 20 µm thick film of solvent cast VF2/VF3 blend. SAXS and WAXS data exhibit strong correlation and reflects the non reversibility of the long period (SAXS) while the Curie crystalline phase transition seems reversible (WAXS).

In this paper, we will present recent results on the thermal behavior of polymeric films undergoing quasi-reversible crystalline phase transformation investigated in-situ with heating rate usually encountered in standard DSC (typically 1°C/min). If the advantage of collecting simultaneously SAXS and WAXS was described long time ago [1], the capability to perform such study at heating rate similar to DSC is of the utmost importance. The case of neat prepared film from solvent cast compared to complex annealing protocols will be highlighted.

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STRUCTURAL IMACT OF TRANSITION METAL HALIDES ON THE REACTIVE HYDRIDE COMPOSITES FOR SOLID-STATE HYDROGEN STORAGE

F. Karimi[a], **P. K. Pranzas**[a], **A. Hoell**[b], **M. Wasbrough**[c], **U. Vainio**[d], **D. Mildner**[c], **T. Uduvic**[c], **A. Heinemann**[a], **H. Eckerlebe**[a], **M. Dornheim**[a], **T. Klassen**[a], **and A. Schreyer**[a]
[a]*Helmholtz-Zentrum Geesthacht, Max Planck-Str. 1, 21502 SH, Germany*
[b]*Helmholtz-Zentrum Berlin GmbH, Albert-Einstein-Str. 15, 12489 Berlin, Germany*
[c]*NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, MD 20899-6102*
[d]*Deutsches Elektronen-Synchrotron (DESY), Notkestrasse 85, 22607 Hamburg, Germany*

Hydrogen is one of the most promising renewable energy sources for mobile and stationary applications. Hydrogen stored in solid state systems circumvents the safety issues and increases the volumetric hydrogen capacity significantly, in comparison to gaseous or liquid hydrogen. A promising class of materials is the so called "Reactive Hydride Composites" (RHCs) [1], *e.g.*: $LiBH_4$-MgH_2 and $Ca(BH_4)_2$-MgH_2. These systems show reduced total reaction enthalpies at high storage capacities. However, these systems show very sluggish hydrogen sorption kinetics and they can therefore be presently operated only at temperatures very much above their thermodynamic equilibria. With suitable transition metal halide (TMH) additives the kinetics can be improved by considerably. To determine the size distribution of the hydride-matrix in the $LiBH_4$-MgH_2 composite system SANS/USANS measurements were carried out. Here, the isotopes of Li (^{7}Li, Li) and B (^{11}B, B) were used to follow selective the decomposition products in the particles. In the case of $Ca(BH_4)_2$-MgH_2, ASAXS on the calcium K-edge was performed to determine the Ca-containing nano structures [2]. To investigate the size distribution and chemical state of the additives in the hydride matrices, ASAXS and XAS measurements at the K-edge of the transition metals were carried out. These results shed light on the complex reaction mechanism of TMH in the hydride matrix and lead to improvement of the RHCs for a possible application in short terms.

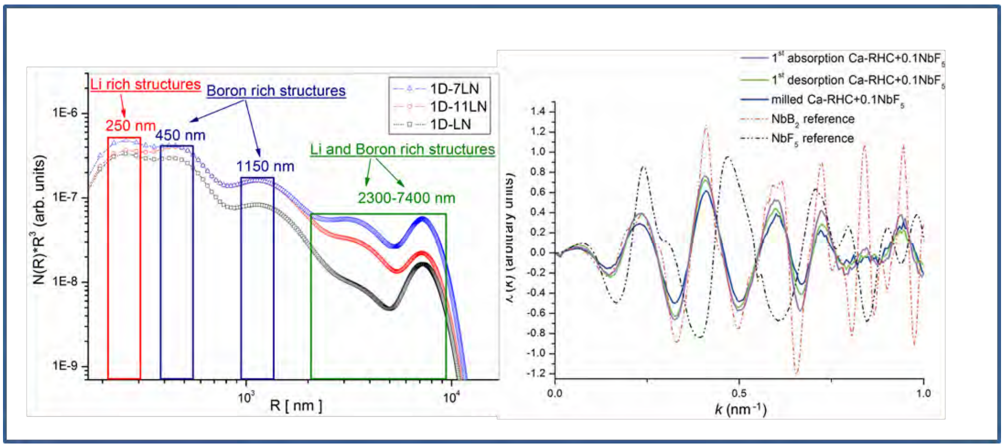

Figure 1-Size distribution of LiH-MgB_2 (1D-LN), LiH-$Mg^{11}B_2$ (1D-11LN), and ^7LiH-$Mg^{11}B_2$ (1D-7LN) doped with 0.1NbF_5 (left). EXAFS pattern of Nb in the $Ca(BH_4)_2$-MgH_2 with some references (right).

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fahim.karimi@hzg.de

ANOMALOUS SMALL ANGLE X-RAY SCATTERING OPERANDO ON A LITHIUM BATTERY AND CERAMIC FUEL CELL ASSEMBLIES

A. Braun[a], **S. Seifert**[b] **P.R. Jemian**[b], **J. Ilavsky**[b], **A.J. Allen**[c], **and E.J. Cairns**[d]
[a]*Empa. Laboratory for High Performance Ceramics, Überlandstr. 129*
CH-8600 Dübendorf, Switzerland
[b] *Advanced Photon Source, Argonne National Laboratory, 9700 S. Cass Avenue*
Argonne, IL 60439, United States
[a] *U.S. Department of Commerce, National Institute of Standards and Technology, 100 Bureau Drive, Gaithersburg, MD 20899, United States*
[b]*University of California Berkeley, Dept. of Chemical and Biomolecular Engineering*
Berkeley, CA 94720, United States

The functionality of electrochemical energy storage and conversion devices depends primarily on the electronic structure of the materials of their electrodes and electrolytes. Secondarily, their microstructure determines much of their actual performance. The microstructure of electrodes in batteries and electrodes and electrolytes in ceramic fuel cells is actually some convolution of chemical and topological heterogeneity, which is difficult to conceptually grasp and very difficult to actually map out. We investigated the microstructure changes of a complete lithium battery cell with anomalous small angle x-ray scattering (ASAXS) while in operation (Figure 1 – left panel). The resonant x-ray energy was the Mn K-edge, because Mn was the element of the chemically active redox species $LiMn_2O_4$ in the battery cathode [1,2]. The other study was an ASAXS study on a solid oxide fuel cell electrode assembly, where we scanned with Ni and Zr resonant X-rays with a micro focus beam across the thickness of the assembly in steps of 10 micrometers so as to map the microstructure heterogeneities particularly at the electrode-electrolyte interfaces. With the full quantitative analysis of the ASAXS data (Figure 1 – middle panel) we were able to sketch the pathogenesis of the electrochemical interfaces and triple phase boundaries as a result of exposure to sulfur impurities in the fuel gas (Figure 1 – right panel).

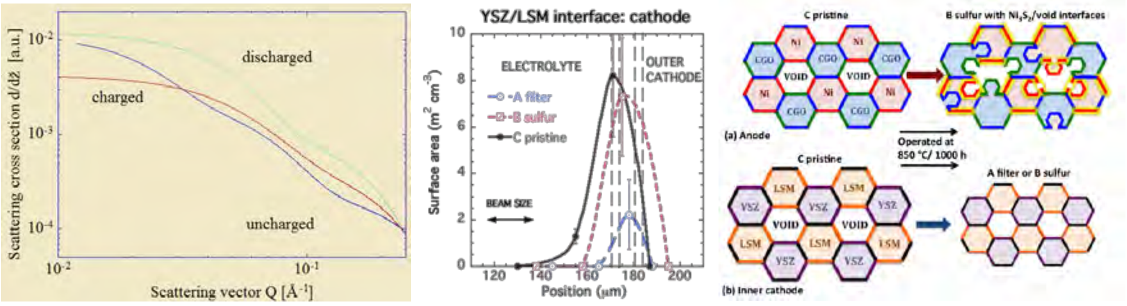

Figure 1: (left) Change of the Mn ASAXS scattering cross section of lithium battery $LiMn_2O_4$ cathode from uncharged – charged to discharged state. (middle) Internal surface area derived from Ni and Zr resonant ASAXS data near electrolyte – cathode interface from SOFC assembly in pristine state, pure fuel operated state and sulfur poisoned fuel state. (right) Schematic of microstructure degradation in SOFC anode upon sulfur poisoning.

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SORPTION-INDUCED DEFORMATION OF HIERARCHICAL POROUS SILICA

R. Morak[a], **C. Balzer**[b], **A. Waag**[b], **F. Putz**[c], **M Elsaesser**[c], **N. Hüsing**[c], **G. Reichenauer**[b] **and** **O. Paris**[a]

[a] *Institut für Physik, Montanuniversität Leoben, Franz Josef Strasse 18, 8700 Leoben, Austria*
[b] *Bavarian Center for Applied Energy Research, Am Galgenberg 87, 97074 Würzburg, Germany*
[c] *Fachbereich Materialforschung und Physik, Paris-Lodron Universität Salzburg, Hellbrunner Str. 34, A-5020 Salzburg, Austria*

Sorption-induced deformation of nanoporous materials is a widely recognized phenomenon with potential impact in diverse fields such as sensing, actuation or energy storage. It has been demonstrated that adsorption and condensation of fluids in ordered mesoporous silica materials lead to a fully reversible deformation of the ordered pore lattice[1]. Theoretical work has confirmed that the physical origins for this deformation are the change of the interfacial energy (and thus, the surface stress) due to the fluid adsorption at the pore walls, and the Laplace pressure acting at capillary condensation, respectively[2],[3]. Recently, we have for the first time studied a monolithic silica material with hierarchical porosity[4]. This material consists of a macroporous network of struts (see Fig. 1), each strut containing cylindrical mesopores of roughly 8 nm in diameter on a 2D hexagonal pore lattice. In-situ dilatometry (macroscopic strain) and in-situ small-angle X-ray scattering (pore lattice strain) during ad- and desorption of n-pentane revealed differences of the fluid pressure dependent deformation, which were attributed to the complex geometry of the pore network[4]. New experiments show that by changing the synthesis conditions, the mechanical response of the network at both, the macroscopic and the mesoscopic scale can be varied over a wide range. Moreover, we also managed to introduce anisotropy into the macroporous network, opening the possibility to study directional macroscopic deformation.

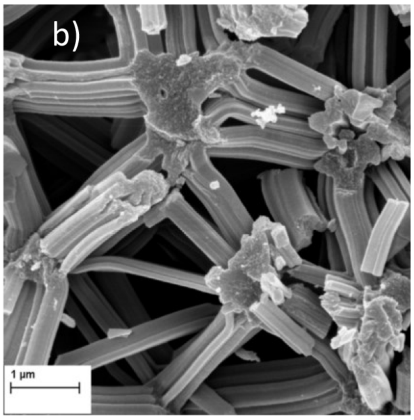

Fig. 1. Scanning electron microscopy image of a monolithic silica sample with hierarchical porosity.

Here we present new in-situ small-angle scattering data on this fascinating class of materials upon ad- and desorption of different fluids. In particular we demonstrate that the combination of small-angle scattering with dilatometry is an excellent tool to study sorption induced deformation at different levels of hierarchy at great detail opening the possibility to tailor these materials for specific functions.

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Submitting Author: oskar.paris@unileoben.ac.at

ABSORPTION-CONTRAST SAXS OF THIN-FILM PHOTOVOLTAIC CHALCOPYRITE COATINGS

R. Winter[a], **M. E. Jones**[a], **J. Wychowaniec**[a], **J. Ash**[a], **P. Staniec**[b] **and N. Terrill**[b]
[a]*Department of Physics, Aberystwyth University, Penglais, Aberystwyth SY23 3BZ, Wales*
[b]*Beamline I22, Diamond Light Source, Didcot OX11 0DE, England*

Chalcopyrites such as Cu(In,Ga)S_2 (CIGS) are promising candidate materials for efficient thin-film dye-sensitised photovoltaic cells. Their absorption spectrum in the visible and consequently their photovoltaic efficiency is governed by the particle size and the In:Ga stoichiometry. When preparing CIGS nano-particle inks, the In and Ga sources are usually two separate compounds, so homogeneity at the atomic scale isn't necessarily guaranteed, and particle size and stoichiometry may be correlated.

Even in the absence of microscopic phase segregation, such coatings are complex structures combining porosity with nano-particles subject to a distribution of sizes. In this case, segregation into particles with different stoichiometry is also a possibility. Clearly, additional information will be needed beyond a simple scattering pattern in order to establish with confidence a model of the structure.

In this study, we have used energy-dependent SAXS around the Cu and Ga *K*-edges during an in-situ dip-coating experiment to obtain scattering patterns with chemical sensitivity in order to correlate CIGS particle and agglomerate sizes with local stoichiometry. As anomalous scattering (ASAXS) in a dynamically changing system is error-prone due to chemical shifts of the absorption edge, we instead contrast energies substantially below and above each edge and correct for fluorescence, which is measured using a separate energy-dispersive point detector placed at right angles with the x-ray beam. This *absorption-contrast SAXS (ac-SAXS)* technique allows us to obtain chemical contrast with useful time resolution.

Using the attenuation of the potassium fluorescence from the mica substrate, we are able to determine the effective thickness of the coating. This is used to calibrate the background resulting from the copper and gallium fluorescence. After removal of this fluorescence background from the scattering patterns obtained above the respective edges, difference patterns are calculated at each absorption edge, revealing the scattering features resulting from particles containing copper and gallium, respectively. The former allows us to distinguish nano-particles from porosity, while the latter reflects variations in the In:Ga stoichiometry.

We demonstrate that ac-SAXS provides chemical contrast even in dynamic systems where the exact position of the absorption edge may not be known with sufficient accuracy for ASAXS. This comes at the expense of an additional energy-dependent point measurement taken at the same time as each SAXS exposure. The data analysis can be straightforward if integrated into the workflow of a scattering data analysis package such as Dawn.

Submitting Author: Rudolf Winter, ruw@aber.ac.uk

Precipitation kinetics in an Al-Mg-Zn alloy under friction stir welding thermal cycles studied by high-energy small-angle X-ray scattering

Peter Staron, Torben Fischer, Andreas Stark, Andreas Schreyer

Institut für Werkstoffforschung, Helmholtz-Zentrum Geesthacht, Geesthacht, Germany

Friction stir welding (FSW) is used for the production of Al structures e.g. in aerospace and shipbuilding industries. It is a solid-state joining process producing joints with good mechanical properties. Various Al alloys (e.g. AA2xxx or AA7xxx) are strengthened by nano-precipitates. The strengthening precipitates are strongly influenced by the welding thermal cycles that can reduce alloy performance under service conditions. Thus, the precipitation kinetics in an Al-2.1Mg-8.4Zn alloy (wt%) developed for aircraft construction were studied under thermal cycles as they occur in friction stir welding.

A dilatometer was used for simulating the welding thermal cycles in small samples. The TA instruments dilatometer 805A/D is a standard sample environment at the high-energy synchrotron X-ray beamline HEMS of HZG at DESY. Small-angle X-ray scattering (SAXS) at a photon energy of 70 keV was used to monitor volume fraction and mean size of nano-precipitates during thermal cycles. High X-ray energies allow using thick samples that can be further processed afterwards. With the dilatometer, the thermal influence of the friction stir welding process can easily be studied in-situ, varying the maximum temperature and cycle time.

In addition, a numerical model was implemented for predicting the precipitation kinetics in the ternary Al-Mg-Zn alloy during thermal welding cycles. The model calculates the development of precipitate size distributions of the metastable η' phase and the stable η phase during all stages of precipitation, i.e. nucleation, growth, and coarsening. After calibrating the model parameters with the results of the SAXS measurements, predictions in a wider range of temperatures and cycle times and for different initial tempers could be calculated. Based on such a precipitation model, also predictions of mechanical properties connected with precipitates become possible.

STABILITY AND GROWTH OF TaC PRECIPITATES IN Co-Re SUPERALLOYS FOR ULTRA HIGH TEMPERATURE APPLICATIONS STUDIED BY SANS

L. Karge [a], R. Gilles [a], D. Mukherji [b], P. Strunz [c], J. Roesler [b]
[a]TU München, Heinz Maier-Leibnitz Zentrum, Lichtenbergstr. 1, 85747 Garching, Germany
[b]TU Braunschweig, IfW Langer Kamp 8, 38106 Braunschweig, Germany
[c]Nuclear Physics Institute (NPI), 25068 Rez near Prague, Czech Republic

Co-Re alloys are being developed in order to supplement Ni-base superalloys in future gas turbines for ultra-high temperature applications. Measurements by means of small-angle neutron scattering (SANS) and neutron diffraction (ND) were an essential part of their development in the past several years [1]. The complex interplay between the different existing mesoscopic phases could be studied in-situ at high temperatures. Especially with SANS, it was possible to observe the size distribution of precipitating phases and their evolution, when heating to temperatures up to 1380°C [2]. It was shown that the amount and distribution of the stabilizing mono-carbide of TaC phase strongly depends on the stoichiometry of alloyed components. A Ta content of 1.2 %at with varying C/Ta ratio from 0.5-1 was studied to investigate its influence on the TaC stability. The stability of a fine distribution of TaC in the CoRe matrix could be shown at temperatures up to 1300°C. The finely distributed TaC precipitates strengthen the alloy by interacting with dislocations during creep deformation at high temperatures. Currently, the effect of different heat treatments is under investigation and in-situ SANS and microscopic studies show long-term stability of very small (< 80 nm) TaC precipitates. Figure 1 shows the evolution and growth of TaC during aging at 900°C in the alloy with C/Ta = 0.5.

