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SAS2015 - Berlin

16TH INTERNATIONAL CONFERENCE ON SMALL-ANGLE SCATTERING

13th – 18th September 2015, Berlin

Poster Abstracts

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STRUCTURE AND PHASE BEHAVIOR OF C_{28}-PEO STAR-LIKE MICELLES AS SOFT COLLOIDAL MODEL SYSTEM STUDIED BY SANS

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In this contribution we present the structural characteristics of star-like C_{28}-PEO polymer micelles in water as a function of polymer concentration and PEO chain length by small-angle neutron scattering (SANS). A key feature of our model system is the tunable unimer exchange kinetics with temperature, assuring thermodynamic equilibration of the micelles at high temperature and frozen micelles at low temperature. This was exploited to determine single particle properties like the micellar aggregation number N_{agg} at higher concentrations with a specially designed freezing and diluting experiment.

Furthermore, we examined the phase behavior of our model system at high concentrations with a new time-of-flight option of the KWS2 SANS instrument at MLZ in Garching, Germany, significantly improving the instrumental resolution (high resolution SANS). The HR-SANS experiment revealed the formation of crystalline phases at concentrations around ϕ^*. The improved instrumental resolution enabled an unambiguous determination of the crystal structure by analyzing the experimental structure factor. Depending on the PEO chain length (5, 10 & 20 kg/mol) different crystal structures (fcc & bcc) were observed. For short PEO chains also a solid-solid phase transition from fcc to bcc was found. From the experimental data we could extract the lattice constants of the crystals which were then used to calculate N_{agg} by geometrical arguments.

By combining the results of the freezing and diluting experiment and the crystal structure analysis we could investigate the concentration dependence of N_{agg} over a wide concentration regime from dilute up to $6\cdot\phi^*$. It was found, that $N_{agg}=100$ (PEO 5kg/mol) is constant with increasing concentration up to a critical concentration around three times ϕ^*. When exceeding this concentration, N_{agg} slightly increases with increasing concentration. These results are compared to predictions from scaling theories for star-like micelles [1], showing a complete disagreement between experiment and theory.

The observed phase behavior of our model system was compared to a theoretical phase diagram for soft colloids derived from an established ultrasoft interaction potential [2] which is sensitive to N_{agg}. The interactions were modeled in the liquid phase and compared to experimental data at different concentrations to test the validity of the interaction potential for our system. A good description with the potential could be achieved for long PEO chains (10 & 20 kg/mol) while it fails for short PEO chains (5 kg/mol). Even though, the observed phase behavior is in good agreement with the theoretical phase diagram.

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VISCOSITY OF HYALURONIC ACID/SURFACTANT COMPLEXES NEW INSIDES TO AN OLD TOPIC

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Self-assembled complexes of polyelectrolyte and oppositely charged surfactant in aqueous solutions have been studied over decades and are used in various applications especially for healthcare products. They are thermodynamically favoured due to their electrostatic attraction and the release of counter ions and water. Besides all possible polyelectrolyte and surfactant combinations, there are many parameters which are controlling the structure of these complexes[1,2]: The mixing ratio of both components, the ionic strength of the solution, the MW, charge density and persistence length of the polymer as well as the morphology of the micelle formed by the surfactant.However, besides a lack of knowledge of fundamental principles, much uncertainty still exists about the relation between the mesoscopic arrangement in these complexes and their macroscopic viscoelastic behavior.This contribution will focus on the polysaccharide Hyaluronic acid (HA), which has a carboxylic group on each repeating unit and an intrinsic persistence length of 4.0 nm in aqueous solutions.[3] As oppositely charged surfactant we use TTAB (tetradecyl-trimethylammonium bromide). Homogeneous mixtures of these components were studied rheologically by shear flow experiments and structurally by SANS and light scattering. Three fundamentally different cases were found: 1. Polymer rich solutions showed a lower diffusion coefficient but no change in viscosity; 2. Mixtures near the charge equilibrium were precipitating; and 3. Surfactant rich solutions possess a faster diffusion but an increase in zero shear viscosity. SANS measurements showed that in this system the viscosity increase is caused by the entanglement of the HA chains (see figure) and not by a change in micellar structure as it is stated for similar systems. Upon shear flow an alignment of the complexes of surfactant rich solutions could be observed in Rheo-SANS experiments (concentrations below wormlike conditions). Thereof and from comparison to carboxymethyl cellulose/TTAB complexes a comprehensive structural picture will be derived.

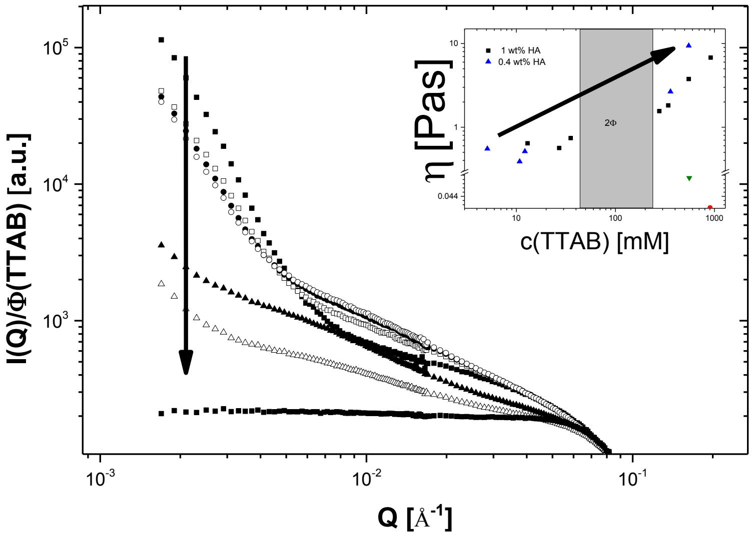

Figure 1: SANS-Data of HA/TTAB complexes with different mixing ratios weighted by volume fraction of TTAB.Inset Shows corresponding zero shear viscosity.

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HOW DEFECTS ON LIPID MEMBRANES CAN BE INVESTIGATED FROM SMALL ANGLE X-RAY SCATTERING (SAXS) DATA

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Biological processes occurring at the level of lipid bilayers and their interfaces are of great significance to shed light on the complex cellular mechanisms of membrane response. In this work we explore the effects of the presence of defects on the biophysical properties of lipid membranes, such as those caused by membrane interaction with actinoporins, pore forming toxins, and those promoted by lipid chemical transformations induced by photo-oxidation, which result in membrane pore formation. Prediction of Small Angle X-Ray Scattering (SAXS) curves from defect-containing mimetic membranes (figure 1), represented by large unilamellar (LUVs) and multilamellar (MLVs) vesicles, was achieved taking advantage of the GENFIT package [1] for the analysis of SAS data. Within its framework an ad hoc model was developed that takes into account the presence of cylindrical defects within the membrane, whose dimensions and electron densities are allowed to vary, their correlation defined in terms of the para-crystal theory and the stacking of bilayers and their correlation defined via the modified Caillé theory. With the above mentioned approach we focused on different types of membrane defects, in particular the cases of water pores, transmembrane proteins and protein forming pores. This theoretical work could be employed as the ground on which plan and execute future SAXS experiments with the aim of understanding the complex interactions between toxins and biological membranes as well as the effects of oxidative stress on membranes.

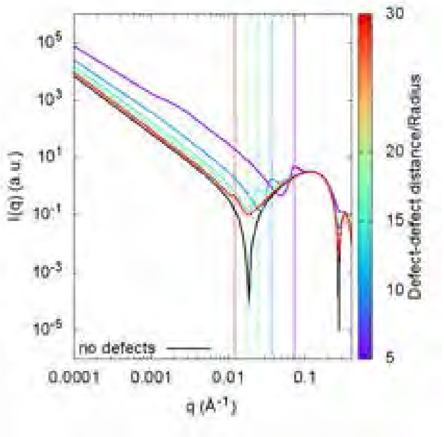

Figure 1: Example of simulated curves of defect-containing LUVs.

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SOLVENTE EFFECTS ON THE SUPRAMACROMOLECULAR STRUCTURE OF IONIC SELF ASSEMBLED AMPHIPHILIC MACROMOLECULES

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The search for smart building blocks with controllable and well defined properties is of prime relevance in the design of addressable soft-matter-based. Synthesis of such systems is a major challenge and, usually, requires several reaction-purification steps. Synthetic strategies based on the use of non-covalent interactions like ion-pair interactions have emerged as versatile tools for the assembly of soft nanostructures. A simple route to the synthesis of Ionic Self Assembled amphiphilic structures is the ion-pairing in low-ε solvents between components.

The flexibility of the synthetic procedure raises also questions about the stability of the macromolecular assemblies regarding thermal changes and solvent properties (like polarity, viscosity, H-donicity, etc.).

In the present communication we assembled amphiphilic core-shell structures with polar Hyperbranched Polyethileneimine (HPEI) as core polymer and different carboxylic fatty acids as shell. The different shells were chosen in order to investigate the effect of chain length, volume and grafting density. In an effort to understand the general trends governing the stability of these systems we performed SAXS experiments at different temperatures and solvent compositions.

General trends were clearly observed:

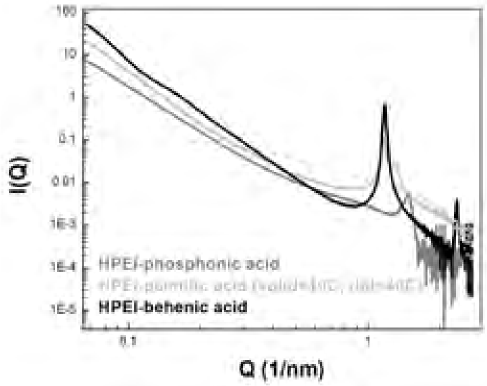
a) Long chain shells tend to stabilize the formation of ordered structures.

b) Higher grafting densities move the phase diagram from simple lamelar structures to hexagonal structures or mixed states.

c) The “order-disorder” temperature is highly dependent on shell thickness.

d) Ordered phases (lamellar or hexagonal) are adopted in low ε solvents. Mixtures as low as 30% higher polarity solvent strongly influence the phase diagram of the system.

The figure bellow shows (just as an example) the dramatic effect on the SAXS diagrams due to different capping molecules and, for the same capping, different temperatures.



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HIGH-THROUGHPUT SYNCHROTRON SMALL-ANGLE SCATTERING STUDIES ON LIPIDIC MESOPHASES FOR PROTEIN ENCAPSULATION

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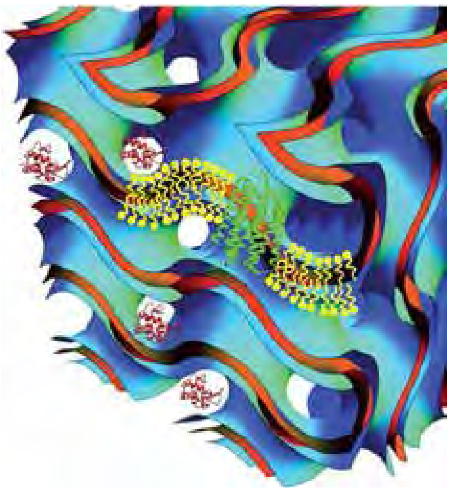

Figure 1: Schematic of a representative soluble protein and integral membrane protein contained within a lipidic cubic phase.

Self-assembled lipidic cubic phases are attracting increasing interest as biocompatible carriers of large biomolecules including proteins, peptides, DNA and drugs, Figure 1.[1] A suite of new high-throughput techniques to synthesise and formulate libraries of lipidic mesophases will be described.[2] Structural characterization of these materials for protein and peptide encapsulation, carried out at the SAXS/WAXS beamline at the Australian Synchrotron, will be described. High-throughput assessment of functionality for membrane proteins and peptides contained within cubic phases is also presented.[2, 3] Robust and predictive computational models are used to predict how the lipidic material changes over time and under the influence of additives.[4] We demonstrate how this high-throughput method allows screening of the extremely large variable physiochemical space for *in meso* crystallization, which would be unreasonable to explore using traditional experimental methods.[5, 6] In addition the application of this technique to a wide variety of applications for lipidic mesophases will be described, including pharmaceutical (drug discovery, drug delivery, gene therapy and medical imaging), materials science (biosensors, detergent industries), biology (long-term storage of fragile proteins, crystallization) and chemistry/physics (fundamental surfactant and lipid phase behaviour studies), which are currently restricted by difficulties in handling and characterizing this highly viscous material.

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MICROSTRUCTURE OF FATTY ACID ORGANIC SOLUTIONS BY SANS COMBINED WITH MOLECULAR DYNAMIC SIMULATIONS

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The small-angle neutron scattering (SANS) data for diluted (< 3 vol. %) organic solutions of saturated monocarboxylic acids, namely, myristic ($C_{13}H_{27}COOH$) and stearic ($C_{17}H_{35}COOH$) acids, in deutarated (d-) benzene (C_6D_6) and decalin ($C_{10}D_{18}$) are interpreted with the help of molecular dynamic (MD) simulations [1-3]. The SANS curves from these comparatively small molecules can be well treated in terms of the Guinier approximation, which is, however, incorrect regarding the determination of the residual incoherent background (*bkg*) produced by hydrogen in the acid structure. The reason is a short-range solvent ordering near the acid molecules. While for the d-benzene-based solutions the corresponding inhomogeneity effect on the scattering is small, it becomes more significant for the d-decalin-based solutions, which correlates with the larger effective size of decalin as compared to benzene.

We used the method of classical MD simulations to obtain the atomic number density distributions, and, as a consequence, the spatial modulations of the scattering length density (SLD) in the solute–solvent interface area (about 2 nm around the acid molecules). First, to prove the inhomogeneity effect the modelling of the SANS curves was made assuming the acid molecules to be in the rigid (all-*trans*) conformation and in a non-associated state. A number of cylindrical approximations to the simulated SLD distributions based on the linear structure of the acid molecules were probed to achieve the best consistency with the experimental SANS curves by varying the *bkg* parameter only.

As the second step, the solvation shell formation effect was considered together with other possible structural peculiarities of the acids in solutions including the acid molecule dimerization through the hydrogen bonding and alkyl chain *trans*/*gauche* isomerization. The degree of dimerization at the considered concentrations was found to be around 95 % from the additional spectroscopic (FTIR) measurements and was assumed to be 100% in the consequent modelling. The conformational flexibility was modelled in terms of the effective length and cross-sectional radius of the cylinders corresponding to the acid dimers. These two parameters were also varied in the fitting procedure in addition to the *bkg* parameter. As a result, the effective size characteristics of the acids in the two solvents were determined and compared. An increase in the solvent excluded volume for the d-decalin-based solutions was revealed showing higher lyophobic properties of the acids in decalin. This correlates with the SANS data from the concentrated solutions revealing specific differences for the two types of solvents in the nematic transition which occurs with the acid concentration growth.

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ANOMALOUS SMALL ANGLE X-RAY SCATTERING (ASAXS) STUDY OF BIMETALLIC CORE/SHELL NANOPARTICLES

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Unlike traditional solvents, ionic liquids (ILs) can be used to generate metallic nanoparticles (NPs) in the absence of any additive. Indeed, ILs can dissolve organometallic (OM) precursors, which readily form metallic NPs by decomposition (or reduction) under H_2 [1]. This process provides suspensions of metallic NPs, with accurate size control and high stability.

Such approach was extended to Ru-Cu binary mixtures of OM precursors. ASAXS measurements performed at the Ru K-edge on the CRG-BM02 beamline at the ESRF (Grenoble) have allowed to characterize the Ru-core/Cu-shell morphology of the as-formed nanoparticles. Such morphology results from the faster decomposition of the Ru precursor into Ru NPS of 2 nm size, followed by the reaction of the Cu precursor and agglomeration as a Cu shell [2].

Figure 1 shows the variation of the diameter of the bimetallic NPs with Cu content measured by TEM and ASAXS. Figure 2 shows the signature of the core-shell morphology for Cu contents equal to 0.75 and 0.9. It is characterized by a slower decrease of the differential intensities, $\Delta I = I_{NPs}(E=21.60keV) - I_{NPs}(E=22.10keV)$ with the scattering vector q, compared to the total intensities I(q). For $x_{Cu}=0.1$, the NPs consist of pure Ru, therefore I(q) and ΔI(q) behave similarly. More recent ASAXS experiments show that a core/shell morphology could be obtained through the decomposition of Ta precursor on a pre-formed Ru NPs suspension. In contrast, starting from a Ta NPs suspension, two populations of Ta and Ru NPs are obtained.

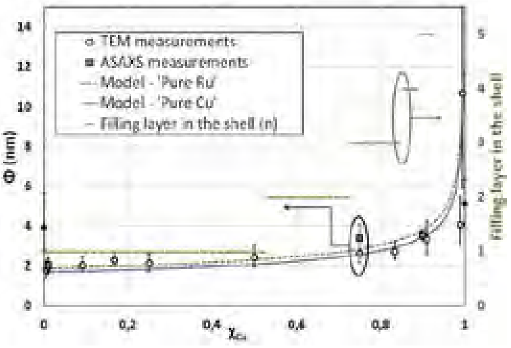

Figure 1: Diameter evolution of Ru/Cu NPs with copper content as measured by TEM and ASAXS, and comparison with a model developed in the present work.

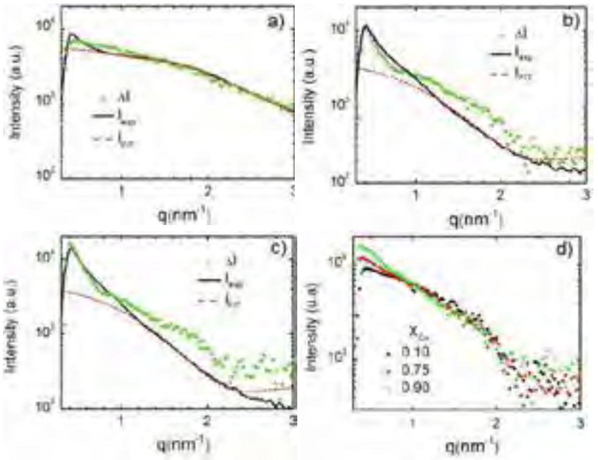

Figure 2: Experimental (black line) and simulated [3] (red dots) intensities for χ(Cu) = (a) 0.1, (b) 0.75 and (c) 0.9; the green points are the differential intensities (ΔI); (d) Comparison of the ΔI obtained for each composition.

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SHAPE AND VOLUME CHANGES IN OSMOTICALLY AND METABOLICALLY CHANGED HUMAN RED BLOOD CELLS BY USANS

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The rheology of red blood cell (RBC) suspensions, and indeed whole blood, is highly influenced by the shape of the RBCs [1]. The surface area of an RBC is fixed within tight limits, while the regulation of its shape is achieved metabolically. The transmembrane ionic disequilibrium in which $[Na^+]$ outside is much higher than inside, and vice versa for $[K^+]$ arises from the activity of Na,K-ATPase and cation-exchange pathways [2]. Thus at a fundamental level the cell's metabolism strongly influences the behaviour of blood as a complex fluid. In this work we aimed to understand the relationship between average cell volume , shape, and rheology of RBC suspensions.As a first step we used the S18 instrument at the Institute Laue Langevin (Grenoble, France) configured as a Bonse-Hart-type of double crystal diffractometer to measure directly average structure parameters of RBC suspensions. Ultra-small angle neutron scattering (USANS) rocking curves from suspensions of RBCs in different D_2O-based media: (1) isotonic with and without glucose; (2) RBCs that had been swollen and shrunken osmotically; (3) and RBCs that underwent metabolically-induced shape and volume changes.

A simple comparison of the scattering curves from RBC suspensions with and without added glucose over a 24-h period indicated the importance of metabolism in maintaining average RBC shape. While undoubtedly requiring a sophisticated interpretation, neutron scattering measurements from RBCs are weighted overwhelmingly by the signal from the concentrated solution of protein (mostly haemoglobin) that is constrained by the cell's plasma membrane. A simplification of the scattering problem to essentially that of a two-phase system allowed us to use the Porod law, with its typical 3-exponential decay for slit-smeared intensity (Figure 1). Thus we could calculate an average volume per cell. Deviations of the Porod law from the data, at the lowest scattering angles was indicative of average cell shape. Deviation from the data at the highest scattering angles was indicative of aggregates of haemogobin tetramers within the RBCs. Overall we conclude that USANS, when applied to the study of RBC suspensions, provides a simple means of determining average structural parameters of metabolically active cell suspensions in a milieu closely approximating that in the cardiovascular circulation.

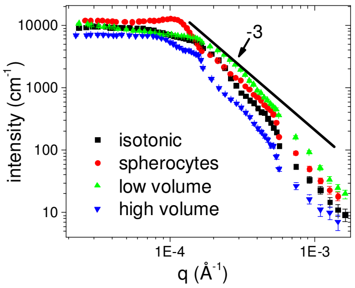

Figure 1: USANS curves from RBC suspensions containing D_2O and: 154 mM NaCl (isotonic); metabolically poisoned using NaF .and 154 mM NaCl (spherocytes); 200 mM NaCl (low volume); and 100 mM NaCl (high volume).

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INVESTIGATION OF PHENYLALANINE OLIGOPEPTIDES ACTION ON LIPID BILAYERS ORGANIZATION

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The incorporation of proteins, peptides to lipid bilayers [1- 2] affect their mechanical properties as well as their three-dimensional organization. It has been shown that peptides, at low concentrations, are adsorbed at interface with little disturbing effects on membrane elasticity. Above a given concentration, the peptides self-assembly in more complex structures, like filaments and fibrils inducing the formation of pores and eventually membrane disruption.

In this work we investigate the effect of a small sequence of amino acids, diphenylalanine (FF), on lecithin bilayers. This sequence is particularly interesting due to their ability to self assemble in nanotubes and nanowires and are part of a longer sequence (LVFFA) found in in patients with Alzheimer's disease [3]. In particular, the presence of FF groups in peptides has been related to the formation of amyloid fibrils. In the present study we also investigate two other sequences; tri diphenylalanine (FFF) and cysteine diphenylalanine (CFF). The interests in using these three distinct sequences lies in their ability to self assemble in distinct structures; while FFF form plate-like nanostructures [4], CFF form spheres [5]. The first step of this work consisted in adding a given peptide to the lecithin, varying the proportion between them, in a diluted regime, where we expected to obtain vesicles.

The peptide was co-solubilized with lecithin and then dispersed in water and sonicated. X-ray scattering experiments were performed on solutions of vesicles, with the quantity of lipid fixed in 1% wt and the molar ratio between peptide and the lecithin (P/L) was varied from 1/5 to 1/200. For FF and FFF sequences, two order of a lamellar structure are clearly observed for low concentration of peptides, indicating the presence of multilamellar vesicles. The fitting of experimental curves allows determination of membrane thickness and the number of bilayers. With increasing peptide concentration the peaks become broader and diffuse indicating a decreasing correlation length for positional ordering. The scattering curves obtained for the mixture lecithin - CFF exhibits a completely different behavior, without correlation peaks. DLS, FTIR and microscopy experiments are in course to complement our study and support our conclusions.

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A Time-Resolved Turbidity Study on the Ripening of $C_{12}E_5$ Microemulsion upon Temperature Quench

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Abstract

In this study we report the turbidimetric analysis of a ternary system consisting of pentaoxyethylene glycol dodecyl ether ($C_{12}E_5$), water, and 1-chloroalkane (such as 1-chlorodecane, 1-chlorododecane, 1-chlorotetradecane, and 1-chlorohexadecane) subjected to a systematic temperature quench. The volume fraction of the droplet was fixed at 0.010. The change in turbidity of the system on its way to the new equilibrium was measured systematically. The influence of alkyl chain length of the chlorinated oil and the concentration on the growth of the oil droplet was studied and discussed. This study further demonstrate the usefulness of a spectrophotometer in the size determination of an oil-in-water microemulsion droplets upon perturbation in equilibrium.

COMPLEXES OF CHITOSAN AND OPPOSITELY CHARGED SURFACTANT – RICHNESS IN STRUCTURE AND PROPERTIES

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Ionic co-assembly of polyelectrolytes and surfactants is a way to obtain rather complex colloids, which combine the hydrophobic domains of surfactant with the hydrophilicity and flexibility of polyelectrolytes, thereby leading to a rich variety of structures, which depends on the molecular architecture of the components. Here parameters such as persistence length and spacing of the charges have a remarkable effect on the structures formed [1]. Accordingly, pronounced differences are observed between the behavior of complexes with polysaccharide basis and synthetic polymers (typically based on vinyl monomers).

Here, we present the co-assembly of the biopolycation chitosan with weakly anionic alkyl oligoethyleneoxide carboxylic acids as a fully biocompatible alternative to conventional synthetic polyelectrolytes [2-3]. From a detailed investigation by means of SANS and SLS/DLS the resulting structures were determined which allows to correlate phase behaviour and the stuctures formed with the molecular structures of the components, e.g., rigidity of the polymer or packing parameter of the surfactant (see Figure 1 below). Furthermore these complexes are very interesting due to their high pH-responsiveness arising from both components.

The structural evolution of these complexes in aqueous solutions as a function of the mixing ratio Z of chitosan/surfactant and pH shows that, depending on Z or pH one may end up with a weak attachment of micelles to the chitosan network, a linear arrangement of micelles facilitated by the rather stiff chitosan, or densely packed micelles “glued together” by the chitosan. For bilayer forming surfactant also the formation of multilamellar vesicles can be induced where the degree of multilamellarity is controlled by the addition of oppositely charged chitosan. Such systems allow for the formulation of highly responsive systems, which can be employed for a wide range of applications. This was demonstrated by a series of showcase experiments in which chitosan/alkyl oligoethylene-oxide carboxylic acids mixtures were employed for selective removal or release of target molecules, sequestering multivalent cations [4]. In summary, these are highly biocompatible systems with a large tunable structural versatility, which can easily be employed for a multitude of interesting applications in aqueous dispersion.

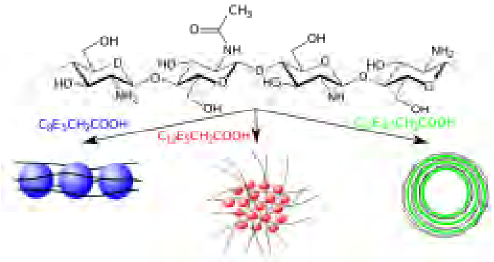

Figure 1: Self-assembled structures formed in chitosan / alkyl oligoethylene- oxide carboxylic acids mixtures.

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TUNINING THE AGGREGATION AND MIXING BEHAVIOUR OF BOLAAMPHIPHILES VIA CHAIN LENGTH AND HEADGROUP VARIATION

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The self-assembly process of bolaamphiphiles in aqueous suspension on supramolecular level as delicate balance between hydrophobic self-aggregation of alkyl chains and repulsion among headgroup is followed by small angle X-ray and neutron scattering. Wide polymorphism of formed complexes from nearly spherical micelles to rigid or flexible nanofibers [1], lamellar aggregates [2] or square lamellas [3] have been observed and their transition have been investigated. The information on packing possibility of bola molecules depending on size and symmetry, pH sensitivity of head groups and length, rigidity and modification of alkyl chain is obtained and compared with other techniques and calculations. Phenylene-modified bolaamphiphiles [4,5] in aqueous suspension show that the alteration of para- to meta- and ortho-substitution of the alkyl chains on the central phenyl ring leads for the pure bolaamphiphiles to the preferred formation of small micellar aggregates rather than to nanofibers. The mixing of these novel phenylene-modified bolaamphiphiles with bilayer forming phospholipids, *e.g.*, DPPC and DSPC, leads to the formation of small bilayer fragments or disk-like aggregates with increased thermal stability if the ortho-substituted bolaamphiphile is used [5].

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ASAXS INVESTIGATIONS ON BIMETALIC NANOPARTICLES SYNTHESIZED BY MICROWAVE ASSISTED METHOD

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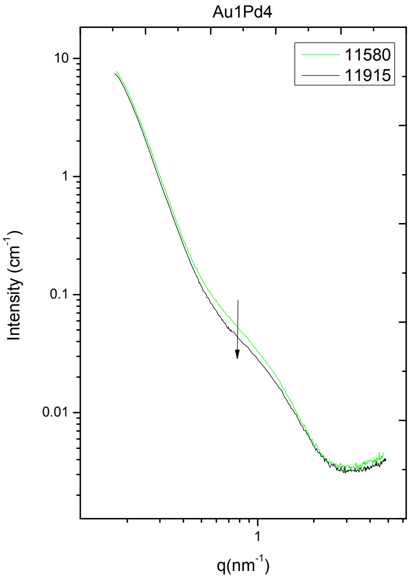
Bimetallic nanoparticles are a novel class of materials usable for catalysis, fuel cell, water splitting, photo-catalysis and thermoelectric applications. They offer a larger panorama for achieving a wider variation of electronic, optical and catalytic properties over their monometallic counterparts [1-3]. Controlling the distribution of a particular element in bimetallic nanoparticle systems, as well as shape and size of the bimetallic nanoparticles allows property variations for specific applications. Here, a two-step microwave-assisted polyol fabrication is applied to prepare bimetallic nanoparticles of Au/Pd and Au/Pt of different ratios [4]. ASAXS investigations are performed on the X-ray absorption edges of elements present in the bimetallic nanoparticles. Complementary investigation methods as UV-Vis spectroscopy and Transmission Electron Microscopy were applied to for further clarifications on the structure of nanoparticles [4]. The aim is to evaluate shape, size, size distribution of the nanoparticles and moreover, the special distribution of particular elements in the system. The figure exemplifies an ASAXS effect near Au X-ray L3 absorption edge (11919 eV) on the sample with the ratio Au1Pd4. Clearly, the ASAXS effect is seen in the *q*-range of 0.5 nm^{-1} to 2.0 nm^{-1}. Information on the structure of the investigated nanoparticle was calculated by nonlinear fitting of respective SAXS curves and it is found that all the samples can be described by a spherical core-shell model. ASAXS effect near the Au edge is explained by the formation of Pd enriched layer surrounding the Au nanoparticles. During synthesis in microwave, first the Au nanoparticles were formed that is followed by the reduction of Pd salt. Moreover, ASAXS data analysis reveals that with increasing concentration of Pd leads to formation of larger particles with a thicker alloyed layer. It is expected that this thick layer is enriched with Pd because that suppresses the ASAXS effect at Au K-edge at lower *q*-values. There is also a possibility that for higher Pd concentration, a pure Au NPs is followed by the formation of thin layer of AuPd alloy region followed by a thick layer of Pd. Similarly, ASAXS measurements were performed and presented on different other ratios of bimetallic nanoparticles (Au/Pt, AuPd).



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IMPACT OF THE SYNTHESIS CONDITIONS ON THE AGGREGATION OF BOEHMITE CRYSTALLITES: IN-SITU SAXS CHARACTERISATION

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The transition aluminas, obtained by dehydration of the boehmite γ-AlOOH, are widely used as catalyst supports in refining. Precipitation of aluminum salts is one of the pathways to synthesis boehmite, and that allows optimizing the textural properties. The resulting precipitate consists in boehmite crystallites of size of few nanometers, aggregated in structures of thousands of nanometers which are themselves aggregated in the form of agglomerates of few microns. Previous studies [1-2] had been performed to investigate the impact of operating parameters at once on the morphology of the crystallites. They had highlighted the difficulty in correlating only the crystallite morphology to the textural properties (BET, pore diameter/volume) of the final and dried boehmite. It appeared that the arrangement of the crystallites could also strongly affect the final texture of the boehmite gel.

The objectives of this study were double. First, it was expected to study the relationship between the process parameters and the arrangement of the crystallites during the synthesis, monitoring the formation of different size and shape of aggregates. In the second time, it was expected to establish the link between the characteristics of the crystallites and the aggregates with the textural properties of alumina.

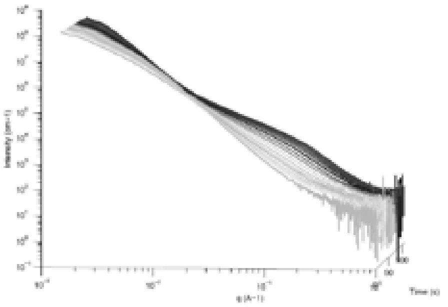

Figure 1: SAXS measurements obtained with a time feeding of 9 min.

To success in investigating these two points, various syntheses with different process parameters (feeding flows, mixing, etc.) have been monitored by *in situ* Small-Angle-X-Ray Scattering thanks to the high X-ray flux available at SOLEIL, on the SWING Beamline (see Figure 1). The model of Beaucage [3] has been used to analyze the spectra. It has allowed describing throughout the synthesis, the evolution of, first the primary particles sizes, secondly the size and the fractal dimension of the aggregates and finally the size and the fractal dimension of the agglomerates. It has appeared that the time feeding of the reactants that controls the local supersaturation inside the reactor on the surface of the particles does drastically impact the phenomena of aggregation and agglomeration of the crystallites. Besides, cryo-TEM and textural analyses have been performed to attempt linking the multi-scale structure of the boehmite crystallites in suspension with the porous structure of the boehmite dried powder.

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ALIGNMENT OF SPINDLE –SHAPED PARTICLES IN A LIQUID JET STUDIED BY TIME RESOLVED SAXS EXPERIMENTS

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Liquid jet injection systems have become an attractive tool to study complex fluids at modern synchrotron and XFEL light sources. In particular, they offer the possibility to investigate soft condensed matter on ultra-small length and ultra-fast time scales using a small volume of sample, e.g. in non-equilibrium states, and avoiding background scattering [1]. Microfluidic jets are injected into vacuum by Gas Dynamic Virtual Nozzles (GDVN). Here, the sample is pressed through a tiny aperture forming a jet, which is compressed and focused by a surrounding gas stream [2]. In this way, broad shear stress distributions and high shear rates are formed at the liquid-gas-interface [2]. In order to study the influence of the shear rates on the sample, we performed a small angle X-ray scattering (SAXS) experiment on a colloidal dispersion of spindle-shaped hematite particles [3] in a liquid jet. In Figure 1 patterns measured at different jet locations are shown. Depending on the distance from the nozzle exit and across the jet a change of particle orientations is suggested [4]. Close to the nozzle exit, the particles were aligned with the long axis parallel to the flow direction, while further away from the nozzle, particles were aligned with the long axis perpendicular to the flow. The rotation of the hematite spindles occurs on a time scale of less than 100 µs indicating a shear rate of around 10^4Hz [4].

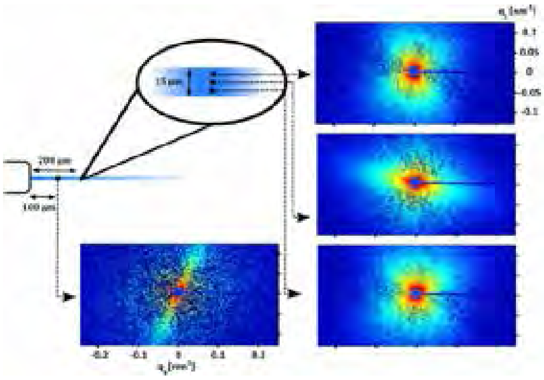

Figure 1: Schematic overview of the measured SAXS patterns at different jet locations. Jet diameter is 10 µm and jet velocity is 10m/s [4].

In this presentation these results will be compared to similar results reported from microfluidics experiments on micelles [5] and the possibility of performing rheology studies at small length scales and high rates using liquid jets will be discussed.

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TIME RESOLVED STUDIES ON THE FORMATION MECHANISM OF IRON OXIDE NANOPARTICLES USING COMBINED FAST-XANES AND SAXS

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Iron oxide nanoparticles find application in different areas like sensing [1], catalysis [2], magnetic storage media [3], and biomedicine [4,5], due to their magnetic properties and environment-friendliness. Different synthesis routes are intensively studied, one of which is the co-precipitation. The synthesis is performed by precipitating the iron precursor in an alkaline, aqueous solution. Despite many studies based on *ex situ* investigations, information on the particles formation mechanism in the aqueous solution is still scarce [6,7]. Time-resolved *in situ* investigations allow to clarify the pathways and intermediates occuring during the formation.

In the present contribution, we report on the *in situ* investigation of an iron oxide nanoparticle synthesis by coupled X-ray absorption near-edge structure (XANES) and Small Angle X-ray Scattering (SAXS) (see Fig. 1). The combination provides simultaneously information about the size and shape of particles (SAXS) and on the oxidation state and the local structure of the iron atoms (XANES). The co-precipitation synthesis was exemplary studied, using a stabilization agent to decelerate the fast precipitation of the iron oxides. This allows to detected intermediates *in situ*. The measurements were performed using a custom-made acoustic levitator as sample holder. From the data, a mechanism was derived indicating different phases of particle formation and oxidation state changes. The information obtained provided the basis for an improved control of the product of the synthesis.

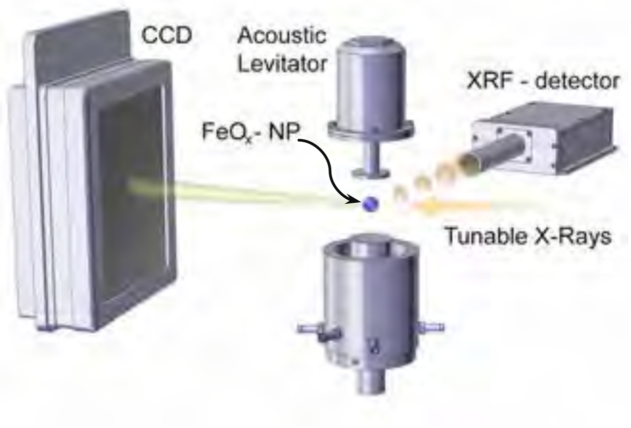

Figure 1: Experimental setup of coupling XANES and SAXS using an acoustic levitator as sample holder. XANES spectra were collected using an XRF-detector.

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THE SOLUTION STRUCTURE OF ESSENTIAL PROTEINS IN THE PRESENCE OF ULTRA-SMALL SILVER NANOPARTICLES

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We report on the synthesis of ultra-small silver nanoparticles and their quantitative characterization by small-angle X-ray scattering. The size distribution was derived by utilizing a Monte-Carlo data evaluation procedure reported by Pauw et al. [1]. Mean volume-weighted sizes are 3 nm with a size distribution width of 18 % (see Figure 1). The particles should be used as reference materials [2] for comparison of the result of different analytical methods among which are field-flow fractionation (FFF), dynamic light scattering (DLS), nanoparticle tracking analysis (NTA) and electron microscopy (EM). In addition further use of the particles is foreseen for comparison of studies on the toxicology of nanoparticles [3].

It is known that silver shows antimicrobial behavior at the macroscopic scale, but there are controversial articles where the potential toxic effect of silver is discussed. Typically the studies about the toxicology or antibacterial effect of silver species are focused on the interaction with single cell organisms or cell cultures. So far comparatively little attention has been paid to the effects of different silver species like ions or nanoparticles on proteins. Especially the interaction of nanoparticles with essential proteins is of interest regarding their cytotoxicity. The characteristics of nanoparticles can change dramatically after the transfer from water into a complex biological media by adsorption of biomolecules. A key issue, therefore, is whether silver ions or nanoparticles induce the formation of large multi-component macromolecular complexes in the presence of essential proteins. With the help of small-angle X-ray scattering we quantify changes in the structure of the proteins. This enables the investigation regarding to denaturation or aggregation behavior of essential proteins. Due to the high variety of proteins the work focused on the solution structure of four proteins: At first the interaction of different silver species with the mammalian proteins albumin, cytochrome c and hemoglobin will be investigated. If one of these proteins is inhibited in its function as a result of aggregation or denaturation the usage of silver species in consumer products has to be reconsidered due to the negative impact on the biological system of mammals and plants.

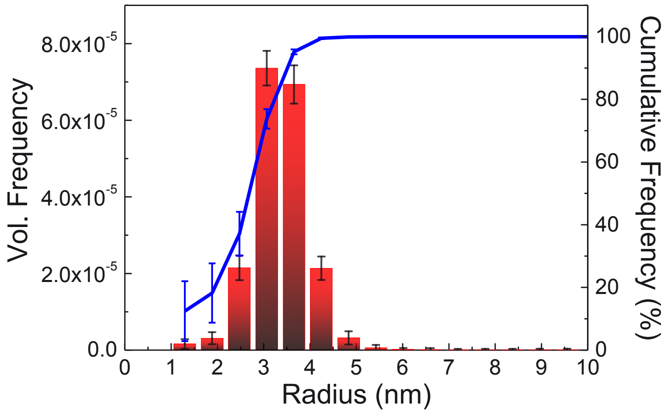

Figure 1: Volume-weighted size distribution of ultra-small silver nanoparticles in differential and cumulative presentation (left and right-hand y-axis) derived from SAXS.

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SMALL ANGLE STUDY ON VARIOUS NANOSTRUCTURES OF AMPHIPHILIC MOLECULES IN AQUEOUS SOLUTION

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Amphiphilic molecules including the surfactant and block copolymers, self-assemble into various micellar structures and represent excellent phase behaviors according to their geometrical molecular shape in aqueous solution. The self-assembled nanostructures of amphiphilic molecules can be easily controlled by the external conditions such as temperature, pH and additives that can induce a variety of geometrical molecular shapes without a chemical reaction. Therefore, the amphiphilic molecules have been of interests for a wide range of potential applications such as nanotemplates, nanobuilding blocks or drug delivery. However, the phase behavior of amphiphilic molecules under various external conditions, which is key information for practical use of amphiphilic molecules, has not been fully studied yet. Here, we report the various self-assembled structures of block copolymers under different external conditions, which have been investigated by using the small angle scattering (SAS). Depending on the external conditions, the SAS intensity showed that the block copolymer formed a variety of nanoparticle such as sphere, cylinder micelle and vesicle in low polymer concentration [1], and rich phase behaviors in high polymer concentration [2].

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LIQUID CRYSTAL REORIENTATION UNDER FLOW AT SOLID AND LIQUID INTERFACES: SAXS STUDIES IN A MICROFLUIDIC DEVICE

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We present results of synchrotron small-angle-x-ray-scattering (SAXS) studies of flow and boundary condition effects on the orientation field of liquid crystals under flow and confinement in a microfluidic device. In the first experiment with solid interfaces, a nematic liquid crystal is flowed through a square-channel cross section at varying flow rates, while the nematic director orientation projected on the velocity/velocity-gradient plane is measured by SAXS using a 2D detector. At moderate-to-high flow rates, the nematic director is predominantly aligned in the flow direction, but with a small tilt angle ≈±11° towards the velocity gradient direction. The director tilt angle is constant throughout most of the channel width, but switches sign when crossing the channel center, in agreement with the Ericksen-Leslie-Parodi (ELP) theory. At low flow rates, boundary conditions begin to dominate, and a flow profile resembling the escaped radial director configuration is observed, where the director is seen to vary more smoothly from the edges (with homeotropic alignment) to the center of the channel. In the second experiment with liquid interfaces, hydrodynamic focusing is employed to confine the nematic phase into a sheet of liquid sandwiched between two layers of Triton X-100 aqueous solutions. The average nematic director orientation shifts to some extent from the flow direction towards the liquid boundaries, although it remains unclear if one tilt angle is dominant through most of the nematic sheet (with abrupt jumps near the boundaries), or if the tilt angle varies smoothly between two extreme values (~90° and 0°). The technique presented here could be applied to perform high-throughput measurements for assessing the influence of different surfactants on the orientation of nematic phases, and may lead to further improvements in areas such as boundary lubrication and clarifying the nature of defect structures in LC Displays. Research primarily supported by the U.S. Department of Energy (DOE), Office of Science, Basic Energy Sciences (BES), under award DE–FG02–06ER46314 (dissipative out-of-equilibrium structures in complex material systems), and the National Science Foundation (NSF) under award DMR-1401784 (phase behavior of confined matter).

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TIME-RESOLVED SAXS STUDY ON THE AGGREGATES FORMED BY MIXING OPPOSITELY CHARGED LIPID BICELLES

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Time-resolved small-angle X-ray scattering (TR-SAXS) was applied to study the charged lipid exchange between oppositely charged disc-shaped bicelles at close contact. Using disc-shaped bicelles eliminates the effects of flip-flop and curvature on the lipid exchange. Disc bicelles can be doped with charged lipids to control their surface charge density [1,2]. The oppositely charged bicelles form alternatively stacked aggregates right upon mixing [3]. The number of stacked layers is correlated to the bicelle surface charge density. The exchange of the charged lipids would gradually reduce the surface charge density and turn the stacked bicelle aggregates to become shorter and shorter. Eventually, the stacked bicelles will all dismantle into free bicelles once they are neutralized. Following the structural evolution of the stacked bicelle aggregates by as a function of time would reveal the trend of the charged lipid exchange process between the oppositely charged bicelles in close contact (Fig. 1). It was found that initially at high surface charge density with almost no free water layer between the stacked bicelles, a fast exchange kinetics dominates the charged lipid exchange process. At later stage with lower surface charge density and larger water gap between the stacked bicelles, a slow exchange kinetics takes over. The fast exchange kinetics is correlated with the close contact of the bicelles when there is almost no free water layer existed between the tightly bound bicelles with a charged lipid exchange time constant as short as 20~40 min. When the water gap becomes larger to have free water layer existed between the stacked bicelles, the fast lipid exchange kinetics is taken over by the slow lipid exchange kinetics with time constants around 200~300 min, which is comparable to the typical time constant of lipid exchange between vesicles in aqueous solution. These two kinds of exchange modes fit well with the lipid exchange models of transient hemifusion for the fast mode and the monomer exchange for the slow mode.

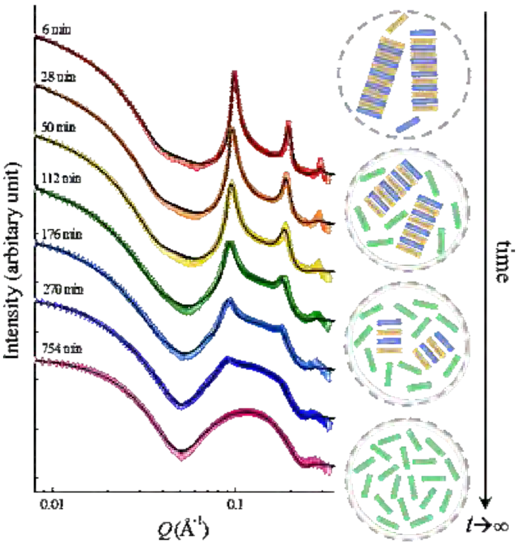

Fig. 1 TR-SAXS profiles of mixing oppositely charged bicelles of 15% charge doping at room temperature and the schematics of the structural evolution of the mixed bicelle system.

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SHEAR-INDUCED MACROSCOPIC “SIAMESE” TWINS IN SOFT COLLOIDAL CRYSTALS

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Soft materials such as micelles or polymers can form highly ordered crystals which are inherently very susceptible to shear. Large shear strains lead to the formation of macroscopic Siamese twinning in lyotropic fcc crystals formed by block copolymer micelles. The twins exist over the whole gap of the shear cell with the twin boundary located inside the gap. Our experiment indicates that the deformation twinning mechanism is analogous to the plastic deformation of nanocrystalline metals under high shear stress and high deformation rates.

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INVESTIGATION OF OSMOTIC DESWELLING OF POLYSTYRENE MICROGELS ON POLYMER ADDITION

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In colloid science the interplay of theory and experiment often enables creating and customizing novel soft materials. Theory predicts that introducing short-ranged attractive interactions by adding linear polymer chains to colloid suspensions leads to a melting of the repulsive glassy state. On further increasing the attraction strength (i.e. the polymer concentration) the colloidal particles form a novel glassy state, the attractive glass. According to theory this fluid region grows when the attraction length δ shrinks. Experimentally, this amounts to reducing the ratio $\delta = R_g/R_c$ of the radius of the added polymer coils to the radius of colloidal particles. Recent studies of our group showed experimentally in colloidal systems of polystyrene (PS) microgel colloids with added linear PS that the theories' predictions that the fluid region grows when attraction length shrinks can be realized qualitatively as shown in Fig.1[1].

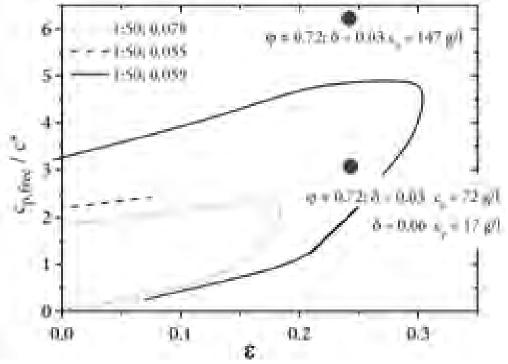

Figure1: Re-entrant region of PS-microgel systems with two different attraction lengths studied by our group. Data are given in rescaled units: cp,free/c* and $\varepsilon = (\varphi - \varphi_g)/\varphi_g$, cp,free was calculated within the framework of scaled particle theory following [2].The larger attraction length of δ = 0.08 lead to a smaller re-entrant area as the smaller one of δ = 0.06. The points represent the states of the samples investigated within this work.

However, the extent of the refluidization was much stronger than predicted and then found for PMMA hard sphere colloids. One possible reason for this unexpected behaviour could be the osmotic deswelling of the microgels on polymer addition. We studied the influence of polymer addition to colloidal systems of PS microgels with regard to their osmotic deswelling. This was possible by performing SANS experiments on D11 at ILL employing contrast variation techniques in toluene/toluene-D8 mixtures with host-tracer-mixtures of our colloidal system. We measured the dependence of the particle form factor P(q) of fully deuterated PS microgel tracers in colloid polymer mixtures for two different attraction lengths of δ = 0.06 and 0.03 at very high colloidal volume fractions of φ = 0.72 and sufficient high polymer concentrations (cf. points in Fig. 1). In the course of the experiments we wanted to resolve even a slight change in radius, so it was necessary to improve the resolution of the experiment. Therefore the detectors' pixel density was increased from 128 x 128 to 256 x 256 pixels and additionally we measured three closely spaced sample-detector distances. As a result the radius can be determined with an accuracy of $\Delta R < 1$ nm. Despite within experimental accuracy there is no osmotic deswelling identifiable for the larger attraction length of δ = 0.06, but the system with δ = 0.03 showed a significant change in radius.

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MICROFLUIDIC-SANS: PROCESSING OF COMPLEX FLUID AND HIGH THROUGHPUT CHARACTERISATION

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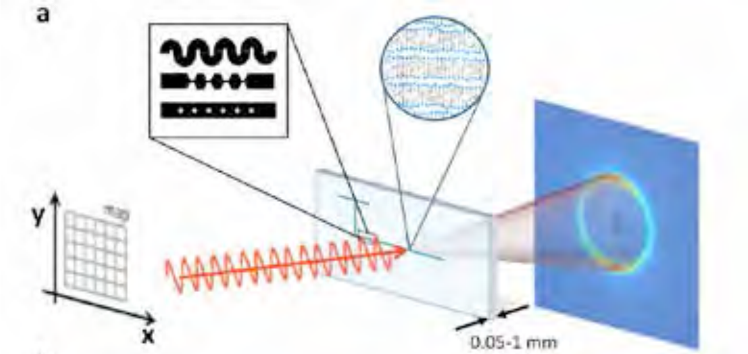

Figure 1: Schematic of a microfluidic-SANS experiment, depicting patterned microchannel geometries and an illustration of a lamellar system along with a 2D scattering pattern.

The coupling of microfluidics and small angle neutron scattering (SANS) is successfully demonstrated [1]. We have developed novel microfluidic devices with suitably low SANS background and high pressure compatibility for the investigation of flow-induced phenomena and high throughput phase mapping of complex fluids. We have obtained scattering profiles from 50μm channels, in 1 - 100 second acquisition times. The microfluidic geometry enables the variation of both flow type and magnitude, beyond traditional rheo-SANS setups, and is exceptionally well-suited for complex fluids due to the commensurability of relevant time and lengthscales. We study three model flow responsive systems, including surfactant/co-surfactant/water mixtures, with well-known equilibrium phase behaviour: (i) sodium dodecyl sulfate (SDS)/octanol/brine, (ii) cetyltrimethyl ammonium chloride (C_{16}TAC)/pentanol/water and (iii) a model microemulsion system ($C_{10}E4$ /decane/ $D_2$0).

Using an online micromixer we implement a high throughput approach, scanning in excess of 10 scattering profiles/minute for a continuous aqueous surfactant dilution over two decades in concentration, as shown in figure 2.

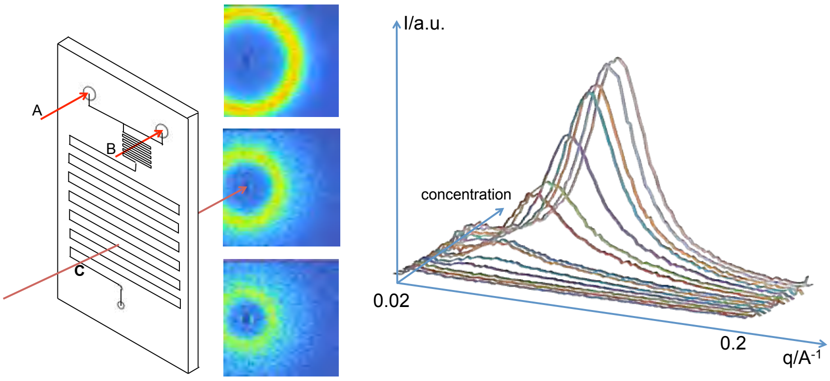

Figure 2: Left: Schematic of microfluidic mixer: A concentrated CTAC/D2O solution is pumped through inlet **A** and pure D_2O is pumped through inlet **B**. By varying the ratio of flowrates, a continuous dilution is generated, which is measured as a function of time at position **C**. Right: scattering profiles, obtained at a rate of 12/minute, plotted as a function of concentration.

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KINETIC PHENOMENA OF SURFACTANT MICELLES STUDIED BY TIME-RESOLVED SAXS

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Surfactant molecules have the ability to aggregate into a wide variety of interesting and highly dynamic nanostructures. Most studies relate to the statics, in particular the structure and macroscopic properties such as surface tension, conductivity foaming etc. [1]. However, concerning their dynamics much less is known and very much limited to relaxation studies where the system is slightly perturbed off its equilibrium and monitored back a new equilibrium. Here we take advantage of the time resolved small-angle scattering (TR-SAS) to follow typical non-equilibrium kinetic processes in surfactant micelle systems over time scales starting from a few milliseconds. In the first part we will focus on the formation kinetics of maltose-based non-ionic surfactant system (dodecylmaltoside) [2] by dissolving the system in pure DMF and rapidly induce micellization by adding water using a stopped-flow apparatus. The results show that the process can be described using a nucleation & growth model where only unimer exchange is allowed. We will relate these results to those for block copolymer micelles studied previously [3]. In the second part of the presentation we will address the sphere –to-cylinder transition of surfactant micelles [4]. We use an archetypical, simple surfactant system consisting of sodium dodecyl sulphate (SDS) in aqueous NaCl solutions and “film” the process for the first time using small-angle X-ray scattering combined with stroboscopic stopped-flow schemes. The results show that worms are formed by fusion of globular micelles and short cylinders in a fashion that bears similarities to step-like polymerization mechanisms. In the last part we will address the self-assembly of light sensitive surfactants which forms micelles that can be reversibly manipulated dissolved and reformed upon UV/blue light illumination. By integrating synchrotron SAXS with a photospectrometer, we are able to follow both processes *in situ*.

In the presentation we shall give an overview over the different results and discuss the strength of the time-resolved methods based on neutrons and X-rays in studies of surfactant kinetics.

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COMPARATIVE ANALYSIS OF SUPRAMOLECULAR AGGREGATES FORMED BY TAPERED DENDRONS OF DIFFERENT NATURE AND CHIRALITY IN BULK AND IN SOLUTIONS

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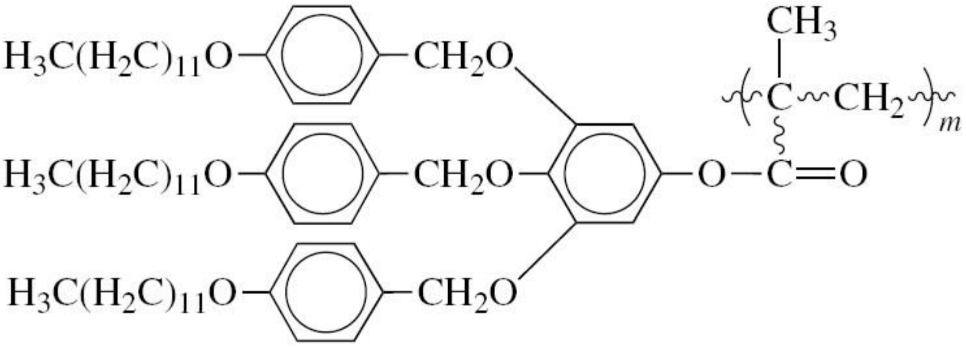
This report is devoted to the comparative analysis of self-assembling of tapered amphiphilic dendrons in bulk state and in solutions. X-Ray structural analysis of dendrons on the basis of gallic acid together with differential scanning calorimetriy, polarizing optical microscopy and molecular modeling revealed a rich phase behavior: 1-D smectical layers, 2-D ordered and disordered columnar phases of different symmetry, 3-D crystalline hexagonal phase, cubic primitive, Pm3n and Im3m micellar phases as well as bicontinuous gyroid mesophase of Ia3d symmetry were discovered in such compounds.



However, such variety follows several rather simple rules. To study the general features of self-organization related to the action of weak noncovalent bonds, it is interesting to characterize the structure of supramolecular objects not only in the condensed state but also in solution. To determine the character of mutual interaction and the packing of mesogenic groups, the shape and dimensions of the formed supramolecular aggregates were studied. The effect of the molecular mass of polymers with tapered dendrons as side substituents on their self-assembly ability was studied as well. It was shown that in fresh solutions of a low-molecular-mass polymer, extended piles composed of several molecules are formed. Each molecule form a disc with a diameter of ~4.4 nm, which is similar to the diameter of columnar phase cylinders in the solid state. In solutions of a high molecular-mass polymer, several molecules form a wormlike particle.

We have also conducted comparative analysis of helical supramolecular columnar aggregates formed by the amphiphilic dendrons with chiral dipeptide groups in their cores: L-Tyr-L-Ala, D-Tyr-D-Ala and D-Tyr-L-Ala -OMe. It was revealed that such compounds self-assemble into porous elliptical and circular columns which, in turn, self-organize into centered rectangular columnar or hexagonal columnar 2-D lattice. Solutions of enantiopure compounds contain similar aggregates. Racemic mixtures however do not contain any supramolecular particles due to the formation of D-L dimers.

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AGGREGATION AND DISPERSION PROCESS OF POLYMER-CONJUGATED GOLD NANOPARTICLES USING MODEL-POTENTIAL-FREE METHOD

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Uehara *et al.*[1] reported the glutathione-triggered dispersion of gold nanocomposites composed of gold nanoparticles and copolymers [poly(N-n-isopropylacrylamide-co-acryloyldiethyletriamine)] attached to the surfaces of the nanoparticles. The localized surface plasmon band of the aggregated nanocomposites shifts from 520 nm to 650 nm, because of the assembled nanoparticles that are conjugated with the diethylenetriamine groups incorporated into the copolymers. Glutathione added to the nanocomposite solution adsorbs onto the surface of the gold cores to liberate diethylenetriamine groups, resulting in spontaneous disassembly that changes the plasmon band to 520 nm as observed in dispersed nanoparticles.

Sumi *et al.*[2] devised model-potential-free (MPF) method for evaluation of structure factor and interaction potential using small-angle X-ray scattering (SAXS) data, instead of using the Derjaguin–Landau–Verwey–Overbeek (DLVO) model. The method is free from assumption and approximation by specific model potential functions. Thus, the MPF method is applicable for investigation of the interaction in significantly complex system such as the present polymer-conjugated nanocomposites.

SAXS measurement systems such as in-situ apparatus for SAXS/UV-vis spectra, in-situ beam monitoring devise, entirely titanium sample holder were constructed by our group[3]. We have struggled to investigate the mechanism of the aggregation/dispersion of the nanocopmosites based on combination of the developed nanocomposite system, the MPF methodology and the in-situ experimental technique.

The results indicated that valley of the primary minima of the obtained interaction potential becomes deeper with an increase of the reaction time. It was also found that the energy barriers that suppress the dispersion processes were observed as significantly lower maxima compared to potential profiles evaluated in nanoparticles dispersed by coulombic repulsion. Furthermore, distance of inter-nanoparticles estimated from radial distribution functions remained to be the same during whole of the dispersion process.

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STRUCTURE OF PHOSPHOLIPID MIXED MICELLES (BICELLES) INVESTIGATED BY SMALL ANGLE X-RAY SCATTERING

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Mixed phospholipid micelles are widely applied in NMR studies of membrane proteins in solution, as they can solubilize them and be aligned in the magnetic field. Mixing of dihexanoyl phosphatidyl choline (DHPC) and dimyristoyl phosphatidyl choline (DMPC) in certain ratios leads to the formation of anisotropic micelles, called bicelles. It has been proposed that the DMPC molecules with relatively long C14 hydrocarbon tails constitute a flat bilayer, whereas the DHPC molecules with shorter C6 tails form the rim of the bicelles [1,2]. Thus, according to this idealized picture, the DMPC/DHPC ratio (Q) determines the size of the bicelles. Although SAXS [3,4] and SANS [5,6] data have previously been published for this system, only limited analysis in terms of a geometric model for the shape of the bicelles has been done for SANS data [5,6], and no modeling has been performed for SAXS data. In this work, SAXS data were collected for a wide range of DMPC/DHPC ratios at 37 °C. Samples with concentrations as applied for NMR measurements with 30 wt% lipids were diluted to avoid structure factor effects in the SAXS patterns. Dilution with pure solvent, however, leads to an increased DMPC/DHPC ratio in the micelles, as DHPC has a relatively high solubility. Dilutions with solutions of different DHPC concentrations were performed to find the concentration which does not lead to a change in the micelle composition. For the correct concentration, the structure factor effects decrease upon dilution, whereas the form factor does not change. Absolute-scale modeling of the SAXS data using molecular constraints reveals a relatively complex set of morphologies as a function of DMPC/DHPC ratio with different morphologies of the aggregates, which do not follow the suggested trends for the ideal bicelle model. At $Q = 0$ (pure DHPC) the SAXS data can be modeled as an oblate core-shell micelle. At $Q = 1$ and $Q = 2$, the data can be modeled as cylinders, in agreement with [6], with a core and two shells for which the cylinder length increases with Q. At $Q = 3.2$ the SAXS data are in agreement with coexistence of similar cylinders as at $Q = 2$ and infinite bilayers. Data at $Q = 4$ is modeled as infinite bilayers and at $Q = \infty$ (pure DMPC) there is coexistence between multilamellar structures and free bilayers.

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A STRUCTURAL SAXS STUDY OF MYOGLOBIN AND α-LACTALBUMIN IN COMPLEX WITH THE BIOSURFACTANT RHAMNOLIPID

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Biosurfactants are surface active molecules that can be produced in microorganisms [1]. If biosurfactants, as for example rhamnolipids, are to replace common surfactants, it is important to study their interactions with macromolecules such as proteins. The structure of micelles of the biosurfactant rhamnolipid (RL) and of RL in complex with, respectively, myoglobin (Mb) and α-Lactalbumin (αLA) was determined by small angle x-ray scattering (SAXS). For comparison, also some investigations of sodium dodecyl sulphate (SDS) micelles and SDS-αLA complex structures were performed. The SAXS data from the pure RL samples could be modeled as prolate cores-shell micelles with a remarkably small core of 4 Å, shell thickness of 16 Å, and an aggregation number of 50. The scattering data for the αLA-RL complex (Figure 1) could also be described by a prolate particle with a similarly sized core and a shell thickness of 19 Å. This shell includes both RL head groups and partly unfolded αLA. Above saturation by surfactant, the complex consists of one protein and about 30 RL molecules. For the Mb-RL complexes, an additional shell is needed for modeling the SAXS data. It only contains protein and has a significantly smeared interface due to disorder in the shell. Mb-RL complexes also has one protein but varies in number of RL molecules from 41 to 57 with increasing RL concentration, suggesting that the studied RL concentration range is not sufficient to reach a surfactant saturated complex. The SAXS data of the SDS micelles could be modeled with an oblate morphology with a core having a short axis of 12 Å, fixed shell thickness of 5.5 Å, and aggregations number of 74. Data for αLA-SDS complexes are described by a prolate particle with a core radius of 11-14 Å and a shell of thickness 8-12 Å. The particles consist on average of more than one (up to three) αLA and up to 43 SDS per αLA. The number of surfactants in the αLA-SDS complexes does not increase continuously with increasing surfactants concentration as seen for the RL-containing complexes. The difference in surfactant aggregation number and number of protein per complex between αLA-RL and αLA-SDS indicates that αLA interactions with RL are more important than the RL-RL interactions for the formed complexes, whereas the SDS-SDS interactions in the SDS micelles are relatively more important than the αLA-SDS interactions in these complexes.

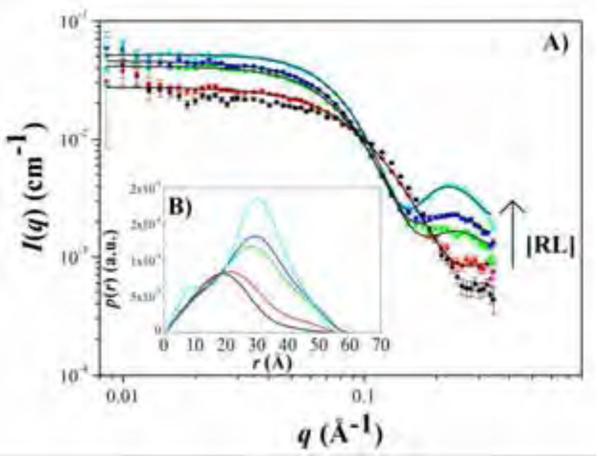

Figure 1.A) Scattering from pure aLA (black) and with increasing RL concentration. B) p(r)-functions for pure aLA and increasing RL concentration.

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CHARGE EFFECTS ON SHEAR THICKENING AND ONION FORMATION IN A NONIONIC SURFACTANT SOLUTION

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A shear-induced onion formation from a planar lamellar structure in a surfactant solution has known for decades. Such onions fill all the space of the solution without excess water and cause shear thickening [1]. In a nonionic surfactant aqueous solution, pentaethylene glycol monododecyl ether ($C_{12}E_5$) and D_2O, onion formation associated with shear thickening is observed in 40 wt% $C_{12}E_5$ solution at T=55˚C [2]. Effects of charge on this phenomenon were investigated using anionic-nonionic surfactant mixed membranes [3].

Here we studied a rheological behavior of a dilute solution of $C_{12}E_5$ (10wt%) and D_2O, and also effect of charge was investigated with adding either sodium dodecyl sulfate (SDS) or an antagonistic salt ($RbBPh_4$). From conventional small-angle neutron scattering (SANS) experiments, we confirmed that a disordered structure of $C_{12}E_5$ membrane at T=59˚C transforms to an ordered lamellar structure by adding charge molecules. The antagonistic salt behaved almost identical to the charged surfactant. As shown in Figure 1 shear thickening is observed at various molar ratio of SDS and $C_{12}E_5$, S. We measured rheo-SANS, which confirmed that planar lamellar layers are oriented parallel to the flow direction at low shear rate, while onion structure is formed as evident by isotropic scattering pattern, which is eventually broken by further increase of the shear rate. Even in the case of a non-charged bilayer (shown as S=0) a shoulder in shear rate dependence of solution viscosity was originated from the onion-like structure formation. In order to understand the bilayer elastic property at a steady state, we measured bending elastic modulus using neutron spin echo (without shear). We will combine these data to understand the onion formation mechanisms, especially in the dilute and low inter-membrane interaction cases.

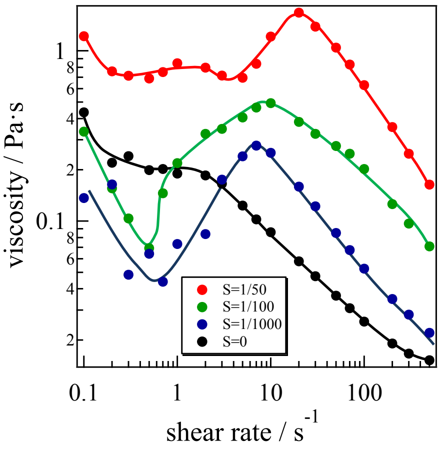

Figure 1. SDS concentration dependence of shear viscosity against shear rate of mixtures of $C_{12}E_5$ (10 wt%), D_2O and SDS. Black; without SDS (S=0), Blue; S=1/1000, Green; S=1/100, Red; S=1/50.

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CHARACTERIZATION OF PROTEIN-NANOPARTICLE INTERACTIONS: INSIGHT FROM SCATTERING EXPERIMENTS

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Nanoparticles (NPs) have been widely used in the fields of biology and biomedicine due to their unique properties as biological sensors, drug and gene carriers and targets for imaging of life cells and tissues [1]. When NPs are placed in physiological environments, a very large surface is exposed to the biomolecules present in these biological fluids, i.e. proteins, inducing thereby specific protein-NP interactions. The specific binding and the affinity of the proteins to the nanoparticles result very often in the formation of core-shell complexes constituted by a NP core surrounded by a protein corona [2-4]. This has a direct impact on the way cells and membranes recognize and absorb the NPs [5]. In addition, the formation of an adsorbed protein layer around the NPs may decrease their colloidal stability, causing a dramatic effect in biomedical applications as blockage of blood vessels in intravenous injections. Thus it is crucial to understand and characterize the interactions that arise between proteins and nanoparticles.

In the present work we report on the study of the behavior of functionalized gold nanoparticles (AuNPs) in the presence of different biological fluids. We have used AuNPs with different surface functionalization: citrate-stabilized bare particles and sterically stabilized PEGylated particles with positive, negative and neutral functionalized surfaces. The dynamic and structural properties of the AuNPs were studied with a combination of direct and indirect space techniques such as transmission electron microscopy (TEM), small-angle x-ray scattering (SAXS) and small-angle neutron scattering (SANS). The latter allowed us to quantitatively investigate the core-shell structure of the AuNPs by performing contrast variation studies. Moreover we took advantage of the special optical properties of AuNPs, which results in a considerably enhanced depolarized component of the scattered light. We used depolarized dynamic light scattering (DDLS) to discriminate scattering contributions from the complex biological background and obtain the translational and rotational diffusion coefficients of AuNPs and AuNP-protein complexes as a very sensitive tool to investigate the behavior of NPs in complex biological fluids with unprecedented resolution [6-7].

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KINETICS OF SPONTANEOUS SOLUBILIZATION OF OLEIC ACID BY THE PLANT-BASED INGREDIENT METHYL ESTER ETHOXYLATE

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The plant-based ingredient of nonionic surfactant, methyl ester ethoxylates (MEE) has found great utility as fabric liquid detergent products because of great advantage of it for the formulation of highly concentrated liquid detergent and the high detergency of odor stain. Recently some reports have been published on the influence of odor stain on micelle properties. However, characterization of micelle properties is very difficult due to the mutual influence of a lot of factors like a size, shape and micellar interaction in mixtures. The present study aims to characterize the micelle properties of aqueous solutions relationship between surfactant and odor stain.

In this study, we used MEE and alcohol ethoxylates (AE) as surfactants and examined the influence of odor stain of oleic acid on micelle properties. We determined the solubilized solutions using time-resolved small angle X-ray scattering (SAXS). Static structure factor deduced the pair distance distribution function of micelles by a generalized indirect Fourier transformation (GIFT) methods and the radial electron density distribution of the micelles by Deconvolution analysis of the SAXS data.

Figure 1 shows the solubilization of the oleic acid in AE and MEE micellar solutions under the no stirring condition. As a result, AE didn't change the micellar size, while MEE changed the micellar size with time. We could clarify that MEE micelles solubilized oleic acid spontaneously using time-resolved SAXS applying GIFT methods. And we calculated micellar electron density by Deconvolution analysis. Oleic acid was solubilized into the lipophilic part of the MEE micelles under the no stirring condition.

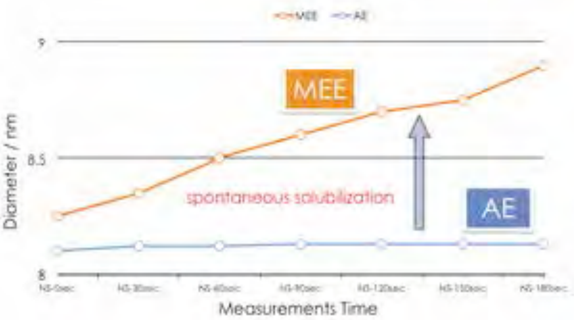

Figure 1. The micellar sizes of MEE and AE from time-resolved SAXS

In addition, it was confirmed the micelle properties were in agreement with other measurements of FT-IR and QCM-D. We have successfully clarified the characteristic of spontaneous solubilization of oleic acid in MEE aqueous solutions.

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A THERMODYNAMIC AND STRUCTURAL STUDY OF SDS/TWEEN MIXED MICELLES

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It is known that the surfactant molecules can self-assemble forming aggregates of various types, sizes and shapes. For example, globular and cylindrical micelles, vesicle bilayers, among others. In general, the physical and chemical properties of micellar systems have always been of great interest due to the applicability of these systems in daily life [1]. More recently, such interest has turned to micelles composed of more than one surfactant (the so called mixed micelles). This is due to the fact that such mixtures, which have many industrial applications, provide features that are primarily controlled by the amount of each surfactant in the mixed micelle [2]. For this reason, mixtures of ionic-ionic, nonionic-nonionic and ionic-nonionic surfactants have been studied by different techniques.

In this work a study of mixed micelles was performed using a combination of Small Angle X-ray Scattering (SAXS), Conductimetry, Surface Tension and Isothermal Titration Calorimetry (ITC). These techniques are widely used for the study of colloidal systems in solution and they provide a structural and thermodynamic understanding of the system as well as interesting information about its properties. The mixed micelles were composed by two kinds of molecules: an ionic surfactant, Sodium Dodecyl Sulfate (SDS), and one of four non-ionic surfactants, Tween 20, 40, 60 or 80. SDS has wide application in many branches of industry, from personal hygiene to chemical processes [1]. The Tween surfactants are non-toxic, being widely used as emulsifiers for nutritional, domestic, scientific, and pharmaceutical products [2]. The SDS-Tween system has been investigated in the literature but to date no structural study using scattering techniques on such a system (or even the combination SAXS/ITC/Conductimetry/Surface Tension) was found, thus highlighting the contribution of this work [3].

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STRUCTURE AND STACKING ORDER IN CRYSTALS OF ASYMMETRIC DUMBBELL-LIKE COLLOIDS

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The crystalline structure assembled out of charge-stabilized asymmetric dumbbell-like colloidal particles in ethyl alcohol by sedimentation has been probed using small-angle X-ray scattering with microradian resolution [1]. The existence of plastic face-centered cubic crystals was inferred from the observed Bragg peaks. The presence of stacking faults and the mosaic structure of the sample lead to the appearance of diffuse scattering, forming Bragg scattering cylinders in the three-dimensional reciprocal space. The quality of the crystalline structure, as ascertained from a detailed analysis of the diffuse scattering intensity distribution, indicates the presence of only 1.5% of stacking faults between the hexagonal close-packed layers.

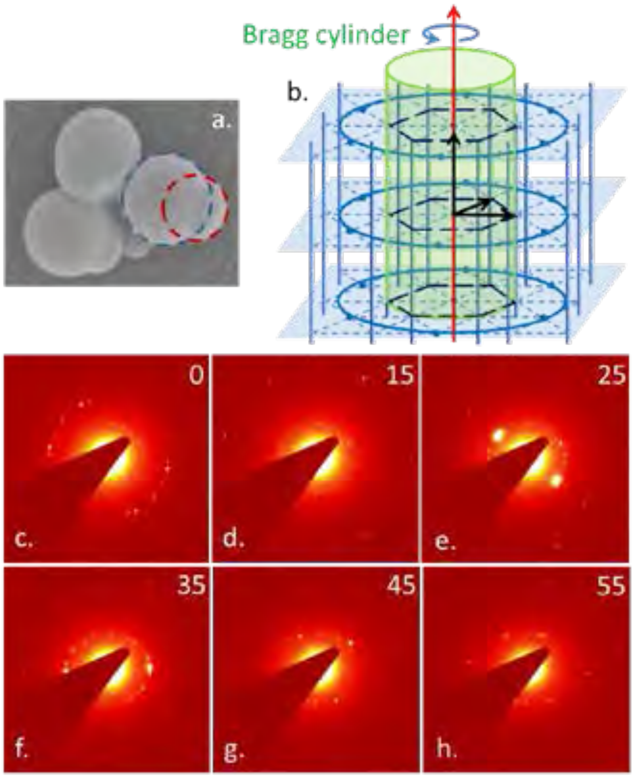

Figure 1. (a) Scanning electron micrograph (SEM) of the dumbbell-like colloids, (b) General reciprocal lattice of close packed structure with the illustration of Bragg cylinder, (c-h) Diffraction patterns of the crystal at different rotation angles.

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TUNING THE COLLOIDAL CRYSTAL STRUCTURE OF MAGNETIC PARTICLES BY EXTERNAL FIELD

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Manipulation of the self-assembly of magnetic colloidal particles by an externally applied magnetic field paves a way toward developing novel stimuli responsive photonic structures. Using microradian X-ray scattering technique we have investigated the different crystal structures exhibited by self-assembly of core–shell magnetite/silica nanoparticles [1]. An external magnetic field was employed to tune the colloidal crystallization. We find that the equilibrium structure in absence of the field is random hexagonal close-packed (RHCP) one. External field drives the self-assembly toward a body-centered tetragonal (BCT) structure in agreement with simulation results [2]. However, the *c*/*a* ratio is found to deviate by as much as 15% from the expected bct structure of touching spheres.

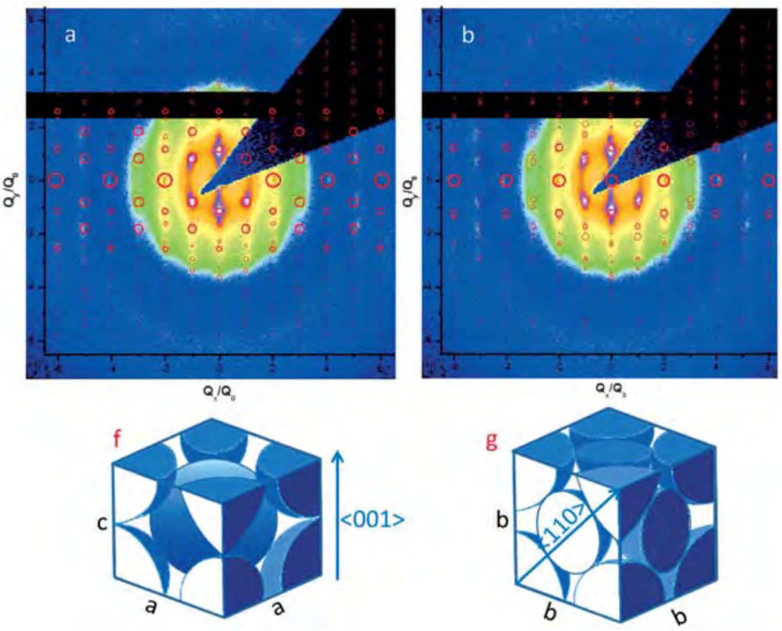

Figure 1. Small-angle x-ray diffraction pattern of crystalline sediment of 170 nm magnetic core-shell particles in magnetic field compared to BCT (a) and face-centred cubic (b) structural models. Detailed analysis clearly shows excellent agreement for the BCT model with the *c*-axis parallel to the magnetic field.

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FORMATION, STABILITY AND TIME DEVELOPMENT OF POLYELECTROLYTE ASSEMBLIES

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Owing to the advances in organic synthesis, the availability of well-defined synthetic charged polymers has increased widely in the last years. This has allowed starting more systematic studies on the interactions between charged species in solution. Being a relatively new area of research, there are a lot of possibilities to be explored yet and most of the work so far has been focused on interactions of polyions with small oppositely charged molecules (salts or ionic surfactants) and between oppositely charged homopolymers.

In this work we studied the case of block copolymers constituted of a hydrophilic chain covalently linked to a polyelectrolyte chain, which we mix either with an oppositely charged homopolymer or a block copolymer with an oppositely charged block. The chosen blocks were poly(*N*-isopropylacrylamide) or poly(ethylene oxide) for the hydrophobic part, Poly(styrene sulfonate) as polyanionic block, and poly(3-acrylamidopropyl trimethylammonium chloride) as polycations. The samples were mixed as diluted aqueous solutions and characterized by use of Small-Angle X-Ray Scattering (SAXS), Photon Cross Correlation Spectroscopy (PCCS) and Zeta Potential Measurements.

Most of the samples have a limpid appearance and the assemblies were found to have nano-sized globular micellar-like structures, with a core formed by the charge-neutralized polyelectrolytes and an outer shell formed by the hydrophilic component of the block copolymers. For the different aggregates, the SAXS data of the assemblies was related to those of the pure polyelectrolyte to obtain a reliable value of aggregation number. The calculated aggregation number varies between 50 and 100 depending on the polyelectrolytes used.

For samples containing block copolymers with a long hydrophobic tail a time development of the sample was observed, from a turbid solution with a network-like structure to a limpid solution containing globular micelles. Using SAXS and PCCS it was possible to follow the evolutions of those samples. Presence of added salt was seen to influence strongly the kinetic and phase state of the systems. Addition of low amount of electrolytes increases the stability of the assemblies in solution and speeds the aggregation, in some cases from hours to minutes. However, when increasing salt concentration a critical point is reached where the polyelectrolytes are not soluble anymore and form a separate solid phase. Phase diagrams for different assemblies as a function of salt concentration were obtained through turbidity measurements on the systems.

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ANISOMERIC POLYELECTROLYTE/MIXED SURFACTANT NANOASSEMBLIES FORMED BY THE ASSOCIATION OF POLY(DIALLYLDIMETHYLAMMONIUM CHLORIDE) WITH SODIUM DODECYL SULFATE AND DODECYL MALTOSIDE

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Complexes of oppositely charged polyelectrolytes and surfactants are widely present as components of personal care products. Different studies have addressed the formation of such complexes and one of the common findings is that they are generally water soluble at low surfactant to polyelectrolyte ratios and insoluble at higher ratios. There is, however, a lack of studies on their structure, especially in the one phase region, where the complex is assumed to have a "beads on a string" structure [1], with interconnected micelles with a structure similar to that of the micelles formed by the surfactant alone.

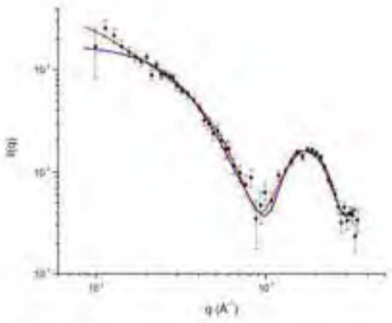

Figure 1: SAXS data for PDADMAC and SDS complex in aqueous solution and the corresponding fits as globular (blue line) and cylindrical (red line) complexes.

In this work we measured and modeled small-angle x-ray scattering (SAXS) data on a series of aqueous samples containing 1000 ppm Poly(diallyldimethyl ammonium chloride) (PDADMAC), a long chain cationic polyelectrolyte mixed with the negatively charged surfactant Sodium Dodecyl Sulfate (SDS) and the nonionic surfactant dodecyl maltoside (DDM). The SDS concentration in the different samples varied between 1 and 16 mM, while the DDM concentration varied between 1 and 10 mM.

Samples with low SDS/PDADMAC ratios without DDM were fitted at first with a "beads on a string" model, as suggested in literature. Even though such a model fits the data reasonably well, we found out that a better fit is obtained for a cylindrical model, as can be seen in Figure 1; this show a strong correlation with the structure of the precipitated complexes in samples with high SDS/PDADMAC, which can be described by an ordered hexagonal structure.

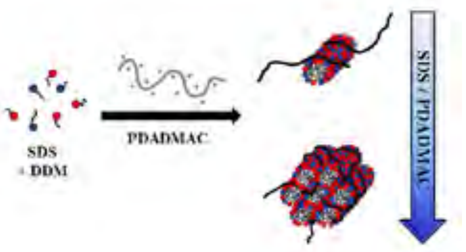

Figure 2: Structure of the SDS/PDADMAC complexes, with incorporated DDM.

The effect of DDM on the complexes has also been investigated. DDM forms mixed micelles with SDS, getting incorporated in the complexes and leading to a decrease in the critical micellar concentration and critical aggregation concentration. DDM is, however, not causing variations neither in the structure of the complexes nor in the critical SDS/PDADMAC ratio for formation of insoluble complexes (Figure 2).

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TEMPERATURE DEPENDENCE IN SURFACTANTS CORE-SHELL MICELLES: CORE FREEZING AND SIZE SEGREGATION

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Surfactants and block copolymers containing Poly(ethylene oxide) (PEO) are chemically simple, bio-compatible and form core-shell micelles in a wide range of conditions and they have been widely investigated. We and others [1] have found irregularities in their behavior as a function of temperature, and more specifically in the low temperature region. Those irregularities can be associated with a phase transition in the micellar cores. In this work we expand the focus from the case of single component systems to mixtures of surfactants and show that a similar transition is present also in mixtures.The study is on micelles obtained from pure surfactants of the kind [$CH_3(CH_2)_nO(CH_2CH_2O)_mH$], abbreviated CnEm. The surfactant used are C18E20 and C18E100, both pure and mixed in different ratios. The samples were analyzed combining Small-Angle X-ray Scattering (SAXS), Differential Scanning Calorimetry (DSC), Nuclear Magnetic Resonance (NMR) and density measurements at temperature between 1 and 15°C at a concentration of 1 wt% in milliQ water.

NMR and DSC were used to confirm the presence of a phase transition, while SAXS was a powerful tool to investigate the segregation of the surfactants. Due to the positive excess scattering length of PEO and the negative one of C18 and the different chemical composition of the two surfactants, the scattering of mixed micelles is very different from that of coexisting pure micelles of the two components. To investigate the mixing, linear combinations of data from solutions containing single surfactants were compared to the data from the mixtures in terms of χ^2 values (Figure 1). Data acquired upon multiple cycles of heating-cooling, demonstrate a remarkable reversible segregation of the surfactants into separate micelles, when the temperature is lowered below 7 °C. From what can be observed, there is no significant difference between the micelles present in the mixture at low temperature and those present in the non mixed samples, meaning that the surfactants segregate in extremely pure micelles.

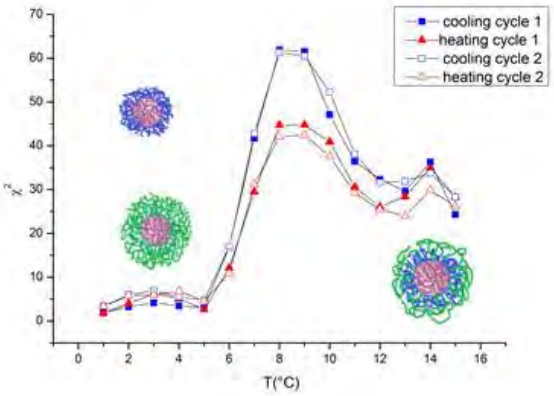

Figure 1: Discrepancy (χ^2) between experimental SAXS data from mixtures of C18E20 and C18E100 and a linear combination of SAXS data from the single surfactants, as a function of temperature. Below 7 °C the surfactants segregates in two different micellar structures.

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GISAXS INVESTIGATION OF LARGE AREA GOLD-PNIPAM LINEAR ASSEMBLY

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Nanostructures with plasmonic properties have attracted considerable attention during the last decades because of their interesting optical properties that can be used for sensing, imaging and light management in photovoltaic devices. A key challenge is the integration of such nanostructures into functional devices. While lithography can provide structures with very well-defined components from a broad range of materials, this method is rather expensive and limited to fairly small structures. In contrast using colloidal building blocks offers many advantages due to the enormous progress in the synthesis of tailored plasmonic particles in the last decades.

In this work we show the assembly of gold/poly(N-isopropylacrylamide) core-shell particles to create linear arrays of gold nanoparticles on macroscopic glass substrates (Figure 1a). GISAXS is used to fully characterize the linear assembly. In particular, high resolution GISAXS analysis allows one to study at the same time the inter-particle and the inter-line spacing (Figure 1b). Unique information about the polymer shell conformation and about the core-core interaction can be extracted.

High resolution GISAXS analysis shows that the order of the deposited colloidal gold/polymer particles extends over a very large area, making these systems useful for applications such sensing and photovoltaics.

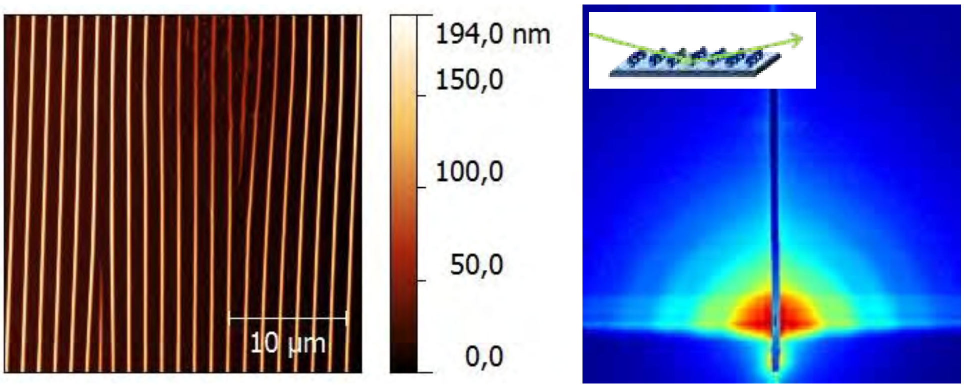

Figure 1. (left) linear assembly of Au-PNIPAM colloidal particles. (right) GISAXS patter collected for the Au-PNIPAM linear assembly with the beam perpendicular to the lines.

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SURFACTANT MOLECULES BEHAVING AS SURFACE-INACTIVE AGENTS

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Generally, oil mixes with water when surfactants are added. In other words, surfactants act as a "surface-active" agent in a mixture. However, we recently discovered that surfactants can also behave as a "surface-inactive" agent in some cases. Figure 1 (a) shows the phase diagram of D_2O / 2,6-lutidine. The two-phase region of the mixture shrinks when an ionic surfactant, SDS, is added. In contrast, the addition of a non-ionic surfactant, $C_{12}E_5$, expands the two-phase region; that is, the mutual solubility of water and 2,6-lutidine decreases in the presence of $C_{12}E_5$.

According to the theoretical consideration by Onuki [1], the mutual solubility of water and organic solvent increases when an amphiphilic molecules adsorbs at the interface between each solvent, while decreases when an amphiphilic molecule preferentially solvates solely in water or organic solvent. Therefore, it is suggested that SDS molecules adsorb at the interface between water-rich and 2,6-lutidine-rich domains, while $C_{12}E_5$ molecules preferentially solvate solely in water-rich or 2,6-lutidine-rich domains.

On the basis of this assumption, we investigated the nanostructure in the mixture by using 18m- and 40m-SANS in HANARO. The SANS result for SDS mixtures suggests that monolayers are formed at the interface between water and 2,6-lutidine (see Fig. 1(b)). On the other hand, sponge structures composed of $C_{12}E_5$ are formed in the mixture (see Fig. 1(c)). The thickness of the membrane corresponds to the molecular length of $C_{12}E_5$, i.e., 15 Å, and this fact indicates that no 2,6-lutidine molecules are contained inside the micelle. Therefore, $C_{12}E_5$ does not act as "surface-active" agent. On the contrary, the hydrophilic group of micelle should attract water preferentially, and this results in the demixing of 2,6-lutidine. The similar tendency was also observed in a mixture of water / acetonitrile / surfactants by QUOKKA in ANSTO.

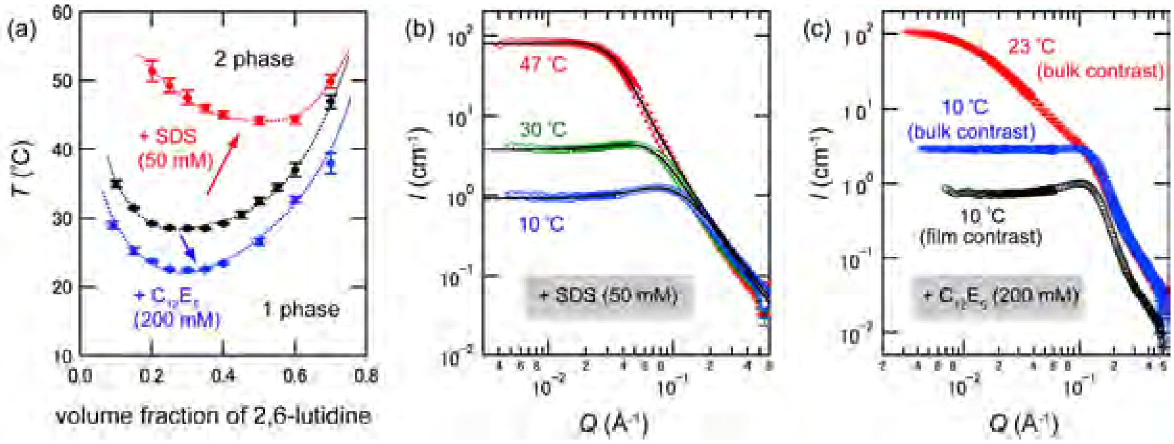

Figure 1: (a) The phase diagram of D_2O / 2,6-lutidine / surfactants. (b) The SANS profiles for SDS mixtures. (c) The SANS profiles for $C_{12}E_5$ mixtures.

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MICELLE STRUCTURE IN A PHOTO-RESPONSIVE SURFACTANT FROM SMALL-ANGLE NEUTRON SCATTERING

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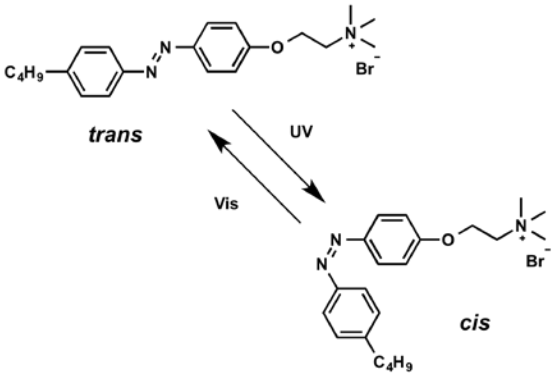
Photo-responsive micellar systems of 4-butylazobenzene-4'-(oxyethyl)trimethylammonium bromide (AZTMA, Scheme 1) [1, 2] were examined with and without ethylbenzene using small-angle neutron scattering (SANS). Analysis of SANS profiles showed that an aqueous solution containing 5, 10 and 50 mM AZTMA forms prolate spheroids with a long radius (Ra) of 38 Å and a short radius (Rb) of 21 Å. In the 5 mM AZTMA solution, the concentration of micelles decreased upon UV light irradiation, while their size and shape remained almost unchanged (Fig. 1). Subsequent visible light irradiation reversed the decrease and increased the number of micelles. In contrast, 10 and 50 mM AZTMA solutions showed that the number and long radius of the micelles decreased with UV light irradiation, while subsequent exposure to visible light irradiation restored them. For AZTMA micellar solutions equilibrated with excess ethylbenzene, the solubilized amount of ethylbenzene increased upon UV light irradiation due to enhanced swelling of the micelles with cis-AZTMA. This photoinduced uptake of the solubilizate has potential applicability for the collection and removal of hazardous oily substances.



Scheme 1 *trans/cis* photoisomerization of AZTMA

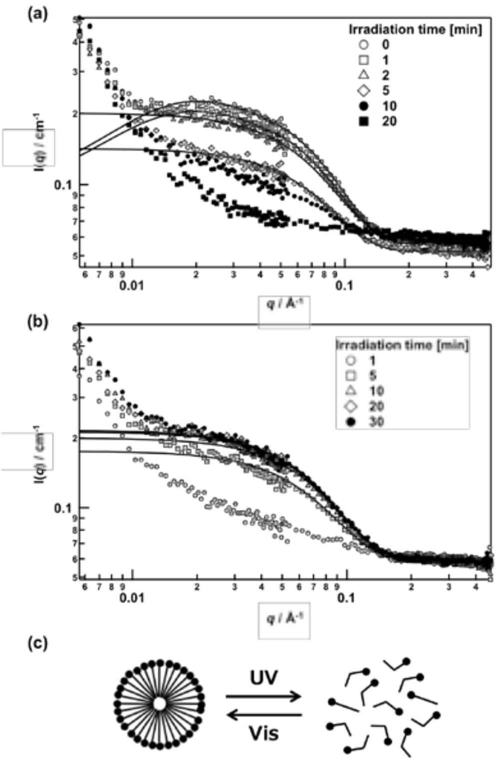


Figure 1 SANS profiles with fitting results after UV and visible light irradiation of (a) 5 mM and (b) 10 mM, and (c) schematic illustration of photo-induced change in micelle structure.

