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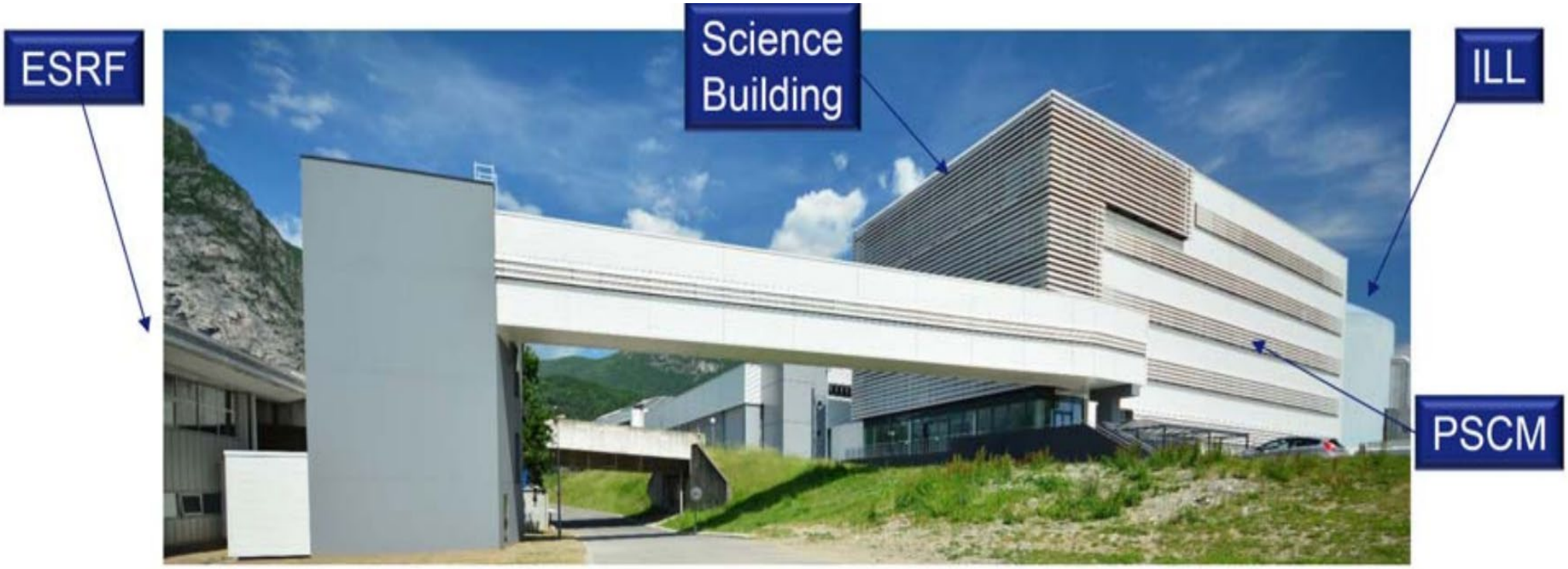
4th – 6th March 2024