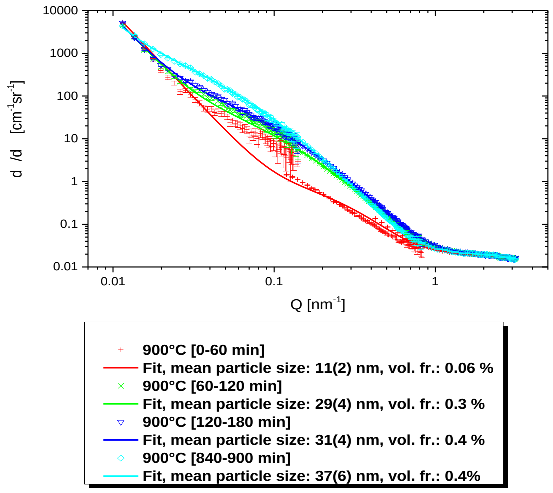

Figure 1: Long-term stability of TaC precipitates at 900°C, measured by in-situ SANS. The discontinuity of the first dataset (red) is caused by the quick evolution in the first 10 minutes.

Additionally, due to the high flux of the SANS-1 instrument at MLZ, it was possible to observe time resolved phase transformations of large precipitates (~100 nm) in-situ with a time resolution of 10 seconds. This method makes it possible to observe fast changes in the particle size with any associated change in volume fraction. This is not easy to observe with other techniques.

In this presentation we show that TaC is stable in Co-Re-based alloys with different C/Ta ratio and with the addition of Cr, which is added for oxidation resistance at high temperatures.

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Submitting Author: lukas.karge@frm2.tum.de

HIGH TEMPERATURE STUDIES OF γ′ PRECIPITATION IN A W-RICH NICKEL-BASE SUPERALLOY USING SANS AND SAXS

R. Gilles[a], **D. Mukherji**[b], **L Karge**[a], **P. Strunz**[c], **H. Eckerlebe**[d], **P. Staron**[d], **Th. Lippmann**[d]

[a]*Heinz Maier-Leibnitz Zentrum (MLZ), TU München, Lichtenbergstr. 1, 85747Garching, Germany*
[b]*TU Braunschweig, IFW Langer Kamp 8, 38106 Braunschweig, Germany*
[c]*Nuclear Pysics Institute (NPI), 25068 Rez near Prague, Czech Republic*
[d]*Helmholtz-Zentrum Geesthacht, Max-Planck-Str. 1, 21502 Geesthacht, Germany*

Nickel-base superalloys are widely used for gas turbine application due to their excellent properties of high temperature strength and oxidation resistance. They are the material of choice in the hot section of gas turbines, both land-based and aero-engines, and derive their strength from the precipitation of the Ni_3Al type γ′ phase in a Ni solid solution γ matrix.

In these superalloys, particularly the new generation of single crystal alloys, the kinetics of γ′ precipitation is very fast and it is generally not possible to suppress precipitation during cooling from the single phase region. However, because of this it is also difficult to experimentally determine the precipitation kinetics or to find the temperature when the nucleation first starts during cooling. Small angle scattering, particularly, in situ SAXS measurements with the high flux allow studying very fast transformation including the early stages of precipitation and growth of the γ′ precipitates. By recording scattering patterns on a TFT flat panel detector with an exposure time of 1 sec and a readout-time of 1.5 sec, it became feasible to detect the onset of γ′ precipitation during the cooling from supersolvus temperature at the cooling rate of ~ 750 K min^{-1}. After dissolving all existing γ′ precipitates at 1573 K and then cooling down at 1535 K the first scattering contribution during the cooling was clearly observed, already after 1 second of reaching 1535 K. Even with in situ SANS measurement, where the scattering contrast for this tungsten rich superalloy is very low, it was possible to record the integral intensity counts in intervals of 5 minutes with a fixed medium Q range resolution and to observe a scattering increase due to the formation of the γ′ precipitates.

Commercial single crystal Ni-superalloys contain a bimodal γ′ distribution with large cuboidal particles (300-500 nm) arranged in a 3D array and smaller spherical particles (50-100 nm) in the channel between the larger γ′ precipitates. This is also a result of the two step ageing heat treatment adopted by the industry (the sample is cooled to RT after the first ageing and reheated to the second ageing temperature to cut costs). At the higher temperature the diffusion is faster and allows quick growth of precipitates to reach the cuboidal shape in shorter times and the lower temperature ageing is used to equilibrate the γ′ volume fraction with longer holding.

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Submitting Author: ralph.gilles@frm2.tum.de

TEMPORAL EVOLUTION OF MESOSCOPIC STRUCTURE DURING HYDRATION OF CEMENT

S. Mazumder[a]
[a]*Solid State Physics Division, Bhabha Atomic Research Centre, Mumbai 400 085, India*

Though cement is a ubiquitous material with global production exceeding that of any other material of technological importance, the mechanism of its hydration and evolution of cement-water mixtures into gels of high compressive strength is poorly understood, despite extensive research over the past century. Recent investigations, based on neutron scattering measurements, aims at unraveling this enigma and outlines, for the first time, the evolution of the mesoscopic structure of the cement paste which exhibits temporal oscillations, strongly dependent on the scale of observation and on the medium of hydration (light or heavy water). While the formation of hydration products is synchronous for hydration with H2O, the process is non-synchronous for hydration with D_2O. The reason why morphological patterns of domains at different times look dissimilar, as seen before [1,2], for different hydration media emerges as a natural consequence of this finding. Mesoscopic structure of cement paste exhibits isotope effect. The structures arise from well-characterised chemical reactions as water diffuses through the porous material to bring about the water-surface interactions within the complex local geometry. The noteworthy observations point to the effect of hydrogen bonding on mesoscopic structure resulting from hydration although hydrogen bond with deuterium is only slightly stabler yielding a longer lifetime vis-a-vis bond involving hydrogen. Aforementioned investigations [1-10] also provide an explanation for disagreement with the hypothesis of dynamical scaling for hydration of cement with heavy water and is a step forward towards general understanding of hydration process.

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Submitting Author: smazu@barc.gov.in

CCP-SAS – a community consortium for the atomistic modelling of scattering data

Joseph E. Curtis[1], Emre Brookes[2], David W. Wright[3], Hailiang Zhang[4], Jianhan Chen[5], Stephen M. King[6], Paul Butler[1], Stephen J. Perkins[3]

[1] NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, Maryland, U.S.A. [2] University of Texas Health Science Center, Department of Biochemistry, San Antonio, Texas U.S.A. [3] Department of Structural and Molecular Biology, Darwin Building, University College London, Gower Street, London, U.K. [4] Department of Chemistry, University of Tennessee, Knoxville, Tennessee U.S.A. [5] Biochemistry and Molecular Biophysics, Kansas State University, Manhattan, Kansas U.S.A. [6] ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot U.K.

Email: joseph.curtis@nist.gov

The major infrastructural investment worldwide in multiuser X-ray synchrotrons and neutron sources during the last two decades has been immensely successful in allowing external (university and commercial) users to perform data collection on ever more challenging and important systems. There is however a need for the hardware investment to be matched by software developments. For example, macromolecular crystallography has been able to exploit the fruits of CCP4 software, and the result has been an explosion of new crystal structures.

In solution scattering, huge advances have been made in the throughput and accuracy of the experimental measurements. However, the software used to analyze, and in particular to model, this data has lagged behind. Closed-source non-atomistic approaches have been most beneficial for visualizing and rationalizing many problems. In order to realize the full benefit of instrumental investments, links to atomistic modelling approaches are needed to develop novel applications and address different classes of problems. This requires integrating the SANS and SAXS data with user-friendly, high-throughput, molecular modelling software in order to reveal how these structures change under varying experimental conditions. We are funded by the EPSRC and the NSF in a joint UK/USA collaboration called CCP-SAS (1). The goal is to produce a new generation of open-source software that facilitates atomistic modelling based on solution SANS/SAXS data.

We have implemented a web-based application incorporating the SASSIE and SCT suite of programs developed at NIST and UCL. The web-based technology was enabled through the development of the GenApp framework that enables automatic application generation for general scientific software programs that run on both standard and high-performance computing hardware. The web-based SASSIE program will be available for open-access (beta) testing from May 2015. The inclusion of analytical ultracentrifugation data for additional constraints will also be incorporated within the same framework using the popular US-SOMO suite. In order to ensure the long-term future of our code and its usability worldwide, we plan to make the software open source, easy to install and stable to use. We have completed several successful atomistic modellings with this package, and examples will be presented in other abstracts at this meeting. These indicate future new directions that will become possible with atomistic modelling in the CCP-SAS package.

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QUANTITATIVE ASSESMENT OF THE USEFUL ANGULAR RANGE FOR SMALL-ANGLE SCATTERING DATA FROM SOLUTIONS

P.V. Konarev[a] **and D.I. Svergun**[b]
[a]*Institute of Crystallography RAS, Leninsky pr. 59, 119333 Moscow, Russia*
[b]*EMBL, Hamburg Outstation, Notkestraße 85, 22603 Hamburg, Germany*

Small angle scattering of X-rays or neutrons (SAXS and SANS) usually rapidly decay with the scattering angle and very often, especially *e.g.* for biological systems, the contrast of the particles in aqueous solutions is rather small and the useful signal at higher angles may be weak compared to the background. This leads to low signal-to-noise ratio of the data especially at higher scattering angles. A question arises on how to determine the useful angular data range of the experimental scattering pattern that can be taken for the subsequent interpretation and model building. A usual practice is to use only the portion of the scattering curve where the signal-to-noise ratio exceeds a certain threshold but the choice of the threshold remains a rather subjective procedure. Also, relying only on the signal-to-noise ratio does not take into account the degree of oversampling of the data.

Here we propose an approach using the Shannon sampling [1] to determine the useful range in a given experimental scattering data from dilute monodisperse (or slightly polydisperse) systems. The range is defined *via* the number of Shannon channels that can be reliable determined from this data set. To establish a robust algorithm for the determination of this number, simulated data sets with different signal-to-noise ratio and different oversampling corresponding to typical X-ray and neutron scattering experiments are generated and analyzed. The algorithm is implemented in a computer program SHANUM and applied to experimental SAXS and SANS data sets recorded at various conditions and on various instruments. The proposed method is easy to incorporate into automated analysis pipelines, it can be employed to select fitting range in *ab initio* shape determination analysis and also during data deposition/publication to discard the portions of the (higher angles) SAXS/SANS data containing no useful information.

The authors acknowledge the support of the Bundesministerium für Bildung und Forschung (BMBF) project BIOSCAT, grant 05K20912.

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P.V. Konarev: konarev@ns.crys.ras.ru

X+: A COMPREHENSIVE STRUCTURE ANALYSIS TOOL FOR SOLUTION X-RAY SCATTERING FROM SUPRAMOLECULAR SELF-ASSEMBLIES

Uri Raviv

Institute of Chemistry, The Hebrew University of Jerusalem

Our software(*1*, *2*), X+, are the state-of-the-art for modeling supramolecular self-assembled structures. In this program, we are using geometric models of various shapes (for example, slabs, spheres, cylinders, or helixes), multi-layers or multi-shells of each shape with various sizes and/or electron density profiles. The models can be either isolated in solution or be subunits in a lattice, which is in solution. Using this program we modeled microtubules, assuming a hollow cylinder model that its wall has a Gaussian electron density profile (*1*). This program was very useful to determine tubulin alternative structures (*3*) as well as other self-assembled structures including lipid bilayers (*4*-*6*) or viruses (*7*).

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Submitting Author: uri.raviv@mail.huji.ac.il

TACKLING HIGH DATA RATES IN SAXS AND GISAXS

G. Benecke,[a,b] W. Wagermaier,[b] C. Li,[b] M. Schwartzkopf,[a] G. Flucke,[a] R. Hoerth,[b,c] I. Zizak,[d] M. Burghammer,[e,f] E. Metwalli,[g] P. Müller-Buschbaum,[g] M. Trebbin,[h] S. Förster,[h] O. Paris,[b,i] S. V. Roth[a] and P. Fratzl[b]
[a] *Deutsches Elektronen-Synchrotron, Notkestrasse 85, D-22607 Hamburg*
[b] *Dep. of Biomat., Max Planck Inst. of Coll. and Interfaces, Am Mühlenberg 1, D-14476 Potsdam*
[c] *Berlin-Brandenburg School for Regenerative Therapies (BSRT), Charité – Universitätsmedizin Berlin, Augustenburger Platz 1, D-13353 Berlin*
[d] *Helmholtz-Zentrum Berlin, Albert-Einstein-Strasse 15, D-12489Berlin*
[e] *European Synchrotron Radiation Facility, 6 Rue Jules Horowitz, F-38000 Grenoble*
[f] *Department of Analytical Chemistry, Ghent University, Krijgslaan 281, S12, B-9000 Ghent*
[g] *Lehrstuhl f. Funktionelle Materialien, Physik-Dep. E13, Techn. Univ. München, James-Franck-Strasse 1, D-85747 Garching*
[h] *University of Bayreuth, Physical Chemistry 1, 101251, D_95440Bayreuth*
[i] *Inst. f. Physik, Montanuniversität Leoben, Franz-Josef Strasse 18, A-8700 Leoben*

The large and constantly increasing amounts of data stemming from X-ray scattering experiments at synchrotron sources often is a limiting factor in the analysis of the data. This is due to the fact that appropriate software is rarely available to perform fast and tailored data processing. Moreover, online data reduction and analysis during the experiment are often necessary in order to interactively optimize experimental design. We present an open-source software package - DPDAK (directly programmable data analysis kit) – which is capable of processing large amounts of data from synchrotron scattering experiments. The data reduction processes involve calibration and correction of raw data, one- or two-dimensional integration, as well as fitting and further analysis of the data, including the extraction of certain parameters. The software is based on a plug-in structure and allows individual extension in accordance with the requirements of the user. We demonstrate the use of DPDAK for on- and offline analysis of scanning small-angle X-ray scattering (SAXS) data on biological samples and microfluidic systems, as well as for a comprehensive analysis of grazing-incidence SAXS data. We discuss the structure of DPDAK and the possibilities, limitations, and future capabilities. [1]

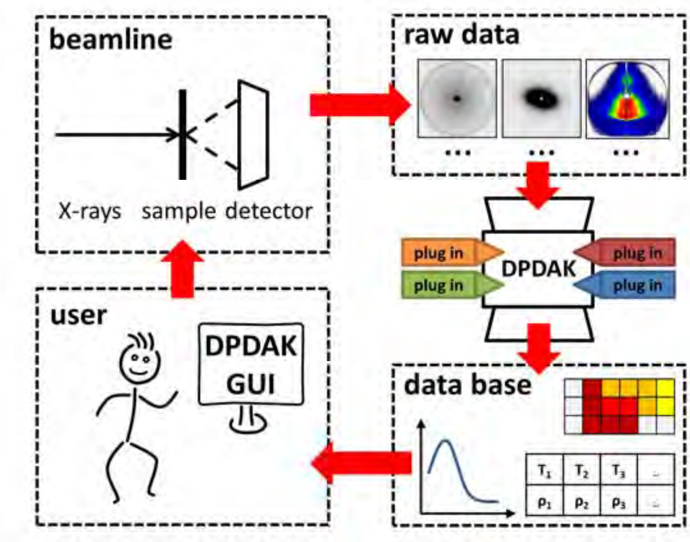

Figure 1: Plug-in concept of DPDAK [1].

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Submitting Author: stephan.roth@desy.de

STUCTURAL INVESTIGATIONS OF DETONATION NANODIAMONDS BY SMALL-ANGLE NEUTRON SCATTERING

O.V Tomchuk[a,b], **M.V. Avdeev**[a], **V.L. Aksenov**[c,a], **L.A. Bulavin**[b] **and V.M. Garamus**[d]
[a]*Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research,*
Joliot-Curie-Str. 6, 141980 Dubna, Russian Federation
[a]*Physics Department, Taras Shevchenko National University of Kyiv,*
Volodymyrska-Str.-64, 01601 Kyiv, Ukraine
[c]National Research Centre 'Kurchatov Institute', Academician Kurchatov Square 1,
123182 Moscow, Russian Federation
[d]*Centre for Materials and Coastal Research, Helmholtz-Zentrum Geesthacht,*
Max-Planck-Str., D-215 02 Geesthacht, Germany

Experimental structural studies of detonation nanodiamonds (DND) were made using the small-angle neutron scattering (SANS) [1-3]. DND are formed during an explosion of oxygen-imbalanced explosives. The DND particles are diamond crystallites with a typical size of less than 10 nm. The extremely large specific surface area and some spectral properties of DND together with their high biocompatibility make them very attractive material for nanotechnology. The intensive present day research is associated with purification and synthesis of stable DND suspensions based on various solvents.