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FORMATION OF ANISOTROPIC GOLD NANOPARTICLES WITH DIFFERENT MORPHOLOGIES ANALYSED BY UV-VIS SPECTROSCOPY, SAXS AND TEM

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Anisotropic Au nanoparticles like nanorods (AuNR) have been the subject of widespread research in the last two decades. AuNRs are of large interest because due to their ability to absorb visible light at two distinct wavelengths (Figure 1a). Applications are expected in biological imaging, drug delivery and phototherapeutics.[1]

The common wet chemical synthesis of AuNRs is the seed-mediated growth synthesis route.[1] Therefore small seed particles (2 nm) are used to grow nanorods (10x35 nm) in a solution of CTAB (Cetyltrimethylammonium bromide) as structure directing agent.

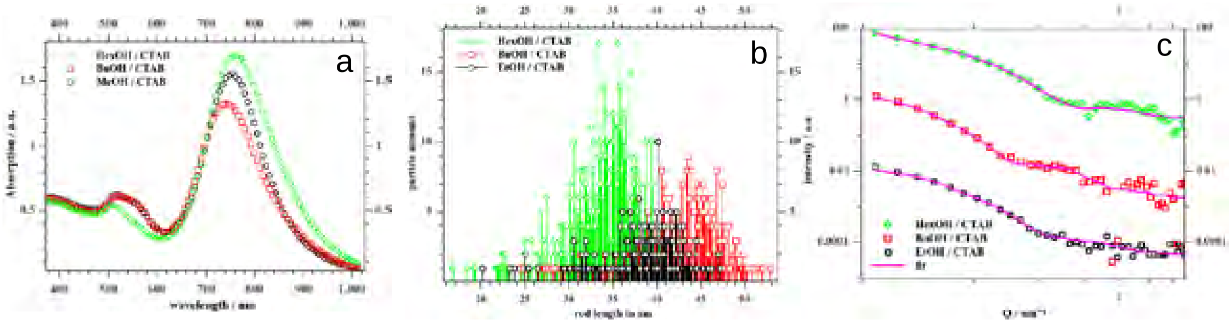

Figure 1: UV-Vis spectra (a), results of quantitative TEM analysis of AuNR length measurements (b) and SAXS data with multiplied intensities for better comparability (c) of gold nanorods (AuNRs) synthesized by seed particles formed in aqueous CTAB solutions containing additional methanol/ethanol (black circles), buthanol (red squares) or hexanol (green diamonds). Using a combination of these three techniques it is possible to fully characterize the products of AuNR synthesis using seed particles formed in different alcohol containing CTAB solutions

The micellar solution of CTAB can be influenced structurally by alcohols. Synthesis of Au seed particles in these modified CTAB solutions lead to colloidal suspensions that are more stable against aggregation than particles in pure aqueous CTAB solutions. Regular synthesis of AuNRs using seeds formed in different alcoholic CTAB solutions show different UV-Vis spectra (Figue 1) which indicates morphological differences of the formed AuNRs. The exact shape as well the ratio of isotropic to anisotropic particles differs in the product solutions which can be seen by transmission electron microscopy (TEM). The exact morphology can be analysed by quantitative TEM (Figure 1b) whereas fitting of small angle X-ray scattering (SAXS) data (Figure 1c) enables to reveal the correct composition of particles with different morphologies by using fit parameters obtained by TEM. Systematic studies using these three complementary techniques were made with AuNR solutions synthesized with seed particles in different alcohol containing CTAB solutions as educts.

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HIGH PRESSURE SAXS ON COLLOIDAL CRYSTAL SUSPENSIONS

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Colloidal suspensions serve as model systems to study structure formation processes. The effect of external perturbations like temperature, ion concentration or electric and magnetic fields on the phase diagram and transitions of concentrated colloidal suspensions has been investigated in great detail. In contrast, the influence of hydrostatic pressure on these systems is largely unexplored although pressure is a fundamental thermodynamic parameter.

Here, small angle x-ray scattering (SAXS) offers an excellent possibility to study matter under high pressure due to the high transmission of radiation through the high absorbing sample environment. It is especially powerful to investigate pressure-induced structural changes in various soft matter systems, e.g. protein solutions [1-3], yet only few studies deal with colloidal solutions [4-6].

In order to fill this gap we performed high pressure SAXS and x-ray cross-correlation analysis (XCCA) [7-9] on colloidal crystal suspensions in water. We find a complex pressure dependence of the lattice spacing and the orientational order which is based on the specific pressure properties of water. Our findings can be understood by a delicate balance between water compression, changes of the electrostatic properties of the system, and the breakdown of the second coordination shell of water. This highlights the power of pressure to affect colloidal systems in aqueous suspension [10].

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LOCAL STRUCTURES IN GLASS-FORMING FLUIDS STUDIED BY HIGHER-ORDER INTENSITY CORRELATIONS

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Many of the remaining mysteries in condensed matter science today lie in the field of the materials' self-assembly and the glass transition. Liquids and glasses do not exhibit long-range order but they are suggested to organize in a variety of different local symmetries. However, the lack of long-range order makes the structure determination much more challenging. Therefore, despite the huge amount of studies during the past decades, the (local) structure of liquids and glasses remains an open question.

Colloidal dispersions have been an excellent model system which provided useful insights into the phase behavior of liquids and glasses [1]. The crystallization process of colloidal system is often studied to understand the self-assembly processes [2]. In hard-sphere colloids the phase transitions depend on the volume fraction and degree of polydispersity. For soft colloids the interparticle interaction potential can be varied from steeply repulsive to deeply attractive [3], by changing the solvent properties. Hence, the phase diagram is more complex than for pure hard sphere systems.

In the present study we employ X-ray Cross Correlation Analysis [4-6] to probe the local orientational order in colloidal dispersions (hard and soft systems) at different volume fractions – from the liquid to the glassy states. The experiments on hard sphere colloidal systems suggest a formation of crystalline and glassy precursors [7]. Furthermore, we have studied the influence of interaction potentials on the local order by changing the salt concentration in soft-sphere colloidal dispersions. The higher-order correlation analysis reveals an increase in the degree of the orientational local order for systems with higher salt content.

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UNFOLDING AND REFOLDING PATHWAY OF LYSOZYME INDUCED BY SODIUM DODECYL SULFATE

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Sodium dodecyl sulfate (SDS) has consistently been shown to induce secondary structure, particularly alpha -helices, in polypeptides, and is commonly used as a model system for hydrophobic environments. In present work, we focus on the di®erent binding stages of hen egg white lysozyme (HEWL) with SDS at pH 6.9 PBS buffer (ionic strength 16 mM). Combining transition points obtained from isothermal titration calorimetry (ITC), which provided invertigation routes for other techniques, such as fluorescence spectra and circular dichroism, it was possible to investigate the unfolding and refolding of HEWL induced by SDS, and the relationship of hydrophobic and electrostatic interaction during the binding Structural information about the formed complex in each binding stages was obtained by small angle X-ray scattering (SAXS) measurements and modeling procedures. These results permitted the proposition of a general model for the protein-surfactant complex as a core-shell structure with a dodecyl chains composing the core and a shell consisting of SDS head groups and molten-globule HEWL, which showed a novel, generic structural model of SDS-HEWL complexes (Figure 1). The results of presented in this work [1] not only helps the understanding of the interaction process of HEWL/SDS binding and complexation, but also provides molecular insights into the role of surfactant on the unfolding and refolding of proteins, in general.

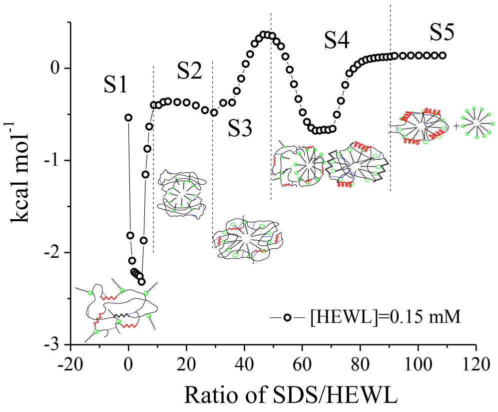

Figure 1: The model of HEWL with SDS in different binding stages.

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METROLOGY OF MAGNETIC IRON OXIDE NANOPARTICLES

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Due to upcoming regulations and the broad application of magnetic nanoparticles (MNP) in industry and medicine there is a strong demand for reliable and standardized characterization methods of structural and magnetic properties of these systems. This task is tackled by the EU project NanoMag. Within this project the small angle x-ray scattering (SAXS) technique has a prominent position in the characterization of the particle core sizes. The challenge is to establish SAXS a standard method for the sizing of MNP cores. Because of its sensitivity to high density matter SAXS has a uniqueness factor among other sizing methods. The mean size of the core itself is crucial for other characterization techniques, especially those addressing the magnetic properties. This is owed to the fact that the MNPs are single domain particles and the particle size, or precisely the iron oxide core size, determines their magnetic behavior. Hence, the iron oxide core size is a very important input parameter for almost any magnetic method. Otherwise, assumptions must be made about the mean magnetic particle size which drastically limits the reliability of the result obtained. Thus, there is a great opportunity for SAXS to become an essential link in this analytical chain, once a standard sizing method of iron oxide particle cores is established.

In the study presented we follow a double tracked approach in the data analysis. First, we use the standard model tool kit based on superposition of analytical scattering curves and distribution functions. Here for we use the SASfit software [1]. The second method of analysis are Monte Carlo (MC) calculations done with the software package McSAS [2]. The main advantage of the MC approach is its statistical nature that gives size distribution histograms with uncertainty estimates in a quite straightforward way (Figure 1). In this work we compare these two approaches applied to the analysis of MNP cores. At this stage of the study it can be reported that the MC calculations deal better with broad and complex size distributions, whereas the standard method of modelling provides an easier access to the investigation of interactions, which of course play a role for the MNP systems, since the particles are magnetic dipoles.

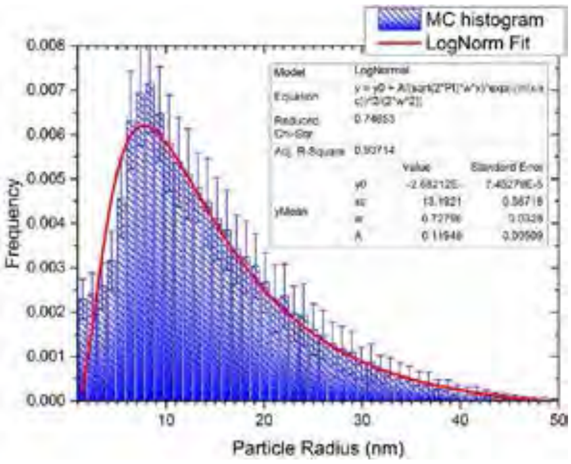

Figure 1: Example for a histogram of the core size distribution (blue bars) of multi-core magnetic nanoparticles from Monte Carlo calculations plotted together with the log-normal fit to this distribution (red)

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RESOLVING PARTICLES SIZE DISTRIBUTIONS IN BI- AND TRI-MODAL NANOPARTICLE SUSPESIONS

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The possibilities in using small-angle X-ray scattering (SAXS) for characterization of bi- and tri-modal size distributions of nanoparticles is presented. Size distributions were derived by utilizing a Monte-Carlo data evaluation procedure reported by Pauw et al. [1]. A comparison with classical data evaluation procedures such as implemented in the program SASfit is given. Examples are presented from mixtures of super-paramagnetic nanoparticles [2] as shown in Figure 1. The SAXS results are in good agreement with results from complex ac-susceptibility (ACS) [2]. Further examples are mixtures of gold nanoparticles with nominal sizes of 10 nm, 30 nm and 60 nm. Here a limit of detection was found as low as 10^{-4} volume percent of nanoparticles. Another example is a mixture of silica nanoparticles FD102 with nominal sizes of 20 and 40 nm [3]. Intensity-, volume- and number-weighted size distribution analyses will be discussed. Especially the quantification of number-weighted size distribution is of tremendous interest for regulation and declaration of nanomaterials in Europe. Reference materials and methods are a key factor for standardization on the level of the ISO. The first SAXS ISO standard for the use in particle size analysis is briefly reviewed (ISO standard 17867).

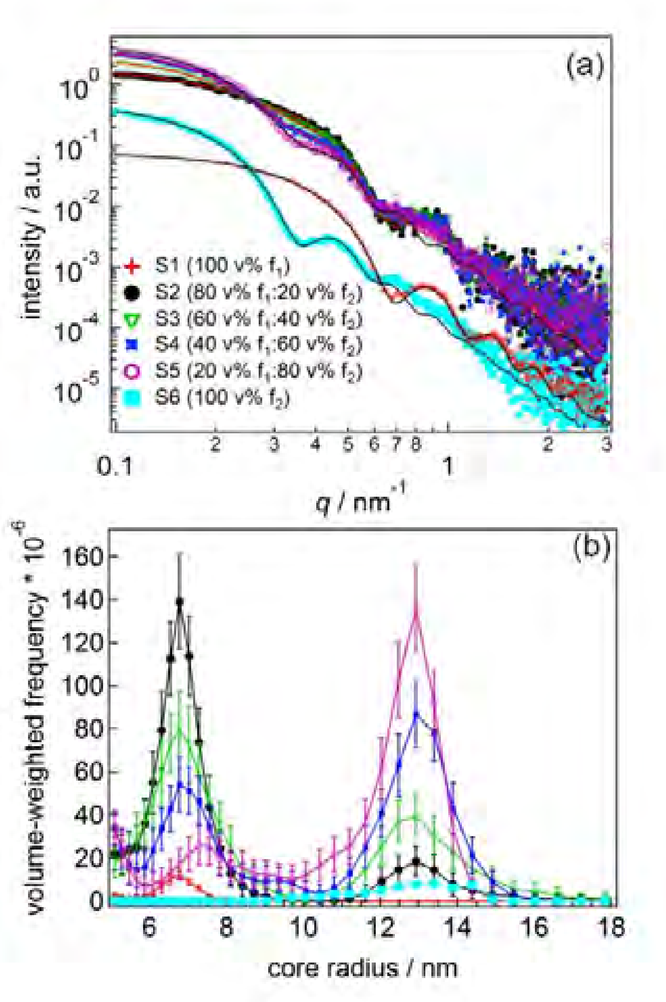

Figure 1: Experimental (markers) and reconstructed (solid lines) SAXS curves of mono- and bi-modal samples and (b) resultant volume-weighted particle cores size distributions [2].

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SELF-ASSEMBLY OF UNILAMELLAR VESICLES: TOWARDS A GENERALIZED UNDERSTANDING OF BILAYER STRUCTURE AND KINETICS

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Controlling the self-assembly of small unilamellar vesicles (SUVs) has been successfully done recently by the addition of amphiphilic copolymers to the model system tetradecyldimethylamine oxide (TDMAO) and lithium perfluorooctylsulfonate (LiPFOS).[1] In order to extend the results to systems of more practical interest, a generalized understanding of the self-assembly process of monodisperse SUVs on a molecular level is needed. Previous investigations of the system TDMAO and lithium perfluorooctanoate (LiPFO) have shown that intermediate structures leading to SUVs can be disk- or torus-like, depending on the overall concentration.[2] An exemplary formation of SUVs via disks is partly shown in figure 1. Nevertheless, the distribution of molecules within the bilayer remains unknown, but is important for understanding its properties. Due to the relatively small size of the resulting vesicles ($R \sim 10$ nm), osmotic pressure and the distribution of ions inside and outside the vesicle are relevant for this system.[3]

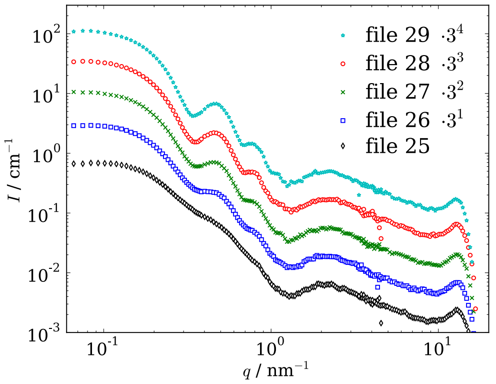

Fig. 1: Subsequent datasets for 12.5 mM TDMAO + 12.5 mM LiPFO as a function of time showing vesicle formation

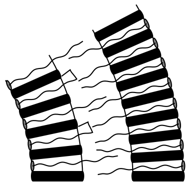

Fig. 2: Schematic bilayer structure. Black cylinders: LiPFO; long flexible molecules: TDMAO.

The analysis done so far on combined stopped-flow SAXS and WAXS data (ID02, ESRF) has shown that in the radial direction it is sufficient to use a simple scattering length density profile consisting of three concentrical shells. Currently, we are refining our models for the detailed structure of the bilayer (see figure 2) thereby describe in further details the kinetics of structure formation as that is the key for controlling in a systematic way the formation of well-defined vesicles, as they are important for many of their applications.

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Title: A small-angle scattering study of the biomineralizing protein Mms6 and its membrane environment emulated by bicelles.

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Abstract:

Mms6 (wild type), is a biomineralizing protein isolated from a magnetotactic bacterium, Magnetospirillum magneticum strain AMB-1. It plays a central role in mediating the formation of magnetite nanocrystals of regular-shape and uniform size (~30 nm) under mild conditions both in vivo and vitro. The presence of the artificially made bicelles that emulate the native membrane environment for the protein is considered as an effective strategy to promote the protein's iron binding activity and capacity. Both the x-ray and neutron small angle scattering techniques are employed to examine the structure of the bicelles and Mms6 and its mutants in an aqueous environment and the morphological changes of protein assembly in response to the presence of iron ions.

Investigation of complex solutions under shear and pressure

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The unmatched tribological performance of articulated joints is due to both the properties of the cartilage itself and the assumed self-organization of the molecules in the synovial fluid (SF) and at the surface of cartilage [1]. The components of the SF account for the response of synovial tribological system to different load and shear conditions by re-structuring. Thereby they provide extremely low friction coefficients under low and high pressures up to several tens of MPa and different shear rates [2,3].

In order to investigate how the different constitutes of the synovial fluid work under high pressure and shear conditions we have developed two sample environment units which allow us to investigate their self-assembly behaviour in situ by means of small angle scattering. A microfluidic setup allows for measuring the structure of macromolecules in solution at shear rates of more than $100ks^{-1}$ with nanofocused x-ray beams. The second environment utilizes a fully working rheometer with pressure option (300bar) to test the effect of shear and pressure on the bulk solution and on interfaces as this rheometer has the option to place wafers inside.
In first experiments we investigated highly concentrated protein solutions of lysozyme, which show a shear thinning behaviour. In the course of the experiments we observed a decrease in the structure factor showing an influence of the shear rate on the protein/protein interaction.

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NOVEL BICELLS-DNA COMPLEXES

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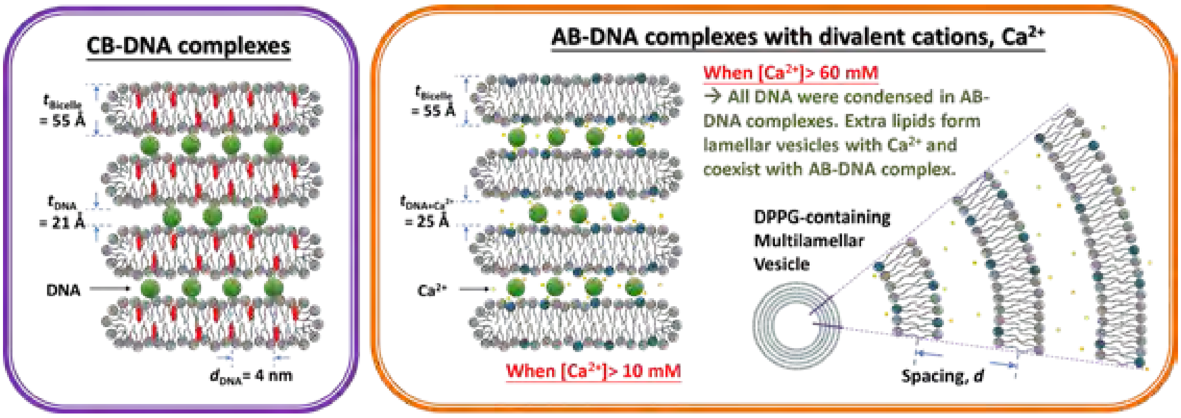
The liposome-DNA complexes were well-known to be used as non-viral vectors for improving the transfection efficiency of gene delivery. Here we demonstrate novel types of cationic and anionic lipid-DNA complexes based on typical disk-shaped bicelles. First, we have developed a cationic bicelle–DNA (CB-DNA) complex system by mixing cationic bicelles with DNA to form alternating stacks of disc bilayered plates and DNA arrays with a repeat distance of 7.5 nm. SAXS and TEM revealed that the DNA molecules were encapsulated between the disc bilayered plates, forming ordered arrays with a spacing of around 4–5 nm. The number of stacking layers can be easily tuned from just a few layers to more than one hundred layers by adjusting the doping percentage of the charged lipids. This CB–DNA complex is also quite stable against increases in temperature above the chain-melting temperature of the long chain lipids. [1] Having lower cytotoxicity, the other approach is proposed to induce anionic DPPG doped bicelles for forming the similar lamellar stacked structure with negatively charged DNA in the presence of sufficient divalent ions. It was found that the anionic bicelle could not form stable complexes with DNA at low calcium ion concentrations, such as 1 mM. The AB–DNA complexes can be formed in the investigated range of 10 mM to 100 mM calcium ion concentrations. However, for an equal anionic lipid charge and DNA charge system, an ion-membrane phase (multilamellar vesicles) would gradually appear as the calcium ion concentration is increased above a critical concentration. It indicates that DNA could be packed closer at above the critical divalent ion concentration. If more DNA is added to such a two-phase coexistence system (originally with the total anionic lipid charge equal to that of DNA), the ion-membrane phase could be transformed into the AB–DNA complexes. As a result, more DNA can be packed in the form of AB–DNA complexes at above the critical calcium ion concentration. [2]



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NANOSTRUECTURED HYBRID DRUG-DELIVERY SYSTEMS FOR ULCERATIVE COLITIS TREATMENT: SMALL ANGLE X-RAY SCATTERING (SAXS) STUDY

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Systemic glucocorticoids have been used to treat an inflammatory bowel disease such as ulcerative colitis (UC), due to their potent anti-inflammatory effects. Currently, budesonide (BUD) is a glucocorticoid available as controlled ileal release formulation or as enema. However, the capsules do not deliver BUD to the left colon and therefore are not optimally designed for the treatment. The enema formulation causes losses during the administration and discomfort to the patient because of the large volume of the application and low viscosity of the formulation. In this context, it is expected the improvement of physicochemical properties through complexation with cyclodextrin (CD) and the incorporation of inclusion complex into PL-based hydrogels, contributing to a longer duration of anti-inflammatory effect associated with high bioadhesion.

In this work [1], we propose the study of the system BUD-HP-β-CD inclusion complex incorporated into PL 407 and PL407-PL403, since the micelles assembling to the thermoreversible hydrogels considering structural parameters related to sol-gel transition phase, as well as the interaction between BUD:HP-β-CD complex and PL, using small angle X-ray scattering (SAXS). The SAXS experiments were performed at SAXS1 beamline at the Brazilian Synchrotron Laboratory (LNLS, Campinas-SP, Brazil) at two temperatures: 25 °C. Our results showed the presence of a lamellar structure for PL407 (at 25°C) (for two different concentrations). After addition of HP-β-CD, BUD and the BUD-HP-β-CD inclusion complex, the lamellar structure is maintained (Figure 1). Besides, the addition of PL403 (a more hydrophobic co-polymer compared to PL407) to the hydrogel formulation, maintaining the lamellar structure and favoring the incorporation of HP-β-CD, BUD and the BUD-HP-β-CD inclusion complex into the formulation, being interesting for pharmaceutical applications, particularly for ulcerative colitis treatment.

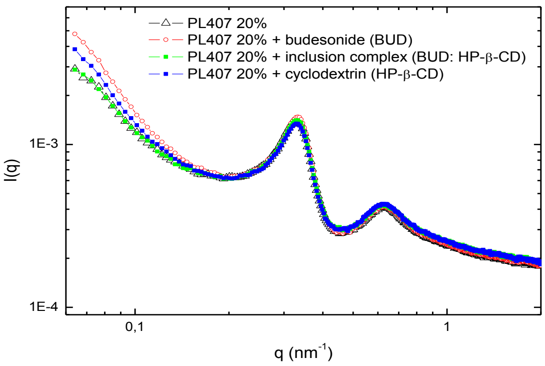

Figure 1: Comparison between PL407 20% with HP-β-CD, BUD and the BUD-HP-β-CD at 25°C.

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In situ Study the Assembly of Spray-deposited Gold Nanoparticles on Polymer Substrates Using GISAXS

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The well dispersed metal nanoparticles on substrate can present enhanced properties and the preparation of designed nanoparticle thin film is a hot topic in material science [1]. Especially, for the large scale industrial production like roll to roll and inkjet printing of functional nanoparticles, the controlled fast solvent evaporation and designed homogeneous structure is preferred. However, inhomogeneous material dispersion for example, coffee-stain-like or clumps of nanoparticles is observed in the dried thin film[2]. To overcome this obstacle, controlling the solution evaporation and promoting the ordering of nanoparticles on the templated substrates is a smart and feasible choice. Spray deposition is one of the desirable techniques to manipulate solvent evaporation by atomizing the solution[3, 4]. It offers a fast and economic deposition of organic/inorganic-based nanoparticles showing high structural uniformity over large areas and is thus of great interest in industrial applications. Here we present our recent in situ studies on the directed assembly of spray deposited gold nanoparticles on patterned polymer substrates. By manipulating the assembly process, we compared the optical properties of the as-prepared gold nanoparticle thin films. These findings are attractive for the applications such as solar cells and antireflection coatings.

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CRYSTALLIZATION IN MICELLAR CORES – MELTING POINT DEPRESSION AND INFLUENCE ON EXCHANGE KINETICS AS SEEN BY SMALL ANGLE NEUTRON/X-RAY SCATTERING

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We present the influence of crystallization on the molecular exchange kinetics in polymeric micelles that are formed by very well-defined poly(ethylene oxide) polymer chains end-capped with a single n-alkyl group (C_n-PEO). The spontaneous self-assembly of C_n-PEO into micellar aggregates in aqueous solution and their equilibrium structure has been well understood [1]. Polymer micelles attain their thermodynamic equilibrium via active molecular exchange that is thermodynamically understood as a first order kinetic process characterized by a single rate constant that follows a simple Arrhenius behavior [2,3,4]. Experimentally, time-resolved small-angle neutron scattering (TR-SANS) in combination with a kinetic zero average contrast experiment (KZAC) is a powerful technique to access the chain exchange in-situ [2]. It is generally assumed that the process can be described by an activated diffusive motion of a single chain from the melt-like core [2,3]. The corresponding activation energy is solely given by the immiscibility between the n-alkyl tail and the solvent which is proportional to the length of the hydrophobic block [2,5,6].

By using a range of techniques including small-angle X-ray scattering, densitometry and differential scanning calorimetry we show that the n-alkyls crystallizes with the nanometer-sized core microdomain [7].

Upon varying the temperature, we find a discontinuity in the scattered intensity at high Q with SAXS. This is confirmed by densitometric measurements where we find a discrete jump at the same temperature. The specific heat capacity also shows a clear peak and thus shows that the micellar core exhibit a 1st order phase transition that can be associated to the melting of the n-alkanes. Interestingly, we find that a melting depression with respect to pure n-alkanes that can be accurately described by the Gibbs-Thomson equation [6]. By comparing thermodynamic data with TR-SANS kinetic results we show that there is a considerable entropic and enthpalic contributions from the crystallization that play a central role in the kinetic stability of micelles.

In the presentation we will provide an overview of the interrelationship between kinetics and thermodynamics and discuss the basic mechanisms for molecular exchange in partially crystalline nanostructures.

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↘ Flash Talk: Mon-F-C1

Rheo-SANS STUDY OF REVERSIBLE POLYMERIC GELS: SHEAR-INDUCED STRUCTURE FORMATION AND MELTING

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We present a Rheo-SANS study on physical reversible cross-linked polymeric networks formed by well-defined functionalized poly(ethylene oxide) (PEO) polymer chains in aqueous solution. The rheology and the physical properties of PEO hyrdrophobically end-capped with n-hexadecyl ($C_{16}H_{33}$) on both ends are of great interest for commercial use. It is well known that these telechelic polymers form physically reversible cross-linked, micellar networks [1,2,3] and thus are well suited to study the general mechanism of self-healing in transient networks. In concentrated aqueous solution the polymer self-associates into a network of connected (ordered) spherical micelles with dynamic junction-points formed by the associative block [4]. Depending on the length of the hydrophobic end-group (sticker), the molecular weight of the PEO polymer (spacer) or the degree of functionalization the network shows a complex and non-linear flow behavior [5,6]. It is of particular interest how rheology and the exchange kinetics of the individual bridging polymers are related. A shear deformation of about 40% completely destroys the formed structure and then only slowly recovers within several hours. Moreover, we observe that time for the recovery of the crystalline ordering greatly differs in the flow (~ 10h) and gradient direction (~ 1h). The exact time dependence mainly is associated to the exchange kinetics of the polymers i.e. the rate at which the stickers enter or leave the hydrophobic knot points [7] and temperature. For this reason the microscopic lifetime of the "living" knots determines the macroscopic rheological behavior.

In the presentation we will demonstrate results showing the shear-induced structure formation and melting. Moreover, we will address the structure recovery i.e. the self-healing of the network and attempt to relate this to the microscopic dynamics.

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ORGANIC-INORGANIC NANOCOMPOSITE GEL IN SITU GELATION BIOMATERIAL FOR OCULAR LENS

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Polymer solutions, capable forming a gel in a body cavity or tissues with latent space, have potential uses in ophthalmology as intra-ocular lenses, vitreous substitutes, and drug-delivery devises. Such in situ forming gels have the advantages to form gel that completely fills any irregular cavity and provides the elastic modulus, and of being delivered using minimally invasive techniques. We focus on the development of a novel injectable accommodative lens for intraocular applications, which is based on a thermosensitive hydrophobically-modified poly(ethylene glycol), E5KMC18 containing hydrophilized silica nanoparticles, OCAPS. We distinguished macroscopically, with changes in the temperature or concentration, two regions in the phase diagram for aqueous solution of E5KMC18/OCAPS in weight: transparent sol and transparent gel. These changes occurred reversibly, without hysteresis, when the temperature is decreased. The temperature and concentration regime in which gel formed are reduced by adding OCAPS in the gel matrix. Small-angle neutron scattering measurements for nanocomposite gels provide good proof of a gel phase where the high shear-modulus is gained by a high inter-micellar correlations originating in the crystalline order. Under the condition of uniform distribution of OCAPS with small size (2-5 nm) in the gel matrix, an increase in refractive index up to 0.0667 were obtained for nanocomposite gel compared with native gel matrix without an increase in turbidity. This composite system could be formulated to match the modulus and the refractive index of the natural lens (~1.411), and was easily extruded through narrow-gauge needle. Rapid endocupsular gelation yielded optically clear gel within the lens capsular bag. This technique enables us to validate methods to determine the biomechanics of the lens and its role in accommodation. The modification of the mechanical response and stability of the E5KMC18 network by addition of OCAPS was also investigated in detail.

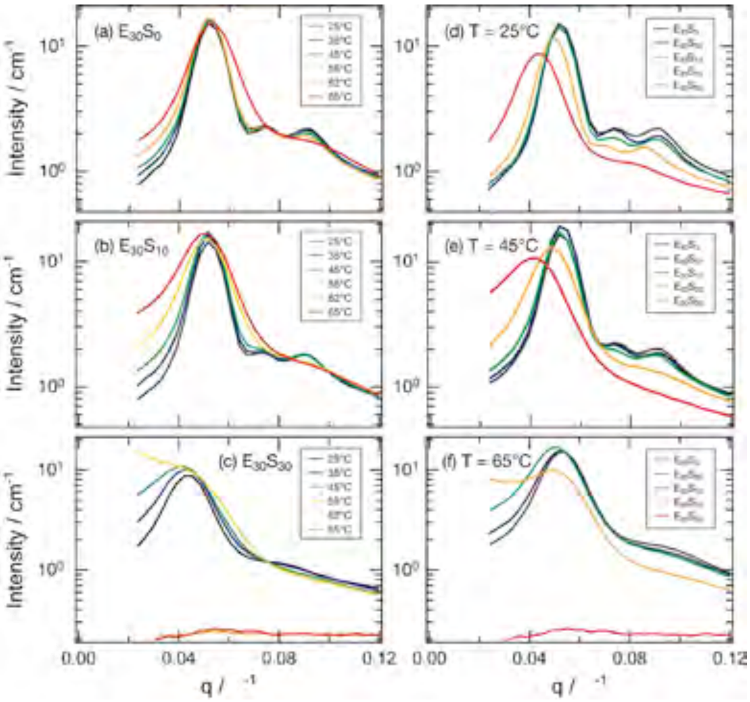

Figure 1: SANS profiles, of E_mS_n (m: E5KMC18 conc., n: OCAPS conc.). (a), (b) and (c) highlights the temperature dependence of $I(q)$ for $E_{30}S_0$, $E_{30}S_{10}$ and $E_{30}S_{30}$, respectively, plotted for temperatures at 25, 35, 45, 55, 62 and 65°C. (d), (e) and (f) highlights the OCAPS concentration dependence of $I(q)$ for 25, 45 and 65°C, respectively, plotted for OCAPS conc. at 0, 5, 10, 20 and 30wt%.

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Small-Angle X-Ray Scattering Investigation of PVDF Microstructure due to Exposure to Supercritical CO_2

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A subsea flexible pipe has been subjected to cyclic rapid decompression. The poly(vinylidene fluoride) (PVDF) layers have flowed radially into gaps of adjacent metallic coils forming whitened noses. Microbeam small-angle X-Ray scattering (SAXS) scanning is applied. PVDF layers (inner: wear, outer: barrier) in two zones (undamaged and damaged) are tested. Far from noses and damage zone the samples are isotropic without voids. Their morphological parameters are determined and compared to virgin material. Approaching the noses, the structure turns into highly oriented microfibrils perpendicular to the local flow into the gaps. Here voids extend parallel to the microfibrils. At edges of the metallic structure they turn more perpendicular to the layer. Crystallite orientation extends out to both sides of the whitened nose regions, but in the undamaged samples tilting of the orientation direction and void-formation are restricted to the white regions: successive mechanisms of cold drawing are mapped into space. Under the damaged spot voids and crystallite orientation are observed everywhere[1].

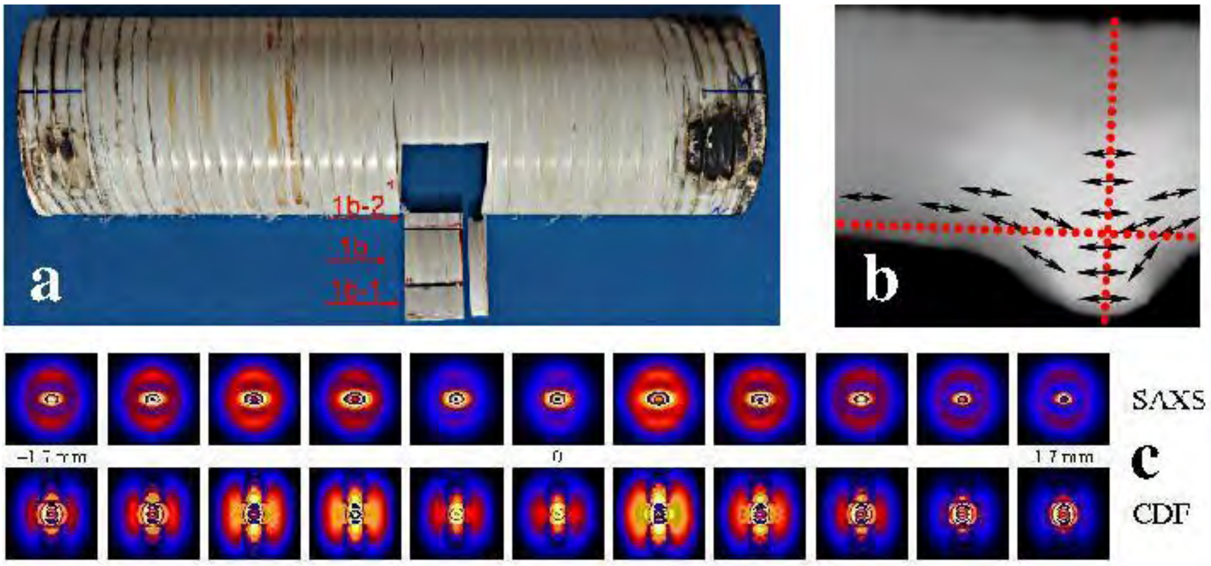

Figure 1. **a**) PVDF layer after test. **b**) thin cut, scan points and orientation directions. **c**) selected scattering data from one of the scans

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CONTROL OF INTERFACIAL MORPHOLOGIES BY COLUMNAR LIQUID-CRYSTALLINE PHASE IN DENDRON-JACKETED BLOCK COPOLYMERS

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In this study, we extend from the previous three published studies [1-3] on morphology transitions of a supramolecular dendron-jacketed diblock copolymer (DJBCP), and report specifically the interfacial morphology control resulted from manipulating the competing between the orderings of LC phase and the dendron-jacketed blocks. We have demonstrated that the two-dimensionally ordered hexagonal columnar LC phase can substantially flatten the intermaterial dividing surfaces (IMDS) and direct the self-assembly of the global microdomains with a long-range ordering. Interfacial morphologies of hierarchically phase-separated domains in DJBCP are directed via liquid-crystalline (LC) phases of the dendronized blocks. The DJBCP is formed with a dendron 4'-(3,4,5-trioctyloxybenzoyloxy)benzoic acid (TOB), selectively incorporated into the P4VP block of poly(styrene)-*block*-poly(4-vinylpyridine) (PS-*b*-P4VP). Revealed from small- and wide-angle X-ray scattering as well as transmission electron microscopy, the hexagonally packed columnar LC phase (HEX_{col}) of the dendronized blocks P4VP(TOB) can substantially decrease the curvature of the IMDS of the DJBCP. Consequently formed are hierarchically structured DJBCP with hexagonally packed hexagon PS cylinders. As the locally 2D-ordered HEX_{col} phase reduces to 1D ordered smectic (Sm) phase with weakened LC packing strength, the planar IMDS of the DJBCP relaxes into curved IMDS for circular PS cylinders. IMDS flattening effect imposed by the columnar LC phase is further strengthened via a triblock DJBCP of $P4VP(TOB)_x$-*b*-PS-*b*-$P4VP(TOB)_x$, leading to a highly oriented honeycomb structure with an ordering length up to sub-millimeter. The LC-controlled IMDS morphology of the DJBCP might facilitate fabrication of templates toward nano-periodic arrays with sharp channel edges for lithography applications.

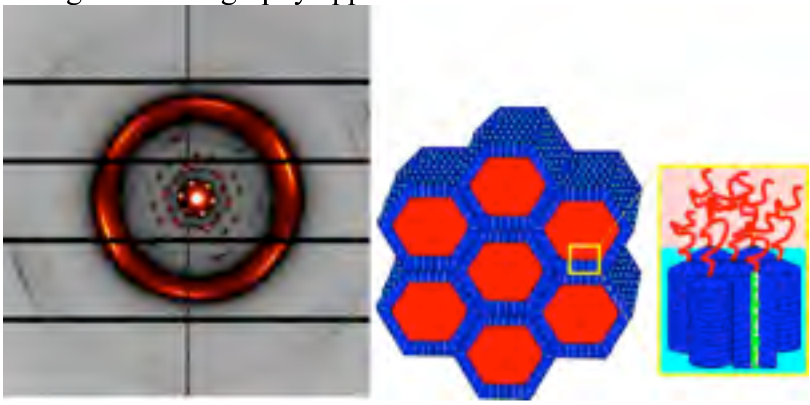

Figure 1 : 2D SAXS pattern with X-rays incident along the axial direction of PS cylinders (Y- direction) of a stretching-annealed film of $P4VP_{43}(TOB)_{0.7}$-*b*-PS_{260}-*b*-$P4VP_{43}(TOB)_{0.7}$, and cartoons for the hierarchically structure HEX_{col}-*within*-OBL_{CYL} with hexagonal PS cylinders.

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INVESTIGATION OF ANISOTROPIC STRUCTURES IN POLYMER MATERIALS USING USAXS

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Mechanical properties of polymer materials can be designed through chemistry and process. They are related to the internal structure of the system, from the local to the mesoscopic scale and sometimes even up to the macroscopic scale. Understanding of the involved mechanisms is essential to control the final structure and develop materials with enhanced mechanical performances.

Small Angle X-Ray Scattering (SAXS) is a technique well suited for investigating nano-materials and nano-structures of polymers. Information is collected on sample structure parameters such as particle shape or size, size distribution, orientation, surface to volume ratio… in the range from 1 nm to beyond 100 nm. Furthermore, orientational functions of stretched matrices or of self assembled polymers can be derived from 2-dimensional x-ray patterns. In the case of samples with internal structures larger than 200 nm, USAXS (Ultra Small Angle X-Ray scattering) experimental conditions are required. The progress in the performances of x-ray components and subsequent assembly offers such characterization methods in the laboratory.

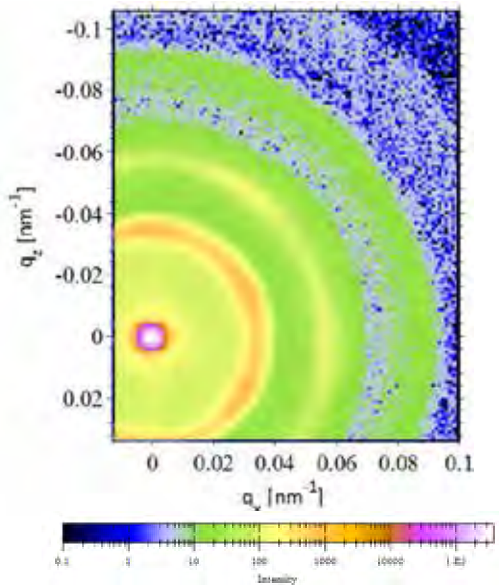

Figure 1: 2D-USAXS pattern of a Latex film with a hexagonal lattice signature. Characteristic dimension of the system = 178 nm.

Soft colloidal crystalline structure can be obtained from drying Latex dispersions. As they strongly scatter or absorb visible light, X-ray scattering is well applied to investigate their structure. How the solvent evaporation process affects the film structure is not well understood. Precise definition of the lattice parameters can be obtained. USAXS measurements performed on a Latex film with a characteristic dimension of 178 nm of the hexagonal lattice [Figure 1] show the new insights achievable with a laboratory beamline. Samples with such a scattering power allow performing experiments without any beamstop.

USAXS allows also to access heterogeneities about some hundreds of nanometers while providing the opportunity to investigate the large-scale structure evolution during the deformation of polymeric materials [1]. Recent results obtained on in-situ stretched Polybutene-1 (PB-1) illustrate the capability to perform lab measurement equivalent to Synchrotron USAXS [2] highlighting microscopic structural evolution and macroscopic strain-whitening phenomenon correlation.

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Microstructural origins of yield, strain hardening and hysteresis in thermoplastic elastomers under uniaxial deformation: an in-situ tensile-SANS study

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In-situ morphological characterization of elastomeric materials under periodic deformation is crucial to understand the structural origin of equilibrium mechanical properties and time dependent properties like hysteresis and fatigue. We present unique measurements that combine the power of small-angle neutron scattering (SANS) and precision mechanical measurements to measure the morphology on the nanoscale and the mechanical properties simultaneously. To this end a new instrument was developed at the NIST Center for Neutron Research (NCNR), consisting of a Sentmanat extensional rheometer (SER) to measure the uniaxial stress response during SANS measurements.

The first *in-situ* tensile-SANS (tenSANS) measurements were performed on two commercial thermoplastic elastomers (TPEs) consisting on styrene-isoprene-styrene (SIS) triblock copolymers with two styrene contents: 14 wt% (SIS14) and 22 wt% (SIS22). Under quiescent conditions, SIS14 forms a bcc lattice with glassy (polystyrene) spheres, whereas SIS22 forms glassy rods arranged in hexagonal structures. The glassy domains are connected by (polyisoprene) amorphous tie chains. By using advanced SANS nano-metrology techniques, we were able to quantify the special arrangement of the glassy domains and thereby determine affine deformation at low strains (in the linear regime), and cluster formation at high strains where yield and strain hardening is measured. Remnant nano-deformation is observed after loading-unloading cycles, which is directly correlated to the macroscopic permanent set and deformation hysteresis. In addition, the orientation angle of the clusters associated to yield and the alignment of the rods in the SIS22 system were quantified. Complementary techniques (in-situ WAXS and SALS and birefringence measurments during extension) are being used to quantify cavitation, strain-induced crystallization, and molecular alignment during uniaxial extension, and ultimately correlate these microstructural features with the measured stress.

↘ Flash Talk: Wed-F-P1

INSTALLATION FOR IN-SITU X-RAY SCATTERING MEASUREMENTS DURING POLYMER INJECTION MOLDING AT TOYOTA BEAMLINE

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Injection molding is a widely used technique to manufacture parts of semi-crystalline polymer. The mechanical properties of the parts have been controlled by the processing conditions: the mold temperature, the injection velocity, and the keeping pressure and so on. The processing condition should affect the hierarchical structure of the semi-crystalline polymers, which determines the mechanical properties. However, the process-structure-property relationship is a growing subject to develop high-performance polymer more efficiently. X-ray scattering is a standard tool to study the hierarchical structure of the semi-crystalline polymers. In the polymer parts produced by injection molding, the structure and the property depend on the position in the molds, that is, the history of the temperature, shear, and pressure along the flow path from the injection gate. Although the effect of the temperature, shear and pressure on the structure has been separately investigated, combination of the each factor should be considered to understand the injection molding process [1]. Therefore, we have designed an injection molding machine compatible with in-situ measurements of X-ray scattering at Toyota Beamline.

A picture of the installation is shown in Figure 1. An incident X-rays with 15 keV from the undulator of BL33XU in SPring-8 were irradiated on the mold and the scattered X-rays were monitored with a hybrid photon counting pixel detector PILATUS 300K of DECTRIS. The mold with beryllium windows was fabricated to produce dumbbell-shaped test pieces. A compact injection molding machine was vertically set on the stage.

A result of an in-situ wide-angle X-ray scattering measurement of isotactic polypropylene during injection molding is shown in Figure 2. Since the scattering pattern is anisotropic, sector average in the vertical direction against the flow vector is presented. Each spectrum was obtained in every 0.8 seconds. The time when the melt polymer passed the X-ray beam was set at 0 second. After appearance of amorphous halo for a few seconds, we could observe an increase of the crystalline peak intensity during injection molding.

Figure 1: Injection molding machine at BL33XU.

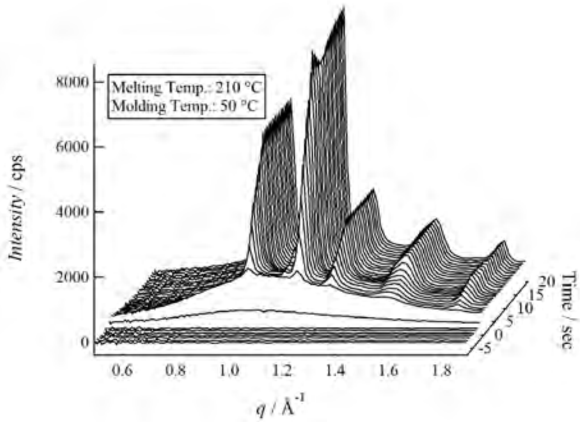

Figure 2: Structure change of a polymer in a mold.

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DIFFERENCES IN MESOSCOPIC STRUCTURE AND MACROSCOPIC FLOW BEHAVIOUR BETWEEN CATIONIC HEC/SDS AND PDADMAC/SDS MIXTURES

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Systems composed of oppositely charged polyelectrolytes (PE) and surfactants show rich self-aggregation behavior that varies over a large size range and have many applications e.g. in cosmetics, detergency and drug delivery[1]. While mixtures of the cationically modified hydroxyethyl cellulose JR 400 show a remarkable increase in viscosity by 3 to 4 orders of magnitude[2-4] (Figure 1) near charge equilibrium, no such pronounced effect can be observed in mixtures of pDADMAC and SDS at similar concentrations, despite a similar length of the PE.

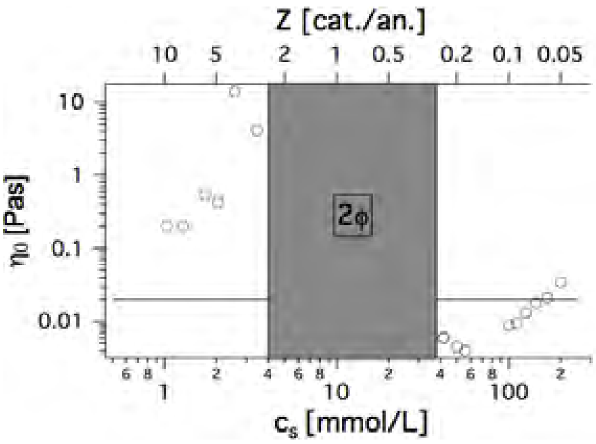

Figure 1: Viscosity of mixtures of SDS with 1 wt% JR 400, horizontal line: viscosity of 1 wt% JR 400 without added surfactant

With the help of mainly small-angle neutron scattering, complemented by other methods, such as neutron spin-echo (NSE), dynamic light scattering (DLS) and fluorescence correlation spectroscopy (FCS), we are aiming at elucidating the mesoscopic origin for the striking differences in macroscopic behaviour. The ability to change the contrast in neutron scattering, simply by changing the isotopic composition of the sample proofs particularly useful, as it allows to observe the individual components of the sample.

It is shown that mixed aggregates are formed in both JR 400/SDS and pDADMAC/SDS mixtures. However, subtle differences in their structure and composition result in a remarkable difference in macroscopic flow behaviour.

In summary, we investigated different mixtures of cationic PE and the anionic surfactant SDS and used SANS to identify the structural differences, which determine whether a strong increase in viscosity occurs or not.

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↘ Flash Talk: Wed-F-P1

STRUCTURE OF DNA-DENDRIMER COMPLEXES AND ITS IMPLICATION ON DNA-HISTONE INTERACTION IN NUCLEOSOME

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Eukaryotic organisms efficiently package their genetic information into the nucleus by compacting DNA into chromatin in a hierarchical way [1]. The fundamental repeating unit of chromatin is nucleosome, which is composed of 147 bp of DNA bound to a central octamer of histone proteins [2]. Polyamidoamine (PAMAM) dendrimer consisting of a central core and well-defined number of layers of branches can be protonated spontaneously under physiological or acidic condition. The positively charged PAMAM dendrimer thus formed can form electrostatic complexes with polyanionic DNA [3]. Considering the similarity in geometric characteristics between PAMAM G6 dendrimer and histone octamer, the G6 dendrimer may serve as a synthetic model of histone protein for understanding the DNA-histone interaction which governs the hierarchical structure of chromatin [4].

Using small angle X-ray scattering (SAXS), here we show that the electrostatic attraction between DNA and polyamidoamine (PAMAM) dendrimer of generation six (G6), which is geometrically similar to histone, led to the formation of beads-on-string structure, where DNA wrapped around the spherical dendrimer macrocations to yield the "chromatin-like fiber" composing of the interconnected "nucleosome-like particles". A "wormlike chromatin-like fiber model" was introduced to obtain the theoretical scattering patterns closely resembling the experimentally observed ones, from which the pitch length of the DNA superhelix wrapping around the dendrimer and the interparticle distance of the nucleosome-like particles were deduced. The pitch length (ca. 3 nm) was similar to that associated with the nucleosome; however, the wrapping of DNA around the dendrimer was not tight, but showed obvious fluctuations of the superhelix radius. The interparticle distance in the chromatin-like fiber was close to that of the dendrimer diameter, indicating that the linker DNA was very short. On the other hand, the SAXS profile in the intermediate to high q region of the nucleosome array in aqueous solution was fitted very well by the form factor of the mono-nucleosome particle based on the rigid crystal structure model. This means that the fluctuation of the beads-on-string structure of nucleosome was strongly suppressed and the linker DNA was long. The comparison between the structure features of the dendriplex and those of the nucleosome revealed that the attraction free energy arising from the electrostatic interaction energy and the counterion entropy was not sufficient to stabilize the beads-on-string structure and regulate the length of linker DNA in chromatin. Additional binding forces and regulation factors are hence involved in creating the chromatin structure in vivo.

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↘ Flash Talk: Wed-F-P1

NANOSTRUCTURE OF THE POLYMER-GRAPHENE COMPOSITES

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PVDF and PET is a polymer of high chemical resistance, good mechanical strength, and additionally is easy in processing. Its properties prefer it to be used in technical solutions where you need a long-term chemical and thermal resistance for outdoor conditions. Graphene is a planar sheet of sp 2-bonded carbon atoms in a hexagonal network. It can be considered as the final member of the series of fused polycyclic aromatic hydrocarbons, such as naphthalene and anthracene. There are many publications that describe the testing of composites in which graphene is used as an additive to polymers to improve their properties. These results indicate that using the graphene may increase the mechanical strength of the composite, the thermal and electrical conductivity. The combination of the properties of PVDF and PET and graphene suggests that the resulting composite will be a new material for technical applications. In the literature there are no reports on the receiving polymer-graphene fiber nanocomposite. Mixtures prepared by their own patent. In the process of thermoforming there were obtained fibers with very interesting properties containing graphene. This paper will present the results of nanocomposites determining by SEM, structural studies WAXS and SAXS, and DSC thermal analysis.

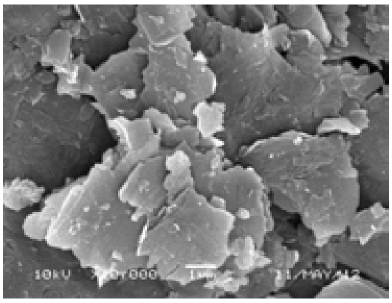

Fig .1. *SEM micrograph of graphene oxide (GO)*

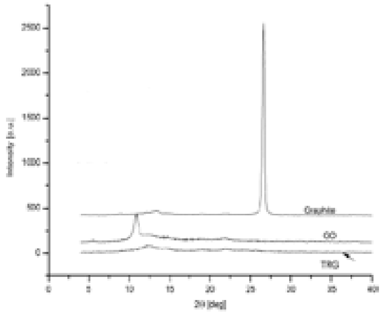

Fig.2. *WAXS curves for graphite, graphene oxide (GO), graphene prepared by thermal reduction (TRG)*

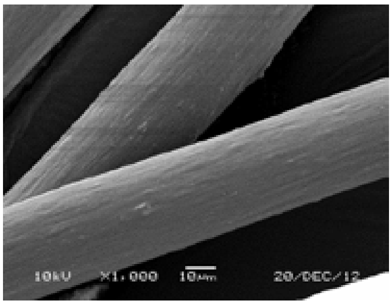

Fig. 3. *SEM micrograph of composite fiber PVDF / graphene (TRG)*

Keywords: *Nanocomposites, graphene, supermolecular structure, PVDF, PET*

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SEMI-CRYSTALLINE POLYMER NANOCOMPOSITES: INTERPLAY OF MATRIX CRYSTALLIZATION AND NANOPARTICLE SELF-ASSEMBLY

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The creation of ordered (layered) biomimetic materials typically follows a series of steps: first mix nanoparticles with water, organize the NPs by ice templating, evaporate the ice and then back fill with metal or polymer. We propose a simple method exploiting the in situ self-assembly of a crystalline polymer in the presence of nanoparticles to facilitate this process, and provide a completely new pathway for the synthesis of biomimetic materials. A suite of complementary experimental tools are used in this analysis. In parallel, we are developing theoretical tools to a priori predict the morphologies adopted by semicrystalline polymers. The convergence of these novel experimental developments in the venerable field of semicrystalline polymers could lead to new applications for this largest class of commercially relevant polymeric materials. We investigate a new class of nanocomposite materials made of semi-crystalline poly(ethylene oxide) and poly(methyl methacrylate) grafted silica nanoparticles (NPs). The results indicate that NPs do not act as nucleating agents as indicated from the lowering of the onset of crystallization temperature with addition of NPs. Although the crystal sizes and rate of crystallization are reduced in the presence of NPs, the equilibrium melting temperature seems to be unaffected. Furthermore, no remarkable change was observed in the spatial dispersion of NPs upon fast crystallization [1]. However, for slow crystallization when NPs diffusion is faster than the crystal growth rate [2], both TEM and SAXS scattering reveal that the system starts to be organized in a "layer-by-layer" architecture, where the NPs are aligned in the amorphous phases intercalated by the crystalline lamellar phases.

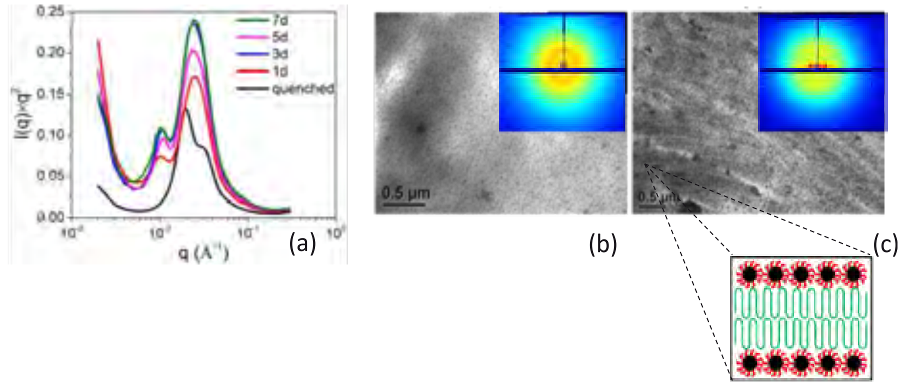

Figure 1: (a) $I(q)$ *vs* q^2 for silica (20wt %) in PEO based PNCs isothermally crystallized at 57.5 °C for different amounts of time, (b) TEM micrograph for silica PEO based PNC quenched from melt. (c) TEM micrograph for silica PEO based PNC isothermally crystallized at 57.5 °C for 3 days. The insets correspond to 2D SAXS scattering patterns isotropic for the quench (b) and strongly anisotropic after crystallization (c). The sketch illustrates the organization of the NPs intercalated by the crystalline lamellar phase.

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STRUCTURE OF CHAIN-GRAFTED POLYSTYRENE-FULLERENE STAR SYSTEMS INVESTIGATED BY SANS

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The performance of entangled polymers is extremely important both for understanding their fundamental behaviour and for industrial applications, as it provides insight into mechanical properties as well as processing of polymers. The behaviour of linear chains is well understood, however the behaviour of branched polymers is hindered by the difficulty in defining branched polymers precisely. The synthesis of star polymers provides more control over the number and molecular weight of the arms. Therefore, these structures can be viewed as model systems to carry out dynamic and structural studies.

There is particular interest in star polymers containing a fullerene core, as grafting polymer chains to the surface of the fullerene overcomes their incompatibility [1]. The development of controlled polymerisation grafting techniques have allowed for the synthesis of well-defined polymer-filler star systems which are ideal for structural analysis.

Using living anionic polymerisation, 6 polystyrene (PS) chains of molecular weights both above and below the entanglement molecular weight of PS have been attached to fullerene cores. These structures have shown unusual viscoelastic properties in solution: there is shear thickening behaviour in concentrated solutions contrary to results for polymer brushes grafted onto nanoparticle cores in the literature [2]. A full structural study of these stars in solution at a range of concentrations provides some insight into their physical behaviour.

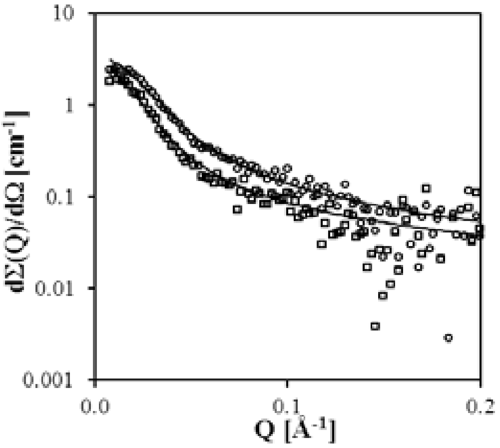

Figure 1: I(q) of PS-fullerene stars at 1wt% (□) and 2 wt% (o). The lines show a fit using a core-star model.

We present the results from dynamic light scattering (DLS) and small-angle neutron scattering (SANS) experiments on grafted PS/fullerene nanocomposites in solution at concentrations ranging from the dilute to the semi-dilute region. The stars were studied in both good and θ solvent conditions at a range of temperatures. The well-defined structure allows for use of a core-star model (Figure 1) in dilute conditions to describe the size and the shape of the nanocomposites. At higher concentrations, an adjusted model is used that takes into account the formation of clusters and change in the dimensions of the stars at different concentrations.

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THERMOPLASTIC POLYURETHANES WITH VARYING HARD SEGMENT CONTENT. MORPHOLOGY EVOLUTION MECHANISMS UNDER STRAIN

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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]. 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].
3 groups of TPU materials with different hard-segments content are compared.

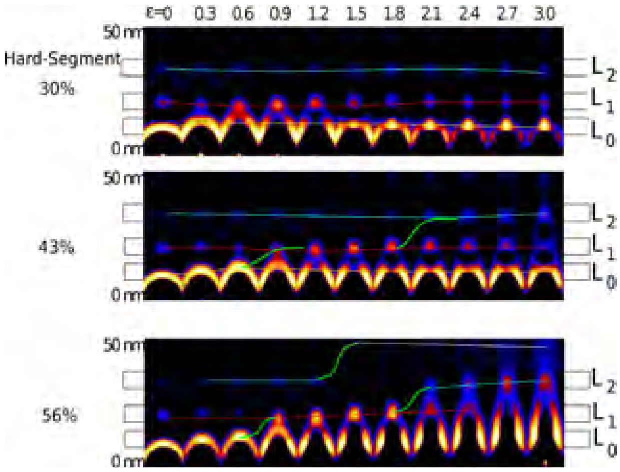

Figure 1: Nanostructure evolution as a function of strain viewed in meridional long period regions cut from CDFs, from different of Hard-Segment percentage base on TPU

Figure1 demonstrates a fundamental morphological difference between hard-segment (MDI+BD) for HSC=30% , HSC=43% and HSC=56%. An interesting result concerns the occurrence of relaxing HHS sequences when stretching. The systematic variation of sample parameters has led to clear indications herein. Correspondingly, more domains are sacrificed and less experience relief when the HSC is rising from 30% to 43%. Finally relaxation is absent in the material with HSC = 56wt.-%. Material in HSC=56% , the long period increases linearly with strain. Materials with lower HSC% have CDF long periods that reside in stationary bands. Their positions form a Fibonacci series. This sequence of hard and soft domains relates to the synthesis route (polyaddition). The differences are explained by different homogeneity of the reacting mixture of raw materials. Straining mechanisms are discussed.

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PHASE BEHAVIORS OF BLOCK COPOLYMER AND IONIC LIQUID MIXTURES

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Ionic liquid is a special type of solvent owing to its unique properties such as negligible vapor pressure, high ion conductivity, and chemical stability. The mixture of block copolymer and ionic liquid can make periodic nanostructure if ionic liquid could be selectively incorporated into a one block copolymer phase. Here, we studied phase behaviors of PS-*b*-P2VP (polystyrene-block-poly-2-vinylpyridine copolymer)/ionic liquid mixture with ionic liquid amount. We selected two different ionic liquids, [EMIM][TFIS] and [HMIM][TFSI] to find the effect of number of alkyl chains on the phase behaviors of PS-*b*-P2VP. The overall volume fraction of ionic liquids in block copolymer/ ionic liquid mixtures was varied from 0 to 0.4 and nanostructures of each mixtures and thermal stability of the structures were measured by small angle neutron and x-ray scattering. The distributions of ionic liquid in block copolymer were confirmed with contrast variation of block copolymer/ ionic liquid mixtures by small angle neutron scattering.

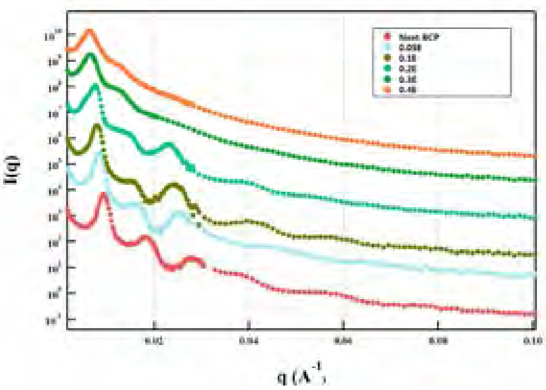

Figure 1: structure changes of block copolymer /ionic liquid mixtures with ionic liquid amount

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THE INTERACTION OF PEO-PPO-PEO TRIBLOCK COPOLYMER WITH BILE SALT

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Bile acid diarrhea is a disease resulting from malabsorption of bile acids in the small intestine. We investigate the possibility of using nonionic triblock copolymers based on poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO) instead of ion-exchange resins [1] in the treatment of this disease. For that purpose the interaction in aqueous solution between a PEO/PPO triblock copolymer, EO_{20}-PO_{69}-EO_{20} (P123), and the bile salt sodium glycodeoxycholate (NaGDC), has been studied by a series of methods: small angle neutron scattering (SANS), small angle X-ray scattering (SAXS), dynamic and static light scattering (DLS/SLS), as well as differential scanning calorimetry (DSC) and zeta-potential measurements. Alone, this triblock copolymer forms micelles with a PPO core and a PEO corona above a critical micelle concentration, CMC, and a critical micelle temperature (hydrodynamic radius ca. 10 nm). NaGDC also forms micelles in aqueous solution, but with a smaller radius of around 1.6 nm [2]. The results from the abovementioned techniques show a significant interaction between the bile salt and the triblock copolymer. At low bile salt concentrations the NaGDC monomers associate with P123 micelles forming a mixed polymer-rich complex. With increasing concentration of bile salt, this complex becomes more charged. Furthermore, at sufficiently high bile salt concentrations a disintegration of the block copolymer micelle begins, and bile-salt-rich mixed complexes coexist with the polymer-rich complexes.

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↘ Flash Talk: Wed-F-P1

SURFACTANT EFFECT ON THE STRUCTURE OF HYDROGELS INVESTIGATED BY SANS

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Epoxy-based hydrogels prepared by swelling of hydrophilic epoxy networks containing polyoxyethylene (POE) and polyoxypropylene (POP) in water have a nanophase separated structure consisting of water-rich and water-poor domains [1]. Presence of a surfactant in the swelling solution results in an additional amount of water absorbed by the networks. Consequently, structure of the hydrogels has to be rearranged to cope with the volume change. The aim of this communication is a study of the effect of a cationic surfactant (cetyltrimethylammonium bromide, CTAB) on the structure of the epoxy-based hydrogels by SANS.

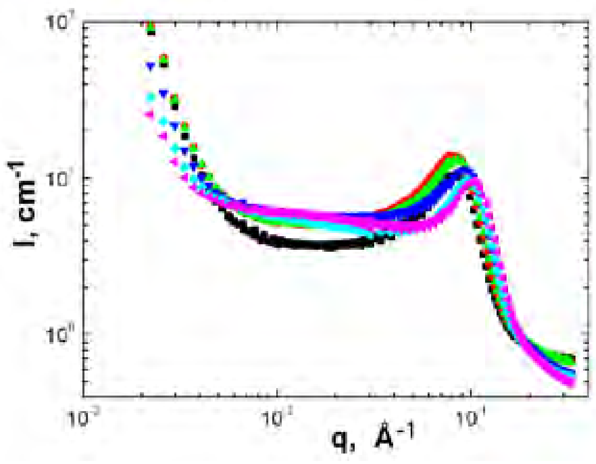

Figure 1: SANS patterns obtained from D-2000/POEBGE networks swollen to equilibrium at 25 ^oC in: D_2O (■) and 0.001M (●), 0.002M (▲), 0.005M (▼), 0.01M (♦), 0.1M (◀) CTAB in D_2O.

Figure 1 shows SANS patterns obtained from the stoichiometric epoxy network prepared by end-liking reaction of *α*,*ω*-diamino terminated POP of molar mass 2000 g.mol^{-1} (Jeffamine D-2000) with POE diglycidylether of molar mass 525 g.mol^{-1} swollen in D_2O and aqueous CTAB solutions. Nanophase separated structure of the hydrogels is preserved at all CTAB concentrations as proved by presence of the distinct scattering peak (q_{max}) and q^{-n} scaling ($n \approx 4$) in Porod's region of SANS. Characteristic length of the structure, D_B ($=2\pi/q_{max}$), decreases from 80 Å (in D_2O) to 60 Å (in 0.1M CTAB). Therefore, presence of CTAB in the swelling solutions reduces average size of both phases in the hydrogels.

These observations are in good agreement with the effect of ionic surfactants on aggregation behavior of POE-POP-POE molecules in aqueous environment observed by Hecht *et al* [2]: the surfactant binds cooperatively on the block copolymer molecules and increases miscibility of hydrophobic network building blocks (POP) with water.

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POLYURETHANE MORPHOLOGIES AND THEIR RESPONSE TO STRAIN STUDIED BY SAXS

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Extension of polyurethanes (PUs) synthesized of varying topology and functionality (f =2..4) of the polyols are monitored by small-angle X-ray scattering (SAXS).[1] PUs with different polyols exhibit different failure mechanisms[2]. Chord distribution function (CDF) computed from the recorded SAXS patterns[3] reveals the characteristics of nanostructure evolution of poorly developed domain structure under strain. The nanostructure variation uncovers the failure mechanisms. PU-Hs – a H-shaped (f =4) polyol with short arms – is not nanostructured. Isolated hard domains at random in PU-Hl (long arms) are not destroyed during straining. PU-X (f=4, star-shaped) develops microfibrils: one-dimensional correlations among hard domains, as deduced from a CDF analysis. PU-I and PU-Y are based on 2- and 3-functional polyols. They contain many well-separated hard domains with 3D connectivity. Their arrangement of hard domains evolves identically, but not the population density. In PU-I (and PU-X) hard domains fail during straining, in PU-Y the interdomain soft phase density decreases. Fig. 1 shows the straining mechanisms.

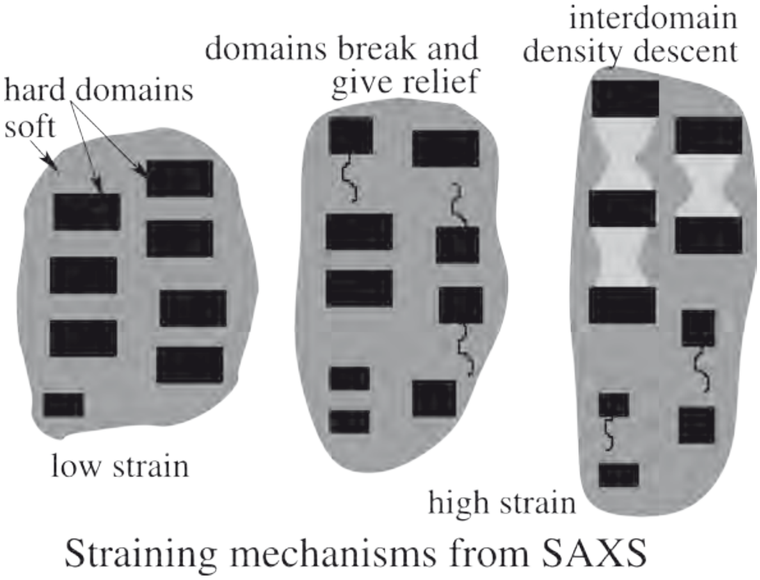

Fig. 1. The straining mechanisms concluded from SAXS

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↘ Flash Talk: Wed-F-P1

OBSERVATION OF PROTEIN UNFOLDING AND REFOLDING WITH SELECTIVE SURFACTANTS

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The protein-surfactant complexes are of great interest because of their use in many fields including pharmaceuticals, cosmetics and protein separation. The resultant structure of protein and surfactant complex is governed by the competition of electrostatic and hydrophobic interactions between the components [1]. We have used the interplay of these interactions to refold an unfolded protein using combination of selective surfactants. Small-Angle Neutron Scattering (SANS) has been used to characterize these structures. Measurements are carried out from the complexes of anionic BSA protein with anionic SDS, cationic DTAB and nonionic C12E10 surfactants. Ionic surfactants (both cationic and anionic) strongly bind to BSA protein at lower concentration and the protein is unfolded through the formation of micelle-like clusters along the protein chain at higher surfactant concentrations. Nonionic surfactants do not show any significant interaction with protein and the two components mostly coexist individually. The folded protein structure is characterized by oblate shape, whereas the unfolded protein by the mass fractal. The overall size of complex (extent of unfolding) increases and fractal dimension (packing of micelles) decreases with the increase in surfactant concentration [2].

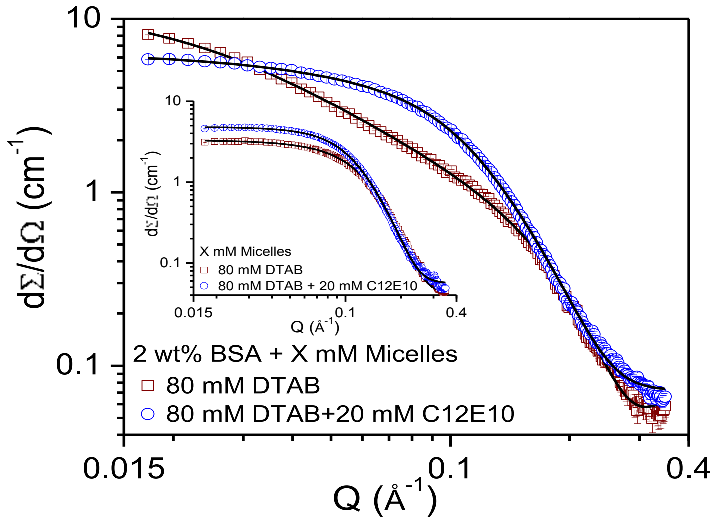

Figure 1: SANS data from BSA protein with selective surfactants for the protein undergoing unfolded to folded state. (Inset shows the data of corresponding surfactants without protein).

The unfolded protein with ionic surfactant refolds back in the presence of nonionic surfactants (Figure 1). The ionic surfactant molecules move out themselves from the unfolded protein and form mixed micelles with nonionic surfactants. The refolding is governed by the dominance of hydrophobic association of ionic and nonionic surfactants over the electrostatic binding of ionic surfactant with protein [3]. The mechanism of protein refolding involves number of micelles attach to protein decreasing with increase in nonionic surfactant concentration.

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↘ Flash Talk: Wed-F-P1

INVESTIGATION OF CAVITATION IN RUBBER UNDER HIGHLY CONSTRAINT CONDITIONS

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Rubber exhibits a high reversible stress strain relation under cyclic uniaxial tension. Under constraint conditions with high local hydrostatic stresses irreversible damage occurs by local cavitation. The damage process within the material was investigated in-situ by SAXS, x-ray computer tomography and dilatometry to identify elementary steps of failure. In contrast to semi-crystalline materials here generally could be found, that cavitation took place in that way, that small cavities merge abruptly to larger bubbles which are responsible for remarkable local stress release and stabilization of local stress distribution. Therefore the material at failure is finally dominated by only few well-distributed large cavities, visible finally on the fracture surface. Figure 1 show as example the fracture surface of a Styrene-Butadiene Rubber with 20 phr CB as filler, diameter 20 mm, thickness 1 mm.

Figure 1: Fracture surface of a SBR-sample with 20 phr CB.

Scanning SAXS measurements show during the whole loading cycle small but characteristic changes in the structure on nm-scale within the material as well as the changes of those structures with ongoing deformation. These changes will be discussed on the basis of cord distribution functions according to the extended presentations of Stribeck [1].

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↘ Flash Talk: Wed-F-P1

IN OPERANDO STUDIES ON REVERSE OSMOSIS DESALINATION WITH SMALL-ANGLE NEUTRON SCATTERING

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Formation of aggregates caused by the interaction of organic and inorganic molecules, in particular those involved in the formation of calcium phosphate minerals, has strong negative influence on membrane permeability in reverse osmosis (RO) waste water desalination. Presently, RO is an important tool for gaining and recovering potable water. A better understanding of the origin of these aggregates is urgently needed for economic reason but also for scientific purpose as these phenomena are very much related to the broad and versatile field of biomineralization [1]. Small-angle neutron scattering (SANS) is a very strong tool in this field as it is a non-destructive technique, allows quantitative analysis on microscopic length scale and differentiates between organic and inorganic components when using the technique of contrast variation [1-3].

One of our goals was the realization of in operando SANS experiments on RO desalination under most realistic conditions. For this purpose we developed a cell for real-time SANS experiments simulating the process of reverse osmosis (RO) wastewater desalination up to 30 bar [4]. These studies are quite complex as scattering originates from three different sources of the sample, namely from the feed (salt water to be desalinated), the fouling layer at the surface of the membrane, as well as from the membrane itself, as its structure is changing due to large exposed pressure. In parallel we always measured the permeability of the membrane which is an important parameter for the engineer.

In the presentation we first will give a short description of the cell which is followed by SANS data from the various topics of this project. These are: (i) Formation and characterization of aggregates formed in a simulated secondary effluent (SSE) after adding various organic molecules as partly described in refs. [2,3], (ii) the characterization of RO thin-film composite (TFC) membranes using contrast variation, as well as (iii) in operando results from desalination experiments performed at KWS3 of the FRM II (TUM in Garching). It came out that the VSANS transmission coefficient, as a measure of the total scattered neutrons, is a proper parameter which is discussed together with membrane permeability measured in parallel [4].

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↘ Flash Talk: Wed-F-P1

Small-angle X-Ray Scattering from poly(*L*-glutamic acid) in quaternary ammonium salt aqueous solutions

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The helix-coil transition of polypeptide in aqueous solution is a well-known phenomenon. For example, poly(*L*-glutamic acid)(PLGA) shows the phenomenon by changing pH of solution. It remains unclarified, however, effect of quaternary ammonium salt on the local conformation of PLGA in aqueous solution. In this work, the local conformation of PLGA in quaternary ammonium salt aqueous solutions was studied by SAXS.

Sodium salt of poly(*L*-glutamic acid)(PLGA-Na) of $M_w = 6.4 \times 10^4$ was purchased from Sigma-Aldrich Chemical Co. The degree of neutralization $\alpha = 0.8$ of the sample was employed in SAXS measurements. C_s of added salts, ammonium chloride(NH_4Cl), and tetramethyl-(TMAC), tetraethyl-(TEAC), tetrapropyl-(TPAC), and tetrabutyl- ammonium chloride(TBAC) were 0.1M and polymer concentration C_p was 0.01 g/mL.

SAXS measurements were performed at the Photon Factory of High Energy Accelerator Research Organization, Tsukuba, Japan. The wavelength of incident X-ray was 0.1488 nm. The sample cell was made of stainless-steel and had quartz windows of 20 μm thickness whose interval is 1 mm. The exposure time was 5 minutes and the measurement temperature was at room temperature. From the scattering profiles of samples, the root-mean-square radius of the cross-section of polymer chain was evaluated to be 0.4 ± 0.05 nm independently of the added salt species, which was the same the case in PLGA in 0.2M NaCl[1]. Figure 1 shows Kratky plot of PLGA in quaternary ammonium salt aqueous solutions. The data were fitted to the scattering function of a semi-flexible polymer chain[2][3][4] which involves parameters the contour length and the persistence length L_p of polymer chain. The fitting gave L_p of 0.94(TBAC), 0.94(TPAC), 1.07(TEAC), 1.18(TMAC), and 1.27(NH_4Cl) nm, respectively, and L_p of the chain decreased with increasing ionic radius of counter-ion. This result might suggest that the expansion of PLGA chain decreases as counter-ion radius increases and simultaneously hydrophobic interaction among quaternary ammonium salts becomes effective.

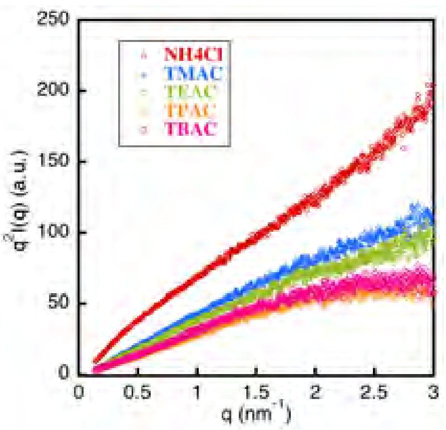

Figure 1: Kratky plot of PLGA in quaternary ammonium salt qaueous solutions.

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↘ Flash Talk: Wed-F-P1

THE FIRST LABORATORY *IN-SITU* GISAXS AND GIWAXS STUDIES OF THE SOLVENT AND THERMAL ANNEALINGS OF THE BULK HETEROJUNCTION ORGANIC SOLAR CELLS

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In this study, we report on the first laboratory *in-situ* GISAXS and GIWAXS studies of the solvent and thermal annealings of the bulk heterojunction organic solar cell with the blend composed of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C61-butyric acid methyl ester (PCBM). The solvent and thermal annealings are used to optimize the bulk heterojunction morphology due to an improved phase separation between P3HT (donor) and PCBM (acceptor) domains. The larger domains and improved donor/acceptor interface facilitate the charge transport and exciton dissociation, respectively [1]. The P3HT/PCBM blend morphology evolution during the solvent and thermal annealings was explored *in-situ* by GISAXS method with the time resolution of 10 s (Figure 1). This high resolution was achieved due to the high-flux liquid metal-jet X-ray source Excillum that allows measurements of organic materials confined solely to synchrotron beamlines before. Simultaneously, the crystallization of P3HT molecules during solvent and thermal annealings was monitored by GIWAXS method with the identical time resolution of 10 s. The improvements in the blend morphology of the bulk heterojunction and crystallinity of P3HT were correlated with the impedance spectroscopic measurements that provide a fingerprint of the electronic structure of both components of the blend.

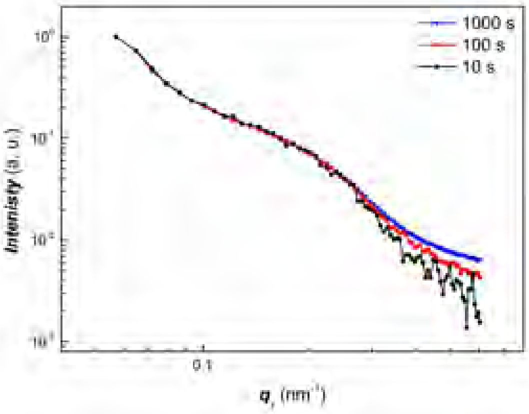

Figure 1. The GISAXS horizontal cuts of the P3HT/PCBM bulk heterojunction plotted in the log-log scale for different exposition times: 10 s, 100 s and 1000 s. The horizontal cuts were taken at q_z=0.32 nm^{-1}.

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Network structures of triblock copolymer by two-step phase separation

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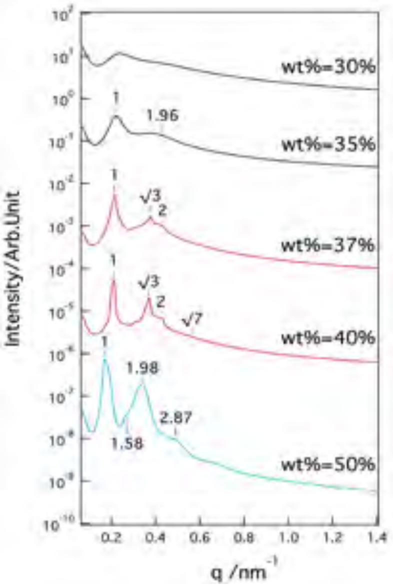

Figure 1. SAXS profile of SID1 solution.

We have previously found the Ordered Bicontinuous Double Diamond network structure (OBDD) in polystyrene-*b*-polyisoprene-*b*-polydimethylsiloxiane (SID) (M_n = 324000 g/mol, $f_{PS} = 0.29$, $f_{PI} = 0.43$, $f_{PDMS} = 0.28$), by toluene cast process. Though OBDD structure is not an equilibrium structure of triblock copolymers, we still found OBDD structure in triblock copolymer. Therefore, we expect that complex phase transition occurs during the solvent casting process, prior to the formation of OBDD. Thus, we investigated the mechanism of OBDD-forming process by probing the morphological transition during solvent cast process via SAXS experiment.

Figure 1 shows the concentration dependence of SAXS profile of SID solutions. The broad peak observed at 35 wt% corresponds to the micelle structures in solution. At 37 wt%, peak position ratio of $1:\sqrt{3}$ indicates hexagonally packing cylinders are formed in the solution. At 50 wt%, series lattice peaks of $1:\sqrt{3/2}:\sqrt{2}:\sqrt{5/2}:\sqrt{3}:\sqrt{4}:\sqrt{9/2}$ match up with Pn3m double-diamond structure, indicating the cylinders structure transformed into OBDD network structures. This order-order transition is caused by a two-step microphase-separation as shown in Figure 2. In the first step, as the result of insoluble PDMS chains in toluene and the unfavorable enthalpic interaction between PS and PDMS, PDMS blocks microphase separated first as PDMS-cylinders in PS/PI matrix. Then, as toluene evaporated gradually, PS and PI blocks finally microphase separated and the morphology transformed into OBDD network structure. This two-step phase separation result in a OBDD network structure during the self-assembling process of PS-PI-PDMS in solvent cast process.

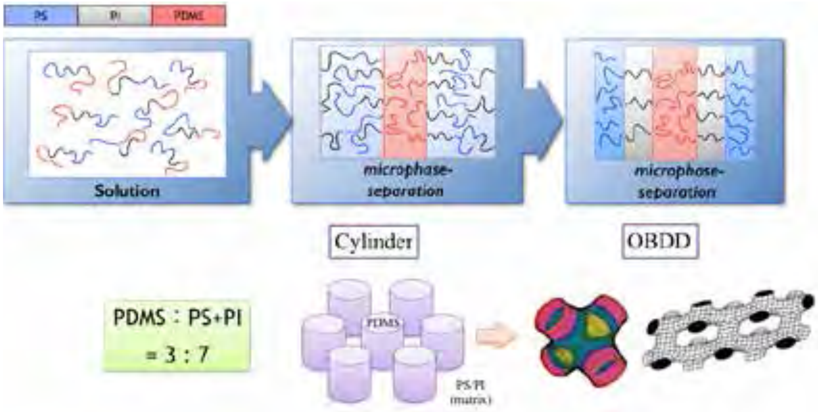

Figure 2. Two-step Microphase Separation.

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POLOXAMER-BASED HYDROGELS AS DRUG-DELIVERY SYSTEMS FOR MIGRAINE TREATMENT: SMALL ANGLE X-RAY SCATTERING (SAXS) STUDY

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Migraine is a neurological disorder characterized by unilateral throbbing headaches, lasting from 4 hours to 3 days and affecting around 12 % of the world population. In order to treat the acute symptoms of migraine, sumatriptan (SMT) has been considered due to its safety and clinical efficacy. Nevertheless, SMT presents some limitations related to its permeation across the blood brain barrier and its commercially available formulations have low bioavailability.

Therefore, in these circumstances, the research of new carrier systems is of great interest and importance in the development of new controlled-release formulations containing SMT, favoring the prolonged action of this drug. The present study [1] proposed to characterize the structure formed by isolated and binary systems of poloxamers (PL) (Pluronic® PL407and/or Pluronic® L-81)-basedhydrogels as controlled release formulations for SMT, using small angle X-ray scattering (SAXS), and the sol-gel process applying rheology. SAXS experiments were performed at SAXS1 beamline at the Brazilian Synchrotron Laboratory (LNLS, Campinas-SP, Brazil) at two temperatures: 25 and 37°C. The rheology measurements were performed using a Haake Mars-III rheometer at 37°C, with a plate-plate geometry.

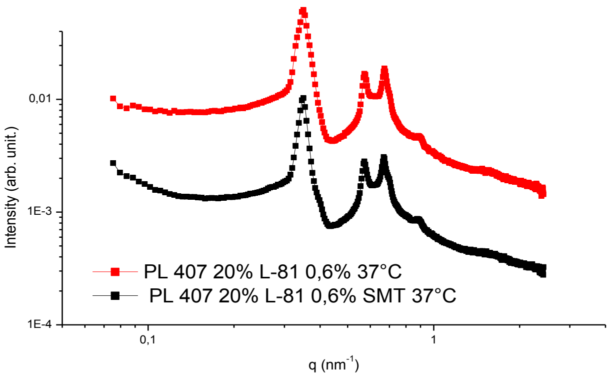

Figure 1: Comparison between PL407 20% L81 0,6% with and withouth SMT at 37°C

Our results showed the presence of a lamellar structure for PL PL407 (at 25°C) and for PL PL407+PL-L81 (25°C). At 37°C, the system PL F-127+PL-L81 presents a hexagonal structure pattern. After addition of SMT, the hexagonal structure was maintained (Figure 1). Besides, the addition of PL L-81 (a more hydrophobic co-polymer compared to PL PL407) to the hydrogel formulation, maintaining the hexagonal structure and favoring the incorporation of SMT into the formulation, being interesting for pharmaceutical applications, particularly for migraine treatment.

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SINGLE AND DOUBLE NETWORKS FROM AMPHIPHILIC STAR BLOCK COPOLYMERS

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Amphiphilic conetworks comprise hydrophilic and hydrophobic chains which microphase-separate when swollen with water. This way, a large amount of internal interfaces is created which is of interest for, among others, tissue engineering [1]. To improve the mechanical stiffness, especially regarding compression, a second hydrophilic polymer network is introduced into these amphiphilic networks (Figure 1).

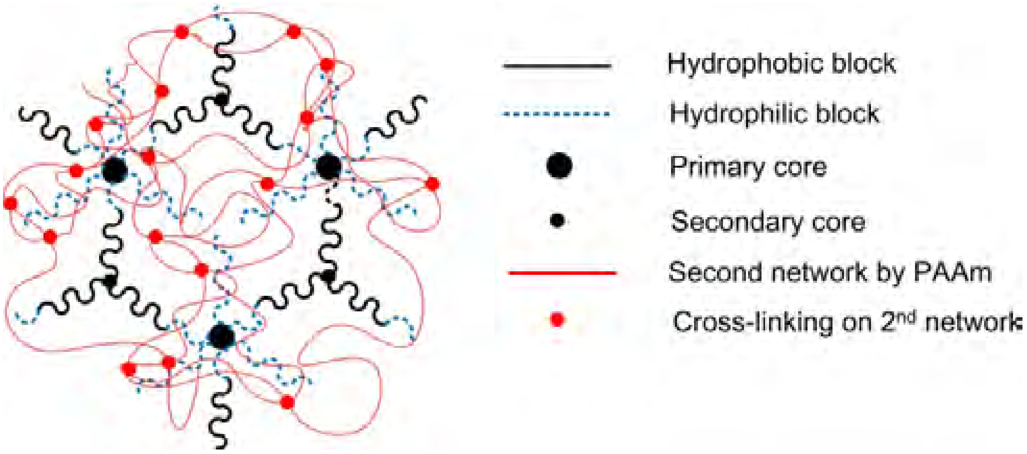

Figure 1: Schematic of the double network

We investigate amphiphilic conetworks from various acrylic blocks which differ in composition, water solubility and mechanical properties. We have studied the structures of the single and the double networks using small-angle X-ray scattering which reveals information about the microphase-separated morphology. We find that their degree of swelling in water as well as the underlying mesoscopic structures depend strongly on these characteristics.

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↘ Flash Talk: Wed-F-F1

IN OPERANDO APPLICATIONS OF COMBINED USAXS/SAXS/WAXS MEASUREMENTS AT PRESSURE OR TEMPERATURE

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Simultaneous *in situ* small-angle scattering and wide-angle (diffraction) measurements, combined with realistic sample environments (pressure, temperature, processing conditions), provide a powerful means to follow in real time the correlated phase composition and microstructure evolutions that occur in response to changes in environmental conditions. Examples of major applications in materials science are as diverse as measuring, *in operando*, the effects of precipitation heat treatments in metals and alloys, or determining the response of flexible metal organic frameworks during adsorption and desorption of H_2, CO_2 or other gases.

For such measurements to be quantitative and accurate, several requirements must be met, which place severe constraints on the experimental configuration. For example, in order to retain a parallel-sided sample geometry needed for SAXS or SANS, while having sufficient q-ranges for both small-angle and wide-angle diffraction regimes, a short X-ray or neutron wavelength is needed. When coupled with requirements for sufficient q- and time-resolution for real-time experiments, these constraints point to such measurements being done at a major facility: either using hard X-rays at a synchrotron, or short-wavelength neutrons at a pulsed neutron source. Over recent years [1], the USAXS facility at the Advanced Photon Source (Argonne National Lab., IL, USA) has been continually upgraded and adapted to conduct rapid USAXS/SAXS/WAXS measurements under *in operando* conditions – currently over a structural and microstructural scale range from sub-Å to micrometers in about 6 minutes.

In applying this capability, major issues to address have been the intensity, geometry and q calibrations and, in particular, the accuracy with which Bragg diffraction patterns in the WAXS regime using a SAXS-type transmission geometry can be correlated with separate results from dedicated powder diffraction instruments. This is a critical issue for USAXS/SAXS/WAXS *in operando* studies, because complex, minor or modified phases must frequently be recognized from weak diffraction peaks (perhaps strained) over a more limited q-range than available in conventional powder diffraction, and the integrated peak intensities must be quantitatively correlated with the changing absolute-calibrated (and interpreted) SAXS intensity data curve.

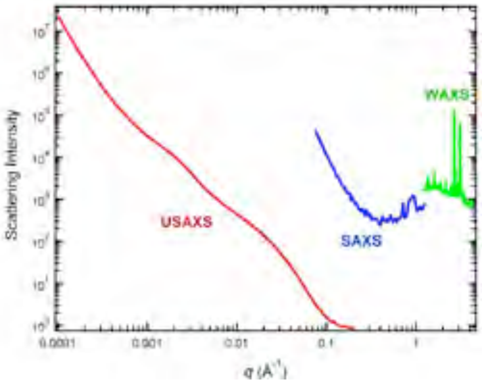

Figure 1: USAXS, SAXS & WAXS data

We explore these issues (see Figure 1) in connection with *in operando* studies of alloy heat treatments at elevated temperatures, and CO_2 sorption studies of novel solid sorbents under pressure. *In operando* USAXS/SAXS/WAXS capabilities also show potential for providing important insights regarding post-build heat treatments for additive manufacturing or for operation of solid oxide fuel cells and batteries.

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SUPERMOLECULAR SELF-ASSEMBLY DYNAMICS OF PERYLENE BISIMIDES AND OXYGENIC POLYOXOMETALATES

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Upon addition of perylene bisimide (PBI2+) to ruthenium polyoxometalate (RuPOM) in aqueous solution, a spontaneous self-assembly into a nano-scaffold occurs [1]. In both TEM and SEM images of the hybrid material, various morphologies were observed from which no detailed information on the intermolecular structure could be gained. Subsequent solution SAXS measurements reveal the formation of superstructures. Scattering behavior in the Guinier-regime suggests plate-like assemblies in the range of 4-7 nm, depending on solvent conditions. Further, disordered correlation peaks allow conclusions on the lateral arrangement. Based on this evidence, a molecular structural model is suggested. AFM measurements confirmed the predicted nano-plate morphology as building blocks with potential application as photocatalysts.

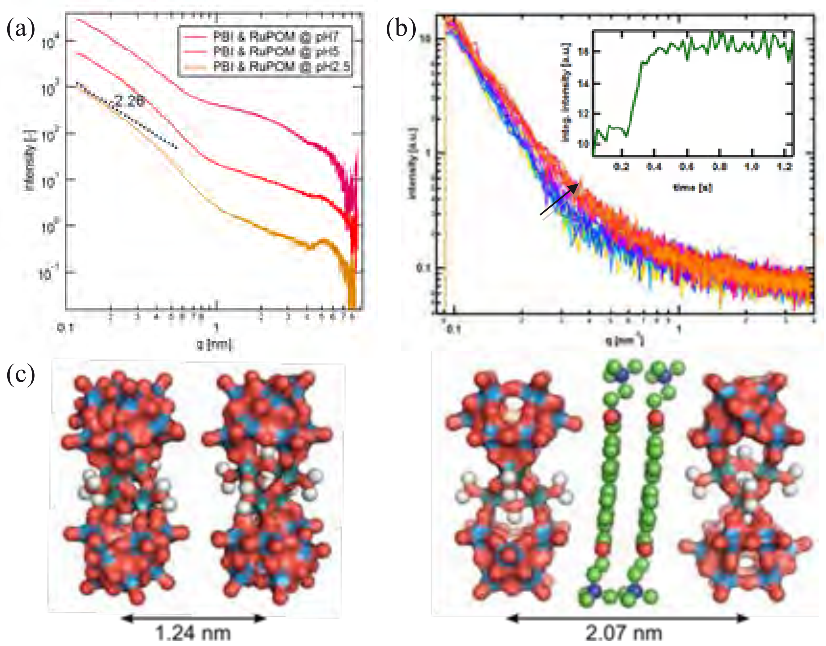

Figure 1: (a) Solution SAXS data of the nano-scaffolds after mixing of PBI and RuPOM. (b) Stop-flow SAXS spectra with a time resolution of 25ms of the first second after mixing. (inset) Evolution of the integrated intensity of the curves over time. (c) Proposed molecular model based on detailed evaluation of the SAXS data in (a).