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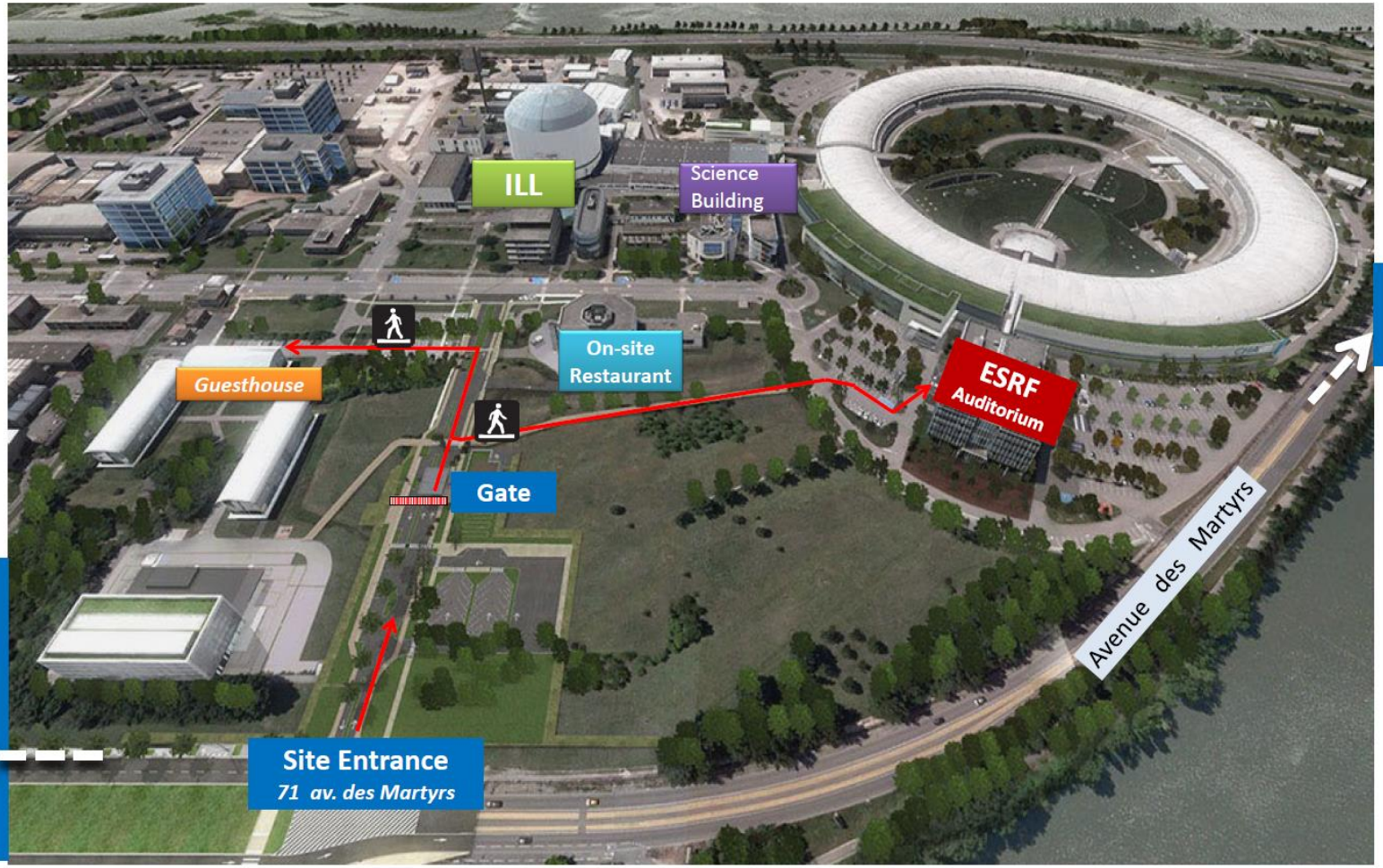

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Partnership for Soft Condensed Matter User Meeting

Monday 4 March

from 11:00	**Registration** at ESRF Central Building Entrance Hall **Poster installation** at Science Building 2nd Floor
12:00 – 13:30	**Lunch** at Common Restaurant

Opening – ESRF Auditorium		
13:45 – 13:55	General ESRF introduction	**Michael KRISCH** ESRF, France
13:55 – 14:05	General ILL introduction	**Jacques JESTIN** ILL, France
14:05 – 14:15	PSCM introduction	**Leonardo CHIAPPISI** ILL, France **&** **Diego PONTONI** ESRF, France
Session 1 - Chair: Michael KRISCH		
14:15 – 14:55	Soft and responsive: exploring the structure and dynamics of microgels	**Roberta ANGELINI** CNR, Italy
14:55 – 15:20	Mixed, stirred or shaken: The nanoscale structure of ionic liquid cocktails	**Moshe DEUTSCH** Bar-Ilan University, Israel
15:20	Coffee break (Group photo – ESRF Entrance hall)	
Session 2 - Chair: Jacques JESTIN		
15:40 – 16:20	Scanning Small Angle X-Ray Scattering for Cell Imaging	**Sarah KÖSTER** University of Göttingen, Germany
16:20 – 16:45	Solvent extraction in the spent nuclear fuel field: correlation between interfacial structure and kinetic of ion transfer at the liquid/liquid interface	**Olivier DIAT** ICSM, CEA, France
16:45 – 17:05	Investigation of aqueous foam from pea-based albumins using small-angle neutron scattering	**Ruifen LI** Aarhus University, Denmark
17:05 – 18:00	**Free Open Discussion** **Moderators**: Leonardo Chiappisi, Diego Pontoni **Available for discussion**: Jacques Jestin, Michael Krisch, Ralf Schweins, Oleg Konovalov	
18:30	**POSTER SESSION** with Wine & Cheese - **SCIENCE BUILDING 2nd FLOOR**	