SANS allows one to obtain rather full structural information about the multi-level organization of the DND suspensions due to sufficiently high contrast between DND and solvents and availability of stable concentrated solutions, which makes it possible to apply the contrast variation technique. It is shown that DND particles in suspensions form stable and reproducible branched clusters with a wide size distribution (size 10-100 nm and above). The mechanism of clusters formation is close to the diffusion-limited aggregation (observed fractal dimension range 2.3-2.5) independent of the type of stabilization, producer, series of samples and even their surface modifications. The interaction between clusters is of repulsive character but the developed structure allows the interpenetration of the aggregates in concentrated solutions, which leads at some concentration to a reversible transition to a micro-gel state.

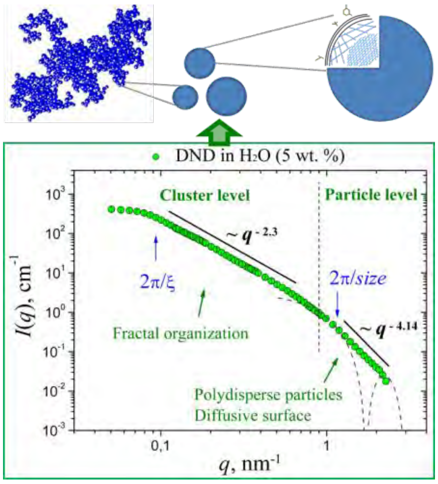

Figure 1: Structural level of DND suspensions as seen by SANS.

The DND particles themselves are highly polydisperse (size range of 2-10 nm) and have a non-uniform inner structure. There is almost a continuous spatial transition from diamond inner states to graphitic surface states over the whole crystallite volume. It can be parameterized in terms of the power-law type radial distribution function of scattering length density and is responsible for the diffusive properties of the particle surface observed in scattering experiments as a specific deviation from the Porod law.

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Submitting Author: tomchuk@jinr.ru

ANALYSIS OF THE CRITICAL CASIMIR EFFECT IN BINARY LIQUID MIXTURES BY VERY SMALL ANGLE NEUTRON SCATTERING (V-SANS)

G. Goerigk[a], N. Grimm[a], D. Wallacher[a], J. Groth[a], Y. Lu[a], M. Ballauff[a] and V. Pipich[b]
[a]*Helmholtz-Zentrum Berlin GmbH, Albert-Einstein-Str. 15, D-12489 Berlin, Germany*
[b]*Jülich Centre for Neutron Science (JCNS), Forschungszentrum Jülich GmbH Outstation at MLZ, Lichtenbergstr. 1, D-85747 Garching, Germany*

Confining structures in fluctuating media cause Casimir-like forces. Near the continuous phase transition of such a critical medium the corresponding order parameters cover all length scales and in the neighborhood to the critical point universality occurs i.e. the critical phenomena become to a large extent independent of the microscopic (atomistic) details of the system under investigation. Recently theoretical and experimental results have been reported on the direct measurement of the critical Casimir forces by total internal reflection microscopy (TIRM) [1] and confocal microscopy [2]. As a soft-matter analogue of the quantum-electrodynamic Casimir effect, the confinement of the concentration fluctuations within a near-critical binary liquid mixture by the surfaces of colloidal particles results in an attractive or repulsive interaction [3].

Because the spatial extension of critical fluctuations diverges when approaching the critical temperature, the confinement of such large correlations cause Critical Casimir forces between large scale structures in the micrometer range (i.e. between large colloids immersed in a critical mixture) which can be analyzed for instance by V-SANS (Very Small-Angle Neutron Scattering). V-SANS experiments are highly sensitive to the structure factor of large colloids thereby giving access to the attractive respectively repulsive forces between them.

In a 1st step the divergence of the critical correlation length of a critical D_2O(72%)/2.6-Lutidine(28%) mixture for selected temperatures near the critical point T_C have been measured with the V-SANS instrument KWS3@FRM II [4]. For this purpose a sample cell was developed, which meets the special requirements of the neutron beam at KWS-3 providing a temperature stability of 1 mK at RT. Results are presented which deduce the critical exponent ν from the correlation length via $\xi \sim T_C^{\nu}/(T_C-T)^{\nu}$. In a 2nd step the critical Casimir forces between large colloids acting upon the critical mixture are analyzed.

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G. Goerigk: guenter.goerigk@helmholtz-berlin.de

NANOMETER-SIZE POLYOXOMETALATES ANIONS ADSORB STRONGLY ON NEUTRAL SOFT SURFACES

Pierre Bauduin[a], Bappaditya Naskar[a], Veronique Nardello-Rataj[b], Olivier Diat[a]
[a]Institut de Chimie Séparative de Marcoule (ICSM)
UMR 5257 (CEA/CNRS/UM/ENSCM)- bat. 426, BP 17171, 30207, Bagnols sur Céze, France
[b]Université Lille Nord de France, Université Lille 1, EA 4478, Chimie Moléculaire et Formulation, F-59655 Villeneuve d'Ascq, France

Polyoxometalates (POMs) are nanometric metal-oxide anions with unique chemical and physical properties.[1] During the last ten years, significant efforts have been made to graft alkyl chains on POMs to acquire surface activity and self-assembly properties, which is essential for catalysis applications and for producing organic-inorganic hydrid materials with desired nanostructures.[2-3] We show here that POMs based surfactants are produced spontaneously through non-covalent interactions in water by simply mixing non-ionic surfactants with a POM using SAXS method onto a Xenocs bench and modelling the CMC variation. The most common POMs of Keggin's type, tungstosilicate (SiW12O404-) and tungstophosphate (PW12O403-), have indeed an unexpected strong tendency to adsorb on polar and electrically neutral interfaces i.e. here on water-micelle and water-air interfaces [4]. The highlight of this general property of POMs deepens our understanding of the many biological effects of POMs, such as their antiviral and antitumor activities.

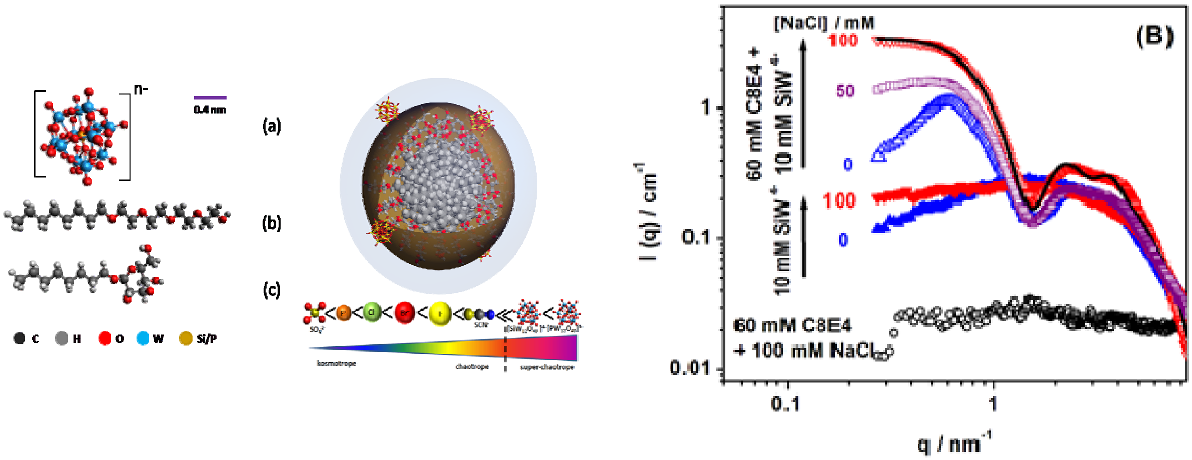

Figure 1 – Chemical structures of (a) POM: [SiW12O40]4- (SiW4-) or [PW12O40]3- (PW3-); n = 4 (Si) and 3 (P), (b) tetraethyleneglycol monooctyl ether (C8E4), and (c) n-octyl-b-D-monoglucoside (C8G1). Sketch of a C8G1 micelle covered by a POM anion. Hofmeister's series from kosmotropic (salting-out) to chaotropic (salting-in) anions, POM were found to act as super-chaotropic anions. SAXS spectra of POM decorated micelles

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Submitting Author: olivier.diat@cea.fr

SOME GLOBULAR PROTEINS UNFOLDES BY SDS CAN BE REFOLDED BY ADDITION ON NONIONIC SURACTANTS: A SAXS STUDY

A. Søndergaard[a], Daniel E. Otzen[b], and J.S. Pedersen[c]

[a] *Interdisciplinary Nanoscience Center (iNANO) and Department of Chemistry, Aarhus University, 8000 Aarhus C, Denmark*
[b] *Interdisciplinary Nanoscience Center (iNANO) and Department of Molecular Biology and Genetics, Center for Insoluble Protein Structures (inSPIN), Aarhus University, 8000 Aarhus C, Denmark*

Sodium dodecyl sulphate (SDS) is a rather aggressive surfactant and the globualar protein Bovine Serum Albumin (BSA), α-Lactalbumin (αLA), β-lactoglobulin (β –LG), and lysozyme (LYZ) denature and unfold when exposed to SDS. In a previous study, it was shown that the non-ionic surfactant, octaethylene glycol monododecyl ether (C12E8) has a protective effect against unfolding by SDS, as BSA was found not to unfold when exposed to mixtures of SDS and C12E8 [1]. In the present study we decided to investigate whether the protein-surfactant complexes formed when BSA, αLA β –LG and LYZ are unfolded by SDS could be refolded when increasing amounts of C12E8 are added.

Small-angle X-ray scattering (SAXS) measurements were performed in order to provide structural descriptions of the pure SDS micelles, the mixed micelles, and the protein-surfactant complexes. Circular Dichroism (CD) measurements were done in order to provide complementary information regarding the structural changes of secondary structure of the proteins. Especially changes in the α-helical content, when exposed to SDS alone or to SDS and C12E8 were investigated by CD.

The SAXS data collected showed that all proteins are denatured by SDS and modelling on absolute scales shows that the systems form core-shell particle. The core consists of the SDS tails and the shell consists of the SDS head groups and the protein. The modelling gives additional information on surfactant aggregation numbers and number of proteins per complex. Addition of the nonionic surfactant to the protein-SDS complexes led BSA and β-LG to refold, and thus C12E8 is able to extract the SDS from the proteins and make them refold. In contrast, α-LA and LYZ did not refold when nonionic surfactant were added to the protein-SDS-complexes.

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Submitting Author: jsp@chem.au.dk

SURFACTANT-FREE MICROEMULSIONS AS INTERFACELESS DICHOTOMIC SOLVENTS

O. Diat[b], **S. Prévost**[c], **J. Marcus**[a], **T. Lopian**[a,b], **D. Touraud**[a], **Th. Zemb**[b] **and W. Kunz**[a]
[a] *Institute of Physical and Theoretical Chemistry, University of Regensburg, Universitätsstraße 31, D-93040 Regensburg, Germany*
[b] *Institut de Chimie Séparative de Marcoule (ICSM), UMR 5257 (CEA/CNRS/UM2/ENSCM), F-30207 Bagnols-sur-Cèze, France*
[c] *ESRF – The European synchrotron, 71 avenue des Martyrs, F-38000 Grenoble, France*

The phase diagrams of ternary mixtures of partly miscible solvents exhibit large monophasic areas. When approaching the immiscibility gap, in a region we dubbed "pre-Ouzo", nm-scale fluctuations of composition are observed by Small Angle Scattering techniques.

The pre-Ouzo region corresponds to a range of composition where a micro-emulsion separates under moderate centrifugation, and shows the presence of an interfacial accumulation of the hydrotrope molecule, in most cases ethanol, that produces a labile interfacial film between oil-rich domains and water-rich domains of nanometric size.

We performed complementary SWAXS (Small and Wide Angle X-ray Scattering), SANS (with contrast variation) as well as DLS and SLS to elucidate the structure of these surfactant-free micelles,[1,2] and we corroborated these results with molecular dynamics simulations.[3,4]

A striking characteristic of these domains is the absence of a sharp interface, and correspondingly the scattering spectra are modelled by a Lorentzian profile according to the Ornstein-Zernicke formulation for composition fluctuations. Pre-ouzo formulations are an excellent substrate for enzymatic reactions, separation chemistry as well as organic synthesis.

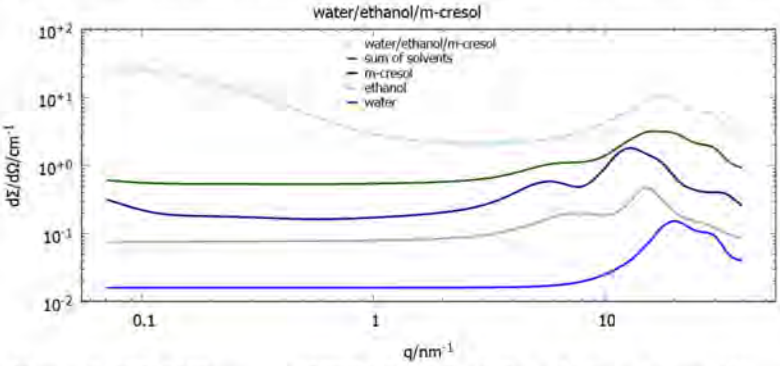

Figure 1: SWAXS spectra (ID02@ESRF) of, from bottom to top, (1) water, (2) ethanol, (3) m-cresol, (4) the volume fraction weighted sum of these solvents, and (5) the ternary mixture in the pre-Ouzo region exhibiting a large scattering intensity at low q modelled as a Lorentzian.

Far from being restricted to some particular ternary mixtures, we propose that these surfactant-free micro-emulsions are in fact ubiquitous, and only need a hydrotrope as cosolvent between two immiscible phases, with a quasi-equilibrium between formation of an interfacial film and water/solvent partition of the hydrotrope. We will show how hydration forces are responsible for the stability of these micelles, and the possible manipulations of their static structure and dynamics e.g. by tuning electrostatic interaction or encapsulating hydrophobic compounds or large biomolecules.

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Olivier Diat: diat@cea.fr

HIERARCHICAL SOFT MATTER SYSTEMS: STRIPED VESICLES, CUBOSOMES AND HEXOSOMES

Liliana de Campo[a,c], Minoo Moghaddam[b], Christine Rehm[a], Trond Varslot[c], Nigel Kirby[d], Chris Garvey[a], Rainer Mittelbach[c], and Stephen Hyde[c]
[a]*ANSTO, Bragg Insitute, Sydney, Australia*
[b]*CSIRO, North Ryde, Australia*
[c]*Australian National University, Canberra, Australia*
[d]*Australian Synchrotron, Clayton, Australia*

Cubosomes and hexosomes are hierarchically organized materials, where sub-micron sized dispersed particles contain an internal liquid crystalline nanostructure. [1] This nanostructure is usually based on lipids that self-assemble due to their amphiphilic character, i.e., they have two immiscible parts linked together in the same molecule.

As an extension, we have been developing star-polyphiles, which are small lipid-like molecules, but with three mutually immiscible parts (a hydrophilic, hydrocarbon and fluorocarbon chain) attached to a common center (Fig1). [2-4]

Here we present our combined USANS/SANS/SAXS study of vesicles, cubosomes and hexosomes based on star-polyphiles, which show hierarchical ordering on three length scales: submicron-sized particles with internal liquid crystalline phase, in which the membrane of the liquid crystals consists of hydrocarbon and fluorocarbon stripes.

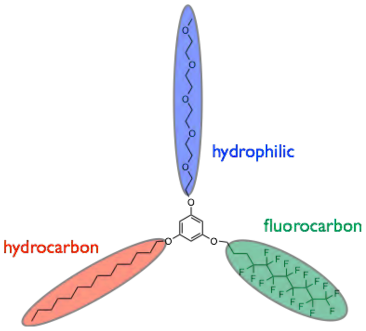

Fig.1 Star-polyphile molecule

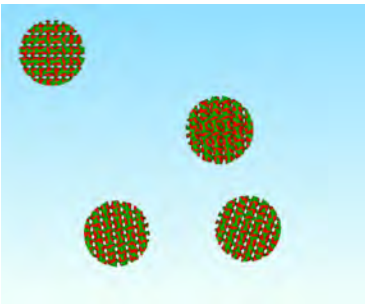

Fig.2
Schematic picture of striped cubosomes

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Submitting Author: liliana.decampo@ansto.gov.au

MEASUREMENT OF THE BURIED STRUCTURE OF BLOCK COPOLYMER LITHOGRAPHY PATTERNS USING RESONANT X-RAY SCATTERING

D.F. Sunday, A.F. Hannon, C. Liman, and R.J. Kline
National Institute of Standards & Technology, 100 Bureau Dr., Gaithersburg, MD 20899, USA

The semiconductor industry is pushing the limit for patterns made using conventional optical lithography. New lithographic methods are required for the continued shrinking of the feature sizes of the nanostructures in integrated circuits. One of the potential technologies being evaluated as a next generation lithographic method is block copolymer (BCP) lithography using directed self assembly. BCP lithography uses a chemical or topographic template to direct the orientation of the BCP domains during self assembly. The dimension of the pattern are defined by the chemistry of the BCP. The prototypical BCP lithography system is PS-b-PMMA for making patterned lines with sub-30 nm pitch. One of the greatest challenges for implementing BCP lithography in the semiconductor industry is reduction of defects and the development of metrology methods that can differentiate between the PS and PMMA phases. This is particularly important because theoretical modeling predicts cases where the top surface of the BCP appears to have well defined lines, but the buried structure of PS and PMMA domains is quite complex. Conventional measurement methods such as electron microscopy and X-ray scattering have very little contrast between the blocks without physically altering them by etching or staining.