To obtain a comprehensive understanding of the self-assembly behavior of this system, stop-flow SAXS measurements were performed. The obtained data suggests a full aggregation in the observable size regime within a few hundred milliseconds. We will further present the influence of varying precursor and solvent parameters on the final structure as well as on the aggregation dynamics of this promising combination with potential application as photocatalysts.

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IN-OPERANDO SANS ANALYSIS OF LITHIUM SULFUR CELLS

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Due to their high theoretical electrochemical capacity of 1675 mAhg-1 Lithium/Sulfur (Li/S) batteries are subjects of intense research [1]. However, there is still a loss of capacity with the number of charging cycles and the complicated processes within the Li/S battery are still not understood. Here we present an operando setup (Figure 1) that allows us to analyze the cathode of the Li/S cell with five different measurements.

The small angle neutron scattering (SANS) measurement gives information about the macroscopic formation of the solid sulfur phase (S8) that is present at the end of each charge cycle. The contrast matching method was used to match the elemental sulfur phase in the electrochemical cell. Simultaneous performance of electrochemical impedance spectroscopy (EIS) and UV/vis spectroscopy enables the access to kinetic processes at the solid electrolyte interface as well as the composition of the electrolyte. The cell temperature of the electrochemical cell is also monitored during the cycling process.

The use of a monolithic carbon cathode material and the non-application of a separator layer make this cell design a model system for LiS batteries. The authors have also developed an operando setup for X-ray radiography with the same parallel performed characterization methods. The results of the SANS measurement extend the view into the formation process of elemental sulfur to lower length scales.

The SANS measurements were performed at PSI (SANS II) in Villingen, Switzerland and at MLZ (KWS-II) in Garching, Germany.

Figure 1: Sample environment for in-operando analysis

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MESOSCALE STRUCTURES OF HOMOGENISED PLANT FIBERS STUDIED BY SAXS

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Plant fibers are widely used as natural structurant in many consumer products such as foods and beverages. There has been a long standing interest in understanding how the naturally present cellulose particles (i.e. elementary fibrils) are organized in these systems and how this changes when fibers are subjected to mechanical agitation. The objective of this study is to understand the impact of homogenization of plant cellulose dispersions at the meso length scale. Small-angle X-ray scattering (SAXS) experiments were performed at the high brilliance ID02 beamline of the European Synchrotron Radiation Facility (ESRF), France.

The observed SAXS patterns are the product of the form function of the individual elementary fibrils, an interference function derived from their packing arrangements and an exponential background arising from larger-scale scattering features [1]. The radius of the elementary fibrils was calculated from the first minimum of the Bessel (Form) function [1] and this yielded a diameter of 3.8 nm. Fitting the experimental data with models where we assume packed cylinders with circular cross-sections also resulted in a diameter of the elementary fibrils of 3.8 ± 0.32 nm. The structure factor could not be determined from model fitting due to lack of strong packing order [1]. Hence we adopted a model-free approach [1] where by means of Porod and Kratky plots the observed interference peak became more evident and the mean center-to-center spacing of elementary fibrils within a microfibril as well as the mean center-to-center spacing between microfibrils were calculated. From the dimensions derived from the fitting of the form factor and the observed weak interference peaks, the idealistic structural model presented in Figure 1 can be compiled. The evolution of 'within' and 'between' microfibrillar packing was studied for the number of homogenization passes during processing, the effect of the fiber concentration and the addition of solutes. The strongest effect was observed for the 'between' microfibrillar packing.

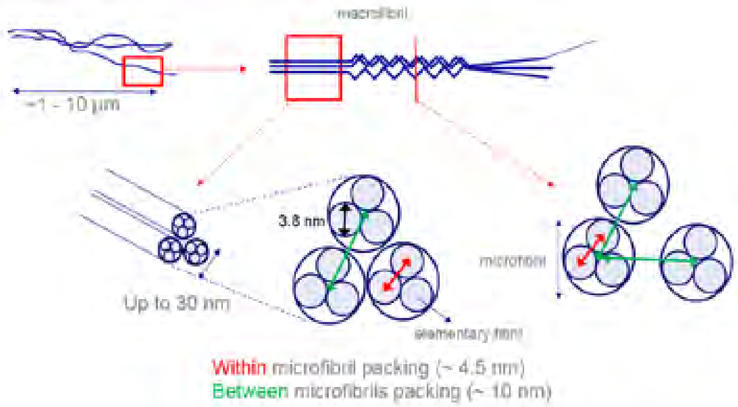

Figure 1: Schematic representation of the idealistic model used for the microfibrillar structural arrangements.

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MULTI-SCALE FILLER STRUCTURE AND DYNAMICS IN SIMPLIFIED INDUSTRIAL NANOCOMPOSITES

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Nanocomposites made of hard inorganic nanoparticles (NPs) embedded in a soft polymer matrix may have mechanical and electrical frequency-dependent properties of interest for various applications. These properties depend crucially on the dispersion of the filler NPs, which has been studied in simplified industrial (i.e., without crosslinker and related chemistry) styrene–butadiene nanocomposites with silica filler NPs of high structural disorder.

We have developed a quantitative structural analysis based on a combination of electron microscopy and small-angle X-ray scattering [1]. It leads to a global model, where primary silica beads are organized within small aggregates, which themselves fill large-scale fractal branches. Experimental parameters have been varied independently, starting with the silica volume fraction Φ_{si}, the matrix composition (percentage of graftable chains, %D3), and the chain mass. The grafting density on the silica NPs was shown to be the structure- (Figure 1) and rheology-determining parameter.

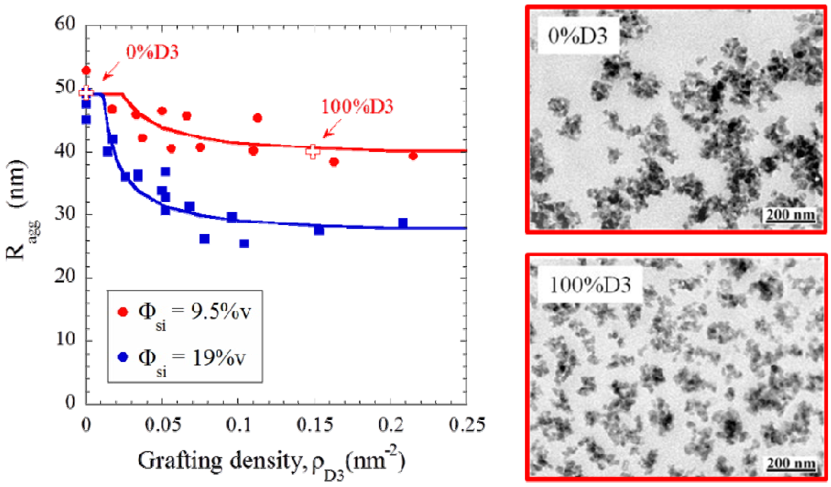

Figure 1: Average aggregate radius versus the nominal grafting density for nanocomposites with different mass (M_{SB} = 40 to 280 kg/mol) and matrix composition (0 to 100%D3) at 9.5%v and 19%v silica. Right: TEM pictures of two nanocomposites, which are indicated by crosses in the graph.

Moreover, dynamical properties have been followed by broadband dielectric spectroscopy (BDS) recently, and the detailed characterization of two high-temperature silica-related processes provided evidence that one of them can be linked to the structural evolution of these nanocomposites [2]. Our work thus suggests that such high-temperature BDS-measurements can be used to detect reorganizations in structurally complex silica nanocomposites.

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↘ Flash Talk: Wed-F-F1

ANALYSIS OF SMALL ANGLE NEUTRON SCATTERING FROM NANOCRYSTALLINE NIOBIUM CARBIDE POWDERS

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Small angle neutron scattering (SANS) from nanocrystalline niobium carbide material was investigated. Four powder samples of nonstoichiometric niobium carbide NbC_y ($y \approx 0.93$) were prepared by high-energy ball milling technique [1] of the initial coarse grain powder with different milling duration: $T = 0, 1, 5, 15$ hours. Initial single-phase powder was synthesized by high-temperature solid-phase vacuum sintering. SANS experiments have been performed on the YuMO spectrometer at the IBR-2 pulsed reactor in FLNP JINR (Dubna, Russia).

Measured SANS curves *I(Q)* were analyzed using the model suggested by G. Beaucage [2]. The model uses unified global scattering function over the whole available *Q*-range as a combination of exponential and power-law parts to fit the Guinier and Porod regions with a smooth transition region between them.

The SANS results revealed that two hierarchical structural levels are clearly observed in the scattering data from ball milled nanocrystalline niobium carbide powders. First structural level corresponds to aggregates with fractal surface and it is characterized by its own gyration radius R_g in the range from 424 to 305 Å depending on milling duration. Second structural level corresponds to compact non-aggregated nanocrystalline subparticles. The analysis of deviation from the Porod power-law asymptotic behavior in small-angle scattering curve allowed characterizing them as subparticles with diffusive interface [3]. Estimated gyration radius R_{gS} of subparticles varies from 83 to 43 Å. Using normalized polydispersity index PDI_n lognormal distributions of subparticles sizes were calculated assuming their spherical shape.

This work was supported by the Russian Foundation for Basic Research and Moscow Region Government (project No. 14-42-03585_r_center_a).

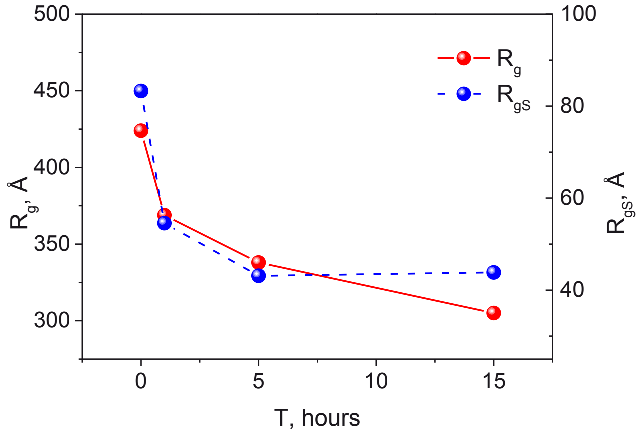

Fig. 1. The gyration radii of aggregates R_g and nanocrystalline subparticles R_{gS} vs. milling duration.

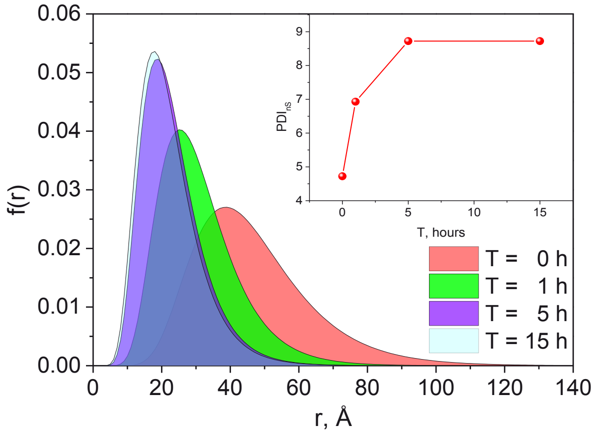

Fig. 2. Size distributions of subparticles for different milling durations. The inset shows polydispersity index.

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↘ Flash Talk: Wed-F-F1

THE INTERNAL STRUCTURE OF THE SPHERICAL SILICA PARTICLES

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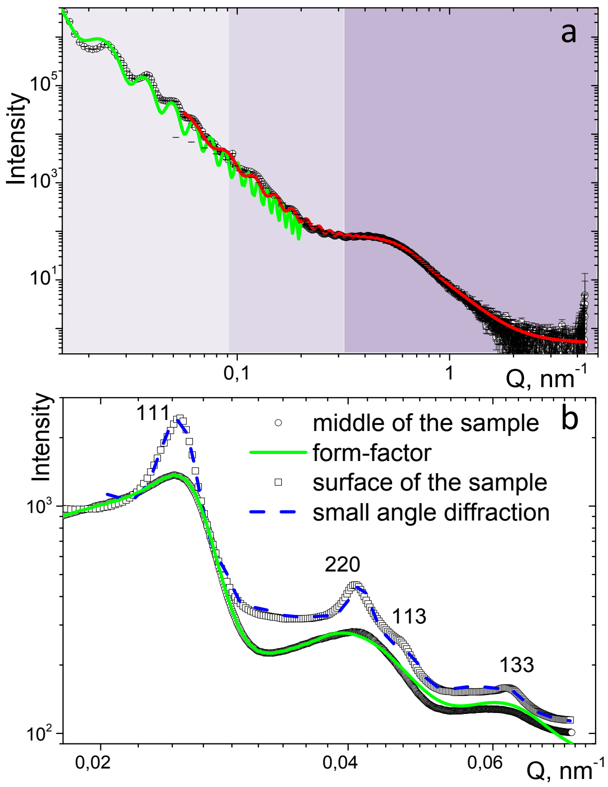
The internal structure of monodisperse spherical silica particles synthesized by a multistage Stöber - Fink method [1] was investigated by small-angle scattering of synchrotron radiation. It has been suggested that relatively large spherical particles of silica (more than 1000 nm in diameter) have the shell-hierarchic structure and consist of smaller particles ("secondary" particles). The last ones, in turn, consist of even smaller spherical particles with diameter of 5 - 10 nm ("primary" particles) [2]. To prove or refute an existence of the hierarchical model of the internal structure, as well as to describe the geometry of the particles and to determine their ordering at the process of sedimentation from aqueous colloidal solution by gravity, the Q-dependencies of the scattering intensity were obtained and analyzed.



It was found (Fig. a) that the silica particles with diameters from 300 nm to 2200 nm compose of smaller nanoparticles (diameter about 10 nm) which form a short-range order. In the Q-range of 0.09 nm^{-1} < Q < 0.3 nm^{-1} the features (maxima) on the scattering curve were detected, which, however, could not be definitely interpreted as a "secondary" particles. Although the size of the scatterers in this Q range should be about 70 - 100 nm that corresponds to the "secondary" particle size predicted in [2]. The Q-range of 0.01 nm^{-1} < Q < 0.09 nm^{-1} is well described by the form-factor curve of the spherical particles and determines their size.

The samples of artificial opals were synthesized from silica spheres on the surface of colloidal precipitate (Fig. b). It is shown that increasing the spheres diameter from 300 nm to 850 nm leads to an increase in the quality of the opal crystal structure resulting in the appearance of a well-detectable Bragg reflections corresponding to a face-centered cubic lattice. Quality of packing drops abruptly to a complete disorder with a further increase of the particle diameter from 1050 nm to 2200 nm.

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↘ Flash Talk: Wed-F-F1

CORE-SHELL NANOPARTICLES – INSIGHTS IN THEIR GROWTH AND DYNAMIC BEHAVIOR BY SMALL-ANGLE X-RAY SCATTERING

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Functional nanoparticles for which an inorganic, e.g. superparamagnetic, core can be used to localize or actuate the responsive (spherical) brush polymer shell of the nanoparticle are receiving immense interest as building blocks for biomedical and smart materials applications. The shell density profile and its change in solvation upon external stimuli determine the functionality for the diverse biotechnological applications.

In the present study, core-shell nanoparticles consisting of an iron oxide superparamagnetic core and a highly dense and stably grafted polyethylene glycol (PEG)shell [1] have been investigated by small-angle x-ray scattering (SAXS). This study proved for the first time the ability to directly investigate the shell in such a core-shell system using x-rays under static as well as dynamic conditions. The scattering curve shown in Fig 1. was directly compared to a mean-field scaling model of the shell, developed to describe dense spherical brushes [2].

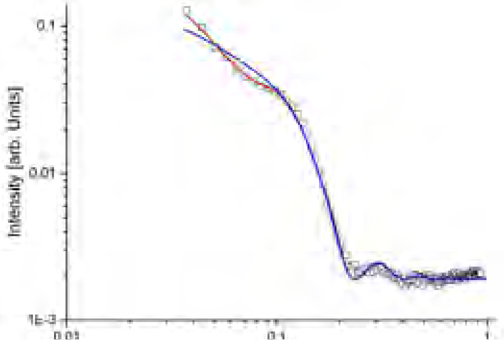

Figure 1 Scattering curve from core shell particles (open squares) with a fit based on the Daoud-Cotton model (red line) and a parabolic brush profile (blue)

The response of the shell to varying solvent conditions was monitored by the usage of a cloud point buffer that allows decreasing the solubility of the PEG as a function of the temperature. Here a collapse of the shell structure above a critical temperature could be observed.

Ligand assisted synthesis is used to create monodisperse iron oxide nanoparticle cores, which are a prerequisite for structural investigations as those above. Until now the understanding of the nucleation and growth of those nanoparticles has remained elusive and the involved mechanisms are under strong discussion in the scientific community. We present results from an in-situ SAXS/WAXS synchrotron experiment, which allowed for extracting the kinetics of nucleation and growth with unprecedented time resolution under minimal disturbance of the synthesis. The influence of parameters that could govern size and polydispersity, especially the ratio of monomer and surfactant was shown to play an important role. Also the point of phase transformation as well as the reaction kinetics could be resolved [3].

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SAXS AS HIGH THROGHPUT METHOD TO CLASSIFY THE MODE OF ACTION OF NOVEL ANTIMICROBIAL COMPOUNDS

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Multi-drug resistant pathogens are currently undermining our health care system. Urgently needed are novel antimicrobial drugs that have a new mode of action, however determining the mode of action is often not easy and not available in a high throughput approach. Here we present a high throughput method that can be used to classify the mode of action for novel antimicrobials and therefore support drug development. We applied small angle X-ray scattering as a sensitive structural tool to rapidly screen the drug induced morphological signatures in whole *Escherichia coli* cells in similar way as by determination of organelles (melamosomes) structural variations [1]. We could demonstrate that different modes of action result in different drug induced changes in the morphology of the bacteria. These changes of known antimicrobials can be classified using principle component analysis and then compared to novel antimicrobial compounds. In contrast to conventional imaging techniques, millions of cells can be probed within seconds and as consequence, statistically significant information on nanometer sized structural units in the sample is obtained. The experiments show that SAXS on synchrotron source or even modern lab source has potential to become standard procedure in the high-throughput screening pipeline in modern drug discovery.

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LINEARLY SWELLING NON-NIPAM BASED MICROGELS: STUDYING ARCHITECTURE BY SMALL ANGLE NEUTRON SCATTERING USING CONTRAST VARIATIONS

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Smart microgels have been increasingly recognized as potential building blocks for a lot of different applications like e.g. photonic materials, catalytic carriers, smart surface coatings and sensors.[1]

In the first part of this contribution, we treat statistical copolymers from N-n-proplyacrylamide (NNPAM) and N-isopropylmethacrylamide (NIPMAM) [2]. In its second part, this contribution studies non (N-isopropyl acrylamide)-based core-shell microgels that exhibit a unique linear thermoresponsive behavior in a temperature range between 25°C and 40°C.

It is the combination of distinct materials in core and shell, that gives the particles this unique property. Our approach was inspired by the work of the Richtering group [3].

The properties of these novel materials are studied by means of dynamic light scattering (DLS) and small angle neutron scattering (SANS). A major finding of these experiments is that the swelling becomes linear dependent on temperature and the crosslinker content of the core is directly related to the linear response. Hence, the core-shell particles behave piezo-like and might be useful as actuators on the nanometer scale [4].

Aiming at a better understanding of the underlying mechanism of the swelling of such core-shell structure, we prepared particles with deuterated cores and used contrast variation in SANS to reveal additional structural features related to the de-swelling and swelling of these microgels.

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Controlled fibrillation of monodisperse self-assembled low molecular weight hydrogelators

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The structure-activity relationship and the gelation process that drives the self-assembly of potential gelators into gels is not fully understood and the majority of gels are found serendipitously.[1] However, it has been established[1] that gelation is mainly controlled by the gelator design, gelation temperature, gelator concentration and solvent effects. Attempts to understand the molecular assembly of the gelators into molecular-scale fibrils and the subsequent hierarchal organization of the fibrils into spanning network that percolates the solution by fibril-fibril interaction has also been investigated. The mechanism development of a molecular solution into insoluble fibrillar gel network is a phase separation process driven thermodynamically by solution saturation. Furthermore, the molecular conformation has been found to be critical to enable packing in a specific manner to facilitate the self-assembly of 3-D gel-networks.[2] Recently, we reported[3] the low molecular weight hydrogelator (LMWH) as a very strong hydrogelator (MGC 0.3mg/ml) and presents interesting properties as a result of its low minimum gelation concentration, pH-sensitivity and for its fascinating semi-crystalline layered structure in the self-assembled fibers. Extensive investigations at different length scales during the slow hydrolysis of a Lewis acid in order to control homogenously throughout the solution at the local scale the pH turning of an aqueous solution, by several combined techniques. H^+ NMR, FT-IR, Rheology offline as well as simultaneous Rheo SAXS have revealed high monodispersity morphology of the fibers obtained by modifying the pH media as well as the association rate of the fibrillation process. Moreover, Microfluidic flow reactors have been used as a substitute to chemical species to modify the pH at the nanoscale in a controlled fashion. Importantly, at each point of the flow path of the microfluidic device, the self-assembly is a steady state process. SAXS studies[4] in combination with microfluidic reactor have enable us to probe the formation of the self-assembled LMWG fibers in a static fashion significantly at early stages. Moreover, the self-assembled system possess great industrial interest as a result of their applications such us remarkable selectivity with pharmaceutical targets methyl blue and Doxorubicin as well with common industrial dyes as indigo carmine.

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USAXS IN SITU QUANTIFICATION OF VOID NETWORK EVOLUTION DURING ANNEALING OF NANOMETER-SIZED YSZ

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Suspension plasma spraying (SPS) uses a stabilized suspension of nm or μm-sized feedstock particles to form 20 to 100 μm thick coatings with unique microstructures and properties (*e.g.*, **[1-2]**). Yttria-stabilized zirconia (YSZ) is a standard material for thermal barrier coatings (TBC) for use in high heat applications (e.g., turbines). It has been discovered, that SPS coatings made from the nm-sized feedstock exhibit significantly lower thermal conductivities compared to conventional coatings (*e.g.*, **[3]**), probably as results of unique voids/porous structure. Quantification of this void network architecture is challenging, especially due to their small sizes **[4]** – but it is critical for the development of the future SPS coatings applications.

USAXS (Ultra-Small Angle X-Rays Scattering) is highly suitable tool to characterize the voids with sizes in the critical range for these applications – from few nm to μm (*e.g.*, **[5]**). Original ex-situ results indicated, that as-sprayed SPS coatings exhibit unusual porous architectures where the average void size is comparable to the size of the feedstock particles - with about 80% of the voids, by number, having a characteristic dimension smaller than 30 nm, while the total void content was between 13 to 20%, similar to the conventional TBC coatings.

We have used *in situ* USAXS experiment to gain insight into structural evolution during simulated *in operando* conditions, which delivers much more relevant results compared to common *ex situ* measurements. It has been observed that, even at temperatures as low as 800°C, the microstructure is being transformed - while the total void content does not change significantly even after thermal annealing at 1250°C for almost 5 hours. Results show two mechanisms, which occur depending upon the temperature: sintering (corresponding to a decrease of both the void content and the void specific surface area) and coalescence (corresponding to a decrease of the specific surface area while the void content remains constant). The paper will review these experiments and document, how USAXS can be applied for industrially relevant applications providing quantitative *in operando* characterization of complex porous microstructures.

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IMPACT OF THE CORE/SHELL STRUCTURE OF NANOCRYSTALS ON THE OPTICAL OUTPUT REVEALED BY ASAXS AND WAXS

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The chemical synthesis of core/shell colloidal nanocrystals (NCs) has led to a pronounced improvement in the optical properties and the chemical stability of semiconducting NCs [1, 2].

The infrared emission of lead chalcogenide nanocrystals (NCs) can be drastically increased by stabilising the core with a hard protective shell [1] due to cationic exchange, e.g. for the case of PbS/CdS NCs [3]. Here, we have very recently shown that metastable crystal phases in the chemical homogenous CdS shell influences significantly the photoluminescence (PL). This was only achieved by retrieving the chemical profile of NCs in sub-nanometer resolution (see Fig. 1a) by using anomalous SAXS (ASAXS). This knowledge allowed to deduce from the recorded crystal peaks in WAXS geometry the metastable rock salt phase fraction within the CdS shell (see Fig. 1b) and hence, to directly relate the PL output to the phase fraction (see Fig. 1c).

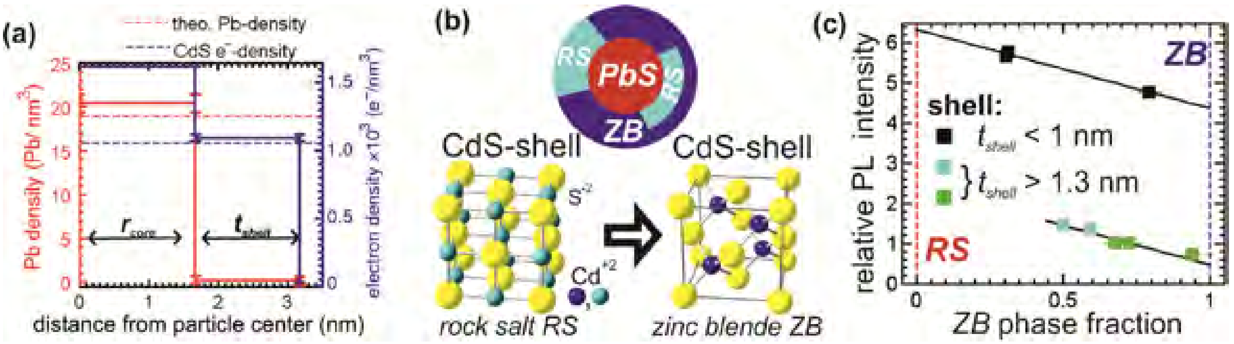

Figure 1: (a) Chemical core/shell profile of PbS/CdS NCs derived from ASAXS. (b) Crystalline core/shell structure derived by WAXS. (c) PL enhancement as a function of the phase fraction within the CdS shell [3].

In a current study performed at the beamline ID02 at the ESRF, we have investigated CdSe/CdS core/shell NCs with different core/shell dimensions by recording simultaneously ASAXS and WAXS spectra. In contrast to the CdS shells around PbS cores that were grown by cationic exchange [3], here the CdS shells were grown epitaxial [2]. We aim to reveal, if the epitaxial core/shell structure depicts the same sharp chemical interface as found for the PbS/CdS system (see Fig. 1a). Especially, we want to probe the crystal structure of the shell to check, if the core influences the shell's structure as strongly as shown for the cationic exchange growth [3]. The exact understanding of the core/shell growth mechanisms will allow a more precise tuning of the optical properties of core/shell NCs.

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GISAXS/WAXD CHARACTERIZATION OF MATERIALS MESO/MICROPOROSITY TUNED BY DEEP X-RAY LITHOGRAPY FOR FLUIDICS APPLICATIONS

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Microfluidic systems for handling and sensing chemical and biological samples will improve their performance through the employment of materials with selected functionalities in specific regions of the device. To obtain this goal, top-down techniques can be employed to pattern bottom-up synthesized functional materials. To guarantee the tailoring of the structure for the specific application, suitable investigation techniques must be employed [1].

In this communication, we will present two examples of the combination of GISAXS/WAXD measurement technique and deep X-ray lithography (DXRL) top-down fabrication technique to tune the porosity of meso and microporous materials that can be used as "bricks" to build new generation lab on chips. DXRL induces chemical and structural changes in materials due to the effect of high energy X-rays (3–20 keV), providing high aspect ratios, almost vertical sidewalls after development, and 200 nm lateral resolution.

First, we will show the effect of increasing irradiation dose on the structure of thin mesoporous silica films (pores in the order of 2-10 nm) that, using DXRL as patterning technique, can be used for example as DNA arrays [2], or can be functionalized with enzymes to achieve selective bioactive areas [3]. We will present the results of the structural investigation through GISAXS, leading to the optimization of the dose, and showing that high quality patterns can be obtained while still retaining the hexagonal structure, making them a good choice for microfluidics.

Then we will describe the use of DXRL with Thermally Rearrangeable (TR) polymers, engineered micro-porous polymers having interconnected microcavities with up to 30% free volume and excellent permselective functionality. We will describe the effect of increasing irradiation dose, investigated with WAXD and other techniques, showing that it leads to smaller micro-pores on thermal rearrangement compared to the not irradiated ones. Surprisingly, the permeability of small molecules through TR-polymers increases with the X-ray dose. This can be explained considering that such smaller pores are better interconnected. This patterning method will allow obtaining highly accurate microstructures that are chemically and mechanically stable with improved permselective properties, suitable to be implemented in miniaturized devices where selective gas exchange is required [4].

Both DXRL and GISAXS experiments have been performed at Elettra Sincrotrone Trieste synchrotron radiation source.

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SMALL ANGLE SCATTERING TECHNIQUES TO INVESTIGATE THE DISTINCT INTERACTION MECHANISMS BETWEEN CELLULOSE AND PLANT CELL WALL MATRIX POLYSACCHARIDES

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Plant cell walls are extremely complex structures in which cellulose microfibrils are hierarchically assembled and embedded in a multi-component matrix. While the cellulose microfibrils represent the basic building unit providing mechanical strength, the matrix components are able to tune the properties of each specific tissue, increasing the flexibility or limiting the transport of moisture, for instance.

In this work, a multi-technique approach based on the combination of small angle neutron and X-ray scattering (SANS and SAXS) with X-ray diffraction (XRD), NMR spectroscopy and morphological characterisation, has been applied to investigate the structure of native hydrated bacterial cellulose pellicles and their composites with plant cell wall (PCW) polysaccharides. Bacterial cellulose fermentation is an efficient strategy to mimic the cell wall biosynthesis process and investigate the interactions established between cellulose and matrix polysaccharides by incorporating these latter components into the culture media.

The different scattering length density contrast obtained with neutrons and X-rays, enabled the identification of distinct structural features within the hierarchically-assembled bacterial cellulose pellicles. The SANS data of pellicles soaked in different D_2O/H_2O mixtures suggested the existence of regions with different solvent accessibility within the cellulose ribbons. Accordingly, a core-shell cylinder model combined with an interfacial scattering term was able to accurately fit the experimental data. PCW polysaccharides affected the ribbons' solvent exchange differently depending on their interaction mechanisms. On the other hand, SAXS provided information on the packing of the individual microfibrils found within the ribbons and revealed a more loosely packed structure when strong cellulose-PCW polysaccharide interactions were established. Additionally, XRD results highlighted the ability of certain PCW polysaccharides to interfere with the cellulose crystallization process, altering the crystallinity and crystallite cross-sections and in some cases, even promoting the crystallization into the I_β allomorph typically found in plants, as opposed to the predominant I_α allomorph found in native bacterial cellulose.

These results highlight the potential of small angle scattering in combination with complementary techniques to reveal the distinct cellulose-PCW polysaccharides interaction mechanisms.

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STRUCTURAL CHARACTERISATION AND SORPTION-INDUCED DEFORMATION OF HIERARCHICAL SILICA MONOLITHS WITH ANISOTROPIC POROSITY

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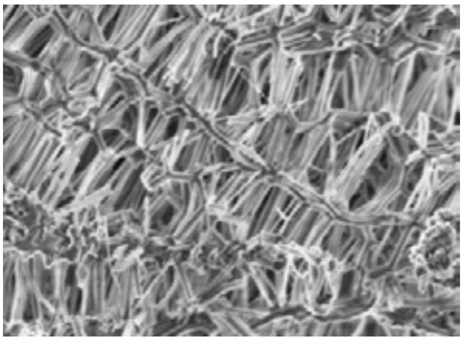

Fig. 1. Scanning electron microscopy image of a monolithic silica sample with anisotropic macroporosity

Sorption-induced deformation of nanoporous materials is of considerable interest in science and technology. Especially ordered porous systems with well defined pore sizes provide unique possibilities to be used in technical applications, such as in catalysts and sensors as well as in microelectronics or medical diagnostics [1]. We have investigated hierarchically organized, porous silica monoliths consisting of a macroporous network of struts, each strut containing well-defined cylindrical mesopores of about 8 nm arranged on a 2D hexagonal lattice. The deformation of this material induced by the sorption of n-pentane at the level of the mesopores has been studied with in-situ SAXS and in addition, deformation on the macroscopic level was monitored with in-situ dilatometry [2]. Recently, we have developed a new synthesis strategy to influence the orientation of the mesoporous struts to obtain a macroscopically anisotropic network (see Fig. 1). The struts are thus preferentially oriented in parallel to the axis of the cylindrically shaped macroscopic monoliths. Position resolved 2D-SAXS patterns reveal that the ordered cylindrical mesopores follow this macroscopically preferred orientation of the sample (see Fig. 2) with a gradient from the center towards the rim of the macroscopic sample.

Here we present in-situ SAXS results of sorption induced deformation in these macroscopically anisotropic samples and compare these data with the overall macroscopic deformation obtained from in-situ dilatometry.

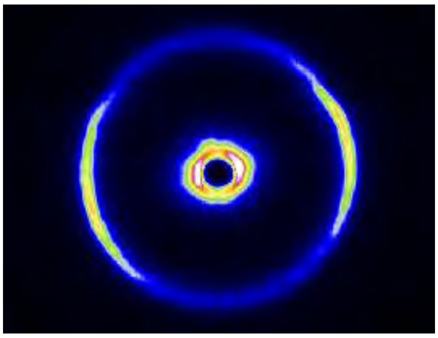

Fig. 2. 2D SAXS detector image of an anisotropic monolithic silica sample. The powder ring is the 10 reflection from the 2D hexagonal mesopore

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ORGANOGEL FORMATION VIA SUPRAMOLECULAR ASSEMBLY OF OLEIC ACID AND SODIUM OLEATE

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To create materials with novel functionalities, the formation of gels within hydrophobic media has become popular. This is often accomplished through the assembly of low molecular weight organogelators into a variety of complex phases through intermolecular interactions. In the case of edible materials, the assembly of saturated fatty acids to form fat crystal networks is often used for structuring. Here, the first example of structuring with unsaturated fatty acids is reported, namely mixtures of oleic acid and sodium oleate, to structure edible lipid phases. Small-angle neutron scattering demonstrates that the resultant structures, which vary with oleic acid and sodium oleate molar ratio, comprise either inverse micellar or lamellar phases, combined with the formation of crystalline space-filling networks. Network formation was found for filler concentrations above 8.0 wt%. Rheological measurements show that gel strength depends on the ratio of oleic acid to sodium oleate, and is greater when only oleic acid is used. The addition of up to 1.5 wt% of water enhanced the strength of the organogels, probably through supplementary hydrogen bonding but, for concentrations greater than 2.0 wt%, the assembly was inhibited leading to collapse of the gel. Polarized microscopy along with rheology, differential scanning calorimetry, and neutron scattering techniques were used to investigate the assembly structures to provide insight into the gelation mechanism.

↘ Flash Talk: Wed-F-F1

UV-LASERSINTERING OF TIO_2 NANOPARTICLES THIN FILMS INVESTIGATED BY μGIWAXS AND μRAMAN MEASUREMENTS

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Titanium dioxide (TiO_2) is an interesting material because of its application as a transparent conductive oxide, in dye sensitized solar cells and photo catalytic active material. The use of TiO_2 nanoparticles provides a low-cost fabrication method for TiO_2 thin films. The optical, electrical and thermal properties of the TiO_2 nanoparticles are closely related to structural properties like phase composition, defect density, micro strain and crystallite size. For example, the photo catalytic activity of TiO_2 is directly related to the phase composition present[1]. To achieve the designed property, a post treatment of the nanoparticle films is often needed to adjust the porosity, size(distribution), adhesion and phase composition. A promising technique to tailor the properties of the TiO_2 nanoparticle thin films is laser sintering. Compared to other methods like furnace sintering, it has the advantage of short processing time and the controllable, localized heat load. For a targeted tailoring of the thin films, an in depth understanding of the laser sintering process is needed.

Recently, we have shown that the use of continuous UV lasers allows sintering of TiO_2 nanoparticle films with power densities down to 38 kW/cm^2 and a precise control of the bed density tuned through the applied laser power [2]. Using a thin TiO_2 film on Si, we observe a complete phase transition from pure anatase phase to rutile by laser sintering. We combine microbeam grazing incidence wide angle X-ray scattering (μGIWAXS) and micro Raman spectroscopy (μRaman) to obtain a local and detailed picture of the sintering process on the atomic and nanoscale level.

We present first μGIWAXS measurements performed at the P03 beamline [3] and μRaman investigation on laser sintered TiO_2 nanoparticle films. The spatially resolved measurements show a significant difference between furnace sintered, area laser sintered samples and a single laser sintering track.

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QUANTUM DOT LIQUID CRYSTAL MICRO-SHELL SELF ASSEMBLY

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Thermotropic liquid crystals provide an active basis for organization of nanoparticles. Using a bottom-up approach, nanoparticles (NPs) well dispersed in the isotropic phase can be self-assembled by exclusion into the nematic phase as the material cools (Figure 1a). A ligand exchange reaction can be used to create nanoparticles with mesogenic ligand coatings to allow better dispersion and assemble novel structures [1-2]. These meta-materials have tunable properties with applications in quantum dot based electro-optic devices and more.

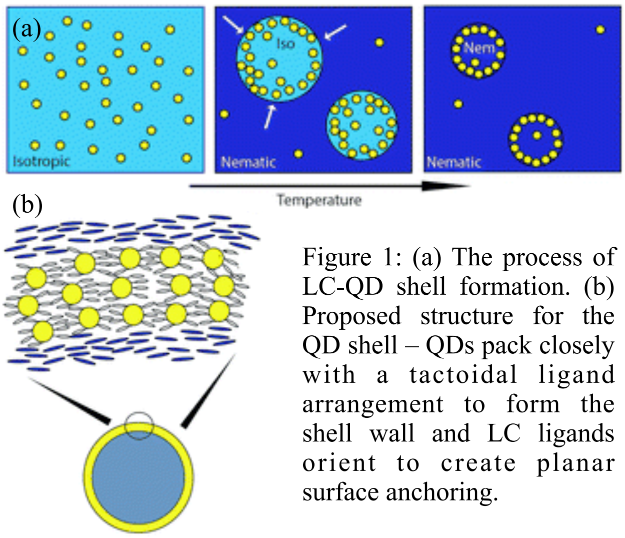

Figure 1: (a) The process of LC-QD shell formation. (b) Proposed structure for the QD shell – QDs pack closely with a tactoidal ligand arrangement to form the shell wall and LC ligands orient to create planar surface anchoring.

We report a liquid crystal (LC) droplet templated process that takes advantage of the phase dependent miscibility of mesogen-functionalized quantum dots (QDs) in a nematic liquid crystal to produce micron-scale vesicles or spherical 'shells' of QDs [1]. The orientation and arrangement of particles in the shell (Figure 1b) was determined by small angle X-ray scattering. Chemical control of shell size and structure is achieved by varying NP concentration and connecting ligand design. Since these parameters are independent of particle type, the process can be easily adapted for use with any appropriately sized NPs or combinations thereof, including mixtures of metallic, semiconducting and magnetic particles. These shells are mechanically robust, stable up to temperatures of ~110 °C, and can be extracted intact from the host LC phase. Addition of a UV cross-linkable ligand further enhances shell stability following formation, demonstrating the applicability of these structures to a wide variety of photonic and materials applications.

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STRUCTURE FORMATION IN THE BULK LASER-IRRADIATED GLASSES

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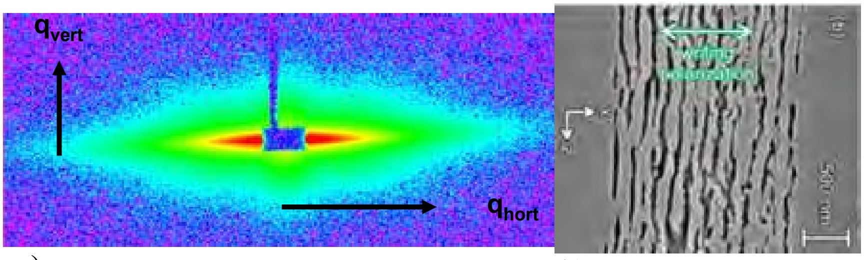
Femtosecond-laser irradiation of transparent media, such as glasses can produce permanent modification via nonlinear interaction between the laser field and the material, such as refractive index changes or pore formation. Under defined conditions the voids in side the glass start to self-organize to form nanogratings [1,2]. The period of these gratings can range from 60 to 300 nm, generally scaling with λ/2*n (λ wavelength, n refractive index) but also λ/10*n has been found [3]. Irradiated areas appear as homogeneous with appearance of strong birefringence as the aligned nanosheets (periodicity along laser polarization) form structures below the wavelength of visible light.

Structure formation and nanoscale determination of the formation of the voids and relation to birefringence have been analysed by synchrotron SAXS at the beamline cSAXS (SLS) [2]. High q span together with micrometer-sized X-ray beam allows for a comprehensive determination of structural features from the 10 to the 400 nm scale [3,4].



a) b)

Figure 1: False-color representation of scattering intensity (a) of aligned sheet-like nanovoids inside laser-irradiated fused silica together with a scanning electron micrograph of a polished and etched section through the region of pore formation (b). The sheets extend perpendicularly to laser polarization [2].

Insight in the formation mechanism and the relation between X-ray pattern and optical birefringence is discussed and successive rewriting by orientation reversal is demonstrated [5].

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↘ Flash Talk: Wed-F-F1

USE OF *IN-SITU* SMALL ANGLE SCATTERING TO PROBE THE DYNAMIC STRUCTURE OF GRAPHENE-BASED MEMBRANES

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Engineered membranes that are selectively ion, gas, or liquid permeable are key aspects of emerging technology especially in the fields of gas separation [1], water purification [2], and energy storage [3]. Recent reports have shown that graphene-based membranes consisting of chemically converted graphene (CCG), graphene oxide (GO), or partially reduced GO sheets are tunable structures with unique membrane properties that also exhibit responsive behavior. Currently, no definitive models exist to describe the structure of these multi-layer graphene-based materials, and initial results presented here are discussed in relation to a disordered lamellar system. Because the structure of each graphene sheet varies and has features across a very broad range of length scales, X-ray and neutron scattering techniques are able to provide valuable insight on the variation in surface corrugation and interlayer spacing for these materials. As shown in Figure 1, 2D SAXS images from different geometries detail both the inter-lamellar spacing and surface roughness, which are the features believed to correspond with the level of corrugation or wrinkling along the graphene sheets. This disorder induced from corrugation is the main determinant of the pore size and pore size distribution and thus controls the transport properties of the membrane. *In-situ* studies of hydration have shown extremely interesting information about the dynamic behaviour of these materials (Figure 2), and these results have guided design of further experiments with dynamic system perturbation using an applied electric field, humidity controls, or gas sorption/desorption systems. Suggested scattering models for these new materials are also discussed alongside the data.

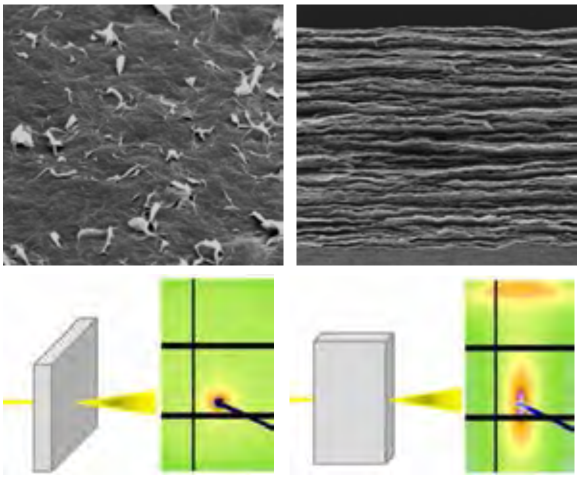

Figure 1: SEM (top) and 2D SAXS (bottom) images detail the structural differences normal to the surface (left) or through the edge (right).

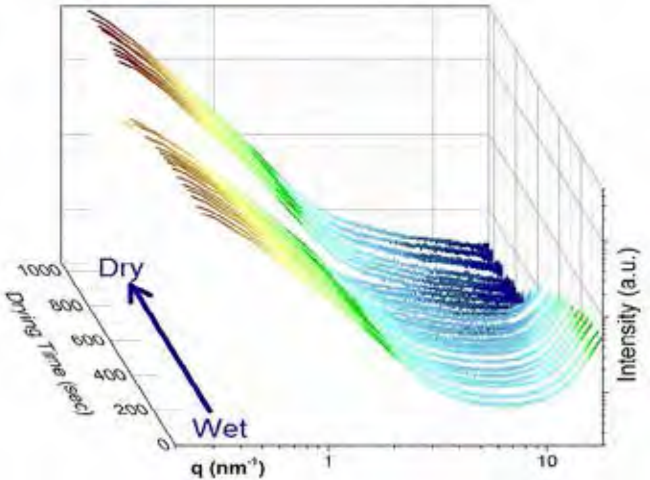

Figure 2: 1D SAXS radial averages from a CCG hydrogel as it dries. Structural changes are seen in the inter-lamellar spacing (high q) and roughness along the sheets (low q).

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CRYSTALLOGRAPHY-AFFECTED LONG-RANGE PORE ORDERING IN ANODIC ALUMINA FILMS

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Anodic aluminum oxide (AAO) films possess vertical cylindrical channels that self-organize into a periodic hexagonal network upon film growth. The degree of pore ordering into a close-packed lattice depends on many experimental parameters such as the electrolyte composition, applied voltage, etc. Recently, the influence of crystallographic orientation of Al substrate on the positional [1], orientational [2] and longitudinal [3] order of the pores has been found. Nevertheless the mechanism of the self-organization of pores into an ordered hexagonal lattice remains a topic of debate.

In the present study the AAO films obtained on single crystal substrates with different crystallographic orientations were quantitative characterized by SAXS technique. The diffraction experiments were performed at the beamline BM26B “DUBBLE” of ESRF.

Typical diffraction patterns are presented in Figure 1. The AAO porous film, grown on Al(111) substrate exhibits a spot-like diffraction pattern that corresponds to the long-range orientational order. In case of substrate with (100) orientation several rings with uniform distribution of intensity indicate that porous domains are completely disoriented in the plane of the oxide film.

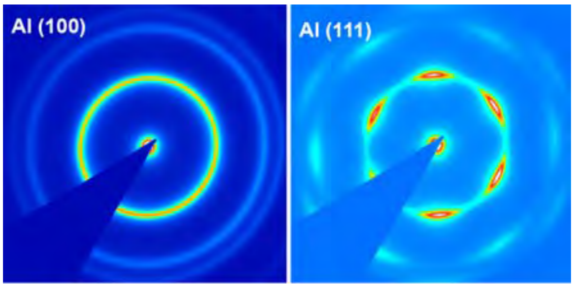

Figure 1: Small-angle X-ray diffraction patterns recorded from AAO films, obtained in 0.3M sulfuric acid at 25 V (the interpore distance is 65 nm) on Al(100) and Al(111) substrates.

In order to observe the influence of the crystallographic orientation on the longitudinal pore arrangement, a specially designed Al(100) single crystal with the vicinal edges tilted from the (100) plane by 5° was used. It was shown, that the grown direction of AAO channels is tailored by two competing factors: (i) electromigration of ions under external electric field, which push it along the normal to the Al surface; (ii) presence of stable crystal faces of (100) family, crossing of which by the pore is energetically unfavourable due to hampered diffusion of oxygen ions through dense atomic planes. Aforementioned factors lead to coexisting of two preferable pore grown directions in AAO with disorientation of about 0.3°.

This work is partly supported by the Russian Scientific Foundation (Grant No. 14-13-00809) and Russian Foundation for Basic Research (Grant No. 15-08-09012).

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↘ Flash Talk: Wed-F-F1

SAXS STUDY OF SILICA MESOSTRUCTURE FORMATION IN THE GAS PHASE: THE EFFECT OF SOLVENTS COMPOSITION

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The synthesis of mesostructured silica nanoparticles can be achieved by various adjustments of synthesis conditions. Control of the morphology, particle size, and uniformity is getting more and more important for applications in catalysis, adsorption, optical devices, bio-imaging, drug delivery, and nanomedicine.

The spray-drying of aerosol droplets is an attractive route to obtain mesostructured silica nanoparticles, as it is cheap if compared to alternative methods, is environmentally benign, and allows a good control of the synthesis conditions.

Two common solvents used in the spray-drying production of silica mesoporous nanoparticles are water and ethanol. During the self-assembly of mesoporous silica, the templating agent, cetyltrimethylammonium bromide (CTAB), drives the condensation of tetraethyl ortosilicate (TEOS) molecules into an organized structure. This process was successfully studied in-situ at the Austrian SAXS beamline at Elettra Sicrotrone Trieste [1, 2]. A model to describe the dynamics of evaporation of the solvents in the aerosol droplets supported by simulations was recently presented [3]: as the solvent evaporates radially in the droplets, different solute concentration leads to the formation of the mesophase from the outer shell to the inner part of the nanodrops.

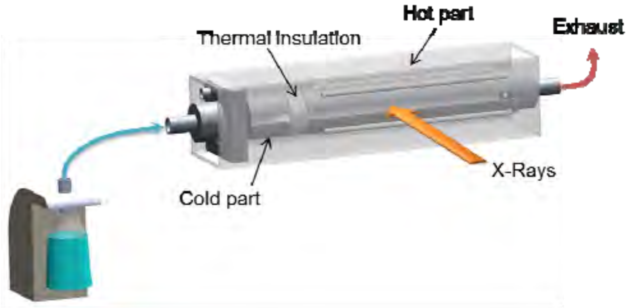

Figure 1: aerosol setup scheme

With our custom built reaction chamber (Figure 1), the evolution of the mesostructure can be followed in-situ with SAXS during the evaporation of the solvent [4, 5]; in the present communication we will show how the presence of two different solvents and their respective molar ratio in a water/ethanol system influence the silica mesostructure.

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↘ Flash Talk: Wed-F-F1

MICROSTRUCTURAL CHARACTERIZATION OF POLYMER ELECTROLYTE MEMBRANES BASED ON SULFONATED SYNDIOTACTIC POLYSTYRENE IN THE δ CO-CRYSTALLINE PHASE

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Syndiotactic polystyrene (*s*-PS) is able to form different kinds of co-crystalline phases with guest molecules of various size, shape and property. Several advanced materials have been produced starting from *s*-PS co-crystalline films [1-2]. In particular, sulfonated *s*-PS (*s*-SPS) can be used as proton-conductive membrane for fuel cells, as it presents high proton conductivity (comparable with *Nafion*). Besides, it shows a high chemical and thermo-mechanical stability and a low cost [3]. The morphology of different *s*-PS clathrates and the structural behavior of *s*-SPS upon hydration can be more thoroughly understood by combining X-rays scattering and FT-IR with SANS [4-5]. In fact, exploiting the neutron contrast variation between various hydrogenated and deuterated components of *s*-PS and *s*-SPS clathrates, additional and unique information about the distribution of guest molecules in the crystalline and amorphous regions and about the hydrated domains of the polymer were obtained. Moreover, the stretching of films leads to occurrence and distribution of scattering features from typical morphologies on specific directions and sectors of detection plan, which enables an accurate structural study of such complex polymeric systems. A complete SANS investigation on *s*-PS samples, starting from their crystallization with guest molecules to the subsequent sulfonation and hydration, was performed at SANS diffractometer KWS2 of MLZ. This experimental analysis has highlighted that the morphology of these polymeric films is characterized by hydrated channels in the amorphous phase alternated to staples of crystalline lamellae, along the stretching direction.

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SELF-ASSEMBLING SUPRAMOLECULAR SYSTEMS OF DIFFERENT SYMMETRY FORMED BY WEDGED MACROMOLECULAR DENDRONS

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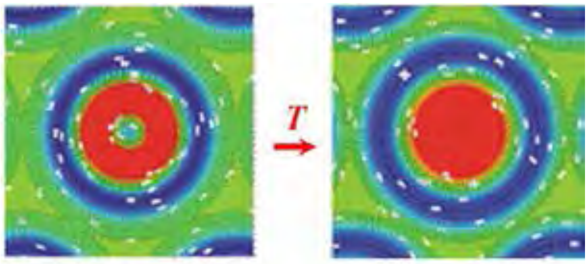
Using a unique combination of experimental methods (wide- and small-angle X-ray diffraction, molecular simulation, differential scanning calorimetry, atomic force and optical polarization microscopy) structure of supramolecular aggregates formed by conical and tapered dendrons could be studied due to the application of. The use of two different X-ray diffraction techniques (the reconstruction of the local mutual ordering of mesogenic groups from a wide-angle X-ray diffraction pattern, on the one hand, and the determination of EDD maps from small-angle reflection intensities, on the other hand) makes it possible to establish the structure of self-assembling particles with a very high degree of reliability.

Studies of the phase behavior of self-assembling dendrons based on gallic and benzenesulfonic acids revealed a rich phase behavior: 1D smectical layers, 2D ordered and disordered columnar phases of different symmetry, 3D crystalline hexagonal phase, cubic primitive, Pm3n and Im3m micellar phases as well as bicontinuous gyroid mesophase of Ia3d symmetry were discovered in such compounds. It was possible to detect the main stages in the organization of supramolecular ensembles. First of all, it is the formation of individual supramolecular aggregates (long cylinders and spherical micelles) due to weak noncovalent interactions of mesogenic groups and to their subsequent mutual ordering. In turn, supramolecular aggregates are organized into 2D or 3D lattices, depending on the rigidity of their peripheral regions. The shape of supramolecular aggregates and its change with temperature depend on the chemical structure of the mesogenic group; hence, one can perform the directed design of complex self-assembling systems characterized by a “smart” response to external stimuli.



Col$_{HO}$ Col$_{HD}$

We report a number of mesophase transitions studied in detail by a method of reconstruction of electron density using relative intensities of X-Ray reflections. Of great interest is the possibility of the creation of ion-selective membranes with controlled switch on/off temperature: a wide number of compounds based on symmetric benzenesulfonic acid form an ordered hexagonal columnar mesophase at room temperature. It’s important feature is the presence of central channel of a few angstroms wide inside each supramolecular cylinder. With increasing temperature, transition to the disordered columnar mesophase takes place, and ion-selective channels close respectively.

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↘ Flash Talk: Wed-F-F1

NANOSCALE CHARACTERIZATION AND IMAGING OF BIOLOGICAL SOFT TISSUES BY TABLE-TOP SMALL-ANGLE X-RAY SCATTERING SET-UP

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In recent years, Small Angle X-ray Scattering technique has found interesting applications in medicine for the study of healthy or pathologic tissues from breast, brain, cornea, bone, etc., to detect structural changes at supramolecular level, and in some cases also to derive clear relationships between tissue changes and disease development or onset. In addition, scanning SAXS microscopy has become a suitable technique to quantitatively map the nanostructural heterogeneity of biological materials over extended areas [1], thanks to the recent progress in the development of X-ray microbeam sources combined with scanning methods for imaging [2].

A key issue in most of these experiments was the need for a high brilliance synchrotron radiation X-ray source to obtain high-quality scattering patterns, although a limited number of papers made use of laboratory systems mainly for bone and breast tissues analysis [3]. The possibility to use a laboratory X-ray source for SAXS studies in nanomedicine is extremely important, because - in order to transfer this knowledge into a clinic - a room-sized system is mandatory.

In this work, we will show the application of a table top super-bright microfocus laboratory X-ray source coupled to a three-pinhole camera [4], which was used to investigate the supramolecular structure of soft matter in SAXS ex-situ experiments. In particular, the combination of the microsource brilliance and an original theoretical approach allowed to restore diffraction features from SAXS profiles collected from low scattering biomaterials or soft tissues, reaching data quality compared to synchrotron radiation data.

As relevant examples we will show SAXS data obtained with the optimized set-up on:

i) solid residues of exosomes' drops from healthy epithelial colon and colorectal cancer cell lines;
ii) engineered tissues of collagen/human elastin artificial scaffolds for vascular applications
iii) proteins in solution
iv) bovine cornea studied by SAXS scanning microscopy.

Our results show how precious morphological/structural nanoscale information can be gained by mapping biomaterials and tissues, even if a table-top source is employed.

Acknowledgements

"Con il contributo del Ministero degli Affari Esteri e dalla Cooperazione Internazionale, Direzione Generale per la Promozione del Sistema Paese "

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RESONANT SOFT X-RAY SCATTERING STUDY OF LIQUID CRYSTAL HELICAL NANOFILAMENT STRUCTURE

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Bent-core liquid crystals (LCs) exhibit rich phase behavior[1-3] (B1, B2, … B7, $SmAP_F$, $SmAP_{Fmod}$) and have potential applications, including displays and fast electro-optic devices. Of particular interest, the B4 helical nanofilament (HNF) phase[4] has been proposed to be made of helices formed by twisted smectic layers composed of aromatic and aliphatic sublayers, an indication that not only molecular chirality but layer chirality drives the formation of helical structures. This current structural model for HNF is almost solely based on freeze-fracture transmission electron microscopy (FF-TEM), which has limitations, e.g. it only provides local information and is not suitable for *in situ* temperature-dependent studies. Attempts to probe the helical structure with hard x-rays have been made with limited success.

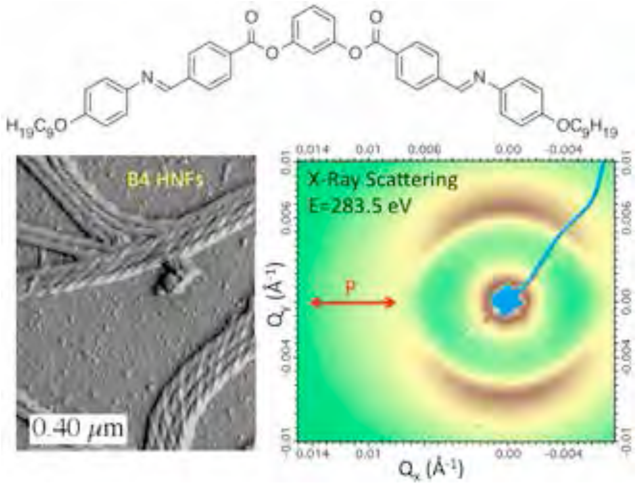

Fig. 1: (Top) The liquid crystal molecular structure. (BL) FF-TEM image of B4 helical nanofilaments (HNFs), formed of twisted smectic layers. (BR) 2-D scattering pattern of B4 HNFs of random orientation, with linearly polarized (horizontal) incoming x-rays at C K edge.

We report the first *In situ* measurement of the helical pitch of B4 HNFs, using linearly polarized, resonant soft x-ray scattering at the carbon K-edge. A strong scattering peak corresponding to the half-pitch of the twisted smectic layer structure was observed, due to the bond orientation sensitivity enabled by linearli polarized x-rays at C K edge. Measurements suggest that the HNF pitch can be tuned by mixing guest organic molecules with the bent-core host, followed by thermal annealing. The equilibrium helical half-pitch of NOBOW is found to be 120 nm, essentially independent of temperature.

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SMALL-ANGLE SCATTERING IN STRUCTURE RESEARCH OF MAGNETOFERRITIN: STABILITY IN SOLUTIONS AND INTERACTION WITH PROTEIN AMYLOID AGGREGATES

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SAXS and SANS small-angle scattering techniques have been applied [1,2] to magnetoferritin solutions and their mixtures with protein amyloid aggregates in the frame of the comprehensive structure analysis. Magnetoferritin is a synthetic derivate of ferritin consisting of a quasi-spherical protein shell (apoferritin) loaded with a magnetic iron-based core of $Fe_3O_4/\gamma\text{-}Fe_2O_3$, which significantly increases the magnetic moment of the biological macromolecule as compared to the native ferritin with a ferrihydrite core. It is of current interest for various biomedical applications, which make use of the magnetic properties of nanoparticles, such as targeted drug transport, magnetic resonance imaging, etc.

Both techniques have shown that in average the structure of magnetoferritin is unstable in slightly acidic solutions (effective apoferritin concentration range of 5-20 $mg \cdot mL^{-1}$) and strongly depends on the effective loading factor (LF), the mean number of iron atoms per one molecule of apoferritin. Starting from moderate loads ($LF < 500$) a partial decomposition of the appoferritin shell takes place, which increases with the LF growth. Also, the structural polydispersity (deviation of the iron-protein ratio distribution over magnetoferritin molecules from its mean value) increases. These effects correlate with the aggregation of the macromolecules in solutions. At LF above 500 it sharply intensifies and at LF exceeding 900 the loss of solution stability with partial sedimentation is observed. At the same time, the supernatant solutions contain mainly macromolecules with a complete apoferritin shell, thus showing that at all stages studied there is a complex mixture of structures in the solutions.

It has been discovered that magnetoferritin affects fibrillar amyloid aggregates of lysozyme (egg white) in acidic solutions. In SAXS experiments, the effect has been detected by comparing the scattering from the mixed (magnetoferritin plus amyloid aggregates) solutions and the sum of the scattering from the separate solutions. The determination of the partial scattering contributions has shown that the presence of magnetoferritin leads to a significant reduction in the size of the amyloid aggregates. The effect has been found to be more pronounced for higher loading factors of magnetoferritin. The change in the helical structure of amyloid fibrils in terms of the simplified model [3] has also been analyzed.

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INTERACTION BETWEEN HYBRID INCLUSIONS MEDIATED BY SURFACTANT MEMBRANES

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We perform a systematic investigation of the interaction between hydrophobic inorganic particles (butyl-functionalized tin oxide clusters) inserted in highly aligned lamellar phases of a zwitterionic surfactant as a function of particle concentration and temperature.

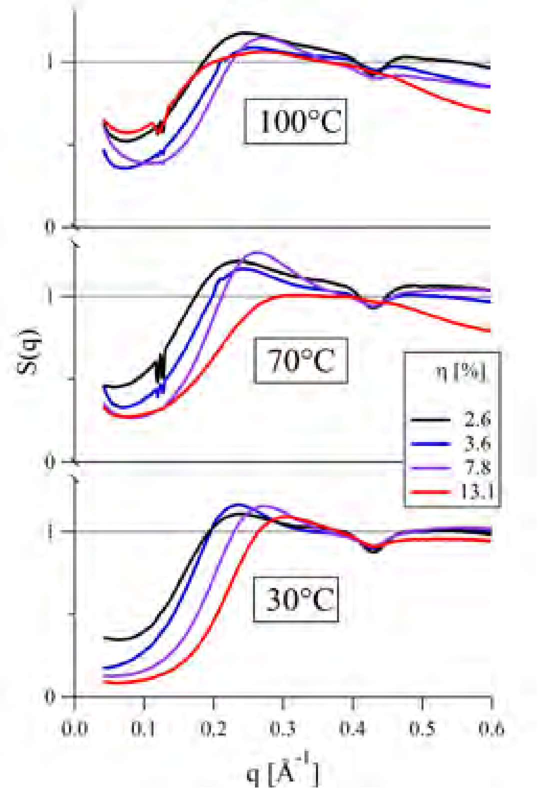

Figure 1: Two-dimensional structure factor of the particle fluid within the membrane, for selected concentrations and at different temperatures. The small dip around 0.4 Å^{-1} is due to imperfect subtraction of the peak from a kapton window.

The SAXS measurements (with the beam incident along the layer normal) give access to the in-plane signal $I(q_r)$ (at q_z=0) of the two-dimensional fluid formed by the inclusions within the bilayer. The background-subtracted intensity divided by the form factor of the particles yields the structure factor $S(q)$, shown in Figure 1 for 30 °C, 70 °C and 100 °C (the highest temperature reached) at various surface fraction of inclusions η.

The differences are visible: at high temperature, the flattening of the primary peak and a small-angle upturn indicate a more attractive interaction. By numerically solving the Ornstein-Zernicke equation [1]–[3], we extract from the structure factor the membrane-mediated interaction potential $V(r)$, determined by the elastic properties of the membrane.

We will fit the experimental data using analytical and numerical models for the membrane-mediated interaction between inclusions, developed in collaboration with a theory team of the MSC laboratory in Paris (J.-B. Fournier and P. Galatola.) [4]. The comparison should yield a detailed image of the elastic properties of the membranes, as well as of their temperature dependence.

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↘ Flash Talk: Mon-F-H1

INFLUENCE OF EMBEDDED GOLD NANOPARTICLES ON STRUCTURE OF DNA CHOLESTERIC LIQUID-CRYSTALLINE DISPERSION REVEALED BY SAXS

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From medical point of view the interest to gold nanoparticles is caused by their possible applications in anti-cancer therapy. However, using cholesteric liquid crystal dispersions (CLCD) DNA models it has been demonstrated that the gold nanoparticles disrupt the structure of the genetic apparatus causing genotoxic effects [1]. It was also shown that 2 nm gold nanoparticles being incorporated into the space between adjacent molecules of DNA ordered layers of the CLCD DNA form linear clusters [2]. The aim of the present work is to determine the effects caused by incorporation of the gold nanoparticles of different sizes on the CLCD DNA structure. Structural analysis was performed using two complementary methods: small-angle X-ray scattering (SAXS) and circular dichroism (CD). It allowed us to consider structural changes on two different levels. We found out that the amount of ordered regions in the CLCD DNA exponentially decreases with increasing of concentration of the embedded gold nanoparticles. This fact can be explained by a formation of gold aggregates at higher concentrations of the nanoparticles. Being too large the aggregates cannot be incorporated in the ordered DNA structure without disintegration of the latter. The experiment with gold nanoparticles of larger size (15 nm) demonstrates that the disruption of the CLCD DNA structure occurs significantly faster confirming the assumption that only small nanoparticles can be embedded into the space between adjacent molecules of DNA without structural violation. The obtained results correlate well with those of the CD analysis. Generally, our data allows one to conclude that analogous structural changes can occur in the mutual arrangement of the DNA macromolecules in chromosomes causing serious genetic changes. It explains the observed genotoxic effects at interaction of the genetic material with gold nanoparticles [3].

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POLYMER-STABILIZED PHOSPHOLIPID NANODISCS

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Phospholipid bilayer nanodiscs are a patch of lipid bilayer, with the hydrophobic disc edges surrounded and stabilized by a polymer [1] or protein belt [2]. They are used as a model membrane support for membrane proteins, to allow structural and functional studies of this class of proteins, which are difficult to stabilize outside of the native cell membrane. We are studying the properties and formation of nanodiscs stabilized by poly(styrene-alt-maleic acid) (PSMA). PSMA can be made in bulk quantities, far more cheaply than the protein stabilizer, enabling large quantities of nanodiscs to be prepared. Polymer stabilized nanodiscs can also be prepared directly from lipid suspensions or disrupted cell membranes simply by adding the polymer and shaking, without requiring addition of detergent or ultrasound to assist dispersion.[1, 3] Recently we have identified a second polymer which forms discs, poly(styrene-alt-maleimide) (PSMI), which has a similar structure to that of PSMA but contains amines rather than acid groups. This chemistry allows PSMI to be used at acidic pH where PSMA becomes insoluble, and also overcomes problems with PSMA binding to Ca^{2+} ions, which are commonly found in biological systems. Both polymers can easily be deuterated for SANS contrast variation studies.

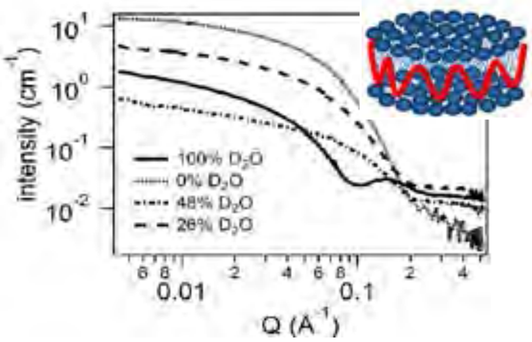

Figure 1: Small angle neutron scattering patterns from lipid nanodiscs stabilized with PSMA at several solution contrasts. Inset: schematic of polymer-stabilized lipid nanodisc structure.

We have carried out systematic studies on the effect of polymer molecular weight, and styrene to maleic acid (or maleimide) molar ratio on formation of phospholipid nanodiscs made using PSMA and PSMI. Disc stability and structure has been determined at a range of temperatures, pH and salt concentrations using small angle X-ray and neutron scattering, dynamic light scattering and cryo-TEM.

Initial scattering data analysis was carried out using a model based on concentric cylinders to mimic the polymer-wrapped lipid nanodisc structure, however atomistic simulations of polymer-lipid nanodisc structures, used in combination with the SASSIE program suite to compare scattering data from the models directly to experimental data, will also be discussed. Funded by the BBSRC (BB/J017310/1) and a joint EPSRC (EP/K039121/1) and NSF (CHE-1265821) grant; http://www.ccpsas.org/

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MORPHOLOGY OF SURFACTANT AGGREGATES IN PORES STUDIED BY SANS

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The self-assembly of amphiphilic substances in confined geometries plays an important role in many technological fields, such as size exclusion chromatography, biomolecule sensing, and drug delivery. In previous work we have developed a method to characterize the morphology of surfactant aggregates adsorbed in the pores of periodic mesoporous silica materials like SBA-15 by small-angle neutron scattering (SANS) [1]. The SANS intensity profiles can be approximated by a sum of two terms, one accounting for diffuse scattering from surfactant aggregates in the pores, and the other for Bragg scattering from the pore lattice of the silica matrix. The Bragg scattering contribution is modeled with the form factor of morphologies of the surfactant aggregates in the pores, ranging from hollow cylinders to rods and wormlike structures. The diffuse scattering contribution is represented by a Teubner-Strey type scattering function which accounts for the 3D spatial correlations between the adsorbed surface aggregates in the pores. This approach allows us to distinguish between surfactant morphologies of a laterally uniform adsorbed layer, patchy surface aggregates [1] and situations in which surfactant aggregates in the pores are essentially not in contact with the pore wall [2].

Here we present a SANS study of the adsorption of the cationic surfactant dodecylpyridinium chloride (DPC) in the 8 nm cylindrical pores of SBA-15. Analysis of the Bragg peak intensities shows that unlike nonionic surfactants, DPC forms a laterally homogeneous adsorbed layer at the pore walls up to high relative loadings *f* (Fig. 1). The different aggregation behavior of nonionic and cationic surfactants in the pores can be attributed to the difference in binding energy of the head groups to the pore walls. Hence the SANS study provides valuable information about the self-assembly of soft matter in confined geometries, which is hardly accessible by other techniques.

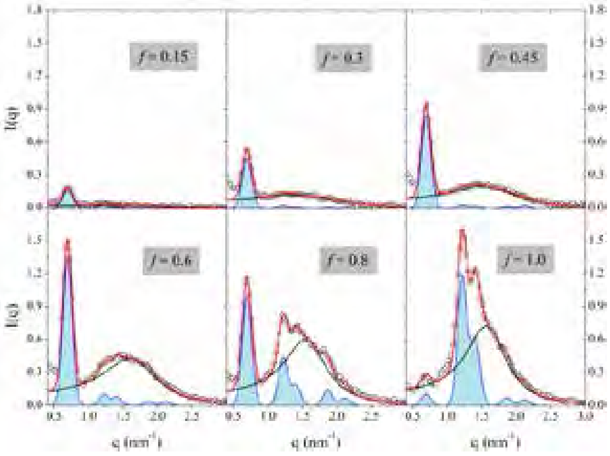

Figure 1 SANS scattering intensity I(q) profiles in SBA-15 contrast matching conditions at increasing DPC pore loadings *f*.

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SIZE DETERMINATION OF A LIPOSOMAL DRUG BY SMALL-ANGLE X-RAY SCATTERING USING CONTINUOUS CONTRAST VARIATION

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The usage of nanoparticles for drug-delivery applications has opened the continuously growing field of nanomedicine. For example, doxorubicin is an anticancer drug known for its high cardiotoxicity, though a liposomal formulation can reduce this side-effect significantly and improve the pharmacokinetics of the drug. The nano-drug applicability is closely related with its physicochemical properties and thus the drug-carrier must be accurately characterized.

In this work, the mean size and average density of pegylated liposomal doxorubicin (Caelyx® [1]) was determined by continuous contrast variation in SAXS with iodixanol, an iso-osmolar suspending medium. The study is focused on the isoscattering point position and the model-free analysis of the Guinier region of the scattering curves recorded at different solvent densities at the four-crystal monochromator beamline of PTB at the synchrotron radiation facility BESSY II [2]. The response of the liposome to increasing solvent osmolality and the structure of the liposome-encapsulated doxorubicin fiber after the osmotic shrinkage of the liposome are evaluated with sucrose contrast variation in SAXS/WAXS.

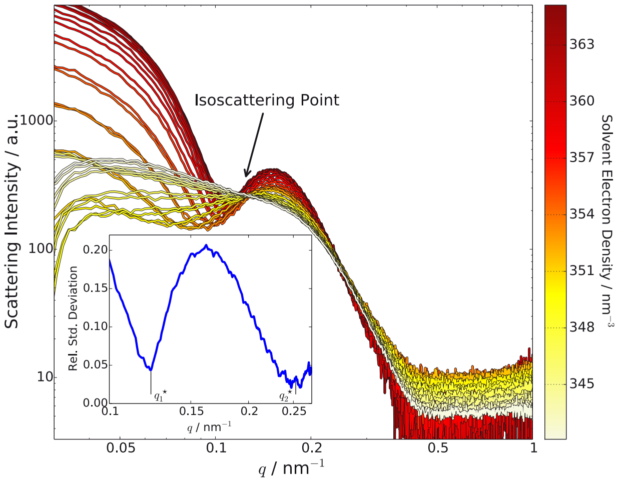

Figure 1: Scattering curves at different solvent densities obtained with a iodixanol density gradient. The inset shows the position of the isoscattering points.

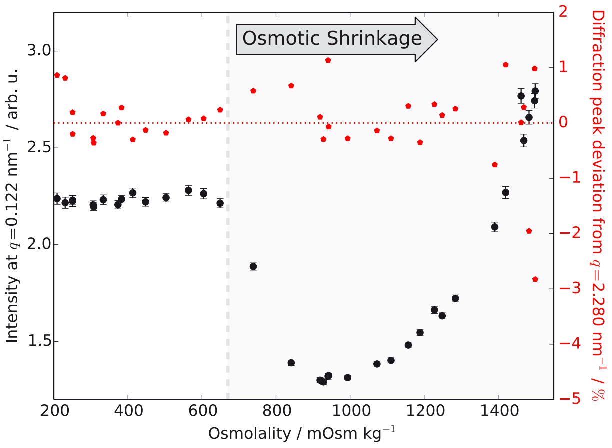

Figure 2: The isoscattering point intensity (black) and the shift of the doxorubicin-aggregate diffraction peak (red) are shwon as a function of the aqueous sucrose solution osmolality.

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SAXS/WAXS STUDY OF PHASE TRANSITIONS IN STRATUM CORNEUM MODEL LIPID MEMBRANES

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The outermost layer of mammalian skin – *stratum corneum* – provides essential barrier towards various external substances and water loss through skin. It consists of dead cells (keratinocytes) embedded into extracellular lipid matrix. This extracellular matrix exhibits layered structure which can be easily observed in electron microscope – the "brick-and-mortar" model. Bricks are dead cells and mortar is lipid matrix [1].

Essential role in nanostructure formation of this lipid matrix played by various types of double-chained amphiphilic molecules – mostly ceramides. Mixing of synthetic components allows one to create model matrix membranes and possibly separate roles of different lipid species in formation of ordered structures [2, 3].

Present study conducted at synchrotron facility "Siberia-2" at NRC Kurchatov Institute (Moscow, Russia) shows that lamellar structure of model membranes correlates with pH and temperature changes. Lamellar phase transition occurs near 70°C. No structural changes are observed under 60°C.

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PHYSICAL CHEMICAL PROPERTIES OF MAGNETIC MICROGELS FOR DRUG TARGETING APPLICATIONS

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Magnetoresponsive microgels with high saturation magnetization values have been obtained by a strategy based on the miniemulsion method using high colloidal stability organic carrier ferrofluid as primary material. Hydrophobic nanoparticles Fe_3O_4/oleic acid are densely packed into well-defined spherical nanoparticle clusters coated with polymers with sizes in the range 40–350 nm. Physical– chemical characteristic sofmagnetic microgels were investigated by TEM (Fig. 1), SAXS, XPS and VSM measurements with the focus on the structure–properties relationship. SAXS data build important connection between information on individual particle obtained from imaging technique with additional information interface profile due to influence of polymers and magnetic responce of system as total in connection with distribution of magnetic nanoparticles within microgel complexes. Our results show that microgels are promising structures for applicationin magnetic drug targeting [1].

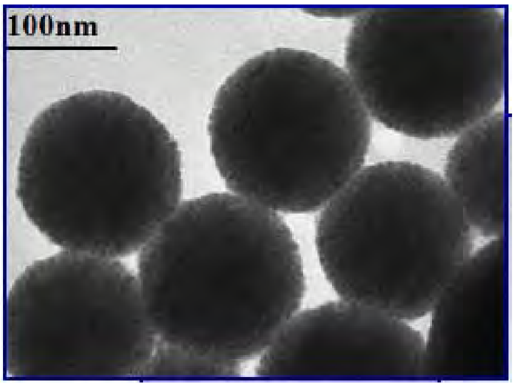

Figure 1. TEM images of magnetic microgels.

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↘ Flash Talk: Mon-F-H1

IN-SITU SMALL ANGLE X-RAY SCATTERING OF SINGLE HAIR FIBRE UNDER STRAIN

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Human hair exhibits a complex structure promoting structural hierarchy from atomic to macroscopic scale. A two-phase model [1] generally describes hair structure at the nanoscale: intermediate filaments (IF) consisting of crystalline alpha-helix keratins embedded in an amorphous matrix (AM) of IF-associated proteins. Such fibrilar keratin structures in human hair are found in the range of 0.1-10 nm [2]. An investigation of the changes in the nanostructure of human hair in response to strain as a function of relative humidity is presented. Single hair fibres were investigated by means of small angle X-ray scattering using synchrotron radiation at ID02 beam line, ESRF Grenoble. Information about the inter-filament spacing can be obtained in the small angle region (q value 0.01- 2nm^{-1}). Ordering of the coiled coils along the surface of the IF and isotropic lipid scattering are the other features observable at the low angle regime.

SAXS measurements were conducted on single hair fibre at different equatorial positions along the fibre axis. The fibres were mounted in a humidity-controlled cell and positioned vertically such that the strain was achieved by loading weights. It was found that the peak corresponding to the IF is consistent and reproducible at all measurement positions while the inconsistency in the lipids scattering indicates their heterogeneous distribution/ordering along the hair fibre. An increase in the distance between the IFs was detected at high humidity suggesting the swelling of the AM upon hydration. Results revealed a shift of the peak position at 0.7 nm^{-1} towards higher q values with the increase in strain. This is indicative for a shortening of the mean distance between the IFs.

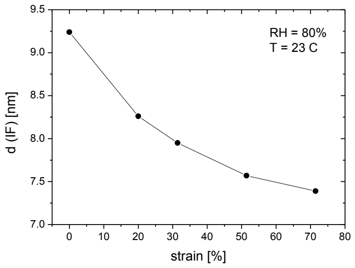

Figure 1: Inter-filament distance reduces with increasing strain

Understanding the link between mechanical and molecular/structural properties of hair presents a prerequisite in designing superior hair care products that can provide a wide range of consumer benefits.

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↘ Flash Talk: Mon-F-H1

REASSEMBLY OF SlpA OF *L. BREVIS* ON CATIONIC LIPOSOMES STUDIED BY SAXS

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Liposomes are hollow structures formed by phospholipids in aqueous solution. Coating them with surface (S-) layer proteins stabilizes them against environmental changes. We have previously studied the reassembly of the S-layer protein SlpA from *Lactobacillus brevis* ATCC 8287 on cationic liposomes composed of 1-palmitoyl-2-oleyl-*sn*-glycero-3-phosphocholine (POPC) and 1,2-dioleoyl-3-trimethylammonium-propane (chloride salt) (DOTAP) with SAXS. We showed that SAXS is a valuable method in studying S-layer reassemblies on liposomes and that the reassembled S-layer differs from that on native cell wall fragments [2].

To study whether the phase behavior of the lipid bilayer affects the reassembly process of the S-layer proteins, we have reassembled SlpA on cationic liposomes composed of 1,2-dipalmitoyl-*sn*-glycero-3-phosphocholine (DPPC) and DOTAP (70/30 mol%). The DPPC/DOTAP mixture is in gel state at room temperature, as it has a transition temperature of ~30°C [3]. The POPC/DOTAP liposomes are in fluid state at room temperature.

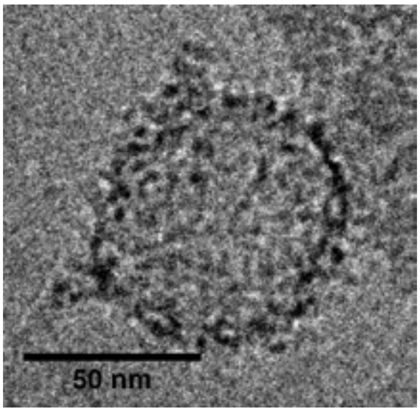

Figure 1: Cryo-EM image of SlpA coated DPPC/DOTAP liposome. Scale bar, 50 nm.

Even though the liposome surface charge of DPPC/DOTAP liposomes is the same as that of POPC/DOTAP liposomes, zeta potential and size measurements indicate that SlpA does not reassemble on DPPC/DOTAP liposomes at room temperature. However, if the reassembly is done at 41°C, the liposomes are coated by SlpA, as can be seen in Fig. 1. An uncoated liposome is shown in Fig. 2 for comparison.

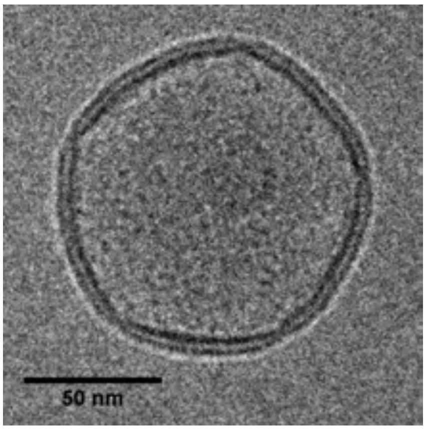

Figure 2: Cryo-EM image of DPPC/ DOTAP liposome. Scale bar, 50 nm.

Forthcoming SAXS experiments at MAX IV Laboratory will enable us to look at the crystal lattice of SlpA on top of DPPC/DOTAP liposomes. The results will be discussed in the presentation.

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SMALL ANGLE X-RAY SCATTERING (SAXS) OF THERMOPLASTIC PROTEIN: INTERLINK BETWEEN NANO-STRUCTURE AND THERMAL STABILITY

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A key factor behind the massive usage of thermoplastic polymeric materials for everyday life products relates to the ease of processing. The synthesis, however, relies on petro-chemical products which is problematic from a sustainability standpoint. Natural biopolymers are derived from renewable sources and exhibit inherent biodegradability. Their processing is usually not as straightforward as synthetic thermoplastic and induces irreversible deterioration of the mechanical and macroscopic properties. As only exception to this rule we recently described the sucker ring teeth (SRT) coating the arms and tentacles of cephalopods [1]. SRT is assembled entirely from a protein family that exhibit mechanical properties that compare with the strongest synthetic polymers, such as high molecular weight polyethylene [2]. Because it is stabilized by hydrogen bonds contained within the protein β-sheets, SRT can be melted by simple heating in water and reshaped multiple times just like standard thermoplastic, thus providing intriguing lessons in eco-processing. Here we studied the structure and thermal stability of SRT with a variety of *in situ* x-ray scattering and spectroscopic techniques. Wide angle and small angle X-ray scattering (WAXS and SAXS) were used to gain insights into molecular and nano-scale building blocks of the SRT structure (Figure 1a). The results show that SRT are semi-crystalline polymers, consisting of β-sheet domains in an amorphous matrix organized into a hexagonally packed network of nano-fibrils. SAXS 2D scattering patterns (Figure 1b) provided valuable information on the degree of orientation, via the ρ- and χ_0 parameters (Figure 1c). *In situ* X-ray and vibrational spectroscopy tools combined with the thermal treatment were crucial in understanding thermo plasticity of SRT. The results are consistent with a model of a biphasic semi-crystalline polymer in which the amorphous matrix exhibits viscous flow at a temperature below the melting or degradation point of the β-sheets nanoconfined phase.

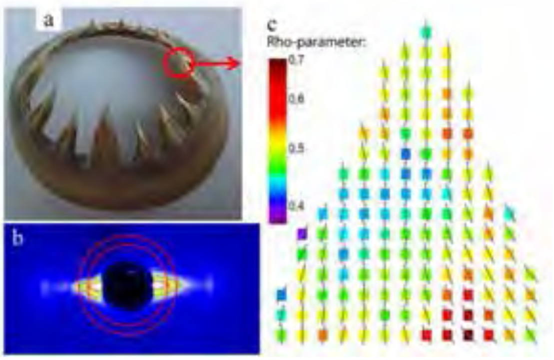

Figure 1: a) Schematic illustration of SRT, with teeth lining the basal ring, measured region is indicated with red box b) 2D scattering pattern of SAXS region c) Map of ρ-parameter and χ_0 for entire tooth.

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UNDERSTANDING THE EFFECT OF CATIONS ON SILK FIBER FORMATION

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Silk is a natural polymer having outstanding mechanical properties, close to the ones of high performance man-made fibers. Understanding how the silkworm makes such a high quality fiber, without using any solvent or high temperature and pressure conditions, is the challenge to address in order to replicate this process and tune parameters to tailor the properties of the fiber.

The main constituent of the silk fiber is a heterodimeric protein named Fibroin (Fib), which sequence presents several hydrophobic blocks separated by hydrophilic spacers and termini. Within the fiber, the hydrophobic blocks are folded into nanocrystals of pleated β-sheet embedded in an amorphous matrix consisting of the hydrophilic parts. Fibroin is produced at the posterior extremity of the silk gland and migrates through it up to the spinneret close to the caterpillar mouth. Along this journey, the physico-chemical environment of the protein changes dramatically. Amongst the parameters progressively varying, the pH, the shear forces and the presence of several cations are known to influence Fibroin maturation. The results presented here focus on the role of some of these cations: Ca^{2+}, Cu^{2+}, Mg^{2+}, Na^{+} and K^{+} on the structural organization of the protein.

A mild protocol has been set to regenerate non-degraded Fibroin from silkworm cocoons. The protein is then mixed with each ion separately, and analyzed by Small-Angle Neutron Scattering (SANS) and Circular dichroism (CD). The secondary, tertiary and quaternary structures of the protein are influenced in different manner by the different cations: Cu^{2+} would promote a directional self-assembling while the other ions would influence the folding and compactness of the protein. Dynamic light scattering revealed the dual effect of Ca^{2+}, promoting aggregation at low concentration while preventing it at high concentration. A Neutron-transparent dialysis cell has been recently developed to mimic the sequence of ionic environments of Fibroin along its natural processing and appreciate the reversibility of each step as well as the importance of their order. Structural evolution along these sequences will be presented.

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BIOMIMETIC MULTIFUNCTIONAL MAGNETITE/GEL COMPOSITES

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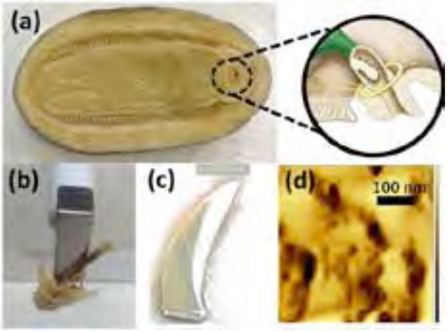

***Fig. 1.** (a) Chiton, (b) Chiton radula teeth, (c) a microscopy image of Chiton radula tooth (cross section), (b) AFM of Chiton tooth (on the tooth mineral shell)* .

Nature provides many archetypes of highly ordered systems, some of these biomaterials are known for their remarkable mechanical properties. An amazing example of biomaterials is the tooth of chitons consisting of a magnetite/protein-polysaccharide hybrid shell. The fully ineralized chiton tooth displays remarkable functional properties such as outstanding fracture toughness, wear resistance and has the highest reported hardness among known biominerals [1]. Inspired by this biomaterial design concepts, we aim to investigate the mechanism of bio-inspired magnetite mineralization and the organic-inorganic hybrid structures by Small Angle Neutron/X-ray Scattering methods.

In the present work we have investigated an in situ mineralization process to fabricate magnetic nanoparticles inside the chitin gelatin composite with controllable mineral content varying from 20 wt % up 70 wt % [2,3]. We could show that with increasing mineral content the gelatin hydrogel structure changes and therefore the mechanical and magnetic properties of the material. Gelatin hydrogels show a spatially confined cavity structure appearing as homogeneously distributed meshes throughout the gel matrix and which allows the magnetite particles to form. We explore the role of gelatin hydrogels on bio-inspired magnetite mineralization by using small (SANS) and very-small (VSANS) angle neutron scattering in conjunction with TEM/AFM/XRD measurements. The scattering contrast of aqueous solution was adapted by the choice of D_2O content in order to determine separately the organic and inorganic components. We aimed to provide novel insight establishing a direct relation between the spacing confinement of the gelatin matrix and the mineralized particles producing such highly and optimized sophisticated materials properties. These structural and mineralization mechanism are compared with the biological samples (Chiton teeth). The comparative studies of the structural features will help to optimize the materials structure for improved mechanical performance.

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NANOSTRUCTURE OF WHEAT PROTEIN GLIADIN EXTRACTED IN WATER

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Wheat protein gluten plays an important role in determining the texture, taste, strength, and stability of wheat flour foods. Gluten is composed of two types of proteins: glutenin and gliadin, which are responsible for the elasticity and the viscosity of dough, respectively. Although gliadin had usually been extracted into ethanol/water solutions or weak acids, it has previously been found that gliadin can be extracted even in distilled water from NaCl-containing dough [1]. Gliadin thus extracted is likely to have characteristics similar to that in real dough. In this study, we investigated nanostructure of gliadin in aqueous solutions by SAXS over a wide range of concentrations to reveal the behavior of gliadin molecules in water.

Gliadin was obtained by the method described in the previous report [1]. NaCl-containing dough was washed repeatedly in distilled water. NaCl was added to particular washing solutions and the resultant precipitates were collected by centrifugation. After dialysis, final products were obtained by freeze-drying. Gliadin thus obtained was mixed with various ratios of water to give wide range concentrations of solutions. SAXS experiments were carried out at the beam line BL-10C of Photon Factory, a synchrotron radiation facility of Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK). Solutions were measured with 1-mm thick aluminum cells with 20-μm-thick quartz windows. The wavelength of X-ray was 0.1488 nm, the sample-to-detector distance was around 2 m, and the q-range was 0.06–2.5 nm^{-1}. The detector used were an imaging plate (RIGAKU R-AXIS VII) and a silicon detector (DECTRIS Pilatus 2M).

Figure 1 shows the SAXS profiles of gliadin solutions in water for 0.1, 1, and 10 wt%. Above 10 wt%, gliadin is no longer soluble in water. From a Guinier analysis for 0.1 wt%, the radius of gyration is found to be around 5.7 nm, indicating that most of gliadin is present as monomeric molecules. However, it is likely that a small amount of dimers and oligomers are also present. At 1 wt%, a broad shoulder peak appears around 0.2 nm^{-1} corresponding to the size of *ca.* 30 nm in real space. This result shows that interparticle interference between aggregated gliadin molecules emerges probably due to electrostatic repulsion. At 10 wt%, the shoulder peak is shifted to a lower q value and the corresponding size is around 50 nm, suggesting that the gliadin aggregates become larger and separation distance of those aggregates increases.

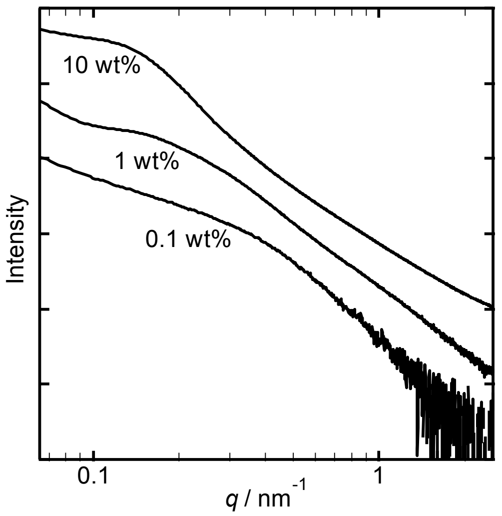

Figure 1. SAXS profiles of gliadins solutions in distilled water over a wide range of concenrations. The curves are vertically shifted for clarity.

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HYBRID THERMOELECTRICS BASED ON A POLYMER/NANOPARTICLE COMPOSITE

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In recent years, the demand for energy in general has increased dramatically. Moreover, with society facing the threat of global climate change, a need for the usage of renewable energy sources has arisen.

In many daily life processes energy is lost in the form of heat, e.g. in combustion engines, solar cells and the human body. However, it is feasible to turn this low-quality energy into usable electrical power. Thermoelectric materials make use of temperature differences across the device in order to generate electrical power. Thus, thermoelectric devices can be regarded as a complementary technology to classical photovoltaic devices. So far, thermoelectric devices are not well established and comprise semiconducting ceramics made of elements such as bismuth, tellurium, lead, or selenium. The low abundance, high costs and potential toxicity of these elements has limited the wide-spread application of thermoelectric devices for power generation.

Recently, thermoelectrics based on conducting polymers have attracted the attention of researchers due to their feasibility regarding facile fabrication of devices, low cost and high abundance, since they are carbon-based. In the research work presented, we use the conducting polymer blend PEDOT:PSS, which exhibits high electrical conductivities when treated with high-boiling solvents such as ethylene glycol [1] or dimethylsulfoxide [2]. Apart from the Seebeck coefficient and the electrical conductivity, the thermal conductivity of the material also plays a significant role. Through the use of silicon nanoparticles, we aim to decrease this quantity, which contributes negatively to the device efficiency. The particles are to act as scattering centers for the phonons carrying heat across the material.

It is very important to investigate the influence of particle distribution within the film on the thermoelectric properties of the device. For this purpose, we investigated thin films of PEDOT:PSS in combination with different concentrations of silicon nanoparticles using grazing incidence small-angle resonant x-ray scattering. Measurements at sulfur K-edge were performed at the four-crystal monochromator beamline of PTB at BESSY II using an in-vacuum Pilatus detector to increase the scattering contrast for the sulfur-containing component PEDOT:PSS with respect to the nanoparticles. By determining the particle distribution, it will be possible to correlate this to potential changes in the thermal conductivity.

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INVESTIGATING THE MORPHOLOGY OF MAPBI$_{3\text{-}X}$CL$_X$ HIGHLY EFFICIENT PEROVSKITE SOLAR CELLS

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In the past two years, organic-inorganic hybrid materials with perovskite crystal structure have received much attention as promising absorber materials for future photovoltaics. In spite of their easy processing comparable to organic and dye-sensitized solar cells, perovskite solar cells nowadays already exhibit power conversion efficiencies (PCE) challenging conventional thin film technologies. However, fundamental understanding of some basic working principles lacks behind the fast progress in device efficiency. The most challenging questions tackled by scientist are the origin of the hysteresis observed in current-voltage characterization and the reproducibility of devices, both of which are strongly linked to the preparation protocol.

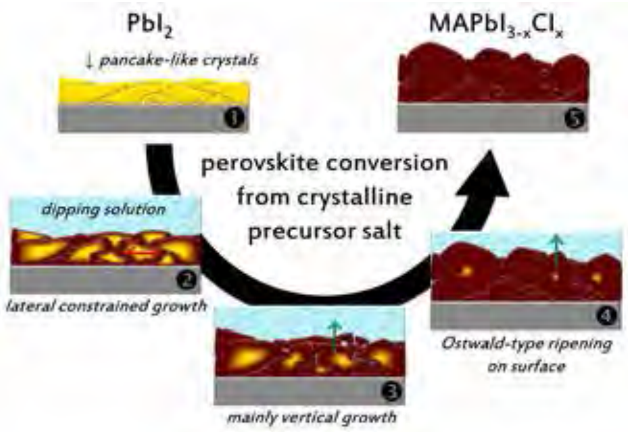

Figure 1: Proposed mechanism of the 2-step technique [2].