Tuesday 5 March – ESRF Auditorium

Session 3 - Chair: Sarah KÖSTER		
9:00 – 09:40	Liquid crystal science at the ESRF: from bulk structural properties to thin film ordering	**Francesco VITA** Università Politecnica delle Marche, Italy
9:40 – 10:05	X-ray diffraction identification of smectic layer distortion in thin films	**Emmanuelle LACAZE** CNRS UPMC, France
10:05 – 10:25	Investigation of ganglioside GM3 in model membranes for cancer therapy	**Caterina RICCI** University of Milan, Italy
10:25	**Coffee break**	
Session 4 - Chair: Roberta ANGELINI		
10:40 – 11:20	Uncommon Phase Behaviour and Structures Induced by Addition of Cosurfactant to Nonionic Micelles – Cylindrical Assembly of Small Micelles	**Michael GRADZIELSKI** Technische. Univ. Berlin, Germany
11:20 – 11:45	Microtube self-assembly leads to conformational freezing point depression	**Jasper LANDMAN** Wageningen University, The Netherlands
11:45 – 12:05	Aging of a natural colloidal gel investigated by time-resolved mechanical spectroscopy	**Thomas GIBAUD** ENS de Lyon, France
12:05 – 12:25	Polyethylene glycol-based polymer bottlebrushes: Synthesis, stability and anti-fouling properties	**Larissa DOS SANTOS** ILL, France
12:25 – 13:30	**Lunch**	
Session 5 - Chair: Oriano FRANCESCANGELI		
13:30 – 14:10	Insight on the myoglobulin interaction with lipid bilayers within sponge phases using polarized neutron reflectometry	**Tommy NYLANDER** Lund University, Sweden
14:10 – 14:35	Electrostatic interaction between lipid layers: beyond Poisson-Boltzmann theory	**Thierry CHARITAT** CNRS, France
14:35 – 14:55	Spontaneous formation of a cushioned lipid membrane? What we have learned	**Amanda ERIKSSON SKOG** Lund University, Sweden
14:55 – 15:15	Orthotropic organization of a cellulose nanocrystal suspension realized via the combined action of frontal ultrafiltration and ultrasound as revealed by in situ SAXS, SALS and dichroism.	**Frederic PIGNON** Univ. Grenoble Alpes, France
15:15	**Coffee break**	
Session 6 - Chair: Michael GRADZIELSKI		
15:30 – 15:50	Salt-induced temperature dependent liquid-liquid phase separations in protein solutions	**Christian BECK** Univ. Tübingen, Germany
15:50 – 16:10	Polypeptide/surfactant films: three-dimensional structure control	**Javier CARRASCOSA** ILL, France
16:10 – 16:30	Structure and dynamics of protein-nanoplastic complexes	**Stefano DA VELA** Alfred-Wegner-Inst. Bremerhaven, Germany
16:30 – 16:50	Multi-scale diffusion in therapeutic monoclonal antibody solutions	**Ilaria MOSCA** ILL, France
16:50 – 20:00	**Free Time / PSCM Lab visits upon request**	
20:00	**Social Dinner in town with "one feedback per table" game**	

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Wednesday 6 March – ESRF Auditorium

Session 7 - Chair: Tommy NYLANDER		
9:00 - 9:20	NR determination of the structural profile of asymmetric myelin membranes and their interaction mechanism with Myelin Basic Protein (MBP)	**Julio Martin PUSTERLA** Forschungszentr. Jülich, Germany
9:20 – 9:40	Simultaneous Interfacial Rheology and Neutron Reflectometry studies of interfacial films	**Pablo SANCHEZ PUGA** ILL, France
9:40 – 10:00	Between tribology and soft matter: understanding the fundamentals of Organic Friction Modifiers behaviour	**Inga KICIOR** ESRF, France
10:00 – 10:20	Structural changes in lipid monolayers induced by synapsin and vesicles investigated using X-ray reflectivity and GID	**Titus CZAJKA** University of Göttingen, Germany
10:20	Coffee break	
Session 8 - Chair: Moshe DEUTSCH		
10:40 – 11:00	Structural and thermodynamic variations occurring during protein denaturation	**Judith PETERS** UGA + ILL, France
11:00 – 11:20	Unfolding and refolding of Albumin induced by a time-programmable dissipative pH-jump	**Alessandra DEL GIUDICE** Università di Roma La Sapienza, Italy
11:20 – 11:40	Phase behaviour of cotton-derived cellulose nanocrystal suspensions in water and in the presence of salts	**Vladimir GRACHEV** KU Leuven, Belgium
11:40 – 12:00	New Insights on the Molecular Structure of Tear Film Lipids Revealed by Surface X-ray Scattering	**Ryan TREVORAH** University of Helsinki, Finland
12:00 – 12:30	**Wrap-up** Summary of discussions and conclusions	**Leonardo CHIAPPISI** & **Diego PONTONI**
12:30 – 13:30	Lunch and departure	

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SoftComp SOFT MATTER COMPOSITES

Speaker Abstracts

Soft and responsive: exploring the structure and dynamics of microgels

Roberta Angelini[1,2]

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2Dipartimento di Fisica, Sapienza Università di Roma, Roma, 00185, Italy

Microgels are soft particles made by cross-linked polymer networks with a hybrid nature between that of polymers and colloids. They are widely used as a colloidal model system because of their swelling properties and their responsivity to external control parameters such temperature or pH. The phase behaviour of microgels has attracted great attention thanks to the large variety of new phenomenology emerging from their ability to pack at very high volume fractions. Combining rheology [1,2], x-ray photon correlation spectroscopy [3] and small angle x-ray scattering, we perform an extensive experimental study of a thermo- and pH-sensitive microgel composed of Interpenetrated Polymer Network (IPN) of poly(N-isopropylacrylamide) (PNIPAM) and poly(acrylic acid) (PAAc) at fixed PAAc content as a function of weight concentration with the ultimate goal of understanding its complex phase behavior. We distinguish three different states: liquid, glass and jammed characterized by three different rheological, dynamical and structural regimes. The possible molecular mechanisms driving the formation of these states is discussed [1] and a preliminary T- C_w phase diagram is drawn [4].