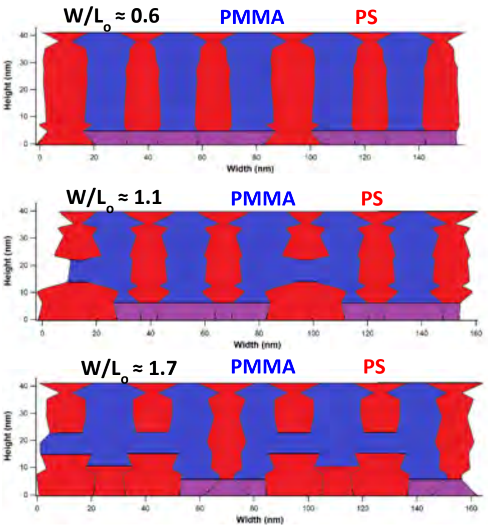

Fig. 1 – 2D shape profiles determined for 3 different template conditions for PS-b-PMMA.

We report on the application of soft X-rays to obtain resonant scattering contrast between the two phases and are able to solve the resulting diffraction pattern to determine the original buried structure of the block copolymer.[1] The method is equivalent to variable-angle transmission small angle X-ray scattering where single crystal diffraction from nanopattern grating is used to determine the size and shape of the nanopattern.[2] We used resonant scattering at the carbon, oxygen, and nitrogen edge to obtain scattering contrast for several BCP systems. The near-edge contrast comes from differences in molecular bonds present in the different blocks. We were able to determine the buried structure of a variety of BCP systems where the top surface was different from the bulk (fig. 1). Our results matched well with theoretical predictions for the structure based on the process parameters.

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Submitting Author: joe.kline@nist.gov

IN-SITU GISAXS INVESTIGATION OF ALUMINUM THIN FILM GROWTH ON NANOSTRUCTURED DIBLOCK POLYMER SUBSTRATES

B. Beyersdorff[a], M. Schwartzkopf[a], D. Chekrygina[b], V. Cantelli[c], E. Metwalli[d], S. Xia[d], W. Wurth[b], C. Bähtz[c], P. Müller-Buschbaum[d] and S. V. Roth[a]
[a]Deutsches Elektronen-Synchrotron DESY, Notkestraße 85, D-22607 Hamburg, Germany
[b]Universität Hamburg, Jungiusstraße 9, D-20355 Hamburg, Germany
[c]Helmholtz-Zentrum Dresden-Rossendorf, Bautzner Landstr. 400, D-01328 Dresden, Germany
[d]Physikdepartment, Lehrstuhl für Funktionelle Materialien, Technische Universität München, James-Franck-Straße 1, D-85747 Garching, Germany

Targeted installation of nanostructured metal films for application devices is of utmost importance in many areas of modern science and technology, including organic photovoltaics and sensors [1,2]. Sputter deposited Aluminum is frequently employed in nanotechnology for sensors, e.g. surface-enhanced Raman Scattering (SERS), as well as a contact layer material in organic-electronics and organic photovoltaics [3]. When installing a metal layer on a nanostructured diblock polymer substrate, a variety of processes occur such as selective wetting of specific polymers and embedding of metal atoms into the polymer. These processes lead to a strongly meso- and nanostructured metal film as well as to changes in the thin polymeric layer [4,5].

We report on the formation of Aluminum (Al) nanoclusters and a subsequent Al layer formation by sputter deposition on a poly(styrene-block-methylmethacrylate) [P(S-b-MMA)] diblock copolymer thin film by means of grazing incidence small-angle X-ray scattering (GISAXS) performed at the ROBL-BM20 beamline at ESRF. The resulting GISAXS pattern yield information on the different growth regimes during nanostructural evolution on the polymer substrate as well as on the existence of an embedding layer on the diblock copolymer substrate.

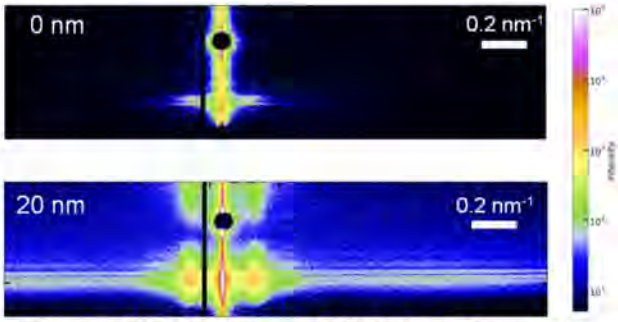

Figure 1: GISAXS images of diblock copolymer thin film before and after sputter deposition of 20 nm Al.

Complementary to GISAXS, X-ray reflectivity (XRR) gives access to analyzing the roughness and thickness of the embedding layer at different Al coverages.

Furthermore, the morphological characterization is completed by atomic force microscopy (AFM) and scanning electron microscopy (SEM) in order to connect the scattering patterns with real space observations.

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Submitting Author: bjoern.beyersdorff@desy.de

IN-SITU SAXS AND X-RAY TRANSMISSION AS COMPLEMENTARY TOOLS TO STUDY ION ELECTROSORPTION IN CHARGED NANOCONFINEMENT

C. Prehal[a], **M. Burian**[b], **H. Amenitsch**[b], **R. T. Lechner**[a], **V. Presser**[c,d] **and O. Paris**[a]
[a]*Institute of Physics, Montanuniversität Leoben, Franz-Josef Straße 18, 8700 Leoben, Austria*
[b]*Institute of Inorganic Chemistry, Graz University of Technology, Stremayrgasse 9/IV, 8010 Graz, Austria*
[c]*INM – Leibniz Institute for New Materials, Campus D2 2, 66123 Saarbrücken, Germany.*
[d]*Department of Materials Science and Engineering, Saarland University, Campus D2 2, 66123 Saarbrücken, Germany*

A fundamental understanding of ion transport and electrosorption in nanoporous confinement is important for a variety of different fields, like energy storage or capacitive de-ionization. Supercapacitors are devices used for efficient energy storage, where the opposed charges at the electrode-electrolyte interface within highly porous carbons reveal a huge capacitance and hence a large amount of electrostatically stored energy. However, information on the mechanism how ions facilitate charge storage is limited using conventional electrochemical methods. In-situ scattering methods allow a direct probing of ion transport phenomena being sensitive to scattering length density changes within the nanopores.

We employ in-situ small angle X-ray scattering (SAXS) and X-ray transmission (XRT) measurements to study ion re-arrangements within the disordered, nanoporous structure of carbon based supercapacitors. While applying various voltage signals to the supercapacitor in-situ cell via a Potentiostat, the SAXS pattern and corresponding transmission value are recorded simultaneously with a time resolution of seconds. It turns out that the experimentally easy accessible transmission signal is very useful to calculate cation and anion concentration changes upon charging or discharging.

Although the SAXS intensity of disordered, nanoporous carbons is rather featureless, the intensity changes upon charging contain a rich amount of information (see Fig. 1: a carbide derived carbon (CDC) electrode with 1M aqueous CsCl electrolyte). Using different aqueous electrolytes we were able to vary the X-ray contrast of the individual ions, while the actual electrosorption mechanism remains essentially the same. This contrast variation approach helps to unravel the complex SAXS intensity changes. Beside the *global* information on ion transport obtained from XRT, the in-situ SAXS signals allow us to track the *local* re-arrangement of ions across the nanopores. By using a simple two-phase model, the preferred adsorption of ions near the pore walls (*local ion re-arrangement*) can be modeled by an effective decrease of the pore width in the electron density profile of a nanopore [1].

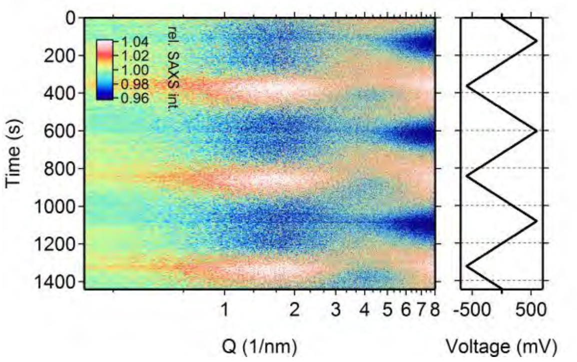

Figure 1: Change of the SAXS intensity visualized in a color coded plot (Time vs. Q) as a function of the applied voltage (right).

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Submitting Author: christian.prehal@unileoben.ac.at

ENTROPY DRIVEN TWO-DIMENSIONAL BINARY SUPERLATTICE OF A SWNT/CYLINDERICAL-MICELLAR SYSTEM

S.-M. Choi[a], **S.-H. Lim**[a], **H.-S. Jang**[a], **J.-M. Ha**[a], **T.-H. Kim**[b], **P. Kwasniewski**[c],
T. Narayanan[c], **and K.S. Jin**[d]

[a]*Dept. of Nuclear and Quantum Engineering, KAIST, Daejeon, 305-701, Republic of Korea*
[b]*Neutron Science Division, KAERI, Daejeon 305-353, Republic of Korea*
[c]*European Synchrotron Radiation Facility, Grenoble, 38043, France,*
[d]*Pohang Accelerator Laboratory, Pohang, 790-784, Republic of Korea*

Synthesis of binary or multicomponent superstructures of nanoparticles, which may provide new emerging properties through synergetic coupling between different types of nanoparticles, are of great interests for various potential applications as well as its own scientific merit. Recently, exciting progresses have been made for the fabrication of binary or ternary spherical nanoparticle superlattices with various symmetries using solvent evaporation or programmed DNA. However, systematic experimental studies on the mixtures of two different types of 1D nanoparticles to form highly ordered binary superlattices have been very rare and the reported structures have been limited to simple liquid crystalline structures such as nematic ordering. In this talk, a hierarchically self-assembled intercalated hexagonal binary superlattice of hydrophillically functionalized single wall carbon nanotubes (p-SWNTs) and surfactant (C12E5) cylindrical micelles investigated by small angle neutron and x-ray scattering [1] will be presented together with a brief overview of highly ordered self-assemblies of 1D nanoparticles in block copolymer [2,3] and lipid [4] systems.

When p-SWNTs (with a diameter slightly larger than that of the C12E5 cylinders) were added to the hexagonally packed C12E5 cylindrical-micellar system, p-SWNTs positioned themselves in such a way that the free volume entropies for both p-SWNTs and C12E5 cylinders were maximized, thus resulting in the intercalated hexagonal binary superlattice. In this binary superlattice, a hexagonal array of p-SWNTs is embedded in a honeycomb lattice of C12E5 cylinders. The intercalated hexagonal binary superlattice can be highly aligned in one direction by an oscillatory shear field and remains aligned after the shear is removed. The understanding obtained in this study may provide new insights for designing new methods for synthesizing highly ordered binary or multicomponent superlattices of other 1D nanoparticles (such as metallic, semiconducting, and magnetic nanorods which are of great current interests) with new synergetic functionalities.

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Sung-Min Choi : sungmin@kaist.ac.kr

CORRELATION MAP: KNOWING THE DIFFERENCE

D. Franke[a], **C. M. Jeffries**[a] **and D. I. Svergun**[a]
[a]*European Molecular Biology Laboratory, Notkestr. 85 c/o DESY, 22607 Hamburg, Germany*

Small Angle Scattering (SAS) is a universal technique to study the nanostructure of disordered systems. SAS analysis, e.g. of macromolecular solutions, are nowadays highly automated, generating unprecedented amounts of scattering data and structural models. A vital component of data interpretation is to provide adequate answers to the questions “Are these data sets identical?” or “Does this model fit the data?”. Traditionally, quantitative assessments of similarity between independent data sets, or between models and data, have been performed using the reduced χ^2 test, which in addition to the provision of experimental data and fit, also requires that the experimental errors have been correctly estimated. However, error estimates can be difficult to ascertain, potentially rendering statistical comparisons invalid.

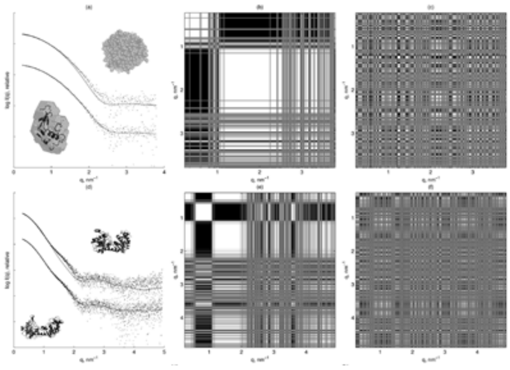

Figure 1. CorMaps (right) calculated for experimental data and model fits (left). CorMap highlights misfit regions and quantifies similarity.

Due to the lack of viable alternatives to the reduced χ^2 test, investigators may discard unlikely test outcomes, e.g. due to incorrect error estimates, and apply empirical decision rules instead. Such decision rules may lack statistical validity, leading to incorrect data interpretation.

Here we present the Correlation Map (CorMap), an approach that sidesteps the problem of explicit error estimation [1]. This pair-wise test only takes into account the distribution of signs of the residuals, but maintains a statistical power to detect differences comparable to that of the reduced χ^2 test. Figure 1 depicts a visual representation of the test. Large black or white ‘patches’ appearing in the CorMap panels are indicative of systematic deviations between one dataset and another; a randomised lattice pattern indicates a good fit to the data. Based on the size of the largest patch, exact probabilities of difference in data-data and data-model fits can be deduced [1].

We conducted extensive simulation studies to compare the statistical validity and power of the CorMap with the reduced χ^2 test and the recently proposed χ^2_{free} resampling variation test [2]. CorMap shows a statistical power to detect systematic deviations comparable to that of a valid reduced χ^2 test. Notably, when correct error estimates are provided, the reduced χ^2 test and χ^2_{free} are identical, i.e., χ^2_{free} affords no advantage over the χ^2 test. In turn, if no, or incorrect, error estimates are available, both the reduced χ^2 and χ^2_{free} tests are invalid whereas the CorMap always maintains its power to detect differences. The proposed approach can be used not only for SAS and also for other physical experiments yielding one dimensional oversampled data.

This work was supported by the Bundesministerium für Bildung und Forschung project BIOSCAT, Grant 05K12YE1, and by the European Commission, BioStruct-X grant 283570.

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Submitting Author: franke@embl-hamburg.de

SAXS INVESTIGATION OF VIMENTIN ASSEMBLY AND BUNDLING: CONTINUOUS AND SEGMENTED MICROFLUIDICS APPROACH

O. Saldanha[a], **M. Brennich**[a,b], **C. Hémonnot**[a], **R. Graceffa**[a] **and S. Köster**[a]
[a]*Georg-August-University, Institute for X-ray Physics, Friedrich-Hund-Platz 1, 37077 Göttingen, Germany*
[b] current address: *Structural Biology Group, ESRF, Grenoble, France*

Mechanical support in eukaryotic cells is provided by a class of cytoskeletal fibrous proteins, called intermediate filaments (IFs), together with actin filaments and microtubules. Vimentin, a member of this protein family, is found in cells of mesenchymal origin. Vimentin filaments, like other IFs, are made up of monomers containing a centrally placed α-helical domain flanked by non-structured head and tail domains. *In vitro*, these rod-like IF monomers assemble in a hierarchical manner to form µm-long filaments with a diameter of about 10 nm [1,2] and, upon addition of additional ions, form bundles and networks [3-5]. Interestingly, many of the distinct mechanical properties of IFs seem to be encoded in their specific architecture; however, the precise assembly mechanisms leading to this architecture are still under study.

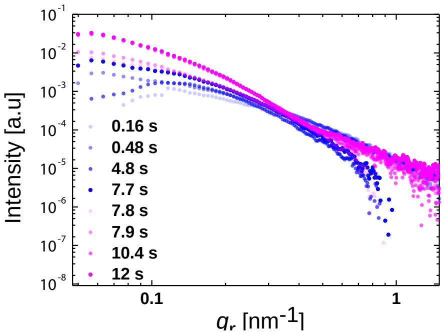

Figure1: SAXS profiles seen due to the effect of KCl (blue) and MgCl$_2$ (pink).