In our present work we have prepared perovskite thin films with an established 2-step synthesis method that has led to highly efficient solar cells [1]. It comprises the deposition of a precursor layer (PbI_2) from solution by spin-coating and the subsequent conversion to perovskite. We have investigated both films with grazing incidence small angle X-ray scattering GISAXS and modeled the scattering data within a distorted wave born approximation (DWBA) using three from factors (FF) [2]. We observe a strong correlation of lateral crystal sizes before and after conversion which we attribute to constrained crystal growth. Additionally, by contemplating the intensities of individual FF, we find an accumulation of smaller crystals within the film in contrast to the surface (Figure 1) which reveals laterally differing conversion processes [2].

Thus, our results shed light on the conversion process itself and can be useful to understand and further improve a range of 2-step methods, which may eventually lead to reproducible high PCE.

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A SMALL-ANGLE X-RAY SCATTERING STUDY OF BIOINSPIRED HYBRIDMATERIALS USING PEPTIDE PEO-CONJUGATES TO ADHERE MAGNESIUMFLUORIDE PARTICLES TO A PEO MATRIX

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Specially designed hybrid materials made from an organic and inorganic part can be used as a model system to compare its properties and structural design principles with those of biological materials such as bone. To obtain information about deformation processes in hierarchically structured materials and to elucidate the correlation between macroscopic material mechanics and microscopic structure a combination of small angle X-ray scattering (SAXS) with mechanical tensile testing can be applied.

In the current study a hybrid material, composed of submicron magnesium fluoride particles linked via tailored peptide-poly(ethylene oxide) (PEO) compatibilizers to a PEO matrix has been investigated. By applying tensile testing experiments and wide angle-X-ray scattering experiments we were able to define an optimized composition of the material with increased elastic moduli and crystallinity of the PEO matrix.

To characterize the matrix and the influence of the compatibilizers on the nanostructure, SAXS experiments with a rotating sample holder were performed on pure PEO and PEO in combination with the compatibilizers. Furthermore we elucidated shape, size and distribution of the magnesium fluoride particles by SAXS experiments using a synchrotron source. The high time resolution of this setup allowed also the combination with mechanical tensile testing experiments.

The SAXS measurements showed that the MgF_2 particles are not homogeneously distributed nanometer-sized spheres, but rather elongated objects which might be an effect of agglomeration. Our results indicate a fractal agglomeration of the particles. The SAXS data will be correlated with the mechanical properties of the material to understand the deformation processes at different length scales.

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HIERARCHICALLY LINKED STRUCTURE AND DYNAMICS OF PHOSPHOLIPID VESICLES NEAR THE MAIN TRANSITION

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Biomembranes serve as natural carriers in mammal organisms. The most simple representation of a biomimetic membrane is a vesicular system consisting of a single kind of phospholipid in an aqueous solution. It is assumed that the functional properties of a membrane depend strongly on the structure and dynamics of the lipid bilayer which involves a wide range of length and time scales. The mechanical properties as well as the thickness of a biological membrane determine the permeability of small molecules [1]. The potential for a vesicle to function as a carrier in a likewise crowded environment is determined by its size, stability, concentration and polydispersity. Here, we investigate small unilamellar vesicles (ULV's) composed of the phospholipid 1,2-dimyristoyl-sn-glycero-3-phosphaditylcholine (DMPC). The ULV's are probed by X-ray, light and neutron scattering to reveal structure and dynamics while undergoing the temperature-induced main phase transition at around 23.6 °C. The DMPC bilayer anomalous swelling, being previously associated with the bilayer main phase transition, has been the object of a large number of studies [2-3]. We use complementary scattering techniques to cover the probed length scales from the nearest neighbor distances in the bilayer plane to an ensemble of lipid vesicles in solution. The covered time scales range from ns to ms around the main phase transition temperature, whereby the acyl chain correlation peak is observed by wide-angle X-ray scattering (WAXS, (I)) and the lipid bilayer thickness is probed using small-angle X-ray scattering (SAXS, II). The latter represents length scales of the bilayer undulations probed by neutron spin-echo spectroscopy (NSE, (II), (III)). Our experiments relate quantitatively temperature-induced in-plane changes in the in-plane distance of the phospholipid molecules, the lipid bilayer thickness, vesicle size and local lipid bilayer undulations. The molecular reorganization during the main phase transition and its effects on the vesicle diffusion and bilayer interface dynamics is pictured intrinsically from the results by our experiments.

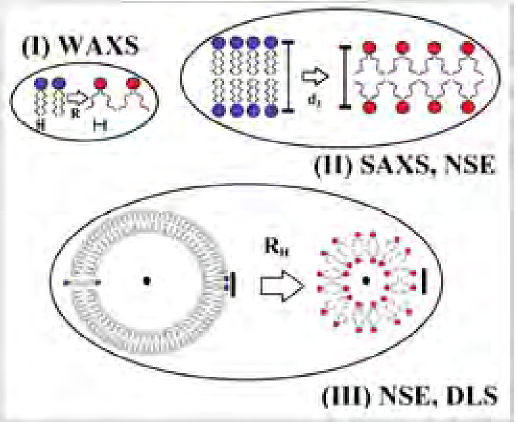

Figure 1: Structure and dynamics of a unilamellar DMPC vesicle. (I) lipid chain correlation (WAXS); (II) lipid bilayer thickness (SAXS), local lipid bilayer undulations (NSE); hydrodynamic vesicle radius (DLS), vesicle center-of-mass diffusion (NSE, DLS).

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↘ Flash Talk: Mon-F-H1

Competition between entropy and enthalpy in the binding of melittin with ULV vesicles and the ULV chain length effects

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Membrane-active peptides with genetic codes are known to interact directly with cell membranes, rather than via specific protein receptors, in carrying out their biological functions. In the very recent years, melittin, an antimicrobial peptide, was found to form transmembrane pores of toroidal type in membranes of lipid vesicles [Lee, PNAS]. As membrane pores are believed to be one of the primary causes for cell lysis and/or act as membrane crossing channels for ions/bio-molecules, understanding the peptide-membrane binding behavior and pore formation process and mechanism is of broad interest, and carries hints in designing target drug carriers with lipid ULV. In this study, temperature-dependent binding behavior of melittin with zwitterionic phosphate lipid membranes of 1,2-dioleoyl-*sn*-glycero-3-phosphocholine (DiC20:1PC) is studied using small-angle X-ray scattering (SAXS), low-angle X-ray diffraction, and circular dichroism (CD). SAXS result shows a successively enhanced thinning behavior of the melittin-bound unilamelar vesicle (ULV) bilayers upon increased solution temperature from 280 to 318 K, attributed to thermally enhanced peptide-membrane binding. The melittin-ULV bilayer thinning percentages measured are further scaled to that measured by X-ray diffraction from the correspondingly premixed multilamellar membrane of prescribed peptide-to-lipid binding ratio χ_b, thereby establishing the binding isotherm χ_b of peptide-ULV bilayers vs. free peptide concentration. Compared with the stronger χ_b established from the corresponding CD result obtained in a much lower peptide concentration range of μM, the SAXS result suggests a secondary stage of peptide-membrane binding behavior prior to membrane pore formation. On the basis of Gouy-Chapman theory with screened charge interactions, we further extract the temperature-dependent binding constants $K(T)$ values and binding free energy of a model peptide melittin to the zwitterionic phospholipid ULV from the X-ray-determined binding isotherms. The binding constant of melittin with di20:1PC ULV bilayers is found to increases more than two folds in a marginally temperature change from 293 K to 311.5 K, revealing an enhanced entropic effect over the hydrophobic interactions at high temperatures. Based on the Van't Hoff expression, we have further deduced quantitatively the entropy effect on reducing the system energy by a few kcal/mol, from 293 to 311.5 K. Our results illustrate clearly the modulated competition between the hydrophobic interactions of membrane lipid chains favoring membrane integrity and the entropy favoring peptide's partitioning into lipid membranes. The entropy effect can override the hydrophobic interactions (enthalpy) at high temperatures, especially with lipids of longer chain lengths of non-linearly increased entropy effects. Accordingly, the ULV lipid chain length effects on the melittin-ULV binding are shown.

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↘ Flash Talk: Mon-F-H1

Resonant Soft X-ray Scattering for Soft Materials

Cheng Wang

To meet the challenge on investigating new and complex materials that is relevant to mesoscale energy science, it is essential to connect microscopic dynamical processes to activated kinetic processes and macroscopic function in diverse soft and hard materials. We need sharper tools in order to discover, understand, and control mesoscale phenomena and architectures. Over the past a few years, we have developed Resonant Soft X-ray Scattering (RSoXS) and constructed the first dedicated resonant soft x-ray scattering beamline at the Advanced Light Source, LBNL. RSoXS combines soft x-ray spectroscopy with x-ray scattering thus offers statistical information for 3D chemical morphology over a large length scale range from nanometers to micrometers. Using RSoXS to characterize multi-length scale soft materials with heterogeous chemical structures, we have demonstrated that soft x-ray scattering is a unique complementary technique to conventional hard x-ray and neutron scattering. Its unique chemical sensitivity, large accessible size scale, molecular bond orientation sensitivity with polarized x-rays and high coherence have shown great potential for chemical/morphological structure characterization for many classes of materials. Some recent development of in-situ soft x-ray scattering with in-vacuum sample environment will be discussed. In order to study sciences in naturally occurring conditions, we need to overcome the sample limitations set by the low penetration depth of soft x-rays and requirement of high vacuum. Adapting to the evolving environmental cell designs utilized increasingly in the Electron Microscopy community, customized designed liquid/gas environmental cells will enable soft x-ray scattering experiments on biological, electro-chemical, self-assembly, and hierarchical functional systems in both static and dynamic fashion. Recent RSoXS results on organic electronics, block copolymer thin films, and membrane structure will be presented.

Use SAXS and SANS to observe the interaction between diblock-copolymer PS-b-P4VPQ and DNA in solution

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We used small angle X-ray/neutron scattering (SAXS and SANS) to detect the complex structure formed by diblock-copolymer PS-b-P4VPQ and DNA in solution, and TEM photos were also taken to justify fitting parameters more accurately. The DNA concentration is our main experimental parameter, we also used charge-matched point (CMP) to represent the total amount of negative charges contributed by DNA in solution is equal to the total amount of positive charges contributed by PS-b-P4VPQ.

When there's only diblock-copolymer in solution, the micelle structure is formed because of their self-assembly property. As the DNA is added in solution, DNA will help polymer micelles to fuse into a core-shell cylinder structure by wrapping around P4VPQ shell with their electrostatic interaction. The cylinder structure will then be saturated until the CMP is reached, furthermore increasing DNA concentration will not affect the stabilized structure. This observation might be useful in gene delivery or bio-mimicking applications.

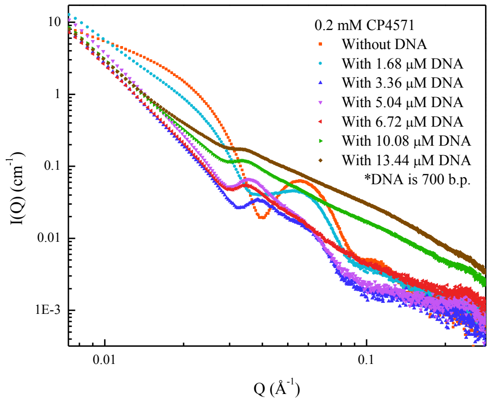

Figure 1: SAXS profile of 0.2 mM CP4571 polymer with different DNA concentrations from 0 μM to 13.44 μM.

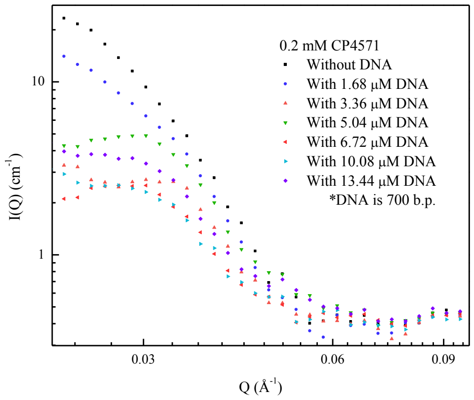

Figure 2: SANS profile of 0.2 mM CP4571 polymer with different DNA concentrations from 0 μM to 13.44 μM.

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SAS STUDIES ON THE INTERACTION OF DPPC AND HYALURONAN

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Articular joints are bio-lubrication systems with exceptional good lubrication properties. Friction coefficients in articular joints are the lowest found in nature and they are kept even under high loads end shear rates. [1] The friction is provided by the synovial fluid, which is an intricate composition of different macromolecules. Two of the most important components are phospholipids and hyaluronan (HA) and it has been shown that these two reduce friction on their own, but that a mixture of both leads to even lower friction coefficients. [2]

In order two reveal which structures HA and phospholipids form, small angle scattering studies (using neutrons as well as X-rays) of mixtures of Dipalmitoylphosphatidylcholine (DPPC) vesicles and HA have been performed. Our measurements show an increase of the radius of gyration of DPPC-vesicles in the presences of HA. Measurements with two different weights of HA have been done in order to reveal if the chain length has an influence on the formed structures. In addition, the influence of the solution condition has been studied. Therefore measurements have been done in sole 150mM NaCl as well as in a mixture of 150mM NaCl and 10mM $CaCl_2$. In the presence of calcium ions a much stronger change in the vesicles structure due to HA addition could be observed.

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↘ Flash Talk: Wed-F-M1

EFFECT OF TRANSITION FROM SPIN GLASS TO FERROMAGNETIC STATE ON TRANSPORT IN $La_{0.54}Ho_{0.11}Sr_{0.35}Mn_{1-x}Cr_xO_3$ MANGANITES

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In this work we aim to establish the correlations between the transition from spin glass to ferromagnetic state on transport phenomena in $La_{0.54}Ho_{0.11}Sr_{0.35}Mn_{1-x}Cr_xO_3$ manganites (synthesized by sol-gel method) at various Cr concentrations (x), by using neutron diffraction, small-angle X-ray and neutron scattering (SAXS/SANS). Neutron diffraction has been performed at room temperature, and SAXS and SANS measurements were performed in the range 258 ÷ 353 K (H = 0). The variation of the molar magnetization and of the resistance with temperature and intensity of the applied magnetic field were determined by using a Foner type magnetometer and, respectively, the four probes method between 77 and 400 K, at H_{max}= 1 T.

We observed a monotonous decrease of the lattice constants and of the unit cell volume with the increase of the Cr concentration. Variation of molar magnetization with temperature at relatively low magnetic fields shows a dependence on the thermal history of the samples, attributed to the transformation from the ferromagnetic to spin glass state. A large variation of the resistance with the magnetic field intensity was observed near room temperature for all investigated manganites.

For samples with x = 0.05, 0.10, 0.15 and 0.20, the SANS data allows us to obtain the volume fraction of the magnetic phase using the Porod invariant. An interesting behavior can be observed for x = 0.15 sample, where we obtain the power-law decay scattering exponent $\alpha \approx 2$ for T = 293 K, which indicates the formation of 2D disk-like structures. We found that for x = 0.00, 0.05 and 0.20 at T = 343 K, we have $\alpha = 1$ and show that the magnetic nano-domains have a 1D rod-like shape with the radius in the range 2.5 − 5Å and the height in the range 40 − 60 Å. For these concentrations the general characteristic is that a decreasing of the temperature determines a slight increasing of the scattering exponent α, which indicates that the rod-like magnetic structures expand to form worm-like structures.

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COMPACT SMALL-ANGLE SYNCHROTRON DIFFRACTION TECHNIQUE WITH TUNABLE PROBE SIZE: STUDY OF THE ANODIC ALUMINA MEMBRANE

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The compact high-resolution small-angle synchrotron radiation technique with tunable probe size was suggested. Preliminary test experiments were carried out at the microoptics test bench of the ID06 beamline, ESRF. The microradian X-ray diffraction with the beam energy of about 12 keV ($\lambda = 1$ Å , $\Delta\lambda/\lambda \sim 10{-}4$) was realized using the set of compound refractive lenses (CRL), which consists of 30 parabolic lenses with 200 µm curvature radius, giving a focal length of 1.45 m and providing coherent illumination on the sample. The beam was focused at the two-dimensional high resolution Sensicam CCD detector (0.645×0.645 µm^2 pixel size). Using of the distance between the compound lenses and the detector as a sample position is a novel approach. The probe size could be vary from 4 to 500 µm depending on the sample position.

In the capacity of the test sample we have used an anodic alumina membrane with the thickness of 96 µm and self-ordered pore structure (pore diameter – 40 nm, distance between the centers of the pore – 102 nm). The membrane was installed perpendicularly to the incident beam on the distance from 246 to 16 mm from the detector. In this way the adjustment of an exposing area size from 87 to 4.2 µm and focusing on the area of one or few pore structure domains became possible. If the irradiated sample area consists of a few domains, the diffraction peaks on the 2D-diffraction pattern split into the speckles.

The source of the important information about the real ordering and orientation of the pores into the each domain is the azimuthal and radial location of the speckle and their intensity. The analysis of speckles allowed to reveal that the pores into each domain have high degree of ordering in transversal direction, and they are longitudinal for all thickness of the membrane. At the same time using method of analysis of the all diffraction peak area usually gives the average information and distorts the data about the features of the real sample structure [1]. The ordering of the pores in neighboring domains is distinguished. The pores are contorted and their growth is stopped mainly on the domain borders. The suggested diffraction technique with tunable probe size can be applied successfully for the detail studying of the different nanostructured materials.

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↘ Flash Talk: Wed-F-M1

COMPARATIVE SANS INVESTIGATION OF 9CR AND OF AISI304 OXIDE DISPERSION STRENGTHENED (ODS) STEELS FOR NUCLEAR APPLICATIONS

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This contribution presents the results of a small-angle neutron scattering (SANS) investigation carried out to characterize the microstructure of oxide dispersion strengthened (ODS) steels, developed for nuclear applications due to their irradiation resistance and high temperature strength. The following two different steels were investigated in the as-received state:
austenitic (ODS 304) 18 Cr 8 Ni 1 Mo 0,15 Si 0,5 Ti 0.35 Y_2O_3 wt%
ferritic/martensitic (9Cr-ODS) 18 Cr 1 Mo 1,5 W0,15 Si 0,5 Ti 0.35 Y_2O_3 wt%.
The SANS measurements were carried out at the D22 instrument, at the ILL-Grenoble, under a 1 T external magnetic field to distinguish the nuclear and the magnetic SANS component; a 6 nm wavelength was utilized with sample-to-detector distances of 2 m and 11.2 m, covering a Q-range sufficiently large to explore the experimental window relevant from a metallurgical viewpoint. The samples were platelets, approximately 1 mm thick and 1 cm^2 in surface area. A strong magnetic anisotropy is detected in the 9Cr-ODS steel, while the ODS 304 one is almost completely non-magnetic. Based on already published metallurgical characterization by electron microscopy [1] and by neutron diffraction measurements on these same steels [2], the observed SANS effects are tentatively attributed to Y-Ti-O non-magnetic complexes, giving rise to strong magnetic contrast in ferritic/martensitic steel.

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SMALL ANGLE NEUTRON SCATTERING STUDY OF OXIDE DISPERSION STRENGTHENED ALLOYS FOR FUTURE NUCLEAR APPLICATION

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The nano sized microstructures in Fe base ODS(Oxide Dispersion Strengthened) alloys and Ni base ODS alloys for future nuclear application were studied by SANS(Small Angle Neutron Scattering). The ODS alloys were manufactured by MA(Mechanical Alloying) and Hot working process with various chemical compositions and fabrication conditions. The SANS experiments were performed by the 40 meter SANS instrument at HANARO[1]. The scattering vector ranged between 0.0007 Å^{-1} and 0.5 Å^{-1} during SANS experiment. The nano sized microstructures such as yttrium oxides and carbides were quantitatively analyzed by SANS. The yttrium oxides and carbides were also observed by the electron microscope. The microstructural analysis results by SANS were compared with those by the electron microscope. The effects of chemical compositions and thermo-mechanical treatments on microstructure was discussed according to the quantitative microstructural analysis results by SANS. For Fe base ODS alloys, The ratio between magnetic and nuclear scattering components was calculated and the characteristics of the non-magnetic nano sized microstructures in experimental Fe base ODS alloys were discussed from the SANS analysis results[2].

Figure 1: 40m small angle neutron scattering instrument at HANARO.

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CHARACTERIZATION OF BIMETALLIC AG/AU NANOPARTICLES AS PREPARED BY ARF-EXCIMER LASER IRRADIATION BY MEANS OF SAXS AND ASAXS EXPERIMENTS

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The generation of plasmonic Au/Ag nanostructures in glass surfaces showing a tunable surface plasmon resonance in a wide range of wavelengths (400 – 650 nm) could be realized by UV laser irradiation (193 nm). These are promising materials for optoelectronics and nanoplasmonics. Here, Au containing glasses after an Ag ion exchange or Au coated Ag/Na ion-exchanged glass has been used as base glasses. The subsequent irradiation by ArF excimer laser in the sub-ablation threshold regime induced patterning in micron and submicron dimensions as result of formation of bimetallic Au/Ag nanoparticles. The particle formation has been investigated by combination of optical spectroscopy and ASAXS to identify the mechanism of precipitation as well as to characterize size, structure (homogeneous or core-shell) and the composition of bimetallic nanoparticles. With it, the correlations could be identified between the applied laser process parameters and the resulting structures as well as the generated optical properties.

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FAST, QUANTITATIVE, AND NONDESTRUCTIVE EVALUATION OF HYDRIDED LWR FUEL CLADDING BY SMALL ANGLE INCOHERENT NEUTRON SCATTERING OF HYDROGEN

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A nondestructive neutron scattering method to precisely measure the uptake of hydrogen and the distribution of hydride precipitates in light water reactor (LWR) fuel cladding was developed. Zircaloy-4 clad- ding used in commercial LWRs was used to produce hydrided specimens. The hydriding apparatus consists of a closed stainless-steel vessel that contains Zr alloy specimens and hydrogen gas. Following hydrogen charging, the hydrogen content of the hydrided specimens was measured using the vacuum hot extraction method, by which the samples with desired hydrogen concentrations were selected for the neutron study. Optical microscopy shows that our hydriding procedure results in uniform distribution of circumferential hydrides across the wall thickness. Small angle neutron incoherent scattering was performed in the High Flux Isotope Reactor at Oak Ridge National Laboratory. Our study demonstrates that the hydrogen in commercial Zircaloy-4 cladding can be measured very accurately in minutes by this nondestructive method over a wide range of hydrogen concentrations from a very small amount (~20 ppm) to over 1000 ppm. The hydrogen distribution in a tube sample was obtained by scaling the neutron scattering rate with a factor determined by a calibration process using standard, destructive direct chemical analysis methods on the specimens. This scale factor can be used in future tests with unknown hydrogen concentrations, thus providing a nondestructive method for determining absolute hydrogen concentrations.

This research was sponsored by the Laboratory Directed Research and Development (LOIS-6502) Program of Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the U.S. Department of Energy under Contract No. DE-AC05-00OR22725), and EBSD through a user project supported by ORNL's Center for Nanophase Materials Sciences (CNMS), which is sponsored by the Scientific User Facilities Division, Office of Basic Energy Sciences, U.S. Department of Energy. Beamline CG3 is supported by the Office of Biological and Environmental Research of the U.S. Department of Energy through the ORNL Center for Structural Molecular Biology. The High Flux Isotope Reactor and beamline CG2 of ORNL was sponsored by the Scientific User Facilities Division, Office of Basic Energy Sciences, U.S. Department of Energy. We are grateful to Dr. Jeremy Busby for his technical inputs and stimulating discussions.

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SMALL ANGLE NEUTRON SCATTERING – A POWERFUL TOOL TO STUDY MICROSTRUCTURE OF HIGHLY IRRADIATED REACTOR PRESSURE VESSEL STEELS

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Some of the current fleet of nuclear power plants is poised to reach their end of life and will require an operating lifetime extension. Therefore, the main structural components, including the reactor pressure vessel (RPV), will be subject to higher neutron exposures than originally planned. These longer operating times raise serious concerns regarding our ability to predict the reliability of RPV steels at such high doses. In this work, we studied high nickel (1.58 and 1.66 wt%), low copper (<0.08%) steel weld samples from the surveillance program of the Swedish Ringhals Unit 3 and 4 pressurized water reactors by small-angle neutron scattering (SANS) in a saturating magnetic field and by atom probe tomography. The SANS results were analyzed by non-linear least square fits to the scattering cross-section data assuming spherical, non-magnetic features following a log-normal size distribution to obtain the irradiation-induced feature dimensions: mean precipitate radius, volume fraction, and number density. Large number densities of ultra-fine precipitates were observed in the surveillance welds. However, annealing of the welds at 450C for 24 hours resulted in almost complete disappearance of ne Ni-Mn-Si precipitates. The relationship between ductile-to-brittle transition temperature (DBTT) shifts and precipitate volume fractions from these experiments is in general agreement with previous data. This work demonstrates that nondestructive SANS and high-resolution, real-space APT provide comparable descriptions of irradiation induced precipitates in these steels and compliment each other.

Research was sponsored by the Light-Water Reactor Sustainability Program of the Office of Nuclear Energy. Atom probe tomography research at the Oak Ridge National Laboratory ShaRE User Facility was sponsored by the Scientific User Facilities Division, Office of Basic Energy Sciences, U.S. Department of Energy. The High Flux Isotope Reactor and beamline CG2 of ORNL was sponsored by the Scientific User Facilities Division, Office of Basic Energy Sciences, U.S. Department of Energy. We are grateful to Dr. Brian Wirth of the University of Tennessee for the electromagnet used in the SANS experiments.

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↘ Flash Talk: Wed-F-M1

RADIATION TOLERANCE OF FE-CR-AL ALLOYS: ROLE OF AL AND CR ON PHASE STABILITY UNDER NEUTRON IRRADIATION

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Fe-Cr-Al alloys are an emerging alloy class for fusion energy applications. This is due to Fe-Cr-Al alloys having similar materials performance but improved compatibility with corrosive environments like Pb-Li when compared to Fe-Cr alloys. This work examines the radiation tolerance of Fe-Cr-Al alloys with an emphasis on developing a mechanistic understanding on the role of Al and Cr on the formation of Cr-rich α' precipitates under neutron irradiation. Model Fe-(10-18)Cr-(2.9-4.9)Al (wt %) alloys were irradiated in the High Flux Isotope Reactor (HFIR) to 0.3-9 dpa between the temperatures of 300-400°C. Irradiation conditions were selected to enable the direct comparison of Fe-Cr-Al results to the rich database on irradiated Fe-Cr alloys. Comprehensive testing and characterization was conducted on the non-irradiated and irradiated specimens with mechanical testing, small angle neutron scattering (SANS), atom probe tomography (APT), and advanced electron microscopy.

Results indicate that radiation-induced hardening, represented by a yield strength increase, can be observed in Fe-Cr-Al alloys as high as 350 MPa. Initial structure-property relationships indicate radiation-induced hardening was directly related to the formation of dislocation loops with Burgers vector of a<100> and a/2<111> and the precipitation of nanometer scaled Cr-rich α' under irradiation. Alloy Cr content was found to strongly influence precipitation, a result that mimics findings for Fe-Cr alloys. Al content had little effect on phase stability at the compositions studied. Significant precipitation ($\geq 10^{24}$ m^{-3}) was found to dominate the hardening response in the Fe-Cr-Al alloys. Damage dose (dpa) and irradiation temperature were also found to influence the size, number density, and composition of Cr-rich α' precipitates. This presentation will present a detailed analysis on the irradiation performance of Fe-Cr-Al alloys and provide guidance on the development of Fe-Cr-Al alloys for fusion energy applications from the perspective of composition refinement for enhanced radiation tolerance.

Research was sponsored by DOE Office of Nuclear Energy, Advanced Fuel Campaign of the Fuel Cycle R&D program. The High Flux Isotope Reactor and beamline CG2 of ORNL was sponsored by the Scientific User Facilities Division, Office of Basic Energy Sciences, U.S. Department of Energy. We are grateful to Dr. Jeremy Busby for his technical inputs and stimulating discussions.

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MAGNETIC SANS CORRELATION FUNCTIONS OF BULK MAGNETIC MATERIALS

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We present model calculations, based on the continuum theory of micromagnetics, for the correlation function of the spin-misalignment SANS cross section of bulk ferromagnets (*e.g.* elemental polycrystalline ferromagnets, soft and hard magnetic nanocomposites, nanoporous ferromagnets, or magnetic steels). For such materials, the spin disorder which is related to spatial variations in the saturation magnetization and magnetic anisotropy field results in strong spin-misalignment scattering $d\Sigma_M/d\Omega$ along the forward direction [1]. When the applied magnetic field is perpendicular to the incoming neutron beam, the characteristics of $d\Sigma_M/d\Omega$ (*e.g.* the angular anisotropy on a two-dimensional detector or the asymptotic power-law exponent) are determined by the ratio of magnetic anisotropy-field strength H_p to the jump ΔM in the saturation magnetization at internal interfaces. Here, we analyze the corresponding one and two-dimensional real-space correlations as a function of applied magnetic field, ratio $H_p/\Delta M$, single-particle form factor, and particle volume fraction. Finally, we compare the theoretical results for the correlation function to experimental data on a Nd-Fe-B-based nanocomposite.

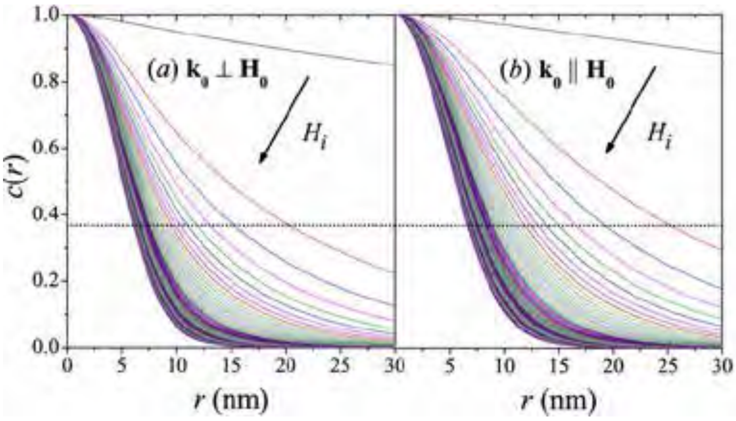

Fig.1 Normalized correlation functions $c(r)$ at several applied-field values H_i. H_i increases from 0.001T to 10 T in steps of 0.1 T; the arrows specify the direction of increasing H_i. Dotted horizontal lines: $c(r) = e^{-1}$.

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MAGNETIC SMALL-ANGLE NEUTRON SCATTERING: BEYOND THE PARTICLE-MATRIX CONCEPT

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Small-angle neutron scattering (SANS) is a very powerful technique for the investigation of magnetic materials, since it provides information from within the bulk of magnetic media and on a length scale between a few nanometers and a few hundred of nanometers (~ 1-300 nm). In this talk, we summarize recent theoretical and experimental work in the field of magnetic SANS of bulk ferromagnets [1-3]. The response of the magnetization to spatially inhomogeneous magnetic anisotropy and magnetostatic stray fields is computed using micromagnetic theory, and the ensuing spin-misalignment SANS is deduced. This approach – originally pioneered by Kronmüller, Seeger, and Wilkens [4] – goes beyond the traditional description of SANS in terms of particle form and structure factors. Analysis of experimental magnetic-field-dependent SANS data corroborates the usefulness of the approach, which provides important quantitative information on the magnetic-interaction parameters such as the exchange-stiffness constant, the mean magnetic anisotropy field, and the mean magnetostatic field due to jumps ΔM of the magnetization at internal interfaces. Besides the value of the applied magnetic field, it turns out to be the ratio of the magnetic anisotropy field H_p to ΔM, which determines the properties of the magnetic SANS cross section of bulk ferromagnets; specifically, the angular anisotropy on a two-dimensional detector, the asymptotic power-law exponent, and the characteristic decay length of spin-misalignment fluctuations. Unpolarized and polarized neutron data on various magnetic materials will be discussed.

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SANS AND BRAGG-EDGE TRANSMISSION ANALYSIS USING PULSED NEUTRON

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Small-angle scattering (SAS) is a powerful tool to characterize nano- and microstructures in metals and alloys. It enables *quantitative* characterization due to large observable sample volume. In the field of metallurgy, SAS is frequently used to evaluate the representative morphological information about nano-sized particles precipitated in metal matrix. However, it provides no crystallographic information about the matrix such as crystal structure, residual strain, crystallite size, and texture.

To quantitatively evaluate the crystallographic information of the matrix, diffraction technique is useful. Synergistic use of SAS and diffraction allows the total quantitative characterization of both the precipitates and matrix in the metals and alloys. Although simultaneous measurement of small- and wide-angle scattering (SAS/WAS) is well established, sample and sample environment are restricted by the experimental requirements for both SAS and WAS. With recent development of pulsed neutron sources, a new technique to measure the diffraction, Bragg-edge transmission analysis, attracts attention in the field of neutron imaging [1]. It is a kind of diffraction experiment and analyses the wavelength dependence of transmission. In the pulsed small-angle neutron scattering (SANS), the transmission spectrum can be simultaneously measured with SANS intensity. Using both SANS intensity and transmission spectrum, the precipitates and matrix in the metal can be simultaneously characterized. In this study, we propose the combined technique of SANS and Bragg-edge transmission analysis using pulsed neutron source.

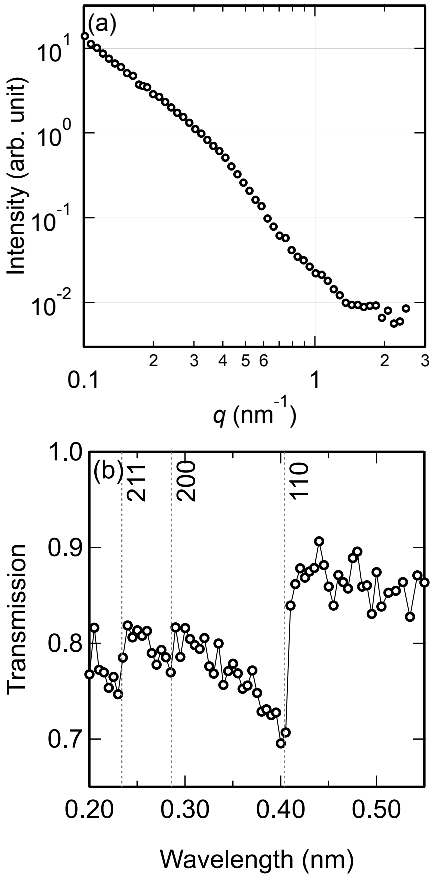

Figure 1: (a) SANS profile and (b) transmission spectrum of ferritic steel with nano-sized precipitates. Dotted lines indicate the wavelength of Bragg edges in bcc Fe.

The experiments were carried out at the pulsed SANS instrument TAIKAN at J-PARC. Ferritic steels with nano-sized precipitates were measured.

Figure 1 shows the SANS profile and the transmission spectra of the steel measured at the same time. A shoulder is observed at $q\sim0.4$ nm^{-1} in the SANS profile. This indicates the presence of nano-sized particles. In the transmission spectrum, a jump is observed around 0.40 nm. This corresponds to the Bragg edge of {110} crystal lattice planes of the ferritic steel. Other two small Bragg edges are also observed. In conclusion, we successfully observed the SANS and Bragg edge of the steel at the same time.

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HETEROGENEITY IN MARTENSITE PHASE OF STEELS

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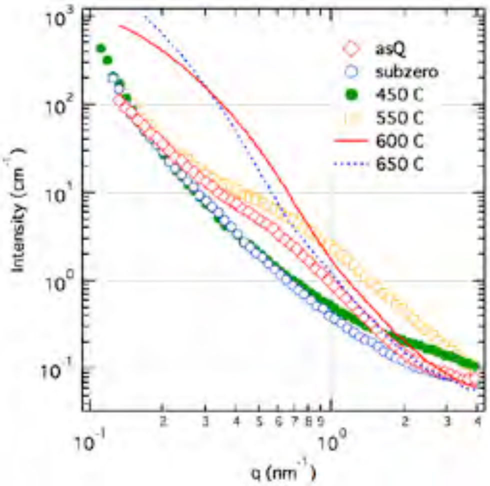

Fig.1 evolution of SAXS profiles of high-nitrogen martensitic stainless steel

Martensite is one of the most important phase in the field of metallurgy, especially in the steels. Since light element such as carbon and nitrogen are solved in an fcc phase of the steels at high temperature range, they are quenched in a bcc phase with much smaller solubility limit at room temperature when the cooling rate is sufficiently high. This is called as martensite transformation in steels and we expect uniform composition including those light elements in martensite. However, a certain number of quenched steels show strong scattering in small-angle scattering. As an example, the evolution of SAXS profiles of high-nitrogen martensitic stainless steel, are shown in Fig.1. The strong scattering in the observed q-range appears in the as-quenched state, indicating the formation of particles with a few nanometer size. The following sub-zero treatment in which sample is quenched in the liquid nitrogen from room temperature, makes this scattering much weaker than as-quenched state. After subzero treatment, the samples were tempered at 450 C and 550 C. Clear signal in higher-q region than $1nm^{-1}$ appears by comparing with subzero-treatment, indicating the formation of finer heterogeneity with less than 1 nm in diameter. For determining the crystalline structure of the corresponding particles, we use transmission electron microscope and find the nano-scale hetero-structures with the size of 1 nm inside the martensite phase. In this area, the diffraction pattern of hexagonal phase co-exists with bcc phase. By careful observations from different zone axis, we conclude that hexagonal phase with the same crystalline structure of omega phase in Ti alloys are formed in the martensite of all samples described above. Under the assumption of the crystalline structure of omega phase, we discuss the composition of omega phase from the intensity ratio between SAXS and SANS measured in absolute unit. The change of the ratio suggests the change in composition during this tempering process. For omega particles formed by tempering at 450 C, only nitrogen enrichment can explain the SAXS/SANS ratio, while both chromium and nitrogen enrichment are required for explaining the ratio of the intensity obtained in the sample tempered at 550 C. X-ray diffraction measurements for the same samples with transmission mode, we found the peak that can be indexed by (001) omega phase in as-quenched and 550 C. In contrast, 600 C, and 650 C show peaks only from equilibrium phases, i.e. Cr_2N and bcc-Fe peaks. These results suggest that the martensite of this steel consists of two components, one is bcc-Fe and the other is nanometer size particles enriched by nitrogen. Similar SAXS profiles and diffraction patterns have been obtained in the as-quenched carbon steels with martensite phase, suggesting that the formation of omega phase commonly occurs in most of the maetensite transformation of steels with different carbon and nitrogen contents.

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FORMATION OF LONG-PERIOD STACKING ORDERED STRUCTURED IN RAPIDLY/SLOWLY QUENCHED $Mg_{85}Y_9Zn_6$ ALLOYS

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Phase transformation of synchronized long-period stacking ordered (Sync.LPSO) structures having 18R order from mold-cast crystalline samples and rapidly quenched amorphous ribbons is presented for $Mg_{85}Y_9Zn_6$ alloys, which is the stoichiometric composition for 18R LPSO phase. The cast sample showed intergrowth microstructures of 18R and 10H with short-range ordering of clusters at the stacking fault/ segregation layers[1]. The quenched ribbons are amorphous in the as-RQ conditions. The formation/destruction process are examined by in-situ simultaneous small and wide angle scattering/diffraction measurements during heating the sample at a constatnt rate of 10K/min from room temperatures upto the melting point. Amorphous ribbon shows weak association between Y and Zn, while larger clusters observed upon crystallization showed rather similar chemical nearest neighbor structures as that for stable LPSO structures when examined by XAFS at the Zn and Y K absorption edges. In-situ SWAXS measurements of the sample showed a sequential process of relaxation, crystallization, segregation and LPSO formation. These characteristic temperatures that the structure changes were observed agreed well with those where changes in the specific heat were observed. These transformation process will be discussed in light of the transformation process observed for the isothermal process of cast (ingot) sample with the same composition1, exhibiting two-dimensional ordering kinetics of clusters[2,3].

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OBSERVATION OF MAGNETIZATION REVERSAL PROCESS IN (ND,DY)-FE-B SINTERED MAGNETS USING MAGNETIC VSANS

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There have been strong interests in the mechanism of high coercivity in Nd-Fe-B sintered magnets due to increasing demands for automotive applications. Motors used in hybrid and electric vehicles are operating at high temperature and approximately more than 30% of Nd is substituted with Dy in the current Nd-Fe-B sintered magnets for automotive motor applications to increase the anisotropy field. Since Dy is comparatively rare natural resources with supply risks, a new technology that can increase the coercivity of Nd-Fe-B sintered magnets is strongly desired.

Magnetic Small Angle Neutron Scattering (SANS) is very powerful to observe bulk magnetic microstructures of Nd-Fe-B nanocrystalline magnets [1-4]. The length scale of standard SANS instrument is not suitable for "sintered" magnets, i.e. magnet used for motors and industrial applications, since the grain size of sintered magnets is a few micrometer. The use of Very Small Angle Neutron Scattering (VSANS) is indispensable for sintered magnet. In this study, we performed VSANS experiments for (Nd,Dy)-Fe-B sintered magnet at KWS-3 in FRM-II, Munich, Germany. We observed clear changes in magnetic VSANS patterns for both Nd-Fe-B and (Nd,Dy)-Fe-B sintered magnets in the q-range of 0.003 ~ 0.03 nm^{-1} during magnetization reversal process. It is suggested that the change in magnetic microstructure inside the bulk sintered magnet is occurred with the size of 200 ~ 2,000 nm. We also found that there are two different origins for the change in magnetic VSANS intensity. In lower q region, magnetic scattering is mostly affected by macroscopic magnetization. On the other hand in higher q region, magnetic scattering is mostly caused by a formation of magnetic domains.

This work was partly supported by the JST under Collaborative Research Based on Industrial Demand "High Performance Magnets: Towards Innovative Development of Next Generation Magnets."

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SANS STUDY OF ND-FE-B SINTERED MAGNETS

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The magnetic microstructure of an isotropic sintered Nd–Fe–B permanent magnet was studied by means of unpolarized magnetic-field-dependent small-angle neutron scattering (SANS). The experimental observation of a 'spike' in $d\Sigma_M/d\Omega$ along the forward direction (see figure below) implies the presence of long-wavelength magnetization fluctuations. Using micromagnetic theory, it is shown that this type of angular anisotropy is the result of the presence of unavoidable magnetic poles in the bulk of the magnet. Although the microstructure of the material consists of micron-sized $Nd_2Fe_{14}B$ grains that are separated by a (low volume fraction) nanometer-sized Nd-rich phase, the SANS signal contains a significant contribution due to spin misalignment, which is evidenced by an enhanced scattering signal along the direction of the applied field. The origin of this spin misalignment is presumably related to the perturbing effect of the Nd-rich interphases. Analysis of the SANS data in terms of the autocorrelation function of the spin misalignment provides an almost field-independent length scale $l_C \sim 40$ nm. Comparison of our results with a phenomenological expression for l_C based on micromagnetic theory suggests that the large anisotropy field of the $Nd_2Fe_{14}B$ phase reduces the size of gradients in the spin microstructure, so that, for hard magnetic materials, l_C represents the (field-independent) size of the characteristic defect in the microstructure.

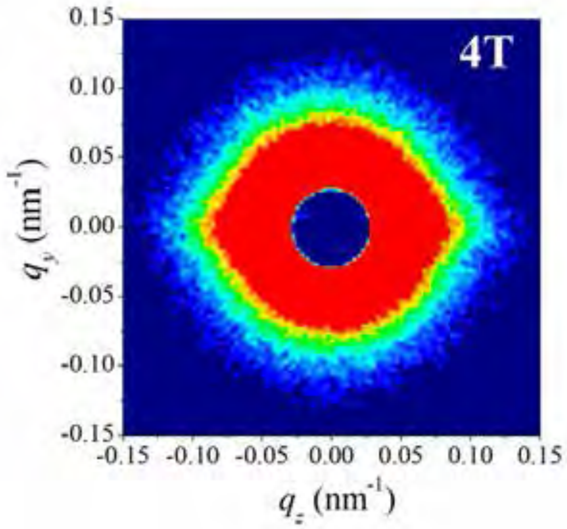

Figure 1 – Color-coded map of the experimental unpolarized scattering intensity $d\Sigma/d\Omega$ of a sintered (untextured) Nd–Fe–B permanent magnet at 4T (taken from Ref. [1]).

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↘ Flash Talk: Wed-F-M1

EVALUATION OF LOCAL STRUCTURE AND NANO QUASICRYSTAL-FORMATION IN Zr-BASED GLASSY ALLOYS CONTAINING NOBLE METALS

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Recently, development of alloy composition with a high stability of supercooled liquid state (*i.e.*, a metastable liquid state below melting temperature) has enabled us to produce the glassy metallic materials with bulky shape. It has been suggested that the unique local structure contributes to form such the stable supercooled liquid. Due to a number of reports on the primary precipitation of the nano scale icosahedral quasicrystalline (QC) particles in several Zr-based glassy alloys by addition of minor elements [1-4], we have investigated that an icosahedral local atomic configuration exists and significantly plays a role for the stability of supercooled liquid [5].

Noble metals such as Pd and Pt are known as QC-forming elements in $Zr_{70}Cu_{30}$ glassy alloy [6]. These elements might change the local atomic structure, leading to a change in transformation behavior with QC precipitation. The QC phase usually precipitates with a compositional partition from the glassy structure. Such precipitation takes place abruptly above a certain temperature, which might result from a cooperative-like motion of icosahedral clusters [7]. We have investigated the two types of icosahedral polyhedra in the glassy state: one is a large cluster having a relatively perfect icosahedral structure formed around the Zr atoms [8]. The other has comparatively small size in a distorted configuration around the solute atoms. The medium-range order (*i.e.,* QC nucleus) has a core of the Zr-centered icosahedral cluster, and the QC grows via aggregation of possible small icosahedral clusters surrounding QC nucleus. Noble metals stabilize individual Zr-centered icosahedral clusters, facilitating the formation of the nucleus and growth of the QC phase.

In the presentation, we intend to survey the nano QC phase precipitation process related to the icosahedral local structure analysis using X-ray scattering, TEM and so on. The study is evaluated as a novel approach of investigation of the formation and structure of glassy structure.

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INITIAL MAGNETIZATION PROCESS OF NANOCRYSTALLINE ND-FE-B MAGNETS

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After the discovery of $Nd_2Fe_{14}B$, enormous efforts have been made to improve magnetic performance of Nd-Fe-B permanent magnets as the importance of strong permanent magnets is growing to build the society with high energy efficiency[1,2]. However, some basic phenomena such as initial magnetization and reversal processes in the magnets have not been deeply understood due to the complexity from inhomogeneity and multiscale structures of real magnets. Most of the related researches are based on the microscopic observations and there are only few bulk experiments except some attempts to understand the physical picture of initial magnetization via macroscopic measurements[3,4]. SANS is a suitable probe to investigate initial magnetization and reversal processes inside bulk magnets which involve the development of magnetic domains with nano/micrometer size. We have conducted SANS experiments on the initial magnetization process in nanocrystalline Nd-Fe-B magnets with different grain boundary width to investigate the relation between microstructure and initial magnetization. SANS experiments were carried out at QUOKKA, ANSTO. 2D SANS images for a sample with the shortest grain boundary width is shown in Figure 1. Strong intensities along a direction perpendicular to the easy axis is observed for thermally demagnetized state at 0 T (upper image) and it decreases with increasing external field *H* (lower image). Qualitatively difference in 2D SANS images between samples with different grain boundary width and their origin will be discussed.

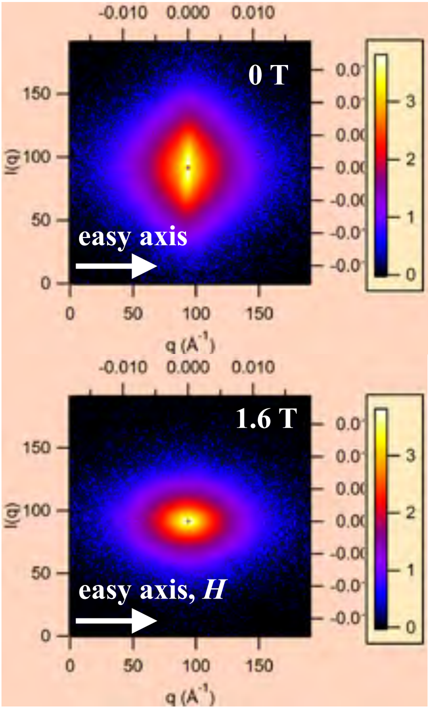

Figure 1: SANS images of a nanocrystalline Nd-Fe-B magnet in the initial magnetization process.

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↘ Flash Talk: Wed-F-M1

CU PRECIPITATION ANALYSIS IN STEEL USING SANS

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The Cu precipitation kinetics during martensite tempering of an Fe-0.44C-0.60Mn-0.21Si-0.11Cr-1.53Cu (wt.%) steel was quantitatively investigated by separating the Cu precipitation from the cementite precipitation through electrical resistivity, small-angle neutron scattering (SANS) and thermodynamic calculations. The cementite precipitation was already finished during continuous heating to 450 ^{O}C, and then Cu precipitation occurred above 450 ^{O}C. The Cu precipitation kinetics was accelerated with increasing tempering temperature. The fcc ε-Cu particles were precipitated mainly at cementite interfaces, while bcc Cu-rich particles were formed in the tempered martensite matrix, and transformed to 9R, 3R, and fcc ε-Cu during further tempering, resulting in higher hardness of a medium C steel.

STUDY OF TEMPERATURE BEHAVIOR OF CRITICAL FIELDS IN FERROMAGNETIC INVERSE OPAL-LIKE STRUCTURES

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Inverse opal-like structures (IOLS) can be synthesized by filling the voids of opal templates with suitable structure-forming precursors and subsequent removal of the initial microspheres to leave three-dimensionally ordered porous materials. The inverse opals based on the ferromagnetic metals (Ni, Co, etc) represent a new class of the 3-dimensional nanoscale ferromagnetic structures, which are geometrically frustrated at room temperature.

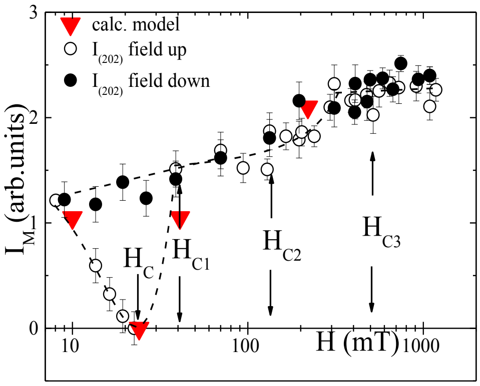

Fig. 1 The dependence of intensity on the external magnetic field for Co IOLS

By small-angle neutron diffraction intensities of magnetic scattering as a function of external magnetic field for crystallographic planes of {202}-family at room temperature were obtained [1]. The presence of the Bragg reflections of the magnetic nature in the same area where the structural reflexes, indicates a strong correlation of magnetic and spatial structures of IOLS. It is assumed that the magnetic structure of inverse opals is a system of 4 magnetic subsystems, directed along four different <111> axes of the fcc structure. Different subsystems are magnetizing in different critical fields, so the magnetic scattering function has a stepped look (Fig. 1). One can distinguish critical values of the magnetic field H_C, H_{C1}, H_{C2}, H_{C3} – coercivity; inflection field point; field point, where two branches come together; saturation field.

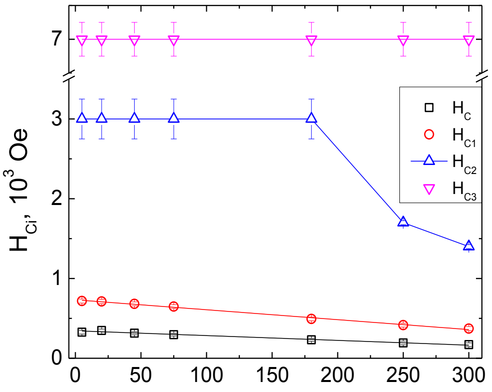

Fig. 2 Dependencies of critical fields on the temperature for Ni IOLS

For more detailed analysis of the behavior of the critical fields as a function of temperature the method of SQUID-magnetometry was used. Remagnetization curves for Co and Ni IOLS with thickness of 13 mkm at temperatures of 5, 20, 45, 75, 180, 250, 300 K were obtained. For all the dependencies the critical fields were determined (Fig. 2). It was found that coercive force and value of H_{C1} field linearly decreases with increasing of temperature for Co and Ni IOLS. The value of H_{C2} at first has a constant value, but further decreases sharply at 180 K for Ni and at 75 K for Co IOLS. Saturation field H_{C3} does not change value in the whole temperature range for Ni IOLS, and linearly decreases with increasing of temperature for Co IOLS.

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FORMATION AND DISSOLUTION OF γ' PRECIPITATES IN IN792 SUPERALLOY AT ELEVATED TEMPERATURES

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The important high-temperature materials - nickel based superalloys - are natural composites consisting of γ' precipitates ($L1_2$) with an ordered structure coherently embedded in a γ solid solution (fcc) [1]. Morphology of γ' precipitates after the standard heat treatment is mostly cuboidal with dimension in range 100 – 700 nm.

The neutron scattering offers a unique tool for ex- and in-situ bulk investigation of microstructure of superalloys. A full characterization of medium and also small additional precipitates by small-angle neutron scattering (SANS) was carried out in the past e.g. for Inconel type superalloy IN738LC [2]. It was found that the equilibrium volume fraction of γ'-precipitates in the temperature range RT-825°C is significantly higher than previously reported.

From the ex-situ SANS test with IN792 superalloy, it was known that an additional precipitation occurs at 700°C also in this superalloy. The subsequent in-situ experiment focused on formation and dissolution of γ' precipitates at elevated temperatures in IN792.

The temperature profile (Fig. 1) used in the present in-situ experiment (SANS-II at SINQ, PSI Villigen) enabled to asses formation of small precipitates (slow kinetics) in the temperature range RT-800°C, their dissolution up to 900°C as well as the dissolution of larger precipitates above 900°C. Fig. 1 displays the integral scattered intensities at small angles (for SDD=1.2m, λ=6.21 Å) at various temperatures. The integral intensities at selected temperatures indicate the evolution of volume fraction of small precipitates which are created on heating above 575°C. Their disappearance above 700°C is caused by their growth and (at higher temperatures) also by their dissolution which results in their complete vanishing at 900°C. The small and medium-size γ´ precipitates influence mechanical parameters which exhibit an anomaly around 700°C.

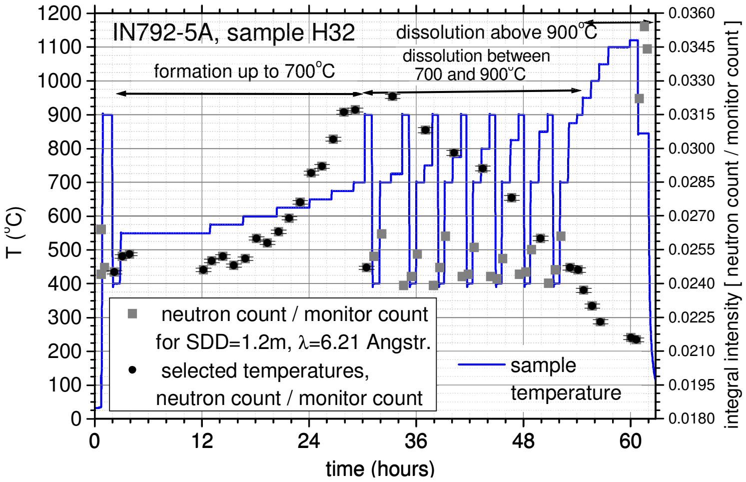

Figure 1: Integral intensities at small angles in dependence on thermal treatment of the IN792-5A superalloy.

GACR project No. 14-36566G support is acknowledged.

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MULTIPLE-SCATTERING EFFECT ON SMALL-ANGLE NEUTRON SCATTERING FOR ND-FE-B MAGNETS

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Small-angle neutron scattering (SANS) have been recognized as a powerful experimental technique to characterize bulk properties of ferromagnetic materials such as Nd-Fe-B permanent magnets [1–3]. However, multiple scattering often arises if the sample is and blurs “true” signal from the single-scattered neutrons. In this study, we investigated the multiple-scattering effect on SANS for sintered (^{11}B substituted) and hot-deformed Nd-Fe-B magnets. By utilizing the continuous-wavelength neutrons from the pulsed neutron source, one can simultaneously measure wavelength and scattering-vector (q) dependent SANS intensities and transmissions.

SANS experiments were performed at BL15 TAIKAN at the J-PARC/MLF, at the Quokka at the OPAL, ANSTO, and at the V4 at the BER-II, HZB. Nd-Fe-B magnets were cut to plate-shaped samples with various thicknesses (sintered: 0.5 and 1.0 mm, hot-deformed: 0.91, 0.47, and 0.24 mm). All samples were thermally demagnetized at 400ºC in a vacuum furnace in advance. Pulsed neutron beam with continuous-wavelength (λ = 0.7–7.5 Å) was used at the TAIKAN. The experiment was performed at room temperature.

Wavelength-dependent transmission (Tr) shows a steep reduction for the hot-deformed 0.91-mm-thick sample (Tr ~ 0.8 for λ = 0.7 Å to Tr ~ 0.2 for λ = 6 Å). It indicates the sizable effect of multiple scattering for longer wavelength neutron in this sample. On the other hand, for the hot-deformed 0.24-mm-thick sample, Tr is more than 0.8 for λ < 4 Å. Detailed analysis of the multiple-scattering effect on the transmission and the wavelength dependent SANS intensities for the samples with various thicknesses and ^{11}B substitution will be discussed.

This work was supported by ESICMM under the outsourcing project of MEXT, Japan. Sample preparation was performed under the future pioneering program “Development of magnetic material technology for high-efficiency motors” commissioned by NEDO, Japan. SANS experiments were performed at J-PARC/MLF (proposal No. 2014E002), at ANSTO proposal No. 4140), and at HZB (proposal No. 14100745-ST).

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MAGNETIZATION REVERSAL PROCESS OF ND-FE-B NANOCRYSTALLINE MAGNETS OBSERVED BY MAGNETIC SANS

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Development of the permanent magnet materials with high coercive force is highly demanded from the viewpoint of industrial application such as motors for hybrid or electric vehicles. Phenomenological model of the coercive force proposed by Kronmüller is following: $H_c = \alpha H_a - N_{eff}M_s$. The coercive force ($H_c$) is determined from the anisotropy field (H_a), the saturation magnetization (M_s), and microstructural parameters: α and the effective demagnetization factor (N_{eff}). Rare-earth iron boride $Nd_2Fe_{14}B$ exhibits both high anisotropy field and high saturation magnetization and the $Nd_2Fe_{14}B$-based permanent magnets are widely used. However, in order to enhance the coercive force farther, the heavy rare-earth elements Dy, which is one of the critical elements with supply instability, are substituted to Nd. Therefore, the development of Dy-reduced and/or Dy-free permanent magnet material is a matter of urgency. Reduction of the $Nd_2Fe_{14}B$ grain size is a way to realize Dy-free Nd–Fe–B magnet with high coercive force. Hot-deformed Nd–Fe–B nanocrystalline magnets consist of $Nd_2Fe_{14}B$ grains of several 100 nm. Furthermore, the infiltration of RE–Cu (RE = Pr or Nd) eutectic alloy enhances their coercive force.

In order to unveil the microscopic mechanism of the coercive force, we have conducted magnetic small-angle neutron scattering (SANS) study on as-deformed and RE–Cu-infiltrated Nd-Fe-B nanocrystalline magnets. The SANS experiment was performed at the V4 beamline at the BER-II in Helmholtz-Zentrum Berlin. SANS intensities were obtained during the magnetization reversal process from the fully magnetized initial state. Scattering intensities along the perpendicular direction to the nominal [001]-axis were maximized at the coercive force in all samples. External magnetic field dependence of the magnetic scattering intensity showed the suppression of the intensity variation in the RE–Cu-infiltrated samples compared to the as-deformed sample [1,2]. It is indicated that the $Nd_2Fe_{14}B$ grains are magnetically isolated in the RE–Cu-infiltrated Nd-Fe-B nanocrystalline magnets that result in the higher coercive force than that of as-deformed one.

This work was supported by ESICMM under the outsourcing project of MEXT, Japan. Sample preparation was performed under the future pioneering program “Development of magnetic material technology for high-efficiency motors” commissioned by NEDO, Japan. We thank HZB for the allocation of neutron beamtime (proposal No. MAT-04-2110).

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Quantitative analysis of nanometer precipitates in copper foil by using small-angle X-ray scattering

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The electrolytic copper foil is applied in printed circuit board and Li ion secondary batteries. Recently, the high-strength copper foil is called for in Li ion secondary batteries which carried the silicon as cathodes materials. This mechanical property of the electrolytic copper foil is controlled by adding some organic substances to an electrolysis solution. It is thought that these organic substances are decomposed minutely and taken into the electrolytic copper foils. However, the metallographic structure of the electrolytic copper foil in nano-scale has not been analyzed yet in detail. Therefore, we investigated this nano-structure.

We succeed in observing nanometer precipitates in the electrolytic copper foil by using Transmission Electron Microscope (Figure.1). On the other hand, the quantitative analysis of these precipitates was performed by Small-Angle X-ray Scattering (Figure.2). We estimated that these precipitates are organic substances added when making electrolytic copper foil and play a role of Zener's pinning effect of stopping crystal growth.

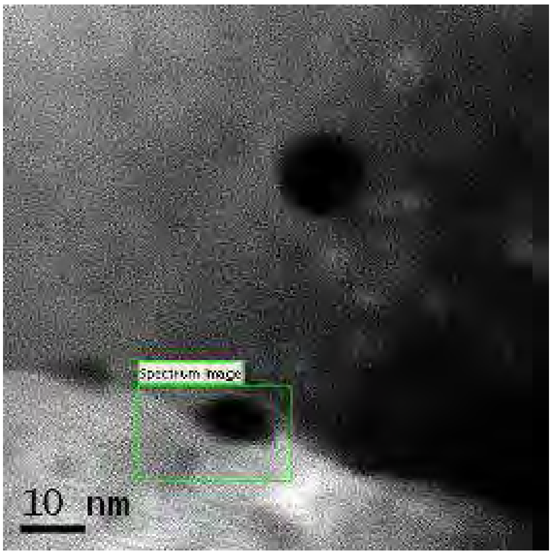

Figure 1 : HAADF-STEM image of nanometer precipitates.

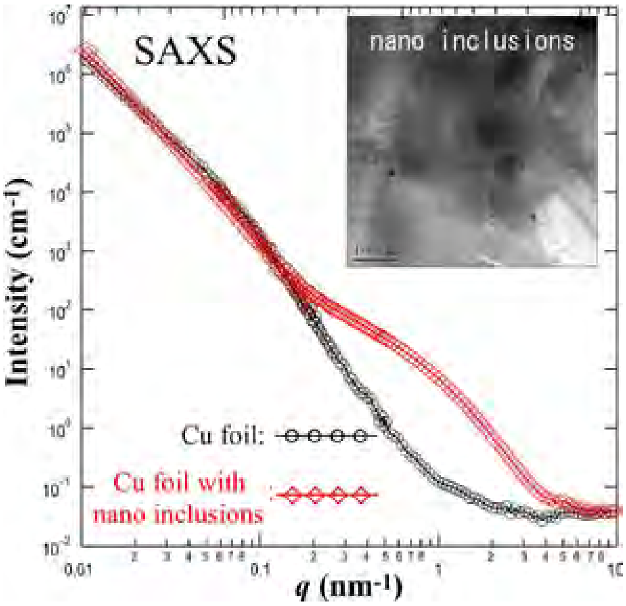

Figure 2 : SAXS profile of the electrolytic copper foil.

References

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DEFECT STRUCTURE IN CERIA/SILICA IRRADIATED WITH SWIFT HEAVY IONS

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High electronic excitations generated by swift heavy ion irradiation produce characteristic defects in insulatior materials. These defects, so called ion tracks are expected to be modifications for optical properties and are concerned as crucial dameges to fuel materials in nuclear power plant. Ceria (CeO_2) has received considerable attention as a surrogate material for investigating radiation effects of uranium dioxides, because of its identical crystal structure and similar material's properties [1]. Moreover, amorphous silica (a-SiO_2) also draws much attention for nano-fabrication by ion tracks. The present study aims to gain insights into the defect structure evolution in CeO_2 deposited on a-SiO_2 by using synchrotron SAXS.

Ceria samples were prepared by Pulsed laser deposition (PLD) technique using an excimer KrF* laser source (λ= 248 nm). The sintered CeO_2 was used for targets of PLD. High purity a-SiO_2 plates were used as substrates. The thin film samples were irradiated with 200 MeV Xe ions at an ambient temperature to a fluence of 3×10^{11} ions/cm^2. The SAXS measurements were carried out at the beamline 10C at the Photon Factory in KEK using an X-ray wavelength of 1.5 Å and a camera length of 1 m. Images were taken in transmission geometry with using the Pilatus 2M detector.

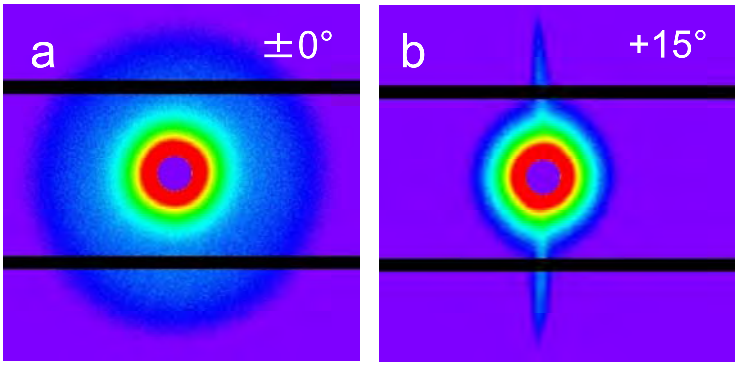

Figure 1: SAXS images of CeO_2/SiO_2 irradeated with 200 MeV Xe ions to a fluence of 3×10^{11} ions/cm^2. (a) Traks collinear with the X-ray beam and (b) 15° tilted with respect to the X-ray beam.

Figure 1 shows SAXS images of the sample irradiated with Xe ions recorded on the detector under different angles of the X-ray incidence (0° and 15°) with respect to the direction of the incidence of Xe ion beam. Under tilted X-ray beam incidence, the scattered intensity is highly anisotropic and concentrates in curved steaks, due to the anisotropic originates from the high aspect ratio of cylindrical shape of the ion tracks [2].

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FOLLOWING VIRUS LIKE PARTICLES ASSEMBLY USING TIME RESOLVED SMALL ANGLE X-RAY SCATTERING

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Viruses are evolved examples of self-assembled structures. This ability to self-assemble can be harnessed for nano- and biotechnology. Viral capsids and capsid proteins have been used to assemble structures for guided synthesis of inorganic and organic nanostructures, as cages for packaging cargos, and as vectors for gene therapy. The mechanisms by which spherical viruses assemble from hundreds of capsid proteins around nucleic acid, however, are yet unresolved.

In our previous work [1], by using time resolved small angle x-ray scattering (TR-SAXS) we were able to directly visualize Simian Virus 40 (SV40) viral proteins encapsidating short ssRNA molecule. The assembly process yields $T = 1$ icosahedral virus like particles (VLPs) comprised of 12 protein subunits and one RNA molecule. The reaction is nearly 1/3 complete within 35 milliseconds, following a rapid two–state kinetic process with no detectable intermediates.

As opposed to SV40 derived VLPs, core capsid proteins of the Hepatitis B Virus (HBV) can assembled without a nucleic acid template, forming either $T = 4$ or $T = 3$ icosahedral empty particles, comprised of 120 and 90 protein subunits, respectively. This one component, assembly system presents a simplified, yet a much more challenging case for studying the basic principles governing the assembly process of spherical viruses.

In order to follow the assembly process of HBV derived empty VLPs, we are combining static and time resolved SAXS data from 3rd generation synchrotrons, structural data form x-ray crystallography and unique SAXS analysis tools, developed in our lab. Using our modeling tools we are able to generate scattering intensities of a large number of possible assemblies, ranging from a single dimer to a complete 120-mer capsid. Together with global fitting procedures we are trying to find the distribution of assemblies that best fit our TR-SAXS data at each measured time point during the assembly process.

Our most recent results indicate that only a small number of intermediates structures is dominant throughout the assembly process. The same intermediates appeared throughout the assembly at different solutions conditions implying these are possible critical stages for a successful assembly of the capsid.

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PROBING pH- AND CO-FACTOR DEPENDENT CONFORMATIONAL TRANSITIONS OF VON WILLEBRAND FACTOR BY SMALL ANGLE X-RAY SCATTERING

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Von Willebrand factor (VWF) is a large blood glycoprotein sensing shear flow irregularities in the blood stream. At sites of vascular injury, VWF extends and subsequently promotes platelet adhesion (2). Since formation of a platelet plug is essential for primary hemostasis, defects in or deficiency of VWF can lead to severe bleeding symptoms, as for instance found in von Willebrand disease (3). VWF exists as a multimer with a variable number of dimeric subunits, which have a mass of ~ 500 kDa. Recently, it was found that pH conditions influence the static structure of VWF dimers (1). At pH 6.2, characteristic of the environment in the Golgi apparatus, VWF dimers form an elongated dimeric bouquet (Fig. 1), as judged from class averages of EM images. In contrast, at a pH of 7.4 (the physiological pH in blood) the dimeric bouquet structure was lost and dimeric VWF was suggested to be completely flexible. However, single-molecule AFM force spectroscopy and AFM imaging data indicate conformational transitions in the dimer even at pH 7.4, a finding at odds with the proposed complete flexibility of the dimer under these conditions.

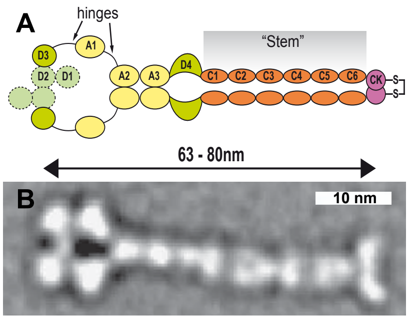

Figure 1 (A) Structure of dimeric VWF at pH 6.2 and the corresponding EM image **(B)** as observed by Ref. (*1*).

We have used SAXS to probe the solution structure of dimeric VWF both at pH 6.2 and 7.4, as well as both in the presence and absence of the co-factor Ca^{2+}. We find that the overall conformations in solution are similar for pH 6.2 and 7.4 when Ca^{2+} is present, indicating that the structure of the dimer stem is not completely lost upon changing pH. However, we find that VWF dimers exhibit a flexible behavior when EDTA is dissolved and no Ca^{2+} is added to the solution. Our preliminary results indicate that SAXS is well suited to dissect the conformational changes under varying solution conditions for this very large protein complex.

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ADVANCED SAMPLING AND ATOMISTIC MODELING FOR STRUCTURAL INTERPRETATION OF SMALL ANGLE SCATTERING

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As part of an US-UK Collaborative Computational Project for advanced analyses of structural data in chemical biology and soft condensed matter (CCP-SAS), we have been developing new sampling algorithms and exploring appropriate atomistic models for more reliable structural interpretation of small angle scattering data of soft matter. In this poster, we will present our latest development of hybrid Monte Carlo (MC) and torsion angle molecular dynamics (TAMD) implemented the SASSIE software package. The basic idea is to first generate a broad conformational ensemble using MC moves along a small number of selected backbone dihedral angles and then perform short TAMD simulations on representative configurations for detailed sampling of local conformational space. A particular advantage of TAMD compared to traditional Cartesian molecular dynamics is that TAMD allows arbitrary classification of “rigid” and “flexible” regions for detailed sampling. At present, the new sampling protocol is coupled to an efficient solvent-accessible surface area (SASA) implicit solvent and tested on a range of biomolecules including proteins, nucleic acids and carbohydrates. The results demonstrate clear improvement over the previous MC sampling in terms of detailed sampling of relevant conformational space. At the same time, our initial tests also reveal important limitations in the SASA implicit solvent model and substantial challenges in identifying efficient atomistic force fields that maybe suitable for the general application to high-resolution SAS analysis.

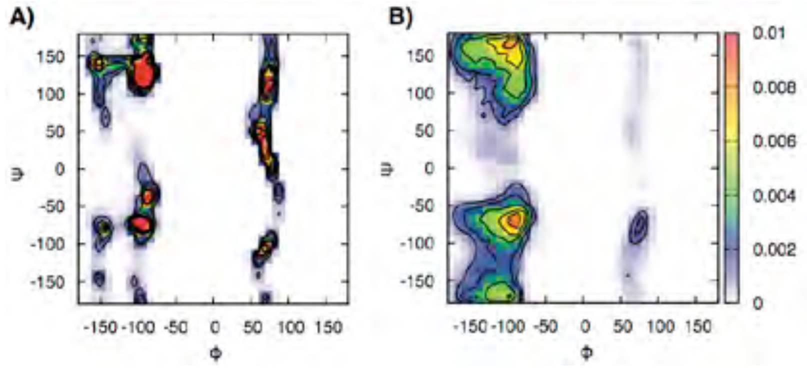

Figure 1. A representative Ramachandran plot for residue 124 in the Gag protein A-B system. A) Dihedral space sampled by 17500 MC configurations generated using only residue 124 as the flexible region. B) Dihedral space sampled by MC combined with TAMD simulations. 175 representative configurations are pick out from 136281 MC con- figurations and performed 1 ns of TAMD simulation. Totally 17500 structures are used in calculating Ramachandran plot.

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BIOSAXS-2000 ADVANCES FOR BIOLOGICAL SOLUTION SCATTERING

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Small angle X-ray scattering (SAXS) is a useful technique for extracting structural information from biological samples in solution. However, the X-ray scattering signal from macromolecules is challenging to measure because of low particle concentrations and high background from solvent. As a result, instrument designs for home laboratories, where X-ray intensities are lower than synchrotrons, require special scrutiny. In particular, collimation design, X-ray source and area detector contribute greatly to improved data quality for home laboratory experiments.

Recently, Rigaku introduced the BioSAXS-2000, a SAXS instrument for the home lab, which combines 2D Kratky collimation with confocal optics to achieve maximum X-ray flux on the sample without the hassle of data desmearing. The BioSAXS-2000 uses a hybrid pixel array detector (HPAD), the PILATUS3 R 100K, manufactured by Dectris. HPADs are ideal for measuring weak scattering from biological solutions because they combine ultra low noise, high dynamic range and direct detection of X-ray photons. In fact, HPADs are the detector of choice for most SAXS beamlines and modern home laboratory SAXS instruments. Results with the BioSAXS-2000 consistently show that this instrument produces high quality SAXS data in minutes.

The BioSAXS-2000 includes an AUTO package that includes automation tools to achieve unattended SAXS data collection and analysis. The BioSAXS AUTO package includes a 96-sample Automatic Sample Changer and an Automatic Analysis Pipeline (AAP). The AAP uses the industry standard ATSAS package for automatic data processing and analysis. Here, we describe advances to the BioSAXS-2000 system and updates for automated tools

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STRUCTURE OF INORGANIC PYROPHOSPHATASE AND OF ITS PROTEIN-PARTNERS IN SOLUTION STUDIED BY SAXS

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E. coli inorganic pyrophosphatase (PPase) [1] supports a lot of endergonic metabolic processes where diphosphate is produced. It is well-characterized both functionally and structurally, but a PPase's role in the interactome is poorly understood. Biochemical analysis gave evidence of interaction between PPase and other enzymes involved into metabolic regulation [2]: fructose-1,6-bisphosphate aldolase class I (FbaB) with unknown up to now structure and functions [3]; 5-keto 4-deoxyuronate isomerase (KduI) involved in pectin degradation [4]; and glutamate decarboxylase (GadA) catalyzing the decarboxylation of glutamate to γ-aminobutyrate [5]. Investigation of interacting proteins is an important instrument to elucidate mechanism of the regulatory networks formation. However, such kind of structural analysis, first of all, requires information on structure and behavior in solution of each of the components of the expected complexes. That is why the present work focuses on comprehensive analysis of structural aspects of the behavior in solution of the above enzymes. It allows one also to get insight into their functional properties and to understand the role of the enzymes in cell activity. To reach the goal of the work we used small-angle X-ray scattering as one of the powerful tool to study biological objects in solution, i.e. in nearly physiological conditions.

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STRUCTURAL INSIGHTS INTO THE SHAPE AND ASSEMBLY OF PHOTOSYNTHETIC GAPDH/CP12/PRK COMPLEX BY SMALL ANGLE X-RAY SCATTERING

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Photosynthetic organisms produce sugars through the Calvin-Benson cycle, consuming carbon dioxide and energy provided by the conversion of light to chemical energy. The smooth proceeding of photosynthesis is controlled by different regulatory systems including the transient formation of protein complexes. Through the scaffold protein CP12, which is predicted to be intrinsically disordered, two enzymes of the cycle, glyceraldehyde-3-phosphate dehydrogenase (tetrameric GAPDH) and phosphoribulokinase (dimeric PRK), are regulated by formation of a supramolecular ternary complex of 498 kDa with stoichiometry [GAPDH-$(CP12)_2$-$(PRK)]_2$ [1,2]. The activities of GAPDH and PRK enzymes are inhibited by complex formation and fully recovered upon dissociation of the complex at the onset of light, providing an effective means for regulation of the Calvin cycle *in vivo* [3].

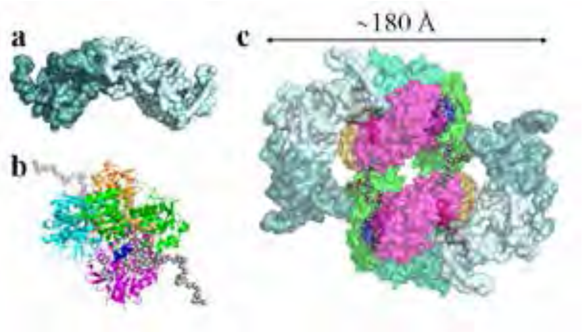

Figure 1: Proposed low-resolution models of: a)PRK dimer, b)GAPDH-CP12 binary complex, c) GAPDH-CP12-PRK ternary complex.

Small angle X-ray scattering analysis was performed on the pre-formed complex and its free components all from *Arabidopsis thaliana*, and the ATSAS package was used for data analysis and modeling [4]. A concave bent and screwed *ab-initio* shape of the PRK dimer was recovered, while a combined rigid-body/dummy-residue model was obtained for the GAPDH-$(CP12)_2$ binary complex in order to take into account a small rearrangement of the known crystallographic subunits positions [2] and the missing CP12 aminoacids (Figure 1, a and b). These models were then used in the rigid-body modeling of the ternary complex against the experimental scattering curve, allowing for partial dissociation [5]. The known stoichiometry of the complex was confirmed and from the sorting of a big number of models obtained with multiple runs of the minimization procedure, an overall reproducible assembly emerged (Figure 1, c). The structure of the ternary complex appears more compact with respect to the previous pictorial models and the two GAPDHs proximity suggests an unsuspected involvement of an interaction between them in the overall complex stabilization.

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NEW LIGHTS ON MULTIMERIC ENZYMES – A COMBINATION OF CHROMATOGRAPHY, SAXS AND SPECTROSCOPY

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While the importance of structure-function relationships has been recognized and their correlation sought after, the underlying molecular mechanisms linking structure to function are elusive. The complexity of sample reactivity and polymorphism are only few reasons amongst other for such difficulties. A relevant way to approach the problem is the combination of techniques that can report on structure and chemistry of the samples. To address this need, we have developed a platform called SURF that consists of synchrotron SAXS, UV-Vis, Raman and fluorescence techniques. The SURF platform provides simultaneous measurements on the same sample volume and a multivariate framework to correlate the spectroscopic and X-ray scattering information.

In this contribution we will illustrate the benefits of SURF in combination with size exclusion chromatography (SEC) to resolve multimeric enzymes structure activity relationship. The enzyme of interest in this case is beta-galactosidase [1], most commonly known as lactase (used to produce lactose free milk). We have combined [2] SEC with a post column reaction loop and our unique multimodal characterization platform (i.e. SURF) [3]. Figure 1 shows the UV trace from the SEC, figure 2 shows the simultaneous and correlated activity (ONPG substrate hydrolysis) of the beta-galactosidase using the reaction loop. Figure 2, confirms that the shoulder from figure 1 is indeed an active oligomeric form of beta-galactosidase. Figure 3 shows the fluorescence emission of the eluted peak, and figure 4 the SAXS intensity at zero-angle, I(q=0) directly proportional to the size and molecular weight of the eluted species.

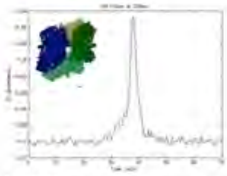

Figure 1. UV trace at 280nm. Inset beta-galactosidase tetramer

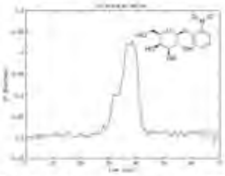

Figure 2. UV-Visible trace at 405nm, characteristic of the catalysis of ONPG. Inset ONPG.

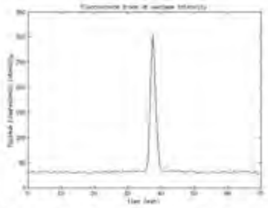

Figure 3. Beta-galactosidase fluorescence emission trace at maximum emission intensity

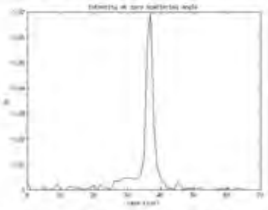

Figure 4. Zero angle intensity (Io) from SAXS

In this contribution, we will show that the combination of techniques with a suitable analysis framework has the inherent capacity to resolve the structural composition of complex system.

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MODELING THE COMD/COME/COMCDE INTERACTION NETWORK USING SMALL ANGLE X-RAY SCATTERING

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Natural transformation contributes to the maintenance and to the evolution of bacterial genomes. In *Streptococcus pneumoniae*, this function is reached by achieving the competence state, which is under the control of the ComD-ComE two component system, via the phosphoregulation of ComE. The crystal structure of non-phosphorylatable ComE^{D58A} mutant revealed an asymmetric dimer, each chain comprising two domains, a regulation domain REC and an effector domain LytTR, separated by a linker. In contrast, Small-angle X-ray scattering (SAXS) measurements showed that ComE^{D58A} is monomeric in solution, whereas the ComE^{D58E} active mimic mutant dimerizes via its REC domains. In a second step, we investigated the binding between ComE, the catalytic domain of ComD (ComD^{catdom}) and the promoter region *comcde*, using SAXS. ComD^{catdom} appears to be a dimer that accommodates two monomers of ComE, one on each side, positioning ^{ComE}D58 residue in front of ^{ComD}H248, a location that is convenient for the intermolecular transfer reaction of the phosphoryl group. All three complexes of *comcde* with LytTR, ComE^{D58A} and ComE^{D58E} have a stoichiometry of two protein molecules per DNA duplex. Modeling the complexes against small angle X-ray scattering data using EOM indicated that ComE^{D58E} bound to *comcde* forms a compact dimer similar to the crystal structure, whereas ComE^{D58A}–*comcde* adopts more than one conformation with or without dimer contacts (see Figure 1). The monomeric and dimeric states of ComE induce different bending angles of the promoter, thereby providing a mechanistic scenario for the activation of ComE: the phosphorylation of ComE forces additional bending of *comcde*, while the release of this bending strain on DNA via the disruption of the ComE dimer may signal the shut-off of the competence state.

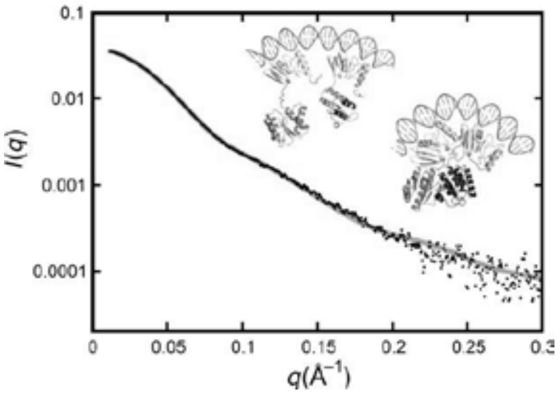

Figure 1: ComE^{D58A}-*comcde* complex SAXS analysis.

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THE SMALL-ANGLE X-RAY SCATTERING CORE FACILITY OF CENTER FOR CANCER RESEARCH OF NATIONAL CANCER INSTITUTE

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Small-angle X-ray scattering (SAXS) is a complementary technique to Macromolecular Crystallography and NMR techniques and is becoming more widely used in structural biology. Crystallography requires good crystals and NMR limits to biomolecules with low molecular mass. SAXS allows studying the structure of macrobiomolecules and their complexes in near physiological environments and studying structural changes with external conditions. The SAXS core facility of Center for Cancer Research (CCR) of National Cancer Institute, NIH includes in-house state-of-art SAXS instrument and routine access to beamtime from the Advanced Photon Source at Argonne National Laboratory through the existing Partnership User Program agreement. The mission of SAXS core facility is to provide support to research projects from CCR researchers, NIH intramural and extramural research groups/laboratories. It is open to research communities. The research field includes but not limited to structural studies of nucleic acids, proteins, protein assemblies, virus particles, lipid membranes and membrane-protein/DNA complexes. This presentation gives introduction to SAXS core facility of CCR and highlights recent scientific achievements produced by SAXS core facility users.

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EFFECT OF UREA AND TMAO ON LIPID BILAYERS

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Lipid bilayers can display a wide range of morphologies and are simple models for the cell membrane, that not only defines the cell limits but also provides a matrix for anchoring a variety of substances, e.g, membrane proteins, glycolipids, etc., that play an essential role in the cell.

Recently, we have been studying the structural effects of synthetic quinones on lipid model membranes, in order to investigate their contribution to morphologies possibly involved in the electron transfer process. Summarizing, we can say that the insertion of these synthetic additives lower the temperature of the structural phase transitions comparative to pure lipids and in many cases induce the formation of cubic phases at low temperatures, e.g. 30°C, which corresponds to an increase of the lipid matrix surface curvature. The scattering patterns of the cubic phases are clearly identifiable, despite their intrinsic low resolution. In some cases micellar cubic phases were observed.

In this study we shifted our attention to the influence of small molecules such as urea and TMAO. It is accepted that they have antagonistic effects on the fluidity of lipid membranes. In red blood cells, urea slightly increases the gel-phase domains, but this effect is counteracted by TMAO. We intended to determine how these organic solutes affect the structure of a lipid membrane and determine their contribution to the possible curvature induced on them. We could see a change on the temperature of phase transitions and the formation of induced phases or structures.

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THE EFFECT OF ICE ON GLUCOSE DISTRIBUTION IN LIPID MESOPHASES

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In this study we build on our quantitative understanding of the effects of small solute molecules on the phase transitions of lipid mesophases[1-3]. Such systems are used as models to understand the cryoprotective mechanisms of sugars. Previously we have observed the unequal solute partitioning of cryoprotectants in lipid mesophase systems[2]. The concentration of sugar in the lipid mesophase is a significant factor in the efficacy of membrane protection during dehydration and freezing[3]. The formation of ice within a system would be expected to redistribute solutes (excluded from the ice) between the lipid phases and coexisting excess solvent phases. Contrast variation small angle neutron scattering (SANS) is used to measure the match point of the lipid mesophase. We experimentally examine an assumption that the scattering problem may be approximated by two phases (lipid and coexisting excess solvent phases) to directly measure glucose concentration changes in the lipid phase and excess solvent phase of a hydrated dioleoylphosphatidylethanolamine (DOPE) system above and below the freezing point. If this assumption is correct a large change in the partitioning behaviour of glucose was observed which we attribute to the formation of ice in the system, with the ratio of glucose concentration in the excess phase to that in the lipid phase decreasing significantly following cooling from 25 °C to -15 °C. Small angle x-ray scattering measurements correlate these results to the structural changes observed in the system

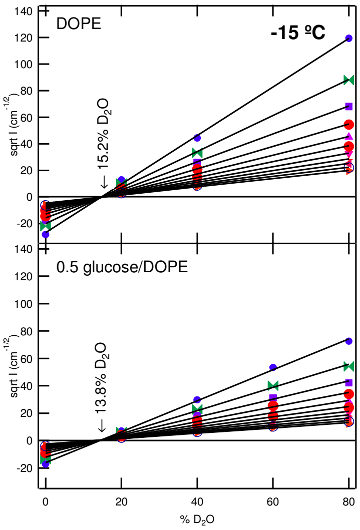

Figure 1: The square root of intensity vs. percentage of D_2O relative to the total water volume for DOPE in abscence and precence of sugar.

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SANS INVESTIGATION OF THE STRUCTURE AND INTERMEMBRANE INTERACTION OF THE ULVs DMPC IN THE SULFOXIDES PRESENCE

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The structure and intermembrane interaction of the fully hydrated unilamellar vesicles (ULVs) DMPC in the Dimethyl sulfoxide (DMSO) and Diethyl sulfoxide (DESO) presence was investigated by small angle neutron scattering (SANS). SANS experiments have been performed on the YuMO spectrometer at the IBR-2 pulsed reactor in FLNP JINR (Dubna, Russia).

The spontaneous formation of the multilamellar vesicles (MLVs) PC membranes from extruded ULVs has been observed (Fig.1). It turned out that the ULVs fusion is caused by two factors: time and increasing of the DMSO and DESO molar concentration. The present work confirms the hypothesis about a crucial role of the hydrophobic interactions in the intermembrane interaction in the presence of sulfoxides. However, it should be noted that these hydrophobic interactions are stronger in the presence of DESO. At first, DESO causes the fusion of the ULVs about 1/2 hour after samples preparation, while this process occurs in an hour in the presence of DMSO. At the second, the investigation in short-term time scale shown that formation of the MLVs take place at X_{DESO} = 0.3 and X_{DMSO} = 0.4. And finally, a number of sulfoxides molecules strongly bound with lipid molecules was determined using contract variation method (Fig.2).

This work was supported by the Romania – JINR (Dubna) Programme 2014 – 2015.

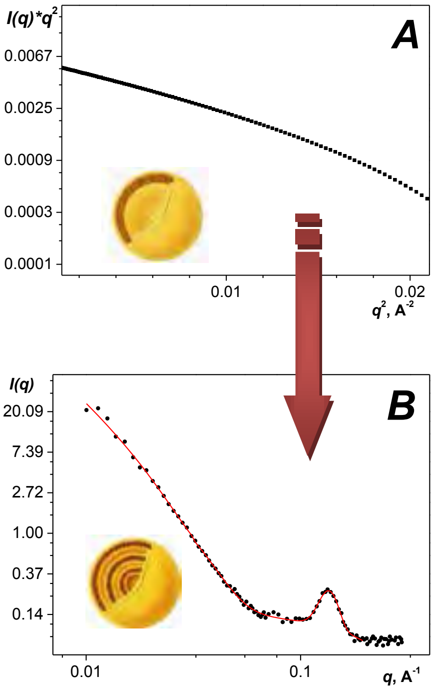

Fig. 1. SANS curves on ULVs DMPC (2 wt %) in DMSO/D$_2$0 mixture at X_{DMSO} = 0.2 in liquid-crystalline phase at T = 55 ºC after preparation (A) and 1 hour later (B).

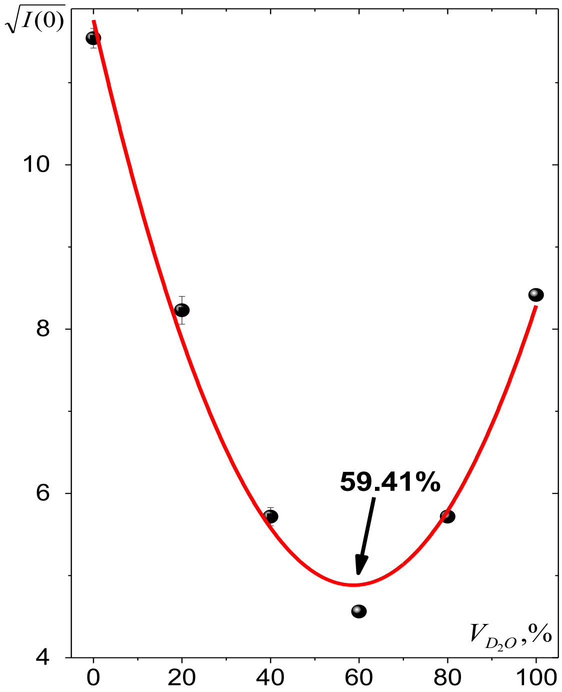

Fig. 2. Square root of intensity vs. D2O volume fraction for ULVs DMPC$_{d54}$ (2 wt %) in DESO/water mixture at X_{DESO} = 0.2 in liquid-crystalline phase at T = 60 ºC.

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FITTING SOLUTION X-RAY SCATTERING DATA BASED ON THE ATOMIC COORDINATES: THE EFFECTS THE DISPLACED AND SURFACE SOLVENT TREATMENT

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Accurate prediction of solution scattering data from atomic coordinates of the biomolecules is extremely important for SAXS applications in structural biology as the errors in data interpretation can propagate into inaccuracies of the models selected by the best fit against the experimental data. Currently available software packages that predict and/or fit SAXS data from the atomic coordinates differ mainly in the manner in which the scattering intensity contributions are calculated for the solvent displaced by the macromolecule and the thin layer of solvent surrounding the macromolecule, either positioning the displaced and/or surface solvent exactly on top of the atomic coordinates, or treating the solvent and the ionic atmosphere via explicit molecular dynamics simulations.

Our own approach AXES is a hybrid between the two as it calculates solvent contributions from snapshots of a simulation of a uniformly filled water box placed on top of the macromolecular coordinates. In this study we investigate the impact of varying the parameters describing the contrast of the surface solvent layer relative to protein/RNA/DNA, on the quality of the SAXS data fit.

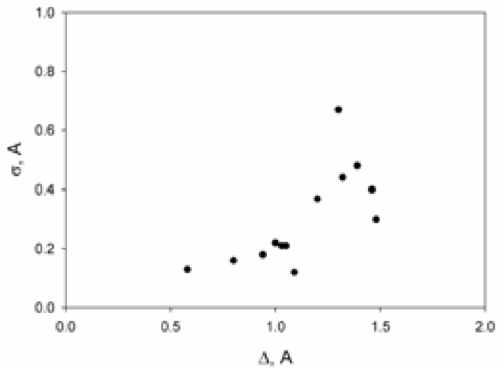

Figure 1: Correlation between the fitted thickness of the surface solvent layer around proteins and its offset relative to the protein atomic coordinates.

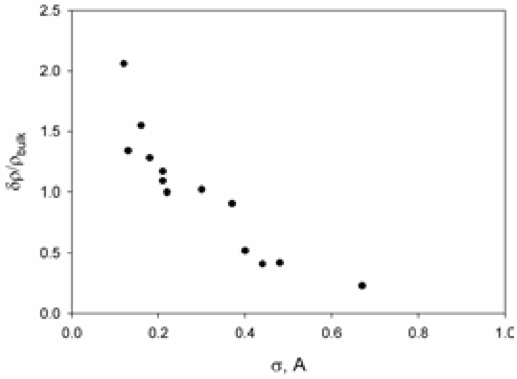

Figure 2: Correlation between fitted contrast and the thickness of the protein surface solvent layer.

In order to increase the confidence in the conclusions reached, the evaluation is performed over an extensive set of high-quality data and the associated structural models that includes the BioISIS database, making for ~20 protein, RNA, and DNA entries in total. The fitted values of the surface solvent parameters support a thin and dense surface layer positioned relative to the macromolecular surface in general agreement with the results obtained via molecular dynamics simulations in explicit water (Figures 1 and 2). The parameters of the optimized solvent model are expected to improve our ability to accurately interpret SAXS data based the biomolecular coordinates.

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SOLUTION X-RAY STUDIES OF NAD$^+$- and NADH-BOUND ALKYLHYDROPEROXIDE REDUCTASE FROM ESCHERICHIA COLI

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Redox homeostasis is significant for the survival of pro- and eukaryotic cells and is crucial for defense against reactive oxygen species like superoxide and hydrogen peroxide. In *Escherichia coli*, the reduction of peroxides occurs via the redox active disulphide center of the alkyl hydroperoxide reductase C subunit (AhpC), whose reduced state becomes restored by AhpF. The 57 kDa *Ec*AhpF contains an N-terminal domain (NTD), which catalyzes the electron transfer from NADH via an FAD of the C-terminal domain into *Ec*AhpC. The NTD is connected to the C-terminal domain via a linker. The NADH-bound form of *Ec*AhpF reveals that the NADH-binding domain is required to alter its conformation to bring a bound NADH to the *re*-face of the isoalloxazine ring of the flavin, and thereby render the NADH-domain dithiol center accessible to the NTD disulphide center for electron transfer. The NAD$^+$-bound form of *Ec*AhpF shows conformational differences for the nicotinamide end moieties and its interacting residue M467, which is proposed to represent an intermediate product-release conformation [1,2]. The structural alterations in *Ec*AhpF due to NADH- and NAD$^+$-binding in solution are shown by small angle X-ray scattering studies (unpubl. data). The *Ec*AhpF is revealed to adopt many intermediate conformations in solution to facilitate the electron transfer from the substrate NADH to the C-terminal domain, and subsequently to the NTD of *Ec*AhpF for the final step of AhpC reduction. In addition, the extent of conformational flexibility of the NTD in solution will be presented (unpubl. data).