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Mixed, stirred or shaken: The nanoscale structure of ionic liquid cocktails

PSCM User Meeting 2024

Moshe Deutsch[1], Diego Pontoni[2], Marco DiMichiel[2]

[1]Bar-Ilan University, Israel , [2]ESRF, Grenoble, France

Room temperature ionic liquids (RTILs) are organic salts comprising bulky and irregular-form ions which prohibit their solidification down to room temperatures and often well below. First reported in 1877, then in 1914, they were practically forgotten until the 1990's when their potential for a plethora of applications, ranging from batteries to embalming fluids was realised [1]. They have since enjoyed an explosive growth in research due to their rare complex-liquid, hierarchical, bulk structure, and unusually broad variety of interactions, ranging from the major Coulomb and Van der Waals ones, to solvophobic, dispersion, hydrogen bonding, dipole-dipole, electron-pair donor/acceptor interactions, and more [2]. Although the over-1000 RTILs synthesized to date (more than all naturally-occurring salts) already present a broad range of physical and chemical properties to choose from, RTIL mixing is a cheap and easy way for fine-tuning RTILs' properties to specific application. Yet, such mixtures' nanoscale structure, and its relation to that of its pure components has scarcely been studied at the molecular level.

"To understand function, study structure!" [3]. So, we have studied by x-ray scattering the nanostructure of binary mixtures of the model RTIL family $[C_nmim][NTf_2]$. One study [4] explored the temperature and composition structure evolution of n=8,12 mixtures, and the other [5] – that of equimolar n_1=12 and n_2=1-22 mixtures. Following a brief introduction on the layered nanoscale structure of the pure $[C_nmim][NTf_2]$ RTILs [6-7], we'll discuss our mixtures' results, including their nanostructure evolution with composition, n-difference, and temperature. While the layered nature of the pure components is mostly preserved and observed to be dominated by the mixture's longer-chain species, the studies reveal a surprising evolution with n_2 from a solution-like to a conventional layering behaviour. The mixtures' layer spacings deviate significantly from classical Vegard's Law (VL) of ideal mixtures, but agree well with the *modified* VL of soft-solids, yielding powers akin to rotator phases of alkanes and of alcohol mixtures. Finally, our mixtures' layer spacings are found to depend linearly on the normalized n-difference of the components, squared. The same dependence was found [8] for the mismatch energy due to chain lengths' difference, dominating the surface-frozen phases of binary alkane and alcohol mixtures. This may indicate a dominant impact of the mismatch energy of the cationic alkyl chains on the nanoscale structure of our RTIL mixtures as well.

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Scanning Small Angle X-Ray Scattering for Cell Imaging

S. Köster[1], M. Burghammer[2], C. Cassini[1], B. Yu[1], M. Sinha[1]

[1]Institute for X-Ray Physics, University of Göttingen, Germany, [2]ESRF – The European Synchrotron, Grenoble, France

Arguably the most well-established methods for imaging biological cells are fluorescence microscopy and electron microscopy. While each of them provides unique advantages and both have seen tremendous advancements over the last years, one serious draw back remains the need for invasive sample preparation and labeling, and the low penetration power of visible light photons and electrons. Here, X-ray imaging as a complementary technique can help to address these challenges. X-Rays probe electron densities, thus work without specific labels and they can enter deep into material, thus enabling the imaging of whole cells or even tissues. Among the many X-ray imaging modalities that have been introduced over the past decades, scanning small angle X-ray scanning (SAXS) combines imaging in real space with a resolution of the order of the beam size, with structural information derived from analyzing scattering signals in reciprocal space. Others and we have shown that scanning SAXS can be applied to image single cells in freeze-dried, fixed-hydrated or even living state [1]. More recently, we have applied a special fast scanning mode available at ID 13 of ESRF combined with very short exposure times and intense beams that are provided after the EBS (extremely brilliant source) upgrade to scan statistically relevant ensembles of cells [2]. We combined these scans of hundreds of cells with semi-automated segmentation and data analysis algorithms to derive meaningful quantification of cellular parameters. Our current work includes the design of a versatile, yet robust flow chamber [3] so as to keep fixed-hydrated and eventually living cells in liquid conditions throughout the measurements.