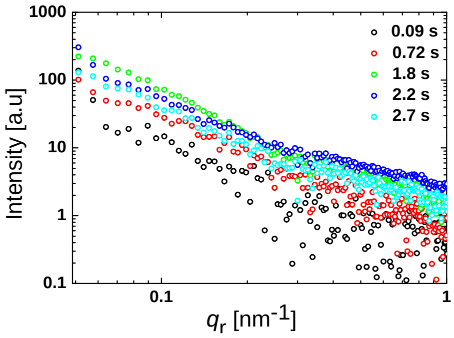

Figure2: SAXS profiles seen due to the effect of KCl in droplets

Our interest is to access the relevant time and length scales of vimentin assembly in the presence of monovalent K$^+$ ions and the bundling process in the presence of Mg^{2+}. Previously, we have performed bulk SAXS studies on vimentin assembled in the presence of mono- and divalent ions [2], as well as microscopy studies on network aggregation in microfluidic droplets [3-5]. Here, we employ small angle X-ray scattering (SAXS) in combination with (i) continuous microflow (Figure 1) and (ii) droplet microfluidics (Figure 2). The continuous flow approach offers the possibility of successive mixing in of different ion species with precise control, whereas the droplet flow technique enables us to encapsulate the micro-reaction in a unique picoliter environment. Both complementary approaches ensure decreased radiation damage as compared to bulk SAXS due to the flow. Given the sensitivity of SAXS measurements to the size of the molecular aggregates, we can distinguish between different stages of the hierarchical architecture and relate the structural results to the flow conditions in the device, thus quantifying the time scales involved in the assembly and aggregation process.

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Submitting Author: oliva.saldanha@phys.uni-goettingen.de

MECHANISM OF FATTY ACID COMPLEXATION WITH PROTEINS STUDIED BY SMALL ANGLE X-RAY SCATTERING

H. V. Sørensen[a], **J. N. Pedersen**[a], **B. Plazzotta**[b] **J. S. Pedersen**[b] **and D. E. Otzen**[a]
[a]Interdisciplinary Nanoscience Center, Department of Molecular Biology, Faculty of Science, University of Aarhus, Gustav Wieds Vej 14, 8000 Aarhus, Denmark
[b]Department of Chemistry and Interdisciplinary Nanoscience Center (iNANO), Aarhus University, Gustav Wieds Vej 14, 8000 Aarhus C, Denmark

Since the discovery of the complex HAMLET (human α -lactalbumin made lethal to tumour cells) between the milk protein human α-lactalbumin and the fatty acid oleic acid[1], which shows targeted cytotoxicity towards tumor cells[1], HAMLET-like complexes have attached great research interest. In the HAMLET complex, human α-lactalbumin is partly unfolded[2], suggesting that the cytotoxicity of HAMLET is not associated with the native functionality of the α-lactalbumin protein. Complexes similar to HAMLET have been made by combining oleic acid with other proteins like bovine serum albumin and β-lactoglobulin, proteins with different shapes and functionality[3][4]. We and others suggest that the cytotoxicity of these protein-fatty acid complexes towards cells is related to the fatty acid, and that the proteins' main function is the delivery of the fatty acid to the cells[3][5].

We have carried out extensive small angle X-ray scattering (SAXS) studies to determine the structure of these protein-fatty acid complexes (also called liprotides[4]), and have derived a model, where a cluster of fatty acid makes up a core (a micelle-like structure) and the partly unfolded protein is attached on the outside, forming a shell around the fatty acids[4]. For sufficiently high molecular mass proteins, a single protein can bind several clusters of fatty acids forming a beads-on-a-string structure[4]. The stoichiometry between fatty acid and protein as well as the number of beads in the structure varies between proteins[3].

The present study uses SAXS to investigate complex formation between proteins and oleic acid over time at different temperatures. SAXS allows us to see the transition from native protein to liprotide, which happens within minutes. The influence of different temperatures on the final structure as well as the structural changes over time has been investigated. Furthermore the changes in structure when cooling down to room temperature have been studied, as well as the stability of the liprotides over time. The proteins used in the study are bovine serum albumin, ovalbumin and bovine α-lactalbumin.

We find that the temperature at which the protein and fatty acid are incubated influences the final structure of the liprotide and in particular on the number of fatty acids bound per protein. Furthermore, cooling down the complexes results in a decrease in the level of fatty acid bound per protein.

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Henrik Vinther Sørensen: henrikvinther@live.dk

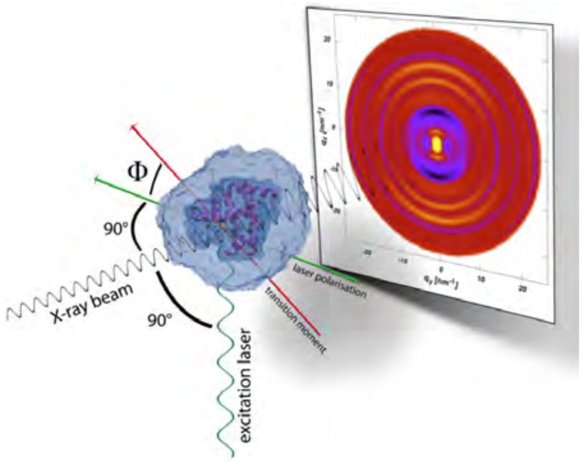
INTERPRETATION OF SWAXS DATA BY EXPLICIT-SOLVENT MOLECULAR DYNAMICS

Po-chia Chen[a], Levin Brinkmann[a], Christopher J. Knight[a], and Jochen S. Hub[a]
[a] *Georg-August-University Göttingen, Institute for Microbiology and Genetics,*
Justus-von-Liebig-Weg 11, 37077 Göttingen, Germany

Small and wide angle X-ray scattering (SWAXS) and molecular dynamics (MD) simulations are complementary approaches that probe conformational transitions of biomolecules in solution, even in a time-resolved manner. However, the structural interpretation of the scattering signals is challenging, while MD simulations frequently suffer from incomplete sampling or from a force field bias.

To combine the advantages of both techniques, we present a method that incorporates SWAXS data as an energetic restraint into explicit-solvent MD simulations, termed SWAXS-driven MD, with the aim to direct the simulation into conformations satisfying the experimental data. Because the calculations fully rely on explicit solvent, no fitting parameters associated with the solvation layer or excluded solvent are required, and the calculations remain valid at wide angles [1-2]. The underlying prediction of SWAXS curves based on explicit-solvent MD is now freely available on the webserver WAXSiS [3].

The complementarity of SWAXS and MD is illustrated using three biological examples, namely a periplasmic binding protein, aspartate carbamoyltransferase, and a nuclear exportin. The examples suggest that SWAXS-driven MD is capable of refining structures against SWAXS data without foreknowledge of possible reaction paths. In turn, the SWAXS data accelerates conformational transitions in MD simulations and reduces the force field bias.



Time-resolved WAXS is an emerging technique to probe conformational transitions of biomolecule up to picosecond resolution, yet the interpretation of the signals as remained challenging. We use explicit-solvent MD to predict both isotropic and anisotropic time-resolved WAXS patterns [4]. The new methodology is used to probe if conformational transitions in protein crystals are compatible with the transitions in solution.

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Submitting Author: jhub@gwdg.de

AN APPROACH TO ESTIMATE RESOLUTION OF SAXS-BASED *AB INITIO* MODELS OF BIOLOGICAL MACROMOLECULES

Anne Tuukkanen[a], Gerard Kleywegt[b] and Dmitri I. Svergun[a]
[a]EMBL Hamburg, Notkestrasse 85, 22607 Hamburg, Germany
[b]EMBL-EBI, Wellcome Genome Campus, Hinxton, Cambridge, CB10 1SD, United Kingdom

Small-Angle X-ray Scattering (SAXS) is becoming an increasingly common method in the characterization of biological macromolecules due to the availability of novel data analysis algorithms and its wide applicability to systems that are difficult to study by other means, for example large protein assemblies or intrinsically disordered proteins. Often, no prior structural knowledge about the studied molecule is available and structural models are generated using solely SAXS data by employing computational *ab initio* methods [1,2]. The first *ab initio* approaches used an angular envelope function to describe the global shape of a molecule. Recently developed bead-modeling techniques produce more detailed models at a resolution of about 10 to 20 Å. In the latter case, a molecule is represented as a densely packed assembly of beads whose theoretical scattering profile fits optimally the measured SAXS data.

Despite the wide usage of SAXS in structural studies by the biological community, at the present no objective resolution criteria or structural assessment tools such as available for X-ray crystallographic or NMR structures are present for SAXS-based models. Validation of *ab initio* models is an essential issue with respect to the growing interest to make them available in the Protein Data Bank. To address these problems, we present an approach to evaluate the resolution of an *ab initio* reconstruction using an ensemble of structural models. The approach was benchmarked against a set of proteins with known high-resolution X-ray crystallographic structures with synthetic SAXS data. The novel resolution measure was tested on *ab initio* reconstructions based on experimental SAXS data of several well-characterized proteins and cross-correlated with the corresponding X-ray crystallographic structures. Our approach is able to obtain resolution values that are in an excellent agreement with the resolution values provided by cross-validation.

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Submitting Author: a.tuukkanen@embl-hamburg.de

COHERENT X-RAY DIFFRACTION IMAGING AT THE ESRF BEAMLINE ID10: POSSIBILITIES AND CHALLENGES

Y. Chushkin[a], **F. Zontone**[a], **B. Maillot**[a], **P. Pernot**[a], **and G. Faraci**[b]
[a] *European Synchrotron Radiation Facility, avenue des Martyrs 71, 38000 Grenoble, France*
[b] *Dipartimento di Fisica, Università di Catania, Corso Italia 57, 95129 Catania, Italy*

Coherent X-ray diffractive imaging (CXDI) is a novel scattering technique [1,2] that exploits the unprecedented degree of coherence of modern synchrotron sources. It has potential for high resolution imaging of isolated microscopic objects beyond the values achieved with X-ray lenses and represents an interesting tool to bridge the gap between high resolution electron and visible light microscopy. The image in the real space is obtained by applying phase retrieval algorithm to the diffraction pattern measured with sufficient oversampling. Because of the high penetration power of the X-rays the imaging of thick object (<10μm) without sectioning is possible in 3D [3,4,5].

In this work we report the current status of the CXDI at the ESRF beamline ID10. We discuss the possibilities and challenges of CXDI by presenting examples of 2D reconstruction of *Deinococcus radiodurans* (DR) bacteria (Figure 1 (left)) and 3D reconstruction of a porous Si cluster (Figure 1 (right)). High quality of the reconstructed images reveals DR's cellular structure and individual Si nanocrystals in unprecedented detail. The improvement in the biological sample preparation and the development of large 2D (pixel) detectors are the key elements for achieving the full potential of the technique.

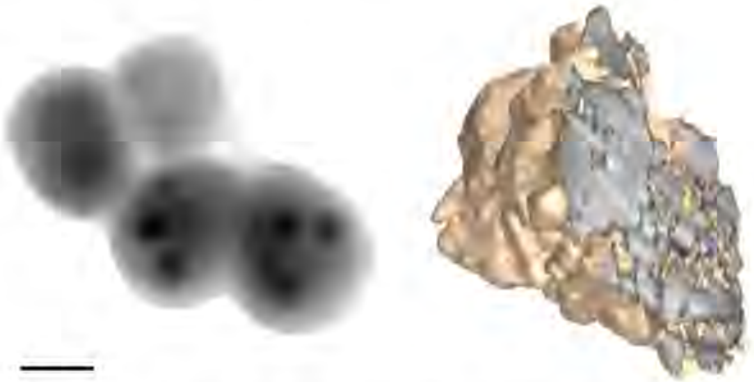

Figure 1: Reconstructed 2D image of bacteria *Deinococcus radiodurans* (left) and a cut through a 3D image of a porous cluster of 100-200nm Si crystals (right). The scale bar in the left image corresponds to 1 μm.

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Submitting Author: chushkin@esrf.fr

NEW METHODS FOR OPTIMISED HIGH THROUGHPUT AND HIGH QUALITY DATA ACQUISITION AT THE ESRF BIOSAXS BEAMLINE BM29

M. Brennich[a], B. Maillot[a], S. Teychené[b], C. Zubieta[a,c], U. Kapp[a], M. Lentini[a], F. Bonneté[d], N. V. Pham[b], D. Radajewski[b], B. Biscans[b], P. Guillet[d], P. Pernot[a] and A. Round[e]

a ESRF-The European Synchrotron, 71 Avenue des Martyrs, Grenoble, France

b Laboratoire de Génie Chimique, 4 allée Emile Monso, Toulouse, France

c CEA Grenoble, iRTSV/LPCV, 17 rue des Martyrs, Grenoble, France

d Institut des Biomolécules Max-Mousseron, 33 rue Louis Pasteur, Avignon, France

e EMBL, Grenoble Outstation, 71 Avenue des Martyrs, Grenoble, France

BioSAXS, or macromolecular solution scattering, has continuously become more important for structural biology. This has led to the development of dedicated beamlines such as BM29 at ESRF which provides a completely *in vacuo* setup with a flow-through capillary for samples and a sample changer robot (SC) for sample delivery [1]. As sample quality is essential for obtaining useful information from a SAXS experiments recent efforts have been focused on achieving optimal samples.

One possible approach is to minimize the time span between sample purification and data acquisition to decrease the effect of dynamic processes such as complex degradation or sample aggregation. To achieve this, the outlet of a size exclusion chromatography (SEC) set-up is directly coupled to the flow-through capillary and SAXS data of the eluent is continuously collected. These SAXS chromatograms not only provide data for each separate oligomeric species present in a sample but can also indicate conformation changes within a single species.

An other approach focuses on high-throughput screening of sample conditions. As this process is typically tedious and sample consumin developed droplet microfluidic devices for automatic screening.. Droplets of protein solution with adjustable protein additive concentrations are exposed to X-rays in a fused silica capillary of 300 μm diameter *in vacuo*. The exposure and data acquistion are synchronized such that only droplets and not the carrying medium are exposed to avoid radiation damage of the carrying medium and total reflection on droplet walls. This setup was applied to *in situ* crystallisation studies of glucose isomerase [2].

All of these approches are completely integrated in the BM29 setup for data aquistion thus users can quickly and easily switch between modes for effecient use of beamtime.

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Submitting Author: brennich@esrf.fr

Thu-T4: Instruments and Techniques 11:00

Title: Monte Carlo simulation of x-ray transport to study in vivo protein-protein interaction fractions using empirically-based cross section data for small-angle scattering

Author List: Mina Choi, Bahaa Ghammraoui, Andreu Badal, Aldo Badano

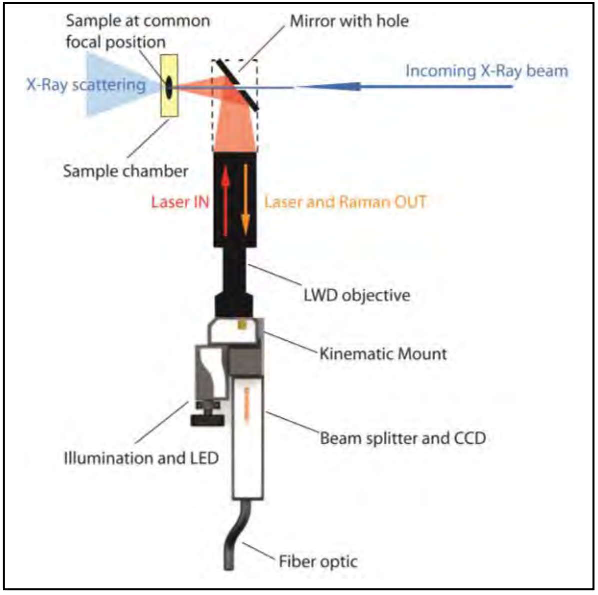
Abstract:

We present a novel method of using existing small-angle, x-ray scattering (SAXS) measurements to model x-ray transport using Monte Carlo techniques and explore different sample and instrument geometries. We use this method to determine the feasibility of quantifying level of molecular interactions in vivo. Our model molecular interaction system consists of solutions of monomer gold nanoparticle probes (GNPs) that are 8 nm in radius, and solutions of dimerized GNP probes representing a non-interacting and interacting system respectively. These samples were measured using a laboratory SAXS system and converted to cross section data for the Monte Carlo simulation using a modified version of the publicly available package mc-gpu. The cross-section materials are embedded within tissue-mimicking materials with varying thicknesses along the beam path. In addition, the energy of the monoenergetic x-ray beam, the source-to-sample and source-to-detector distances were varied to investigate ideal SAXS system specifications for this application. Our Monte Carlo estimates of the interaction fraction exhibit strong correlation with the known input concentration of interacting and non-interacting species.