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CROWDING EFFECT ON PROTEIN STRUCTURE STABILITY CLARIFIED BY X-RAY AND NEUTRON SCATTERING

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As the interior of cell is crowded with macromolecules (30-40 % v/v), proteins are designed to function in crowding environments. Although there would be no room for doubt in the fact that crowding environment changes the equilibrium states of proteins, interpretations of the crowding-effect remain controversial because structural studies of proteins have been conducted under dilute-solution environments in many cases. On the other hand, hydration of biological macromolecules is the key determinant for isothermal, concentration-dependent effects on protein equilibrium states and activities [1]. The studies using inelastic neutron scattering and molecular-dynamics simulation show that the dynamics of proteins is coupled with water molecules surrounding proteins. However, the role of hydration-shells on the structural stability of proteins under crowding environments is still ambiguous and under intensive issues.

By using synchrotron radiation small- and wide-angle X-ray scattering (SR-SWAXS) and small-angle neutron scattering (SANS), we have studied the effect of crowding environment on both the hydration-shell and thermal structural transition of proteins. We previously demonstrated that the SR-SWAXS method is able to clarify the whole hierarchal structure of proteins (quaternary, tertiary, and secondary structures) in solutions and that the details of the structural transition process of proteins can be analyzed at all hierarchal structure levels [2]. The protein measured was myoglobin. The neutral co-solutes (crowders) used were polyvinylpyrrolidone (PVP, Mt. 40,000) and glycerol. At the low concentration of both crowders, the shrinkage of the maximum dimension and the radius of gyration of myoglobin were observed [Figure 1]. These changes can be explained by a change of hydration-shell density accompanying a suppression of the intramolecular fluctuation by osmotic pressure. At the high concentration, the oligomerization of myoglobin was induced, suggesting the excluded volume effect and the change of the intermolecular interaction (decrease of hydration repulsion). The above effect was much evidently seen for the case of high-molecular weight neutral polymer (PVP). The thermal unfolding of myoglobin was affected by PVP and glycerol in different ways. The transition mid-point temperature descended for PVP and ascended for glycerol. The helix-to-cross-β transition temperature was also affected in the same way. The present results suggest that the presence of co-solutes changes the energetic function of protein through the change of hydrated water.

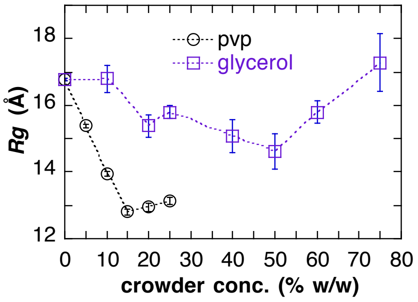

Figure 1. Rg value depending on crowder concentration.

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M.O.S.E.S: MICROSPLITTING FOR ONLINE SEPARATION, EXTENDED CHARACTERIZATION AND SAXS ANALYSIS

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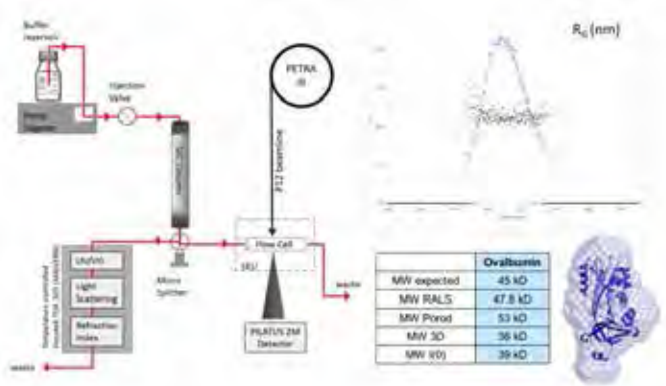
Structural small-angle X-ray scattering (SAXS) studies of proteins in solution typically rely on samples that are both pure and monodisperse in order to extract accurate parameters from the data (e.g. radius of gyration, R_g, forward scattering intensity, $I(0)$, maximum particle dimension, D_{max}) and reconstruct the particle shape. However, in some circumstances, protein samples exist as polydisperse equilibrium mixtures that can complicate data interpretation and modelling. At the P12 bioSAXS beam line of the EMBL (PETRA-III ring, DESY Hamburg), the analysis of these complex mixtures is achieved using a combination of sample component separation via size-exclusion chromatography (SEC) coupled with biophysical characterization using refractive index (RI) and right-angle laser light scattering (RALLS) in parallel with the SAXS measurements. The success of the technique relies on splitting the eluent flow immediately after SEC to divert the chromatographically separated components equally between the SAXS capillary and the RI/RALLS detectors (Figure 1). The M.O.S.E.S approach (Microsplitting for Online Separation, Extended characterization and SAXS analysis) maintains the resolution of the sample components throughout the system by preventing band broadening which can result in component re-mixing in the flow-stream that otherwise occurs using an 'in-series' RI-RALLS-SAXS configuration. The *SASFLOW* software pipeline developed at EMBL-Hamburg [1], fully automates the data reduction and analysis of (up-to) several thousand individual data frames acquired through a SEC-SAXS run. *SASFLOW* performs automated solvent subtraction, extracts R_g and $I(0)$ and correlates these parameters with RI-determined concentrations to obtain component molecular weight information which is then cross-validated with molecular weight estimates independently obtained from RI/RALLS. Consequently, the M.O.S.E.S system goes to increase the overall confidence for interpreting SAXS data acquired from otherwise intractable samples.



	Ovalbumin
MW expected	45 kD
MW RALS	47.8 kD
MW Porod	53 kD
MW 3D	36 kD
MW I(0)	39 kD

Figure 1: Polydisperse sample component separation by SEC, followed by split-stream eluent flow and parallel characterization by RI/RALLS and SAXS. The *SASFLOW* pipeline automatically performs 2D-to-1D radial averaging of the SAXS data, background subtraction and $R_g/I(0)$ analysis of the collected data frames. The molecular weight obtained of the separated components from RI/RALLS (Malvern Instruments) and SAXS are correlated and the *ab initio* shapes of the proteins determined (in this instance ovalbumin).

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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ASSEMBLY OF A STRONG NANOROD FROM TANDEM CLAMPS OF SHORT PROTEIN REPEATS

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Bacteria produce elongated proteins to interact with other bacteria, surfaces and host cells. These proteins contribute to the formation of biofilms by adhering to surfaces and other bacteria, generating protective environments for microbiological communities. Biofilms can form on medical devices to promote exchange of antibiotic resistance genes. SasG is a biofilm-promoting protein from *Staphylococcus aureus* that constructs an extended fibrillar fringe protruding from the bacterial surface. The protein consists of a core region composed of tandem repeats of nearly-identical amino acid sequences. The tandem repeat sequences can be divided into two regions, the E domain (50 amino acids) and the G5 domain (78 amino acids). Surprisingly, when studied in isolation, the E-domain is intrinsically disordered, yet when flanked either side by two G5 domains (G5-E-G5), or before a single G5 domain (E-G5) it undergoes a disordered-to-folded transition [1]. Small-angle X-ray scattering (SAXS) data were collected from monomeric SasG constructs of various lengths consisting of up to seven E-G5 repeats. Scaling relationships extracted from the data including Porod and Flory exponent analysis, dimensionless Kratky plots and correlations between the radius of gyration, R_g, radius of gyration of cross section, R_g^c and maximum dimension (D_{max}), indicate that monomeric SasG adopts a stiff rod-like conformation in solution. Indeed the SAXS data suggest that SasG is one of the most structurally anisotropic monomeric proteins of its size (95 kDa). Modelling the SAXS data using *ab initio* [2] and rigid-body [2] methods (Figure 1) support the stiff-rod hypothesis: at its maximum length, the $G5^1$-$G5^7$ protein extends to 630 Å while is only 20 Å across. The molecular feat of generating a single stiff polypeptide chain utilizing high degrees of folding cooperativity between otherwise intrinsically disordered domains, which form a tandem array of interspersed rigid polypeptide clamps, is quite remarkable.

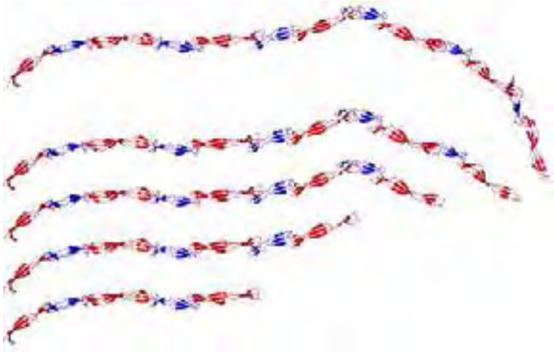

Figure 1: Rigid body models of various SasG protein constructs with different numbers of E-G5 repeats.

This work was in part supported by the Bundesministerium für Bildung und Forschung (BMBF) project BIOSCAT, Grant 05K12YE1 (D.I.S and C.M.J.).

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STRUCTURAL CHARACRACTERISATION OF CHROMATIN PROTEINS IN THE HUMAN MALARIAL PARASITE

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Malaria remains a global public health burden with approximately 600,000 deaths per year, predominantly among young children in sub-Saharan Africa. The human malarial parasite, *Plasmodium falciparum,* causes illness by infecting human red blood cells. Chronic infections depend on antigenic variation of cell surface antigens expressed on these cells. *P. falciparum* erythrocyte membrane protein 1 (PfEMP1) is the major surface antigen and this protein mediates sequestration of infected cells within host blood vessels, which leads to severe malaria. Expression of this protein is controlled by a family of '*var*' genes which are regulated via an epigenetic process through modifications to the encoding chromatin.

The sirtuin enzyme, PfSir2a, is a NAD^+ dependent histone deacetylase whose disruption has been shown to affect the expression of PfEMP1 It has a putative binding partner, PfAlba3, that is a DNA binding protein and may provide a bridge between PfSir2a and DNA, facilitating PfSir2a activity to help to silence *var* genes. We are using small angle neutron and x-ray solution scattering (SANS/SAXS) techniques to characterise the interactions between PfSir2a, PfAlba3 and DNA. This work will give us a better understanding of the molecular mechanisms underlying antigenic silencing and switching - key virulence processes in the malaria parasite.

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EXTENSION OF SASCIF FILE FORMAT AND DEVELOPMENT OF SASCIFTOOLS

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Recent progress in small-angle scattering (SAS) experimental facilities and data analysis methods prompted a dramatic increase in the number of users in projects conducted, in particular for biological solution scattering studies. This progress is causing an upsurge in the amount of objects, experimental data available and the structural models generated. To organize the data and models and make them accessible to the community biological SAS databases were introduced and are being actively developed [1, 2]. Task Forces on SAS and hybrid methods for the International Union of Crystallography and also for the Worldwide Protein Data Bank (wwPDB) envisage developing a federated approach to SAS data and model archiving. In the frame of the federated approach (which is already in the form of the wwPDB for PDB data, with RCSB PDB, PDBe and PDBj as nodes) the existing databases may exchange information and provide independent but synchronized entries to the users. At present, ways of exchanging information between the SAS databases are not established leading to possible duplications and incompatibility of entries and limiting the opportunities for the data driven research for the SAS users. In this work, a solution is developed to resolve these issues and provide a universal exchange format for the community, based on the use of a widely adopted Crystallographic Information File (CIF). A sasCIF format implemented as an extension of the core CIF dictionary is available since 2000 [3] to facilitate the SAS data exchange between laboratories. We have amended sasCIF to comprehensively describe the necessary experimental information, results and models including relevant metadata for SAS data analysis and for the deposition into a database. Processing tools for these files (sasCIFtools) have been developed and are available as standalone programs and integrated into the SASBDB database [1] allowing export and import of the data entries as sasCIF files. Software modules to save relevant information directly from beamline data processing pipelines in sasCIF format are also developed. The update of sasCIF and the relevant tools is an important step in standardization of the way SAS data is presented and exchanged to make the results easily accessible for the users and to further promote the applications of SAS in the structural biology community.

The authors acknowledge support by the European Comission (the 7th Framework Programme) Marie Curie grant IDPbyNMR (contract No 264257) and by the Bundesministerium für Bildung und Forschung project BIOSCAT, Grant 05K20912. The RCSB PDB is funded by the NSF (DBI-1338415), NIH, and DOE)

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CHARACTERIZATION OF THE PHOSPHOLIPID VESICLES VIA SANS AND SAXS

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Vesicles play important role in the intercellular and extracellular transport (Nobel Price 2013 in Physiology or Medicine). Phospholipid vesicles are used as prospective drug delivery system.

SANS on the unilamellar vesicle (ULV) populations was used to characterize lipid vesicles from dimyristoylphosphatidylcholine (DMPC) at three phases: gel $L_{\beta'}$, ripple $P_{\beta'}$, and liquid L_{α}. Parameters of vesicle populations and internal structure of the DMPC bilayer were characterized on the basis of the Separated Form Factor model. Vesicle shape changes from nearly spherical in the L_{α} phase to elliptical in the $P_{\beta'}$ and $L_{\beta'}$ phases. Parameters of the internal bilayer structure (thickness of the membrane and the hydrophobic core, hydration, and surface area of lipid molecule) were determined. DMPC membrane thickness in the L_{α} phase ($T = 30^{o}$C) demonstrates a dependence on the membrane curvature [2]. Water distribution function across the curved lipid bilayer of ULVs was calculated in [3]. This result demonstrates a permeability of the bilayer for the water.

Characterization of the DMPC vesicles in sucrose solution via SAXS at synchrotron requires the development of data evaluation. SAXS curve cannot be described by the layer model of scattering length density across the bilayer. Fluctuation in the position of DMPC molecules is necessary to take into account for the correct description of the experimental SAXS curve [3].

Phospholipid transport nanosystem (FTNS) was developed in the Moscow Institute of Biomedical Chemistry for drug delivery. The morphology of FTNS (micelles or vesicles) has been under discussion. SAXS experiment was carried out to clarify this question. The experimental curve from 25% of the lyophilised FTNS in water is presented at Fig. 1. Sample consists of 20% (w/w) maltose, 5% (w/w) of phospholipid, and 75% (w/w) of water. Experimental curve was fitted by the model of embedded spheres. At above mentioned conditions, FTNS is vesicle population with the average radius 132 Å and the polydispersity 24%.

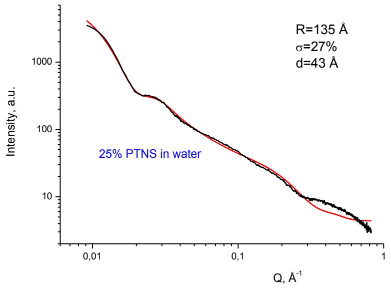

Figure 1: Experimental (black) and fitted (red) SAXS curves from 25 % FTNS in water.

The comparison of SANS and SAXS experiments for vesicle characterization will be discussed. This study was financed by Russian Scientific Foundation, project 14-12-00516.

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AB INITIO BIOMOLECULAR STRUCTURE RECOVERY AND THE HYDRATION LAYER

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Small Angle Scattering of Neutrons (SANS) and X-rays (SAXS) is gaining increasing attention from the structural biology community due to the valuable complementary information that can provide concerning the low resolution structure of biological molecules and their complexes in solution. The popularity of this class of experimental techniques has been boosted in late years by the development of data analysis tools that maximize the amount of information that can be obtained. Among these tools, the so called ab-initio bead models pioneered by Chacon [1] and Svergun [2], treat proteins and nucleic acids as particles of uniform contrast relative to the solvent and represent them as an interconnected and compact collection of dummy-atoms (beads). By proper minimization algorithms the bead arrangement that better reproduces the experimentally acquired small-angle scattering curves is found, and serves as a low-resolution approximation of biomacromolecular shape.

Figure 1: Example of a shape recovery of lysozyme (green) from SAXS data with the proposed biphasic model that takes into account the hydration layer (yellow) scattering contribution.

However consideration of bio-molecules as particles of constant average contrast does not take into account the inherent hydration layer around the molecule, which typically consists of a thin layer of slightly increased contrast relative to the bulk solvent, due to the special packing of water molecules near the outer surface of a protein or nucleic acid.

In a recent publication [3] we have proposed a solution to this problem for SAXS scattering data, by introducing a two-phase bead model where in the final solution, beads that represent the bio-molecule are covered by a second type of beads that represent the hydration layer (see fig, 1). This approach has been implemented in the publically available program DENFERT [4]. In the present contribution we are reviewing the advantages of this approach for the recovery of protein shape, we present a thorough comparison with other existing ab initio programs and also discuss the upcoming extension of the method in the case of SANS experimental data.

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LIPID CORE PHASE TRANSITION AND SHAPE MODIFICATION OF LOW DENSITY LIPOPROTEIN INDUCED BY HIGH HYDROSTATIC PRESSURE

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Human low density lipoprotein (LDL) particles are the principal cholesterol transporter in the blood circulation. The quasi-spherical LDL particles (~20 nm in diameter) are made up of a complex combination of various lipids (primarily cholesteryl esters, triglycerides and phospholipids) and a large single amphipathic protein moiety, named apolipoprotein B-100.

The structural behavior of different types of LDL (native, oxidized and triglyceride rich) was investigated under high hydrostatic pressure (HHP) with SANS (PSI, Villigen, Switzerland) and SAXS (ELETTRA, Trieste, Italy). The HHP conditions ranged from 50 to 3000 bar, whereas the temperature was adjusted in relation to the transition temperature (T_m) of each individual sample. The phase transition of LDL corresponds to the melting of the cholesteryl esters in the inner lipid core from an ordered liquid crystalline phase to a disordered fluid phase. T_m was determined in advance with differential scanning calorimetry (DSC).

The SAXS pattern of LDL below T_m shows a characteristic peak at $q=1.7\ nm^{-1}$ corresponding to the ordered cholesteryl esters in the lipid core. When we measured 10°C above T_m the peak at $q=1.7\ nm^{-1}$ re-emerged continuously by increasing the pressure to 3000 bar (Figure 1). This finding confirms the close relation between temperature and pressure concerning the fluidity state of lipids, as has so far been demonstrated only for lipid/water systems [1]. On the contrary the scattering intensity around $q=0.25\ nm^{-1}$ increases with growing pressure but does not increase when lowering the temperature. In fact, the intensity at small q-values decreases at lower temperatures as we could observe in a temperature scan. So this effect seems to be independent from the pressure induced phase transition of the lipid core and might reflect an overall particle shape alteration.

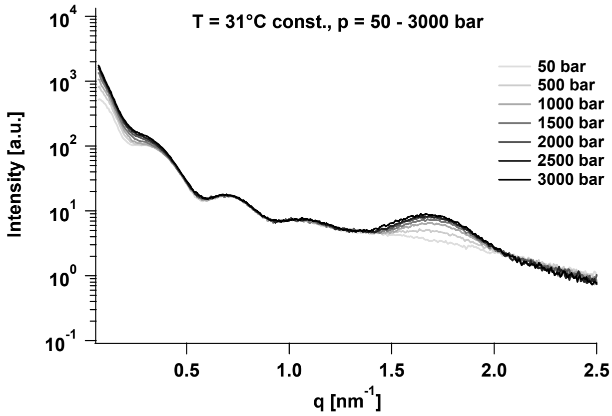

Figure 1: SAXS curves of native LDL measured 10°C above T_m (31°C) from 50-3000 bar

Both observed effects occurred in all investigated LDL types, whereas the triglyceride rich LDL showed the least intensity changes in all q-regions. This might be due to a lack of a lamellar core lipid organization and a lack of ellipsoidal morphology of LDL below T_m [2].

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MEASURING INTRA-MOLECULAR DISTANCES BY ANOMALOUS SMALL-ANGLE X-RAY SCATETRING

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Measurements of molecular distances are key to dissect the structure, dynamics, and functions of biological macromolecules. While FRET and NMR-based techniques have provided invaluable details by measuring intra-molecular distances, they suffer from a limited range (< 10 nm) and difficulties in converting the measured signal into absolute distances. SAXS measurements employing gold-nanoclusters as labels on DNA constructs have demonstrated their ability to provide information about the entire gold label-gold label distance distribution for a considerable range of distances [*1-3*]. The distance distributions are obtained by inverting the gold label-gold label scattering interference term. So far, two approaches have been employed to separate the label-label interference terms from the other contributions (intra-label, label-macromolecule, and intra-macromolecule) to the measured scattering profile. Firstly, the single-labeled and unlabeled samples were measured in addition to the double-labeled macromolecules and from addition and subtraction of the appropriate profiles the interference term could be determined [*1, 2, 4, 5*]. While powerful, this approach requires preparation and measurements of several separate samples for each measured distance distribution. A second approach relies on using relatively large (~ 5 nm) gold particles and neglecting the DNA and gold-DNA scattering terms [*3, 6*]. A drawback of this approach is the large size of the labels, which might perturb the conformational ensemble, and its limited resolution.

Here, we demonstrate measurement of intra-molecular distances on 10, 20, and 30 bp DNA constructs carrying two small (~1 nm) gold labels using anomalous small-angle X-ray scattering (ASAXS). Our approach only requires the double-labeled samples and relies on recording scattering profiles for each sample at different energies. By tuning the X-ray energy through the gold L-III edge (at ~11.9 keV), it is possible to separate out the gold contributions from the DNA only and gold-DNA scattering terms [*7-9*]. Our results demonstrate that ASAXS based determination of label-label distances is possible and provides an attractive alternative to determine absolute intra-molecular distance distributions.

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SERUM ALBUMIN CONFORMATIONAL CHANGES UNDER THERMAL INFLUENCE OBSERVED BY SMALL ANGLE X-RAY SCATTERING (SAXS)

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The all α-helix multi-domain protein SA aggregates at elevated temperatures. The aim of our work is to check that these thermal aggregates may have amyloid-like structure and to track the mechanism of fibrillation process by observing conformational changes of proteins at different conditions. In [1] authors suggest the model of fibril formation from serum albumin, based on the results obtained using fluorescence and circular dichroism (CD) spectroscopy, that contains the following stages: 1) native state, 2) "molten-globule-like" expanded state, 3) molten oligomers, 4) conformationally converted oligomers and 5) amyloid fibrils. Our main idea is to check this model using mostly SAXS technique. For this purpose we are using the beamline at Kurchatov SR source with monochromated ($\lambda = 1.62$ Å) X-ray beam and area CCD-detector. To follow the transitions of proteins we chose to observe the changes of gyration radius (R_g) for different models of scattering particles, of integral intensity near the globule peak at Kratky plot (I_{max}) and of bead model constructed by DAMMIN program which is the part of the ATSAS package. In case of fibril formation we expected to see the diffraction pattern which should provide us with additional data on fibrils structure and kinetics of fibrillation process in general. All methods of sample preparation and experimental process were based on [2].

We have carried out an experiment with SA pH 7.4 and pH 3.0 (sample concentration of 20 mg / ml) at different temperatures up to 70°C. It was noticed that there is a slight decrease of integral intensity at Kratky plot and increase of Rg for temperatures below approximately 50°C and significant changes after it, which is an indicator of aggregation process. The detailed analysis demonstrated the difference of the aggregation process for solutions with pH 3.0 and pH 7.4. Obtained by averaging over 10 exposures of 5 minutes, results of Rg measurements at different pH and 25°C temperature were: at pH 7.4 $Rg = 2.87 \pm 0.007$ nm, at pH 3.0 $Rg = 3.12 \pm 0.008$ nm. For the curve of SA solution at a pH of 7.4 obtained from the database: $Rg = 2.89 \pm 0.003$ nm [3]. Thus, radius of gyration for the solution of SA at pH 7.4 measured at the station DICSY coincided within the error with the value obtained from the database at pH 7.5, and differs from the Rg of SA in solution with pH 3.0 by more than 0.2 nm. Plotting of a pair-distance distribution function by GNOM program and further construction of bead models by DAMMIN program show significant differences in shapes of SA.

We also studied the kinetics of albumin's fibrillation induced by its heating at pH 3. In order to verify results, we compared the results obtained by SXS with fluorescence spectroscopy data.

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HEXAMERIZATION PROCESS OF CYANOBACTERIAL CLOCK PROTEIN KAIC MONITORED WITH SAXS AND FLUORESCENCE SPECTROSCOPY

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KaiC, a core protein of the cyanobacterial circadian clock, self-assembles into its hexameric form upon ATP binding. The hexameric KaiC exhibits rhythmic ATPase, auto-kinase/auto-phosphatase activities in the presence of the other clock proteins, KaiA and KaiB. ATPase activity of KaiC is closely correlated with the frequency of the oscillatory cycle [1], implying that KaiC ATPase defines a circadian periodicity.

KaiC ATPase activity is extremely low (15 ATP d^{-1} $KaiC^{-1}$) compared to those for other ATPases, and exhibits minimum dependency on the ambient temperatures (temperature-compensation) [1]. To reveal the molecular mechanism of such unparalleled properties, it is important to characterize the re-assembly kinetics of KaiC hexamer from nucleotide-free monomer to know the time required for completing this process.

We examined the solution condition, under which nucleotide-free KaiC monomer is stored stably. The use of a phosphate buffer containing L-arginine and L-glutamic acid dramatically increased the stability/solubility of the nucleotide-free KaiC monomer. SAXS analysis revealed that the nucleotide-free KaiC monomer adopts a more compact conformation than that expected for one protomer from the X-ray crystal structure of KaiC hexamer [2]. Reconstructed KaiC hexamer upon addition of ATP was functionally active as wild-type KaiC, supporting the intactness of the nucleotide-free KaiC monomer prepared according to the present protocol.

We investigated the re-assembly process of KaiC hexamer from the nucleotide-free monomer using time-resolved SAXS and fluorescence spectroscopy in combination with stopped-flow technique. The forward scattering intensity, $I(0)$, increased by six-fold on a time scale of 100 s at 10°C, nearly coincident with a major decrease in Trp fluorescence. We also analyzed the temperature-dependency of this process, and found that the re-assembly of the KaiC hexamer completed within 5 min even at 30°C.

In this poster session, we would like to discuss the detailed analysis of ATP-induced hexamerization of KaiC [3] and also present our recent progress in the analysis of KaiC ATPase.

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↘ Flash Talk: Mon-F-S1

STRUCTURE OF THE *E.COLI* CELL CYCLE REGULATOR 6S NON-CODING RNA AND ITS COMPLEX WITH RNA POLYMERASE

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Transcription cycle and the role of RNA polymerase (RNAP) have been extensively studied the last decades. Crystal structures have been solved for the DNA-dependent RNAP in a variety of resolutions from organisms as distant as *E. coli* and *Thermus thermophilus* to yeast and mitochondrial RNAP. RNAP continues to be the subject of intense investigation since its interaction with antibiotics, transcription regulators and other factors is of great importance for gene expression regulation and as a consequence for response and adaptation to environmental changes.

One of the newly identified regulators of bacterial RNAP is a 183 nucleotide non-coding RNA, named 6S. 6S targets specifically the holoenzyme assembly comprising RNA polymerase and the sigma factor σ^{70}. In forming a stable complex with σ^{70}-RNAP, 6S RNA impedes transcription from σ^{70} responsive promoters and enables the alternative σ^{S} dependent transcription of stationary phase expressed genes. Moreover, 6S acts as a template for defined *de novo* transcripts in the absence of DNA.

We are going to present the Small Angle X-ray Scattering determined structure of the 6S RNA and its behaviour under different environmental conditions and in complex with the holoenzyme (σ^{70}-RNAP). The structure of the complex gives hints on the mechanism of the transcriptional regulation through stable yet transitory interactions.

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SAXS TECHNIQUE APPLIED TO PROTEASOME 20S

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The proteasome is a proteolytic complex responsible for protein degradation and this process of intracellular proteolysis is a regulatory mechanism of cellular homeostasis with the same level of importance as gene expression [1]. The proteasome consists of a catalytic core unit called the 20SPT, flanked in one or both ends by regulatory units, called 19S. The 20SPT catalytic chamber is where the hydrolysis occurs and interestingly, the cells have approximately 1/3 of proteasome without regulatory units, i.e. only the 20SPT catalytic unit, which can also degrade proteins independent on poly-ubiquitylation, as in the case of oxidized proteins. Proteins are poorly repaired in comparison to other macromolecules and oxidized proteins have a tendency to form aggregates (a phenomenon that underlies human neurodegenerative diseases), therefore they must be effectively removed from the living cell. Protein degradation has been proposed as the main mechanism of cells to cope with oxidative modification [1,2].

In the literature there is an increasing number of studies about the structural changes of proteasome, in solution, induced by post-translational modifications, such as the oxidative one namely S-glutathiolation. Experimental SAXS data can be described with advanced data analysis and modeling methods permitting the determination of important structural information. In this work we investigated the structural changes and the low resolution model of the proteasomal quaternary structure through redox mechanisms with SAXS experiments. The results (Figure 1) show that when S-glutathionylated, the 20SPT is in the open gate conformation whereas the reduced 20SPT (Proteasome+DTT) form presents important conformational changes its gate is closed, which can be directly correlated with its function and catalytic mechanism [3, 4].

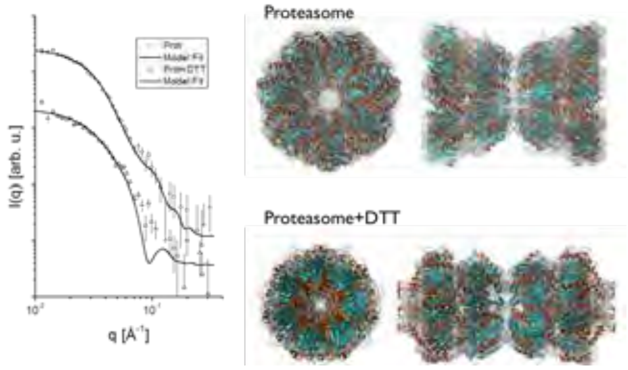

Figure 1: Left: a graph which shows the fitting of scattering curve. Right: grey spheres are an average of 10 independent simulations. Blue and red the most likely structure.

Acknowledgments: FAPESP, USP, CAPES, CNPq, Instituto Butantã

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LIPROTIDES: A NEW CLASS OF PROTEIN LIPID-COMPLEXES

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A cytotoxic complex called HAMLET between the milk protein α-lactalbumin (αLA) and the fatty acid oleic acid (OA) has long been known to form under certain destabilizing conditions [1]. Lately, many other proteins have shown to form protein-fatty acid complexes with similar properties as HAMLET (also known as liprotides) [2]. Due to their size and dynamic structure, neither crystallography nor NMR have been able to provide any structural insight into these complexes. However, we have used SAXS to determine the structure of a number of different protein-OA complexes. Our data reveals a fatty acid micellar core that is stabilized by a shell of partly unfolded protein (core-shell structure) (Figure 1) [3].

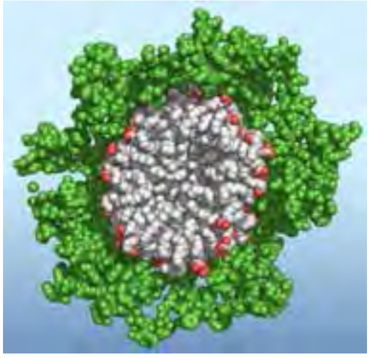
Figure 1: Simple liprotide structure with a micelle core of fatty acid surrounded by partly unfolded protein [3]

To investigate the diversity of this class of complexes, several different fatty acids have been tested for their propensity to form liprotides with αLA. We find that only fatty acids with at least one cis-bond form liprotides. In contrast, we are unable to obtain liprotides from saturated or trans-fatty acids. SAXS of the different cis-fatty acid liprotides show the same core-shell structure as the aLA/OA liprotides, though the dimensions and fatty acid:protein stoichiometry vary.

Remarkably, different liprotide structures can be formed when larger amounts of fatty acid are used for preparing the liprotides. These larger liprotides appear to be multilayered and consist of 3-4 alternating layers of proteins and fatty acids. Their biophysical properties appear to be similar to the smaller core-shell liprotides. SAXS and gel-filtration experiments show that these multilayered liprotides are less stable and easily break down to the smaller core-shell structures when diluted or heated.

The liprotide model opens for the possibility to design liprotides loaded with hydrophobic molecules. Using vitamin E, A and D we have successfully incorporated small molecules in the liprotide structure without changing the overall core-shell structure of the liprotide. The liprotides help stabilize and transport the otherwise poorly soluble vitamins and can potentially be used to fortify foods with vitamin. Future plans involve using other hydrophobic molecules in the liprotide structure that can be used within pharmaceutical and food industry.

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DECIPHERING PROTEIN CONFORMATIONAL CHANGE THROUGH SMALL ANGLE X-RAY SCATTERING AND NORMAL MODE ANALYSIS

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Small-angle X-ray scattering (SAXS) provides important information on conformational states and transitions for macromolecular assemblies in solution. Furthermore, available high resolution models e.g. crystallographic structures can be very useful to build hybrid SAXS models. Given the static nature of the conformational snapshots provided by macromolecular X-ray crystallography (MX) and the typically less-physiological conditions of the crystallization process, MX structures often provide a biased sampling of the conformational space explored by the macromolecule in solution. In such cases (or when studying homologous proteins), the solution conformation may differ from that in the crystal and the experimental SAXS data may not match the theoretical intensities calculated from the MX structure. Still, the latter may constitute a good starting point for the SAXS data interpretation.

Here, we present a methodology to address that situation by exploring the conformational space of the MX structure to find conformations that better correlate with the SAXS experiment. We use normal mode analysis (NMA), particularly the elastic network model [1], as the theoretical framework for protein flexibility, given its speed and accuracy at the coarse-grained level.

The procedure starts by using low frequency normal modes to identify `pseudo-domains' in the structure that shall maintain their internal coordinates during the initial probing of conformational space. Remarkably, these pseudo-domains defined solely on NMA hold close resemblance to traditional protein domains as defined by evolutionary conservation of sequence and/or structure. Once the structure has been partitioned into pseudo-domains (or evolutionary domains, if the user prefers), different combinations of low-frequency normal modes are used to generate alternative conformational states from the input coordinates and these are scored against the SAXS experimental profile by CRYSOL [2].

The best restrained solutions enter a flexible refinement stage, where normal modes are recalculated and applied to minimally deform the entire structure aiming to further improve the overall fit without breaking the macromolecular chain. The overall best structures are then selected and provided to the user.

The method has been implemented in a computer program and benchmarked against a large set of proteins for which multiple conformational states are known. The results are compared to those of previously described approaches [3, 4]. We expect the new approach to be useful for biological SAXS applications given its good performance and ease-of-use. This work was supported by EU FP7 Infrastructures Grant BioStructX (contract 283570).

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DARA: A DATABASE FOR RAPID SEARCH OF STRUCTURAL NEIGHBORS USING SOLUTION SMALL ANGLE X-RAY SCATTERING DATA

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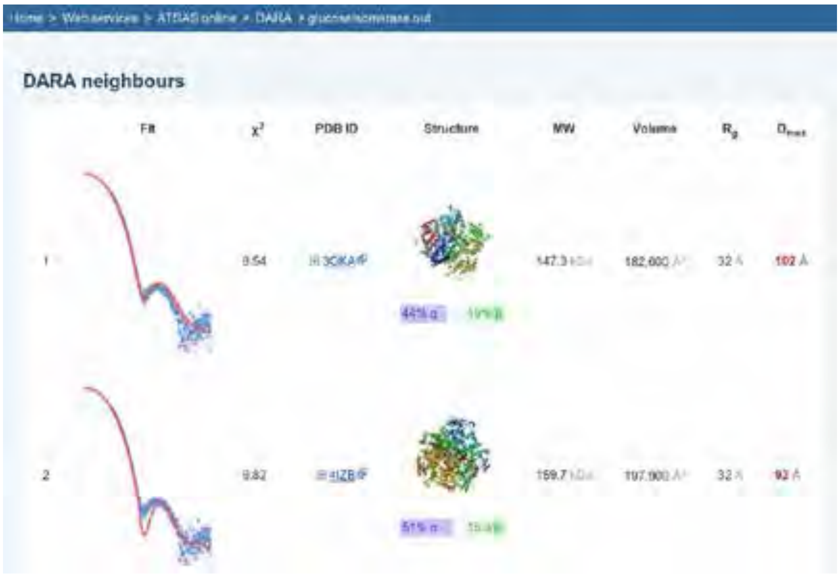
Small angle X-ray scattering (SAXS) is an established method for studying biological macromolecules in solution, whereby the experimental scattering patterns are related to the overall structure of the macromolecule. Here we present a new version of DARA, a web-server that queries over 150 000 scattering patterns pre-computed from the high resolution structures of macromolecules and biological assemblies in the Protein Data Bank, to find nearest neighbors of a given experimental or theoretical SAXS profile. Identification of the best scattering equivalents provides rapid automatic structural assessment of macromolecules based on the experimental SAXS profile. DARA results may further prove useful for tasks related to fold recognition, experiment validation and finding targets for molecular replacement.



Home > Webservices > ATSAS online > DARA > glucoseisomerase.out

DARA neighbours

	Fit	χ^2	PDB ID	Structure	MW	Volume	R_g	D_{max}
1		9.54	3OKA	44% α 10% β	147.3 kDa	182,600 Å³	32 Å	102 Å
2		9.82	4IZB	51% α 15.4% β	159.7 kDa	197,900 Å³	32 Å	93 Å

Figure 1. An example of DARA output displaying nearest structural neighbors as found based on an experimental SAXS profile search.

The current implementation of DARA represents a complete overhaul of the database designed over ten years ago [1]. Among the improvements are a new search algorithm combining principal component analysis and k-d trees for almost instantaneous identification of similar scattering patterns, a new definition of the dataset or search space including nucleic acids and complexes, and a reworked presentation of the results (see Figure 1). DARA is freely available at http://dara.embl-hamburg.de/. The implementation was validated with numerous simulated and experimental data sets. The new server has also been tested by 25 international participants of a recent EMBO practical course on solution scattering (Hamburg, October 2014); at least 13 experimental data sets were used. This work was supported by EU FP7 Infrastructures Grant BioStructX (contract 283570).

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A PREEXISTING EQUILIBRIUM GOVERNS ELECTRON FLUX EFFICIENCY OF A BIDOMAIN DIFLAVIN REDUCTASE: COMBINED SAXS AND NMR STUDY

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Diflavin reductases are bidomain electron transfer proteins in which structural reorientation is necessary to account for the various intramolecular and intermolecular electron transfer steps. Using small-angle x-ray scattering and nuclear magnetic resonance data, we describe the conformational free-energy landscape of the NADPH-cytochrome P450 reductase (CPR), a typical bidomain redox enzyme composed of two covalently-bound flavin domains, under various experimental conditions [1]. The CPR enzyme exists in a salt and pH-dependent rapid equilibrium between a previously described rigid, locked state and a newly characterized, highly flexible, unlocked state (Figure 1). We further establish that maximal electron flux through CPR is conditioned by adjustable stability of the locked state domain interface under resting conditions. This is rationalized by a kinetic scheme coupling rapid conformational sampling and slow chemical reaction rates. Regulated domain interface stability associated with fast stochastic domain contacts during the catalytic cycle thus provides, to our knowledge, a new paradigm for improving our understanding of multidomain enzyme function.

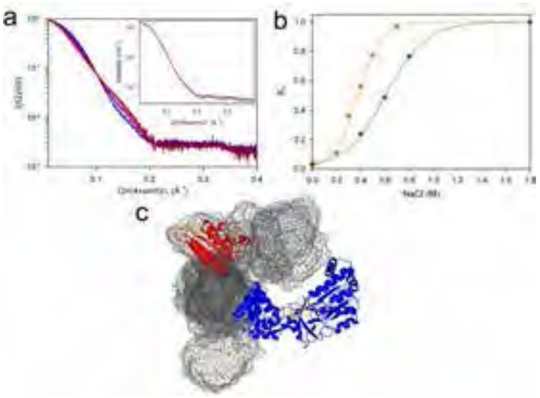

Figure 1: SAXS analysis of the ionic strength mediated conformational transition of CPR. (a) Scattering curves as a function of NaCl concentration. (Inset) Fit of the 0 M scattering curve to the crystal structure of the closed conformation [2] with loop conformation optimized using DADIMODO [3] (b) Fractions of the U state (pU) at pH 7.4 (orange) and pH 6.7 (green) (c) Van der Waals surface of the reunion of the FMN domains determined by EOM [4].

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THE FLEXIBLE SOLUTION STRUCTURES OF MANNOSE-BINDING LECTIN-ASSOCIATED SERINE PROTEASES-1 AND -2 PROVIDE NOVEL INSIGHT ON LECTIN PATHWAY ACTIVATION

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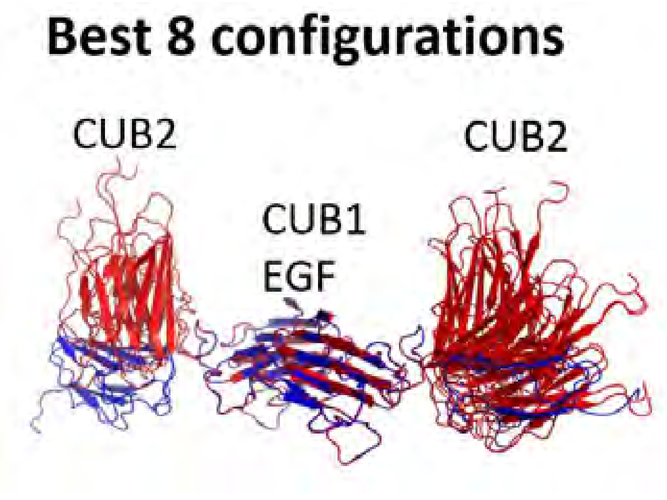
The lectin pathway of complement is activated by the recognition of carbohydrate patterns on pathogen cell surfaces by complexes comprising a recognition component (mannose-binding lectin (MBL), serum ficolins or collectin-K1) and an associated protease (MASP-1 or -2). By MASP-1 binding to MBL, MASP-1 activates MASP-2, and MASP-2 activates the downstream components C4 and C4b-bound C2 to initiate the downstream reaction cascade of complement. MASP-1 and MASP-2 are six-domain proteins.

In order to clarify the molecular basis of lectin pathway activation, we determined two crystal structures for the N-terminal CUB1-EGF-CUB2 three domains of rat MASP-1 and MASP-2 bound with Ca^{2+}, together with their solution structures from X-ray scattering and atomistic modelling using the CCP-SAS atomistic software modelling package. The solution structure for the CUB1-EGF-CUB2 dimer showed that the two CUB2 domains in MASP-1 were tilted upwards (see Figure), unlike its crystal structure, whereas those in MASP-2 remain extended as seen in its crystal structure.



We also determined the solution structures of full-length rat MASP-1 and MASP-2 in their zymogen and activated forms by X-ray scattering. Here, crystal structures of the N-terminal CUB1-EGF-CUB2 and C-terminal SCR1-SCR2-SP regions were used for atomistic scattering modelling. Both the zymogen and activated forms of MASP-1 and MASP-2 showed similar dimeric solution structures with lengths of 30 nm. Both structures were more compact than anticipated from homology models. The best-fit solution structures of the MASP-1 and MASP-2 dimers showed significant domain flexibility in the CUB2-SCR1-SCR2-SP region.

In conclusion, through a comparison of our MASP scattering structures with our previously-determined solution structures for MBL, our novel identification of flexible MASP domain structures changes our understanding of the way in which the MASP proteases activate the lectin pathway through their binding to MBL as a template.

Funded by a joint EPSRC (EP/K039121/1) and NSF (CHE-1265821) grant; http://www.ccpsas.org/

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↘ Flash Talk: Mon-F-S1

DEVELOPING METHODS OF NON-INVASIVE DIAGNOSTICS BASED ON SMALL-ANGLE X-RAY DIFFRACTION STUDIES OF ANIMAL HAIR FIBER

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Hair tissue is likeable for diffraction studies due to its good accessibility and no need in sample preparation (in particular, crystallization) – unlike crystals, hair is already structured.

Experiments were conducted on small-angle station DICSI at the "Siberia-2" storage ring in Kurchatov institute (Moscow). Our representative set of samples was divided into 3 collections:

1) several hundreds of rat hair samples from the animal house "FIB" (Chelyabinsk-40). These animals varied in age, sex, feeding and housing conditions; 2) mice hair samples from Bach Institute of Biochemistry RAS. Descendants of normal females and males with inherited mutation producing a dwarf phenotype [1]; 3) rat hair samples from animals which were housed in two animal houses with significantly different living conditions.

Primary analysis of the diffraction patterns revealed regularity in behavior of the relation of two peaks, typical for hair tissue structure – 6,7 nm, which is 7th order of 47 nm main keratin period, and 4,5 nm, which is the diffraction maximum for intercellular matrix proteoglycan fibrils [2]. Diffraction patterns of animals in relatively good housing conditions showed much lower 4,5 nm intensity in front of 6,7 nm, and the worse conditions, the closer this relation was to 1. Another experiment, in which diffraction patterns from separately primary and fluff hair were taken, showed that this relation differs in these two types of hair. After averaging by 50 experiments, values 1,05±0,32 for primary and 1,68±0,35 for fluff hair were obtained.

This work shows that developed method can be applied for diagnostics of mice mutations (collection 2). After processing data from the first 4 couples of normal-mutant, was obtained:

Intensity relation, a.u.				
№	1	2	3	4
Normal	2,56	2,35	1,87	1,97
Mutant	1,09	1,63	0,96	1,51

Obtained results can be applied to identification of morphological markers suitable for monitoring of functional and physiological states of different animals.

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CRYSOL 3.0 – A NEW TOOL FOR COMPUTATION OF SOLUTION SCATTERING PROFILES FROM ATOMIC MODELS

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A program CRYSOL [1] for computing X-ray small-angle scattering (SAXS) profiles based on the atomic structures of macromolecules and fitting them to experimental data has been rewritten to improve the treatment of the hydration shell and make the calculation more accurate. In the new version CRYSOL 3.0, the hydration shell of a macromolecule is generated by dummy beads attached to the surface. The hydration solvent beads are divided into three classes: *(i)* internal water in cavities, *(ii)* water shell on the outer convex surface and *(iii)* that on the concave surface. The mobility and thus the contrast of the beads may vary depending on the location. In order to optimize the bead positioning, all-atom molecular dynamics (MD) simulations were employed on a large set of test proteins with known high-resolution X-ray crystallographic structures and the MD trajectories were analyzed with respect to average protein – water interactions on surfaces and the average hydration shell occupancies. The approach adopted in CRYSOL 3.0 was validated against solution scattering data from a benchmark set of proteins with known atomic structures. Experimental scattering profiles in SAXS and wide-angle scattering (WAXS) ranges were measured prior and immediately after re-purification of proteins using fast protein liquid chromatography (FPLC). In addition, comprehensive biophysical characterization of samples was done using optical UV absorption spectroscopy, static right-angle light scattering, and refractive index measurements to validate monodispersity and oligomeric state of the species. The influence of the solvent has been further studied by the measurements in the buffers containing additives. The obtained high quality experimental data were analyzed using CRYSOL 3.0 and compared with the results of the previous CRYSOL version and with other available approaches. It has been demonstrated that the CRYSOL 3.0 and its advanced representation of the hydration layer is especially beneficial for accurate calculation of the scattering SAXS/WAXS profiles from biological macromolecules with complex shapes.

The authors acknowledge support by the European Commission, BioStruct-X project (contract number 283570), A.T. was supported by the EMBL Interdisciplinary Postdoc Programme (EIPOD) under Marie Curie COFUND actions and by the BMBF research grant BioSCAT, contract No 05K12YE1.

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STRUCTURAL CHARACTERIZATION OF LIPOPROTEINS UNDER OXIDATIVE AND TEMPERATURE STRESS

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Cholesterol is a hydrophobic molecule, essential for the structure of the cell membrane, precursor of bile acids, vitamin D, and other steroids. The plasma lipoproteins are responsible for the transport of cholesterol between cells. A lipid core composed of triglycerides and cholesterol esters, surrounded by a monolayer of phospholipids, free cholesterol and apolipoproteins (apo), forms these quasi-spherical particles of different sizes and composition. Apolipoproteins are essential for the structural integrity of the particle beyond controlling lipoprotein metabolism through binding to specific cell membrane receptor. The low-density lipoprotein (LDL), responsible for the delivery of cholesterol to peripheral tissues, has only one apolipoprotein (apoB, predominantly B-100), whereas high-density lipoprotein (HDL) which mediate the inverse process of the cholesterol transport, contain several apolipoproteins (e.g., apoA, C and E). It is known that both LDL and HDL are very sensitives to changes in the environment, and this may alter its function.

This work presents [1, 2] a controlled study of low-density lipoprotein (LDL) and high-density lipoprotein (HDL) structural changes due to in vitro oxidation with copper ions and also a systematic study of low-density lipoprotein (LDL) in solutions subjected to subtle temperature changes. In both cases the samples where monitored by Small Angle X-Ray Scattering and the obtained results were combined with additional experimental techniques. As will be shown, by the use of advanced modeling procedures it was possible to obtain unique structural features of the studied lipoproteins due to the environmental changes.

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A COMPREHENSIVE MECHANISM OF FIBRIN NETWORK FORMATION FROM COUPLED TIME-RESOLVED SAXS AND MULTI-ANGLE LIGHT SCATTERING

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Fibrin network formation following fibrinogen (FG) activation is the central event in blood coagulation. It consists basically of two processes: elongation/branching generates an interconnected 3D scaffold of relatively thin fibrils, cooperative lateral aggregation thickens them more than tenfold. Physiologically, the reaction is started by the enzyme thrombin, which sequentially cleaves two couples of small peptides (FpA and FpB) in the central domain of the elongated (~45 nm), dimeric FG molecule. The engagement of newly exposed *A* and *B* "knobs" into constitutively available *a* and *b* pockets in the outer domains of neighboring FG molecules governs the elongation and favors the thickening stages, respectively. A snake venom enzyme ("ancrod") can cleave only the FpA, delaying lateral aggregation.

The early stages up to the gel point were studied by fast FG:ancrod mixing experiments using simultaneous SAXS and wide-angle, multi-angle light scattering (WA-MALS) detection. The coupled evolution of the average molecular weight ($<M>_w$), size ($<R_g^2>_z$), and cross-section ($<R_c^2>_z$) of the growing fibrils were thus recovered. They reveal that extended structures, thinner than those predicted by the classic half-staggered, double-stranded mechanism, must quickly form.

Extensive modeling suggests an initial phase in which single-bonded "Y-ladder" polymers rapidly elongate before undergoing a delayed transition to the double-stranded fibrils. Consistent with the data, this alternative mechanism can intrinsically generate frequent, random branching points in each growing fibril. Our model predicts that some branches in these expanding "lumps" eventually interconnect, forming the pervasive 3D network. While still growing, other branches will then undergo a Ca^{++}/length-dependent cooperative collapse on the resulting network filaments, explaining their sudden thickening, low final density, and basic mechanical properties [1].

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SAXS STUDIES ON HUMAN PEPTIDYLARGININE DEIMINASE (PAD)

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Peptidylarginine deiminase (PAD) is the enzyme that catalyzes the post translational conversion of arginine residues in proteins to citrulline in the presence of Ca^{2+}. In human, there are five isoforms (PAD1-4 and 6). PAD1 and 3 are expressed in the epidermis and hair follicles. PAD2 is expressed in ubiquitous tissues. In hair follicles, S100A3 protein is a representative natural substrate of PAD enzymes. PAD3 converts Arg51 residues of an S100A3 dimer to citrullines specifically, and the citrullinated S100A3 dimers are assembled into homotetramer that have higher affinity with Ca^{2+} and Zn^{2+}. On the other hands, PAD1 and 2 convert all four arginine residues of S100A3. The purpose of this study is to reveal that the mechanism of the substrate recognition of PAD isoforms in hair follicles.

Until now, several crystal structures of PAD isoforms (PAD1[1], 2, 3[2] and 4) were solved. PAD4 localizes in the cell nucleus and catalyzes the citrullination of histones. The PAD4 monomer has an elongated shape. And PAD4s make the head to tail dimer with another PAD4 molecule that is related by a crystallographic two-fold axis. PAD2 and 3 also made the head to tail dimer similar to PAD4 dimer. However the arrangement of PAD1 dimer differs from the head to tail dimer. To elucidate whether the assembly state is the artifact by crystal packing or not, the SAXS measurements were performed on the beamline BL-6A and BL-10C at Photon Factory. The results of SAXS experiments proved that PAD1 is the monomer in solution and PAD3 is the head to tail dimer similar to the crystal structure. To clarify that the assembly state correlates the differences of the substrate specificity between PAD isoforms, we will carry out further SAXS experiment of PAD2.

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AVOIDING PROTEIN RADIATION DAMAGE IN SAXS: HOW A CLEVER COLLIMATION CONCEPT HELPS

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Small-angle X-ray scattering (SAXS) is widely used for characterization of proteins and protein complexes in solution. SAXS is well-suited to study structure and dynamics of proteins in their native state at low resolution and therefore provide important information complementary to high-resolution methods like X-ray crystallography and NMR spectroscopy.

SAXS measurements of proteins in solution are typically performed both at synchrotron SAXS beam lines and by using laboratory SAXS systems. In contrast to other samples, SAXS on protein samples is hampered by the low signal-to-noise caused by the small scattering contrast, the limited sample concentration, and sample stability. In principle, these difficulties can be overcome by carrying out the measurements at the latest-generation synchrotron Bio-SAXS beamlines, where high signal-to-noise data can be obtained in an extremely short amount of time. However, this can be rendered ineffective if samples undergo radiation damage. In principle stabilizing agents such as DTT could be used to prevent radiation damage, but this approach is not generally applicable and limited to proteins that do not contain native disulfide bonds that need to be preserved.

A major advantage of using in-house laboratory SAXS systems is that samples prepared in the lab can be measured immediately at any time. To compensate for the lower signal-to-noise, protein SAXS measurements in the laboratory, substantially longer exposure times are used to obtain data of sufficient quality. For laboratory SAXS systems either powerful sealed-tube sources or brilliant point sources (such as rotating anodes) are used in order to obtain high-quality data within short exposure times. Despite the higher signal-to-noise of brilliant point sources the high flux density of the X-ray beam can lead to radiation damage and render them ineffective.

A straightforward way to overcome radiation damage is to use SAXS instrumentation with slit collimation. The overall intensity and flux of the slit-collimation X-ray beam is high, thus ensuring high-quality SAXS data, however, radiation damage can be avoided due to the lack of high local X-ray flux density.

In this contribution we present different examples of sensitive and low-concentrated protein samples which were successfully measured and analyzed using a laboratory SAXS instrument in slit collimation. The results clearly show that the studied proteins are stable over a long exposure time only when measured in slit collimation which proved to prevent radiation damage which occurred when other instrumentation was used.

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INTERACTION OF AMYLOID-β PROTEIN WITH RAFT-MODEL LIPOSOME UNDER MIMIC ENVIRONMENT OF CELL

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It is now widely accepted that the amyloid *β* -peptide (Aβ), which exists in fibrillar forms as a major component of senile plaques, is central to the development of Alzheimer's disease (AD). Aβ–membrane interactions have been extensively investigated to elucidate the molecular mechanisms of the Aβ-induced cellular dysfunctions underlying the pathogenesis of AD. Particularly, according to accumulating evidence using spectroscopic methods, the importance of ganglioside clusters in the fibrillization of Aβ is emphasized. Gangliosides, major components of glycosphingolipids (GSLs), are acidic lipids and rich in central nervous system. GSL-cholesterol formed microdomains in cell membranes, so-called lipid rafts, are suggested to function as platforms of various membrane-associated events such as signal transduction, cell adhesion, lipid/protein sorting and so on. The interaction between mono-sialoganglioside (G_{M1}) and Aβ is reported to promote the conformational change of Aβ to its cross-beta structure and the G_{M1}-bound form seeds in the process of Aβ polymerization to amyloid fibril [1]. Recently, we reported that that the interaction between the Aβ proteins and the model membrane at the liquid-crystal phase significantly suppresses a bending-diffusion motion, suggesting the possibility of non-receptor-mediated disorder in signaling through a modulation of a membrane dynamics induced by the association of amyloidogenic peptides on a plasma membrane [2].

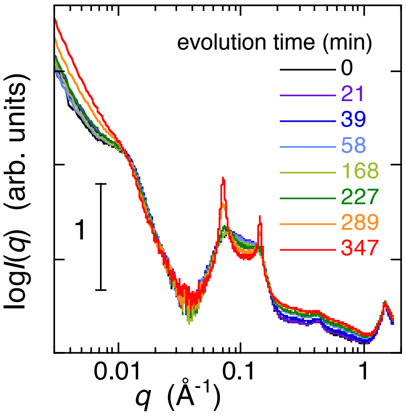

Figure 1. Time-evolution of SAWXS curve of SUV after Ab addition

In the present study, we have investigated the Aβ-membrane interactions under a mimic intracellular environment by using the time-resolved small- and wide-angle X-ray scattering (SWAXS). The membrane used was the small unilamellar vesicle (SUV) composed of G_{M1}, cholesterol, and phospholipid. The mimic intracellular environment, so-called crowding environment, was realized by the addition of the high-molecular weight neutral polymer (polyvinyl-pyrrolidone, PVP). The present results are summarized as follows. Under non-crowding environment, the interaction between SUV and Aβ protein proceeds mostly without affecting the SUV membrane structure. While, under crowding environment, the presence of crowders induces the deformation of the SUV shape and the interaction between SUV, and Aβ protein causes further aggregation to form the lamellar stacking. The time-course of the lamellar distance and the lamellar-peak height suggest the preferential cohesion or intercalation of Aβ proteins in the inter-bilayer region.

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DYNAMIC FEATURES OF THE DENGUE VIRUS NS5 PROTEIN OF SEROTYPE 3 IN SOLUTION

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Dengue virus (DENV) is a member of the Flavivirus genus of the Flaviviridae family, and it consists of four serotypes (DENV1-4). Dengue is a mosquito-borne disease and an infection threat to nearly 40% of the world's population [1]. DENV translates its genomic RNA into a polypeptide that will be processed by host and viral proteases into three structural proteins (capsid, membrane, envelope) and seven non-structural (NS) proteins (NS1, NS2A, NS2B, NS3, NS4A, NS4B and NS5) [2]. Together with NS3, NS5 form the replication complex located on endoplasmic reticulum membrane. NS5 is a multifunctional protein and consists of two domains, methyltransferase which is important in capping of viral RNA, and RNA-dependent RNA polymerase (RdRp) which is essential for viral RNA replication.

In order to characterize NS5 in solution and understand orientation as well as the dynamics of two enzymatic domains in solution, small-angle X-ray scattering (SAXS) experiments were performed. Full-length NS5 protein from DENV-3 was purified in high purity, and its SAXS data were collected with BRUKER NANOSTAR SAXS equipment equipped with a Metal-Jet X-ray source and VÅNTEC 2000 detector. The derived solution models reveal a more elongated conformation with dimension of 10.5 nm x 7.0 nm x 4.0 nm compared to $NS5_{6-895}$ crystallographic structure (PDB: 4V0R) [3], with dimension of 8.7 nm x 7.2 nm x 5.5 nm. Considering the different arrangement seen in solution structure and crystallographic structure, detailed analysis on NS5FL scattering profile was performed, and normalized Kratky plot and Porod-Debye plot showed DENV-3 NS5FL exhibited a more extended conformation and less rigidity. Quantification of the flexibility using ensemble optimization method (EOM) [4, 5] suggests the presence of non-random motion for the methyltransferase relative to the RdRp. To further characterize this dynamic behavior, methyltransferase and RdRp, together with the 10-residues linker, have been generated and purified in high purity. Their SAXS data were collected, and their normalized Kratky plots and Porod-Debye plots reveal that the methyltransferase with linker contributes in part to the dynamic seen in full-length NS5 of DENV-3.

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↘ Flash Talk: Mon-F-S1

THE POTENTIAL OF CSAXS (CORRELATED SAXS) FOR OBSERVING SUPERCOILS IN RANDOMLY ORIENTED ENSEMBLES OF DNA FRAGMENTS

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The advent of X-ray free electron lasers (xFEL's) makes possible the measurement of angular correlations in azimuthal deviations from the angular mean measured in SAXS profiles[1]. We will present simulations of correlated SAXS (CSAXS) from DNA fragments and show that they exhibit a characteristic azimuthal symmetry dependence which measures the relative width to persistence length ratio. We use a wormlike chain model to simulate the size-dependence of this ratio as a function of the size of DNA fragments. We show that CSAXS can measure the degree of supercoiling in DNA plasmids. We discuss the possibility of using this technique to monitor the degree of supercoiling of bacterial chromosomes *in vivo*.

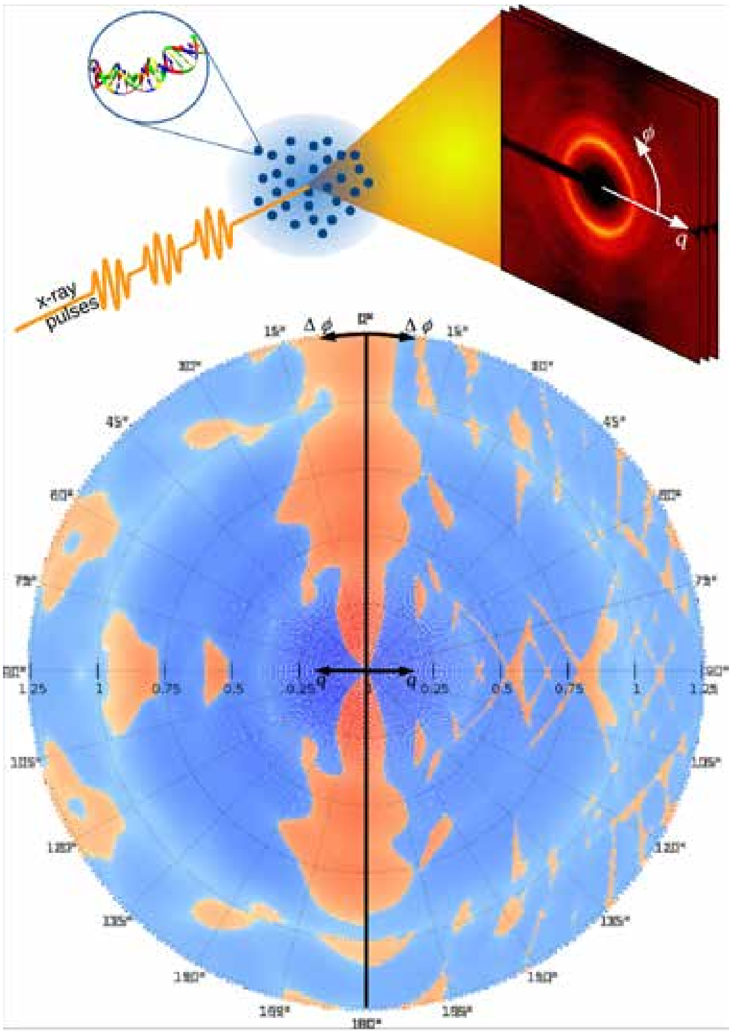

Figure 1: Simulated angular autocorrelations of solution X-ray scattering images. Left:17bp DNA, right: 134bp DNA.

The average over angular correlations of many scattering measurements at low *q* contains information about the thermodynamic persistence length of the DNA molecules and their degree of supercoiling. At higher *q* the correlation patterns relate to the internal molecular structure.

A simple test supports the hypothesis that uncorrelated scattering events from other randomly placed molecules tend to wash out in the correlation average. Because of the inherent three-dimensional information contained in the correlations, CSAXS has the potential to solve new problems inaccessible to traditional solution SAXS.

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↘ Flash Talk: Mon-F-S1

STRUCTURAL TRANSITIONS OF BAX AFTER THE APOPTOTIC ACTIVATION

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In stressed cells, apoptosis ensues when BAX proteins oligomerize and permeabilize the mitochondrial outer membrane [1]. The mechanism utilized by BAX still remains elusive because BAX changes its functional structures along the apoptotic signaling pathway from cytosolic monomer, oligomer, to membrane-associated complex. This polymorphism of BAX poses a great challenge in tracing its structural transitions in functioning. Here we use a combination of electron spin resonance (ESR) and small angle X-ray scattering (SAXS) to study the conformational changes of BAX before and after the apoptotic activation. Particularly, an on-line HPLC is used to separate the BAX monomers, dimers, and oligomers in the eluted sample solution along the flow path for in-situ SAXS data collection at the 23A SWAXS endstation of National Synchrotron Radiation Research Center, Hsinchu, Taiwan [2].

Utilizing a $BimBH_3$ peptide as an apoptotic stimulus, our ESR study determines two possible forms of the BAX dimer and suggests $\alpha 1$ in BAX dimer is highly solvent exposed and disordered. Therefore, we employed the ensemble optimization method (EOM)[3] which selects ensembles of theoretical scattering curves from large pools of structures based on the two dimer forms to fit the SAXS data. Because the eluted samples from the on-line HPLC in the SAXS measurement represent an intermediate state between monomer and oligomer, it was not possible to obtain any adequate fit with a pool consisting of only original compact dimer structures. The introduction of a hypothesized intermediate structure towards oligomer (extended form) is necessary to describe the SAXS data. The optimized ensemble from the new mixed pool provides a better fitting to the experimental scattering data with a large contribution from the extended form and relatively smaller portion from the compact form. For both forms, the two $\alpha 1$ helices tend to stretch out in opposite directions to reach larger R_g values in solution. Together, our findings reveal the possible conformations of activated BAX dimer and precursors for oligomer formation, providing a structural basis for eventually manipulaing BAX activity pharmacologically.

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SELF-ASSEMBLY OF A DESIGNED ALTERNATING ARGININE/PHENYLALANINE OLIGOPEPTIDE[*]

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A model octapeptide peptide consisting of an alternating sequence of arginine (Arg) and phenylalanine (Phe) residues, namely [Arg-Phe]$_4$ was prepared, and its self-assembly in solution studied. The simple alternating [Arg-Phe]$_4$ peptide sequence allows for unique insights into the aggregation process and the structure of the self-assembled motifs. Fluorescence and UV-Vis assays were used to determine critical aggregation concentrations, corresponding to the formation of oligomeric species and β-sheet rich structures organized into both spheroidal aggregates and highly-ordered fibrils. Electron and atomic force microscopy images show globular aggregates and long unbranched fibres with diameters ranging from ~ 4 nm up to ~ 40 nm. Infrared and circular dichroism spectroscopy show the formation of β-sheet structures. XRD diffraction on oriented stalks show that the peptide fibres have an internal lamellar structure, with an orthorhombic unit cell with parameters *a* ~ 27.6 Å, *b* ~ 9.7 Å and *c* ~ 9.6 Å. *In situ* SAXS shows the presence of low molecular weight oligomers in equilibrium with mature fibres which are likely made up from 5 or 6 intertwined proto-filaments. Finally, weak gel solutions are probed under gentle shear suggesting the ability of these arginine-rich fibres to form networks.

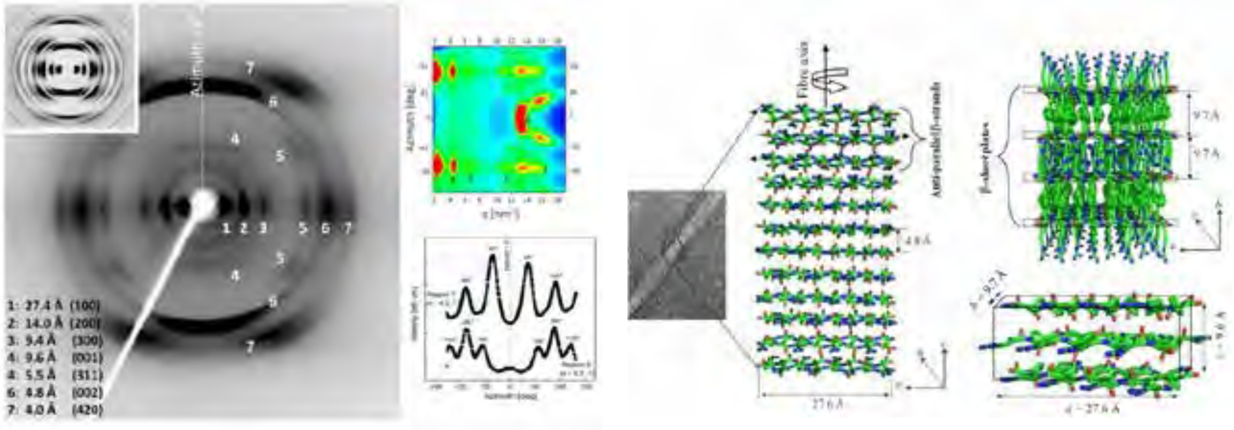

Figure 1: Structural model arising for [Arg-Phe]$_4$ peptide fibres arising from combined SAXS/XRD measurements.

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[*] Published in: ACS *Langmuir* (2015), DOI: 10.1021/acs.langmuir.5b00253

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↘ Flash Talk: Mon-F-S1

SMALL ANGLE X-RAY SCATTERING STUDIES OF MOLECULAR CHAPERONE HSP21 AND CLIENT PROTEINS DURING HEAT STRESS

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When the cell becomes stressed unfolding and subsequent aggregation of proteins is inhibited by molecular chaperones such as Hsp21 (Figure 1). There are many variations of molecular chaperones, each with different functions and target proteins. Common for many molecular chaperones is a high order quaternary structure, dodecamer in the case of Hsp21, which is also highly dynamic under certain conditions [1]. In client proteins the native protein conformation is driven towards partly unfolded states during stress, which may lead to either aggregation or intermolecular interactions with sHsps. Such weak interactions prevent aggregation by kinetic competition[2]. Stable sHsp-substrate protein complexes are formed later but initially the interactions appear weak and transient. We have used small angle X-ray scattering (SAXS) to study the effect of client proteins, as well as temperature, on Hsp21 variants (wild type and point mutant Hsp21d). SAXS data of Hsp21 dodecamer fit well with TEM single particle reconstructions, and confirms that the oligomer is homogenous with little or no contribution from smaller order oligomers at room temperature. We also characterized an Hsp21d point mutant and found that the quaternary structure was heterogeneous and strongly shifted from dodecamer to dimer. We followed the chaperone process during heat stress using SAXS, and data was collected every five or ten minutes. Wild-type, as well as Hsp21d, successfully protected client proteins during short term heat stress. However, after returning the temperature to 25 degrees Celsius the Hsp21d system was aggregated, while the Hsp21 system was not.

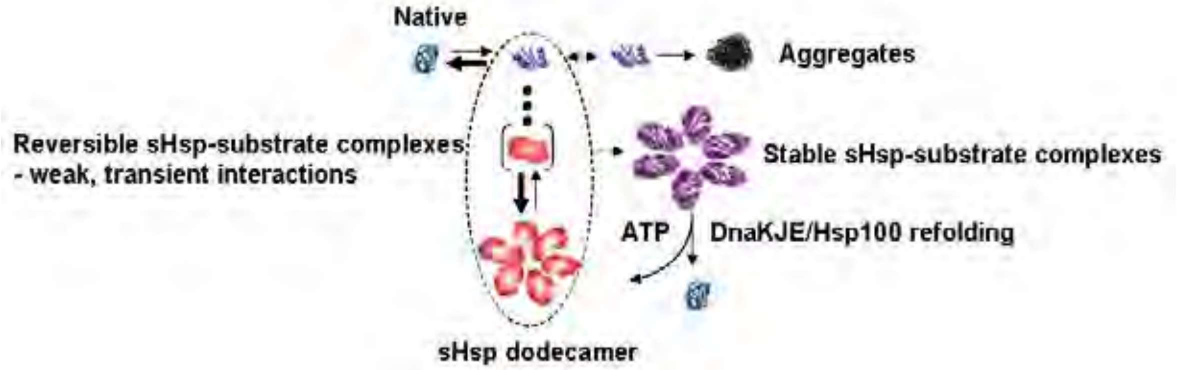

Figure 1: Proteins start to unfold and are either picked up by chaperons such as sHsps, spontaneously refolded, or fully unfolded to form aggregates. The sHsp chaperones are thought to release from their dodecamer complex to bind transiently to partially unfolded proteins. The sHsp-substrate protein complex becomes less transient over time and finally large stable sHsp-substrate protein complexes can be formed, that require ATP for release and refolding of the substrate protein.

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INTERACTION AND STABILITY OF HUMAN SERUM ALBUMIN – A SAXS STUDY

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Human serum albumin (HSA) is used as a functional protein in many different applications where HSAs ability to increase the solution stability of other proteins is utilized. The mechanism of action for this well-known stabilization is well established at low concentration but largely unknown at higher concentrations (>1 mg/ml). The focus of the present study is to utilize SAXSs unique ability to study such dense samples in relevant environment.

HSA is the most abundant plasma protein and is present in concentrations 35-50 mg/ml in blood plasma. Important functions of this protein include regulation of the colloid osmotic pressure and the transport of both endogenous and exogenous compounds, such as fatty acids, hormones and drugs[1]–[3]. The properties of HSA, has made it a protein of interest in the pharmaceutical industry, where it is utilized in many different applications. These include drug delivery systems[4] and in the formulation of other proteins. In formulation, HSA is used as a stabilizer to prevent aggregation, as an anti-adsorption agent or as an antioxidant [5]. Stability of proteins in solution can be affected by a number of factors such as temperature, pH, crowding and ionic strength/tonicity.

To shed light on the observed stabilizing effect, we have used Small-Angle X-ray Scattering (SAXS) to study the solution properties and self-interaction of rHSA molecules in two pharmaceutically relevant buffer systems at various protein concentrations. In one system the tonicity is primarily provided by a salt and in the second system, the tonicity is provided by a non-ionic sugar, trehalose. The behaviour of recombinant HSA (rHSA) in the form of Recombumin® Alpha from Novozymes Biopharma A/S, and its self-interaction with varying ionic strength is investigated. Additionally, the self-interaction of defatted rHSA was studied in pure Milli-Q water. In all three systems, studies at varying NaCl concentrations, at constant protein concentration is performed.

The effective structure factors ($S(q)_{\mathrm{eff}}$) have been extracted from the scattering profiles and fit to the solution of the Ornstein–Zernicke (OZ) equation using a two-yukawa interaction model. The best-fit parameters reveal how the formulation additives (salt or trehalose) alter protein-protein interactions over a large range of protein concentrations. The results are discussed from a pharmaceutical point of view.

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Dedicated setups at Bio-SAXS P12 beamline for microfluidic screening and kinetic experiments

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A high-brilliance beamline P12 of the EMBL (PETRAIII storage ring, DESY, Hamburg) is dedicated to biological small-angle X-ray scattering (SAXS). P12 possesses a versatile and flexible sample environment that caters for diverse experimental needs to study macromolecular solutions. In addition to a robotic sample changer for high throughput SAXS experiments, a novel microfluidic centrifugal mixing device (SAXS disc) and in-air capillary setup for time-resolved stop-flow experiments have been developed to explore multiple equilibrium conditions and time dependent phenomena while optimizing the sample consumption.

The SAXS disc dedicated to high-throughput screening experiments offers the handling and mixing of microliter quantities of sample. The available microfluidic systems for SAXS often require to control and operate multiple devices (pumps, valves, electronics, pneumatics, etc.) and can thus be very bulky and cumbersome to operate. SAXS disc, a centrifugal force driven microfluidic screening disc for solution SAXS, forgoes the need for any external pump or valve attachments during the data collection (Ducrée et al., 2007). Here we present a pilot application of the SAXS disc to detect and characterize folding intermediates during unfolding of ribonuclease A by urea.

For studying time dependent phenomena, SAXS data are collected from the intermediate states of a system as they shift towards a new equilibrium position. Controlled triggering of a reaction can be realized for example by mixing two solutions. Performing time resolved experiments requires appropriate planning and control of the triggering mechanism based on the a priori information on the time scale of the reaction. Kinetic studies at P12 take advantage of the highly brilliant beam source and a rapid detector PILATUS2M, both allowing for measurement times in millisecond range. SFM400 Biologic stop-flow device with a dead time of about 3 ms is mounted on the experimental table and aligned with the beam. All the required hardware synchronization (stopped flow apparatus, detector, shutter etc.) is based on the Programmable Logic Controller technology. Due to the high flux and low instrument background of P12, the data collected in 30 ms exposure time yield interpretable SAXS profiles. The time scale of the stop-flow experiments fits with the repetition rate (30Hz) of Pilatus 2M and kinetic reactions can be followed with a time resolution of 33 ms. Several P12 user groups have employed the stop-flow system for the analysis of their samples, including the analysis of the tRNA-modifying enzyme complex MnmE/MnmG (Fislage et al., 2014). A new multilayer optics, currently under commissioning, will increase the flux by a factor of 50 to about 5 10^{14} ph/s paving the way for yet more rapid experiments with exposure times in sub-millisecond regime. The P12 sample environment allow for time resolved and screening experiments for novice and expert biological SAXS users.

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Aknowledgements

This work was supported by HFSP (RGP0017/2012), the European Community's seventh framework Programme under Biostruct-X (No. 283570) and SAXS-CD (05K10VFB) grants.

STRUCTURE OF PROTEIN COMPLEXES DURING SPLICEOSOME ASSEMBLY

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Splicing is a crucial step in eukaryotic organisms for the processing of pre-mRNA and regulation of gene expression leading to protein diversity. The assembly of the spliceosome involves cooperative recognition and binding of three splicing factors to the 3'-splice site in pre-mRNA introns [1]. SF1 specifically recognises the intron branch point sequence (BPS) while the heterodimeric U2AF (U2AF65/35) binds poly-pyrimidine tracts and AG-dinucleotide, respectively. This step plays a crucial and decisive role for the assembly of the spliceosome and eventual splicing of an intron [2].

In our studies, we focus on different aspects of protein/protein and protein/RNA interactions in the 3'-splice site by combining solution-based methods, i.e. of NMR and SAS. While NMR reveals high resolution structural information of single domains, SAXS leads to a deeper insight in domain interactions and structural information of the overall complex. The interaction with RNA is then further studied by SAXS and SANS.

Using SAS methods, we are investigating the structure and conformational equilibrium of multidomain arrangements of RRM1 and RRM2 in free and RNA-bound U2AF65. We also study the cooperative assembly of SF1 and U2AF65 to the BPS and Py-tract RNA [3] and domain arrangements in the U2AF heterodimer in the presence of Py-tract and the AG-dinucleotide.

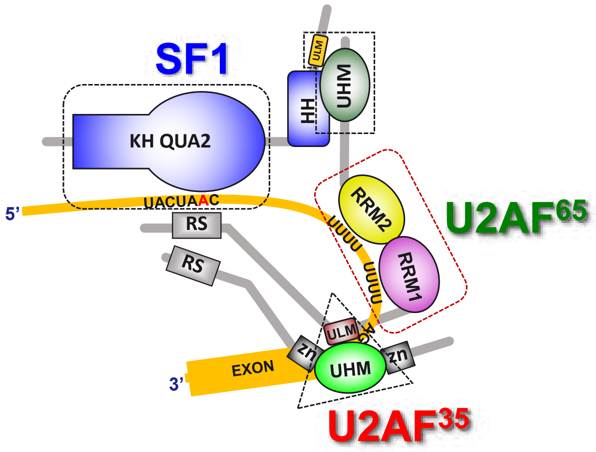

Figure 1: 3'splice site recognition complex containing SF1 and the U2AF65, U2AF35 heterodimer bound to pre-mRNA.

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KINETICS OF SUBUNITS IN α-CRYSTALLIN AS STUDIED BY SMALL-ANGLE NEUTRON SCATTERING

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α-crystallin, which is one of the major structural proteins in the eye lens, exists as huge oligomers consisting of roughly 40 subunits of two homologues: αA and αB. The most fascinating characteristic feature of α-crystallin is its chaperone activity [1], shielding the aggregation of various target proteins under external stresses such as heat, denaturing chemical reagent and UV. In spite of extensive researches, which focused on revealing the mechanism of its chaperone activity the detailed mechanism of it is still far from understanding. One of the proposed concepts is the hybridization of α-crystallin with target proteins. Especially Palmieri et al. [2] reported that the reorganization of quaternary structure of α-crystallin at the temperatures above the onset temperature of its chaperone activity was essential for realization of preferred complexation. Hence it is strongly expected that α-crystallin possesses a dynamical structure, which is submitted to a constant reorganization following certain subunits kinetics. Tracking such kinetics of subunits in α-crystallin must contribute to unveiling the unresolved mechanism of its chaperone activity. For this purpose we resorted to the combination of deuteration-labeling technique and time-resolved small-angle neutron scattering technique.

Figure 1 (a) shows the scattering length densities (SLD) of hydrogenated (h-α), deuterated α-crystallin (d-α) and 82% D_2O buffer. In 82% D_2O buffer the scattering contrasts from h-α and d-α are the exactly same. Upon mixing h-α and d-α in 82% D_2O, if the kinetics of subunits between occurs between them, the scattering contrast will gradually decrease. Namely decrease of the forward scattering intensity (*I*(0)) will be observed. Figure 1 (b) shows the time evolution of *I*(0) after mixing h-α and d-α in 82% D_2O at 298K and we could surely succeed to monitor the kinetics of subunits in α-crystallin. The time evolution of *I*(0) was well fitted with a single exponential function, as shown by a solid line and the evaluated time constant was 20.4±5.2 h. More detailed discussion concering subunits kinetics will be given at the poster session.

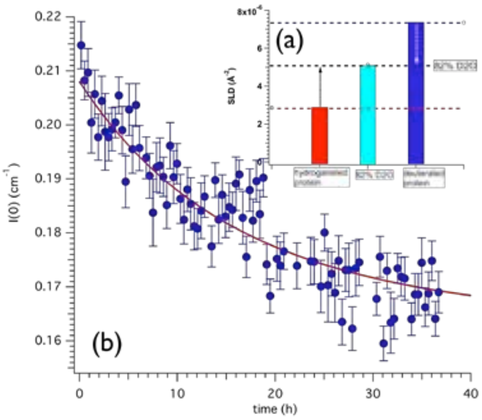

Figure 1(a) SLDs of h-α, 82% D2O and d-α. (b) Time evolution of *I*(0) upon mixing h-α and d-α at 298K.

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SEC-SAXS AS FAST AS BATCH ?

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SWING is the SAXS/WAXS beamline at Synchrotron SOLEIL, mainly dedicated to structural biology and soft condensed matter. For solution biology, Agilent HPLC devices directly coupled to the SAXS measurement cell are available for online purification since 2007 [1]. The HPLC equipment has since been doubled to obtain two independent circuits of purification. We have recently developed an efficient sample injection automated protocol, making possible to alternate batch and SEC-SAXS experiments using a unique interface.

Using columns with smaller volumes (2.5mL) than usual complete elution profiles can be obtained in as short time as 10min, with enough resolution to separate macromolecules from aggregates. During these 10 minutes, a buffer acquisition is performed before the dead volume and then another set of frames are collected during the elution of the sample. The SEC-SAXS procedure results in an optimized buffer subtraction and a range of concentration with a single injection.

Graphical User Interfaces to parameterize and launch the sequences of SEC elutions were largely simplified. The user can program a series of injections and parameterize each of them independently. Two times 54 samples can be injected and recorded without additional human intervention. The twin column system allows to record data under two different buffer conditions without waiting for column equilibration between two shots. Systematic switch between the two columns is actually recommended to obtain a better column equilibration before each injection. In total, a complete SEC-SAXS elution profile can be obtained in 12 minutes.

Improvements have been made on the hardware side as well. A new SAXS cell was designed for an easier replacement of the capillary and of the inlet connecting tubing, and a better alignment of the online fiber-optic dedicated to UV absorption measurement.

All these developments contribute to obtain a much more friendly and efficiently environment for biology users of the SWING beamline.

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AnoSAXS at B21

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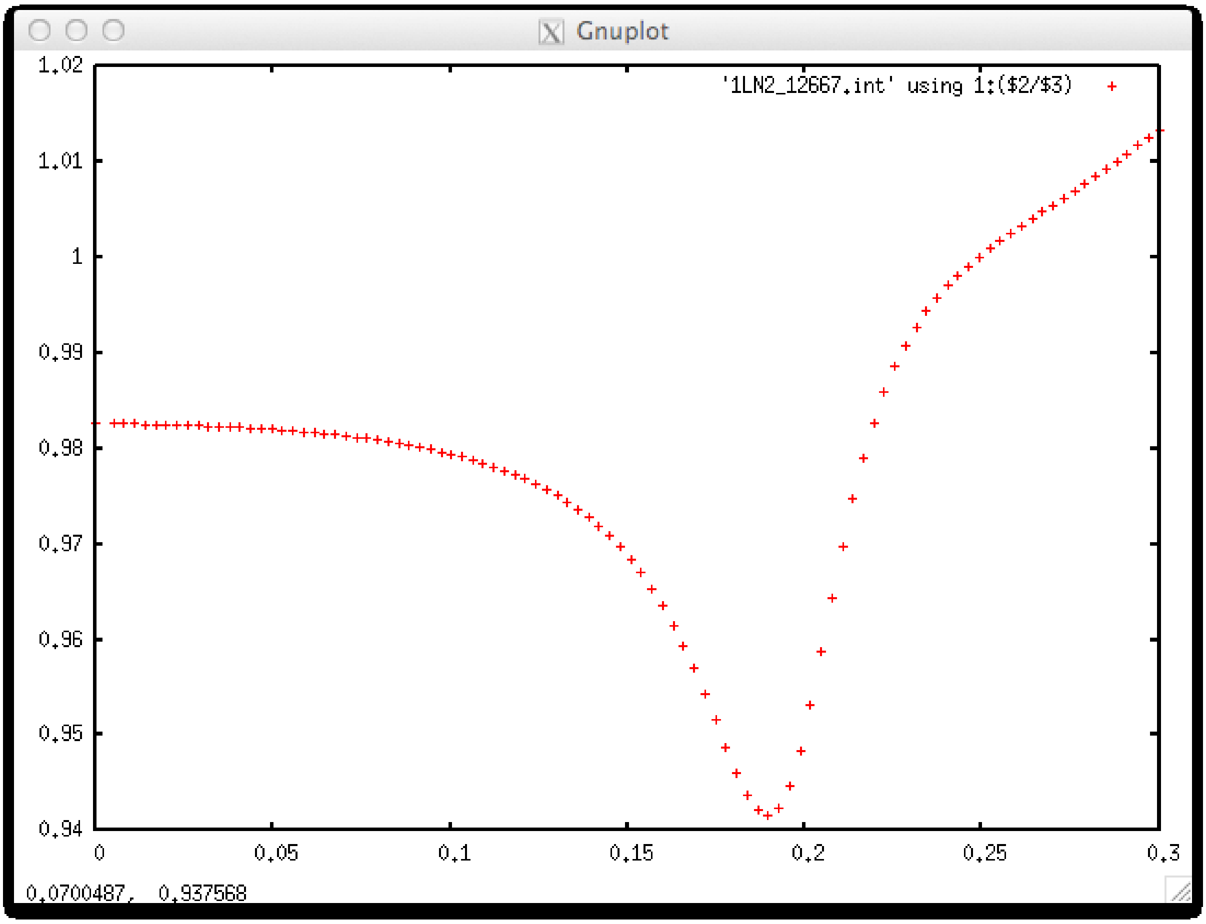
Anomalous SAXS experiments of seleno-methionine or brominated nucleotide labelled complexes has the potential of enhancing structural information from typical SAXS experiments in solution. Anomalous measurements will be difficult, where the magnitude of the anomalous signal will be largely determined by the number of anomalous scatters within the context of the particle. Here, we demonstrate experimental and computational considerations for extracting the anomalous SAXS signal from a protein-protein and protein-nucleic acid complex. We demonstrate using a specialized sample cell that small differences of approximately 6% throughout the observed SAXS profile could be measured by reducing background scatter. Furthermore, we propose using convex optimization routines as a method for extracting the anomalous signal.



SASBDB, a repository of small angle scattering data and models.

Valentini E, Hajizadeh N, Kikhney AG, Jeffries CM, Svergun DI

Small-angle X-ray and neutron scattering (SAXS and SANS) are increasingly popular methods to study the global shapes of proteins, nucleic acids and macromolecular assemblies in solution. Recent advances in instrumentation and analysis methods, the quantity of experimental scattering data and subsequent publications is increasing dramatically. The need for a global repository allowing investigators to locate and access experimental data and associated models was recently emphasized by the world-wide protein databank small-angle scattering task force (wwPDB SAStf) [1], that foresees the development of a consortium of SAS databases for data and model deposition similar to what is currently being done for X-ray crystallography, NMR spectroscopy and electron microscopy at the wwPDB .

The Small Angle Scattering Biological Data Bank (SASBDB) [2] was developed following the wwPDB SAStf requirements. The repository contains SAS experimental data sets together with derived models, relevant experimental conditions and information about macromolecules and publications. SASBDB is a fully browsable database where entries are freely available for download and contains cross-references to other biological databases as well as advanced search options to easily locate SAS data entries.

As of March 2015 SASBDB contains 114 experimental data sets and 195 derived models. The data stored in SASBDB are manually curated by SAS experts, with plans to incorporate automated validation and quality assessments of deposited SAS data and models. Following the suggestions of the wwPDB SAStf, SASBDB includes data in the sasCIF file format [3], that guarantees uniformity in data exchange among different SAS repositories. Furthermore, SASBDB features a set of scattering data from highly purified commercially available proteins, which can be used for algorithm testing purposes. SASBDB comes with multiple help pages and a news feed page where the latest entries are published. The data bank is designed to be fully scalable and so as to cater for the future demands of a rapidly growing user community while at the same time it is hoped that SASBDB will contribute towards improving the overall quality assurance of biological SAS data and modeling for users in the field of biological SAS.

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We acknowledge the European Commission Seventh Framework Programme (FP7) project IDPbyNMR [264257] and the Bundesministerium für Bildung und Forschung (BMBF) project BIOSCAT [05K12YE1].

↘ Flash Talk: Mon-F-S1

EXPLORING THE *IN MESO* CRYSTALLIZATION MECHANISM BY USING SYNCHROTRON SMALL ANGLE X-RAY SCATTERING

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Recently, the development of a novel in meso crystallization method has facilitated the structural determination of several biologically relevant integral membrane proteins (IMPs).[1] However, *in meso* crystallization remains poorly understood as IMPs are difficult to express and handle. *In meso* crystallization is analogous to solution based crystallization and requires extensive screening of precipitant conditions. An improved understanding of the *in meso* crystallization technique can lead to an improved success rate and facilitate the structural determination of more IMPs. These structures are important for rational drug design and designing new treatments for a wide range of diseases.

Bicontinuous cubic phases (Figure 1) are the most commonly used lipid phases for *in meso* crystallization. The proposed mechanism states that the membrane protein or peptide is initially uniformly dispersed in the cubic phase but that crystals grow from a local lamellar phase which acts as a conduit between the crystal and the bulk cubic phase.[2] However, there is very limited experimental evidence for this theory. In this work we have explored this by characterizing the lipid mesophase microenvironment by using synchrotron Small Angle X-ray Scattering with a micro-sized beam during crystal growth of the DAP12-TM peptide of which the structure was recently solved.[3] Crystal growth was indeed found to occur from the cubic mesophase, and for one in four crystals a highly-oriented local lamellar phase was observed consistent with the co-location of the lamellar phase at a crystal face supporting the proposed mechanism for *in meso* crystallization. A new observation of this study is that some crystals may give rise to diffraction at wide angles which is of potential use in locating these crystals.[3]

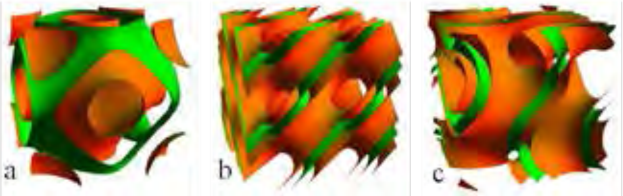

Figure 1: Schematic presentation of self-assembled lipid structures, (a) Primitive cubic phase, (b) Diamond cubic phase, (c) Gyroid cubic phase.[4]

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FUNCTIONAL FLEXIBILITY OF THE INTERLEUKIN-1 RECEPTOR FAMILY

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Interleukin-1 (IL-1) family of cytokines plays significant roles in innate inflammatory response, infectious and autoimmune diseases. IL-1 cytokines exert their function through binding to their respective primary receptor and then recruiting a second receptor to form an activating signaling complex. There are eleven members in the IL-1 family of cytokines, including IL-1β, IL-33 and IL-18. IL-1β promiscuously interacts with receptors IL-1RI and IL-1RII, whereas IL-33 and IL-18 are specifically recognized by receptors ST2 and IL-18Rα, respectively. IL-1RAcP is a shared co-receptor for IL-1 family of cytokines, except for IL-18, which has its own co-receptor IL-18Rβ. Activation of IL-1 signaling cascade, initiated by cytokine binding to ligand-recognition receptor and the following assembly of a co-receptor, juxtaposes the intracellular TIR domains of both receptors triggering the subsequent intracellular signaling pathways. All members of the IL-1 receptor family except SIGIRR have three Ig-like domains, D1, D2 and D3 that are flexibly linked in the extracellular region. Available crystal structures of ternary complexes have illuminated the structural insights into the activation mechanism of IL-1 receptors [1-4]. However, current structures of IL-1 receptors are all captured in ligand-bound state. The degree of flexibility correlated with their dynamic nature relevant to molecular recognition has not been well understood. Therefore, we conducted small-angle X-ray scattering studies to reveal the solution conformations of the ectodomain of IL-1 receptors. Our results show that in unbound state the primary receptors exist in multiple conformations and exhibit the hinge flexibility between the D3 domain and D1D2 module. Interestingly, the co-receptors prefer to stay as a single conformation in solution. The rigidity of the co-receptors explains their inability to directly engage cytokines, while flexibility of the primary receptors offers the accessibility for their respective ligands to interact with D3 domain. Taken together, we have delineated the functionally relevant conformations of IL-1 receptors and provided the fundamental understanding of how the flexibility within IL-1 receptors contributes to specific interactions of cytokine-receptor complexes.

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BL4-2: The Biological Small Angle X-ray Scattering Facility at SSRL

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The small-angle x-ray scattering station BL4-2 at the Stanford Synchrotron Radiation Lightsource (SSRL) is a permanent experimental station dedicated to structural biology and biophysics, providing state-of-the-art experimental facilities for structural studies on nucleic acids, proteins, protein assemblies, virus particles, biological fibers, lipid membranes and their complexes. The beamline is designed to be rapidly re-configurable in order to efficiently optimize the instrument for the specific requirements of the different types of experiments. A customized version of the Blu-Ice/DCS software, originally developed for macromolecular crystallography experiments, is used to control the entire instrument providing an intuitive graphical user interface for all the experiment. Specialized equipments for a variety of different of SAXS experiments are available at the beamline. In particular, we provide a fully automated high-throughput solution sample delivery robot with an attached software pipeline that automatically performs all the necessary steps for data reduction and initial analysis. For aggregation prone samples or unstable complexes a size-exclusion chromatography (SEC) setup can be directly connected to the instrument allowing in-line SEC-SAXS experiments. Furthermore a stopped-flow device with a customized low-volume injection port is available for fast time-resolved SAXS studies at minimum time-resolution of 5ms and above. Here we will inform about new technological developments at the beamline as well as present some recent scientific results.

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↘ Flash Talk: Mon-F-S1

Abstract for SAS 2015

Title: Structural Study of Proteins and their Complex Formation with Polyelectrolytes using Small-Angle Neutron Scattering

Human Serum Albumin (HSA) is an important transport protein that interacts with substances as e.g. fatty acids [1,2] and pharmaceuticals in a specific manner.[3] Also, transport by HSA plays an important role for renal clearance and the interaction of HSA with uremic toxins is an essential factor in the excessive cardiovascular mortality. Patients with a chronic kidney disease suffer from accumulation of a large number of uremic toxins, which are usually excreted by the kidney. [4,5] It is assumed that these patients possess structurally modified HSA which leads to an alteration of its natural function. The structure of such modified protein however is not known.
SANS is a powerful technique to reveal structural information of such small macromolecules due to the high contrast of e.g. proteins to D_2O and the possibility of contrast variation [6]. Furthermore, there have been a great improvement of modelling small-angle scattering data using computational methods.[7] Neutron scattering enables investigation of protein-ligand complexes in solution and under physiological conditions (37°C, physiological salts, etc.), which is not possible by protein-crystallography. We present structural investigations of healthy HSA upon interaction with a model ligand substance and modified HSA from patients suffering from chronical kidney disease in comparison using SANS.