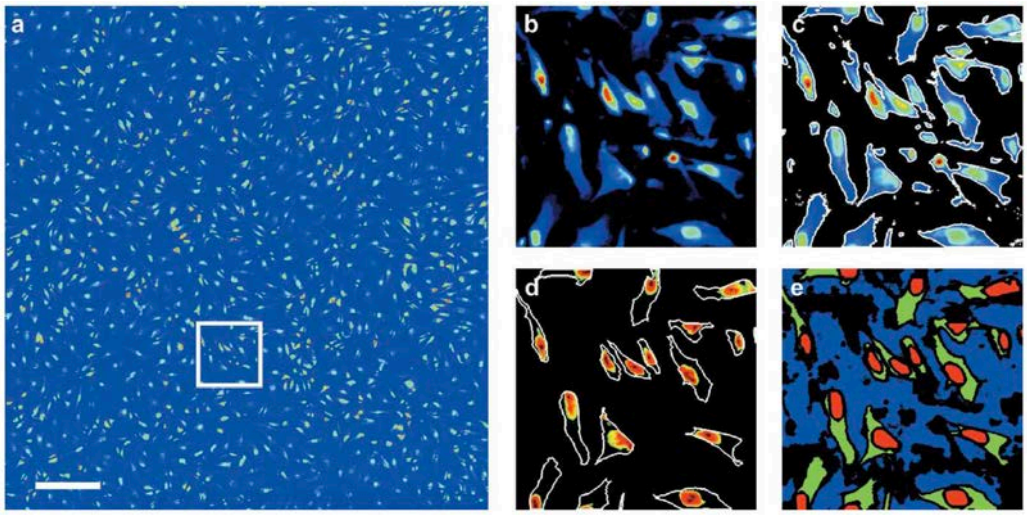

Figure 1: from [2]; a) X-ray dark field image of hundreds of individual cells on a SiN window, scale bar: 200 µm. (b) Detail of the region inside the white box in (a). (c) Result of local thresholding, showing the same region as in (b), but the pixels identified as background have been masked out. (d) Result of global thresholding on single cells, showing the same region as in (b), but only the nuclei. (e) Final regions of interest for the region shown in (b). Background is shown in blue, cytoplasm in green and nuclei in red. Black pixels are disregarded.

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« Solvent extraction in the spent nuclear fuel field: correlation between interfacial structure and kinetic of ion transfer at the liquid/liquid interface»

O. Diat[1], X. Ma[1], J. Dailland[2], L. Girard[1]

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[2]ESRF, Grenoble, France

Tributhyl Phosphate (TBP) extractant is the benchmark ligand molecule in the industry of spent nuclear fuel recycling, used to extract and separate uranium and plutonium elements from other fission products during the first stage of the recycling process (1). Although, its efficiency in the process, it has some drawback such as a chemical degradation under irradiation, formation of phase demixion (3rd phase formation in the solvent extraction language), to be a non-incinerable molecule in the ultime waste management process (due to P atom) and so on. A number of national institutions involved in nuclear spent fuel recycling are looking into new alternatives. The family of monoamide molecules appears to be a strong strategic option with some advantages (2).

A few years back, we worked on solvent extraction within the framework of the PSCM, specifically studying the liquid/liquid interface with ligands (or extractant molecules) from the diamide family, which are designed for the selectivity of lanthanides and actinides, and combining measurements of neutron and x-ray reflectivity (3). The accompanying energy landscape that controls the kinetic of ion transfer (the ienaic) was important to identify by understanding the nature of these interfaces as a function of multiple thermodynamical parameters. Techniques like X-ray and neutron reflectivity are very suitable to investigate these types of buried interfaces at equilibrium and at the nanoscale. We have built a new cell specifically for this investigation and developed a unique data processing protocol, and finally demonstrated that various interfacial organization types could be seen and account for varying ion transfer rates (diffusion- or kinetically limited regime). While diamide self-assemble in compact inverted aggregates in the organic phase that help to the ion transfer from the aqueous phase to the organic phase during the extraction and separation process, simulation and experiment data suggest that monoamide-type extractants have the tendency to self-assemble in polymeric aggregates that significantly affect the organic phase's viscosity according on the composition of ions and acids. What is the structural organization of monoamides at the liquid-liquid interface and how does it influences ion transfer and selectivity? This intriguing question presents a novel inquiry and challenge. This paper aims to delve into the current research landscape in this field and provide insights into the developmental prospects within the PSCM.

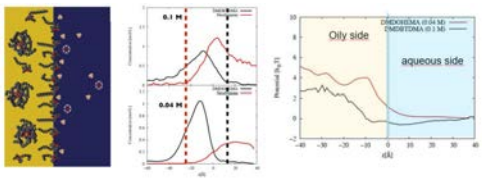

Figure 1: left) schematic view of a liquid/liquid (LL) interface with extractant molecules. Center) ion and extractant distribution at LL interface for two types of extractant. Right) energy barrier at the interface for two types of extractant.