A NEW WORKING PLATFORM COMBINING RAMAN, X-RAY SCATTERING, X-RAY FLUORESCENCE AT BESSY II µSPOT BEAMLINE FOR BIOLOGICAL MATERIALS IN CONTROLLED ENVIRONMENTS

A. Masic[a], **W. Wagermaier**[a], **C. Li**[a], **S. Siegel**[a], **H. T. Metzger**[a],
R. Schuetz[a], **L. Bertinetti**[a], **and P. Fratzl**[a]
[a]*Max Planck Institute of Colloids and Interfaces,*
Department of Biomaterials, Research Campus Golm, 14424 Potsdam, Germany

Biological materials with structural hierarchy are perfectly suited to be investigated by X-ray scattering techniques providing clear structural information at the nanometer level. However, X-ray scattering methods lack information on the amorphous structures, often found in biological materials, as well as the critical chemical information. In this context, Raman has proved to be excellent characterization tool for extracting short range chemical information from crystalline and amorphous phases in biological systems. Furthermore, biological materials and their biomimetic equivalents are tuned to perform most of their extraordinary behavior in very specific environmental conditions (humidity, ionic force, pH, etc.). Therefore methods able to explore different levels of structure *in situ* and in controlled environmental conditions are highly desirable. Here we present a new platform at the µSpot beamline at BESSY II at the Helmholtz-Zentrum Berlin für Materialien und Energie (HZB), combining simultaneous SAXS, WAXS, XRF and changes in environment as well as external stimuli (mechanical, thermal treatment, hydration, etc.) with Raman measurements. In figure 1 a schematic representation of the setup is shown. The setup allows excitation and collection of the Raman spectra through a probe placed in the experimental hutch and is connected with an optical fiber to the spectrometer placed outside the hutch. The micron level repositioning of the Raman probe is performed using x-y-z motors that allows fast alignment of the Raman laser with the X-ray beam. The co-alignment of the X-ray beam with the laser is achieved through a 45° mirror with a hole that permit simultaneous collection of both laser and synchrotron X-ray scattering. Effective spot size of the laser beam is around 20 microns for green (532nm) and 30 microns in the case of near infrared (785nm) laser illumination that matches very well with the X-rays spot size. The working distance of the objective used to focus the laser beam (10 cm) allows the introduction of the sample chamber for environmentally controlled and/or tensile experiments. Combination of X-ray diffraction and Raman spectroscopy offers a unique tool for multi-scale studies of hierarchically organized biologic and synthetic materials that, combined with the specific environmental conditions, will allow unprecedented *in situ* and real-time materials characterization.



Submitting Author: admir.masic@mpikg.mpg.de

Combining SAXS and Crystallography to build intuition in interaction networks and macromolecular engineering

Greg L Hura[ac], Yen-Ting Lai[b], Henry Tang[a], Michal Hammel[a], John A Tainer[a]
[a]*Lawrence Berkeley National Laboratory, 1 Cyclotron Rd. Berkeley CA 94720 USA*
[b]*Department of Chemistry and Biochemistry, University of California Los Angeles, Los Angeles CA 95064 USA*
[c]*Department of Chemistry and Biochemistry, University of California at Santa Cruz, Santa Cruz CA 95064 USA*

Biological macromolecules function by adopting conformationally-distinct states through processes such as phosphorylation, nucleotide binding, ATP hydrolysis, ligand binding, complex formation, or combinatorial post-translational modification. Many of these conformational states may be biologically important, but relatively few are observed and compared by current structural techniques. Crystallography is precise but low throughput, typically captures one low-energy conformation, and often requires truncations or mutations. SAXS experiments can probe the solution state under any condition, provide information at resolutions sufficient to distinguish conformational states, characterize flexible macromolecules and screen in high throughput. Moreover SAXS can be accurately calculated from atomic resolution models forming a valuable complementarity between crystallography and SAXS. Here we present several examples of the application of SAXS which significantly enhance our understanding of biological networks beyond what either a high resolution structure or informatics analysis can yield.

For macromolecular engineering the same combinatorial challenges exist. Because our understanding of the chemical and structural implications of even one point mutation is limited, techniques are required with rapid throughput to build intuition. Moreover crystallography, typically provides perspective in one stochastic solvent condition whereas engineered molecules may be designed for many solvent environments. A crystal structure of one construct combined with computational modelling and SAXS data on mutations and in varying solution conditions can provides remarkable insights for engineering. We will describe experimental and analytical frameworks that have aided in engineering projects with applications in human health and commercial chemical synthesis.

Submitting Author: glhura@lbl.gov

SINGLE SHOT COHERENCE PROPERTIES AND X-RAY PHOTON CORRELATION SPECTROSCOPY AT THE FREE-ELECTRON LASER SACLA

F. Lehmkühler[a,b], **W. Roseker**[a], **B. Fischer**[c], **P. Kwasniewski**[a], **M.A. Schroer**[a,b], **K. Tono**[d], **T. Katayama**[d], **M. Yabashi**[e], **T. Ishikawa**[e], **C. Gutt**[f], **and G. Grübel**[a,b]
[a]*Deutsches Elektronen-Synchrotron DESY, 22607 Hamburg, Germany*
[b]*The Hamburg Centre for Ultrafast Imaging (CUI), 22761 Hamburg, Germany*
[c]*University Hamburg, Institute for Physical Chemistry, 20146 Hamburg, Germany*
[d]*Japan Synchrotron Radiation Institute, 1-1-1 Kuoto, Hyogo 679-5198, Japan*
[e]*RIKEN SPring-8 Center, 1-1-1 Kuoto, Hyogo 679-5148, Japan*
[f]*University Siegen, Department of Physics, 57072 Siegen, Germany*

With the rise of free-electron lasers (FEL) operating in the hard X-ray regime, physical and chemical processes can be studied on ultrafast time scales with molecular resolution. In particular, the proposed superior degree of coherence of the FEL radiation allows, e.g., studies of sample dynamics by X-ray Photon Correlation Spectroscopy (XPCS) or single particle imaging with unprecedented accuracy and at ultrafast acquisition times below 100 fs. Due to the self-amplified spontaneous emission (SASE) process used to generate the FEL radiation, the beam position and intensity fluctuates on a shot-to-shot basis. Thus, the coherence properties of the radiation have to be studied for single shots in order to quantify the influence of such SASE fluctuations on experiments.

First, we present studies of the coherence properties of the free-electron laser SACLA in the hard x-ray regime [1]. We performed a small-angle X-ray scattering (SAXS) experiment on colloidal particles giving rise to coherent diffraction patterns, so-called speckle patterns. These patterns were taken with acquisition times of about 5 fs. The degree of coherence was extracted for single X-ray pulses by performing a contrast analysis on individual speckle patterns. On average, we found an almost full transverse coherent beam with a degree of coherence of 0.79±0.09. These results will be compared to our recent findings at the FEL LCLS [2,3].

Second, we discuss a proof-of-principle sequential XPCS study at SACLA [4]. The performance of single-shot sequential XPCS at FEL source has been challenged recently [5], reporting a decreased contrast in the correlation function g_2 due to beam instabilities originated by the SASE fluctuations. By analyzing speckle patterns from static and diffusive colloidal sample systems we demonstrate the feasibility of XPCS at FEL sources with total acquisition times of 250 fs and a total experimental time below 3 seconds. We extract a contrast from the correlation function of 0.4 which is half of the value obtained from single shots [1]. These results are modeled by simulations of diffusive particles probed by a moving X-ray beam. Most importantly, we did not observe any radiation damage of the samples.

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Submitting Author: felix.lehmkuehler@desy.de

NANOPARTICLE EMISSION AND STRUCTURE EVOLUTION DURING PULSED-LASER ABLATION IN LIQUID (PLAL)

A. Plech[a], **S. Ibrahimkutty**[a,b], **A. Menzel**[c], **P. Wagener**[d,e], **B. Gökce**[d] **and S. Barcikowski**[d]
[a]*Institute for Photon Science and Synchrotron Radiation/ANKA, Karlsruhe Institute of Technology, Hermann-von-Helmholtz-Platz 1, D-76344 Eggenstein-Leopoldshafen, Germany*
[b]*Max Planck Institute for Solid State Research, 70569 Stuttgart, Germany*
[c]*Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland*
[d]*Technical Chemistry I and Center for Nanointegration Duisburg-Essen (CENIDE), University of Duisburg-Essen, Universitätsstrasse 7, D-45141 Essen, Germany*
[e]*NanoEnergieTechnikZentrum (NETZ), University of Duisburg-Essen, Carl-Benz-Strasse 199, D-47057 Duisburg, Germany*

Pulsed-laser ablation in liquid has been established as versatile tool for the synthesis of nanoparticulate matter in liquid suspension [1]. Due to the ablation process a broad range of materials can be used as target for particle production. At the same time the particles are not affected by chemical side products or ligands. The process of laser interaction and particle formation is not fully understood, and the nontrivial interaction between nascent species and the macroscopic bubble formation at irradiation complicate the analytic approach. We have used time-resolved X-ray small-angle scattering in order to follow the kinetics of nanoparticles during the reaction with high temporal (30 µs) and spatial (10 µm) resolution [2] at the cSAXS beamline at SLS (Switzerland). Results have shown that small primary particles are present very early after plasma formation and fill the vapor bubble homogeneously. After collapse and rebirth of the bubble the particles are dragged towards the target and undergo heavy agglomeration [3]. The main portion of release into the liquid only happens afterwards [4]. Particle size quenching is possible already within the vapor bubble for steering the size evolution [5]. The goal is a mechanistic understanding of the particle synthesis process and access to a tuning of final particle quality and modality. This includes a hierarchical resolution of structure evolution.

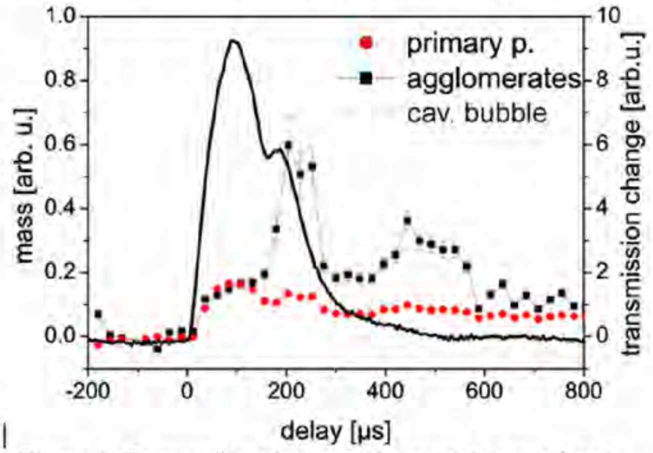

Figure 1: Temporal evolution of the particle mass for the two size species as function of delay after laser impact at 0.17 mm height. The solid line marks the bubble size evolution through change of the direct-beam transmission.

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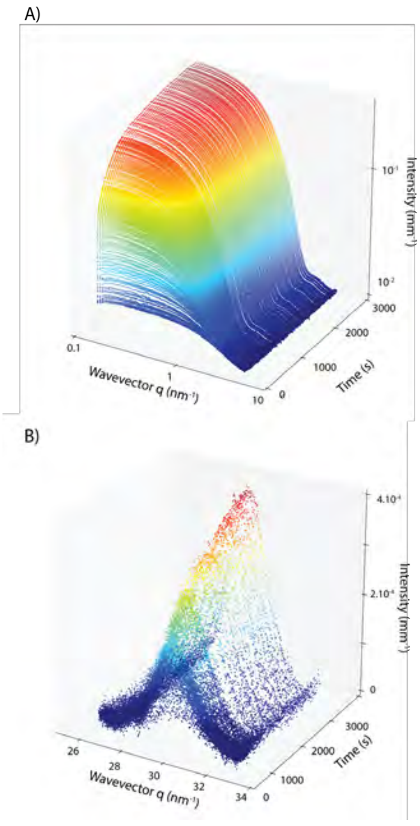
Submitting Author: anton.plech@kit.edu

Fri-D1: Dynamics 11:00

WATCHING QUANTUM DOT GROW IN REAL-TIME USING TIME-RESOLVED SYNCHROTRON SAXS/WAXS

Benjamin Abécassis,[a] **Cécile Bouet,**[b] **Doru Constantin,** [a] **Nicolas Lequeux,** [b] **Sandrine Ithurria** [b], **Benoit Dubertret** [b], **Brian Richard Pauw**[c],¶ **and Diego Pontoni**[d]
[a] *Laboratoire de Physique des Solides, Univ. Paris-Sud, CNRS, UMR 8502, F-91405 Orsay Cedex, France,*
[b] *LPEM, ESPCI-ParisTech, PSL Research University, CNRS UMR 8213, Sorbonne Universités, UPMC Paris 06, 10 rue Vauquelin, 75005 Paris, France.*
[c]*National Institute for Materials Science (NIMS),1-2-1 Sengen, 305-0047, Tsukuba, Japan.*
[d]*European Synchrotron Radiation Facility, Grenoble, France.*



Quantum dots are small fluorescent nanocrystals whose extraordinary optical properties have fascinated researchers for more then 20 years. A variety of different synthesis path exist nowadays and by empirically changing the reaction conditions, various sizes, shapes and topologies can be obtained, often with high purity. However, the discovery of new materials and the optimization of synthesis protocols remain empirical and relies on general principles which are not backed by solid experimental evidence. A better fundamental understanding of the formation mechanism of quantum dots would speed up the discovery process and provide generic rules on which synthetic chemists could rely. Unfortunately, our understanding of the nucleation and growth reactions is still very limited mainly due to the lack of extensive, reliable and quantitative in-situ experimental data. The acquisition of such data has been made difficult by the harsh chemical conditions: high temperature (more than 200°C), corrosive and air-sensitive reagents, at which syntheses of high quality quantum dots take place. Here, we show that the formation mechanism of CdSe quantum dots, a system of wide interest, can be probed in real-time using time-resolved small/wide angle X-ray scattering (SAXS/WAXS) and provide unprecedented details on the nucleation and growth pathways of colloidal nanocrystals.

Our experiment yields a complete movie of the structure of the solution from the self-assembly of the precursors to the formation of the quantum dots. Using a Monte-Carlo for the fitting of the SAXS patterns, size distributions and concentration in nanocrystals are measured in a quantitative fashion as a function of time.

References

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Submitting Author: benjamin.abecassis@u-psud.fr

FOLLOWING NANOPARTICLE SELF-ASSEMBLY BY SAXS OF LEVITATING COLLOIDAL DROPLETS

Michael Agthe[a], German Salazar-Alvarez[a], Tomás S. Plivelic[b], Ana Labrador[b] and Lennart Bergström[a]
[a]Stockholm University, Department of Materials and Environmental Chemistry, Svante Arrhenius väg 16 C, 10691 Stockholm, Sweden
[b]Lund University, MAX IV Laboratory, P.O Box 118, 22100 Lund, Sweden

Self-assembly of nanoparticles into ordered structures is a promising strategy for production and design of nanostructured materials with novel properties. The constrained packing of anisotropic nanoparticles attracts a growing interest as it offers the possibility to tune the electronic, optical and magnetic properties.

We have followed self-assembling toluene dispersed iron oxide nanocubes with an edge length of 10.4 ± 0.5 nm by time-resolved small angle X-Ray scattering (SAXS) on levitating droplets at the MAX-Lab I911-4 beamline. Acoustic levitation uses sound pressure to match gravitational forces of microliter droplets and thus enables substrate-free analysis of temporal processes within a droplet and on the liquid-air interface.

We will present time-resolved SAXS data on the shrinking colloidal droplets that were additionally monitored by a calibrated microscope camera to derive evaporation rates of the solvent. We will discuss the different stages of the evaporation-mediated structure formation of the nanocubes during droplet drying as illustrated in Figure 1. The nanocubes form highly ordered domains characterised by a simple cubic structure and an analysis of the temporal evolution of the primary peak suggests that the ordered domains display Avrami-like growth.

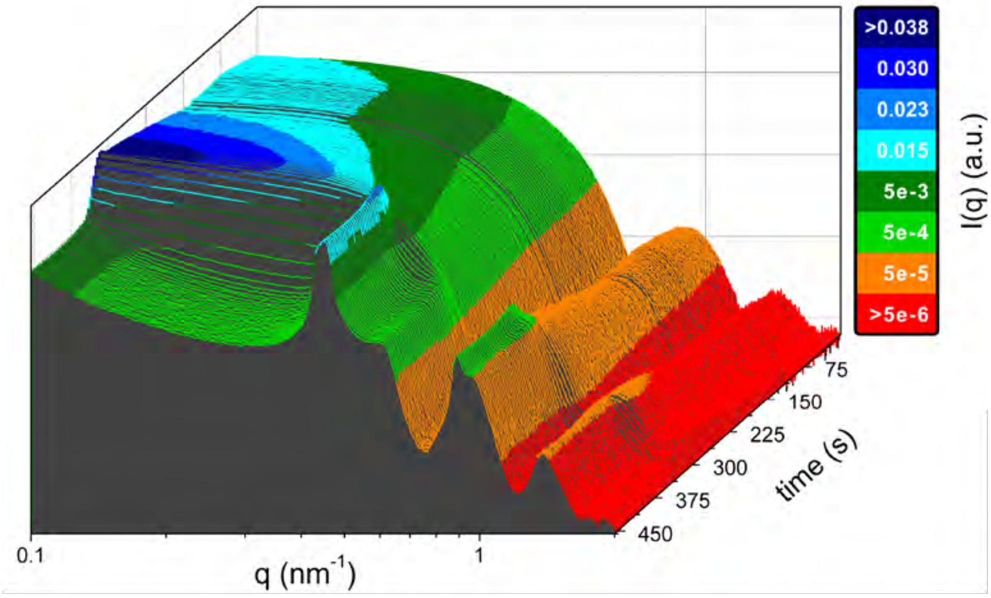

Figure 1: Time resolved SAXS curves of a drying, levitating drop containing iron oxide nanocubes.