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MILLISECOND KINETICS OF THERAPEUTIC DRUGS LOADING IN BICONTINUOUS CUBIC PHASE

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Millisecond time-resolved small-angle X-ray scattering (SAXS) combined with stopped flow rapid mixing at beamline ID02 (ESRF, Gerenoble, France) was used for the study of therapeutic drugs loading in precursors of lipid cubic phases. The concrete realization involved the protein (BDNF, brain derived neurotrophic factor) that modulates the membrane curvature in the cubic phase by steric and electrostatic binding. The produced dynamically assembled lipid/protein architectures are important for both physiological functions and the design of therapeutic nanotechnologies. The kinetic pathway of nonequilibrium lipid/protein states was determined with 4 milliseconds precision.

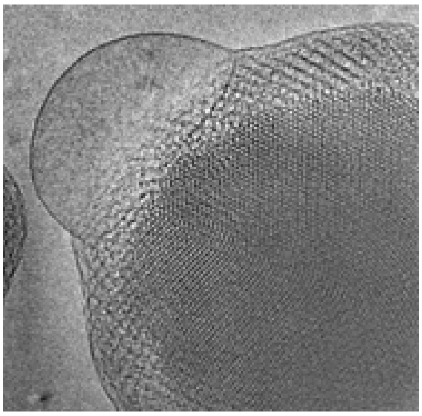
Figure 1: Multiphase liquid-crystalline nanoparticle resulting from stopped flow rapid mixing of lipid cubic precursors and the protein BDNF.

The protein BDNF trafficking and binding to the flexible membranes induced an unusual overlay of nanostructures including two coexisting cubic lattices epitaxially connected to lamellar membrane stacks. These time-resolved membrane processes evidence stepwise curvature control mechanisms based on intercalation of discrete stiff rods (proteins) in continuous soft membranes,. The obtained three-phase liquid-crystalline nanoparticles put forward important advancements in multicompartment soft-matter nanoarchitectonics design.

Acknowledgment. B.A. and S.K.F. acknowledge the Czech Science Foundation Grant No. 15-10527j.

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THE EFFECTS OF DEPOSITION CONDITIONS AND ANNEALING TEMPERATURE ON THE STRUCTURE AND MORPHOLOGY OF TA-N THIN FILMS

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Tantalum nitrides (Ta-N) thin films are used in a wide variety of applications such as an effective Cu diffusion barrier material in integrated circuitry, wear and corrosion-resistant materials, as well as thin film resistors. The structural, morphological and electrical properties of magnetron-sputter-deposited Ta-N thin layers strongly depend on the deposition conditions. Here we focused on the impact of varying nitrogen content in the deposition chamber during synthesis as well as post-deposition annealing in the temperature range up to 950°C. The films were structurally and morphologically characterized with grazing incidence X-ray techniques: specular reflectivity (XRR), diffraction (GIXRD) and small angle scattering (GISAXS). The atomic composition of the films was determined with time-of-flight elastic recoil detection analysis (TOF-ERDA) experiments.

The structure of the films strongly depend on the Nitrogen partial pressure (pN_2); for low pN_2 the film structure is fcc-TaN (pN_2 =20%), while for high pN_2 the film is amorphous N-rich (pN_2 =70%); the density of the films is correspondingly affected. Upon annealing, in low pN_2 film additionally appears a θ-TaN phase, while amorphous film crystallizes into fcc-TaN and concurrently releases nearly 40% of the nitrogen. The porous homogenous structure of the films deposited at high pN_2 develops upon annealing and shows growth of both nanoparticles and voids between them. All these findings are evaluated in relation with electrical measurements of the film resistivity in order to gain a better understanding of the material parameters relevant for electronic devices.

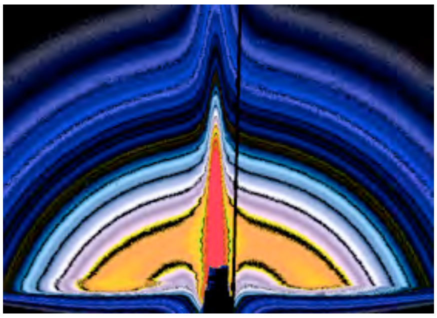

Figure 1: GISAXS pattern for Ta-N film deposited with pN_2=70% and annealed at 750 ^{o}C.

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COMPARISON OF GISAXS AND AFM CAPABILITIES FOR SURFACE SWIFT HEAVY ION TRACK ANALYSIS

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Irradiation of flat solid surfaces by swift heavy ions under grazing incidence angle can result in the formation of surface ion tracks. These ion tracks can be observed directly using atomic force microcopy (AFM) [1-3]. However, to extract statistical information (average ion track length, length distribution etc.), structural investigations of this type are very time consuming. In the present work we apply Grazing Incidence Small Angle X-Ray Scattering (GISAXS) for the structural analysis of surface swift heavy ion tracks and demonstrate its capabilities on a wide range of investigated materials ($SrTiO_3$, TiO_2, quartz and a-SiO_2, amorphous Ge+SiO_2 and Ge+ITO thin films). Compared to AFM, GISAXS allows short measuring times with an excellent statistics. Possible applications of surface patterning of Ge+ITO thin films using swift heavy ions, with respect to the modifications of transparent Ge+ITO electrodes for photovoltaics, will be discussed as well.

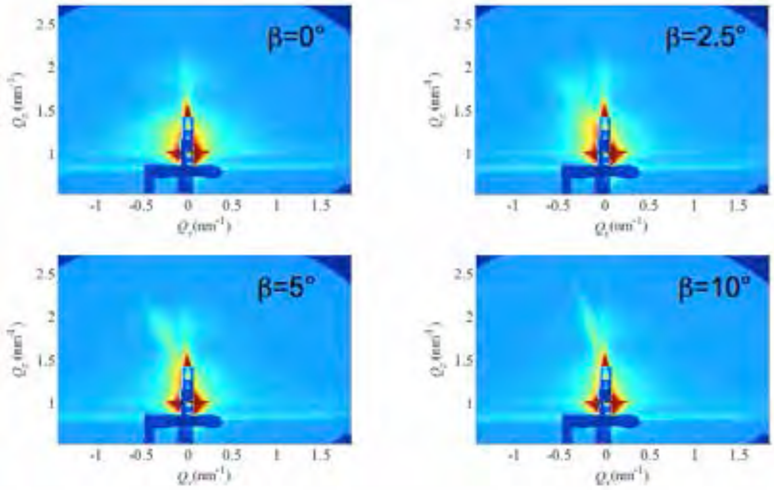

Figure 1: GISAXS pattern from irradiated Ge+ITO thin films: effect of azimuthal angle β.

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FORMATION DYNAMICS AND PLASMON PROPERTIES OF CU NANOPARTICLES

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The metals Cu, Ag, and Au in nanometer shapes present original optical properties due to the presence of a plasmon band. This phenomenon originates from the collective oscillations of the conduction electrons, the plasmons, and corresponds to a narrow absorption band in the visible spectral range. Thus, the optical properties of a dielectric material can be modified by introducing metallic nanoparticles. Controlling the size, shape and chemical environment of nanoparticles, one can modify for example, in a controlled manner, the plasmon band and therefore the macroscopic properties of the host matrix. In this context, our research focuses on the synthesis of Cu nanoparticles in and on silica, forming thus composite materials.

The samples were produced by thermal evaporation in high vacuum of a single Cu layer on top of Si substrate and/or one capped with a thin SiO_2 layer. The samples were deposited on substrates held at different temperatures and were ex-situ annealed in high vacuum. Grazing incidence small-angle X-ray scattering (GISAXS) was used to study the morphology development and the structural properties. The GISAXS results are compared with those from Atomic Force Microscopy and Scanning Electron Microscopy measurements, and the fractality of such formed structures are explored with both techniques. The formation of Cu nanodots was additionally monitored by Rutherford Backscattering Spectroscopy and SAXS/WAXS techniques. However when clustering of Cu was explored within dielectric layers GISAXS was the only choice to provide reliable results. It is shown that the Cu production is critically dependent on the starting configuration of the layers. The plasmonic effect was monitored by UV-Vis reflectance spectroscopy. The oxidation of nanoparticles was further studied by photoluminescence spectroscopy.

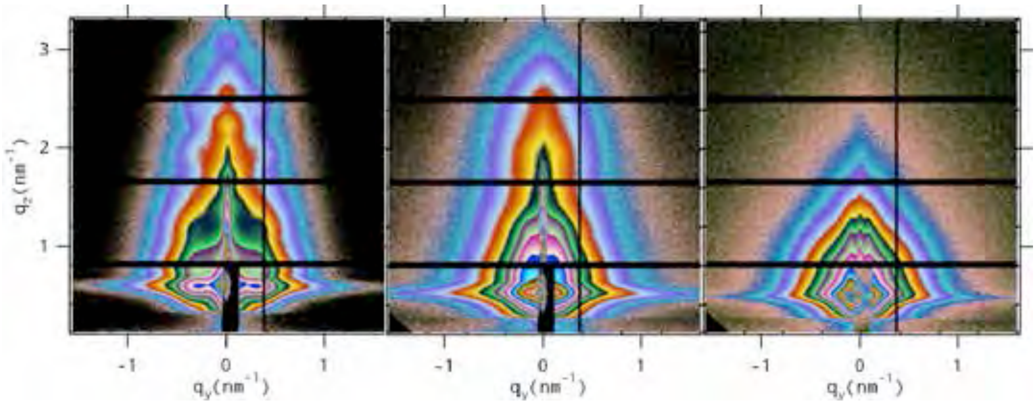

Figure 1: GISAXS patterns of 20 nm Cu thin layers as-deposited on clean Si substrate held at different temperatures (RT, 100°C and 180°C, from left to right).

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THERMODYNAMICS OF PROTEIN-NANOPARTICLE INTERACTIONS A SAXS STUDY

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The use of nanoparticles for biomedical purposes has been under investigation for many years. Some of the most important applications, such as drug delivery, disease diagnosis and treatment, require intravenous delivery and close interaction of nanoparticles with blood. For this reason, the study of interactions of nanoparticles with biomolecules and especially with serum proteins, the most abundant ones in plasma, has received particular attention. The adsorption of proteins and other macromolecules on the nanoparticle surface is determined by their affinity, which depends on several factors such as size, shape and surface chemistry of the nanoparticle [1]. On these grounds, it is essential to understand the behaviour of the protein-nanoparticle interface for a safe use in *in vivo* applications [2]. Recent studies have shown that once nanoparticle are introduced into the plasma, a protein shell is formed around their surface. The role of this coating could be critical in masking the core of nanoparticles to cells and the various receptors that mediate the immune response. Despite the applicative importance of coated nanoparticles, there is a lack of information on the mechanisms and thermodynamics at work. Classical approaches to the characterization of protein-nanoparticle association usually require removal of proteins from the nanoparticle and their subsequent identification [3]. A typical method includes an isolation step via size exclusion chromatography or differential centrifugation, followed by protein identification via gel electrophoresis and mass spectrometry [4]. This is very far from the physiological conditions where these complexes should be studied [5]. Furthermore, quantification of protein binding thermodynamics and kinetics are difficult. Here we propose to take advantage of small angle X-ray scattering (SAXS) to directly inspect samples containing both proteins and nanoparticles without any manipulation, allowing physiological conditions to be used for investigating the stoichiometry and the thermodynamics of the protein-nanoparticle association. A thermodynamic model was developed within the framework of the Genfit software [6] describing the interplay between a protein and one site on the surface of the nanoparticle in terms of the related association constant. Such model is the basis for a theoretical work in which we have inspected the sensitivity of SAXS to detect protein-nanoparticle associations for gold, silver and silica nanoparticles of different sizes with bovine serum albumin (BSA). Experimental curves exploring similar conditions have been analysed to estimate the value of the association constant.

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MICROEMULSIONS AT PLANAR WALLS WITH AND WITHOUT ADDITIVE

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The grazing incidence small angle neutron scattering of microemulsions at planar walls was characterized in terms of structure [1] and dynamics [2] at a SANS instrument, a reflectometer, and a neutron spin-echo (NSE) spectrometer. Using the evanescent (tunneling) wave for incident angles below the critical angle of total reflection, a depth resolution could be achieved for all these experiments.

Bulk bicontinuous microemulsions show a lamellar structure close to hydrophilic planar walls. The number of perfect layers, the decay of the lamellar order, and the dynamics of the surfactant membranes was characterized. The dynamics were three times faster adjacent to the wall, which was connected to a modified theory of membranes in a viscous medium to additional confinement of the hydrodynamic field at solid walls (volume conservation between the first membrane and the wall). The structural characterizations are connected to the depth resolved dynamics, and a complete picture can be drawn. A complementary study of microemulsions adjacent to clay platelets with varying diameter displayed the importance of the confinement of long wavelength undulations [3].

Adding amphiphilic polymers as efficiency boosters to this system [4], the near surface dynamics is slowed down, and the polymers are attracted to the first membranes adjacent to the wall through confinement effects. The more rigid membrane can be connected to the slowing down, and the enrichment of polymers at the wall might facilitate the cleaning of contaminants.

A newly developed resonator enhances the intensity of the evanescent wave dramatically, and would allow for even more difficult experiments. So far we extended the Q-range of the grazing incidence NSE experiments to a more interesting range. In the future, less material or weaker scatterers, i.e. more applicable samples, can be investigated in the vicinity of a planar surface.

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DEFORMATION OF MICROPOROUS FILMS DURING ADSORPTION AND DESORPTION OF WATER

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The mechanical response of porous thin films to changes in humidity was investigated by GISAXS. Porous films prepared by evaporation-induced self-assembly of block-copolymer template silica precursor sols can adsorb water. Two series of films were prepared by spin coating and by dip coating differing in film thickness and degree of orientation of the pores relative to the substrate.

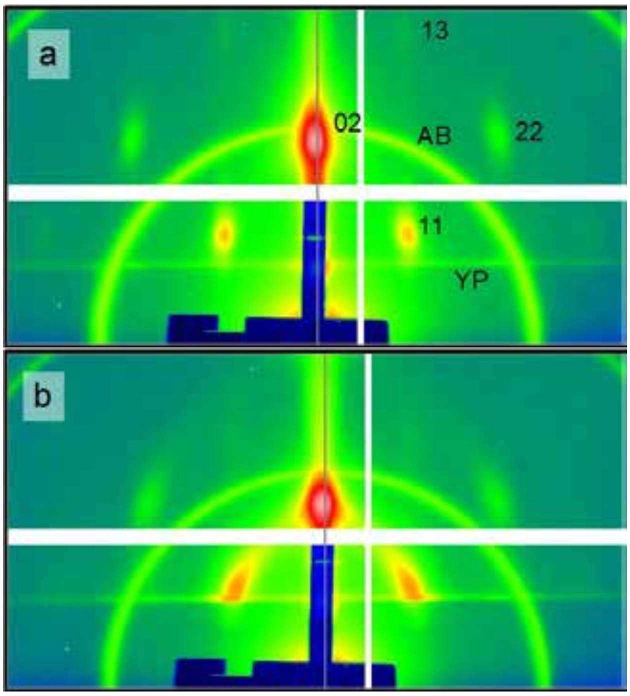

Figure 1: (a) GISAXS pattern of a spin coated film at 2000 rpm. YP indicated the Yoneda peak, AB a silver behenate ring. The numbers are the miller indices of the deformed hexagonal lattice. (b) Dip coated film at 6 mm/s

The liquid phase formed by adsorption within the pores can exert forces onto the pore wall, which leads to a deformation of the material [1]. Such a deformation is anisotropic due to the restrictions in swelling and contraction imposed by the substrate.

Evaluation of GISAXS data (Fig. 1) showed that the deformation in lateral direction is considerably smaller than in vertical direction. The film swells in direction of the surface normal with adsorption and contracts with desorption. Especially the onset of meniscus formation during adsorption and the loss of menisci during desorption is linked to a strong change in lattice parameters. The degree of order as well as the film thickness influences the response to humidity.

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IN SITU GISAXS INVESTIGATION OF THE THERMAL STABILITY OF SELF-ORGANIZED RARE-EARTH SILICIDE NANOSTRUCTURES

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Metallic high aspect ratio rare-earth silicide (RESi) nanowires self-organized on the Si surface have attracted particular attention during the last decades because of their potential applications in the near-future CMOS nanoelectronics as Ohmic contacts and interconnects [1]. For these envisaged applications, however, the systematic investigation of the thermal stability of their crystal phases, chemical composition and morphology is essential since the heat removal became a demanding issue with the continuous downscaling of the electronic circuits.

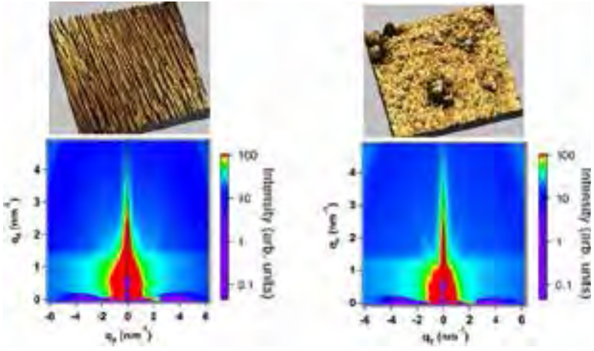

Figure 1: Left - GISAXS and AFM images of $DySi_2$ nanowires obtained at room temperature, Right - GISAXS image obtained at 1273 K along with AFM image obtained at room temperature after annealing.

In order to perform these systematic studies a portable ultrahigh-vacuum (UHV) chamber dedicated to variable-temperature *in situ* (under UHV condition) X-ray scattering and spectroscopy experiments at synchrotron radiation beamlines was constructed and brought into operation at ANKA. RESi ($EuSi_2$ & $DySi_2$) nano-islands and nanowires were grown on vicinal Si(001) substrates at optimized conditions by molecular beam epitaxy [2]. *In situ* GISAXS experiments were performed to investigate the changes of the surface morphology upon high-temperature annealing of RESi nano-islands and -wires. Analysis of GISAXS data have shown that upon annealing at high temperature (~ 1270K) decomposition of the $EuSi_2$ nano-islands takes place and the Eu atoms desorb from the surface leading to an island size reduction by a factor of two. These conclusions are confirmed by the AFM studies performed before and after the in-situ annealing [3]. Upon high temperature annealing $DySi_2$ nanowires degrade forming initially agglomerates of islands and finally faceted islands (Figure 1). The morphology changes from wires to islands can be systematically followed in real time by temperature-dependent *in situ* GISAXS experiment

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IBUPROFEN AND DRYING IN PHOSPHOLIP FILMS

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Nonsteroidal anti-inflammatory drugs (NSAID) such as ibuprofen have a wide range of medical applications, ranging from pain relieve to cancer treatment [1]. However, some applications require long-term application, which can lead to gastrointestinal complications and even fatal ulcers [2]. Neutron reflectometry and grazing incidence neutron scattering (GISANS) investigations of phospholipid films, revealed a change in layer thickness upon the introduction of Ibuprofen [3]. This change in layer thickness can be attributed to a different apparent hydration of the film [4].

We previously investigated the influence of ibuprofen on phospholipid layers of L-α-phosphatidylcholine (SoyPC), as a model system for cell membranes, between 0 and 53.3 mol% of ibuprofen [5]. Our investigations revealed that ibuprofen induces a two-step ordering in such films depending on the concentration. While there is no ordering for the pure SoyPC film, at higher concentrations ordering occurs. There is a re-organization at even higher concentrations of ibuprofen, leaving only a single hexagonal structure. The findings are compared with measurements at different relative humidities of pure SoyPC. Knowledge about this behavior of phospholipid membranes in the presence of ibuprofen may help elucidate the reason for long-term toxicity of ibuprofen.

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IN SITU STUDY BY GISAXS OF THE KINETIC OF FORMATION AND GROWTH OF $CoSi_2$ NANOPLATELETS IN Si(001)

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An in situ study by grazing incidence small angle X-ray scattering (GISAXS) was performed to elucidate the mechanisms of formation and growth of: (i) spherical Co nanoparticles embedded in a SiO_2 thin film deposited on a Si(001) wafer and (ii) hexagonal $CoSi_2$ nanoplatelets endotaxialy buried in the Si(001) substrate, during isothermal annealing at 700 ºC. GISAXS patterns were recorded every 2 min during thermal treatment, over a total period of ~ 180 min. Figure 1 shows the 2D GISAXS intensity patters for the indicated thermal treatment periods.

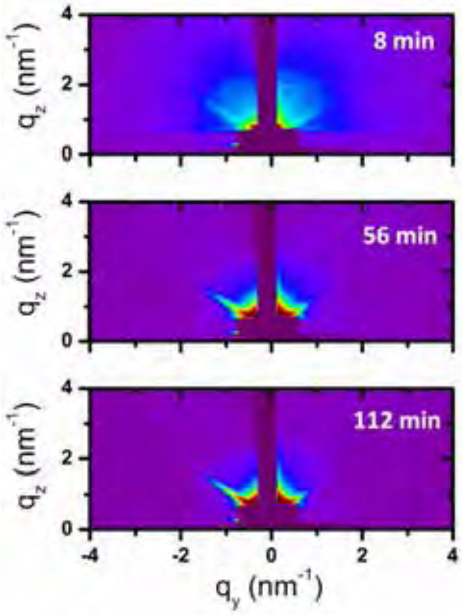

Figure 1: 2D GISAXS intensity patterns due (i) spherical Co nanoparticles embedded in a SiO_2 thin film deposited on a Si(001) wafer and (ii) hexagonal $CoSi_2$ nanoplatelets endotaxialy buried in the Si(001) substrate corresponding to the indicated periods of thermal treatment at 700 °C

Our results evidenced the formation of spherical Co nanoparticles embedded in a SiO_2 thin film promoted by the diffusion of Co atoms through the SiO_2 thin film and the diffusion of Co atoms across the SiO_2/Si(001) interface into a Si(001) wafer leading to the formation of hexagonal $CoSi_2$ nanoplatelets. The sizes of Co nanoparticles continuously grow during the annealing while their number density progressively decreases thus leading to a coarsening of the overall particle structure.

Simultaneously, Co atoms diffuse into the Si substrate, react with Si atoms and build-up $CoSi_2$ hexagonal nanoplatelets. All nanoplatelets have their large surface parallel to Si{111} crystallographic planes with their lattice coherent with the host Si lattice. Since the total volume of Co nanoparticles embedded in the SiO_2 thin film decreases while the total volume of $CoSi_2$ nanoplatelets buried in Si(001) increases, we concluded that the growth of $CoSi_2$ nanoplatelets occurs at the expense of the dissolution of the relatively smaller Co nanoparticles.

In order to obtain all relevant parameters from the experimental GISAXS intensity, we have applied a newly developed routine for full-pattern fitting, which takes into account the experimental counting rates corresponding to all accessible pixels.

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AN IN-SITU µGISAXS INVESTIGATION OF THE GROWTH OF MAGNETIC NANOSTRUCTURES ON RIPPLED TEMPLATES

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Patterning of magnetic materials at nanoscale is so crucial for spintronic applications. The artificial tuning of magnetic properties of ultrathin films by means of the surface and interface modifications is a fascinating issue from both fundamental and technological points of view. Recently, nanorippled Si substrates produced by low energy ion beam erosion have been used as templates for growing nanostructured metallic thin films with tunable functional properties [1, 2]. The structure and the morphology of the nanopatterned substrate are expected to affect significantly the growth behavior of the metallic thin film, inducing anisotropy in the morphology. Therefore it is important to understand the effect of the structure and morphology of the nanopatterned substrate on the growth behavior of metallic thin films.

In this work, investigation of the growth mechanism of magnetic thin films of Co and Permalloy ($Ni_{80}Fe_{20}$) deposited at normal incidence and glancing angle sputter geometry on nano-rippled Si (100) substrates using in-situ µGI-SAXS measurements has been done. We have performed *in-situ* real time µGISAXS at the P03/MiNaXS beamline [3, 4] of PETRA III storage ring during the sputter deposition thin films. Nanorippled Si substrates prepared by low energy ion beam sputtering with average wavelength of 40 nm and depth of 3 nm have been used as a template. A detailed investigation of the effect of various experimental parameters on the formation of patterned templates has been studied using GISAXS. The thickness of the deposited thin films has been calibrated by x-ray reflectivity measurements. In the case of Co thin film deposited at normal incidence the film replicates the morphology up to larger thickness regimes. It has been found that growth is highly anisotropic along and normal to the ripple wave vectors. Magnetic measurements show a strong uniaxial magnetic anisotropy with magnetization in a direction normal to the ripple wave vector. In the case of Permalloy thin films deposited at glancing angle, the shadowing effect leads to the formation of tilted nanowires. The conformity with the template has been observed for low thickness values and it gradually decreases with increasing the film thickness. Annealing followed by the deposition generates large range ordered nanowires. Also tried to correlate the observed magnetic anisotropy with anisotropic nanostructure deduced from GISAXS.

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DISSECTING AMYLOID PEPTIDE EFFECT ON ARTIFICIAL MEMBRANES

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The cytotoxicity mechanism of amyloid peptide is still largely debated. Several hypotheses, all supported by different experimental methods, have been proposed: i) amyloid peptides can oligomerize and form a pore in the membrane; ii) amyloid peptides interaction with the bilayer surface promotes lipid depletion , at the interaction site, which destabilizes the whole bilayer; iii) amyloid aggregation and the subsequent fibril growth destabilize the membrane.

Each of these mechanisms result in the permeation of the membrane to ions, in particular to Ca^{2+}, leading to cell apoptosis.

To clarify the role of amyloid peptides in cell apoptosis, we combine electrophysiology on Droplet Interface Bilayer (DIB) and Neutron Reflectivity (NR). By this way, it is possible to compare the effect of different amyloid peptides on themembrane in terms of permeation (by DIB measurements) and of structural changes (by NR measurements).

We selected human Islet Amyloid Polypeptide (hIAPP) as reference peptide. It is responsible for the depletion of β-pancreatic cells and consecutively, for type II diabetes. Beside the full length peptide (1-37), the amyloidogenic C-ter fragment (23-37) and the non-amyloidogenic N-ter fragment (1-20), are compared in order to understand the role of each part of the peptide in the cytotoxic process. The rodent homologue (rIAPP) and its fragments are used as a control because they are known to be non-amyloidogenic and non-cytotoxic.

On a long time-scale (~ 1 to 4 hours), NR clearly shows a lipid depletion of the leaflet exposed to the peptide solution. In some reproducible cases, peptide fibrillation was also detected. In fact, while the C-ter of the peptide is important for fibrillation, the N-ter is crucial for a deep interaction down to the inner leaflet of the bilayer, not exposed to the peptide solution. Electrophysiology measurements showed that the membrane permeation is not directly linked to the fibrillation.

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↘ Flash Talk: Mon-F-I1

LIPID STRUCTURE, LATERAL ORDER AND INTER-MEMBRANE FORCES

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Using solution x-ray scattering and advanced analysis tools, developed in our lab, we are investigating the high-resolution structure of charged and dipolar lipids under various aqueous solution conditions. These conditions include, different salt solutions containing monovalent, multivalent, or polyvalent ions, as well as ionic liquids. We determine the electron density profile along the normal to the membrane plane and the spacing between bilayers when lamellar phases form.

Using the osmotic stress method, we are determining the forces between these bilayers under different conditions and compare with the predicted interactions based on thermal fluctuations and a modified Poisson Boltzmann theory. This comparison reveals the extent of ion dissociation, entropic effects, membrane elastic properties, and the non electrostatic interactions between the ions and the lipid membranes. We are also revealing the lateral order within the bilayers, using solution wide angle x-ray scattering experiments and our advanced analysis tools.

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STANDING-WAVE X-RAY FLUORESCENCE PROBES ELEMENT PROFILES IN BIOMOLECULAR LAYERS WITH SUB-NANOMETER RESOLUTION

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In nature, biomolecules are often organized as functional thin layers in interfacial geometries. The most prominent examples are the biological membranes which are among the fundamental building blocks of all cells. But biomolecular layers also play important roles in context with biotechnological and biomedical surfaces, for instance when they are the result of desired or undesired adsorption. For the understanding of a wide range of biological or biotechnologically relevant processes, detailed structural insight into the involved biomolecular layers is required. Here, we use standing-wave x-ray fluorescence (SWXF, [1]) to determine element-specific density profiles in solid-supported lipid and protein monolayers with sub-nm resolution. The technique complements traditional reflectometry experiments which merely yield the “global” density profiles of the layers. While earlier work mostly focused on relatively heavy chemical elements and typically dealt with ion distributions, we work in configurations which also allow localizing the comparatively light elements S and P, which are found in many biomolecules and therefore particularly interesting.

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NEUTRON REFLECTOMETRY IDENTIFIES DIFFERENT MODES OF PROTEIN ADSORPTION ONTO POLYMER BRUSHES

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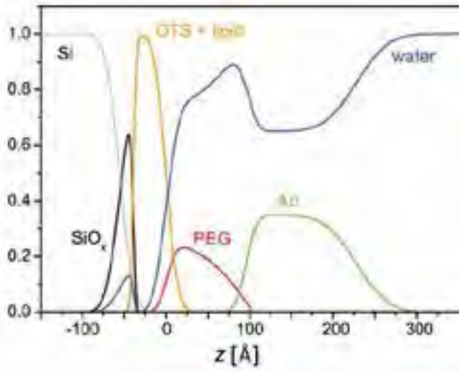
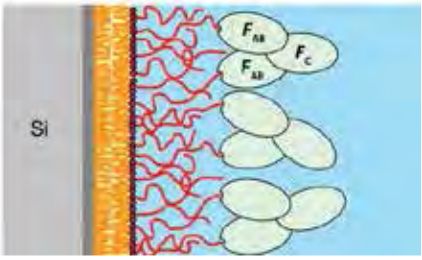
The density profiles of proteins adsorbed onto poly(ethylene glycol) (PEG) brushes are characterized by neutron reflectometry (NR). In contrast to conventional methods, NR allows directly distinguishing among primary adsorption at the grafting surface, secondary adsorption at the brush outer edge, and ternary adsorption to the polymer chains [1]. For hydrophobic grafting surfaces, myoglobin (Mb) exhibits primary adsorption, which consists of two distinct protein layers. The amount of Mb adsorbed in the inner layer is independent of the polymerization degree N but varies with the grafting density σ, while for the outer layer it is correlated to the amount of grafted PEG and thus depends on both N and σ. The sensitivity of NR is enhanced by the use of deuterated Mb [1]. PEG antibodies, whose implications in the field of biocompatible functionalization are still underexplored, exhibit terminal binding to the chain end groups and form dense layers covering the brush periphery [2]. More recent experiments further reveal the distribution of blood proteins adsorbed to brushes from human blood serum. Precise structural studies by NR provide a valuable basis for the rational design of protein-repellent surface functionalization and may help understand the mechanisms by which blood proteins lead to brush failure in in-vivo applications.





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REAL TIME INVESTIGATIONS DURING SPUTTER DEPOSITION FOR TAILORING OPTICAL PROPERTIES OF METAL-POLYMER INTERFACES

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Tailoring optoelectronic properties of metal-polymer interfaces using self-assembly of nanoparticles is of crucial importance in organic electronics and organic photovoltaics [1]. In particular, metal sputter deposition on block-co-polymers is one widely used method to fabricate nanostructured metal layers on a large scale exploiting the selective wetting and doping of metals on polystyrene domains [2,3]. In order to obtain full control over the nanostructural evolution at the metal-polymer interface and its impact on optoelectronic properties, we employed a combination of *in situ* time-resolved microfocus Grazing Incidence Small Angle X-ray Scattering (μGISAXS) with *in situ* UV/Vis Specular Reflectance Spectroscopy (SRS) during sputter deposition of gold (Au) on thin polystyrene films (PS). We monitored the evolution of the metallic layer morphology according to changes in the key scattering features by geometrical modeling [4] and correlate the nanostructural development to optical properties. The changes of optoelectronic properties induced by metal nanoparticle growth during the sputter deposition process were exemplarily monitored using SRS. The morphological characterization is complemented by X-ray reflectivity and electron microscopy. This enables us to identify the different growth regimes including their specific thresholds and permits better understanding of the growth kinetics of gold clusters and their self-organization into complex nanostructures on polymer substrates. Thus, our findings are of great interest for applications in organic photovoltaics [5] and organic electronics, which benefit from tailored metal-polymer interfaces.

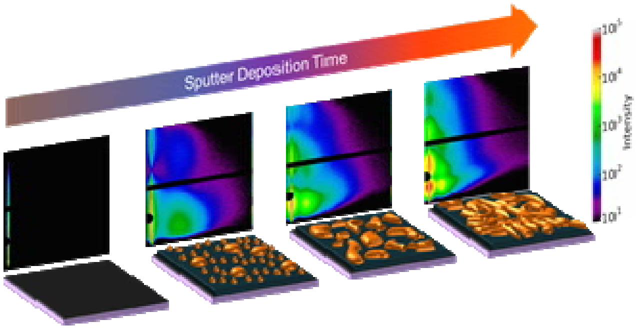

Figure 1: Gold cluster growth morphology and optical properties during sputter deposition on a polymeric substrate using *in situ* GISAXS and SRS. From left to right: before deposition; growth of isolated islands and onset of partial coalescence; branching of domains up to percolation and layer growth.

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LITHIATION OF A CRYSTALLINE SILICON ANODE FOR LITHIUM-ION BATTERIES

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Lithium-ion batteries (LIBs) are frequently used as rechargeable power sources for portable devices with further potential for automotive transportation. In the latter case improvements in cycle life, power density, safety and costs of LIBs are required. Here crystalline silicon (c-Si) is a very promising anode material of next generation LIBs due to its high specific capacity of 3579 mAh/g and further advantages like its abundance in the earth crust and well-developed engineering techniques. The current obstacles in utilizing Si anodes are in their slow and in part irreversible charge/discharge processes. During first lithiation an amorphous Li_xSi phase (with x claime ~3.5) develops and migrates into the c-Si anode with a reaction front from of ~1 nm thickness. At full lithiation (full discharge) the a-Li_xSi phase transforms into the crystalline phase c-$Li_{15}Si_4$, which further hinders fast successive charging (delithiation) After the first discharge/charge cycle c-Si is irreversibly turned into a-Si. The amorphization causes a big volume change and deterioration of the anode material [1]. The underlying lithiation kinetics and its pathways are not well explored until now due to the fact that for the latter techniques with a high sensitivity to Li in amorphous phases with a spatial resolution on the nanometer scale and the capability of operando studies are required. The understanding of lithiation kinetics and its pathways -however- is of outmost importance for the understanding of the volume changes, stress evolution, and mechanical failure during the lithiation/delithiation of Si electrodes.

In this contribution we show that neutron reflectivity is ideally suited to investigate the processes occurring during the electrochemical cycling of silicon anodes under working conditions on the nanometer scale [2]. The measurements we present here are performed on a three electrode electrochemical cell with a crystalline silicon working electrode. Counter and reference electrode are composed of pure lithium. A liquid electrolyte and a housing made of high density polyethylene are used. The first lithiation of the c-Si anode by galvanostatic charging at 2 μA/cm^2 for 12 h might be understood as a two-phase process of Li incorporation into the c-Si working electrode. A $Li_{x(y)}Si$ phase forms during that first cycle with a total thickness $t_{Lix(y)Si}$ of ~50 nm. During the second cycle $t_{Lix(y)Si}$ increases to ~90nm. After delithiation a residual amount of Li is still present in the silicon electrode. Our findings indicate an irreversible degradation of the silicon electrode. The kinetics of lithiation/delithiation in our system is compared with recent MD simulations on the evolution and propagation rate of the phase boundary during initial lithiation of crystalline silicon [3].

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DESIGNING POROUS OVER COATED CATALYTS WITH IN SITU SAXS

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Biomass derived molecules are being converted catalytically to useful products. However, many of these reactions are conducted under harsh conditions such as the hydrogenation of furfural to furfuryl alcohol over copper nanoparticles dispersed on alumina particles in water. The copper particles will rapidly sinter and the reactivity is reduced quickly. It has been shown that over coating with alumina the metal nanoparticles using atomic layer deposition (ALD) will reduce the sintering and if the overcoated particles are thermally treated at 700 °C, the lifetime and reactivity of catalyst increase dramatically compared to the catalyst without ALD over coating. Understanding the mechanism of the pore formation and further controlling the pore size are crucial for the development of the ALD overcoated catalyst. This work demonstrates that SAXS is very powerful technique to characterize these ALD overcoated catalysts. From SAXS analysis it was found that ALD filled the pores of the particles and the thermal treatment resulted in the formation of ~ 3.5 nm pores. This agrees with the BET analysis of the particles [1]. It was thought that it could be possible to control the size of the pores in the overcoat by following in situ pore formation by SAXS as a function of heating rates, final temperature and gas used. As shown in Figure 1, the porosity can be tuned to desired size by how it is heated. Simulation studies suggest that this pore forming process is due to stresses induces because of thermal expansion and densification of the film and surface energy. To better understand the pore formation of ALD overcoats, GISAXS was used to study ALD over coating and thermal treatment on flat substrates as a function of over coat and substrates.

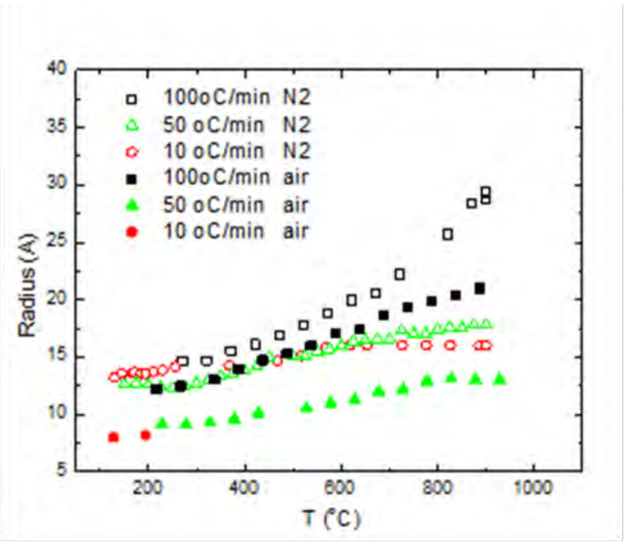

Figure 1. Thermal pore formation followed by SAXS

The SAXS and GSAXS studies were done at beamline 12-ID-B at the APS. For the in situ measurements, samples were heated as a 1 mm thick pellet under the appropriate gas with a Linkam stage. The data was fitted with a spherical shape model using Modeling II tool in the Irena package[2] within the IgorPro application.

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METAL NANOSTRUCTURES ON TOP OF ALQ3 THIN FILM: A GISAXS STORY

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Tris(8-hydroxyquinolinato)aluminium (Alq3) is the active layer in most organic light emitting diodes (OLEDs), an important device as the next generation light source for illumination. Its low cost, easy fabrication and reasonable efficiency have attracted many research interests. The multilayer device structure emphasizes the significance of understanding the interfacial structure and properties. Metals (Al, Ag, et al.) are used as the metal electrical contact. Upon depositing on Alq3, metal atoms can diffuse into the organic layer, modifying both, the morphological and electronic structure, thereby affecting the final device performance. Al and Ag are known to interact with Alq3 differently as probed by different spectroscopic techniques [1–3] and theoretical method3. Nevertheless, the growth mechanism and morphology of Al and Ag on Alq3 is scarcely discussed. For this purpose, in situ grazing incident small angle X-ray scattering (GISAXS) plays a powerful role to characterize the inorganic/organic interfacial structure during the film growth process [4,5]. In this work, we have carried out an in-situ GISAXS characterization to monitor the entire process of Al and Ag metal thin film on top of Alq3 layer during the sputter deposition process [6,7]. Considering the different chemical reactivity of both uses metals, we have completely characterized the different growth mechanisms and final thin film structures: for Al, uniform nanopillar arrays develop; for Ag, the nanostructure morphology changes from truncated spheres to percolated layer. The results benefit the general comprehension of the development of metal/organic semiconductor interfacial structure prepared via sputtering process, which is widely used in the industry.

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↘ Flash Talk: Mon-F-D1

CHARGE EFFECTS ON SURFACTANT BILAYER DYNAMICS

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Surfactant bilayers have long been a focus of study for various academic and industrial applications. The mechanisms of structure formation on nanometer scales have been explained using the concept of membrane elastic properties. Helfrich's bending Hamiltonian successfully explained various characteristic properties of membranes, indicating the importance of such elastic properties in understanding structure formation mechanisms [1]. These membrane elastic properties are coupled with membrane dynamics. Undulation fluctuations are known to be controlled by the bending rigidity of the membrane [2]. Since the original Helfrich model assumes the membranes are thin elastic sheets, intra-membrane properties, such as compressibility, have not been discussed. Recently, localized collective membrane dynamics (thickness fluctuations), have been measured in nonionic surfactant bilayers, as well as in oil swollen nonionic surfactant pseudo-bilayers [3]. Application of a deformation free energy model to the experimental result confirmed that the total bilayer compressibility modulus controls the fluctuation amplitude, and the free energy is actually determining an optimum fluctuation wavelength [4].

Here in the present study, we applied measurements of thickness fluctuation to help understand the effect of charge density in planar bilayers. Historically, charge effects on the lamellar structure and its stability have been measured by scattering techniques to see the change in the Bragg peaks in the scattering profiles. This corresponds to the changing of the structure stability by controlling inter-membrane interactions [5]. This has successfully explained the structural properties in lamellar phases. On the other hand, in the present study, we focused on the stability of the bilayer formation by measuring the membrane thickness fluctuations. We increased the molar ratio of a charged surfactant, SDS, in a nonionic surfactant bilayer, over a range from 1/1000 to 1/20. The bilayer is swollen by small amount of oil while the thickness of the bilayer is approximately 5 nm. The inter-layer interaction changes with the charge density, confirmed by small-angle neutron scattering measurements, while the bilayer dynamics are measured using neutron spin echo spectroscopy. Figure 1 displays the relaxation time, tau, of the thickness fluctuation which become slower as the charge density of the bilayer is increased. We will present details of the experimental procedure and the results, together with the bilayer elastic properties calculated through deformation free energy model.

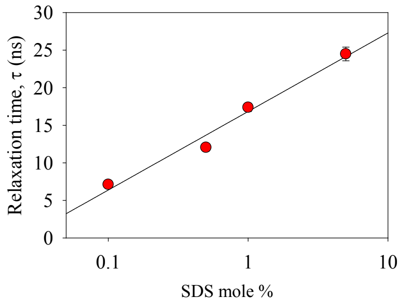

Figure 1: Variation of relaxation time of the bilayer thickness fluctuations as a function of bilayer charge density.

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THE IMPACT OF CARBON SUPPORT ON ACTIVITY AND STABILITY OF PLATINUM NANOPARTICLE FUEL CELL CATALYSTS: AN IN SITU STUDY

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Renewable energy conversion and storage using electrochemistry has become a pivotal issue in solving the global energy challenge. In particular Polymer Electrolyte Fuel Cells (PEMFC), owing to their high efficiency and fuel flexibility, will play a critically important part in electrochemical energy conversion between molecular bonds and free electrons. However, high catalyst costs and limited catalyst durability at the fuel cell electrodes have long hampered a broader technology deployment of fuel cells, in particular of low temperature PEMFC.

The most outstanding challenge for an optimal PEMFC catalyst is an effective performance of the oxygen reduction reaction (ORR). Studies on Pt nanoparticle-based catalysts have evidenced high mass based ORR activity, however, stability tests showed a continuous electrochemical surface area (ESCA) loss [1, 2]. The atomistic details of how ECSA loss is connected to catalyst performance loss are still poorly understood. A variety of studies have focused on the understanding of the ECSA-loss using microscopic techniques. Microscopy, as an *ex situ* method, provided only limited insights into particle degradation [1, 2], requiring sample probing conditions different from conventional PEMFC operation.

In this work we reveal Pt nanoparticle degradation mechanisms as a function of applied potential cycles under *operando* conditions using *in situ* Small Angle X-ray Scattering (SAXS). Employing *in situ* SAXS we derived statistically representative information on particle size, number density and volume fraction of nanoparticles as a function of time of electrochemical treatment. Additionally, we provide insight on the role of morphology of the commonly used conductive carbon supports by answering the question of how the specific surface area of the carbon contributes to catalyst degradation. We conclude from the correlation of derived SAXS parameters for different Pt/carbon-systems that the pore size and its origin in the graphite plane orientation play a crucial role on the catalyst stability performance.

Finally, we discuss which of the degradation mechanisms (coalescence, Ostwald ripening, particle dissolution, particle detachment from conductive support) are mainly affected/determined by carbon characteristics. We answer these questions on the basis of correlating the ECSA-loss curves and time-resolved SAXS-estimates.

Overall, our *in situ* SAXS study helped determining the dominant degradation mechanisms of metal nanoparticles during potential cycling and has identified important parameters for a beneficial selection of catalyst/support couples, enabling improved tailoring of PEMFC catalyst stability and activity.

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INFLUENCE OF TAIL LENGTH MISMATCH ON THE STRUCTURE AND DYNAMICS OF PHOSPHOLIPID BILAYERS

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Cell membranes are composed of an intricate mixture of lipids, protein, and sterols that self assemble into a flexible, dynamic bilayer. It has become increasingly apparent that the complex interplay between lipids and proteins within the cell membrane are essential to cell function. The implication of lipids in membrane mediated processes has motivated theoretical and experimental research to understand the functional significance of lipid chemical structure variations in the biomembrane structure and dynamics. In particular, hydrophobic mismatch between lipids with different acyl chain lengths is expected to play an important role in the local membrane structure and collective membrane dynamics.

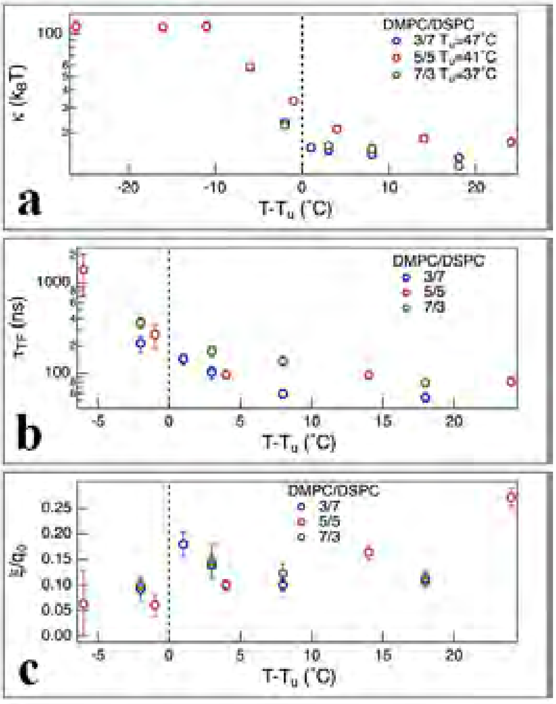

Figure 1. Temperature dependence of (a) bending modulus, κ, (b) thickness fluctuation relaxation time, τ_{TF}, and (c) relative thickness fluctuation amplitude, ξ/q_0, in mixed DMPC/DSPC vesicles

Herein, we investigated the structure and dynamics in large unilamellar vesicles composed of binary mixtures of tail-mismatched lipids using a combination of small angle scattering (SAS) techniques and neutron spin echo spectroscopy (NSE). Small angle X-ray and neutron scattering (SAXS and SANS) were used to probe the structure of binary lipid mixtures as a function of both lipid composition and temperature. The results of the SAS experiments provided additional insights into the bilayer dynamics studied by NSE. Using this method, we studied the impact of the lipid mixing ratio on the bilayer bending (Figure 1a) and thickness fluctuations (Figure 1b and 1c). Notably, the measured bilayer thickness fluctuations were highly dependent on lipid composition.[1,2] Together these studies highlight the importance of lipid composition on the bilayer properties and suggest that nature uses sophisticated mixtures of structurally diverse lipids to tune the rich morphology and dynamics of biomembranes.

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CORRELATED HETEROGENEOUS DYNAMICS IN GLASS-FORMING POLYMERS

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Although glasses are very common in everyday life, the transition from a supercooled liquid to the glassy state is one of the mysteries in condensed matter physics [1]. Upon approaching the glass transition, the sample dynamics slows down by orders of magnitude while the sample structure remains almost unchanged. In addition, relaxation phenomena become non-exponential pointing to a broad distribution of relaxation times and the existence of dynamical heterogeneities that are closely connected to spatial heterogeneities [1,2]. Such heterogeneities can be accessed by higher-order correlation functions, as demonstrated in simulations [3] and recently for coherent X-ray scattering experiments [4].

Here, we study the dynamics of polypropylene-glycol (PPG) with the help of colloidal silica tracer particles by means of X-ray photon correlation spectroscopy (XPCS) [5]. A temperature range from room temperature to the glass transition temperature at $T_g = 205$ K was investigated. Three temperature regimes are identified: At high temperatures, Brownian motion of the tracer particles is observed. Near T_g, the dynamics is hyperdiffusive and ballistic. Around 1.12 T_g we observe an intermediate regime. By analyzing higher-order correlations in the scattering data we find that dynamical heterogeneities dramatically increase in this intermediate temperature regime. This leads to two effects: a) increasing heterogeneous dynamics and b) correlated motion at temperatures close to and below 1.12 T_g.

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MULTIPLE SMALL ANGLE NEUTRON SCATTERING AT HIGH CONCENTRATION OF INHOMOGENEITIES

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The interference of neutron waves from different scatterers makes a significant contribution to the observed intensity of small angle neutron scattering (SANS) at high concentration of inhomogeneities. In the theory of single SANS this phenomenon is described by the structure factor. For SANS measurements in condensed media, it is frequently impossible to ensure a predominant contribution due to single scattering events by reducing the thickness of a probed layer while retaining its structure. In this case, the parameters of inhomogeneities in the sample have to be determined from multiple small angle neutron scattering (MSANS) data. This analysis is usually based on the Moliére multiple scattering theory, which is valid for an independent arrangement of scatterers in the sample.

For the first time the account of interference in MSANS was carried out in [1] for a monodisperse system of scatterers. In [2] MSANS was investigated experimentally. The measurements had been performed for mixtures of Al and Ti–Zr alloy powders. It was shown that the results could be satisfactorily described based on a theory that takes spatial correlations in the arrangement of powder grains into account. Thus, the theoretical and experimental investigation of MSANS on Al powder at a filling factor of $\eta \geq 9\%$ and a scattering multiplicity within $N \sim 5$–10 allowed us to reveal experimentally and validate theoretically the interparticle interference (IPI) effect in the studied system. We had established that, in the region of $\eta \sim 30$–60%, the IPI effect significantly influences the angular distribution of MSANS intensity $I(\beta)$, measured by double-crystal diffractometer, with a two- to threefold variation in the linewidth. Under these conditions, use of the Moliére theory is incorrect, since it leads to significantly overstated sizes of scatterers. These results will be briefly reviewed in the report.

The structure of the theory [1,2] differs significantly from the conventional theory of single SANS. The final expression for the MSANS intensity is too complex for analytical analysis, and numerical calculations are required. In this paper we present a new approach of constructing of MSANS theory for the case when the scattering of neutrons by a single inhomogeneity can be described in the diffraction approximation. A unified description of cases of single and multiple small angle scattering is suggested. A theory of small angle scattering is constructed based on the formalism of the occupation numbers and the method of concentration expansion. A new approach to the analysis of MSANS is based on the synthesis of single-scattering theory and the Moliére theory. A relation of this approach to the existing theory of MSANS [1] is demonstrated. It is shown that the presence of correlations results in the increasing of the number of unscattered neutrons; this explains the effect of narrowing of MSANS spectra [2].

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DYNAMICS NEAR GLASS TRANSITION TEMPERATURE OF IONIC LQIUID STUDIED BY X-RAY PHOTON CORRELATION SPECTROSCOPY

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Room temperature ionic liquids (RTILs) are composed of ions and show liquid state at room temperature or far below room temperature. Because of their unique properties such as non-flammability, low vapor pressure and high ion conductivity, they show promise for the practical application of various fields, for example, a 'green' reaction media in organic chemistry and a novel electrolyte in Li-ion batteries. Thus, numerous RTILs have been designed for many purposes by selecting the combination of cations and anions.

In addition to the application studies, fundamental studies for understanding the structure of RTILs on the molecular level have been vigorously conducted. One of the most interesting findings among the studies is the existence of nanoscale ordered structure in RTILs based on alkyl imidazolium cations with intermediate length (n) for the alkyl tail ($4 \leq n \leq 10$) [1]. Although the detail of the ordered structure is under debate, it has been reported that the ordered structure might affect macroscopic properties of RTILs, such as ion conductivity and viscosity. For example, Watanabe et al. found that the increase in the alkyl length of 1-alkyl-3-methylimidazolium-based RTILs decreases the ionicity, which is an index for the evaluation of the active ions contributing to ionic conduction in the diffusion components [2]. Harris et al. examined temperature dependence of viscosity for 1-alkyl-3-methylimidazolium-based RTILs with different alkyl length and found that the RTILs became more 'strong' glass former as the alkyl length increased [3]. To elucidate the influence of the ordered structure on ion conductivity and viscosity, dynamical properties such as the dynamic motion of cations and anions, as well as the static structure need to be understood.

In terms of the dynamics of the ordered structure, Kofu et al. observed a structural relaxation process using neutron spin echo (NSE) measurement [4]. However, the time-scale covered by NSE precludes the measurement of its whole relaxation behavior, in particular, the relaxation near the glass transition temperature (T_g), which is larger than 100 ns. The observation of the dynamic behavior of the ordered structure by other methods has not been reported, and it has not been clarified.

In this study, we aim to observe the structural relaxation process of the ordered structure near T_g by X-ray photon correlation spectroscopy (XPCS), with which we can observe slower dynamics than that with NSE. From the results of temperature dependence of the structural relaxation time, we discuss the influence of the ordered structure on the glass transition behavior, i.e. temperature dependence of ion conductivity and viscosity.

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TIME RESOLVED X-RAY SCATTERING STUDIES OF PROTEIN UNFOLDING ON ID09B, ESRF

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ID09b is an extremely versatile beamline that can study reactions / mechanisms on very short time scales; from milliseconds to picoseconds. One main area of interest is protein dynamics, including unfolding / misfolding / refolding. The misfolding pathway and dynamics have been of great interest for many years as a result of the health problems it causes [1]. It is thought that the precursors to the amyloidal fibrils are the toxic components therefore research into the very early stages of misfolding and even unfolding is continuing in greater depth.

Here we aim to probe the very early structural transitions of unfolding using time resolved small / wide angle X-Ray scattering, as indicated in figure 1. The unfolding mechanism is initiated using IR laser pulses with lengths of 5 ns or 1 ps (termed the 'pump') which heats the aqueous solvent around the proteins, (exciting the OH overtone in the water), causing the protein to be disturbed through temperature. The structures are then determined using 100 ps X-Ray pulses (termed the 'probe'). This pump-probe method hits a fresh part of sample every event and therefore allows for the sample to return to its native state before being investigated again. Using a combination of SAXS and WAXS enables the internal alpha and beta domains of the proteins aswell as their overall size and shape to be investigated.

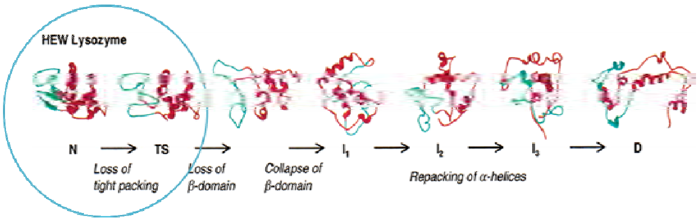

Figure 1: Proposed pathway for HEWL unfolding [2] in which we focus on the N (native) and TS (transition state) structures and dynamics.

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XPCS INVESTIGATION OF THE DYNAMICS OF SILICA NANOPARTICLES IN SWOLLEN RUBBER

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Addition of nanoparticles into rubbery materials improves their viscoelastic and mechanical properties. Understanding of the physical mechanism of this reinforcement effect is important for developing rubbery materials with high performance. Many attempts have been done to elucidate the mechanism, but the detailed physics of this effect has not been clarified.

To elucidate the relationship between the microscopic dynamics and macroscopic viscoelastic structure of rubbery materials, we have been conducting X-ray Photon Correlation Spectroscopy (XPCS) measurements [1-3]. XPCS has been widely utilized for investigating nano-scale dynamics of nanoparticles, as speckle patterns obtained from XPCS measurements are directly related to their exact spatial configuration in real space [4].

In this presentation, we report XPCS of silica nanoparticles in swollen rubber. The results show aging and dynamics showing a compressed exponential behavior. These characteristics have been widely observed for soft condensed matter. Previous studies propose two concepts to account for this behavior: a continuous random time walk model [5] and the relaxation of randomly distributed stress sources on the sample [6]; still, its physical picture is not clear. Aging has also been reported on many systems. As for the dynamics of nanoparticles in uncross-linked rubber, aging behavior is induced by the local stress accompanied with the mixing process of nanoparticles into rubber polymers [2]. We have found that, in swollen rubber, X-ray irradiation itself induces the dynamics characterized by the aging and compressed exponential behavior, indicating that the X-ray irradiation induces local rearrangement of silica particles in swollen rubber [3]. We will show detailed analyses of the XPCS results, and discuss the physical picture of nanoparticles' dynamics in swollen rubber.

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A MICROFLUIDIC CHIP FOR SYNCHROTRON SAXS STUDIES OF PROTEIN KINETICS

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A microfluidic mixing chip for time-resolved SAXS studies has been developed, aimed at investigations of structural transitions of proteins in solution. Whereas ligand induced structural transitions are an important aspect of the functioning of numerous proteins, only limited knowledge on these processes is currently available. By introducing a microfluidic platform in combination with microfocus synchrotron SAXS, it will be possible to obtain sub-millisecond time resolution with a minimal sample consumption, which is crucial for many biological systems.

In the chip, protein and ligand solutions enter inlet channels in a continuous flow, and are merged at a mixing point. A structural transition of the protein is triggered by the ligand diffusing into the protein sheet, and any position downstream of the mixing point represents a certain time after mixing, which can be probed by SAXS. The chip is based on the same principle as the design suggested by Lois Pollack et al. [1,2], but with wider channels (300 µm) and in a UV-cured thiol-ene material, giving a chip which is fast, easy, and cheap to fabricate.

The performance of the chip, was investigated at beamline P12 at Petra III, showing good control over mixing ratios and flow rates. Using the microfocus setup at the BioCAT beamline at APS, it was possible to characterize the profile of the protein sheet. Sheet widths down to 5 µm were successfully obtained, which corresponds to typical mixing times of ca. 1 ms (full diffusion of ligand into the sheet). The unfolding of bovine serum albumin by sodium dodecyl sulfate has been studied as an initial test system, and further studies are in planning.

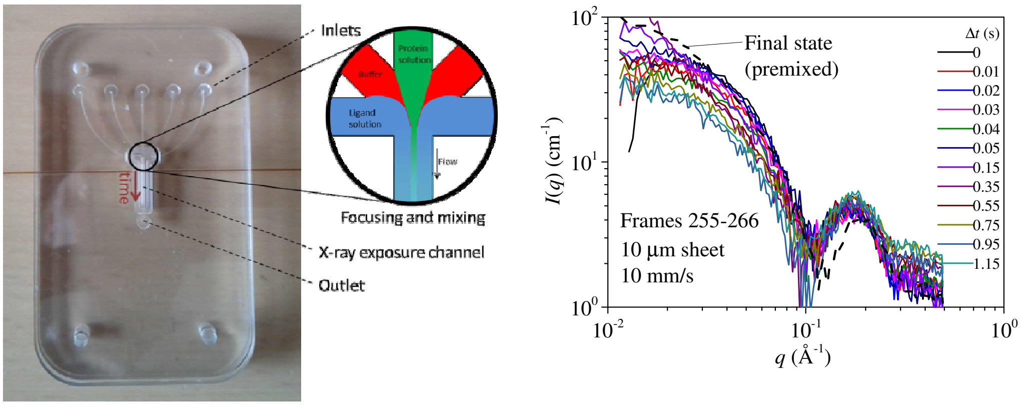

Figure 1. a: Microfluidic chip with X-ray exposure channel. b: Data from mixing of BSA and SDS with a width of the BSA sheet of 10 µm. The flow velocity is v_{flow} = 10 mm/s. The final state of the BSA-SDS complex is not reached.

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SAXS STUDY ON THE GROWTH BEHAVIOR OF SILVER NANOPARTICLES

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Metallic nanoparticles have received great attention due to their unique optical, electronic, magnetic, and catalytic properties, which are highly dependent on the particle size and shape. For controlling the morphology of nanoparticles, the knowledge about the nucleation and growth mechanism of metallic nanoparticles is crucial. There have been some researches on the nucleation and growth mechanism of noble metal nanoparticles, but the initial process of nanoparticle formation and the concentration effect on the resulting nanoparticles are not very clear yet. Small-angle X-ray scattering (SAXS) is a powerful technique to detect the nanoscale structures. In this presentation, a chemical reduction method with polyvinylpyrrolidone (PVP) used as a stabilizing agent was used to prepare silver nanoparticles. In-situ SAXS technique was used to monitor the formation process of silver nanoparticles [1]. In the synthesis of silver nanoparticles, aqueous silver nitrate solutions were used as the precursors and sodium borohydride was used as the reducing agent. Time-resolved SAXS patterns of four silver nanoparticle suspensions were collected with the initial Ag^+ concentrations of 2, 4, 6, and 8 mM in the corresponding precursors. The particle-size change with time was obtained by analyzing the SAXS data. The SAXS results demonstrate that the nucleation size of silver nanoparticle behaves as a linear relation with time in the initial growth stage (<1 s), which can be used to evaluate the critical particle size. The subsequent growth of silver nanoparticles experienced a fast stage and a slow stage. A diffusion-coalescence model as shown in Fig. 1 and the quantitative description about the average particles size has been proposed. The effect of initial Ag^+ concentration on the final particle size and the growth mechanism of Ag nanoparticles are discussed.

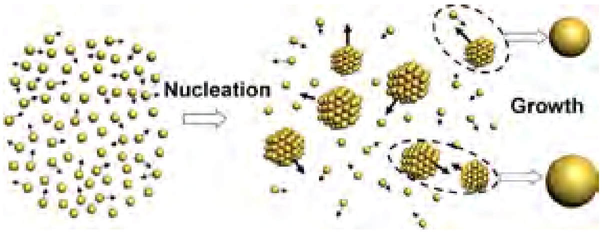

Figure 1: Sketch map of the diffusion-coalescence mechanism of Ag nanoparticles.

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COHERENT X-RAY SCATTERING AT THE ULTRA-SMALL ANGLE REGIME

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Partially coherent radiations generated by high-brilliance third generation synchrotron sources have allowed X-ray Photon Correlation Spectroscopy (XPCS) measurements of slow dynamics in various soft and hard material systems. However, conventional XPCS facilities have generally been limited to microstructure length scales smaller than ≈ 50 nm, thus eliminating large classes of materials that are of major technological importance.

In recent years, we have developed an XPCS technique in the ultra-small angle scattering regime, which bridges the accessible Q ranges of dynamic light scattering and pinhole-based XPCS.[1] This technique is based on the Bonse-Hart ultra-small angle X-ray scattering (USAXS) instrument at the Advanced Photon Source and requires modifications to the beamline configuration and instrument operations for dynamic measurements.

So far, we have successfully applied USAXS-based XPCS to investigations of both equilibrium and nonequilibrium dynamics of scientifically and technologically important materials. In the case of equilibrium dynamics, making use of a point-detection mode, we followed the low-frequency dynamics of colloid-based complex fluids.[2] It is worth noting that with the slower dynamics associated with larger colloids, USAXS-based XPCS makes it possible to directly probe the relaxation dynamics at mesoscopic length scales in aqueous colloidal suspensions, an important area of research that impacts not only understanding of physical principles governing the dynamical behaviors of aqueous fluids but also environmental research.

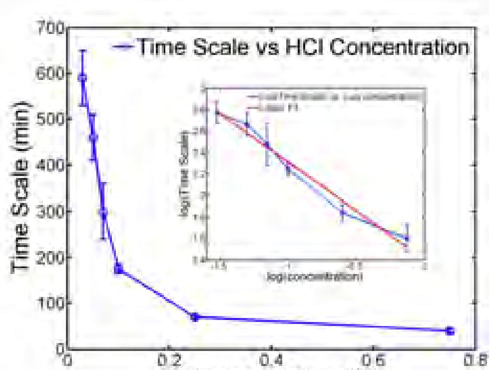

Figure 1: Incipient structural-change time scale as a function of HCl solution concentration.

Using repeated, short scans of the coherent X-ray speckles, we investigated the incipient microstructure changes under non-equilibrium conditions of amorphous calcium phosphate (ACP)-based composite materials.[3] ACP is long regarded as a precursor to crystalline calcium phosphate minerals in organism. However, the detailed transition mechanism was not well understood. With the sensitivity provided by coherent X-rays, we followed the complete solution-mediated transition process from ACP to apatite within a composite material in a controlled aqueous environment (See Figure 1), and were able to unambiguously identify a two-step conversion process from ACP to apatite in which ACP undergoes a local microstructural rearrangement without losing its amorphous characters, followed by an amorphous-crystalline phase transformation.

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BAND-GEM detectors for SANS measurements at the European Spallation Source

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The European Spallation Source (ESS) will be the most powerful neutron source, 30 times brighter than today's leading facilities.

Small Angle Neutron Scattering (SANS) will be among the first measurements to be performed at the ESS because of its broad range of applicability across material science, biology and soft matter research.

The expected high neutron fluxes, with associated high count rate requirements on the detectors, have been the main driver for developing a new type of neutron detector based on the Gas Electron Multiplier (GEM) technique. The GEM technique is well established for charged particle measurements in high energy physics applications at CERN and elsewhere. The new development concerns the neutron conversion to charged particles. It is well known that a single layer of ^{10}B can provide an efficiency that is <5% for thermal neutrons. In the BAND-GEM approach a 3D geometry for the neutron converter was developed that is expected to provide an average efficiency >50% in the wavelength of interest for SANS measurements, while meeting all the requirements to have a good Q resolution for SANS.

In the presentation the Q resolution requirements for SANS will be reviewed, the BAND-GEM detection method will be described and the simulation results will be presented. First results based on counting rate tests with a BAND-GEM prototype and the comparison with ^{3}He will be reported and approaches for optimizing the detector performance will be discussed.

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The P12 BioSAXS beamline of EMBL Hamburg

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The last decades saw a steadily and rapidly growing interest in applications of small-angle-X-ray scattering (SAXS) by macromolecular solutions from the structural biologists community [1], underlining the need for dedicated instruments able to collect high throughput SAXS data on weakly scattering, sensitive, and scarce samples. The EMBL BioSAXS beamline P12 (third generation PETRA-III ring, Hamburg) was built to succeed the extremely successful X33 BioSAXS beamline [2] (second generation DORIS-III ring) and tailored for biological solution SAXS [3].

The optics, double crystal monochromator, bimorph mirrors, deliver a beam of 200x100 microns (full width half maximum), at energy tunable between 4 and 20keV with the flux of up to 10^{13} ph/sec. A multilayer monochromator, currently in commissioning shall deliver up to 5×10^{14} ph/sec (7-15keV) for time resolved applications. The liquid samples are measured in a capillary positioned in vacuum and low instrumental background allows for data collection on weakly scattering objects. The beam transmission is monitored by a radiation-stable miniature active beamstop [4]. Sensitive biological samples often available in limited amounts are reliably and rapidly handled by a robotic sample changer requiring about 20-40 µl per measurement. In an alternative setup, size exclusion chromatography columns and additional spectrometers (UV/Vis, RALS, and refractometer) are connected to the sample exposure unit for on-line purification and biophysical sample characterization.

The sample changer robot makes possible full automatic data collection such that the measurement can be performed with minimal input from the user. The SASFlow pipeline analyzes the data directly after collection and provides the users with the overall parameters of the solutes and low resolution shapes within minutes upon data recording. The high level of automation has permitted us to perform over 85,000 measurements during the last full beamyear and also allows for remote and mail-in measurements.

Description of the characteristics of the instrument and main sample environments will be given along with a glimpse into future developments.

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A VERSATILE LABORATORY X-RAY DIFFRACTOMETER PLATFORM ENABLING USAXS, SAXS, WAXS AND PDF MEASUREMENTS WITHIN A Q-RANGE OF ALMOST FIVE DECADES

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A multipurpose, high-resolution 2-circle laboratory X-ray diffractometer was used as a platform for USAXS, SAXS, WAXS and PDF measurements, thus covering a gapless range of scattering vectors q spanning over almost five decades. The compact instrument with a goniometer radius of 240 mm can be configured with various X-ray tubes, optics, sample stages, anti-scatter devices and high-end detectors. Changing between different setups is easily and quickly accomplished by making use of prealigned hardware modules that can be reproducibly attached to the instrument. A high data quality can be obtained in all these complementary applications as will be demonstrated by results obtained from nanopowders, nanoparticle dispersions and protein solutions.

SAXS/WAXS experiments are done with a line collimation setup using an incident beam mirror in combination with a detachable vacuum path (ScatterX^{78}, PANalytical; Figure 1). A good sensitivity for weakly scattering samples and a q_{min} ($q = 4\pi/\lambda \sin(2\theta/2)$) of 0.006 Å^{-1} can thus be achieved. By scanning the detector around the sample, SAXS measurements can be seamlessly extended into the WAXS region up to 78 deg 2θ. 2D SAXS data are obtainable by reducing the beam size in the axial direction.

Figure 1: SAXS/WAXS setup

USAXS data (Figure 2) are measured by using high resolution incident beam optics and an analyzer crystal. With a q_{min} of 0.00036 Å^{-1}, this setup allows to investigate structural features up to approximately 1 µm.

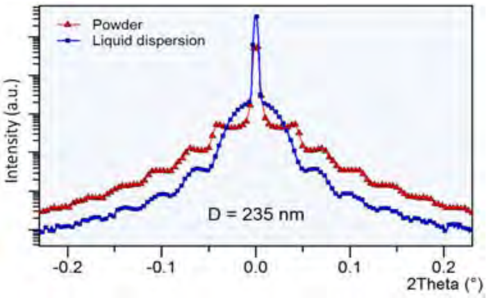

Figure 2: USAXS from silica nanoparticles

At the opposite extreme, for the determination of the atomic pair distribution function (PDF) from which the short range atomic order can be deduced with sub-Angstrom resolution, it is essential to acquire scattering data up to very high q-values. By making use of hard radiation and by scanning the detector up to highest 2θ angles, a q_{max} of 22 Å^{-1} can be reached. Measurement times can be very significantly shortened by using latest detector technology based on a CdTe sensor (GalliPIX^{3D}, PANalytical).

The same X-ray diffractometer platform additionally allows for a variety of other applications, such as powder diffraction, X-ray reflectivity, GISAXS and even CT. It is the only one of its kind that is also commercially available (Empyrean, PANalytical) and widely used as a multipurpose instrument in research labs to yield quality in-house diffraction and scattering data, or for screening samples to be measured at synchrotron beamlines.

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A MO-BASED IN-HOUSE SOURCE FOR SAXS MEASUREMENTS ON BIOLOGICAL MACROMOLECULES

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Biological SAXS experiments are frequently performed at state-of-the art 3rd generation synchrotron X-ray sources, yet measurement time remains a limited resource. As a complementary approach, we demonstrate the applicability of an in-house SAXS setup to study biological macromolecules in solution. Our system consists of a Molybdenum-based microfocus X-ray tube delivering a flux of 2.5 x 10^6 photons per second at a beam size of 1 x1 mm^2 at the collimation path exit. The partially evacuated flight path can be set to a sample-detector distance of up to 2.5 m, which results in observable scattering vectors q (= $4\pi \sin\theta/\lambda$) from 0.3 down to 0.01 $Å^{-1}$, corresponding to real space distances of about 0.2 nm to 60 nm. We integrated a temperature controllable sample stage, which makes it possible to analyze macromolecules under precisely controlled temperatures over a large temperature range, from 0 °C - 120 ºC. In order to verify possible aggregation of the macromolecules, dynamic light scattering (DLS) measurements can additionally performed subsequently after each SAXS measurement.

As a proof-of-concept, we collected SAXS data on both a 24 bp double-stranded DNA sample and a set of proteins including cytochrome *c* and lysozyme, used previously as scattering standards. The employed protein concentrations covered a range of (2 - 24) mg/ml and the exposure times varied between (0.5 - 3) h per measurement. No radiation damage was observable for any of the SAXS measurements, up to 24 h of cumulative exposure.

We analyzed the in-house data by determining global structure parameters and by comparing the experimental profiles to calculated scattering intensities based on the atomic structure of the molecule. We could routinely obtain radii of gyration and D_{max} values in good agreement with literature values. In addition, the data are of sufficient quality to perform *ab initio* shape reconstruction based on the program DAMMIF (Figure 1) [1]. The results demonstrate that it is possible to obtain high-quality SAXS data suitable for low-resolution structure determination at a Mo-based in-house source.

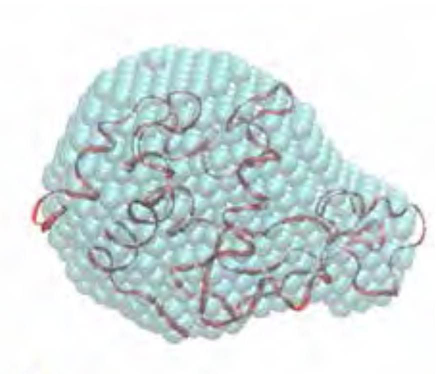

Figure 1: Atomic resolution structure of lysozyme (PDB accession code 2LYZ rendered as red lines) superimposed with the low-resolution bead model based on DAMMIF (blue semitransparent beads).

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A SMALL ACTIVE BEAMSTOP FOR MICROFOCUSING BEAMLINES

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Measuring the sample transmission in a scattering experiment allows a range of sample parameters to be extracted with high accuracy, such as optical thickness. If the sample is radiation sensitive, the transmission can also be used to monitor radiation damage, especially if the acquisition involves multiple exposures. The standard solution to measure the sample transmission is to have a diode embedded in the beamstop. This is simple to implement and works well.

In MX, which is typically performed in air, placing the beamstop closer to the sample allows to reduce the background significantly; in SAXS, the size of the beamstop limits the accessible measurement range (low q) if parameters such as the beam size and divergence are small. However, the current trend to provide ever smaller beams for both crystallography and SAXS presents a challenge. Most microfocusing facilities use passive beamstops, due to the large size of current solutions to measure transmission. While typical beam sizes are in the order of a few microns, the state of the art for diode-based beamstops is around 1.5mm [1, 2].

Here we present an active beamstop with an integrated diode, with a diameter well under a millimeter, optimized for scattering and diffraction applications.

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A DEDICATED MICRO-NANOFOCUS FACILITY FOR X-RAY SCATTERING AT DIAMOND LIGHT SOURCE

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Beamline I14 is the hard X-ray nanoprobe beamline currently under construction at Diamond Light Source in Oxfordshire, UK. It is scheduled to come into operation in 2017. The beamline will be a dedicated facility for nanoscale microscopy and micro-nano focusing SAXS, serving two endstations housed in a new external building, approximately 175m from the main synchrotron ring. This building also houses the new UK National Electron Microscopy Facility, which provides 4 state-of-the-art electron microscopy suites covering the physical and life sciences. The facility combines staff and expertise from a number of different areas which we believe will allow us to make exciting progress in sample preparation techniques and correlative X-ray and electron microscopy studies.

The Nanoprobe endstation aims to achieve the smallest possible focus (initial aim 50nm), with the capability to exploit future optics developments. This endstation is optimized for scanning X-ray fluorescence, X-ray spectroscopy and diffraction mapping, and will be the first to become operational.

The Mesoprobe endstation is dedicated to small and wide angle scattering studies as well as scanning fluorescence mapping. The aim of this facility is to provide a high quality small beam with a variable size in the range 5μm – 100nm, and a flexible sample environment. It will complement the current portfolio of scattering beamlines at Diamond, and expand the scientific and technical capabilities to analyze small and/or inhomogeneous samples.

Here we present the design and key specifications of Beamline I14, highlighting potential applications.

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THE FIRST COHERENT X-RAY SCATTERING BEAMLINE AT TAIWAN PHOTON SOURCE

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Taiwan Photon Source (TPS) is a new 3 GeV ring with the emittance of 1.6 nm·rad. Coherent X-ray Scattering (CXS) beamline, one of the phase-I beamlines designed for TPS, uses the combination of 3-meter-long and 2-meter-long in-vacuum undulators with the period length of 22 mm as source and can provide a highly coherent X-ray with the flux of 10^{10} photons/second at 5.56 keV. The energy resolution of this beamline is about 10^{-4} with using double Si(111) crystals. It can achieve 1-10 µm beam size at sample position in horizontal direction with two-step focusing. The vertical beam size at sample can be switched between 1 and 10 µm with selecting compound refractive lenses (CRLs) or focusing mirror (FM) as focusing optics. High quality focusing mirrors with low slope error and surface roughness are required for preserving the coherent flux. This beamline will focus on performing small-angle X-ray scattering (SAXS), X-ray photon correlation spectroscopy (XPCS), and coherent X-ray diffraction imaging (CDI) experiments. The operating photon energy is designed within the range of 5.56-20 keV and the sample-to-detector distance can be varying in the range from 0.7 to 12 meters. An EIGER X 16M will be the main area detector. The software for beamline control and real-time monitor is EPICS with CSS and the software for data acquisition is GDA. The public opening of CXS beamline will be in the beginning of 2016.

Figure 1: The engineering layout of CXS beamline after front end. On the right (the upstream end of the beamline) are situated a DCM, and a vacuum chamber (in turquoise) housing a set of V-CRLs and the HFM1. One the left are a vacuum chamber (in green) housing a VFM/VDM and the HFM2, and a sample stage. At the end of the beamline is an area detector housed in a 12-meter long vacuum pipe to prevent the signals from being scattered and absorbed by air. (V-CRLs: vertical CRLs; HFM: horizontal FM; VFM: vertical FM; VDM: vertical deflecting mirror)

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↘ Flash Talk: Mon-F-T1

DEVELOPMENT OF AN APPROACH TO LOCALIZE AND TO IDENTIFY BIOLOGICAL SUPRAMOLECULAR STRUCTURES BY µSAXS-CT IMAGES

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In recent years, several researchers are seeking tools to localize and to identify supramolecular arrangements in nanostructured materials such as polymers, wood, but also in amorphous materials like biological tissues [1]. Small Angle X-ray Scattering (SAXS) is the key gold standard in synchrotron laboratories to identify the supramolecular structures. However, it is impossible to know where these structures are spatially localized in the sample volume. In order to provide information about the morphology of sample being investigated, SAXS technique has been coupled to micro-beam computed tomography (µSAXS-CT) [2]. Therefore, in this study we developed an approach based on µSAXS-CT to map and to identify in the sample volume supramolecular arrangements in biological tissues.

A sample containing portions of healthy and pathological breast tissues was used to evaluate the method. The experiments were carried out beamline BW4 at synchrotron radiation facility DORIS III in Hamburg, Germany. A monochromatic beam with a wavelength 1.38Å and size of 36 x 19 μm^2 was used to scan the sample. The SAXS patterns were recorded on a Pilatus 300k detector, using a sample-to-detector of 2320mm corresponding to $0.08 nm^{-1} \leq q \leq 1.71 nm^{-1}$. 5760 projections were acquired following the first generation computed tomography procedures scanning the sample in a 16 linear steps and 360º for each linear step, using a mean exposure time of 30s for projection, in accordance to positron current variation in the ring. SAXS patterns were corrected by several parameters like sample self-attenuation, background, detector efficiency, and then used to reconstruct the sample slice using a standard filtered back-projection algorithm.

The approach developed in this work consists of a procedure to reconstruct the sample slice based on SAXS contrast and to localize and identify supramolecular structures. SAXS contrast has great interest for biological samples because allows to distinguish between supramolecular arrangements even for samples homogeneous in elemental composition and density, but whose nanoscopic structure varies as a function of the position, like breast tissues. In addition, using the approach developed in this work we can select a voxel on the image and to make the reverse analysis in order to yield the SAXS 1-D profile (relative intensity vs q) which allows to identify the supramolecular arrangements at that position in the sample volume.

Therefore, the approach developed in this study based on µSAXS-CT technique arises as a powerful tool for studying biological samples. In this sense, there are several potential applications like to understand the mechanism of breast cancer growth and dissemination which could allow to estimate the prognostic of this disease.

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NON-STANDARD CONFIGURATION OF SANS INSTRUMENTS: MULTIPLE BEAM TECHNIQUES FOR VSANS, SCANNING AND MAGNIFIED NEUTRON IMAGING METHODS

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Small-angle neutron scattering (SANS) instruments offer a unique toy-box of neutron optical devices combined with the high flux of an end-of-neutron-guide beam position. The appropriate combination of optical components such neutron guides, apertures, time-of-flight or monochromatic modes of operation, polarisation and analysis techniques allow a typical SANS instrument to be imaginatively configured for other purposes. Here, we demonstrate how the D33 SANS instrument at ILL can be configured to produce multiple highly collimated beams for measurements in the VSANS regime at the smallest scattering angles. The multiple beam configuration uses the intrinsic properties of the neutron guide system, source and sample apertures with no additional optical devices or precise aperture array alignments. This is particularly useful for the study of small samples, or small regions of a sample, at the smallest scattering angles while retaining sufficient neutron flux due to the use of multiple beams. We also demonstrate how the instrument can be configured to perform magnified neutron imaging and scanning imaging measurements or 'scanning SANS microscopy' using single or multiple beams. Both techniques provide spatial resolution down to ~50μm without the need for high resolution cameras, using only the regular low resolution (5mm x 5mm pixel) SANS detector. Neutron imaging in this way profits from, and allows separation of, both absorption and scattering contrast mechanisms. Examples of multiple beam 'VSANS' and imaging measurements made on D33 will be presented.

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KWS-1 HIGH-RESOLUTION SMALL-ANGLE NEUTRON SCATTERING INSTRUMENT AT JCNS: CURRENT STATE

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The KWS-1 small-angle neutron scattering (SANS) instrument operated by the Jülich Centre for Neutron Science (JCNS) at the research reactor FRM II of the Heinz Maier-Leibnitz Zentrum in Garching near Munich is optimized to relatively high resolution measurements owing to its neutron velocity selector with $\Delta\lambda/\lambda = 10\%$. Combined with the maximum neutron flux on the sample of 1×10^{8} cm^{-2} s^{-1}, this makes KWS-1 one of the best SANS instruments in the world. The covered q-range of the instrument extends from 0.0007 to 0.5 Å^{-1}, which corresponds to real sizes of features in the samples from 10 to 9000 Å.

The KWS-1 instrument has been recently upgraded, from its active collimation apertures to the detector cabling. Most of the parts of the instrument were installed for the first time, including a broadband polarizer, a large-cross-section radio-frequency spin flipper, a chopper and neutron lenses. A custom-designed hexapod in the sample position allows heavy loads and precise sample positioning in the beam for conventional SANS experiments as well as for grazing-incidence SANS under applied magnetic field. With the foreseen *in situ* polarization analysis the main scientific topic of the instrument tends towards magnetism. The performance of the polarizer and flipper was checked with a polarized ^{3}He cell at the sample position.

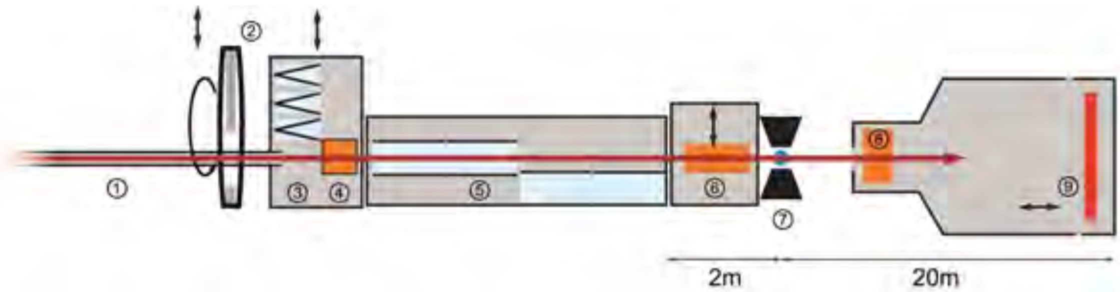

Figure 1: A schematic representation of the KWS-1 SANS diffractometer: (1) S-shaped neutron guide NL3b; (2) high-speed chopper ($\Delta\lambda/\lambda$ = 1-10%); (3) polarizer changer; (4) radio-frequency spin flipper; (5) neutron guide sections (18×1 m); (6) MgF_2 focusing lenses; (7) sample position with hexapod for heavy loading; (8) ^{3}He analyzer with reversible polarization (to be implemented); (9) Anger-type scintillation detector.

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Comparison of Mo and Cu X-ray energy for SAXS from weak scatters in solution

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We compare two SAXS setups based on micro focus X-ray tubes (GeniX3D, Xenocs, France) with Mo and Cu targets (17.4 keV and 8.0 keV, respectively). We use Ge scatterless slits for the Mo target and Si blades for the Cu target [1] to avoid parasitic slit scattering. For Cu radiation, we use the hybrid pixel detector Pilatus 100K (Dectris, Switzerland) with 320 micrometer sensor thickness (97% quantum efficiency QE), while for Mo we use the 1000 micron model (76% QE).

Here, we want to compare the signal-to-noise ratio of SAXS experiments for weak scatterers in solution, e.g. proteins in aqueous solution. In a SAXS experiment, the optimal sample thickness, i.e. the length of the liquid cell along the beam which yield maximal signal, is generally given by the absorption length of the solution. This assumes that absorption is dominated by the solution, which will be the case if the absorption of the scatterers is weak or if the volume fraction of the scatterers is low.

For Cu radiation, the absorption length in water is 1.0 mm (e.g. a capillary), while for Mo, the absorption length in water is 10.0 mm (e.g. a cuvette). Thus, a liquid cell for Mo can be ten times larger, which in turn leads to a ten times higher scattering signal of the scatterer. However, typical Cu tubes have a ten times higher flux, which compensates this effect. Thus, we find that the two setups result in similar counting signal of the sample.

However, when we compare the signal for SAXS experiments with proteins in solution, e.g. cytochrome C, we find that the background is lower for the Mo setup. Apparently, since the incident beam has ten times less photon flux, it gives rise to less background signal. Second, air scattering from gaps between vacuum tubes is less pronounced at higher energies. Therefore, we end up with a higher signal-to-noise ratio at the Mo setup.

The results suggest that it can be beneficial to perform SAXS measurements at higher X-ray energies than the frequently used Cu energy, which also might be an attractive route to enhance signal-to-noise at synchrotron facilities.

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↘ Flash Talk: Mon-F-T1

ACCURACY AND PRECISION OF ASAXS FORMALISMS

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Anomalous small-angle x-ray scattering (ASAXS) uses the energy dependent dispersion correction to the atomic scattering factors, i.e. , to separate the contributions of different atomic species in a sample to a SAXS signal. In order to achieve that separation, several techniques are established [1].

We have simulated the scattered intensity of Pt-Au core-shell nanoparticles to test the partial structure factor (PSF), Stuhrmann and fit method for accuracy and precision in the presence of typical experimental errors. Besides statistical uncertainties at every scattering angle and the effects of a finite beam size, systematic errors in the absolute intensity scale, have a high impact on the reliability of the found solutions.

The PSF and Stuhrmann solutions are evaluated by comparison of a fitted Guinier radius with a theoretical prediction [2]. The fitted parameters of the fit method are compared with the known starting values of the simulation. The accuracy is calculated as and the precision as . Over a threshold value of the scaling errors , all three methods exhibit a dramatic loss in both accuracy and precision: The mechanisms behind this differ though.

PSF and Stuhrmann methods can be written as linear matrix equations. Solving this matrix equation gives the structure factors of the different atomic species for the PSF method and resonant, intermediate and non-resonant scattering factors for the Stuhrmann method. The precision of the solutions will therefore strongly depend on the condition number of the matrix. Even small errors in the measurements will result in large errors in the solution if the condition number is large which will lead to chaotic behavior (Figure 1): Measuring at more photon energies therefore increases the .

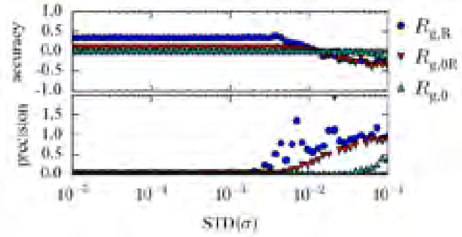

Figure 1: Accuracy and precision of the Stuhrmann method.

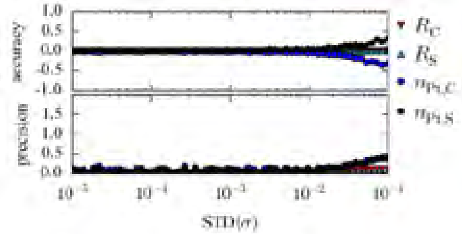

Figure 2: Accuracy and precision of the fit method.

The fit method shows contrary behavior: The threshold is dominated by the average intensity shift: . If the scaling error is of the same magnitude as this shift, the fit method significantly loses accuracy and precision (Figure 2). And since this factor gets smaller the smaller the difference in photon energies gets, more energies in the same range will affect the threshold negatively.

Overall, the most accurate and precise results are obtained from the fit method. The Stuhrmann method is very precise, but the accuracy is affected by the truthfulness of the assumption of only one resonant atom-species. The PSF method, on the other hand, is accurate for high contrasts but lacks precision.

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↘ Flash Talk: Mon-F-T1

ASAXS STRUCTURE INVESTIGATION OF SEMICONDUCTOR QUANTUM DOTS IN THE TENDER X-RAY RANGE

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The Tender X-ray range describes a range of X-ray photon energy, where the K-edges of elements from the 3rd and the first half of the 4th period are situated. These elements are in high interest for industrial applications, because of their abundance on earth. Transition metals from 4th period are candidates to replace noble metals in catalytic applications. Elements of the 3rd period are relevant for applications such as proton- and cation-conductors in fuel cells or batteries, as electrode materials in batteries and for photovoltaic devices.

Anomalous Small-Angle X-ray Scattering (ASAXS) is able to localize elements in nano-structured materials. This is of extraordinary interest for the above-mentioned porous materials. Hence ASAXS measurements require high accuracy in beam stability, beam monitoring and normalization. Especially in the Tender X-Ray regime, it is challenging to achieve this accuracy. A combination of the PTB FCM beamline[1], the HZB SAXS-Instrument[2] and the in-vacuum Pilatus detector of PTB[3] is used to realize the experiments.

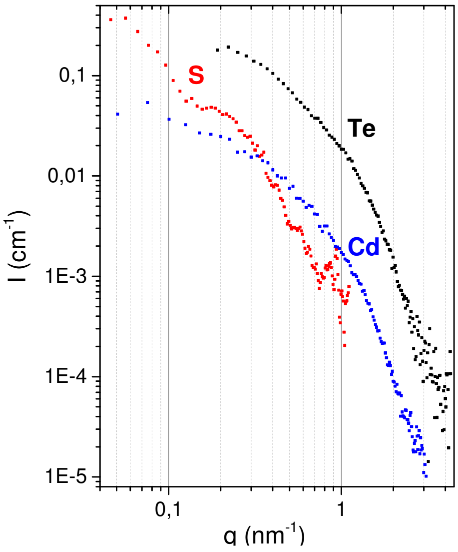

Figure: Resonant scattering of thiolat-stabilized CdTe-QDs at Te L3-edge (black), Cd L3-edge (blue) and difference scattering curve of Sulfur K-edge (red) measurements.

To develop the ability for ASAXS experiments in the Tender X-ray regime, CdTe semiconductor quantum dots (CdTe-QDs) stabilized by a thiolate shell were investigated. The elements Cadmium and Tellurium exhibit L3-edges in this energy range. L3-edges always show a stronger anomalous effect than K-edges, which can be used for prove of concept experiments for the Tender X-ray ASAXS. Also the direct comparison of ASAXS experiments at the Cd K-edge and Cd L3-edge can be used to validate the experimental set up. Finally, sulfur K-edge ASAXS could be realized for the thiolate shell of the CdTe-QDs. On the left hand the terms of resonant scattering at the Cd and Te L3-eges and a scattering intensity difference plot from the ASAXS experiment at the S K-edge are shown.

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SCIENTIFIC HIGHLIGHTS FROM QUOKKA, THE 40 METRE PINHOLE SANS INSTRUMENT AT ANSTO

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Quokka (Figure 1) is the 40 m pinhole SANS instrument at the OPAL reactor serving the growing needs of both domestic and international users [1,2]. In 2014, over 200 days of user experiments were run. Outputs from Quokka have been published covering such diverse fields as magnetism, structural biology, mineralogy, polymers, food science and soft matter. We present here a selection of recent scientific highlights.

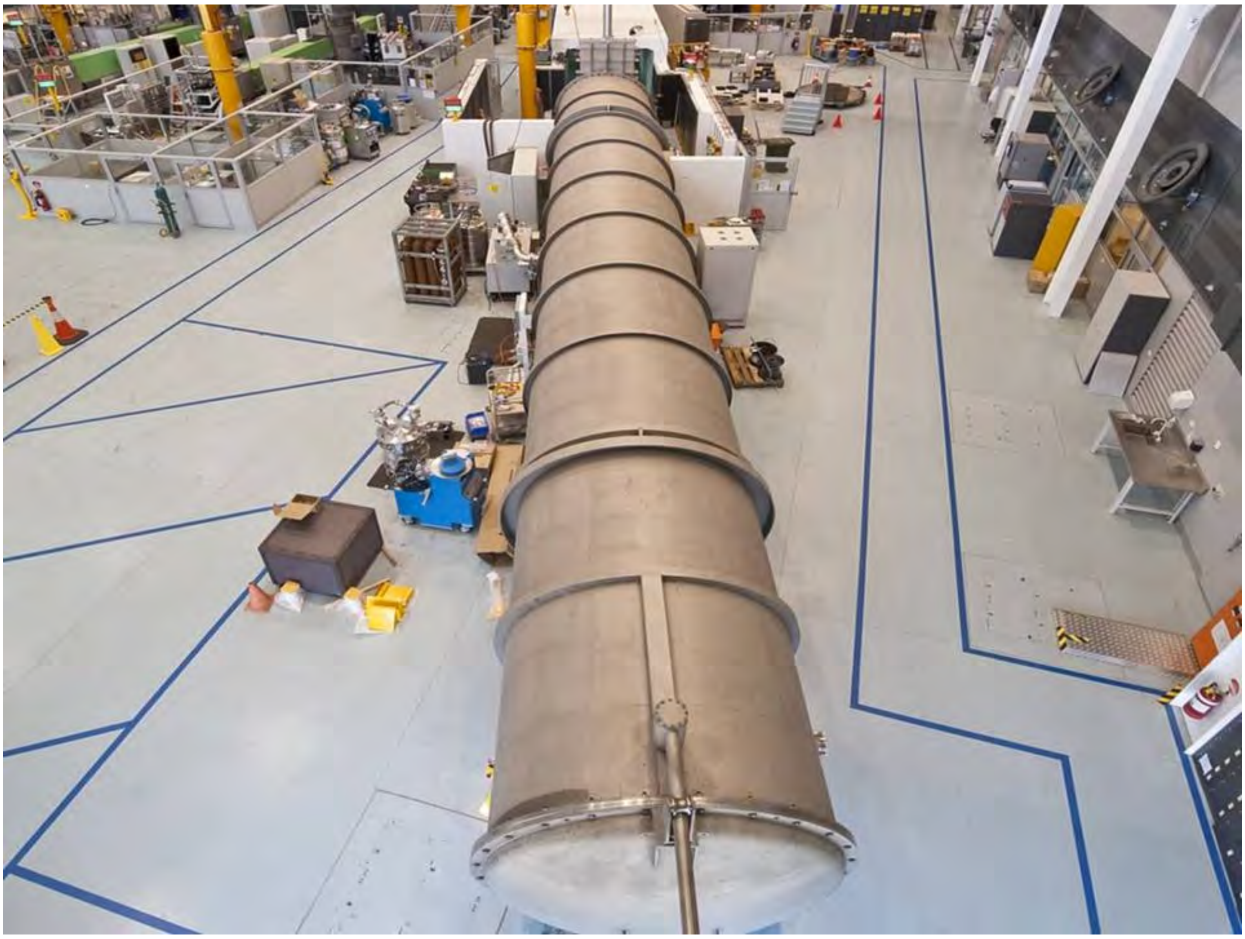

Figure 1 – QUOKKA, located in the Neutron Guide Hall at OPAL. This image was taken before the delivery of QUOKKA’s sister SANS instrument, BILBY.