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« Investigation of aqueous foam from pea-based albumins using small-angle neutron scattering– PSCM User Meeting 2024»

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Aqueous foams are important in creating appealing structures in food, but appealing foams with plant-derived proteins are not yet well developed. Studies on the foaming properties of plant proteins are needed. Albumins, present in the side stream extracts of plant protein have shown promise as functional foaming ingredients. This study investigates for the first time the foaming properties of pea albumins, evaluating them in native and aggregated states. We report the simultaneous time-resolved investigation of foams by small-angle neutron scattering (SANS), together with bubbles imaging, from the nanometer to the millimeter scale. Liquid foams were stabilized by pea albumins treated with different pH (3, 4.5, and 8) and evaluated before and after heating at 90 °C for 1 and 5 min the solutions. The SANS scattering intensity was modeled to quantitatively assess foam properties such as liquid fraction, specific surface area of the Plateau borders and inter-bubble films, and thin film thickness. These parameters were related to the liquid fraction and bubble sizes obtained from image analysis. Results demonstrated that film thickness was the highest for albumins pH 4.5, and at pH 8 the foams had the lowest specific surface area. The liquid fraction did not show significant differences among the different pH during aging time (~80 min). Heat treatment led to the increase of the specific surface area and decrease of the film thickness, especially at pH 4.5. This work will show how with this multiscale approach it is possible to understand the underlying foam destabilization mechanisms of albumins and how using advanced physical techniques in relevant environments it is possible to develop the necessary understanding to design more sustainable food foams with appealing physical properties and stability.

Liquid crystal science at the ESRF: from bulk structural properties to thin film ordering

F. Vita, F.C. Adamo, O. Francescangeli

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Among the several different mesophases formed by liquid crystalline materials, the nematic (N) phase of calamitic (*i.e.*, rod-like) liquid crystals (LCs) is by far the most well-known, as it provides the basis for the widespread LC display technology. Its fundamental feature is the average alignment of the molecules' long axes along a common direction, which typically results in an apolar uniaxial phase symmetry. However, over the years, the synthesis of new mesogenic compounds with more complex molecular structures has led to the discovery of a long catalogue of novel mesophases exhibiting unconventional physical properties. In this regard, bent-core mesogens (BCMs), a class of compounds characterized by a kinked aromatic core between two terminal aliphatic tails, have emerged as promising candidates in the long-standing search for the elusive biaxial and polar N phases [1,2].

Here we summarize our long-standing research activity at the ESRF aimed at exploring the nanostructure of a variety of unconventional LCs (including BCMs) by means of X-ray diffraction and scattering techniques. Our investigations have revealed how the N phase of BCMs is dominated by the presence of nanosized clusters of layered molecules, known as cybotactic groups, which impart unique biaxial and polar properties to the mesophase, together with an unprecedented high sensitivity to external fields [3,4].

More recently, in the frame of the PSCM project, we have undertaken the study of the nanostructure and molecular ordering on thin films of LCs at interfaces, which is key in the surface-to-bulk ordering transfer while still being essentially unexplored. We demonstrated that Langmuir techniques offer an effective strategy for studying and controlling the anchoring of BCMs, inducing biaxial alignment over macroscopic surfaces [5,6].

Finally, we report on our recent study of a liquid crystalline graphene oxide nanocomposite. We show that an extraordinary enhancement of modulus and tensile strength is obtained in polymer films cast from a hybrid biaxial N phase: a mesoscopic lyotropic nematic comprised of stratified GO platelets dissolved in a lyotropic polymeric nematic with respective directors orthogonal to each other. This biaxial nanostructure, which is preserved on drying, is crucial to obtain robust, structural nanocomposite films [7].

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X-ray diffraction identification of smectic layer distortion in thin films

E. Lacaze[1], J.D. Niyonzima[1, 2], H. Jeridi[1, 3], A. Vlad[4], L. Essaoui[1], C. Tosarelli[1], A. Coati[4], D. Constantin[5], D. Babonneau[6], Y. Garreau[4], B. Croset[1]