Submitting Author: michael.agthe@mmk.su.se

MS-TIME RESOLVED SAXS FROM FREE METAL CLUSTERS IN A SUPERSONIC MOLECULAR BEAM

H.Amenitsch[a], **M. Devetta**[b], **P.Piseri**[b]
[a] *Graz University of Technology, Institute of Inorganic Chemistry, Stremayergasse 9, 8010 Graz, Austria* [b] *Università degli Studi di Milano, Dipartimento di Fisica & CIMaINa, via Celoria 16, 20133 Milano, Italy*

The study of isolated nanoparticles produced in the gas phase is a key issue for understanding how the properties of matter evolve from atomic and molecular level to bulk materials. Controlled nanoparticle synthesis combined with manipulation and deposition stages thus plays a major role in the advancement of nanostrustructred materials production e.g. with supersonic Cluster Beam Deposition [1]. Access to information on free nanoparticle morphology, to their aggregate structure and possibly a fractal dimension, i.e. particle characterization beyond size is thus of major importance. Recently a method has been developed, based on the low-pressure aerodynamic mobility of neutral particles, for the quantitative determination of a morphology descriptor of free clusters with a complex nanostructure [2]. Owing to the high cluster beam intensity and stability achievable with a Pulsed Microplasma Cluster Source (PMCS) [3], combined with aerodynamic focusing of particle trajectories in the subsonic part of the aerosol flow [4], a sample density in the range of 10^{14} atoms/cm^3 is typically obtained which is considered enough to allow performing time resolved SAXS as e.g. in ref. [5]. The final setup is shown in Fig. 1.

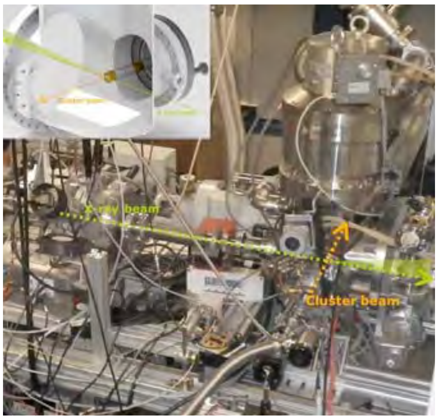

Figure 1: *Picture and sketch of the experimental setup of the cluster source at the ELETTRA SAXS beamline.*

The data have been taken with 8 frames with 9 ms exposure periode (5 ms exposure time) per every single cluster beam pulse. The cluster beam pulses have been generated at 10 Hz repetition rate. The observed signal level is ~1.7 scattered photons per frame at maximum of pulsed beam intensity for Pb clusters in Ar carrier gas.

The acquired SAXS data are the average of 24k single images. The evolution of the structures showed that size is changing from about 2 nm at the top to about 5 nm at the tail of the cluster beam. Further insides of the structure evolution will be given. The experiment proved the feasibility of cluster morphology determination via SAXS on a synchrotron X-ray source.

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Submitting Author: amenitsch@tugraz.at

X-RAY IMAGING AND ANALYSIS OF KERATIN INTERMEDIATE FILAMENTS

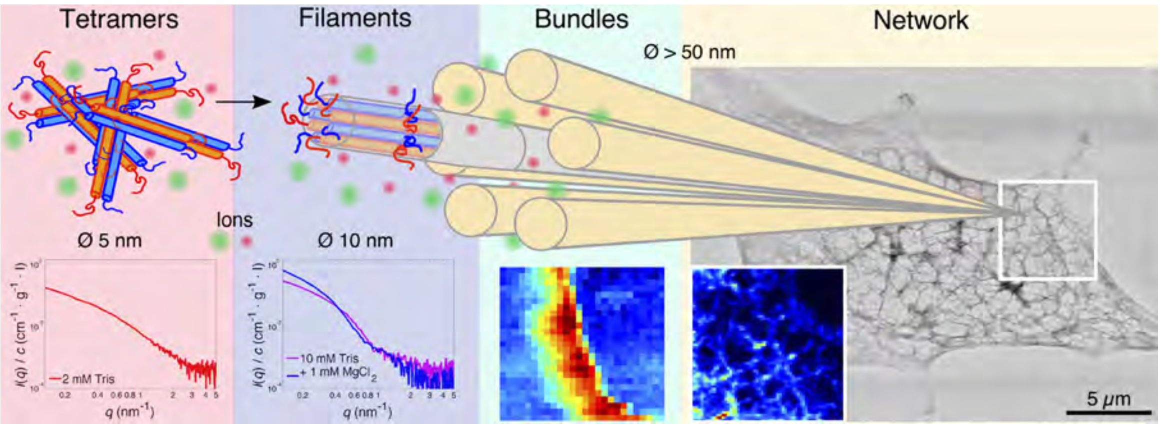
C. Hémonnot[a], **J. Reinhardt**[b], **O. Saldanha**[a], **R. Graceffa**[a], **J. Patommel**[c], **B. Weinhausen**[d], **H. Herrmann**[e], **M. Burghammer**[d], **C. Schroer**[b] **and S. Köster**[a]
[a]*Institute for X-ray Physics, University of Göttingen, Göttingen, Germany*
[b]*DESY, Notketraße 25, 22607 Hamburg, Germany*
[c]*Institute of Structural Physics, TU Dresden, Zellescher Weg 16, 01069 Dresden, Germany*
[d]*ESRF, 71 avenue des Martyrs, 38000 Grenoble, France*
[e]*Division of Molecular Genetics, German Cancer Research Center, Heidelberg, Germany*

Keratin intermediate filament (IF) proteins play an important role for cell mechanics as they form extended filaments (10 nm diameter) and complex, highly ordered intracellular networks, which provide integrity and stability to epithelial cells. We present a study of keratin protein on three different length scales, from single filament to bundles and finally networks in whole cells by using three different X-ray techniques.

First, we investigated the assembly mechanism of keratin IFs into filaments in the presence of monovalent or divalent ions by small angle X-ray scattering. Thus, we demonstrated that the radius of the filaments follows a linear trend with increasing ion concentration. Moreover, we were able to determine where in the filaments the ions accumulated by using a fitting model [1] consisting of a core filament and Gaussian chains representing the N- and C- terminals. Both ion species accumulate at low concentrations in the side chains, then on the core of the filament.

Second, we studied *in vitro* bundles of keratin filaments by scanning X-ray micro-diffraction. We found that the addition of K^+ or Mg^{2+} initiates bundling. We were able to analyse single diffraction pattern in terms of orientation and ordering [2,3] and could thus shed light on the internal build-up of the bundles.

Lastly, we probed the keratin network directly in whole cells by ptychography (low-dose, high-resolution) and scanning X-ray nano-diffraction (internal architecture) on the same sample. In order to characterize the 2D diffraction patterns, we used a model [4] that takes into account the form factor and the structure factor of the system. We were able to determine the average radius of the filaments as well as the distance between filaments of *in situ* networks.



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Submitting Author: clement.hemonnot@phys.uni-goettingen.de

COMBINED SAXS, HDX-MS AND RAMAN STUDY OF A LARGE INTRINSICALLY DISORDERED PROTEIN WHICH FOLDS UPON LIGAND BINDING

D. Durand[a], D. P. O'Brien[b], V. Hourdel[c], B. Hernandez[d], A. C. Sotomayor-Pérez[b], M. Ghomi[d], J. Chamot-Rook[c], D. Ladant[b], S. Brier[c], P.Vachette[a] and A. Chenal[b]

[a]*Département de Biochimie, Biophysique et Biologie Structurale, I2BC, CNRS, Orsay, France*
[b]*Unité de Biochimie des Interactions Macromoléculaires, Institut Pasteur, Paris, France*
[c]*Unité de Spectrométrie de Masse et de Protéomique Structurale, Institut Pasteur, Paris, France*
[d]*Groupe de Biophysique Moléculaire. UFR SMBH, Université Paris 13, Bobigny, France*

The adenylate cyclase toxin (CyaA) is one of the primary virulence factors of Bordetella pertussis, the causative agent of whooping cough. We have shown that the C-terminal (aa 1006-1706), receptor-binding Repeat-in-ToXin (RTX) Domain (RD) of CyaA is intrinsically disordered, and folds upon calcium binding [1]. We propose that this disorder-to-order transition is involved in bacterial toxin secretion. To obtain more details regarding protein conformations, we used a combination of SAXS with Raman spectroscopy and Hydrogen/Deuterium Exchange Mass Spectrometry (HDX-MS) experiments. All three approaches indicated that apo-RD, although essentially unfolded, contained some residual secondary structure elements. Calcium binding to RD induced a dramatic conformational rearrangement of the protein. Raman spectroscopy showed a major increase in β-sheet content, at the expense of structural disorder. A massive masking effect was observed by HDX-MS around the calcium binding regions, proposed to be due to the compaction of the RTX motifs themselves. The flanking regions connecting the RTX motifs exhibited dynamic HDX events, suggesting that these regions are folded but still accessible inter-domain linkers. The SAXS pattern of apo-RD was analyzed in terms of statistical polymer chain with persistence length and thickness. This analysis was completed by an analysis in terms of an ensemble of conformations using EOM. The selected conformations illustrated the presence of residual local structure. Ca-bound RD (holo-RD) appears to be in a compact, significantly folded and monomeric state. It adopts an elongated global conformation as shown by the program Gasbor that yields models looking like a curved elongated cylinder. Using the Webserver Phyre2, we obtained models for six protein regions that exhibited masking effects in HDX-MS. Their mutual arrangement was subsequently refined using the program Bunch. From the resulting models, we conclude that holo-RD is likely to adopt in solution an elongated conformation in which folded domains are linked by regions that are also significantly structured, part or all of which may exhibit some degree of limited flexibility, in agreement with the HDX-MS observations.

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Submitting Author: patrice.vachette@u-psud.fr

THE DIMENSIONS OF INTRINSICALLY DISORDERED PROTEINS: A COMBINED SAXS AND SINGLE-MOLECULE FRET STUDY

Gustavo Fuertes[1,2], Sigrid Milles[1], Christine Koehler[1], Niccolò Banterle[1], Michael Kachala[2], Dmitri I. Svergun[2], Edward A. Lemke[1]
[1] *EMBL Heidelberg, Structural and Computational Biology Unit, Meyerhofstraβe 1, 69117 Heidelberg*
[2] *EMBL Hamburg c/o DESY, Notkestraβe 85, 22607 Hamburg*

As intrinsically disordered proteins (IDPs) are dynamic and populate an ensemble of states in solution, concepts originating from polymer theory have turned out to be particularly useful for the description of their properties. An important experimental parameter quantitatively describing IDPs in solution is the radius of gyration, R_G, which can be determined by two complementary methods, small-angle X-ray scattering (SAXS) and single-molecule Förster resonance energy transfer (smFRET). In the former case, the R_G is measured directly; in the latter case, it is expressed through the end-to-end distance, R_E, which requires attachment of fluorescent labels to the N- and C-termini of the polypeptide. However, the impact of the dyes and linkers, necessary for smFRET, on the measured distances has not been rigorously addressed. In this work we have bridged the gap between smFRET and SAXS by measuring the R_G values of a set of IDPs in a broad range of molecular masses, in the presence and absence of highly concentrated urea in the solvent. Simulations of the protein-linker-dye complex were performed in order to provide a molecular interpretation of the experimentally measured distances. Our results indicate that chemically unfolded IDPs behave as random coils and the dye-linker offset necessary for SAXS and smFRET to yield the same R_G is equivalent to about 10 residues. However, discrepancies between smFRET and SAXS are observed for IDPs in native buffers, which can be explained by considering a polymer model of an IDP with a ratio between R_E^2 and R_G^2 of 4.3. Our results suggest that IDPs in denaturant-free solvents are more collapsed, in terms of R_E, than an ideal Gaussian chain.

Submitting Author: gustavo.fuertes@embl.de

A switch controlling DNA networks, compaction, and bacterial pathogenicity

Michal Hammel[a], Dhar Amlanjyoti[b], Francis Reyes [a], Rochelle Parpana[a], Henry Y. H. Tang[a], John A. Tainer[a,c], Sankar Adhya[b].

[a] Life Sciences Division, Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, CA 94720 USA
[b]Laboratory of Molecular Biology, Center for Cancer Research, National Cancer Institute, National Institutes of Health, Bethesda, MD, USA
[c]Department of Molecular and Cellular Oncology, The University of Texas M. D. Anderson Cancer Center, 1515 Holcombe Blvd., Houston, Texas 77030, USA

Abstract

Bacterial chromosome (nucleoid) compaction and organization at the molecular level is surprisingly enigmatic, but depends upon conserved, histone-like proteins HUαα and Huαβ. Here we determined crystal structures of these chromosome-associated proteins in complex with undamaged DNA [1]. Distinct DNA-binding modes of HUαα- and HUαβ- DNA elucidate fundamental features of bacterial chromosome packing regulating gene transcription. By combining crystal structures with solution X-ray scattering results, we determined architectures of HU's nucleoprotein-DNA networks in physiological conditions[1]. Moreover, characterization of charge-altered HUαα - DNA complex reveals an HU molecular switch that regulates expression of "virulence" genes. Collective findings suggest that shifts between networking, cooperative and non-cooperative HU multimerization on DNA control DNA compaction and supercoiling independently of cellular topoisomerase activity. Defined dynamic HU-DNA networks may promote nucleoid reorganization and transcriptional regulation as efficient general microbial mechanisms to synchronize genetic responses to cell cycle and changing environments.

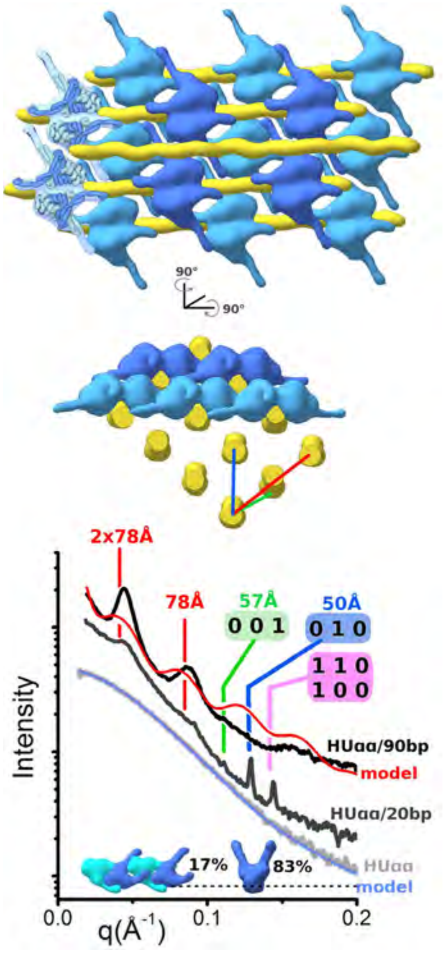

Figure: HUαα-DNA network interactions and assembly

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Submitting Author: mhammel@lbl.gov

SELF-ASSEMBLY OF MATRIX PROTEIN M1: pH DEPENDENCES REVEALED BY SAXS AND AFM

E. Shtykova[a], **L. Baratova**[b], **N. Fedorova**[b], **O. Batishchev**[c], **C. Jeffries**[d], **D. Svergun**[d]
[a]*A.V.Shubnikov Institute of Crystallography, Russian Academy of Sciences, Moscow, Russia*
[b] *A.N. Belozersky Institute of Physico-Chemical biology, Moscow State University, Moscow, Russia*
[c]*A.N. Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, Moscow, Russia*
[d]*EMBL, Hamburg Outstation, Hamburg, Germany*

Recently, small-angle scattering (SAXS), analytical ultracentrifugation (AUC) and atomic force microscopy (AFM) were employed to characterize the overall structure and association behavior of the full length Influenza A Virus matrix protein M1 at acidic pH [1]. This condition occurs at the very beginning of cell infection leading to an acid-triggered fusion of the viral membrane. Moreover, change of pH was found to serve as a switch that allowed M1 to carry out its multiple functions in the uncoating, nuclear transport, and assembly of the viral ribonucleocapsid [2]. It is well known also that the isolated M1 can be soluble without detergents only at pH < 5.0 [3]. Still, it was demonstrated that the M1 self-assembly occurs even at acidic pH: SAXS and AFM experiments revealed well ordered structures formed by M1 both in solution and on the lipid bilayer. These helix-like shapes could be treated as pre-matrix protein superstructures, whose formation is an intrinsic biological property of the M1 protein. It can be assumed, however, that the oligomerization tendency of M1 should increase with pH. The aim of the present work was to analyse the structure and self-assembly of M1 at gradually changing pH (up to the neutral pH condition) in solution and on the bare mica surface using SAXS and AFM, correspondingly. We found that the oligomeization processes occur in a similar way in the solution and on the substrate, and quantitatively described these processes. Moreover, pH 6.0 was found to be the condition at which binding between M1 molecules starts to break. Our results provide new insights into the mechanism of M1 to form matrix and virus-like particles alone without partners and give a basis for a further analysis of the hierarchy of M1 in the virus life cycle.