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QUOKKA - THE 40 M PINHOLE SANS INSTRUMENT AT THE OPAL REACTOR

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Quokka [1] is a conventional pin-hole reactor based small angle neutron scattering (SANS) instrument installed on the CG1 guide from the OPAL reactor at ANSTO (see Figure 1). Quokka is used to study a range of materials: polymers, food, proteins, metals, ceramics, rocks, magnetic clusters, and superconductors. Quokka receives neutrons from a 20 L liquid-deuterium cold source operating at approximately 20 K. Neutrons from the cold source pass through a velocity selector and a variable system of collimation and guides before interacting with the sample position. Recent installation of variable length (bellows) collimation pipe ensures minimum air travel for neutrons and also reduce alignment time significantly. A two-dimensional detector is situated at variable distance from the sample for measurement of the scattered intensity which can be optimized according to the demands of angular resolution or range. Data acquisition may be made in number of modes, including standard time or detector integral counts, stroboscopic, event mode which allows post binning of kinetic data and the summation of multiple time series binned according to an external trigger signal. Calibrated absolute intensity scattering measurements may be made from isotropic scatterers over a standard range of scattering vectors, q (6×10^{-4} Å^{-1} < q < 0.7 Å^{-1}) where the lowest value is achieved by use of focusing optics. Non-standard measurements may be made using a range of collimations, neutron wavelength and wavelength spread, incident beam polarization and subsequent analysis and incident beam dimensions. In the sample position Quokka supplies the user community with a range of measurement environments both standard and unique in the small angle scattering community. Some of these sample environments are, a Rapid Heat Quench Cell enabling a sample to be studied in situ following a thermal shock (-120°C to 220°C) [2]; The neutron Rapid Visco Analyser (nRVA) [3] enables SANS to be measured simultaneously with viscosity via an RVA – an instrument widely used within the food industry; In-situ Differential Scanning Calorimetry (DSC) [4]; A stopped flow cell, and a RheoSANS.

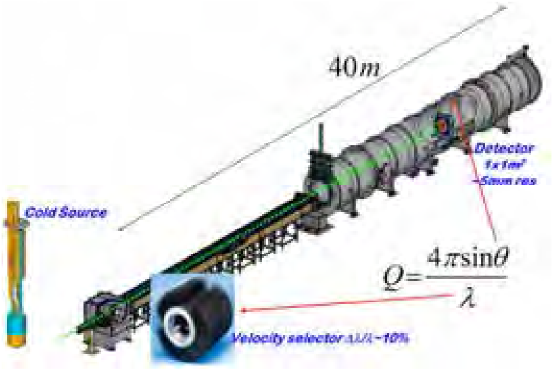

Figure1- Schematic view of the Quokka-SANS instrument at ANSTO

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A DIFFRACTION EFFECT INSIDE THE SENSOR LAYER OF X-RAY AREA DETECTORS

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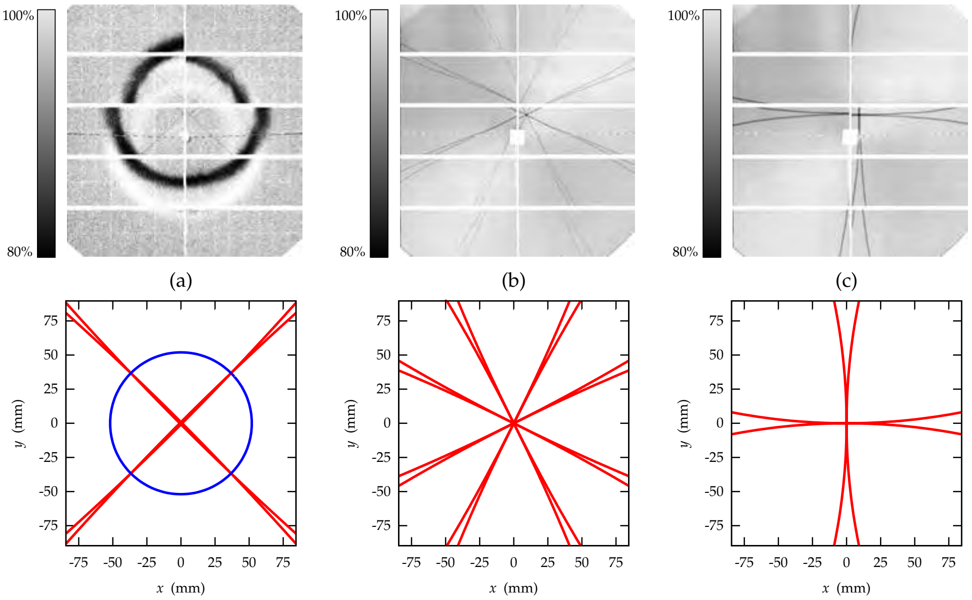
When an X-ray area detector with a single-crystalline sensor layer, such as a hybrid pixel detector, is used to record a scattering or diffraction image, a pattern of lines can appear which overlays the detected images [1]. These lines can be easily found by scattering experiments with smooth patterns, such as small-angle X-ray scattering. The origin of this effect is the Bragg reflection in the sensor layer of the detector.

Figure 1 displays images recorded using a modular PILATUS 1M detector [2] at different photon energies together with a theoretical simulation. The relative intensity of these lines is up to 20 %, which can disturb the evaluation of scattering and diffraction experiments. The effect can be exploited to calibrate the energy of the radiation with an accuracy well below 1 eV and to check the alignment of the detector surface with the direct beam as well as the alignment of individual detector modules with each other in the case of modular detectors.



(a) (b) (c)

Figure 1: Images of the pattern caused by internal diffraction (top row) recorded at $E_{ph} = 4567\,\text{eV}$ (a), $E_{ph} = 7990\,\text{eV}$ (b) and $E_{ph} = 8316.1\,\text{eV}$ (c) together with the simulation (bottom row). The images have been filtered to enhance the visibility of the pattern.

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COMBINATION OF 3D-CROSS CORRELATION LIGHT SCATTERING WITH SMALL-ANGLE NEUTRON SCATTERING

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The combination of 3D-cross correlation light scattering (3D-LS) with small-angle neutron scattering (SANS) will enable researchers to perform simultaneously neutron and light scattering experiments on highly concentrated samples. In particular in the field of soft matter the sample behavior may change with concentration. However the complementary characterization methods, namely LS and SANS, require different sample concentration ranges. Conventional LS-experiments can only be performed on diluted samples to assure that only singly-scattered light is detected, while for a SANS-measurement highly concentrated samples are required. 3D-LS suppress the multiple scattering by performing two simultaneously light scattering experiments. By combining the 3D-LS with the small-angle neutron scattering instrument V16 at the Helmholtz-Zentrum in Berlin, Germany, it will be possible to study samples under exact the same conditions for both scattering experiments. Moreover, this unique setup allows to extract simultaneously information of particles in solution regarding the dynamics of the system and the hydrodynamic volume of the particles (dynamic LS), the structural characteristics (particle-shape and -dimension, interactions) at low q (static LS) as well as the structural characteristics of the sample at high q (SANS).

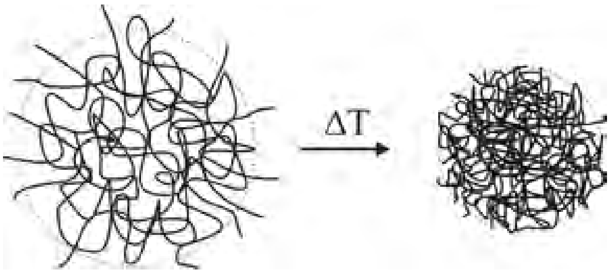

Figure 1: Illustration of the thermosensitive behavior of a PNIPAM microgel particle.

As proof of principle measurements were performed on cross-linked poly-N-isopropyl-acrylamide (PNIPAM) [1] microgel particles, like shown schematically in figure 1. Such thermosensitive microgel particles exhibit a volume phase transition temperature (VPTT). Below the VPTT the polymer chains are water-soluble and the gel particles are swollen (fig. 1, left). However, is the temperature increased, the polymer undergoes a reversible phase transition and the gel collapses (fig. 1, right). This gives rise to a rigorous reduction of the particle volume.

First the phase transition of the microgel particles was characterized with the 3D-LS at a diluted sample. The particles showed an obvious thermosensitive behavior: The hydrodynamic radius decreased from ~280 nm at 10 °C to ~ 140 nm at 40 °C. In further experiments these microgel systems were measured concentration-dependent with the 3D-LS – SANS combination in order to investigate the deformation of the soft particles with increasing concentration.

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CURRENT STATUS OF THE LIQUID-METAL-JET X-RAY SOURCE TECHNOLOGY

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High-end x-ray scattering techniques such as SAXS and GISAXS rely heavily on the x-ray source brightness for resolution and exposure time. Traditional solid or rotating anode x-ray tubes are typically limited in brightness by when the e-beam power density melts the anode. The liquid-metal-jet technology has overcome this limitation by using an anode that is already in the molten state.

We have previously demonstrated prototype performance of a metal-jet anode x-ray source concept [1-3] with unprecedented brightness in the range of one order of magnitude above current state-of-the art sources. Over the last years, the liquid-metal-jet technology has developed from prototypes into fully operational and stable X-ray tubes running in many labs over the world. Small angle scattering has been identified as a key application of the x-ray tube technology, since this application benefits greatly from small spot-sizes and high-brightness, to achieve a high flux x-ray beam with low divergence. Multiple users and system manufacturers has since installed the metal-jet anode x-ray source into their SAXS set-ups with successful results [4, 5].

The influence of the size of the x-ray source and its distance to the x-ray optics on the divergence will be discussed, and how to minimize the divergence in your SAXS experiments.

This presentation will review the current status of the technology specifically in terms of stability, lifetime, flux and brightness. It will also discuss details of the liquid-metal-jet technology with a focus on the fundamental limitations of the technology. It will furthermore refer to some recent SAXS and GISAXS data from users of the metal-jet x-ray tube technology.

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Geometric Corrections of the Tube Detectors on SANS Instruments at ORNL

Abstract The small-angle neutron scattering instruments at the Oak Ridge National Laboratory’s High Flux Isotope Reactor recently installed staggered arrays of linear position-sensitive detectors (LPSDs). The specific geometry of the LPSD array requires that approaches to data reduction traditionally employed be modified. In this work, we will present two methods that are used for correcting the geometric distortion produced by the LPSD array. The first method applies a correction derived from a detector sensitivity measurement performed using the same configuration as the samples are measured. In the second method, a solid angle correction is derived that can be applied to data collected in any instrument configuration during the data reduction process in conjunction with a detector sensitivity measurement collected at a sufficiently long camera length where the geometric distortions are negligible. Both methods produce consistent results and yield a maximum deviation of corrected data from isotropic scattering samples of less than 5% for the scattering angle up to a maximum of 35°. The results are broadly applicable to any SANS instrument employing LPSD array detectors, which will be increasingly common as instruments having higher incident flux are constructed at various neutron scattering facilities around the world.

THE CURRENT STATUS OF RIKEN STRUCTURAL BIOLOGY BEAMLINE I (BL45XU) IN SPring-8

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RIKEN Structural biology beamline I (BL45XU) equipped with tandem undulators consists of two experimental station; small-angle X-ray scattering (SAXS) and small- and wide-angle X-ray scattering (SWAXS) as shown in Fig. 1. Both stations can be independently operated. The beamline was constructed in 1997 for SAXS [1] and protein crystallography (PX). SWAXS station was reconstructed from PX station in 2009 [2]. In the SAXS station, nano- and meso-structure in soft-condensed matters as well as biological materials are studied by using small- and wide angle scattering and diffraction technique.

Optical components of the SAXS station except X-ray focusing mirror have been replaced against the aging degradation. Usable energy range of X-ray is from 7 to 14 keV. Photon flax is ~3 x 10^{12} photons/sec and the beam size is 300 (h) x 150 (v) μm^2 without the size-defined slits. The camera length can be changed from 0.5 m to 3.5 m with 0.5 m increments. At the end of 2014, a photon counting detector, PILATUS3X 2M, was installed. Solution scattering profile from typical biomolecule sample is able to be collected within a few seconds of X-ray exposure while the radiation damage is prevented. Installation of a compact sample changer for film and fiber materials achieved high-throughput measurement in material science. We are also developing a solution sample changer for BioSAXS.

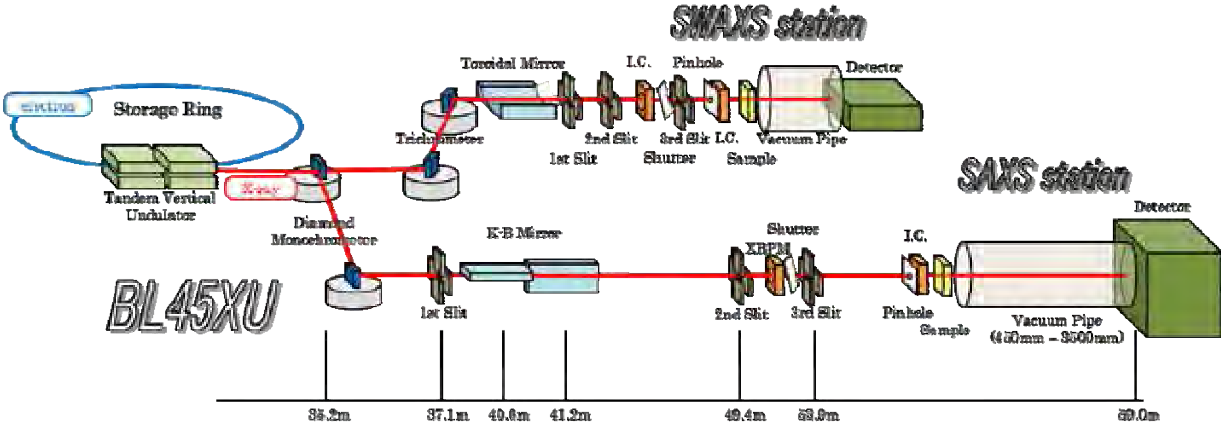

Figure 1: Optics layout of BL45XU.

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THE BESSY ASAXS DEDICATED INSTRUMENT – A REVIEW

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This talk will review some details of the BESSY ASAXS instrument and will elaborate the advantages of ASAXS in the analysis of complex nanomaterials.

First some technical details of the user dedicated SAXS instrument, 7T-MPW-SAXS, at BESSY in Berlin, will be presented. The instrument makes use of a monochromatic beam at the 7T wiggler source and is optimized for Anomalous SAXS (ASAXS) as well as Grazing Incidence SAXS (GISAXS). Details and strategies necessary for ASAXS will be emphasized. Several sample environments are available such as sample changers under air, inert gas, or under vacuum conditions. Various furnaces provided high temperatures up to 1200 °C as well as cooling devices are available down to 50 K.

Some material science applications are chosen to illustrate different aspects and benefits of ASAXS.

AlNiLa alloys have excellent mechanical properties, especially high strength combined with good ductility, high hardness, and corrosion resistance. However, these favorable properties are lost when the alloys crystallize and form grains larger than a few nanometers. Therefore, partial structure functions are derived from ASAXS.

Figure: The moveable detector system (edge welded bellow system) and the sample position of the ASAXS instrument are shown.

Some nanocrystallized oxyfluoride glass ceramics could act as frequency up-conversion glasses by doping with rare earth elements. ASAXS was able to analyse the nanostructure as well as the averaged chemical composition of such nanocrystals [2].

Ruthenium/selenium based catalysts are promising candidates to replace the widely used platinum in fuel cells. ASAXS allows the characteristic length-scales associated with the different elements to be determined [3]. Moreover, in case of bimetallic catalysts for fuel cell applications, made of Pt and Ni, the change of the catalytic nanoparticles was followed during potential cycling [4].

Moreover, ASAXS allows for investigating quantitatively multiphase systems, for example the formation of $ZrTiO_4$ nanoparticles in lithium aluminium silicate (LAS) glass ceramics [5]. Contrast variation in ASAXS allows us to determine the chemical composition of nanoparticles, which helps in determining different crystal growth mechanisms.

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↘ Flash Talk: Mon-F-T1

NEW UNDULATOR SAXS BEAMLINE BL-15A2 AT THE PHOTON FACTORY

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New beamline, BL-15A, was completed at the BL-15 section of the PF-ring in 2014. This new beamline has a short gap undulator which produces high brilliance X-rays ranging from 2.1 keV to 15 keV. The beamline will be dedicated to both activities, XAFS/XRF/XRD studies using semi-micro focus beams (A1 station) and SAXS experiments using collimated softer and hard X-rays (A2 station).

The combination of XAFS/XRF and SAXS experiments gives wide structural information from fine atomic structure to low and medium resolution. However, the XAFS/XRF and SAXS activities require highly focused and collimated beams, respectively. In order to achieve the both requirements, we newly developed a double surface bimorph mirror for the back-end horizontal beamline optics. The mirror surface can be selected by driving the mirror stage, so that quick and easy switching of highly focusing and collimated beams is now realized [1].

At the A2 station, the collimated beams are used for structural studies of functional membranes, large hierarchical structure analysis of soft matter and solution structure determination of biological system. In particular, grazing incidence SAXS (GI-SAXS) using vertically small-size low energy X-rays ranging between 2.1-3.0 keV will help to control the depth of the membrane structure analysis and reduce the roughness defects of an imperfect membrane. For such wide scientific targets, two kinds of SAXS stages are installed in tandem in the A2 station (Figure 1). The upstream stage is used for low energy SAXS experiments in vacuum or helium environment and the downstream one is a conventional SAXS/WAXS stage for various structural researches. The SAXS detector is a vacuum compatible Pilatus3 2M which is used for conventional SAXS experiments and is directly connected to the upstream SAXS stage in order to detect the lower energy x-ray photons. The Pilatus3 300KW is also equipped for wider-angle diffraction measurements.

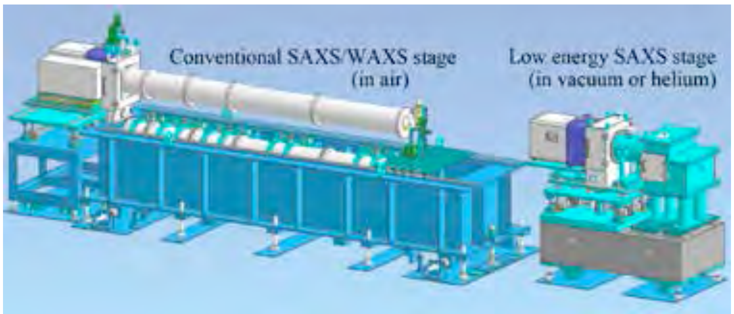

Figure 1: Two SAXS stages in the BL-15A2 station.

The construction was completed in the summer shutdown of 2013 and the first beams were delivered on Oct 17, 2013. The beamline optics tuning was followed by the A1 and A2 commissioning studies. We opened both stations to users in May, 2014. Here, the beamline design and performance, and the preliminary results will be reported.

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USAXS FACILITY FOR CHARACTERIZATION OF HIERARCHICAL STRUCTURES - FROM MICRONS TO ANGSTROMS IN LESS THAN 3 MINUTES

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Hierarchical microstructures spanning multiple length scales are common in wide range of real-world materials – from polymers and polymer composites, metals and alloys, to porous structures of soils, sands, woods, and many other natural and engineering materials. The development and optimization of advanced materials, as well as better utilization of natural resources, require powerful characterization tools with capabilities matching the complexity of the problem. Ideally such tool should also be non-destructive, statistically representative, and quantitative. Availability of such tool or tools is critical step to gain the microstructure understanding and control needed for optimal design/utilization in practical applications.

A versatile materials microstructure and structure characterization facility at the Advanced Photon Source (APS) strives to provide such capabilities by combining Bonse-Hart ultra-small-angle X-ray scattering (USAXS) with pinhole SAXS and wide-angle X-ray scattering (WAXS) measurements [1]. By combining these three techniques users have available unique combination of measurements continually covering up to 5 decades in length scales on one instrument - capable of solving complex materials science problems. An example of such study is presented in Figure 1, where the data from USAXS, SAXS, and WAXS were collected sequentially during isothermal anneal. The total anneal time was over 12 hours and collection of one sequence was about 6 minutes.

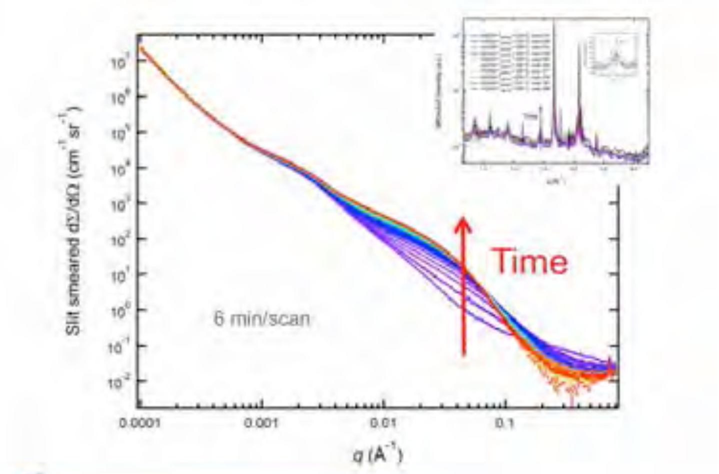

Figure 1: *In situ* 226° isothermal anneal of Al-alloy (courtesy of Lyle Levine, NIST). Data show formation of disk-like precipitates, dissolution of G-P zones and changes in the phase composition.

Recently, by implementation of on-the-fly scanning we have achieved major decrease in data collection time of the Bonse-Hart USAXS instrument. From 4-6 minutes for step scan the same quality data can now be collected in 1 - 2 minutes flyscan. Optionally, by making use of Si 440 crystal optics and higher-energy X-rays (~24keV) we can extend the measured feature sizes range up to about 20 micrometers (matching contemporary USANS instruments) while retaining the USAXS/SAXS/WAXS capabilities through the rest of the size range. Additional capabilities in USAXS imaging and USAXS-XPCS [2] are also available.

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ADVANCES IN SAXS INSTRUMENTS FOR HOME LABORATORY

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Recent advances in SAXS instruments for home laboratory use is describing here. According to increasing the needs for the SAXS applications in the synchrotron radiation facilities with increasing the demands for the nanotechnology, the SAXS instruments in the home laboratories are also attracted for the SAXS community as a complimentary use of the synchrotron radiation beamlines. The SAXS applications are including broad fields not only biological applications such as protein solution scattering but also softmatter applications such as polymers and gels. In addition, advanced materials, composites and devices, used in the nanotechnology has following features: heterogenic and hierarchical structures so that a multi-scale structure analysis is required for such applications. Therefore, it is necessary for the SAXS instruments for home laboratory use to cover a wide range of not only structural scale but also reciprocal space in order to explore the multi-scale structure in the softmatter.

There are three ways of optical configuration: pinhole collimation, Kratky camera [1] and Bonse-Hart camera [2]. The pinhole collimation is widely used in the synchrotron radiation SAXS beamlines, and it is suitable for point-focus X-ray beam and measurement of anisotropic scattering caused from highly oriented materials. We have great technical advantages in the high-brilliance and fine point-focus X-ray generators, and the high-performance focusing optics [3] for home laboratory use. Moreover, a hybrid pixel array detector has been produced, HyPix-3000 [4], having 0.1 mm per pixel spatial resolution and no point spread function smearing. Finer pixel size in the detector enables us to provide more detailed information on the scattering intensity distribution. The combination of these technical advantages and the novel detector technologies enables us to develop the best SAXS instruments for home laboratory use.

In this presentation, we are going to show the newly designed SAXS instruments for home laboratory use, and characterize the performance of the instruments.

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[4] HyPix-3000, Rigaku Corp., http://www.rigaku.com/en/products/xrd/hypix

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IN-SITU 2D SAXS AND 2D WAXS SIMULTANEOUS MEASUREMENT SYSTEM FOR HOME LABORATORY

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A novel in-situ measurement system enabling to record a 2D SAXS and a 2D WAXS information simultaneously has been developed. The measurement system, shown in Figure 1, comprises from a high-brilliance rotating anode X-ray source, a confocal multilayer mirror, two of a state of the art semiconductor detector, PILATUS 100K for WAXS and PILATUS 300K for SAXS, and pinhole collimation optics to suppress the parasitic scattering. Two detector systems are simultaneously controlled from one central software and acquiring the images in different momentum transfer ($Q = 4\pi \sin\theta/\lambda$) regions. Figure 2 shows typical diffraction patterns in different momentum transfer regions: silicon powder (d = 0.32 nm) for WAXS and dried chicken leg collagen (d = 65 nm) for SAXS.

Demands for in-situ measurement are dramatically increasing due to powerful supporting infrastructure in the synchrotron radiation facilities. At the same time, demands for the laboratory SAXS instrument are also increasing. In particular, soft-matters such as polymer and innovative materials have a hierarchical structure. Therefore, wide-coverage of structural scale in both real and reciprocal spaces is really essential.

We are going to present the detailed specification of the instrument and show some results from verification experiments.

Figure 1: Photograph of 2D SAXS and 2D WAXS simultaneous measurement system.

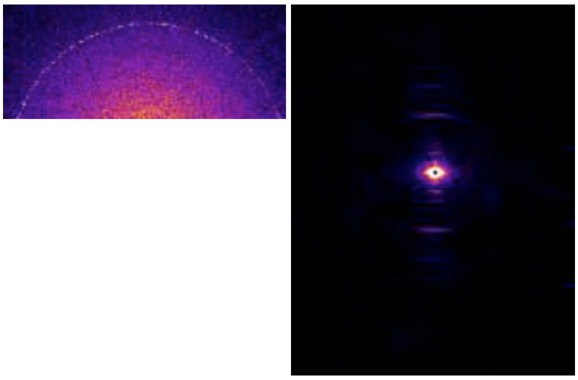

Figure 2: 2D WAXS and 2D SAXS patterns of silicone powder and dried chicken leg collagen.

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HYBRID PIXEL ARRAY DETECOR FOR HOME LABORATORY SAXS INSTRUMENT

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Small-Angle X-ray Scattering (SAXS) technique is a powerful tool for investigating the nano-scale structures and the functional analysis of biological macromolecules. A typical SAXS instrument consists of the X-ray source, optics, and detector. The high-performance X-ray generator and focusing optics such as multilayer mirror have made it possible to improve the performance of SAXS instrument. Moreover, the X-ray detector technology is also advanced during last decade. A hybrid pixel array detector based on the full-depletion photodiode arrays and CMOS ASIC technologies enables the high-precision measurement which is limited by the intrinsic fluctuation of X-ray photons. This representative is PILATUS detector [1].

We, Rigaku Corp., provide the benchtop SAXS instrument, namely NANO-Viewer [2], for the laboratory equipment, and it has been sold more than 50 sets in the world. The combination of the 1.2 kW fine-focus X-ray generator (MicroMax-007HFM), the multilayer confocal mirror, and the in-vacuum three-pinhole system enables us to reach to about 200 nm in size as the maximum dimension of object. This number is very close to that of the SAXS beamline in the 2nd generation synchrotron facility.

The detector is of importance and the key component of the SAXS instruments not only for the synchrotron radiation-based SAXS instruments but also for home laboratory-based SAXS instruments. Recently, we, Rigaku Corp., released a new hybrid pixel array detector, HyPix-3000 [3], for mainly home laboratory instruments. The HyPix-3000 has 775 × 385 pixels with 0.100×0.100 mm^2 pixel size. The counter depth of the HyPix-3000 is 31 bits (=2,147,483,648 $\sim 2 \times 10^9$ counts) and more than 100 Hz frame rate with 3.7 ms readout time. In this presentation, we are going to show the detailed performance characteristics of the detectors in our home laboratory SAXS instruments, and recent progress.

[1] DECTRIS PILATUS 100K/R, http://www.rigaku.co.jp/products/p/pilatus_100kr/
[2] NANO-Viewer, Rigaku Corp., http://www.rigaku.com/ja/products/saxs/nanoviewer
[3] HyPix-3000, Rigaku Corp., http://www.rigaku.com/en/products/xrd/hypix

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SOLID-STATE NEUTRON DETECTOR SoNDe - A NEW NEUTRON DETECTOR FOR HIGH-FLUX APPLICATIONS

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The Solid-State Neutron Detector – SoNDe – project aims to develop a high-resolution neutron detector technique that will enable the construction of position-sensitive neutron detectors for high- flux sources, such as the upcoming European Spallation Source (ESS). This includes also the construction of a full-scale prototype as a research and innovation action. Moreover, by avoiding the use of ^{3}He in this detector the ^{3}He-shortage, which might otherwise impede the construction of such large-scale facilities, can be alleviated. The main features of the envisioned detector technique are:

- high-flux capability, capable of handling the peak-flux of up-to-date spallation sources (gain factor of 20 over current detectors)
- high-resolution of 3 mm by single-pixel technique, below by interpolation
- high detection efficiency of 80 % or more
- no beam stop necessary, thus enabling investigations with direct beam intensity
- strategic independence of ^{3}He
- time-of-flight (TOF) capability, necessary to exploit maximum flux, with a time resolution in the µs regime
- modularity, improving maintenance characteristics of today’s neutron detectors

Compared to nowadays detector techniques a gain factor in counting rate of 20 (for ^{3}He detectors) is possible. Such gain factors will be needed to make the best possible use of sources such as the European Spallation Source (Sweden), the Institut Laue-Langevin (France) and the Maier-Leibnitz Zentrum (Germany). Benefiting instruments at such a facility, among others, would be Small-Angle Neutron Scattering (SANS) instruments such as SKADI [1], but also reflectometers or any other instrument with a need of high-flux capability and a mm resolution. Also applications outside neutron scattering, for example positron emission tomography, are conveivable.

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NEW DEVELOPMENTS IN LABORATORY SMALL-ANGLE X-RAY SCATTERING INSTRUMENTATION

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In this contribution we present a multifunctional laboratory SWAXS system enabling the user to perform combined SAXS and WAXS studies, GI-SAXS, in-situ tensile SWAXS experiments and others. The SWAXS system satisfies the advanced user with a wide range of dedicated sample stages, full experimental flexibility and highest resolution. It is a multifunctional system providing simple operation, short measurement times and an excellent overall angular resolution. This is possible because of the clever beam formation concept which comprises a brilliant X-ray source, specifically designed X-ray optics and an optimized scatterless collimation suppressing unwanted parasitic scattering.

Compared to other laboratory SAXS systems with a long beam path, the presented instrument guarantees an outstanding resolution along with a high intensity of the scattered X-rays, all this at a compact size. This is of particular advantage because a long sample-to-detector distance results in a much longer measurement time: the intensity of the scattered X-rays decreases with the square of the distance between sample and detector.

Different scattering studies were performed with the presented laboratory SWAXS system, including transmission measurements of isotropic and anisotropic materials as well as GI-SAXS studies of thin-film samples at non-ambient conditions. A major advantage is that an excellent resolution, i.e. a very low minimum scattering angle can be achieved. This is essential for measuring large nanoparticles. In addition, a unique sample-positioning mechanism enables to perform WAXS measurements, without re-aligning any part of the SWAXS system.

The presented studies clearly show that high-resolution and high-quality SWAXS data can be obtained with a laboratory SWAXS system.

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INVESTIGATING PARTICLE FORMATION USING SMALL ANGLE NEUTRON SCATTERING WITH IN SITU DROPLET BASED MICROFLUIDICS

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We report on the development of a droplet based microfluidics chip designed for in-situ small angle neutron scattering. Using quartz to provide a low neutron scattering background and high solvent compatibility, the chip allows a small angle scattering (SANS) volume to be positioned close to a source of microfluidic droplets formed at a junction of microchannels. In this way, particle formation within the droplets and probing by SANS can occur in-situ.

Droplet based microfluidics is a rapidly growing field utilizing nano-liter sized droplets that behave as separate compartments in which injected components can rapidly mix and form particles. The nano-scale and nature of the microfluidic particles makes them suitable candidates for small angle scattering[1]. Combining these complementary techniques offers several benefits for the measurement of particle systems. Significantly it allows the chemical composition of the particles to be determined from the injected components while the physical properties of the particles are influenced by the fluidics[2]. In addition, the use of SANS allows contrast variation of the components and solvent within the system to identify and probe the structural property of choice within the microfluidic droplets.

Combing particle formation and SANS measurements on the same chip enables structural changes during particle formation to be probed. By varying the position of the scattering volume relative to the mixing junction, structural information about the particles can obtained at various delay times following mixing. Thus spatial information can be related to temporal information about the particle formation. We demonstrate the utility of the chip with measurements of well defined particle systems undergoing formation and discuss potential applications

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UPGRADING SAXS SETUPS WITH INCOATEC´S SCATTERLESS PINHOLES AND/OR MICROFOCUS SOURCE IµS

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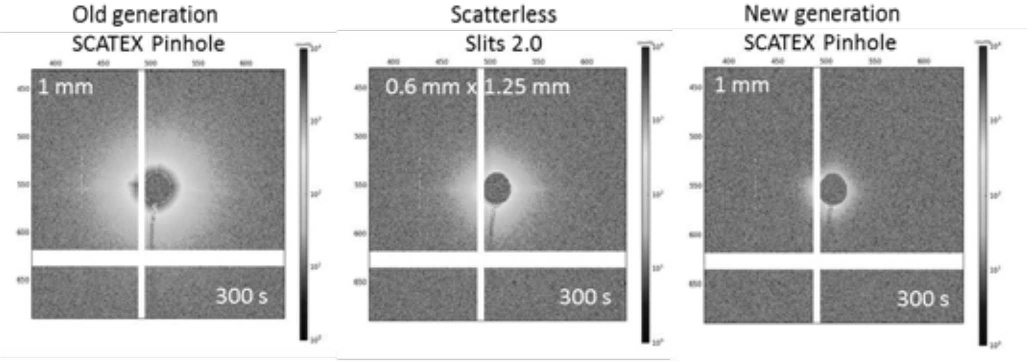
The lately developed SCATEX pinholes, scatterless apertures which significantly reduce unwanted parasitic aperture scattering, enable system upgrades which increase the photon flux, the resolution and signal-to-noise ratio of the whole experimental setup.

SCATEX pinholes are either made of Germanium for energies below 11.2 keV or of Tantalum for energies above 11.2 keV and are available with diameters ranging from 2 mm down to 20 µm and below. Thus, these novel apertures are applicable to a wide range of different applications.

In this presentation we will show several examples on how SCATEX pinholes and our microfocus X-ray source IµS can improve the performance of either home-lab SAXS systems such as the NANOSTAR of Bruker AXS or synchrotron beamlines. We will show results from the Nanofocus Endstation P03 beamline at PETRA III where we compared the performance of our SCATEX apertures with conventional Tungsten slit systems under high flux density conditions. We will further present results collected at the PTB four-crystal monochromator beamline at BESSY II, where we directly compare our old and new generation SCATEX pinholes with commercially available Scatterless Slits 2.0. These measurements show that the new generation of SCATEX pinholes exhibit up to 4 times less parasitic aperture scattering compared to Scatterless Slits 2.0 at the same downstream photon flux (Figure 1).



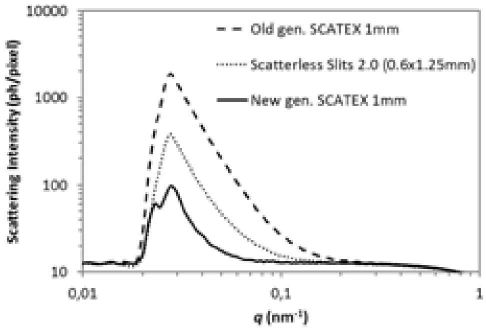


Figure 1: Detector images and the corresponding deduced scattering intensity (360°-integration) of parasitic aperture scattering at 8 keV of old and new generation SCATEX Pinholes and of Scatterless Slits 2.0.

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Contrast Variation Methods Available for Multi-components Small-Angle Scattering Analysis

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Contrast variation is a powerful technique to investigate microstructures or density fluctuations in a multi-component system. Total small-angle scattering is composed of partial scattering functions originating from individual components. The method changes relative balance among the partial scattering functions by changing their front factors, i.e., square of difference in coherent scattering length (Δb^2). Therefore by solving simultaneous linear equations, we are able to analytically decompose the total scattering into the self- and/or cross-term scattering functions for each components. In this presentation, we give an overview of available methods for small-angle neutron scattering (SANS) indicating experimental results.

The most frequently used is isotope exchange between H and D. For conventional contrast variation experiments on Nafion films, we prepared mixed water (H_2O/D_2O) for various ratios every 10%. Nafion films of 50 μm thickness were immersed in the mixed water in order to sufficiently replace water. SANS varies dramatically depending on the mixing ratio.

As for more practical ways, we report a method of solvent swelling and deswelling. These were applied to microstructural analyses on a tire rubber [1] or microbial cellulose [2].

To investigate history of water in an operating fuel cell, we employed deuterium gas (D_2) (deuterium gas fuel cell) [3]. When we operate a fuel cell with D_2, deuteron (D^+) or deuterated water (D_2O), generated from D_2, swells a polymer electrolyte membrane in an operating fuel cell. Thus by switching fuel gas from H_2 to D_2 during operation, scattering contrast for SANS, originating from a swollen membrane (Nafion®) , changes in a course of operation time.

More sophisticated one is dynamic nuclear polarization (DNP) performed at low temperature and under a high & homogeneous magnetic field. Nuclear of hydrogen can be polarized by a hyperfine interaction with electron spin of doped radicals by irradiating miri-electromagnetic wave. Thus scattering length of hydrogen depends on polarization. DNP was applied to a block copolymer system, in which lamellar microdomain is formed by polystyrene and polyisoprene block chains. As a result of selective doping of TEMPO radical into a rebbery phase, neuclear polarizartion was initiated around radical and the spin state spreads by diffusion to glassy phase. By carefully observing a lamellar form factor, we precisely determined spatial heterogeneity of polarization[4]. Finally, complementary use of neutron and X-ray is useful as a probe contrast method [5].

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HYDROSTATIC HIGH-PRESSURE CELL FOR THE SAXS-BEAMLINE AT ELETTRA

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Based on the experience of a previously developed high-pressure SAXS system at the SAXS-beamline at the synchrotron ELETTRA (Trieste, Italy), we have improved and redesigned the existing system [1-2]. The new system consists of a novel and compact pressure cell and an automated pressure control system for numerous applications to study nanostructure as a function of pressure with SAXS. The cell itself is machined out of stainless steel with cube dimensions of 3 x 2 x 2 cm and has two disc-shaped diamond windows with a diameter of 4 mm and a thickness of 0.75 mm each, serving as the X-ray entrance and exit windows, respectively. The cell is connected to a motor-driven spindle press using water as the pressure transmitting medium and the system can be operated in automated pressure or temperature scans. Additionally p-jumps triggered by pneumatic pressure valves, separating two reservoirs of different pressures can be applied, following the nanostructural changes by time-resolved SAXS. The sample in the cell can be pressurized up to moderate 3000 bar and above and its angular range encompasses 0° - 20° (2θ). Changing temperature in the cell can be achieved either by a circulating flow of water through copper plates or by Peltier elements between which the cell is sandwiched.

The application range is widely spread from studying phase diagrams of lyotropic or thermotropic liquid crystalline systems, proteins, lipoproteins or polymers and their barotropic phase transitions. The pressure cell can also be utilized in experiments with super-critical CO_2 and in the grazing incidence mode (GISAXS) for oriented and aligned lipid systems on solid supports.

Selected examples of high-pressure SAXS experiments and their results will be shown. In this example, studies with reversible pressure-scans (at constant T) and T-scans (at elevated p) have been performed on various LDL-samples (low-density lipoprotein) differing in the amount of triglycerides.

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NXUS, AN INDUSTRY PORTAL TO LARGE SCALE FACILITY SAXS AND SANS

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Most large scale X-Ray and neutron facilities have an explicit obligation to reach out to industry to let local and global companies benefit from advanced experimental methods. Despite this, the bridging between large scale facilities and industry is a great challenge and in practice most industrial users enter the facilities via university collaborations. Without understating the importance of such collaborations, it is clear that university collaborations are best suited for companies that can afford a time consuming long term research investment in a project area. Hence, many smaller companies without these resources and without prior experience in the field do not benefit from the knowledge accessible through large scale facility X-ray and neutron scattering.

Following the large public investments in the European Spallation Source in Lund the Capital Region of Denmark and the University of Copenhagen have supported the initiative NXUS (Neutron and X-ray User Support) as a more direct mediator between industry and experiment facilities. The NXUS-initiative is anchored in the neutron and X-ray scattering group at the University of Copenhagen and is a research based industry portal providing expertise in SANS and SAXS data acquisition and analysis.

In its one year pilot phase, the NXUS project identified ten industrial applications of small-angle scattering in collaboration with a broad range of companies ranging from Bio-pharma companies and food industry to manufacturers of paint or catalysts. Besides from contributing new knowledge to the companies, the case studies have introduced new types of users and shown the potential for SAXS and SANS in a broader industrial context. All projects had short term character and could be carried out with a concentrated engagement of 1-2 scientist months from the NXUS project.

Based on this initial success, the NXUS project now works towards consolidating the portal and developing a sustainable collaboration model with significant financial contributions from the participating companies.

Selected cases will be presented along with preliminary conclusions from the pilot phase regarding the structure and organisation of such an industry portal.

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THE ACHIEVEMENTS AT MAX IV LABORATORY DOING SAXS AT THE PERIPHERY OF A MULTIPOLE WIGGLER FAN

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The I911-SAXS beamline at the MAX II 1.5 GeV ring of MAX IV Laboratory was shaped by the strong interest of the Scandinavian soft matter community. The beamline uses 0.5 mrad at the horizontal periphery of the central 2 mrad of the I911 wiggler fan (Figure 1). The predicted photon flux of the focused and collimated beam is $5x10^{10}$ ph/s, the wavelength is fixed at 0.91 Å and the beam size is 0.3 x 0.2 mm^2 (HxV, FWHM) at the detector position. The versatility of the experimental setup permits to select scattering vector ranges within $0.006 \leq q \leq 2$ $Å^{-1}$[1]. I911-SAXS is now a oversubscribed and highly productive multipurpose SAXS beamline that has been running non-stop since May 2011, despite the inherent difficulties of the source and existing optics.

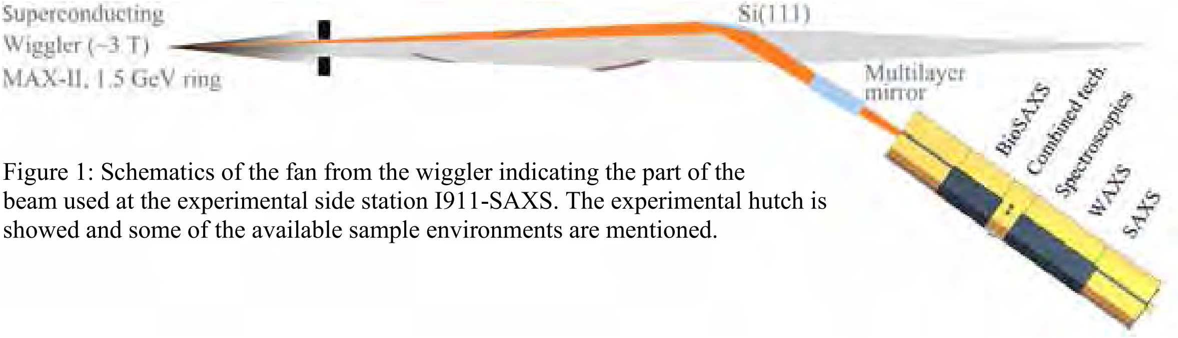

Figure 1: Schematics of the fan from the wiggler indicating the part of the beam used at the experimental side station I911-SAXS. The experimental hutch is showed and some of the available sample environments are mentioned.

Most of the experimental projects at this beamline belong to the fields of soft matter (macromolecules in solution and dense polymers). However, projects on metallic nanoparticles, alloys (hard condensed matter) have also been carried out at I911-SAXS. Over the years a continued development program has been focused on satisfying the interests and needs of the academic and industrial user community. The joint effort led to: competitive sample environments, in-situ and time resolved measurements, as well as experiments combining SAXS with other complementary techniques. These activities consolidate valuable acquired experience towards the future SAXS beamline at the 3 GeV MAX IV ring [2].

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↘ Flash Talk: Mon-F-T1

NEW NCPSS BL19U2 BEAMLINE FOR SMALL-ANGLE X-RAY SCATTERING FROM BIOLOGICAL MACROMOLECULES IN SOLUTION

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The new biological small-angle X-ray scattering beamline (BioSAXS, BL19U2 at the SSRF, Shanghai, China) is dedicated exclusively to the small-angle scattering experiments from biological macromolecules in solution. As a member of the important facilities in National Center for Protein Sciences Shanghai (NCPSS), this BioSAXS beamline is the first in China to serve the rapidly increasing biology communities. Basically, beamline BL19U2 is located in Shanghai Synchrotron Radiation Facility (SSRF). It is an undulator beamline providing high brilliance for BL19U2 end-stations. The RMS source size is 137 µm (H) $_{\mathrm{x}}$ 9.9 µm (V) and divergence 39 µrad (H) $_{\mathrm{x}}$ 9 µrad (V). The beam size at the sample position during normal operation is 0.42 mm (H) $_{\mathrm{x}}$ 0.15 mm (V). A double flat silicon crystal (111) monochromator is used in BL19U2 with a tunable monochromatic lights energy ranging from 7 to 15 keV (Fig.1).

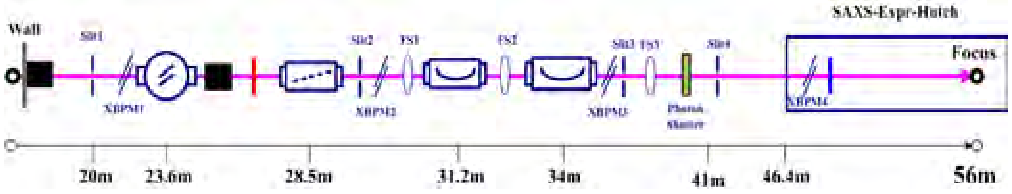

Figure 1: BL19U2 beamline schematic diagram

To meet the rapidly growing demands from crystallographers, biochemists and structural biologists, our BioSAXS beamline allows manual and automatic sample loading/unloading and data collection. A Hamilton syringe pump (Hamilton Robotics Inc., Bonaduz, GR, Switzerland) was used to pump samples/cleaning solutions into the cell unit. The sample cell unit is designed using easily exchangeable quartz capillaries with a short sample flow path. Two motorized x-z stage were employed to serve as the sample cell unit holder and sample tube holder respectively. The Pilatus 1M detector (Dectris) is mounted for data collection characterized with a high dynamic range and a short readout time. The free open-source data-reduction software RAW is employed for data reduction, manipulation and analysis. With the help from EMBL-Hamburg, the highly automated data processing pipeline SASFLOW was integrated in BL19U2, which provides user-friendly interface for 2D image conversion, primary structure parameter characterizing and 3D model building.

The BL19U2 beamline was officially open to the users on March, 2015. Till now, feedback from users is positive and the number of experimental proposals at BL19U2 is increasing, showing that the Bio-SAXS facility of BL19U2 at SSRF is already providing reasonable SAXS results.

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ELECTRONIC RENEWAL OF THE D11 DETECTOR

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The digital electronics of the D11 detector, in use at the instrument since 2009, has been renewed during the long shutdown 2013 – 2014. A center-of-gravity algorithm has been implemented in order to multiply by a factor of 4 the number of detector "pixels", which now results in an improved spatial definition with a mean spatial resolution of 6.8mm. Furthermore, the deadtime of the detector could be improved with the new electronics and has now a value of 330 ns (previously 420 ns).

The improvement of the detector is illustrated with the measurement of a concentrated solution of large microgel particles with added linear polymer in toluene. The small angle scattering of this system is a superposition of the pronounced structure factor due to the high microgel concentration (peak at low momentum transfer Q) and the form factor of the spherical particles (subsequent minima towards higher Q).

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AN AUTOMATED SAMPLE CHANGER FOR THE HIGH BRILLIANCE BEAMLINE ID02 AT THE ESRF

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The High Brilliance Beamline ID02 at the European Synchrotron Radiation Facility (ESRF, Grenoble) evolved after its upgrade in 2014 to a unique time-resolved ultra small-angle X-ray scattering (TRUSAXS) beamline being able to reach a lowest scattering vector of $q < 10^{-3}$ nm^{-1} at 31 m sample-to-detector distance and offering an unprecedented time resolution in the sub millisecond range. Hence, the demand for beam time at the upgraded ID02 beamline on part of the SAXS user community is higher than ever before.

To allow for the most efficient usage of the beam time, we have extended the well-known flow-through capillary concept with an automated sample changer. Within the scope of the development of the presented sample changer two major aspects were pursued: a) the reduction of dead time between sample measurements while preserving high data quality and b) an automated sample environment capable of handling soft matter samples over a relatively wide range of temperature and viscosity. In particular, this sample changer is designed to facilitate high-throughput phase-diagram mapping in the soft matter field as a function of temperature with minimum thermal hysteresis.

The sample changer is composed of a multi-port distribution valve able to hold up to seven different liquid samples with a maximum volume of 1 ml. To ensure a high degree of temperature stability, all sample reservoirs, the multi-port valve, the flow path up to the capillary, and the capillary itself are embedded in an isothermal environment. It is possible to vary the temperature in the range from 10ºC up to 120ºC. A pump with two independently moving syringes manipulates all liquids within the flow path. The first syringe aspirates a sample volume of approximately 350 µl into the flow-through capillary for X-ray exposure under continuous flow to avoid radiation damage. Thereupon, the sample is dispensed back into its reservoir for retrieval waiting for the next cycle. Alternatively, it can be sent to waste. The flow rate is adjusted to the viscosity of the sample. The second syringe administrates the cleaning process via an 8-way distribution valve. Up to six different liquid solutions, e.g. water, various kinds of detergents, large quantities of buffer, can be injected into the flow path ensuring a clean environment, but also allowing for intermediate reference measurements.

In this contribution we will present the design and the functionality of the sample changer being fully integrated into ID02's data acquisition system. First benchmark results obtained on systems such as lysozyme and bovine serum albumin in HEPES buffer and binary and ternary common systems will be reported.

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Non Crystalline Diffraction for polymers on ALBA – BL11

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Non-Crystalline Diffraction is an important method for studying the structural properties of non- or semi-crystalline states of matter. Small Angle X-Ray Scattering (SAXS) and Wide Angle X-ray Scattering (WAXS) is a well suited technique for observing the shape and size of these molecular assemblies and for observing phase changes or conformational rearrangements on a length scale ranging from 10 to 5000 Å.

ALBA is the new synchrotron source located at Cerdanyola del Valles that is mainly used by the Spanish Science community. Bl11 is a versatile beamline where biological macromolecules, synthetic polymers, gels, liquid crystals, oils, paints, ceramics and environmental aggregates can be measured. Scientific and technological challenges on the beamline BL11 are fulfilled by an undulator insertion device on a 3rd generation synchrotron radiation light source. Bl11 is delivering high photon flux (10^{12} ph/s/0.1%b.w.) into a focused 100 x 50 μm^2 spot in the energy range 5-13keV. Grazing Incidence (GISAXS) and µ-focus experiments will be possible in a short future.

Static or time resolved measurements are performed with simultaneous SAXS and WAXS area detectors. A Linkam is available to users for temperature evolution studies to obtain detailed information during crystallisation and melting and the sample platform is very flexible to accommodate user sample environments.

UPGRADE AND NEW SAMPLE ENVIRONMENTS OF D22

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During the one-year long ILL shut down, the D22 small angle scattering spectrometer has benefited from a major upgrade. Collimation, sample zone, detector, shielding have been updated. We briefly review the new capabilities of the instrument which set higher standards. D22 team took also advantage of this year to develop three pieces of equipment for biology and soft-matter studies: a neutron-transparent dialysis cell, an *in situ* UV-visible spectroscopy and a 1-2 shear cell. Preliminary results will be presented demonstrating the new possibilities that such equipment offers.

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TIME-RESOLVED SAXS EXPERIMENTS WITH LOW SAMPLE CONSUMPTION

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Time-Resolved Small Angle X-ray Scattering (TR-SAXS) is an extremely powerful tool to investigate *in-situ* the conformational changes that biological systems are undergoing during the course of their biological function. The time regime of such changes is generally depending on the scale of the event. A TR-SAXS experiment using a stopped-flow mixer is an ideal tool to detect large scale transition like tertiary or quaternary structural changes of macromolecule, which typically occur in the millisecond time scale and above. However the use of stopped-flow mixers for TR-SAXS experiments on biological samples has often been difficult due to the large amount of material necessary.

Stanford Synchrotron Radiation Lightsource (SSRL) Beamline 4-2 is a SAXS/D facility dedicated to structural studies on mostly non-crystalline biological systems [1]. Here we report on the latest status of our fast TR-SAXS setup using a customized stopped-flow mixer in order to reduce the sample consumption. This new setup allows us to obtain a TR-SAXS data set from as little as 30ul of sample volume at the present moment. It also eliminates the sample consuming priming of the tubing inside the stopped flow (no dead volume between shots) and thus substantially reduces the sample amount required for such experiments. An automatic wash cycle for the sample cell is employed after every single shot to ensure that the cell is clean and no residues remain in it from the previous measurement. Recent scientific results using this setup are also being discussed [2].

Use of the Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, is supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Contract No. DE-AC02-76SF00515. The SSRL Structural Molecular Biology Program is supported by the DOE Office of Biological and Environmental Research, and by the National Institutes of Health, National Institute of General Medical Sciences (including P41GM103393) . The contents of this publication are solely the responsibility of the authors and do not necessarily represent the official views of NIGMS or NIH.

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RECENT DEVELOPMENTS ON THE AUSTRALIAN SYNCHROTRON SAXS/WAXS BEAMLINE

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The Australian Synchrotron SAXS/WAXS beamline [1] is an advanced, general purpose Small Angle Scattering undulator beamline, optimised for a low background intensity. Now in its 6th year of user operations, this exceptionally reliable beamline has proven itself to be highly successful with more than 90 papers acknowledging the beamline published in 2014 alone. These publications cover a wide range of science, such as proteins, polymers, metallurgy, coatings, fibres, liquid crystals, and foodstuffs, and various in situ conditions including temperature, pressure, stretching, pH, electric and magnetic fields.

To achieve such a high reliability and excellent rate of publication from the user community, the beamline staff has been particularly proactive in continually developing the beamline. Developments have focused both on new techniques and improvements in reliability and ease of use. Recent examples of this development include an analyser crystal based alignment system for grazing incidence techniques, developing reflectivity capability, an offline sample stage for pre-experiment setup, Python based beamline control, web based applications for data acquisition and analysis, virtualization, and new sample environments.

This paper will describe the beamline, with a particular focus on recent efforts. Examples of user science enabled and improved by these developments will also be presented.

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↘ Flash Talk: Mon-F-T1

CURRENT STATUS OF POLARIZED AND FOCUSED NEUTRON BEAM AT THE SMALL AND WIDE ANGLE NEUTRON SCATTERING INSTRUMENT TAIKAN

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The small and wide angle neutron scattering instrument TAIKAN is designed for efficient measurements in wide-q range of 5.0×10^{-4} Å^{-1} $\leq q \leq$ 20 Å^{-1} by using both neutrons in broad wavelength (λ) bandwidth of 0.7 Å $\leq \lambda \leq$ 7.8 Å and wide angle detectors [1]. In the upper stream of a beamline, optical devices such as six slits, two types of collimators for large or small beam size and three vacuum chambers, which have three devices to be chosen according to the beam condition, i.e., unpolarized, polarized and focusing neutron beams, were installed. At the beginning, only unpolarized neutron beam was available. The beam commissioning was started in January 2012, and users program was started in March 2012. During the summer shutdown of beamtime in 2012, we installed a multi-channel V-shaped magnetic supermirror cavity covering 40 mm × 40 mm beam size. Figure 1 shows the λ dependence of neutron spin polarization obtained with the cavity. It provides polarized neutrons with the polarization higher than 95% for the wavelength above ~ 3 Å. For polarized neutron experiments, we can use various types of equipment, i.e., 0.2 T magnet (vertical or horizontal), 1 T magnet (vertical), 4 T superconducting magnet (horizontal), 10 T superconducting magnet (vertical), 4 K cryostat, and laser furnace (< 1,100 °C). The cryostat and furnace can be combined with the magnets. In 2014, we installed a quadrupole magnet and sextupole magnets to deliver polarized and focusing neutron beam. These magntes and two sets of spin flippers are under commissioning.

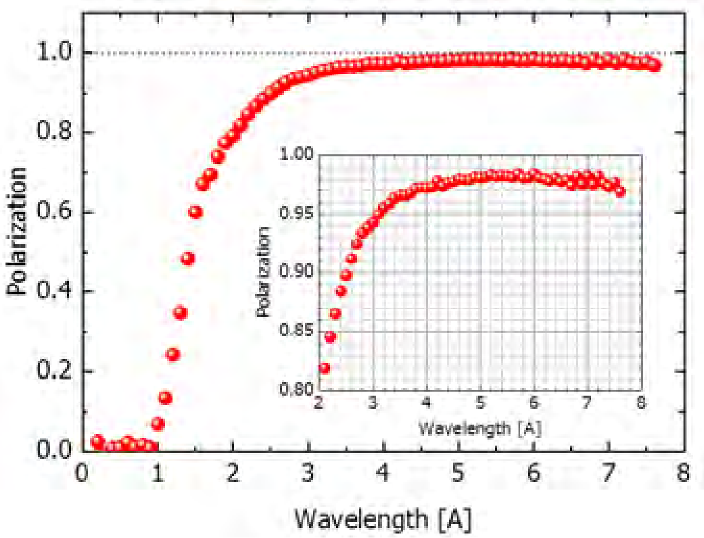

Figure 1: Neutron spin polarization as a function of wavelength provided at TAIKAN.

We will talk about current status of polarized experiments in TAIKAN and show typical data of rare-earth magnets, chiral helimagnetic materials and so on.

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AN ULTRA-SAXS INSTRUMENT ON A SHOESTRING BUDGET

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Laboratory small-angle X-ray scattering (SAXS) typically characterizes one to two orders of magnitude in size. Many materials' properties, however, arise from an interplay of structures spanning a much wider size range. In order to extend the range of small-angle scattering to encompass another two orders of magnitude in size, we must consider complementary instrumentation. As the field of Ultra-SAXS remains somewhat obscure, and with custom Ultra-SAXS instruments prohibitively expensive, the development of inexpensive instrumentation may help to further explore and open up this field.

This poster will present a design and initial results gained from building an inexpensive laboratory Ultra-SAXS instrument for use with higher energy Mo-ka sources (emitting 17.4 keV photons as opposed to the standard 8.0 keV emitted by copper sources). So far, two iterations have been built, the first of interesting but slightly impractical design, and a second version incorporating many improvements.

The first instrument has been demonstrated to work (albeit briefly due to a failing X-ray source) using generously cut two-bounce Si(111) test crystals. The angular precision of the in-house built high-precision rotation stages, the dynamic range of a very inexpensive detector chain, and the feasibility of using a non-evacuated design were all positively proven with this instrument.

The second instrument is mostly comprised of very inexpensive 3D-printed plastic components in combination with off-the-shelf components, to further reduce the build cost, and drastically reduce the prototyping time. Upgrades include rotations on independent rails and jacks to ease alignment, inter-crystal guard slits, and a fast silicon drift detector to reduce the noise floor of the instrument. Furthermore, custom four-bounce Si(220) crystals have been employed.

First results are expected of this instrument between the submission of this abstract and the SAS2015 conference, where they will be presented. It is thus hoped that this inexpensive, open-sourced design may find utility in other SAXS laboratories worldwide.

References

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KWS-3: HIGHEST RESOLUTION FOCUSING SANS DIFFRACTOMETER.

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KWS-3 is a very small angle neutron scattering diffractometer running on the focusing mirror principle at the Heinz Meier-Leibnitz Zentrum MLZ in Garching and operated by Jülich Centre for Neutron Science JCNS. The principle of this instrument is one-to-one imaging of an entrance aperture onto a 2D position sensitive detector by neutron reflection from a double-focusing toroidal mirror.

By variation of the entrance aperture from 0.5x0.5 mm^2 to 5x5 mm^2 the instrument could be optimized to "highest resolution" with minimal momentum transfer $Q_{min}=3\cdot10^{-5}Å^{-1}$ and the intensity 1200 n/sec or to "highest intensity" with $Q_{min}=3\cdot10^{-4}Å^{-1}$ and the intensity $1.2\text{x}10^5$ n/sec. In "standard resolution" mode with 2x2 mm^2 entrance aperture, 12.8 Å wave length and 10 m sample-to-detector distance KWS-3 covers Q-range between 10^{-4} and $2.5\cdot10^{-3}Å^{-1}$ and demonstrates world-wide-best performance: intensity higher than any pinhole SANS instrument and measurement time shorter than any Bonse-Hart camera. A second sample position at 1.3 m distance has extended the Q-range of the instrument to $2\cdot10^{-2}$ $Å^{-1}$ and reached more than one-decade overlapping with the classical pinhole SANS instruments.

KWS-3 can be used for the analysis of structures with between 30nm and 20 µm. The length scale that can be analyzed is extended beyond 20 µm for numerous materials from physics, chemistry, materials science and life science, such as alloys, diluted chemical solutions and membrane systems.

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THE COSAXS PROJECT AT MAX IV LABORATORY: A SMALL ANGLE X-RAY SCATTERING BEAMLINE TO STUDY STRUCTURE AND DYNAMICS

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Structural and dynamics studies at the nanoscale of condensed matter are driving most of the recent efforts of the scientific community to understand complex and multifunctional systems. Among different approaches, the use of x-ray scattering techniques provides a robust method to bring quantitative information of nanostructures.

All modern hard X-ray synchrotron facilities are promoting the upgrade or the development of SAXS beamlines [1]. The new x-ray scattering beamline at the 3 GeV ring of the Swedish Synchrotron MAX IV Laboratory, namely CoSAXS, is planned to be a multipurpose instrument, with modular operation that aims to take full advantage of the unique properties of the source – its brilliance, low emittance and high degree of coherence.

The optical design of the beamline and the results from x-ray tracing simulation [2] are discussed. The source is an in-vacuum undulator with 2 m magnetic length. The monochromator is a Silicon 111 horizontally deflecting double crystal monochromator (hDCM) with inclined crystals. The focusing elements are composed by two pairs of bendable flat mirrors in Kirkpatrick-Baez configuration. The energy range of the beamline is 4-20 keV. Typical spot sizes at the sample are up to 150 x 150 μm^2 (HxV, FWHM) when focalizing at the detector. The scattering vector range is $\sim 6 \times 10^{-4} \leq q \leq 6$ $Å^{-1}$ with simultaneous SAXS/WAXS detection. Photon flux is estimated to be 10^{12}-10^{13} ph/s. The current layout also offers microfocus spot sizes at the sample of about ~25 x 5μm^2.

Sample environments and detection systems are under discussion and preliminary ideas are presented. Different techniques are planning to be implemented in progressing commissioning steps. Among them the priority is on: solution SAXS scattering, SAXS/WAXS, micro-focusing SAXS and Anomalous x-ray scattering down to 4 keV. The coherent properties of the MAX IV machine [3] will be explored mainly through XPCS experiments. The upgrade of diverse sample environments, currently operational at the I911-4 SAXS beamline of MAX IV [4], is envisioned.

The CoSAXS project will have a major positive impact on the current MAX IV SAXS possibilities and the users scattering community in general.

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↘ Flash Talk: Mon-F-T1

NEW SAXS/WAXS, MICROBEAM AND SURFACE SCATTERING CAPABILITIES AT THE BM26B-DUBBLE BEAMLINE AT THE ESRF

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Recently, small-angle X-ray scattering (SAXS) has become a powerful tool to investigate the structure of nanoscaled materials in a multitude of different research fields, from metals to oxides, from polymers to surfactants and from proteins to cells. In particular the use of synchrotron radiation allows one to perform experiments in-situ and with sub second time resolution. As a result, each synchrotron around the world has one or more SAXS dedicated beamlines.

The Dutch-Belgian beamline BM26B at the ESRF is a beamline specialized in performing simultaneous SAXS/WAXS experiments [1]. The beamline is multipurpose and allows to measure samples either in solution or in its bulk solid state.

Thanks to recent upgrades, novel opportunities are available at DUBBLE since the last year. The following fields review the new experimental DUBBLE opportunities available to users:

1. Microbeam scattering/diffraction: post-focusing Kirkpatrick-Baez mirrors and Be lenses have been developed and can be easily inserted in the beam to tune the beam size down to 15 x 5 μm. Micrometer sized polymeric samples, fibers and even thin skin samples can be successfully studied with these post focusing optics [2].
2. Grazing incidence geometries: a novel experimental layout permits to perform scattering and diffraction in a grazing incidence configuration with great accuracy (GISAXS and GIWAXS). 2D GIWAXS setup provides information in the range 0.1 - 10 nm. 2D GISAXS experiments can be conducted in the range 1 – 1000 nm with second and millisecond time resolution.
3. Millisecond SAXS and WAXS: the recent detector upgrade to solid state noiseless fast Si based detectors (i.e. Pilatus) allows the study of structuring of hard and soft matter with millisecond time resolution. Perfect coupling between detector system and devices such as homemade ballistic cooling device [3], modified flash DSC [4] and shear devices allows for the study of polymer crystallization in conditions close to real life ones.

A detailed description of the novel beamline components and performances will be presented in this contribution, together with the most recent research highlights.

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↘ Flash Talk: Mon-F-T1

DEVELOPMENT OF THE BIO-SANS AS A NEUTRON TOOLBOX FOR BIOMACROMOLECULES STUDY

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Bio-SANS is the first small angle neutron scattering beam line dedicated for biological research. Located at the High Flux Isotope Reactor of Oak Ridge National Laboratory, it has been operated by the Center for Structural Molecular Biology. The combination of high neutron flux from the cold neutron source of the HFIR reactor and low experimental background afford users to perform high throughput studies of biomacromolecular complexes. Since commission, we have been developing a suite of tools to make neutron scattering experiment more user friendly to the biological and medical research community.

Here we will showcase our recent and on-going upgrades, opening opportunities that were otherwise non-existent. We have expanded the suite of sample environment to include automatic sample changers, high-pressure cell, ‘tumbler’ or sample changer with constant rotation capability, humidity controlled chamber and three-phase flow cell, etc. An upgraded detector and streamlined operation process together enhance the efficiency of the neutron scattering experiments. Furthermore, we have recently implemented grazing-incident capability, which makes it possible to study planar structures like lipid membrane. We are continuing making upgrades of the instrument for optimizing performance on biomacromolecules. The upgrade includes a wide angle detector for simultaneous data acquisition at both lower and higher angles. A new collimator system with more flexible configurations of optics is also planned.

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A NEW FAST DETECTION SYSTEM FOR THE HIGH-INTENSITY SANS DIFFRACTOMETER KWS-2 OF THE JCNS

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The small-angle neutron diffractometer KWS-2, operated by the Jülich Centre of Neutron Science at Heinz Maier-Leibnitz Zentrum, is dedicated to the investigation of mesoscopic structures and structural changes due to rapid kinetic processes in soft condensed matter and biophysical systems. It was recently subject of a major upgrading aiming for boosting its performance with respect to the intensity on the sample, the instrumental resolution, and the Q-range covered. In the high-intensity mode, up to 12 times intensity gain compared to the conventional pinhole mode for the same resolution can be achieved with lenses based on increasing of the sample size. In the tunable resolution mode, with chopper and TOF data acquisition mode, improved characterization of the scattering features within different Q ranges is enabled by the possibility to vary the wavelength spread $\Delta\lambda/\lambda$ between 2% and 20%. In the extended Q-range mode by means of lenses and a secondary high-resolution detector (pixel size of 0.45mm) a Q_{min} down to 1 x 10^{-4} Å^{-1} can be achieved, which in combination with the pinhole mode permits the exploration of a continuous length scale from 1 nm to one micron.

Following a collaborative work between JCNS and GE Reuter Stokes Inc. the current scintillation detector will be replaced in the summer of 2015 by a new detection system based on an array of ^{3}He tubes and a fast MHz electronics. This achievement will eliminate the actual drawback for an optimal use of the high flux of the instrument (up to $2\text{x}10^8$ n cm^{-2} s^{-1} are available on the sample). The new detector consists of three different lengths of 8mm 8-pack modules, which will be installed on a frame inside the 1.4m tank of KWS-2 and will cover an active detection area equivalent to 0.9 m^2. The new detection electronics is mounted in a closed case in the backside of the ^{3}He tubes frame and will operate at ambient atmosphere under cooling air stream. Recent tests of the prototype (one ^{3}He 8-pack module and electronics) that have been carried out at the JCNS instruments KWS-2 (in high flux conditions) and TREFF have confirmed the outstanding parameters of the new detection system: a) a count rate of ca. 720kHz on the 8-pack module for 10% dead-time for homogeneous illumination of the detector; b) a stability of the pixel response which lies practically within statistical uncertainties and c) a position resolution better than 8mm with a stability better than 1%. It can be thus estimated that a count rate of several MHz will be detected with a very high stability and no dead-time at KWS-2 in the near future. This advantage will open new opportunities for static and time-resolved structural investigations of small soft-matter and biological systems that typically deliver at high Q very weak scattering signal above the buffer or solvent level.

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CONCEPTION AND DEVELOPMENT OF A POLYVALENT PIPETTING ROBOT DEDICATED TO EXPERIMENTS ON LIQUID SAMPLES

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Current autosamplers developed for synchrotron beamlines are optimized for high throughput measurements and are almost permanently integrated to the beamline, often devoted to one main type of experience. The polyvalence of SWING beamline offers to the users a large variety of interchangeable sample environments for biology, chemistry and physics. This versatility imposes to have easily removable, compact and robust equipments. For solution biology, the HPLC chain from Agilent technologies, optimized for on-line purification, is equipped with an autosampler. However, this equipment is hardly compatible with non-conventional liquids such as viscous, semi crystalline or precipitate solutions found in chemical applications or polymers studies.

We have therefore developed a new autosampler offering a wide range of applications, able to load and dispense homogeneous and diluted liquid samples and non-homogenous solutions with untypical physical and chemical properties as well (very concentrated solutions, viscous, partially precipitate or crystalline…), without any dilution effect (Figure 1 Right).

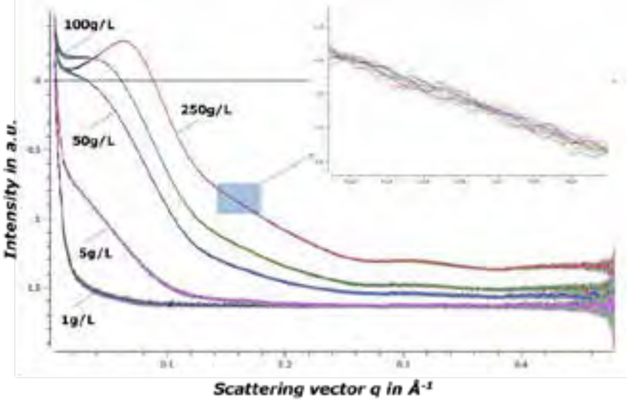

Figure 1
Left : Picture of the pipetting autosampler
Right **:** Series of SAXS collections performed with a set of concentrated solutions of BSA (1, 5, 50, 100 and 250g/l). The SAXS curves obtained for each concentration (picture on the right) show the perfect stability of the measurement (zoomed area) and demonstrate the ability of the autosampler to work with high concentrated solutions.

The autosampler has three motorized axes to position precisely the needle above the sample, and a set of syringe pumps in combination with suitable millifluidic tubing to pipet and precisely transfer the liquid sample to the measurement cell (Figure 1 Left). The autosampler can be also used to prepare a concentration series or perform pre-mixing. The autosampler electronics is based on a programmable PIC microcontroller and the RS232 protocol is used for the steering. The first prototype installed on beamline SWING is fully compatible with the HPLC SEC-SAXS chain, being controlled from the same user interface.

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LATEST DEVELOPMENTS IN LABORATORY SAXS/WAXS SYSTEMS: TOWARDS BROAD, LARGER LENGTH SCALES AND DYNAMIC STUDIES

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Nanostructured materials hold major expectations but understanding their properties requires investigation of a large number of compositions or process combinations necessitating characterization requirements over broad length scales. SAXS technique is a powerful characterization method for such materials developments because of the length scale of analysis between 1nm and 200 nm, as now achieved in the laboratory, together with the capability to investigate the crystalline structure when coupled to WAXS measurements.

Major developments achieved the past years in components and sub-assemblies have extended considerably the measurement capabilities for routine measurements with lower scattering wave vector resolution in SAXS (q_{min}) or for screening of material processing parameters during in-situ analysis. State of the art measurement configurations imply the use of high brilliance microfocus X-ray beam delivery systems coupled to scatterless collimation [1] associated to hybrid pixel photon counting detectors. We will present the latest developments in X-ray components such as new scatterless slits and innovative sample holders reducing the level of background camera to extremely low levels thus improving measurement efficiency for highly diluted samples as it will be demonstrated.

Improved measuring capabilities for in-situ characterization will also be discussed through different examples such as thermal behavior study of block copolymers or semi-crystalline polymers. As it will be emphasized, advanced measuring configurations enable now simultaneous SAXS/WAXS measurements with time resolution in the order of a minute or less, using a 2D divergence controlled X-ray beam thus compatible with anisotropic studies.

A modular SAXS/WAXS system like the Xeuss 2.0 provides the additional capability to extend the range of measurements to high Z materials or absorbing samples holders using motorized dual source holder achieving change of source configuration with automatic realignment for example switching from standard copper radiation to higher penetrating radiation. We will the review the advantage of such versatile design through different application examples emphasizing interest of higher penetration radiation including during in-situ studies.

High brightness, ultra-low divergence beam coupled to increased sample to detector distance now enables to extend the probe length to few hundred of nanometers in the UltraSAXS regime such achieving a unique q range of detection close to 4 orders of magnitude with the same instrument. Capability to perform 2D USAXS measurements such as during thin film Grazing incidence characterization [2] and in-situ stretching characterization will be discussed as examples [3].

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SMALL-ANGLE NEUTRON SCATTERING AT ISIS

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Small-Angle Neutron Scattering (SANS) is a powerful technique for determining microstructure in the range of tens to thousands of Angstroms. SANS on a pulsed source has the significant advantage of a wide simultaneous Q range which is ideal when studying systems containing a broad range of lengthscales. At ISIS there are currently two operational SANS beamlines, Loq and Sans2d, one in a commissioning phase, Larmor [1], and one under construction, Zoom [2].

Loq is positioned on the first target station and has demonstrated the power of the technique at a pulsed source [3]. Building on the success of this beamline, Sans2d was designed and built on the cold neutron optimized second target station, TS-2 [4]. The added flexibility and improved optics of this beamline coupled with the lower rep rate of TS-2 has allowed Sans2d to achieve a uniquely wide simultaneous Q range with increased flux and improved signal to noise when compared to Loq.

Both Larmor and Zoom are positioned on TS-2 and will initially be conventional SANS beamlines with the option of a polarized incident beam. Larmor will additionally offer Spin-Echo SANS (SESANS) as part of an on-going collaboration with TU-Delft, the Netherlands. The second stage of construction for these beamlines will bring further Larmor labelling techniques on Larmor, whilst for Zoom the installation of neutron focusing devices will allow access to smaller Q (~ 0.0003 $Å^{-1}$).

Current science highlights from the existing ISIS SANS beamlines will be displayed here alongside the progress of future beamlines and a taste of the new science to come.

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RECENT DETECTOR UPGRADE OF HIGH-RESOLUTION SANS INSTRUMENT MAUD

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Small-angle neutron scattering instrument is in operation at Czech 10 MW research reactor LVR-15 since year 1983 [1]. This diffractometer is based on two perfect silicon crystals fully asymmetric diffraction geometry with reflecting planes (111) (see Fig. 1). Special mechanism enabling elastic bending of the monochromator and analyzer perfect and due to this horizontal Q_x resolution can be set in range of $10^{-4}\div10^{-3}$ Å^{-1}. Thus SANS data can be measured in 2-3 steps covering total Q-range from about $2\cdot10^{-4}$ to $2\cdot10^{-2}$ Å^{-1}. Monochromatic neutron beam of 2.09 Å wavelength has flux at sample position from $5\cdot10^{3}$ $n\cdot s^{-1}\cdot cm^{-2}$ at high resolution up to $4\cdot10^{4}$ $n\cdot s^{-1}\cdot cm^{-2}$ at low resolution. Maximum samples size is limitted by analyzer crystal cross-section to 4x25mm^2.

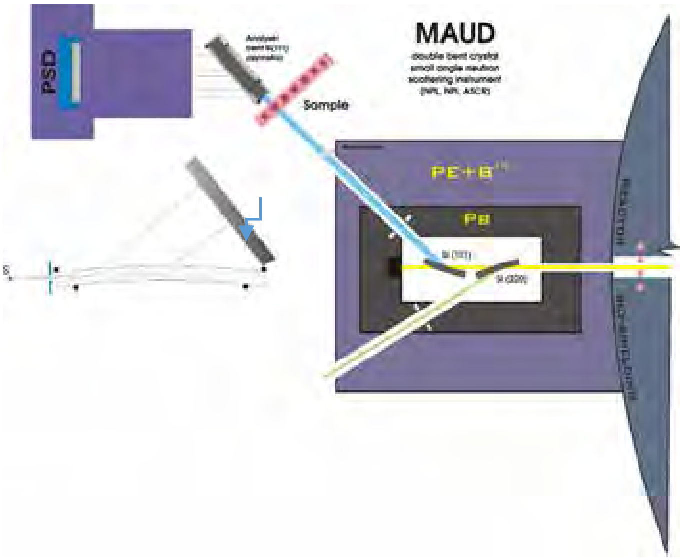

Figure 1: Layout of double-bent-crystals SANS instrument MAUD.

Samples can be mounted in sample changer for 9 samples with step of 12 mm which correspond to standard quartz cells. There are several devices for special sample environments compatible with MAUD facility – high temperature vacuum furnace (T: 400^0 C ÷ 1400^0 C), sample holder with temperature control from 20^0 C up to 200^0 C, deformation rig with maximum loading up to 20 kN and electrical magnet with maximum magnetic field up to 2 T [2].

Recently MAUD has been upgraded with new He^3 position sensitive detector (PSD) [3] with several times higher signal-to-signal ratio. It enables investigation of samples with low scattering cross section. SANS experiments at MAUD are controlled by software Remesys, which allows making very flexible scripts for user. The special software library was developed for effective connection of experiment control software with software at detector Delidaq [3].

MAUD instrument successfully participate in user program of Neutron Physics Laboratory providing major beam time for external experimentalists with NMI3 and CANAM support [4].

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USANS AS OPTION FOR SANS INSTRUMENTS: THE UPGRADE OF D11@ILL AND AN OUTLOOK FOR LOKI@ESS

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The small-angle neutron-scattering (SANS) instrument D11 at the Institut Laue-Langevin (ILL), Grenoble, is one of the first instruments being built and in operation at ILL since 1972 [1]. It is used in various fields of science like soft matter, biology and condensed matter physics. SANS is a workhorse characterization tool, and USANS is the ideal tool to extend its capabilities. Whilst USANS probes similar length scales [≈0.01 – 20 µm] to those accessible by microscopy, it additionally offers all the advantages of neutron scattering techniques, such as probing turbid samples, elucidating one component of a complex structure by contrast variation, statistical averaging of sample structure, deep penetration depth into samples and magnetic sensitivity.

The basis of our approach is the SAMBA principle proposed by Roland Gähler in 2002 (**S**mall **A**ngle **M**ulti **B**eam **A**nalysis) [2, 3]. In the original paper of Gähler et al. [2] this approach is called MSANS (with M standing for Multi hole). This technique is ideally suited as an upgrade of a classical SANS instrument, as it uses its existing components. The only USANS-specific requirement is the addition of a high resolution detector. Therefore a CCD-based detection unit comprising two CCD cameras has been recently purchased for D11, together with a scintillator made of ^{6}LiF and ZnS. The detection unit incorporates optics and mirrors to avoid the cameras being exposed to the direct neutron beam.

The principle may be used on continuous beam as well as time-of-flight instruments. The fundamental idea is to multiplex the scattering experiment in order to achieve a gain in intensity over an equivalent single pinhole geometry. The accessible Q-range can be extended to at least 10^{-5} 1/Å without a loss in intensity.

This contribution will present first results of the upgrade project of D11@ILL with an additional high-resolution detector to allow for USANS experiments utilizing the principle described above. Furthermore, it will present first simulation results on a possible implementation of such an USANS option on the time-of-flight SANS instrument, LoKI, which will be constructed at the European Spallation Source. This is part of the project OPUS (**OP**tion **US**ans), which is financed as in-kind contribution to the ESS by the Italian government.

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FOLLOWING LITHIATION PROCESSES IN LITHIUM ION BATTERIES WITH IN-OPERANDO SMALL-ANGLE NEUTRON SCATTERING (SANS)

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Small-angle scattering is a commonly used method to gain information about the nanostructure of the investigated materials (i.e. size, volume and shape of particles). SANS is well suited for studying any changes of these parameters inside closed battery cells under operation. Up to now only a few publications exist dealing with the SANS method for batteries and battery materials. This is mainly caused by the fact that only new developed batteries provide a reasonable thickness for transmission measurements necessary for the applied method.

In 2012 Bridges et al. used a Li||Graphite coin cell for an in-situ SANS experiment, observing the growth of the anodic SEI-layer [1]. Nagao et al. used the method to investigate the Li-intercalation mechanism in carbon host materials [2].

However, one major drawback in these experiments is that only cells with Li-metal as counter electrode were used.

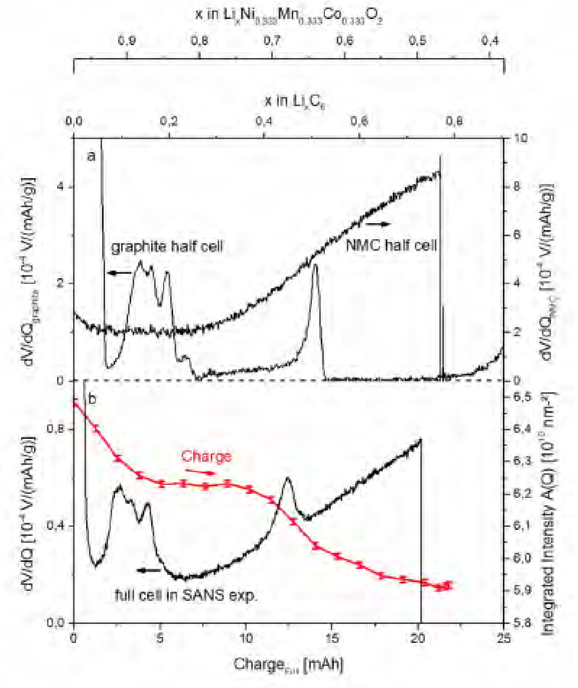

Figure 1: Integrated total scattering intensity vs. transferred charge calculated as x(Li) and dV/dQ plot of the Voltage vs. transferred charge.

In our approach we assembled experimental cells consisting of the same anode and cathode materials as used in commercial cells and perform in-situ SANS experiment during charging/discharging. The cells are assembled as pouch bag or coffee bag cells.

We report on our measurements with the SANS-1 instrument at Heinz Maier-Leibnitz Zentrum (MLZ), Garching. In-operando small-angle neutron scattering data of NMC||Separator||Graphite cells was collected during a complete charging and discharging cycle. In addition single battery components were measured separately to distinguish the various component signals. The in-operando data shows a variation of the integrated total scattering intensity in dependence of the transferred charge. The curve features are directly associated with the lithiation process of the cathode or anode materials.

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CURRENT STATUS OF BIOSAXS EXPERIMENT AT THE PHOTON FACTORY

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The Japanese synchrotron facility, Photon Factory has three SAXS beamlines, BL-6A, BL-10C and BL-15A now. BL-6A and BL-10C have been used for over 30 years, but these beamlines were remarkably upgraded in 2014. The new detector, PILATUS3 1M (Dectris) was installed in BL-6A. Users can change the camera length semi-automatically since the experimental stage was replaced to new one. BL-10C was scrapped and rebuilt in March of 2014. All the optical and experimental components were replaced to new ones. Although the measurement energy had been fixed in BL-10C because of the problem of the monochromator, the installation of new fixed-exit double-crystal monochromator enabled change of the energy from 6 to 14 keV. PILATUS3 2M and 200K (Dectris) were also newly installed for the SAXS and WAXD detector, respectively. BL-15A was newly constructed in the 2013 fiscal year, and opened to the user from 2014 November. The details of BL-15A will be presented by another presentation in this conference.

The experimental apparatus and system for the BioSAXS are improving at the photon factory. We develop and install a solution sample changer (Figure 1) and are constructing the automatic pipeline analysis system for the high-throughput measurement. The software for the pipeline analysis is newly developed. This software, *SAngler* can manage the PILATUS and R-AXIS (Rigaku) images, and perform the making of a mask file, the calibration of camera distance and beam center, the circular average and the subtraction of the background. We are adding several function for analysis of BioSAXS, for example, Guinier, Kratky analysis now. *SAngler* can be used for not only the manual analytic operation through GUI but the automatic analysis through the batch mode.

Figure 1: Solution Sample Changer.

We are also constructing the SEC-SAXS/SEC-MALS-SAXS system (Figure 2) for both the improvement of monodispersity of a sample and more precise molecular weight estimation of a protein complex. HPLC (Alliance e2695, Waters) and MALS (DAWN HELEOS II, Wyatt Technology) were installed, and we are performing the commissioning of these system to suggest the effective measurement condition to users now.

Figure 2: SEC-MALS-SAXS system.

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MODULATED BEAM SAS WITH IMAGE RESOLUTION

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The potential of SAS studies utilizing a spatially modulated beam instead of conventional pinhole collimation has been proposed and demonstrated in very different forms. While from the side of neutron scattering beam modulation through multiple pinholes and spin-echo was suggested and applied [1], in x-ray and neutron imaging phase grating set-ups producing corresponding interference patterns have been employed [2]. In the latter case such were used for qualitative imaging of SAS characteristics of samples, while in the earlier the potential of conventional SAS results was in the focus, through polarization analyses and deconvolution. A deconvolution approach was also proposed for grating interferometric imaging with x-rays, however, could not prove to provide quantitative SAS results.

In this work it is demonstrated, that measuring the relative visibility V of modulation in such SAS or imaging experiments is fully equivalent with Spin-echo SANS measuring the relative polarization. Hence the variation of the autocorrelation length of such set-ups defined by $\xi_{GI} = \frac{\lambda L_s}{\mathrm{p}}$ and dependent on the wavelength λ, the sample to detector distance L_s and the period p of the modulation, provides direct measurements of the real space correlation function of the scattering structures [3].

The application of this theory to imaging data measured with grating interferometers proofs that structural parameters can be determined quantitatively this way and hence SESANS theory can be exploited for spatially modulated beam measurements providing spatially resolved quantitative SAS (Fig. 1).

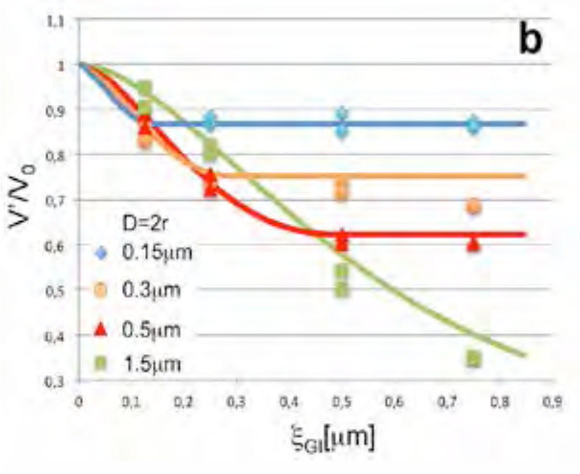

Figure 1 Relative visibility versus autocorrelation length for dispersions of spheric particles with different diameters. Extracted from dark-field imaging experiments utilizing grating interferometers reported in [4] and quantified through the presented theoretical approach [3]. Accordingly the signal represents the real space correlation function and saturates at the value of the structure size.

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A SAXS/WAXS LABORATORY INSTRUMENT FOR NANOMATERIALS

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We present here a custom-made state-of-the-art SAXS/WAXS laboratory instrument (see Figure 1) based on Mo X-ray generator. Its design has been thought and optimized to thoroughly investigate nanostructured material.

Compared to classic samples characterized by SAXS, nanomaterials have inherent physical properties (concentration and composition of samples), which make the use of the Cu-K (8 keV) radiation problematic. To circumvent these difficulties harder X-rays can be used.

The X-ray generator is a molybdenum (17 keV) rotating anode. A combination of a multilayer collimating mirror and a patented hybrid slits [1] gives us a very sharp and high purity beam for a laboratory setup, with a size of 1x1 mm^2 and a flux of 10^9 photons/s.

The motorized sample holder can load 20 capillaries, a temperature controlled system or a circulation environment system for kinetic studies.

A vacuum chamber is placed behind whose output window diameter is designed for the 2D image plate Mar345 detector. The accessible q-range is qmin = 0.03 $Å^{-1}$ to qmax = 3 $Å^{-1}$.

Combining molybdenum energy and the state-of-art experimental setup provide us with a very powerful tool for nanomaterial studies [2][3].

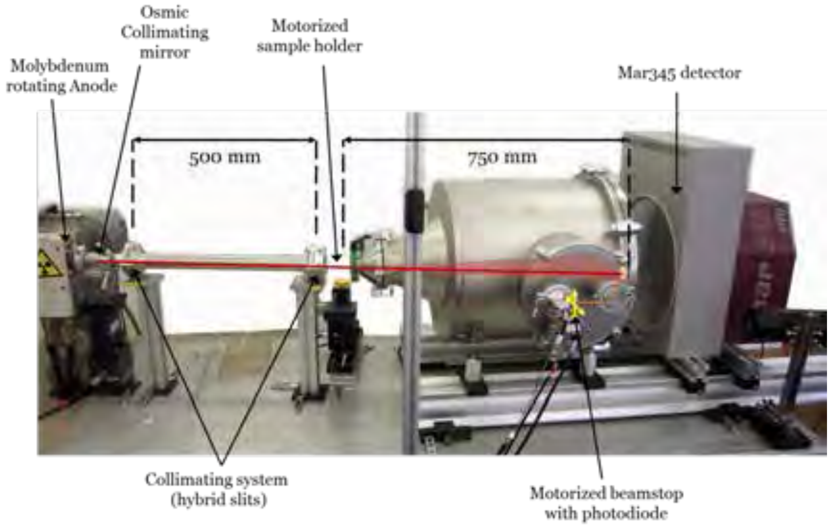

Figure 1 : view of the saxs-waxs setup

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PUSHING THE LIMITS OF SAXS HOME LAB INSTRUMENTATION

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The attractiveness of synchrotron sources is, among other reasons, the extremely high brilliance provided. Traditional lab X-ray sources in this respect are limited by the melting of their solid target. By using liquid metal jet targets (e.g. Gallium alloy) instead of fast spinning solid metal targets much higher power loads can be achieved. In addition, this new technology enables focal spot sizes below 20 micron. The resulting brilliance is comparable to bending magnet sources.

Converting this high source brilliance into highest flux-density at the sample requires dedicated multilayer optics. Further combination with latest beam collimation technologies and state-of-the-art 2D detectors substantially extend the capabilities of SAXS home lab systems for measuring weakly scattering samples, or with very high spatial resolution.

This presentation will discuss the technical advances made, and demonstrate the capabilities of modern SAXS home lab instrumentation.

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New polarimeter for vector analysis of neutron polarization. Application for Small Angle Neutron Scattering.

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There are a number of new objects, such as molecular magnets, new superconductors, spin electronic devices and magnetic nanostructures (e.g. nanoparticles and ferrofluids), which are of great importance because of their exciting possible industrial applications. Detailed understanding of their physical properties, mechanisms involved in their formation (e.g. the self-organization of magnetic nanostructures) and their operation requires the full information about their magnetic properties. For instance, the structural information about magnetic nanoparticles can be obtained by means of SANS. Being joined with 3-D polarization analysis it provides exceptional possibilities for determination of the magnitude and the spatial direction of the magnetization vector inside a magnetic structure.

For this purpose we designed a new polarimeter using mu-metal shielding for the screening of the sample area from external magnetic fields. It is based upon the polarimeter labeled LAP-ND [A. Ioffe et.al., Physica B, 350 (2004) 815], however has the larger size (600×400×400 mm^3) of the zero-field sample chamber. The size of the shielding allows us to host compact magnetic sample environment when avoiding the magnetization of mu-metal thus keeping it able to serve as magnetic shielding from external magnetic fields.

BUILDING AND OPTIMIZING A SAXS INSTRUMENT FROM THE BASICS – LESSONS LEARNED

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Apart from the numerous excellent synchrotron beamlines for small-angle X-ray scattering, which provide cutting-edge experimental possibilities, smaller, more localized laboratory-scale instruments also have the reason for existence. Although the number and the range of measurable specimens are limited (because of a photon flux lower by several orders of magnitude), these are also capable of providing high quality data, or at least can yield valuable results, which may support a subsequent measurement at a larger facility. The optimization of the scattering geometry, i.e. obtaining the highest flux with the highest resolution (lowest value of $q=4\pi\sin\theta/\lambda$, 2θ being the scattering angle and λ the X-ray wavelength) while keeping the background scattering at minimum is of crucial importance.

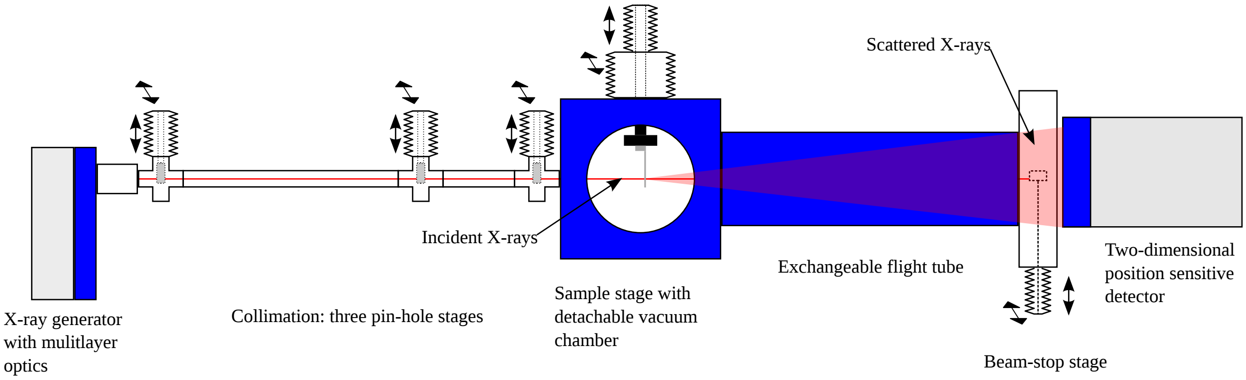

Figure 1: The schematic layout of CREDO. More details of the instrument can be found at http://credo.ttk.mta.hu

This work describes some key points in the design and assessment of a SAXS camera with high flux, high resolution and low background. As a proof of concept the recently constructed CREDO instrument is presented (cf. Figure 1.) [1]. This apparatus – laid out in the conventional transmission point-collimated geometry – was built from the grounds up. Apart from the X-ray source (GeniX3D Cu ULD from Xenocs SA, France) and the detector (Pilatus-300k, Dectris Ltd, Switzerland), all parts have been designed and fabricated in-house. It features a three-pinhole scheme for collimation, and a variable sample-to-detector distance. The fine alignment of the instrument is done by ten stepper motors. To aid the casual guest researcher, an intuitive graphical user interface has been implemented by which common tasks of optimization, measurement preparation and automatic data collection, storage, reduction and evaluation.

In contrast to most commercial SAXS instruments, CREDO has an adjustable collimation geometry: both the apertures and their spacings along the instrument axis are variable in discrete steps. Thus the compromise between intensity and resolution can – and has to – be made for each measurement problem. By this design the inlying possibilities can be fully exploited [2].

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SIMULTANEOUS OVERLAPPING SMALL, MEDIUM, AND WIDE ANGLE SCATTERING DATA COLLECTION ON DND-CAT'S NEW TRIPLE AREA DETECTOR SYSTEM

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A new triple area-detector system is now in regular use at the 5ID-D station of DuPont-Northwestern-Dow Collaborative Access Team (DND-CAT) Synchrotron Research Center at Sector 5 of the Advanced Photon Source. DND-CAT users conduct a wide variety of nano-scale, polymer, and biological materials research.

The detectors were designed by © Rayonix L.L.C. in conjunction with DND-CAT, to maximize the momentum transfer vector coverage, as well as radial coverage for oriented samples. They are high speed, frame transfer, CCD detectors with 44.3 micron pixels. Additionally they are able to collect at 100 frames per sec in higher binning modes.

The wide and medium angle detectors have a 170 x 85 mm active face with a conical groove intersecting a long edge and normal to the phosphor. Matching vacuum chambers and Kapton® exit windows were designed to match the shape of the detectors in order to minimize blind areas of the sample scattering cone.

While the detectors are in air for easy maintenance, the sample scattering and transmitted beam traverse an evacuated chamber expediting incorporation of windowless sample environments. Among these is a thermal capillary flow-cell with Teflon® and Kalrez® seals ideal for solution scattering in water or organic solvents.

This system has a q-range of over three decades overlapping between subsequent detectors, with high speed capability and small pixel size. Thus this system is ideal for collecting data on hierarchal macromolecules and nano-assemblies evolving over multiple length scales in solution as well as solid samples.