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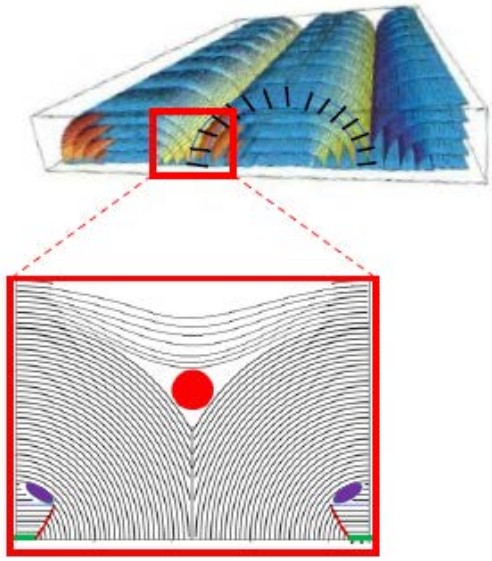
The breaking of continuous symmetry in ordered systems results in topological defects, which are the places where the order melts. Due to their ubiquitous nature and versatility, the topological defects have been of a great interest for over a century in different research area such as cosmology, biology and condensed matter physics. They are important in the determination of dynamic and static properties of the material that host them. However, their intimate structure remains elusive. Liquid crystals are laboratory systems to study topological defects. In such a context smectic liquid crystal thin films are useful since they allow for the use of X-ray scattering to study the defects at an unprecedented resolution. Uni-dimensional patterns of oriented smectic topological defects are obtained in thin smectic-A liquid crystal films of 4-n-octyl-4'-cyanobiphenyl (8CB) due the two strong antagonistic anchorings imposed by Polyvinyl alcohol substrate (planar unidirectional) and air (homeotropic – molecules perpendicular to the air interface). The planar orientation on the substrate is provided by a rubbing machine aimed at rubbing the polymer along a unique direction, the machine being brought to the PSCM laboratory. PSCM spin-coating also allows formation of homogeneous liquid crystal thin films on the rubbed polymer substrate. The defect structure being dependent on the precise sample thickness, a map of the thickness variations for a given sample must be provided by the polarized Optical Microscope available at the PSCM laboratory [1].



We studied a film of 180 nm thickness and found that it is composed of flattened hemicylinders made of superimposed smectic layers (see the figure where the smectic hemicylinders are seen in side view). Combining GISAXS measurements and calculations of the integrated scattered intensity, we could determine the intimate structure of these hemicylinders. We reveal a complex structure associated with different types of coexisting topological defects. These are in particular dislocations (in purple), disclinations (in red) and 2D topological grain boundaries (in green), all oriented in the direction parallel to the axis of the hemicylinder. We demonstrate that the disclination core size surprisingly varies as a function of the film thickness. Large dilation of the smectic layers around the defects is also revealed which appears induced by the non-linear elasticity of these highly distorted smectic layers.

Références [1] – D. Coursault et al. Self-organized arrays of dislocations in thin smectic liquid crystal films, *Soft Matter*3, 629 (2016).

« Investigation of ganglioside GM3 in model membranes for cancer therapy – PSCM User Meeting 2024»

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Gangliosides are glycosphingolipids composed of a ceramide and an oligosaccharide chain, containing at least one residue of sialic acid. The two major sialic acid variants in mammals are N-acetylneuraminic acid (Neu5Ac) and N-glycolyneuraminic acid (Neu5Gc), the difference relying only in one oxygen atom. However, Neu5Gc-sialoconjugates are absent from human normal tissues, while N-glycolylated gangliosides, and in particular GM3(Neu5Gc), have been observed in a wide range of human tumors of the kidney, ovary, uterus, testis, and prostate, as well as in breast cancer and in melanoma. Importantly, in these studies GM3(Neu5Gc) was rarely detected in the corresponding normal tissues, confirming its tumor-specific expression and suggesting to consider this antigen as a target for cancer immunotherapy. [1]
The effect of gangliosides in cancer is strictly linked to their presence in lipid rafts. Changes in rafts by manipulation of sphingolipid and cholesterol content can promote proliferative signaling through lateral membrane microdomain re-organisation. Different results suggest that the quality and quantity of lipid rafts are important for the therapeutic response of cancer cells [2].
Thus, the analysis of the structural properties of model membranes, in particular lipid raft-mimic, in presence of GM3 and the observation of the differences with respect to the behavior of GM3Neu5Gc can be important for the development and optimization of novel therapeutic strategies based on targeting lipid rafts of cancer cell membranes.
Measurements by differential scanning calorimetry, Langmuir deposition and Neutron Reflectometry on model membranes show evident differences in the arrangement and thermotropic behaviour of membranes in presence of ganglioside and as a function of the GM3 variant. The investigation of the structural properties of GM3-containing lipid rafts, also as a function of cholesterol molar ratio can help both in the comprehension of structural changes occurring in tumor tissues and, as the final goal, in the development and optimization of novel therapeutic strategies based on targeting lipid rafts of cancer cell membranes.