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Submitting Author: viwopisx@yahoo.co.uk

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TAILORING DIRECTIONAL HIERARCHICAL METAL-POLYMER NANOSTRUCTURES

S. V. Roth[a], G. Santoro[a], J. F.H. Risch[a], S. Yu[b], M. Schwartzkopf[a], P. Zhang[a], M. A. Rübhausen[c], N. J. Terrill[d], P. A. Staniec[d], Y. Yao[e], E. Metwalli[e] and P. Müller-Buschbaum[e]

[a]*Deutsches Elektronen-Synchrotron (DESY), Notkestr. 85, D-22607 Hamburg, Germany*
[b]*Royal institute of Technology (KTH), Teknikringen 56-58, SE-10044 Stockholm, Sweden*
[c]*Inst. f. Nanostruktur- und Festkörperforschung, CFEL, Advanced Study Group, University of Hamburg, Luruper Chaussee 149, 22761 D-Hamburg, Germany*
[d]*Diamond Light Source, Harwell Science and Innovation Campus, Didcot, Oxfordshire OX11 0QX, United Kingdom*
[e]*Lehrstuhl für Funktionelle Materialien, Physik-Department, TU München, James-Franck-Str. 1, D-85748 Garching, Germany*

Tailoring the metal-polymer interface in hybrid hierarchical materials plays a crucial role in modern advanced material science. Herein, sputter deposition is one method of choice for depositing metal films rapidly and on large scale. Due to self-assembly, the metal film is composed of clusters. Depending on the desired functionality, the nanostructure is tuned to isolated or percolated cluster regimes. On the other hand, diblock copolymer thin films offer the possibility of installing a large variety of morphologies, which can be tuned from cylindrical domains to lamellae. Exploiting the fact, that metals show a strong tendency of selectively wetting one polymer block, one is able to introduce an additional hierarchical structure [1,2].

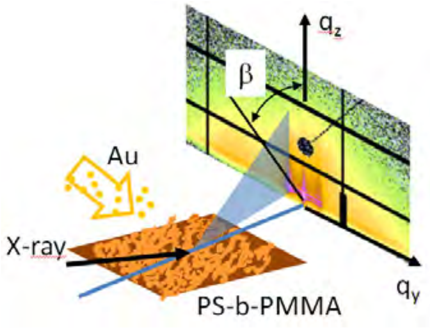

Figure 1: Oblique angle deposition of Au on nanostructured diblock-copolymer film (PS-b-PMMA). The Au nano-structures grow at an angle of with respect to the surface normal.

Using glancing angle deposition of gold (Au) on nanostructured diblock copolymer thin films (PS-b-PMMA), we are able to fabricate *directional* hierarchical structures. This approach exploits the selective wetting of Au on the PS block. We prove the asymmetric, localized growth of the Au nanoparticles, and are able to extract the different growth laws by *in situ* scattering methods as well as microscopy methods [3]. The optical anisotropy of these hierarchical hybrid materials is probed by angular resolved spectroscopic methods and is correlated to the nanostructure. This approach offers the possibility to tailor functional hierarchical thin films for plasmonics and metamaterials, as nanoantennae arrays, in organic photovoltaics and sensor electronics.

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Submitting Author: stephan.roth@desy.de

A COMBINED NEUTRON REFLECTOMETRY AND ATR-FTIR STUDY ON THE EFFECTS OF SHEAR ON LIPID MEMBRANES

M. Trapp[a], F. Schwörer[b] M. Ballauff[a], R. Dahint[b] and R. Steitz[a]
[a]Helmholtz-Zentrum Berlin GmbH, Hahn-Meitner-Platz 1, 14109 Berlin, Germany
[b]RKU Heidelberg, Applied Physical Chemistry, Im Neuenheimer Feld 253, 96120, Germany

Shear forces play a major role in degenerative joint diseases such as osteoarthritis (OA). Due to abrasion cartilage and surface active phospholipids are removed from the bones which lead to increased friction and shows symptoms such as joint pain, stiffness and inflammation. While there are already many different treatments of OA, the understanding of these treatments on a molecular level is still scarce. Medications may include the intra-articular application of hyaluronic acid, one of the main components of the synovial fluid.

In a previous study, we found that solid-supported oligolamellar lipid membranes show an enormous swelling of a factor up to 4 after incubation with HA. In addition, the lipid coating remained on the support even in the liquid phase whereas without HA the coating detached when crossing the main phase transition [1].

In order to investigate shear effects on systems modelling joints, a novel setup was designed and built. We now present first results obtained with this newly developed shear cell which allows the simultaneous measurement of neutron reflectivity and ATR-FTIR data up to shear rates of 6000rpm. The systems under investigation were again solid-supported oligolamellar lipid membranes incubated with the polyelectrolyte poly(allyl amine hydrochloride) (PAH).

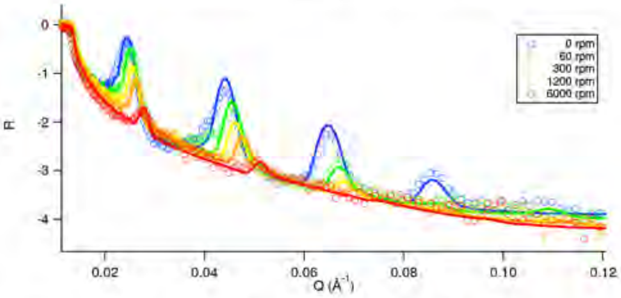

Figure 1: Neutron reflectivity curves of a solid-supported oligolamellar lipid hydrogel lining (11 DMPC lamellae in total) interacting with PAH against water as a function of applied shear load.

After incubation the d-spacing of the system shows an increase of a factor of about 5, similar to the behaviour observed when lipid membranes are incubated with HA [1]. The neutron data reveal a substantially increased water fraction with increasing shear rate. Simultaneously recorded IR data indicate that the applied shear also causes a phase transition into the liquid state. Yet the coating remains attached to the substrate, but changes composition and morphology. This effect can be attributed to the stabilisation introduced through the bridging of individual lipid bilayers by PAH.

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Submitting Author: marcus.trapp@helmholtz-berlin.de

CONSTRAINT SURFACE DYNAMICS OF POLYSTYRENE THIN FILMS BY FUNCTIONALIZATION OF A SILSESQUIOXANE CAGE STUDIED BY X-RAY PHOTON CORRELATION SPECTROSCOPY

T. Hoshino[a], S. Nojima[a,b], M. Sato[b], T. Hirai[a,b,c], Y. Higaki[a,b,c,d],
H. Jinnai[c], A. Takahara[a,b,c,d], M. Takata[a]
[a]RIKEN, SPring-8 Center, Kouto 1-1-1, Sayo-cho, Sayo-gun, Hyogo 679-5148, JAPAN
[b]Graduate School of Engineering, Kyushu University, [c]Institute for Materials Chemistry and Engineering, Kyushu University, [d]JST, ERATO Takahara Soft Interfaces Project

Polyhedral oligomeric silsesquioxane (POSS), a cage structure with high density of silicon, has received much attention as a mean to modify polymer properties. The POSS is often used by mixing it to polymer materials or by chemically attaching it to polymers. In thin films, such mixing or functionalization of POSS should significantly affect the physical properties: for example, the introduction of POSS as a polystyrene (PS) end-functionalization group was reported to prohibit the PS thin films from dewetting [1]. In the present work, the surface dynamics of POSS functionalized PS (PS-POSS) thin films were studied by grazing incidence X-ray photon correlation spectroscopy (GI-XPCS) in order to elucidate the effects of the presence of POSS at the end-of PS chains.

The GI-XPCS measurements were performed on the BL19LXU beamline of SPring-8 with a 27-m-long undulator [2]. The undulator source and Si(111) monochromator were tuned to an energy of 7.30 keV. The sample was irradiated with partially coherent X-rays in a vacuum with the incidental angle of 0.14^o, which is below the critical angle for total external reflection.

As results of GI-XPCS measurements for the homo-PS and PS-POSS thin films above the glass transition temperature, we observed relaxation behavior in time autocorrelation function $g_2(q,t)$ at various q, originating from capillary waves generated by thermal agitation of molecules. Figure 1 shows the q dependence of relaxation rates for homo-PS and PS-POSS film with M_n=2.5k, 60 nm-thick sample at 120 °C, and representative $g_2(q,t)$ at $q=5.65\times10^{-3}$ nm^{-1} are shown in the inset of Fig.1. As shown in Fig. 1, the relaxation rates of PS-POSS were much slower than those of homo-PS thin films at all the measured q range.

The relaxation rates of capillary waves are known to be inversely proportional to the bulk viscosity of fluids, and the enhancement of bulk viscosity of polymers by mixing inorganic materials has been often reported. On the other hand, in the present case, there was no significant difference of bulk viscosity between homo-PS and PS-POSS. Thus the observed difference of the surface fluctuations between homo-PS and PS-POSS should not originate from the bulk properties. The POSS segregation to the surface and film-substrate interface was reported previously. The POSS segregated layer may constrain the dynamical fluctuation of PS-POSS thin films.

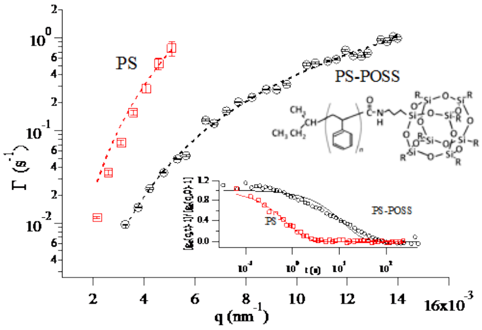

Fig. 1. q dependences of relaxation rate of Γ for the PS film and the PS-POSS film with M_n=2.5k, 60 nm-thick at 120 ℃. Time-autocorrelation functions at q=5.65 $\times10^{-3}$ nm^{-1} are shown in the inset.

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Submitting Author: t-hoshino@spring8.or.jp

TRACING SELF-ASSEMBLY OF A SILICATROPIC TEMPLATE AND THE SUBSEQUENT FORMATION OF MESOSTRUCTURED ARRAYS OF GOLD NANOPARTICLES AT AN AIR-WATER INTERFACE

U. Jeng[a,c,*], Y.-H. Lai[b,*], S.-W. Chen[b], C.-J. Su[a], A.-C. Su[c], C.-Y. Mou[d]

[a] *National Synchrotron Radiation Research Center, Hsinchu 30076, Taiwan*

[b] *Department of Chemistry, Tunghai University, Taichung 407, Taiwan*

[c] *Department of Chemical Engineering, National Tsing Hua University, Hsinchu 30013, Taiwan*

[d] *Department of Chemistry and Center of Condensed Matter Science, National Taiwan University, Taipei 106, Taiwan*

A novel one-trough synthesis via an air-water interface is demonstrated to provide hexagonally packed arrays of densely spaced metallic nanoparticles (NPs) for an ultrahigh number density [1,2]. In the synthesis, a mesostructured polyoxometalate (POM)-silicatropic (with CTAB-TEOS) template (PSS) is first self-assembled at the air-water interface; upon UV irradiation, anion exchange cycles enable the free-floating PSS film to continuously uptake gold precursors from the solution subphase for diffusion-controlled and POM-site-directed photoreduction inside the silica channels. NPs of ca. 2 nm can hence be homogeneously formed inside the silica-surfactant channels until saturation. Time-resolved grazing-incident small-angle X-ray scattering (GISAXS) were adopted to trace the whole formation process at the air-water interface, from the self-assembly of a silicatropic template, followed by the adsorption of gold precursors into the silicate channels of the template, and finally the reduction and aggregation of Au atoms upon UV-irradiation for the channel-directed formation of highly 2D-hexagonally ordered and oriented arrays of gold nanoparticles Au-NP@PSS. SAXS, WAXS, and TEM results for the product Au-NP@PSS harvested from the air-water interface reveal a similar 2D hexagonal lattice with inter-channel spacing of 3.2 nm and a mean along-channel NP spacing of 2.8 nm for an ultrahigh density of gold NPs. The hence synthesized Au-NP@PSS composite exhibits prominent surface-enhanced Raman scattering (SERS) with 4-mercaptobenzoic acid (4-MBA) adsorbed onto the channel-confined Au NPs, for a best 4-MBA detection limit of 5 nM with corresponding SERS enhancement factors above 10^8. Raman spectrum simulation result based on density function theory suggests that these adsrobed 4-MBA could present in both monomer and dimer forms inside the the channels of the Au-NP@PSS, suggesting potential applications of the new material in molecular sensing/reactions with sieving.

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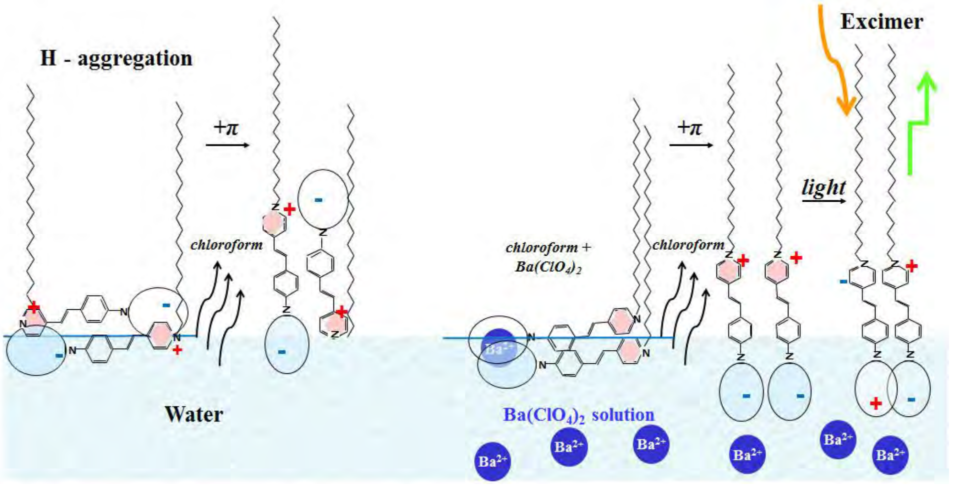
U-Ser Jeng: usjeng@nsrrc.org.tw

EXCIMER PACKING IN LANGMUIR-BLODGETT FILMS OF HEMICYANINE BASED AMPHIPHILIC CHROMOIONOPHORES

M.A. Shcherbina[a], S.L. Selektor[b], , A.V. Bakirov[a], V.V. Arslanov[b], S.N. Chvalun[a]
[a]Enikolopov Institute of Synthetic Polymer Materials RAS, 70 Profsoyuznaya str.,
117393 Moscow, Russian Federation
[b] Frumkin Institute of Physical Chemistry and Electrochemistry RAS, 31 Leninsky prospect,
bg. 4., 119071 Moscow, Russian Federation

Structure of Langmuir-Blodgett films formed by hemicyanine based amphiphilic chromoionophores on water / air interface was studied using compression isotherms, UV-Vis and fluorescence spectroscopy, X-Ray reflectivity, GIXD and GISAXS methods. Comparative analysis of supramolecular aggregates formed at different conditions (pure water or Ba^{2+}, Ca^{2+}, Mg^{2+} containing subphase) was performed.

It was shown for the first time that in the monolayers of amphiphilic crown ether substituted chromoionophores formed on dilute barium or magnesium perchlorate solutions, reversible formation of excimers takes places in compression-expansion cycles. The presence of barium (magnesium) ions in the subphase leads to the organization of neighboring molecules in head-to-head manner due to the generation of crown-ion-crown sandwich structures at the very beginning of monolayer formation while the chloroform is present in the monolayer. We believe that sandwich-type dimers formed at this stage were retained after the evaporation of chloroform despite the fact that the hydration of crown ether groups ejects cations out of the monolayer.



Electrostatic interactions in hemicyanine molecules on water surface lead to “head-tail” aggregation due to opposite charges on the “end” functional groups. Presence of metal cations in water subphase simultaneously with the chloroform at interface leads to the formation of metastable “sandwich” structures in head-to-head orientation, being stabilized by π-π interactions. Moreover the photo excitation leads to local redistribution of electron density in conjugated parts of the molecule. As a result, induced partial charge tends to start fluorescent dimer – excimer formation.

Understanding of excimer organization will result in the ability to control the structure of hemicyanine monolayers and LB films structure as well as their photophysical properties. This allows managing the emission characteristics of dye samples by changes in the subphase cation composition.

Submitting Author: shcherbina@ispm.ru