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A LAB-SCALE SAXS/WAXS EQUIPMENT FOR NANOSTRUCTURAL STUDIES OF NANOPARTICLES IN THE ELECTRICAL DISCHARGE SYNTHESIS PROCESS

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Nanostructured materials are of great importance in a broad range of scientific and industrial applications. Fast non-invasive structural analysis helps to better understand the relation between nanostructured materials and their functionalities, and thus to design and produce nanostructured materials with improved properties.

In this work a physical nanoparticle synthesis process based on an electrical discharge from solid elements in the inert gas [1], which requires no chemical precursors and produces no chemical byproducts or wastes due to avoidance of liquids as compared to other nanoparticle synthesis methods, has been used for generating nanostructured particles. The optimal single unit (OSU) contains two electrodes placed with a certain distance apart inside a chamber. The plasma formed between two electrodes during the electrical discharge will heat the electrode surface rapidly. The melt and vaporized electrode material is mixed with the carrier gas and condensed to form small metallic clusters and primary particles. With the continuous transport in the carrier gas flow, nanostructured particles and agglomerates are formed from the primary particles. The aerosol particles exiting from the OSU can be collected onto different substrates, e.g. TEM grid, PTFE filter, textile or adhesive tape, for further nanostructural studies using TEM and a lab-scale small- and wide-angle X-ray scattering (SAXS/WAXS) equipment [2-3].

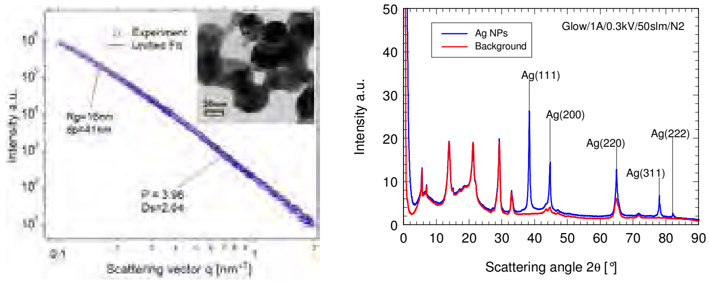

Figure 1: Results of Ag NPs. Left: SAXS and TEM; right: WAXS.

Analysis of the SAXS/WAXS signals detected within a scattering angle up to 90° allows extracting the structural information on the studied particles at different structural levels simultaneously, such as primary particle size, surface morphology, crystalline structure, and mass fractal dimension of the aggregates. The OSU enables the generation of different kinds of nanoparticles by changing the electrode materials. Figure 1 shows exemplarily the simultaneous SAXS/WAXS results of the silver nanoparticles produced by glow discharge (Ag NPs, I=1A, Q=50slm, N_2). Besides, the potential scaling-up by the use of multiple units in parallel can increase the production rate. To systematically study the structural properties of the nanoparticles in the electrical discharge synthesis process using SAXS/WAXS, different kinds of metal electrodes have been used to generate nanostructured particles under different synthesis process conditions. The obtained results are used for optimization of the synthesis process.

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DETERMINATION OF ABSOLUTE SCATTERING INTENSITIES USING A LAB-SCALE SAXS CAMERA

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In our previous work, we have developed a small angle X-ray scattering (SAXS) instrument, which is equipped with a focusing Goebel mirror and a 2D imaging plate detector. In recent years, the SAXS camera was successfully used for the characterization of various systems, e.g. inorganic nanoparticles in form of dispersion and powders. Among others, parameters determined by the SAXS device were the particle size distribution [1], the fractal dimension of particle aggregates [2, 3], the thickness of a diffuse boundary of metal nanoparticles [4] and the shell thickness of silica-coated magnetite nanocomposites [5]. It is of advantage that the calculation of all these parameters does not require absolute scattering intensities. However, measuring scattering intensities in absolute units becomes important if information on the particle mass density or the particle number concentration is of interest.

Thus, the goal of this work was to calibrate the present SAXS instrument to absolute units. The calibration procedure was based on the analysis of pure solvents which can be used to relate the measured intensity to absolute units by means of a calibration factor (CF). Figure 1a shows exemplary SAXS curves of the capillary with and without the solvent (water) and the curve obtained after the background subtraction, which was used to calculate the CF. After the calibration procedure, SiO_2 dispersions of known particle size distributions and particle volume fractions were analyzed in order to validate the CF obtained from pure solvents. Afterwards, the synthesis of SiO_2 nanoparticles was conducted and the absolute scattering intensity was measured for various reaction times t_r. Figure 1b shows the time-evolution of the resulting parameters, the radius of gyration R_g, the exponent P (related to the fractal dimension) and the particle number concentration N/V. Using these parameters, conclusions about the particle formation and growth mechanisms were made and will be presented in this contribution.

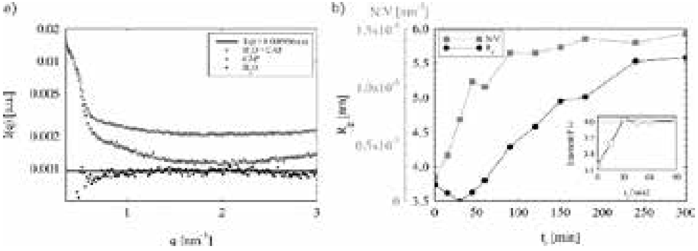

Figure 1: a) Scattering intensity of the capillary with and without the calibration solvent (water) and the background-corrected intensity as a function of the scattering vector modulus q and b) radius of gyration $R_{g,2}$ and the particle number density of Stöber SiO_2 particles at different reaction times t_r

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↘ Flash Talk: Mon-F-L1

NANOPARTICLE CHARACTERIZATION BY CONTINUOUS CONTRAST VARIATION IN SAXS WITH A SOLVENT DENSITY GRADIENT

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Many low-density nanoparticles show a radial inner structure [1] which is often ignored though it can limit their utilization in real-world applications. This work proposes a novel approach to contrast variation with SAXS based on the constitution of a solvent density gradient in a glass capillary in order to resolve this internal morphology. Scattering curves of various polymeric colloids were continuously recorded at different solvent contrasts at the four-crystal monochromator beamline of PTB at the synchrotron radiation facility BESSY II [2]. The mean size and size distribution of the particles as well as an estimation of the colloid density were determined using a variety of evaluation techniques in the Fourier region of the scattering curves and by examining the Guinier region in detail. These results were successfully compared with techniques such as Differential Centrifugal Sedimentation (DCS) and corroborated with a model fit to the experimental data, which provided complementary information about the inner electron density distribution of the suspended nanoparticles.

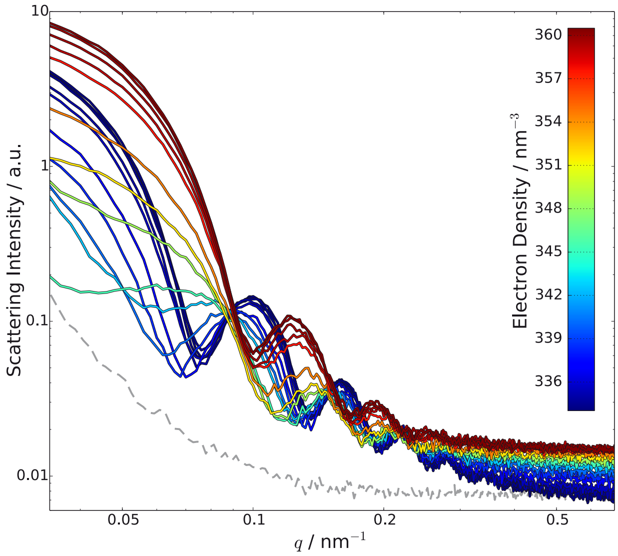

Figure 1: Scattering curves of carboxylated polymeric nanoparticles at different solvent densities obtained with an aqueous sucrose density gradient. Typical contrast variation features such as the isoscattering points can be observed.

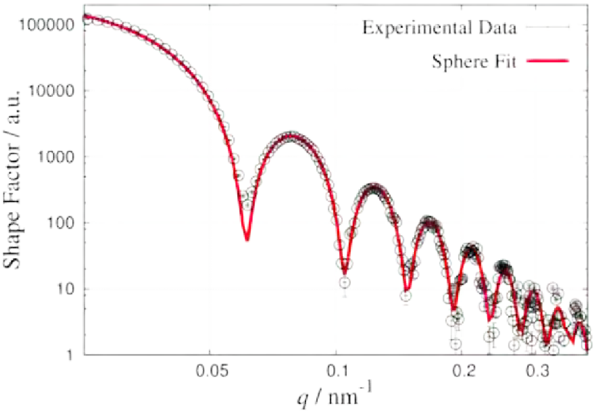

Figure 2: Shape factor of polystyrene beads calculated from 40 scattering curves measured at different suspending medium electron densities. By fitting a simple form factor to the data, the size distribution can be obtained independently of the inner structure.

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HIGHLY ORDERED SBA-15 POWDER WITH TUNABLE BRAGG PEAK POSITION AS SMALL-ANGLE CALIBRATION STANDARD FOR SAXS AND SANS

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The precise determination of the scattering vector, q, is essential for successful small-angle scattering experiments. In experimental set ups with flexible sample position and variable instrument geometry a frequent q-calibration is necessary. The first Bragg reflections of Silver behenate (AgBeh) powder (d_{001} = 5.838 nm)[1,2], which can be found in the small angle range, are widely used for a fast and precise calibration of the scattering vector. Unfortunately, AgBeh causes a few drawbacks in the accessible scattering vector range and radiative and thermal stability. This can be fixed by using SBA-15 complementary to AgBeh as q-calibration standard.

The first Bragg peak of AgBeh appears at a q-value of 1.076 nm^{-1}. This limits the priorly described scattering vector calibration to scattering experiments which cover the scattering range of 1 nm^{-1}. For experiments using exclusively a very low scattering vector range (USAXS, USANS or SAXS in the Tender X-ray range) a complementary q-calibration standard with Bragg peak positions below 1 nm^{-1} is necessary.

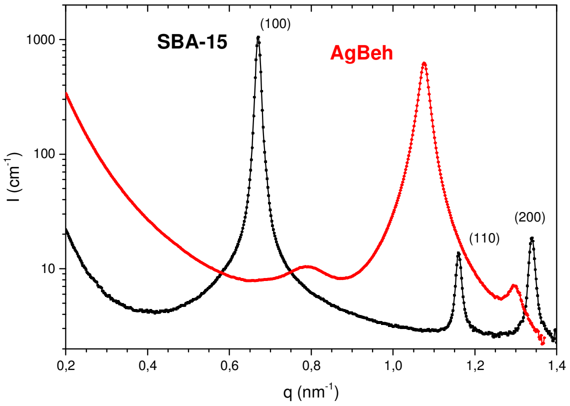

Figure: SAXS measurements of SBA-15 and AgBeh. The Scattering vector is calibrated by a linear regression procedure and normalized against glassy carbon.

SBA-15 as an alternative calibration standard can be synthesized with tunable reflex position from about 0.60 nm^{-1} to 1.2 nm^{-1}. This material is synthesized by a template process and consists of (amorphous) SiO_2. It exhibits negligible radiative damage and the inner structure of SBA-15 is thermally stable up to 600 °C. Furthermore, the peak width is lower by a factor of 2 (Fig. left) and can be described by a Voigt profile.

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↘ Flash Talk: Mon-F-L1

GRAZING INCIDENCE SMALL ANGLE X-RAY SCATTERING FOR DETERMING NANOSCALE DEVICE STRUCTURE

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The scale of semiconductor device is continuously shrinking and line width of the device pattern is already close to ten-nanometers. The current dimension metrology tools are facing difficult challenges to measure such small critical dimensions (CD). For example, the electron beam size of scanning electron microscope (CD-SEM) is comparable with that of the object size itself. The sensitivity of optical proves is very low because the wavelength of the light is much larger than the observed CD. In addition, uniformity of the CD, for example line width roughness (LWR), becomes more crucial for the device performances and the dimension metrology has to have sensitivity for detecting such non-uniformity of the CD. Small angle x-ray scattering (SAXS) is one of a candidate having such capabilities for measuring CD and its non-uniformity. Jones *et al*. demonstrated SAXS measurements with transmission geometry [1]. It is suited for measuring relatively small area, if x-ray brightness of the facility is strong enough (e.g. synchrotron source). However, it is necessary to rotate the sample with certain degrees in order to collect information of depth (height) of the surface structures. On the other hand, grazing incidence (GI) SAXS is sensitive to the surface nanostructures and capable to measure cross sectional profile (depth and width) of the surface structure without such kind of sample movement.

We have developed GISAXS measuring instrument with laboratory source and also developed analysis software, which can solve the cross sectional profile of the surface periodic device structures. We can provide the average value of structural parameters of the periodic grating and dot (hole) patterns, such as pitch of the period, width, height, sidewall angle, rounding of edges, and their fluctuations. We have applied for various kinds of surface periodic nanostructures, e.g., surface one-dimensional grating and two-dimensional dot (hole) pattern samples. X-rays are irradiated on the sample surface with shallow incident glancing angle and scattered x-rays are collected by a two-dimensional pixel-type area detector. A clear two-dimensional scattering pattern, which reflects cross-sectional profile of the surface structure have been detected. The observed scattering pattern is periodic along the horizontal Q_Y direction (parallel to the surface), which is corresponding to the period of surface pattern. In the vertical Q_Z direction (perpendicular the surface), scattering intensity shows modulation corresponding to the depth (height) of the structure. In order to solve the cross sectional profile, we have assumed a certain model for each structure and optimized parameters of those models with minimizing the difference between experimental and calculated data. In our calculation, distorted wave Born approximation is employed to correct reflection and refraction of x-rays at the surface and interface of the structure. The obtained results are compared with cross-sectional SEM and TEM, and fairly good agreements are ensured. The typical examples of our results will be shown in the presented paper.

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↘ Flash Talk: Mon-F-L1

MEASURING NANOSTRUCTURES WITHOUT BREAKING THEM: GISAXS FOR NANOMETROLOGY

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For applications such as quality control of nanostructured surfaces, GISAXS has considerable advantages compared to established techniques such as scanning electron microscopy (SEM). The main advantages are nondestructive and fast measurements and statistical information on a comparatively large sample region. However, analysis of GISAXS measurements and extraction of relevant sample parameters remains challenging. In this talk we present GISAXS measurements of line gratings fabricated by electron beam lithography and etched on a silicon substrate. We compare the results to simulation and complementary methods.

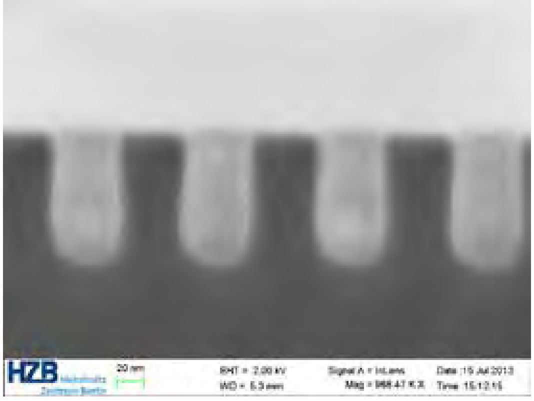

Figure 1: Scanning electron microscopy measurement of a silicon grating cut. Edge and trench rounding are clearly visible.

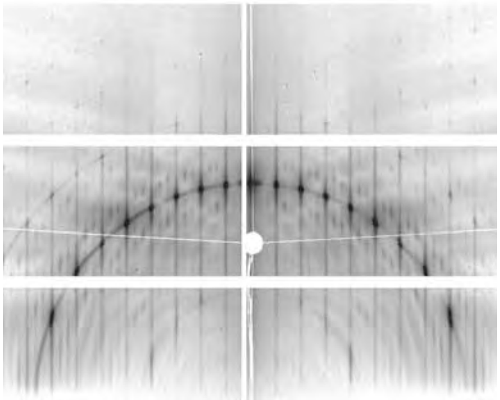

Figure 2: GISAXS measurement of a silicon grating. In addition to the main semicircle pattern, superstructures and diffuse features appear.

In addition to Fourier-based direct methods [1], simulation using finite-element methods (FEM) [2] and distorted wave born approximation (DWBA) is used to analyse the GISAXS measurements and assess parameters such as top and bottom edge rounding, which are not available to most direct non-destructive methods like atomic force microscopy.

GISAXS measurements of large-area (1 mm × 15 mm) gratings are compared to measurements of micrometre-sized patches of gratings, comprised of less than 100 grating lines. Due to the high dynamic range of the used PILATUS photon-counting detector, the weak scattering from grating patches as small as 4.5 µm × 4.5 µm is detectable, although the x-rays illuminate approximately a 0.5 mm × 10 mm region on the sample. As seen for partly disordered gratings by Rueda et al. [3], the GISAXS images change dramatically if the effective length of the grating lines is reduced.

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A NEW NIST REFERENCE MATERIAL FOR SAXS INTENSITY CALIBRATION BASED ON GLASSY CARBON

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Absolute intensity calibration of small-angle scattering data is essential for determining absolute volume fractions, number densities, or surface areas of the scattering features within a sample. As a result, most SAXS and SANS facilities, and lab-based SAXS instruments, have developed methods for absolute intensity calibration. Intensity calibration methods include secondary standard scattering samples (e.g., silica particle Guinier scattering standards with known particle size and concentration), primary scattering samples (e.g., vanadium especially for SANS), geometrical primary calibration using calibrated attenuators to protect the 2D detector, etc. A major challenge in recent years has been to ensure that an absolute intensity calibration, expressed in terms of the absolute differential small-angle scattering cross-section, obtained using one instrument, is reproduced elsewhere using a different instrument. Various round-robin studies have been conducted in connection with proposed standard calibration samples, and glassy carbon has emerged as a desirable intensity calibration material [1].

Glassy carbons are formed by the pyrolysis of a wide variety of polymers. The final glassy carbon morphology and density depend on the chemical composition and morphology of the starting polymer, and the details of the heat treatment. Several glassy carbon treatments give rise to significant small-angle scattering intensity over a suitable *q*-range for SAXS or SANS, and samples are stable over extended time under ambient conditions, at least for SAXS [2].

The new NIST reference material for SAXS intensity calibration is based on an inventory of identical, glassy carbon specimens, from which a carefully selected statistical sub-set have been calibrated for SAXS intensity by a primary calibration method using several different X-ray energies at the USAXS instrument of the Advanced Photon Source, Argonne National Lab., IL, USA [3]. Desmeared USAXS data were compared for consistency with pinhole SAXS data, and were validated using SANS (and the known ratio of contrast factors for SAXS and SANS). Uncertainties for each component were separately estimated, and a calibration curve with 95 % confidence uncertainty bands is shown in Figure 1. Although validated in part using SANS, this intensity calibration standard is aimed primarily at SAXS. Issues to address in possible future certification of the standard for SANS are currently being considered. The new intensity calibration standard [4] should support the validity of SAXS results derived from multiple facilities.

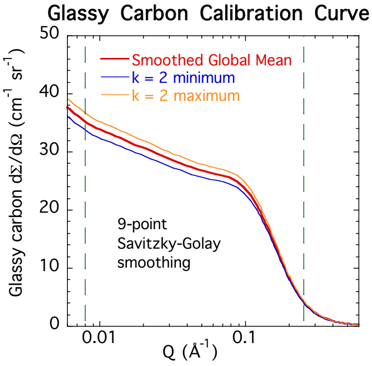

Figure 1: Glassy carbon SAXS intensity calibration curve.

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↘ Flash Talk: Wed-F-A1

SIMULATION AND MODELING OF SCATTERING PATTERNS FOR NANOSCALED SYSTEMS

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Scattering techniques are a powerful tool that can be used to investigate dilute and concentrated systems, retrieving valuable information about size, shape and particle organization. If the system is composed by particles with simple shapes, like spheroids, prisms or cylinders, there are set of analytic or semi-analytical expressions that can be used to describe the scattering data. However, for particles with more complex shapes or geometries, or if the systems are spatially correlated or orientated, the analytic and numerical methods are more restricted.

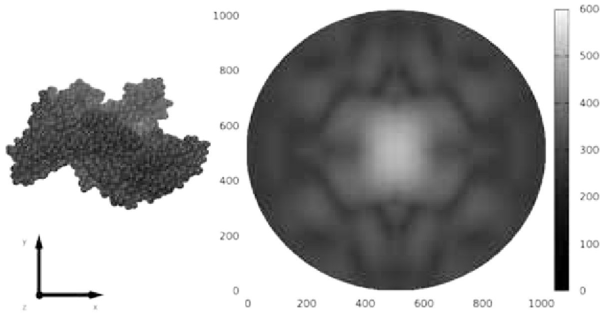

Figure 1: (left) Model of bovine serum albumin (BSA - chain A) - pdb id: 3V03[2]. (right) Scattering pattern of BSA, oriented according to the model at left.

In this work, we present advanced methods to perform simulation, modelling and data analyses of SAS data by using the finite element approach coupled with fast implementations of the Debye equation It will be presented results for the modelling of different systems and the simulation of scattering intensities both for particles oriented or randomly oriented in space. Several examples of the calculations will be shown, demonstrating the method and its applicability.[1].

To perform the modelling and simulation a program package, called *Polygen*, was developed. The modelling can be performed using more than 100 geometries catalogued in a database, besides the possibility to build polyhedral structures from random positions distributed on the surface of a sphere. In these cases the models are generated using the finite element method in several possible modelling strategies, described by a small number of parameters. Also, any model described by a set of subunits (as for example, proteins) can be used as input for the simulation of the scattering intensity.

The set of coordinates is used for the calculation of the scattering intensity, either for an oriented particle (as shown in figure 1) for for randomly oriented systems. It is also possible to optimize the set of parameters describing the models by the fitting of the theoretical intensity against experimental data.

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↘ Flash Talk: Wed-F-A1

EFFECT OF MULTIPLE SCATTERING ON SMALL-ANGLE X-RAY SCATTERING AND X-RAY PHOTON CORRELATION SPECTROSCOPY

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Soft matter often shows hierarchical structures over a wide size scale. The presence of hierarchical structure leads to unique properties of soft matter. A growing interest in its structure-property relationship requires deep knowledge into its quantitative structural information as well as its dynamics. Small-angle X-ray scattering (SAXS) and X-ray Photon Correlation Spectroscopy (XPCS) have been used to obtain these information. Recent advances in the brilliance of X-rays and X-ray optics make it possible to conduct these techniques in an ultra-small-angle scattering (USAS) region, which covers a size scale of hierarchical structure. One of the advantages of using SAXS and XPCS is that the structure and dynamics in reciprocal space are related to the corresponding real space properties via a Fourier transform. This relation is based on the assumption that the effects of multiple scattering are negligible in SAXS and XPCS so that the scattering process is described in the framework of Born approximation. The effects of multiple scattering have been usually ignored in SAXS and XPCS, while they have been explicitly discussed in electron and neutron scattering. In the course of studying hierarchical structure with SAXS and XPCS in a very low-Q range, however, we have found that multiple scattering significantly affects the results of SAXS and XPCS with a sample thickness which the conventional guideline suggests to be optimum on the basis of the absorption effect; consequently too thick samples are often studied in SAXS studies. In the present study, we quantitatively examine the effects of multiple scattering on SAXS and XPCS both numerically and experimentally.

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SCATTERING FROM SURFACE FRACTALS

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It is shown that small-angle scattering (SAS) from surface fractals can be explained in terms of the power-law type polydispersity. The power-law decay of the scattering intensity $I(q) \propto q^{D_s - 6}$, where $2 < D_s < 3$ is the surface fractal dimension of the system, is realized as a non-coherent superposition of three-dimensional objects obeying a power-law distribution $dN(r) \propto r^{-\tau} dr$, with $D_s = \tau - 1$. The distribution is continuous for random fractals and discrete for deterministic surface fractals, since the deterministic fractals are shown to be constructed as a sum of deterministic mass fractals of subsequent iterations. As an example, a surface fractal is constructed by means of the Cantor dusts, and its fractal scattering properties are studied. We suggest the two-dimensional version of the Cantor surface fractal and of the Koch snowflake. If the sample quality is good enough, the present analysis allows us to extract additional information from SAS data, such us the edges of the fractal region, the fractal iteration number and the scaling factor. We derive analytical expressions for the radius of gyration of the three-dimensional Cantor surface fractal and Koch snowflake.

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THE DATA ACQUISITION SYSTEM OF THE ESRF ID02 TRUSAXS BEAMLINE

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In the scope of the ESRF Upgrade phase I the focusing optics, the endstation and the data acquisition system of the small-angle scattering beamline ID02 [1] have been renewed. First experiments at the new TRUSAXS station [2] could be done in July 2014. Time-resolved ultra small angle X-ray scattering experiments probing scattering vectors down to $q=0.001\ nm^{-1}$ are possible now. Today, the beamline is under normal operation. This contribution will present the beamline with emphasis on data acquisition and online processing.

The upgrade of the beamline made it possible to renew the data acquisition hardware and software. On the hardware side a 30 m long vacuum tube with 2 m diameter was installed, housing three 2D SAXS detectors in a movable detector box under atmospheric pressure (Rayonix MX170HS, Dectris Pilatus 300K and ESRF FReLoN 4M Kodak CCD, see [2]). Each detector can be translated automatically into a position where it can record the scattering pattern. This avoids manipulating vacuum tubes, windows and pumps when exchanging detectors or the distance from the sample. Optionally, a WAXS detector (Rayonix LX170HS, see [2]) can be used at the entrance side of the tube close to the sample.

Recording ancillary information for each live frame of a timing sequence is extremely important, e.g. beam intensity, sample temperature, pressure. These parameters are necessary for normalizing or interpreting the scattering data. ID02 uses a well-established technique [3]: a time frame unit (TFU) that generates detector and shutter gates and a multi channel scaler unit (MCS) accumulating calibration data, either coming directly from a counting device or converted from an analogue device with a voltage to frequency converter (VFC). The TFU/MCS/VFC module of ID02 (C216) offers 16 counter channels with 32 bit resolution.

The new beamline computing and network hardware has been dimensioned in such a way that the data stream of up to two synchronously operated detectors (SAXS and WAXS) can be processed and sent to the central server. The maximum raw data rate has been calculated as 240 MB/s. Each 2D detector is controlled by its own server computer that has a direct network link to a common GPU computer for online data processing and saving to the central server.

To avoid writing several detector specific acquisition programs a modern standard library for image data acquisition (LIMA) is used. It offers an identical command interface for all 2D detectors in use. In this way only one set of user macros (SPEC) needs to be written that controls all detectors in the same way. However, for using these features effectively and replacing the previous online processing program (SPD [4]) by a faster, GPU based program (PYFAI [5]) the original data flow became obsolete and needed to be revised. A new system was designed which is able to write HDF5/NEXUS files. The user has the choice between the old (SPD/EDF) and the new (PYFAI/HDF5/NEXUS) system.

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SASFIT: A COMPREHENSIVE TOOL FOR SMALL-ANGLE SCATTERING DATA ANALYSIS

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Small-angle X-ray and neutron scattering experiments are used in many fields of the life sciences and condensed matter research in order to obtain answers to questions about the shape and size of nano-sized structures, typically in the range of 1 to 100 nm. It provides good statistics for large numbers of structural units within short measurement times. With the ever-increasing quantity and quality of data acquisition, the value of appropriate tools that are able to extract valuable information is steadily increasing. SASfit (program icon shown in figure 1) has been a versatile tool with a broad field of application for small-angle scattering data analysis being available for many years.

Figure 1: Program Icon

We describe the basic data processing and analysis work-flow of measured small angle scattering data shown in figure 2 along with recent developments in the SASfit program package. They include (i) more advanced data reduction algorithms (ii) improved confidence assessment in the optimized model parameters and (iii) a flexible plug-in system for custom user-provided models.

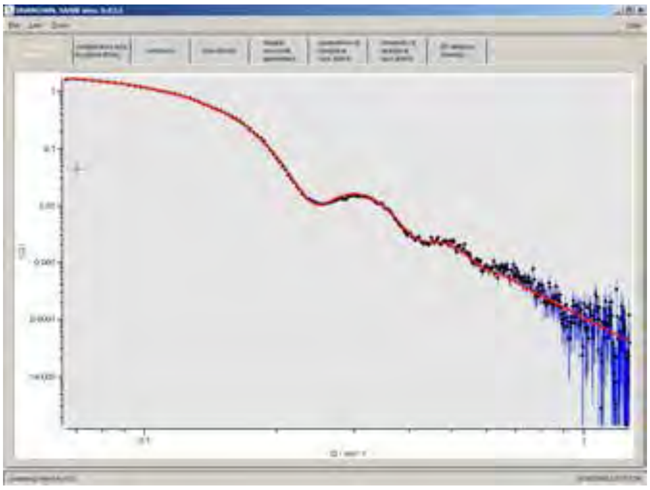

Figure 2: Fit of a model (red line) to a single data set (blue dots with uncertainty bars).

The new SASfit release is available for major platforms such as Windows, Linux and Mac OS X [1]. To facilitate documentation, it includes improved indexed user documentation as well as a web-based wiki for peer collaboration and online videos for guided introduction of basic usage [2].

References

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[2] http://sasfit.sourceforge.net

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GENAPP FRAMEWORK FOR DEPLOYMENT OF SAS SOFTWARE

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The GenApp [1,2] framework was developed as a product of the CCP-SAS [3] to ease deployment of scientific software in a diverse and ever evolving software landscape. To place a module within the framework, the inputs and outputs are defined in a module specific definition file. Collections of modules are arranged in a menu definition file. Running the argument-less single command produces code output for multiple environments, such as a web based client server, or GUI based applications (Figure 1). The framework is extensible to future software technologies without modification to the underlying computational modules. Multi-scale executables are supported and execution can occur locally or on managed compute resources brokered via Apache Airavata [4] middleware.

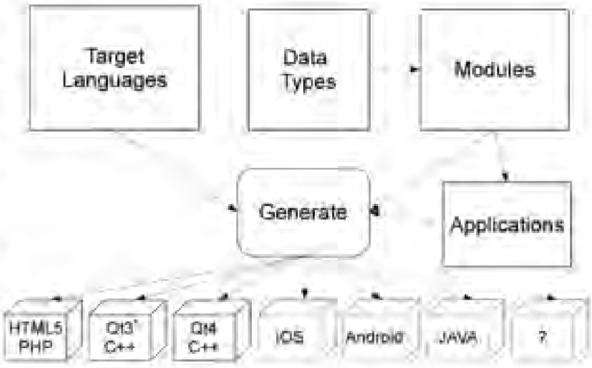

Figure 1: The GenApp framework produces complete code for an extensible set of target languages wrapping easily defined scientific executable modules with a uniform user interface.

SASSIE [5] has been placed with the GenApp framework by the Curtis laboratory to produce SASSIE-WEB, enabling researchers easy access to the SASSIE workflow for the construction of structural ensembles consistent with experimental scattering data. The modular design of SASSIE-WEB allows users to proceed from structural variation using Monte Carlo and molecular dynamics simulation to comparing theoretical and experimental scattering data, or to make use of just the elements they need for a particular project. SCT [6] has been incorporated by the Perkins laboratory [7] as an open source option for scattering curve calculation and comparison. US-SOMO [8] will be placed within this framework by the Brookes laboratory and additional SAS codes for other interested labs will be added to provide an even wider range of simulation and analysis options.

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↘ Flash Talk: Wed-F-A1

NEW DEVELOPMENTS IN THE ULTRASCAN SOLUTION MODELER (US-SOMO) HPLC-SAXS DATA ANALYSIS MODULE

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The on-line coupling of size-exclusion HPLC set-ups to SAXS detectors was developed as an efficient way to collect data on monodispersed (bio)polymers systems. However, two different issues, capillary fouling due to sample accumulation on its walls, and non-efficient peak separation, can severely impair data quality. While these issues should be primarily resolved at the experimental level, this is not always possible. To cope with these issues, we have recently described [1] the development of an HPLC-SAXS module within the UltraScan SOlution MOdeler (US-SOMO) suite of utilities for hydrodynamic and SAS data analysis and simulation [2]. Multiple significant improvements to this module will be presented. To deal with capillary fouling, resulting in SAXS intensities not returning to baseline values after peak elution, an integral baseline correction was developed, replacing the current physically unsatisfying linear approximation. To cope with skewed overlapping peak profiles due, for instance, to interactions with the column matrix, the Gaussian decomposition of non baseline-resolved peaks was enhanced by the introduction of modified Gaussian functions, Exponentially Modified Gaussian (EMG), half-Gaussian Modified Gaussian (GMG) and their combination EMG+GMG (see Figure 1). To evaluate the global Gaussian fitting, a χ^2 vs. q plot was introduced. Assisting guidance and assessment of the decomposition are interactive R_g, I_0 and approximate *MW* [3] computations and plots. For improved *MW* determination, a UV or RI intensity curve can be included with the decomposition. The usefulness of these additions will be demonstrated both with *in silico* simulations and with experimental data processing.

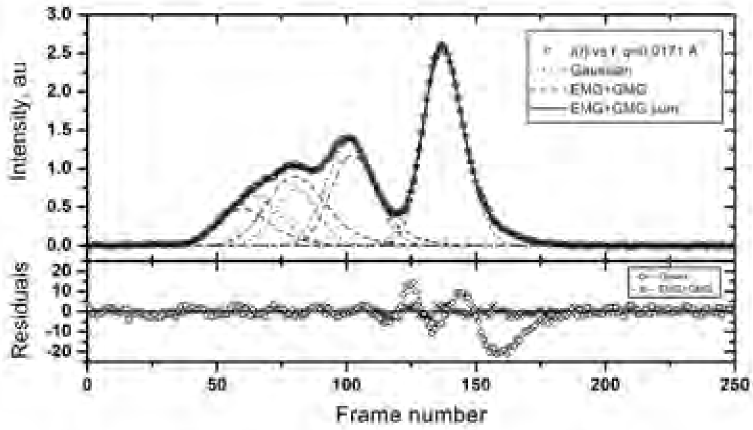

Figure 1. Top: HPLC-SAXS experimental data of aldolase collected at SWING/SOLEIL and processed within US-SOMO, showing the decomposition of an $I(t)$ vs. t chromatogram at a single q value with Gaussians (dotted curves) and EMG+GMG (dashed curves).

Bottom: normalized residuals for the fit of the sum of Gaussians and EMG+GMG curves.

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GisaxStudio: A PROGRAM FOR GISAXS ANALYSIS OF THREE DIMENSIONAL QUANTUM DOT LATTICES

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We demonstrate a new program *GisaxStudio* for processing and analysis of grazing incidence small angle x ray scattering (GISAXS) intensity distributions measured on three dimensional lattices of quantum dots with different types of disorder [1]. Several models are included in the program which enables full 3D structure determination, including lattice type, lattice parameters, the type and degree of disorder in the quantum dot positions, their sizes and the corresponding statistical distributions. Several examples of the analysis are presented and compared with the results obtained by other experimental techniques.

GisaxStudio is a modular, multi-platform program written in Java programming language, featuring a graphical user interface, built-in optimization algorithms and visualization. It can be easily extended with additional models. *GisaxStudio* stores all data in the relational database which facilitates data exchange and reproducibility. It is free for non-commercial use and can be downloaded from the http://homer.zpr.fer.hr/gisaxstudio .

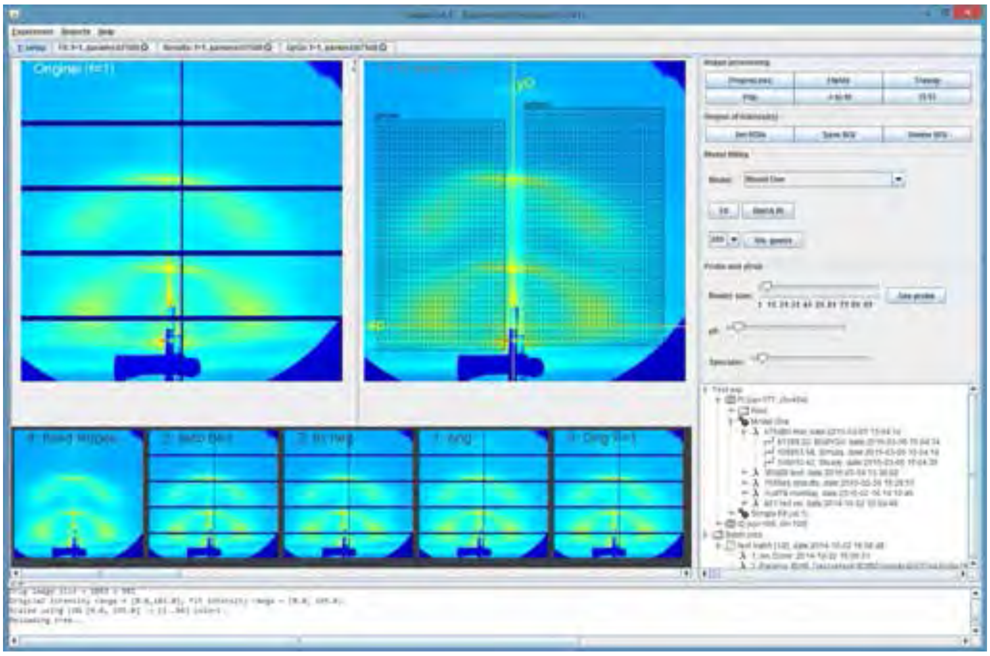

Figure 1: Main screen of the program *GisaxStudio* with the included tabs.

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SASVIEW: ANALYSIS PLATFORM FOR SMALL-ANGLE SCATTERING

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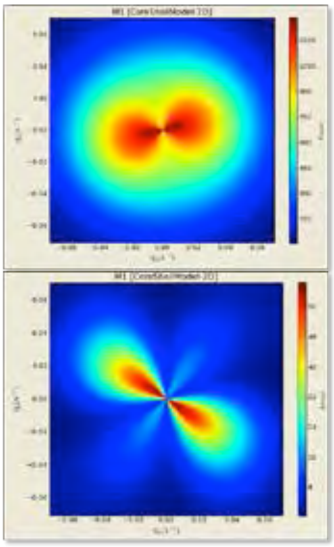
SasView [1] is an open source project to provide data analysis for small-angle scattering. The software is written in Python with C and C++ modules providing some of the heavier computations. SasView is the work of an international collaboration.

SasView reads almost any 1D ASCII column data and the canSAS format. While work is underway to develop a nD data format, SasView currently reads reduced 2D formats produced by various reduction packages including Mantid.

SasView provides several tools for modeling SANS data. About 90 models are available to fit 1D data. Several of those models can also be used to analyze non-azimuthally symmetric 2D data. Wedges tools can also be applied to 2D data to compute I(Q). Although SasView has mostly been focused on modeling, it also offers other tools such as a P(r) calculator, a SLD calculator and image processing tools.



Calculated magnetic scattering from a core-shell structure with the moments in the core and shell oriented in different directions. Top: up-up scattering, Bottom: up-down scattering.

Work is currently underway to develop several aspects of the application. We are working on extending the models and tools to extend modeling to magnetic data and spin-echo SANS. We are also working on refactoring our model implementation to make it easier for users to add in their own models. A long-term goal of the project is to leverage to widespread availability of remote compute resources and GPU computing. We plan on refactoring much of our computation layer to make it compatible with remote job submission, which could open the door to providing SasView computations as web service to be used by other applications.

References

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SIGNAL QUALITY, RADIATION DAMAGE, AND MICROFLUIDICS AT HIGH-FLUX X-RAY SOURCES

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Next-generation high-flux synchrotron sources are delivering more photons for biological small angle solution scattering (BioSAXS) experiments than even before. While this will enable experiments on smaller samples at shorter timescales than previously possible, radiation damage presents a serious challenge. This presentation will introduce SaxsProf, a basic signal quality simulator for BioSAXS experiments. Given solution conditions, concentration, molecular weight, beamline flux and other basic parameters, SaxsProf can serve as a "what if" calculator, giving a realistic preview of experimental signal quality. The modeling considerations will be outlined and a variety of measures of data quality will be simulated and validated against experimental scattering profiles[1]. The calculations are then extended to study the limits of time-resolved and other state-of-the-art methods at future high-flux sources. Radiation damage simulations are also introduced through fluid dynamic convection-diffusion simulations and performed in the context of various microfluidic schemes. Finally, current progress in cryogenic SAXS will be presented, validating SaxProf against actual data and projecting to size and flux scales relevant to next-generation sources.

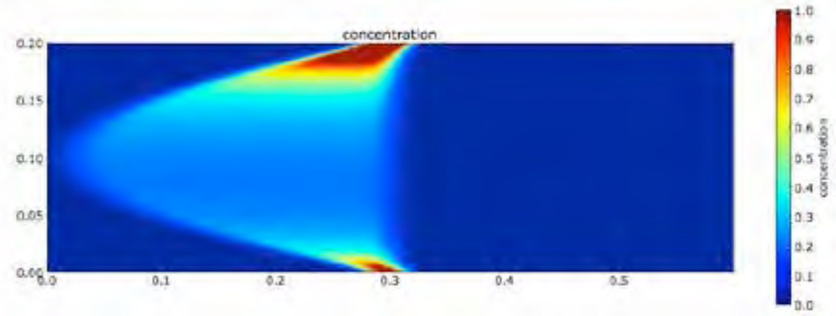

Figure 1: Snapshot of a transient convection diffusion simulation of protein sample damage under typical microfluidic flow conditions. The 250 µm diameter (FWHM) x-ray beam traverses the sample cell vertically (0.2 cm path) at center leaving a wake of damage (red, concentration > 1) in the flow which accumulates near the walls due to no-slip boundary conditions.

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AUTOSAXS - A NEW TOOL FOR SAS DATA FITTING

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Data analysis constitutes a substantial part of a SAS experiment, and thus a number of software tools exists to fit theoretical models to scattering data [1,2]. In case of many models, the parameters are strongly correlated and the number of adjustable parameters is large, which makes the fitting a tedious and error-prone procedure and complicates the determination of uncertainties. autoSAXS is a new tool to fit small-angle scattering data, which focuses on particle dispersions. It employs particle swarm optimization [3], a global optimization technique, in order to find the global minimizer with little user interaction.

Figure 1a displays scattering data from a polymeric core-shell nanoparticle suspension together with the fit found by autoSAXS. In addition to the best fit, an automatic procedure can be started, which varies the assumed mean particle size R around the best-fit value. The resulting dependency of the goodness of fit χ^2 on R (figure 1b) can be used to estimate the uncertainty of the particle size.

Finally, a PDF report can be generated by autoSAXS which contains embedded data files in addition to the fit parameters and plots of the fit data.

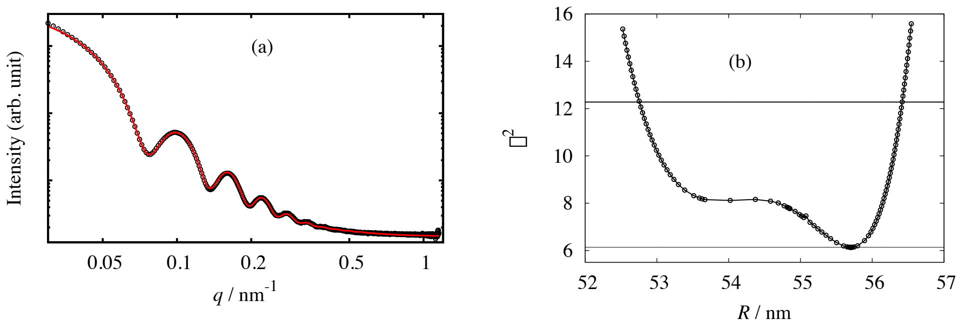

Figure 1: (a) Scattering curve of a polymeric core-shell nanoparticle suspension. The symbols represent the measured data, the solid line displays the best fit found by autoSAXS (b) Goodness of fit χ^2 vs. mean particle radius R. The horizontal lines mark the best achievable χ^2_{min} and $2\chi^2_{\mathrm{min}}$

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SIMPLE BAYESIAN METHOD FOR IMPROVED ANALYSIS OF QUASI-TWO-DIMENSIONAL SCATTERING DATA

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I will present a new method for the analysis of small angle neutron scattering data from quasi-two-dimensional systems such as flux lattices, Skyrmion lattices, and aligned liquid crystals [1].

A significant increase in signal to noise ratio and a natural application of the Lorentz factor can be achieved by taking advantage of the knowledge that all relevant scattering is centered on a plane in reciprocal space. The Bayesian form ensures that missing information is treated in a controlled way and can be subsequently included in the analysis. A simple algorithm based on Gaussian probability assumptions is provided which provides very satisfactory results (Fig. 1), resulting in improvements in signal to noise ratio of a factor of two or more compared to traditional methods.

Whilst highly suited to flux lattice diffraction data, this method is completely general, and I will argue that a generalized model-independent Bayesian data analysis method would be highly advantageous for the processing of all neutron and x-ray scattering data.

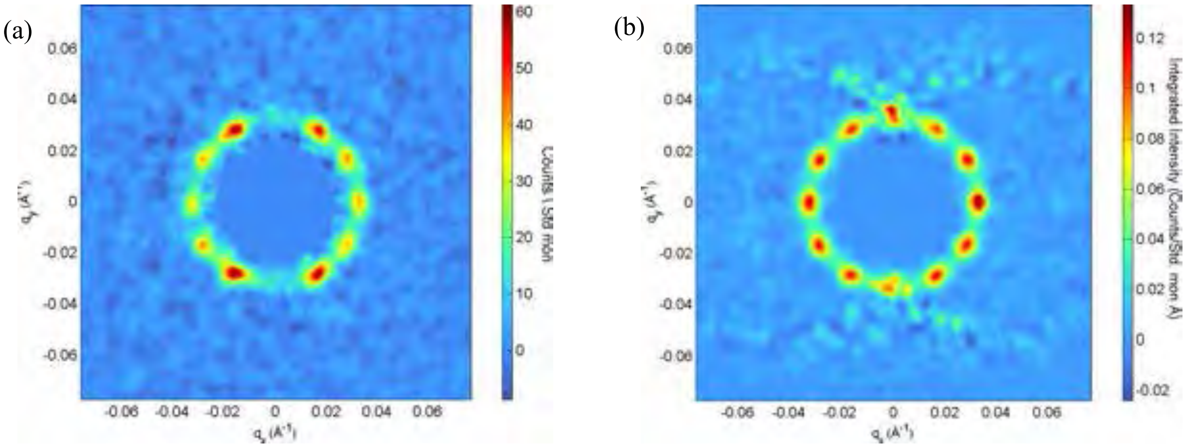

Figure 1: (a) Neutron diffraction pattern from BaFeAs$_{(1-x)}$ P$_x$ (x=0.3) at 5 T obtained by summing a series of [2]. (b) Result of Bayesian fitting method. Note the recovery of spots at the top and bottom, the reduced noise and more even intensity in the main diffraction pattern. A limited amount of processing has been applied to both images (3x3 pixel Gaussian smoothing) allowing some artefacts to remain visible; these can be easily removed in a controlled way.

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THE CANSAS FORMAT FOR SINGLE AND MULTIDIMENSIONAL REDUCED SMALL-ANGLE SCATTERING DATA

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Common data formats provide many advantages for the scientific community, including the easy use of different analysis software packages [1-3], a standard for data deposition [4-5], and establishment of databases for data curation and mining [6-7]. One of the first aims of the canSAS (Collective Action for Nomadic Small-Angle Scatterers) forum of users and facility staff [8] was to discuss better sharing of SAS data analysis software. Establishment of a common data format furthers that aim. In the 2013 annual report [9], members of the IUCr Commission on Small-Angle Scattering reported of their activities in establishing publication guidelines for structural biology applications of SAS [5] and ensuring that conforming datasets could be incorporated into the Worldwide Protein Data Bank [6].

Here we present the *NXcanSAS* format [10], within the scope of the NeXus standard [11], for storage of single and multidimensional reduced data.

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ATSAS 2.7 – AUTOMATED PROCESSING AND ADVANCED INTERPRETATION OF SCATTERING FROM ISOTROPIC SYSTEMS

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Small-angle scattering (SAS) of X-rays and neutrons is actively used to address increasingly complicated questions in structural biology. The ATSAS software package [1] incorporates a broad palette of methods for the analysis of isotropic scattering data and is focused on structural characterization of macromolecular solutions. The package encompasses methods for data manipulation and processing, programs for *ab initio* shape reconstruction, hybrid modelling approaches using high resolution models of subunits, and tools to analyse data from mixtures and flexible systems.

The latest version of ATSAS features a number of new and enhanced modules including: (i) DATTOOLS, a suite of command-line programs for basic data processing, evaluation of overall geometrical parameters and distance-distribution functions. These tools may serve as building blocks for other programs and automated scripts. A new program SHANUM [2] determines the number of meaningful Shannon channels and thus the useful experimental data range; (ii) PRIMUS, a multi-platform interactive data visualisation, manipulation and analysis program with a user-friendly graphical interface. New features include the “correlation map”, a novel approach to statistical comparison of experimental and theoretical data [3] and “wizards” to automate several modelling approaches; (iii) GASBORMX, a program for *ab initio* shape reconstruction based on data from protein monomer-multimer mixtures and (iv) SASREFMX, for rigid body modelling of transient complexes and weak oligomers from polydisperse data; (v) SREFLEX, a program for flexible refinement of atomic structures based on normal-mode analysis; (vi) AMBIMETER, a program to quantitatively assesses the inherent ambiguity of shape reconstruction from a given SAS pattern; (vii) SUPALM, a program for rapid automated superposition of high and low-resolution models using spherical harmonics; (viii) EOM 2.0, an enhanced tool for the analysis of flexible systems utilizing ensemble optimization, redesigned to allow for partially or completely symmetric oligomeric models, to refine the size of the ensemble, and to quantitatively characterize the flexibility (R_{flex}) [4].

ATSAS is freely available for academic users and can be installed on Windows, Mac and various Linux distributions. The package is actively used by the structural biology and condensed matter communities, being downloaded more than 500 times monthly. Many ATSAS programs have online interfaces that can be accessed through a web-browser [5].

The authors acknowledge support by the European Commission, BioStruct-X project (contract number 283570) and by the Bundesministerium für Bildung und Forschung project BIOSCAT, Grant 05K20912.

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AUTOMATED ANALYSIS OF DATA FROM HIGH-THROUGHPUT BIOLOGICAL SOLUTION SAXS EXPERIMENTS

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Small angle X-ray scattering (SAXS) allows studying the structure and interactions of biological macromolecules under near physiological conditions. High-throughput SAXS analysis of solutions of proteins, nucleic acids and their complexes became routine with the introduction of sample changing robots, increased accessibility of dedicated high-flux synchrotron radiation beamlines and advanced laboratory X-ray sources. Typical experiments include screening of various solution conditions, temperature scans and measurement of structural responses to ligand binding. These high-throughput experiments produce enormous amounts of data and a robust automated pipeline for a real-time data analysis becomes an indispensable element of a SAXS infrastructure.

We have developed a set of protocols for automated data reduction and analysis and implemented them in the SASFLOW data analysis pipeline [1]. The pipeline provides the user with an immediate feedback about the sample characteristics and allows e.g. for correcting the sample preparation conditions if necessary.

The primary data processing steps include: radial averaging of the 2D scattering patterns, normalization against the transmitted intensity, radiation damage check, background subtraction and automated merging of data collected from different solute concentrations. Comparisons of the individual data frames using the Correlation Map [2] are performed to check for the radiation damage and comparisons between repetitive exposures of the solvent are done to control the stability of the instrument.

From the processed scattering patterns the pipeline automatically evaluates the overall geometrical parameters of the macromolecules (radius of gyration, volume, maximum size), assesses the particle flexibility/compactness and reconstructs the shape *ab initio*. Automated validation against available a priori data (e.g. expected atomic models) as well as mixture analysis has recently been included. As an option, the pipeline is able to exchange information with the laboratory-information management system ISPyB [3]. This integration allows the user to conveniently pass over the metadata (sample and buffer names and compositions, concentrations, sequence of measurements, relevant high resolution models, if available, etc). The results of SASFLOW are summarized using XML format to be conveniently presented with a Web browser and, if using ISPyB database, to represent and compare the obtained results with previous acquisitions.

This work was supported by EU FP7 Infrastructures Grant BioStructX (contract 283570) and BMBF (Bundesministerium für Bildung und Forschung) Research Grant BioSCAT (contract 05K12YE1).

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RAPID AUTOMATED SUPERPOSITION OF HIGH AND LOW-RESOLUTION MODELS USING SPHERICAL HARMONICS

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Small-angle scattering is more and more actively employed for hybrid modelling in combination with other structural methods. All these methods provide three-dimensional (3D) models of different nature and resolution and comparisons between such heterogeneous models are often required for cross-validation of structural results obtained by different techniques. The comparisons usually require automated best-matching superposition of 3D structures. Such an optimal superposition of heterogeneous models is not a simple task, especially for larger molecules, because of different nature, resolution and representations of the objects to be compared (atomic models, bead models, surfaces *etc*).

We have earlier developed a program SUPCOMB [1] for matching high and low-resolution 3D structures, which used a normalized spatial discrepancy (NSD) as a proximity measure between the objects. Starting from an inertia-axes alignment, the algorithm minimizes the NSD and finds the best-matching alignment of the structures. However, the CPU time used by SUPCOMB is proportional to the product of the number of points in the two objects and for large macromolecular complexes the program becomes computationally expensive.

Here, an algorithm for a fast matching of large macromolecular models in Fourier space is proposed and implemented. It is based on the spherical harmonics representation of the scattering amplitudes and uses a normalized integrated cross-term of the scattering amplitudes calculated by CRYSOL [2] as a proximity measure between 3D objects. The method is implemented in a computer program SUPALM that maximizes this cross-term coefficient of two objects providing the best matching configuration. The performance of the proposed algorithm is tested on a number of high and low-resolution models, and the aligned configurations are in a good agreement with SUPCOMB results. The computing time of SUPALM is comparable to that of SUPCOMB for protein models with molecular weights lower than 100 kDa (represented by about 10^3 atoms). For large (*e.g.* 1 MDa, about 10^5 atoms) macromolecular complexes SUPALM performs ten times faster than SUPCOMB.

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Automation of Data Calibration for GISAXS and GIWAXS Experiments

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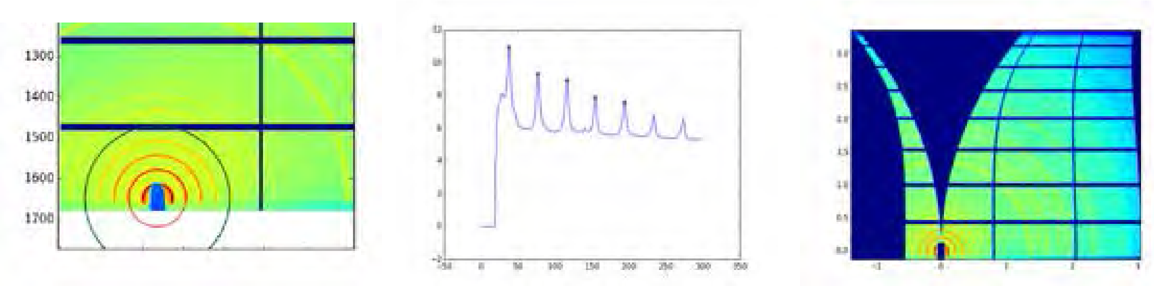
There is a great interest in materials such as thin films of conductive polymers, organic photovoltaics and thin films of nano-particles etc. Grazing incidence small angle scattering and wide angle scattering (GISAXS/GIWAXS) techniques serve as important tools to study the mesoscopic structure of such materials. It is evident from the fact that more than 60% of experiments on SAXS/WAXS beamline at the Advanced Light Source (ALS) are grazing incidence. However before any analysis can begin, one need to determine the coordinates of detector image in resiprocal space. Each set of images taken at beamline come with a corresponding Silver-Behenate (AgB) image as calibrant. Since the peak spacings of AgB in reciprocal space are well establised, if we know the incident angle, we should be able to determine the momentum transfer vector (**q**) for every pixel. We have developed software suite at ALS which, in following steps, (*i*) determine approximate direct-beam, (*ii*) determine approximate sample-detector distance, (*iii*) iteratively refine these values, using part of code from from Dpdak [1]. Every image taken at the beamline is sent to supercomputing facility at the Berkeley National Lab, where it is automatically calibrated, indexed and stored, so that scientists have access to their calibrated data almost in real time. In addition, GIWAXS images are corrected for the curvature of Ewald sphere. Radial average of every image is also calculated and plotted. Users can access the data through a web interface.



(a) Center (b) Sample-det. dist. (c) Remeshing

Figure 1: Calibration Steps

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A PROGRAM FOR SAXS DATA PROCESSING AND ANALYSIS

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A computer program for small angle X-ray scattering (SAXS) data processing and analysis named S.exe written in Intel Visual Fortran has been developed [1]. The program is composed of two modules (see Figure 1). The first module (I) is used for primary data processing as the correction of the position of the centre of the direct beam, the calculation of the radial distance on the scattering profile, the choice of useful data, the calibration of the scattering vector, the correction for the collimation error, the normalization and background subtraction. The second module (II) is used for data analysis to compute structural parameters of the sample such as scatterer shape, scatterers size distribution, specific surface, porosity, interface layer thickness, correlation distance, fractal dimension, etc. A series of subprograms are integrated in the module (II) to compute different structural parameters for different samples with either the desmeared or slit-smeared data. The advantage of this program is to obviate the need of an accurate knowledge of the wavelength and sample-detector distance. The program can be run fully automatically or semi-automatically. It is easy to run the program profiting from the integrated instruction and the step by step operating design. Each module and each subprogram with special function can be called independently. The result of each module is saved separately, which can be viewed and called freely. Furthermore, the program is freely available registered, used and updated and is continuously improved [2].

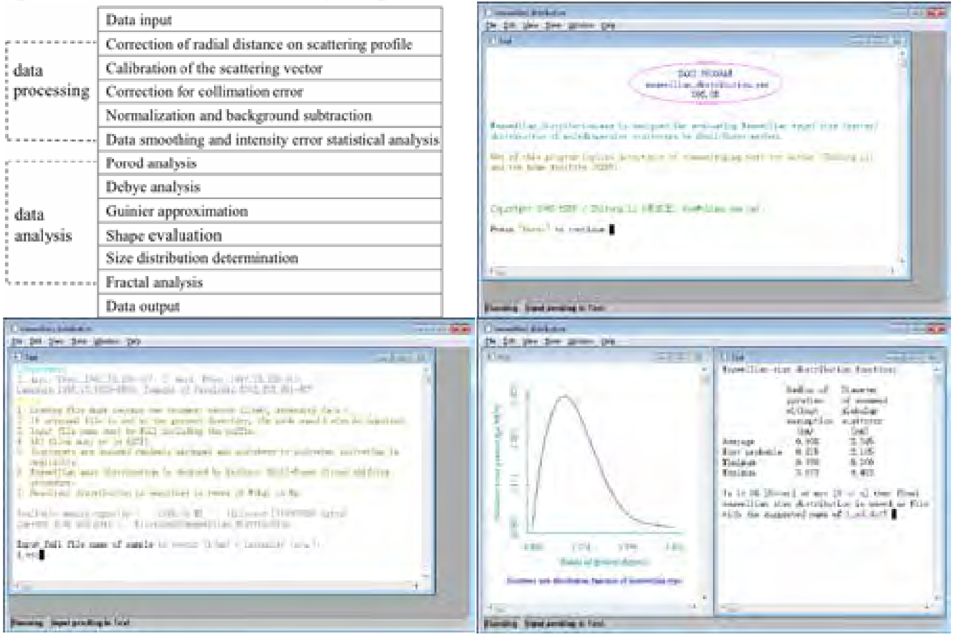

Figure 1: Flow chart of the program S.exe for SAXS data processing and analysis.

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RAPID PHASE ID: ONLINE SPACE GROUP DETERMINATION

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The availability of high flux synchrotron beamlines and fast low noise detectors has driven the development of high throughput data collection techniques. When coupled with robotic sample preparation, data from an enormous number of samples can be collected. The acquisition of numerous SAXS patterns at the Australian Synchrotron SAXS/WAXS beamline for the characterisation of lyotropic drug delivery vehicles is a case in point [1]. *RAPID PHASE ID* was developed in order to efficiently analyse the many SAXS patterns from high-throughput experiments, which may produce thousands of patterns in a 24 hour allocation of beam time. This software was developed to automatically reduce each 1D, radially averaged, small angle diffraction profile to a likely space group and lattice parameter for each sample. These parameters are key for further analysis of these systems.

The *RAPID PHASE ID* analysis pipeline, described here, was initially developed in IDL [2], but has been converted to Python, and is now available as a web service (rapidphaseid.synchrotron.org.au). Although it was originally designed for the specific example described above, the software will work with any data in three column ASCII format, and has found wider application on the beamline for samples exhibiting small angle diffraction.

This paper will describe the analysis methods of the software in detail, demonstrate many of its features, provide examples of its use, and finally explain how to access and use the web service.

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FOXTROT: A VERSATILE JAVA-BASED APPLICATION TO REDUCE AND ANALYSE SAXS AND WAXS PILES OF 2D DATA

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Foxtrot is a Java based application used on beamline SWING to compute Small and Wide Angle X-ray Scattering data. Foxtrot has been developed by the Synchrotron SOLEIL software group and is continuously enhanced with new capabilities, through permanent interactions with the users [1]. Amongst a variety of functions and tools, the user can load files automatically, design/modify a mask for 2D images, perform sector/radial/azimuthal integration, normalize 1D data by transmitted/incoming intensity, convert intensity in absolute unit (e.g. by normalization to water scattering), average/subtract/merge/scale 1D data, perform fits on a series of 1D data, display fitting results as a function of a contextual parameter (e.g. time, to follow the kinetic evolution of Rg and I0), save results in reloadable NeXus files and export results as ASCII files. A simple Macro language is proposed to automate the 2D-to-1D conversion workflow from a pile of images.

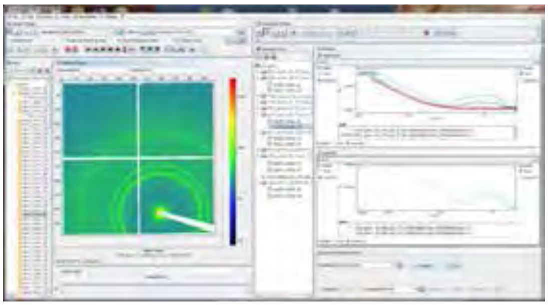

Figure 1: A typical snapshot of the main Foxtrot screen.

Foxtrot application can operate on different data formats thanks to the CommonDataModelAccess (CDMA) software layer it is based upon. The CDMA library gives access to data through so called engines (in charge of handling physical data container: HDF5, Nexus, EDF …) and plugins (managing data organization inside the container) [2]. Using an innovative dictionary "mapping" mechanism between scientific data item definitions (*e.g.* sets of keywords defined by scientists for a given experimental technique) and physical data organization in files, the CDMA framework allows Foxtrot to be used on data produced in different facilities.

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↘ Flash Talk: Wed-F-A1

MEMPROT: A PROGRAM TO MODEL THE DETERGENT CORONA AROUND A MEMBRANE PROTEIN, BASED ON SEC–SAXS DATA

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The application of small-angle X-ray scattering (SAXS) to structural investigations of transmembrane proteins in detergent solution is hampered by two main inherent hurdles. On the one hand, the formation of a detergent corona around the hydrophobic region of the protein strongly modifies the scattering curve of the protein. On the other hand, free micelles of detergent without a precisely known concentration coexist with the protein–detergent complex in solution, therefore adding an uncontrolled signal. To gain robust structural information on such systems from SAXS data, in previous work, advantage was taken of the online combination of size-exclusion chromatography (SEC) and SAXS, and the detergent corona around aquaporin-0, a membrane protein of known structure, could be modelled. A precise geometrical model of the corona, shaped as an elliptical torus, was determined [1]. We have recently revisited the geometrical approach by more thoroughly examining the correlations between all fitting parameters, and derive some rules about which strategy to adopt in further studies with different proteins [2]. The program Memprot has been developed to systematize the SAXS calculations from the geometrical models and is accessible to the community [3]. In a subsequent development of our software, for cases in which the protein contour is less isometric than that of AQP-0, we have considered developing a parameterized geometrical model of the detergent corona which adheres more closely to the actual shape of the protein. New applications of this recent strategy will likely be shown.

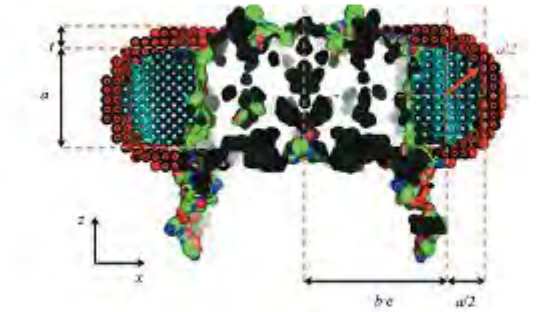

Figure 1: A section of the complex between the full-atom 2b6p structure and its detergent corona optimized from SEC–SAXS experimental data, as modeled in Memprot.

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NEED SOFTWARE FOR SA.S DATA? WHY NOT TO TRY QTIKWS?

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Probably, small angle neutron scattering (SANS) is one of “easiest” neutron-related-method to understand technique and to interpret obtained results for a not experienced user: adjustable pinhole collimator, sample, and 2D-detector. The user could have the same illusion about SANS also after measurement and data reduction: if sample scatters well, instrument works stably, and number of instrument configurations is limited to one... But, in order to measure a sample in the full Q-range at a classical non-TOF SANS instrument, number of instrument configurations should be higher than three. This increases in geometrical progression number of calibration files; and data reduction becomes already really painful.

The aim of SANS data reduction interface “DAN-light” developed within the cross-compiled software package QtiKWS [1] to keep “illusion of simplicity” for a starter and “filling of full control” for a guru of small angle scattering. “Illusion of simplicity” is saved by step-by-step definition of two script tables, namely a table of configurations and sample table. It allows proceeding of all measured datasets within “5 minutes principle”; re-treatment with changed parameters will take only few seconds.

Run-time creation/configuration of data-reduction-algorithm allows to an instrument responsible to optimize data treatment procedure correspondingly to the current status of the instrument or experiment and to control data output at every step. Extraction of needed parameters from files is controlled by universal header-reader tool. The header-reader could read free-format ASCII files with known position of parameters; find parameters by a key sequence; extract data from encoded-data-formats like XML and YAML. It allows integrating most of SANS instruments and data-treatment-procedure looks similar for all of them. “Instrument-free” approach means “independence” from data format; and “dependence” on algorithms of data treatment.

Now, this software package is standard data-reduction-tool for two classical SANS instruments KWS-1 and KWS-2 as well as for very-high resolution focusing SANS diffractometer KWS-3 of the Jülich Centre for Neutron Science (JCNS) at FRM2 reactor in Garching (Germany). Behind current version there are six years of intensive user- and instrument operation as well as source evolution.

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ISPYB AND ADVANCED DATA ANALYSIS: THE POTENTIAL FOR FULLY AUTOMATED AND EFFICIENT HIGH THROUGHPUT BIOSAXS EXPERIMETS

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The advances made in small angle scattering over the past decades have had a large impact on structural biology [1]. Dedicated beamlines such as BM29 at ESRF [2] and P12 at EMBL-Hamburg provide an optimised setup for high throughput data acquisition with the BioSAXS sample changer [3] and online size exclusion chromatography [4]. Automation enables more complex and more thorough experiments which create more data that needs to be processed, analysed [5] and interpreted to enable optimal use of beamtime.

The BioSAXS extension of ISPyB [6] can be used to store all parameters related to the preparation and analysis of SAXS experiments. This includes the definition of all required measurements, shipping details, experimental parameters used and all acquired scattering data as well as online processing and analysis results. It can currently be used at the ESRF, EMBL-Hamburg and other locations as it is independent from local processing software and architecture through use of customisable industry-standard web services. ISPyB's web based GUI provides easy access (from any location) to all data collected at any beamline in order to make the best use of all data collected. Crosschecks of invariants from all measurements of the same samples allow internal verification of consistency and completeness of a data set. The capabilities and potential for cross validation have now been increased by the addition of supplementary *a priori* information (amino acid sequence, molecular mass, biophysical characterisation of size, known high resolution structures or individual domains): as the results obtained via SAXS can be compared to the known parameters, allowing verification or interpretation of mixtures or stoichiometry. Furthermore, the theoretical scattering of all known structures can be compared to the data, as well as mixture analysis and rigid body modeling can be executed automatically. The ISPyB GUI has been updated for visualisation of these additional analysis results to provide the users with maximum feedback as soon as possible, giving the users a less ambiguous indication of the shape and nature of their samples. Furthermore the analysis can provide direct feedback to the data acquisition enabling fully automated data collection taking appropriate action in case of radiation damage, or inter-particle scattering effects to acquire the best data from all samples and to maximise efficient use of beamtime.

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EVALUATION OF ANISOTROPIC SMALL-ANGLE SCATTERING DATA FROM METASTABLE β-Ti ALLOYS

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Metastable β-Ti alloys are technologically important materials used in automotive, aerospace and biomedical industries. They have outstanding mechanical properties (high strength, low density, corrosion resistance, toughness and good hardenability, low elastic modulus). However, the mechanisms producing high level of strength are still not fully understood. Therefore, these alloys are widely studied. One of the microstructural features contributing largely to strengthening for some alloy compositions is metastable ω phase (non-close-packed hexagonal phase) which forms on quenching from β-matrix and grow during subsequent ageing [1].

Small-angle scattering is well suited for investigation of precipitate microstructure in alloys, both *ex situ* or *in situ* at various external conditions (e.g. at elevated temperatures or under stress). Small Angle Neutron Scattering (SANS) data from single-crystal metastable β-Ti alloys have anisotropic character and exhibit interparticle interference maxima due to ordering of the dense system of ω precipitates. For an evaluation of such data, program NOC [2] (previously used for evaluation of data from γ' precipitates in single-crystal nickel based superalloys) was used. Two of the evaluated scattering curves (alloy after ageing at elevated temperatures) are displayed in Fig. 1. The real space model employed for the evaluation used system of spherical particles ordered in 3D. The model is to be tuned in order to take into account the elongation of the ω precipitates in <111> directions, which can bring still better correspondence of the measured and the modelled data.

GACR project No. 14-36566G support is gratefully acknowledged.

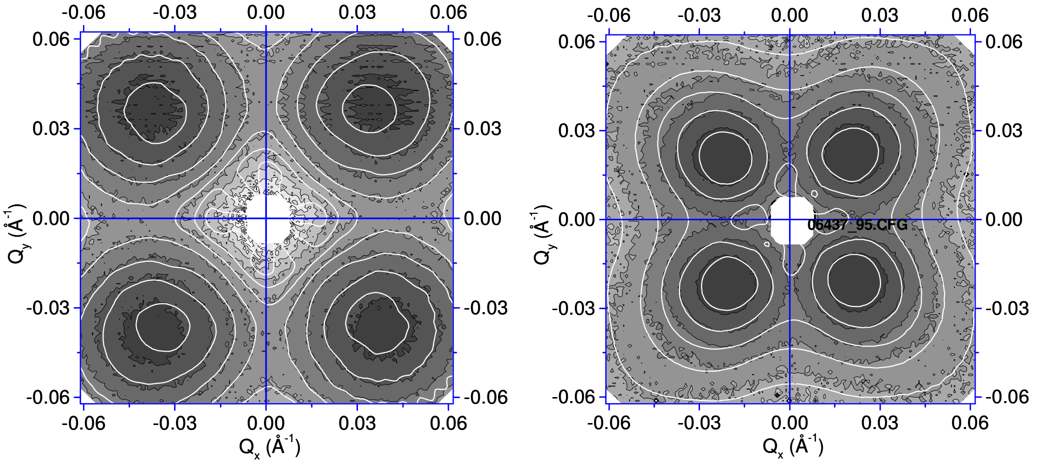

Figure 1: 2D SANS intensity for β-Ti alloy (at %: 88.7Ti-4.1Mo-3.7Fe-3.1Al) after ageing (left: 335°C, 32 hours; right: 370°C, 16 hours). The measured cross section (ILL Grenoble) from ω precipitates is displayed by gray-scale map while the white lines are the equi-intensity lines of the model fitted to the data.

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↘ Flash Talk: Wed-F-A1

PYSAXS, AN OPEN SOURCE PYTHON PACKAGE AND GRAPHIC USER INTERFACE FOR SAXS DATA TREATMENT

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We develop a series of modules entirely written in Python language grouped under the name pySAXS (Python for SAXS), allowing to process the different operations for the SAXS data treatment. pySAXS is open source and based on Numpy and SciPy libraries.

Initially designed for the three homemade LIONS SAXS experiments (USAXS[1], SAXS[2], WAXS), the package is completely independent from experimental details.

pySAXS contains libraries with basic functions for manipulating data (merge, subtract, add,…), setting in absolute scale, processing a deconvolution. Uncertainties are carefully propagated at each step of data manipulation. pySAXS also offer the possibility to easily add user defined modules for computing form and structure factors. Researchers write their own models by simply describing the different parameters and the source code. pySAXS already contain numerous rigorous tested and optimized modules for classical shapes and interactions. Fundamental theorems are also available like Guinier, Porod and invariant computation.

We also added some plugins for using external libraries like xraylib[3] (absorption calculation for compounds at different energies) and pyFAI[4] (a fast radial averaging of 2D detectors images).

A graphic user interface (Figure 1) is proposed for manipulating the data and plot them simultaneously with different type of scales (lin-lin, log-log, or even i.q^n scale) and a publication-ready display. A generic dialog box is shown when the user want to fit data with a given model. It allows to modify the parameters and proposes the fitting functions.

New functionalities offer to process the complete SAXS data treatment on-line.

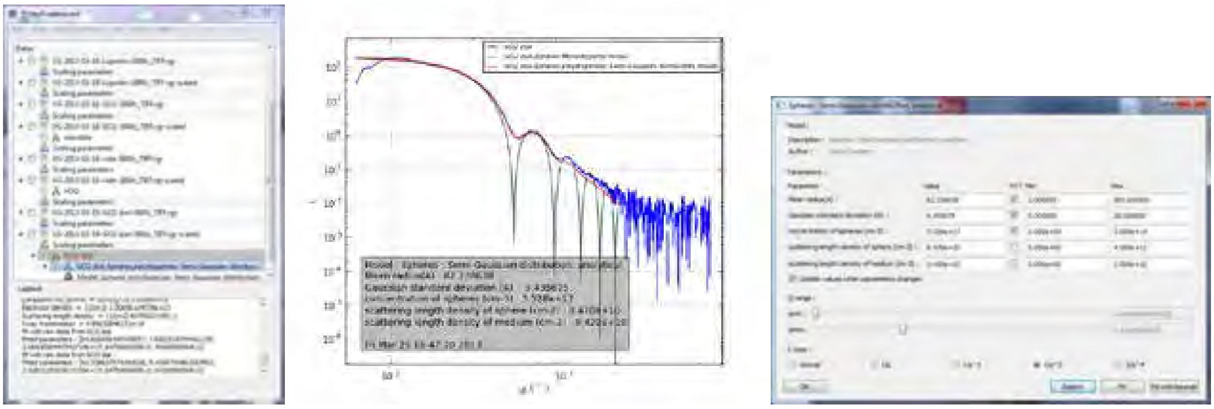

Figure 1 : overview oft the pySAXS graphic user interface allows to manipulate the datas (left),display the corresponding plots (center), and shows a dialog box with the differents models parameters (right).

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↘ Flash Talk: Wed-F-A1

ADVANCED IMAGING ALGORITHMS FOR GISAXS

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Scientists do a large part of GISAXS data processing manually. Furthermore the techniques used for processing the data lag behind the state-of-the-art in image processing and analysis. In this abstract, we present results for processing GISAXS data using state-of-the art techniques from image processing and machine learning. We focus on the problem of improving detector resolution, dealing with gaps in the detector and automatically identifying key features such as arcs and peaks in the data.

The PILATUS-2M detector has a pixel size of 172 microns that may not be sufficient for certain applications. In order to improve this we make use of image super-resolution techniques. We obtain multiple views of the same data by sub-pixel shifts of our detector. The collection of images is then processed to obtain a higher-resolution image. In particular we use a model-based iterative reconstruction approach that models the noise statistics of the detector as well as a characteristics of the underlying image to obtain high quality reconstructions by minimizing a cost function [1]. Fig. 1 shows a result of 4X super-resolved image of the direct beam from our detector.

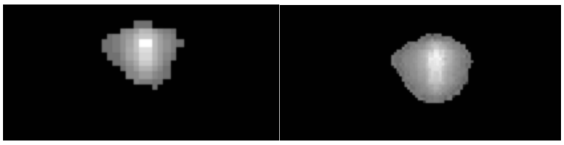

Figure 1: Left – Low resolution image of the direct beam from PILTUS 2M. Right – 4X super-resolved image using the model-based approach.

The PILATUS 2M has gaps that can make it challenging to process the data especially for in-situ experiments. This can hinder the application of other image processing algorithms directly to the data. Hence we propose an image inpainting algorithm based on Laplace's equations with a Dirichlet boundary condition [2] so that the gaps are filled while preserving the continuity in the image. Finally using the in-painted image we identify features that are key to GISAXS data sets – peaks and arcs. For the peak-detection we apply a blob-detection algorithm based on the Laplacian-of-Gaussian filter. We also develop an arc detection algorithm based on sector radial integration to identify the orientation of grains in the data. Fig. 2 and Fig. 3 shows the results of such processing.

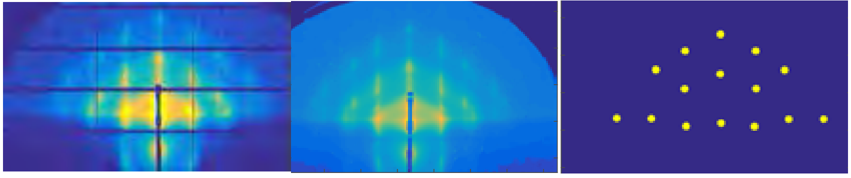

Figure 2: Left –Raw data with missing pixel values. Center - Inpainted image using the diffusion approach. Right - peak-detection algorithm

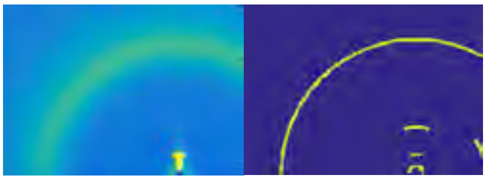

Figure 3: Left – inpainted data. Right - output of arc-detection algorithm.

In conclusion, we presented automated imaging algorithms for GISAXS data sets. Such techniques will reduce manual intervention; help scientists extract more information from data sets and provide good initial conditions for simulators like HIPGISAXS [3].

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More about solution uniqueness and stability in particle shape and size distribution determination from SAS data

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Restoration of 3-dimensional shape of the particles from small-angle scattering data is not only ill-posed, but also ambiguous problem. Both of these factors lead to the spread of solutions, which also depends on the parameters of the models (in particular, bead size) and angular data range. These factors lead to systematic errors in the difference between the experimental and model scattering patterns. In this paper we consider the algorithm of ab-initio shape search DAMMIN. The spread of the solutions can be reduced by modifcation of its search scheme. The basic idea consists in a periodic variation of the relative magnitudes of penalty terms of the objective function. For example, alternating of weight for discrepancy between experimental and model scattering relative to penalties for "looseness" of the structure allows one to find models closer to the right one. In this work, a number of examples of the search for the restoration of the complex models and a new version of the program DAMMIN is considered. This version of the program shows less time of the search and the best quality for the restoration for some formfactors.

The problem of finding the particle size distributions in polydisperse systems was modified in several respects. 1) Improved stability of solutions by introducing nonequidistant angular grid to calculate the R-factor. 2) A more efficient algorithm for finding the minimum of the target function NL2SOL was applied (Levenberg-Marquardt algorithm, enhanced by approximation of Hessian matrix using the variable metric scheme). 3) A secondary search for a solution was applied based on the minimization of the residuals weighted by the inverse function of the relative systematic residuals which are calculated from statistical analysis of the residuals obtained after the first iteration of the search.

Some general quality criteria for solving inverse problems are considered, based on the calculation of the relative systematic error in the difference between the experimental and model scattering data.

Increasing the resolution of SAXS-derived ab initio models

Small angle X-ray scattering measurements of dilute, homogenous particles in solution are resolution limited measurements of the thermodynamic ensemble. Similar to X-ray crystallography and electron microscopy, SAXS observations made at higher scattering vectors (q) imply a greater detail in the structural measurement. This can be readily illustrated by P(r)-distributions derived from SAXS data collected at higher q-values. Here, the P(r)-distribution will demonstrate additional features (i.e., inflection points) as the resolution of the SAXS experiment increases. Therefore, I propose that a true *ab initio* model derived from a SAXS experiment must fully support the resolution-dependent features of the P(r)-distribution.

Here, I present a new *ab initio* modeling method that exploits two fundamental properties of Information Theory (namely, the Shannon Sampling and Noisy-Coding Channel theorems). These theorems allow for the error-free recovery of the SAXS signal, in the form of a real-space, cross-validated P(r)-distribution. The P(r)-distribution contains the structural assessment of the thermodynamic ensemble that is evenly distributed over discrete points determined by the Sampling theorem. As such, a simulated-annealing, bead-density modeling algorithm is proposed that targets the P(r)-distribution using the Kullback-Liebler divergence, an Information Theory difference metric. Compactness is achieved by treating the search space (i.e., the set of equally sized beads within a hexagonal close-packed lattice) as a convex set where the minimization seeks to minimize the feasible set of selected beads (convex hull).

The algorithm scales with resolution. Using a SAXS dataset of a 25 base-pair, double-stranded DNA, the volumetric model illustrates features of the major and minor groove as the resolution of the SAXS dataset increases. Further tests on SAXS of the P4-P6 group I intron RNA domain reveal the large solvent channels observed in the X-ray crystal structure. This method shows that modeling can be made more reliable by exploiting theorems from Information Theory. Information Theory helps mitigate the effects of outliers (e.g., inter-particle interference, aggregation, poor-buffer matching) and determines the effective resolution of the SAXS experiment.

NANOSTRUCTURE OF CALCITE CRYSTAL OF SEA URCHIN SPINE AND ITS MODIFICATION DURING *IN SITU* HEATING: THE ORGANIC - INORGANIC INTERFACE

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Calcite based material are very common in Nature. They often show complex shapes, fulfill various functions, as mechanical reinforcement, and present interesting optical properties [1]. They are therefore very interesting materials to study in order to propose new routes for the synthesis of bio-inspired materials [1]. Sea urchin (SU) spines are Mg^{2+} rich single crystals of calcite with their c-axis oriented along the spine's length (Figure 1) [2]. They are unexpectedly strong, stiff and lightweight partially thanks to the presence of intracrystalline molecules (glycoproteins, less than 1 wt%) selectively adsorbed on (110) planes of the crystal, and the presence of stabilized ACC (8% atom) [3-5].

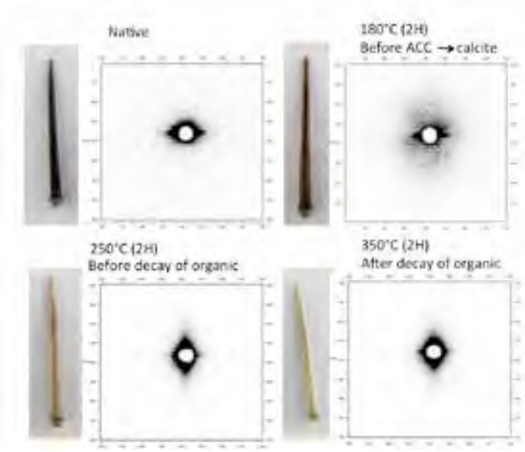

Figure 1: SAXS signals of the SU spines at different temperatures

Using thermogravimetry and differential scanning calorimetry measurements, we determined the temperatures at which the stable ACC transforms into calcite (200°C) and the temperature at which the organic fraction is lost (300°C). Small angle X-ray scattering (SAXS) measurements performed in our lab (Nanostar, MPICI) reveal significant structural modifications occurring at the different annealing temperatures (Figure 1.). Similar changes have been observed in other biogenic systems and have proved valuable for the localization and characterization of the inorganic-organic interface [6, 7].

Here, we present our results of *in situ* heating SAXS analysis performed at the μ-Spot beamline at BESSY II (Berlin). We draw conclusions regarding the crystallographic structure of the mineral phase and the nature of the amorphous-crystalline-organic-inorganic interface in SU spines.

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SAS INVESTIGATION OF SINTERED NIOBIUM POWDER SURFACE INHOMOGENEITIES

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This report presents a method for investigating of solid porous surface inhomogeneities. The method proposed was used to investigate the surface of compact niobium. Samples obtained by high temperature vacuum sintering of Nb powder. The technique described in [1] was used the small-angle X-ray scattering (SAXS). The range of scattering angles is to 2 up to 360 angular minutes. With the collimation process used and the radiation chosen, a resolution is achieved which allows to detect pores with dimensions from 0,1 to 50 nm. The SAXS measurements were treated according to special program which included the background curve substraction of the SAXS diffractometr through the use of the 5-point cubic interpolation technique in the region of every experimental point.

The following characteristic pore dimensions were obtained by SAXS: volume $V=10^6$ nm^3; area $S=10^4$ nm^2; dimension l=20nm. The pores, of which two dimensions exceed the third one (lamella), are approximated by cylinders. The curve of the SAXS data scattering invariant has some peak values. This indicates the polymodality of the surface inhomogeneities system. It should be noted that surface inhomogeneities displays the fractal nature. The approximation procedure of the cylinder shapes is known in the fractal theory as the Swartz area paradox [2].

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SAXS STUDY OF SUPPORTED METAL CATALYSTS: TECHNIQUES AND PERSPECTIVES

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Determination of particle sizes is an important and complicated problem in heterogeneous catalysis. At present, TEM, XRD and CO chemisorption are conventionally used for solving this problem. The SAXS potentially has much advantages compared to these methods. First of all, unlike transmission electron microscopy, SAXS yields information about particle sizes from a macroscopic amount of sample. Second, unlike XRD, SAXS allows for obtaining a particle size distribution instead of an average value of particle sizes. Also SAXS can be applied for study of amorphous and soft samples. However, SAXS is rarely used for determination of particle sizes in heterogeneous catalysts. The reason of low interest is the problem of distinguishing a weak scattering signal originating from supported metal particles from the huge background scattering signal of a porous support. One of the ways for effective separation these signals is a using of liquids with high density for masking support scattering [1].

The main barrier for application this concept is extremely high absorbance of X-ray radiation for typical high dense liquids (such as $CHBr_3$ or CH_2I_2). Despite on the opposite requirement to the masking liquids we design high-density liquid mixtures with relatively low X-ray absorbance. The main compounds of these mixtures are fluorocarbons which has good compromise properties between high density and low absorbance. Using this technique it is possible to mask parasitic scattering signal from any phases with density less 2.8 g/cm^3. In presentation will be discussed prospects and restrictions of new technique, examples of their application to study some catalysts and porous composites. Application of masking liquids for SAXS study of supported catalysts has been revealed advantage of this method versus TEM and XRD. Using this method we can get particle sizes distribution in the wide size range and analyze bulk inactive metal particles more effectively comparing to TEM and XRD. Another technique for getting selective scattering signal from supported metal particles is based on the removal of porous support matrix in catalysts. This technique has no limitation by support density ranges but not available in the cases of very stable oxide supports. Using these techniques we can effectively study different supported catalytic systems.

Acknowledgements

The author is grateful to A.V. Nartova for samples preparation and K.V. Obida for assistance in the investigations of the samples. The reported study was supported by RFBR, research project No. 14-03-31851 mol_a and by MES (Russia).

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LIVING WITH A SAS WEBLOG: HIGHLIGHTS AND LESSONS LEARNT

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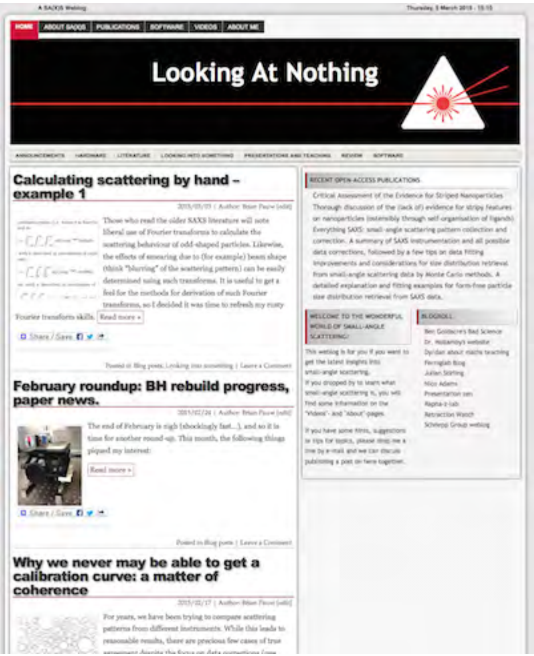
Since 2007, the LookingAtNothing weblog (and associated YouTube channel) has gradually evolved into a well-visited location for learning about small-angle scattering, and exploring aspects thereof [1] (Figure 1). It has led to a series of speaking engagements, improved contact with other scatterers and non-scatterers (leading to several papers), and resulted in interesting exchanges concerning specifics or advice on SAS. However, the weblog also comes with associated downsides: it is not typically considered to be a "valid" working activity for researchers, requires constant attention (about half a day per week), and is inherently biased to brief and small-scoped topics. From the years of blogging, then, several lessons may be percolated.



Looking At Nothing

HOME ABOUT SA(X)S PUBLICATIONS SOFTWARE VIDEOS ABOUT ME

Calculating scattering by hand – example 1

Those who read the older SAXS literature will note liberal use of Fourier transforms to calculate the scattering behaviour of odd-shaped particles. Likewise, the effects of smearing due to (for example) beam shape (think "blurring" of the scattering pattern) can be easily determined using such transforms. It is useful to get a feel for the methods for derivation of such Fourier transforms, so I decided it was time to refresh my rusty Fourier transform skills. Read more »

February roundup: BH rebuild progress, paper news.

The end of February is nigh (shockingly fast...), and so it is time for another round-up. This month, the following things piqued my interest: Read more »

Why we never may be able to get a calibration curve: a matter of coherence

RECENT OPEN-ACCESS PUBLICATIONS

WELCOME TO THE WONDERFUL WORLD OF SMALL-ANGLE SCATTERING!

BLOGROLL

Figure 1: The current look of the LookingAtNothing weblog

The weblog has been the driving force and outlet for many short, interesting (but often unpublishable) curiosity-driven investigations. Highlights include the development of the Live Fourier Transform teaching tool, investigations on the significance and derivation of several data corrections [2], a comparison between line-collimated versus pinhole-collimated instrument data, and comparisons between distance calibration methods.

Furthermore, one positive side-effect from running the weblog is the valuable feedback it provides. Readers of the weblog have been in contact to discuss unclear aspects of small-angle scattering. Their comments serve as powerful indicators (or reminders) of underdeveloped areas in SAS, in need of reinforcement or reiteration. Typical questions ask about introductory methods and materials, data correction software and methods, and data analysis guidelines.

But has blogging proven to be a productive waste of time? The answer depends very much on what results were expected. It certainly does not automatically lead to popularity or fame, and if it does so at all, it does so inefficiently. For more modest purposes, however, it works very well: it provides a central outlet for documenting the odd investigation and highlighting the work of the individual or group. Furthermore, its weakness is its strength: it forces the author to think at least once a week about something!

This talk explores some of these aspects of the weblog environment in a SAS community. It will provide examples of popular blog posts, and explore its need and utility.

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THE FUTURE OF SCATTERING: AN OPINION

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It may be of interest to the early-career small-angle scatterer to investigate the heading of our field. This talk attempts to address that need through an informed opinion on the current state and general direction of the field. Its contents will be based on the polling of peers, recent literature, the experience gained through running the LookingAtNothing weblog, and the small (and larger) curiosity-driven investigations reported therein [1].

The current broad range of applications of SAS indicates that it has to be flexible enough to adapt to broadening future applications, to maintain its status as a reliable and useful characterization technique. A question is thus raised that lies central to the future heading: "How good do we need to be, and where can we improve?".

The metrological approach to answering this is defined by numerical quality: estimating and improving the data accuracy and consistency [2], and determining its effects on the resultant morphological parameters [3, 4]. The numerical quality is dictated by both instrumentation and data correction methods. While we are now enjoying the luxury of bright sources, scatterless collimation, and largely problem-free detection solutions, some questions on (the necessity of) data corrections and reproducibility aspects remain to be answered. The first part of this talk will thus highlight recent advances in standardization, data reduction and analysis, and provide practical examples to estimate their impact.

The personal approach to the central question is defined by our communication: where and how (much) do we need to improve our outreach efforts? Fortunately, the aforementioned weblog has a valuable side-effect: readers of the weblog have been in contact to discuss unclear aspects of small-angle scattering, which serve as powerful indicators (or reminders) of underdeveloped SAS aspects in need of reinforcement or reiteration. Their questions highlight our need to develop and concatenate introductory methods and materials, data correction software and methods, and data analysis guidelines. Examples of these will be given in the second part of this talk.

Lastly, some words of warning may be appropriate, which may prevent alienation of the casual user. Such risks lie, for example, in the development of "black box" SAXS instruments that distance the user from the straightforward technique and its not-so-straightforward caveats, improper application or over-interpretation of the result effecting dissonance in results, or the lack of interoperable data formats and standard analysis methodologies. The final section of the talk will discuss these pitfalls with some examples.

This talk will thus provide a broad overview of the methods for the current state and future aspects of the technique. It will highlight areas of interest and encourage good practices in small-angle scattering. If all the pieces fall into place, our future can be amazing indeed.

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PHASE TRANSITION INDUCED BY 1-BUTANOL ON BINARY ASSEMBLIES OF SODIUM DODECYL SULFONATE AND WATER

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Hexagonal lyotropic liquid crystal (LLC) template is a facile method to prepare mesoporous materials with adjustable uniform pore size (2-50 nm) and large surface area (over 500m^2/g). However, the high inherent viscosity of the system makes the design and fabrication of new materials templated from this LLC mesophase difficult. In this study we examine a system which is lower in viscosity and has a wider tunable range of pore sizes: a ternary system of 1-butanol, sodium dodecyl sulfonate (SDS) and water (Figure 1). The range of the hexagonal phase is enlarged from a SDS concentration of 35-55% to 25%-55% (w/w). The hexagonal phase at lower SDS concentration is stable and less viscous. We aim to use this lower viscosity to modulate the kinetic barrier to an orientation of cylinders in applied field compared to system with a higher SDS concentration. Additionally, the pure cubic phase is converted from hexagonal phase and lamellar phase when the SDS range is 65-75% (w/w) and the coexistence of lamellar phases with two d-spacing in one system is observed when SDS concentration is up to 90% after addition of 1-butanol. The addition of 1-butanol making the binary system of SDS and water more promising for various mesoporous material fabrication templated from diverse LLC mesophases compared to pure SDS system.

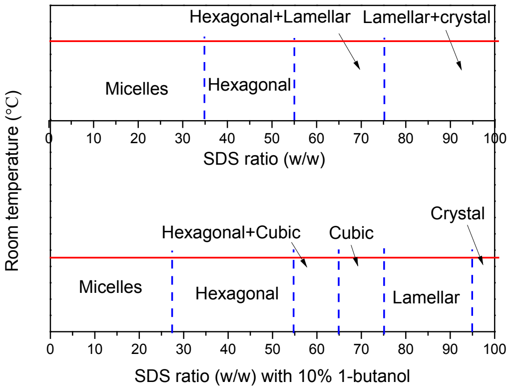

Figure 1 SDS phase diagram before and after adding 1-butanol

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SASCALC—A FAST AND COMPREHENSIVE SCATTERING CALCULATOR FOR CHEMICAL AND BIOLOGICAL SYSTEMS

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Increasingly atomistic models are being used to interpret small-angle X-ray and neutron scattering studies. Often, large structure ensembles (>105 configurations) are required for thorough analysis. Existing calculators, while robust and widely used, are mainly limited to study biological systems over a limited range in momentum transfer, Q. Recently, a new method to account for excess scattering density at molecular surfaces through calibration using atomistic simulations has been developed that extends the range and accuracy of scattering to a wider range of Q. Thus, there is a need to develop an open-source high-throughput accurate small-angle scattering calculator to enable the use of atomistic models to model scattering data.

We have developed a new program, SasCalc, that can be used to calculate small-angle scattering profiles for chemical and biochemical systems. The program utilizes a simple rapid real-space algorithm to calculate scattering profiles using the golden vector method [1]. This method has been shown to scale linearly with the number of atoms and is as accurate as established multipole expansion methods. Solvent contribution has been implemented using Hypred [2] and is being expanded to handle generic co-solvents and conditions. Currently, SasCalc is implemented using CUDA and therefore accesses modern graphical processing units to dramatically reduce the time to calculate accurate scattering profiles for ensembles of structures. SasCal is available in the atomistic scattering analysis package SASSIE [3]

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