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Microtube self-assembly leads to conformational freezing point depression

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Multiwalled tubular aggregates formed by hierarchical self-assembly of beta-cyclodextrin and sodium dodecyl sulphate have a great potential as microcarriers. The highly cited article by Jiang, et al. [1] opened a new trajectory for this system showing that tubes can be a 1D confinement carrier for colloidal materials. However, it left open the question of why this self-assembling system forms in the first place.
Using ultra-small angle x-ray scattering, we are able to follow the multiscale structure of self-assembled microtubes as function of temperature, from the molecular to the micrometer scale and see that concentric microtubes grow from the outside in and melt from the inside out. In particular, we find that the overall conformation of the crystalline bilayer affects the saturation concentration, providing an example of a phenomenon we call conformational freezing point depression.
We propose a model based on freezing point depression, well known from undergraduate physics, and use it to explain the energetics of this hierarchical system, and giving access to material properties without free parameters.[2]

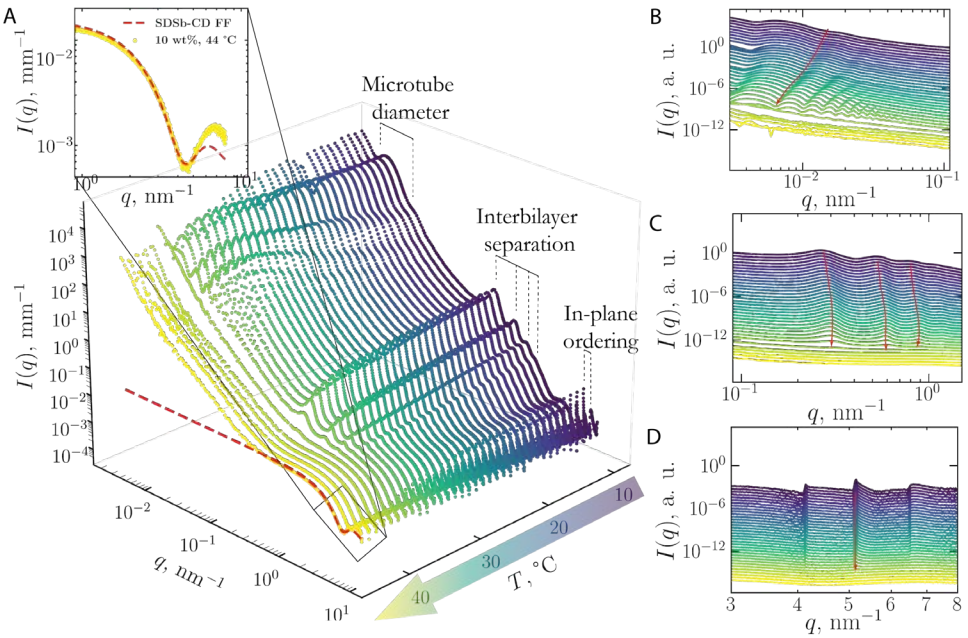

Figure 1: SAXS evolution of the melting of SDS-beta-cyclodextrin microtubes

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Uncommon Phase Behaviour and Structures Induced by Addition of Cosurfactant to Nonionic Micelles – Cylindrical Assembly of Small Micelles

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Properties of surfactant formulations are regularly modified by cosurfactant addition, resulting in systematic control of structure and properties. The structural changes are supposed to proceed by changing continuously the packing parameter of the self-assembled aggregates. According to common textbook opinion, cosurfactant addition to spherical micelles transforms them into increasingly longer wormlike micelles and at still higher cosurfactant concentration to bilayers by proceeding through a first order phase transition.

In this work we show a substantially different self-assembly behaviour, seen for a classical nonionic surfactant (polysorbart Tween 20) upon addition of 2-ethylhexylglycerol (EHG) as cosurfactant. Structural characterisation by light and neutron scattering (SLS, DLS, SANS), and especially cryo-TEM, shows that here elongated assemblies are formed. However, in contrast to normal expectation, they are composed of individual micelles that are locally ordered in a cylindrical fashion, which also explains the much lower viscosity observed in comparison to the normally expected worm-like micelles (WLM). A first-order phase transition takes place at higher cosurfactant content, but here only a smaller fraction of amphiphile is initially forming a bilayer structure and complete transformation to bilayers occurs within the single-phase region for EHG concentrations higher than the ones of the phase transition.

This very uncommon structural evolution has not been reported before, but can be rationalised by the particular structure of the amphiphilic molecules involved. Following up on this very uncommon phase behaviour observed for Tween 20/EHG we did a systematic study of other nonionic surfactants like tetradecyldimethylamine oxide (TDMAO) with a much smaller head group and a group of alcohols as cosurfactants, where the head group and the hydrophobic part were systematically varied. One observes systematic correlations between the molecular architecture of the surfactant and cosurfactant with the tendency for formation of WLM and the phase behaviour. These observations for the formation of different types of aggregates can be rationalised by geometrical arguments that can explain the observed structural and phase behaviour. This finding not only extends the common assumptions about surfactant assembly but should also be of importance for a better general understanding of how to formulate surfactants by the addition of cosurfactants.

Aging of a natural colloidal gel investigated by time-resolved mechanical spectroscopy

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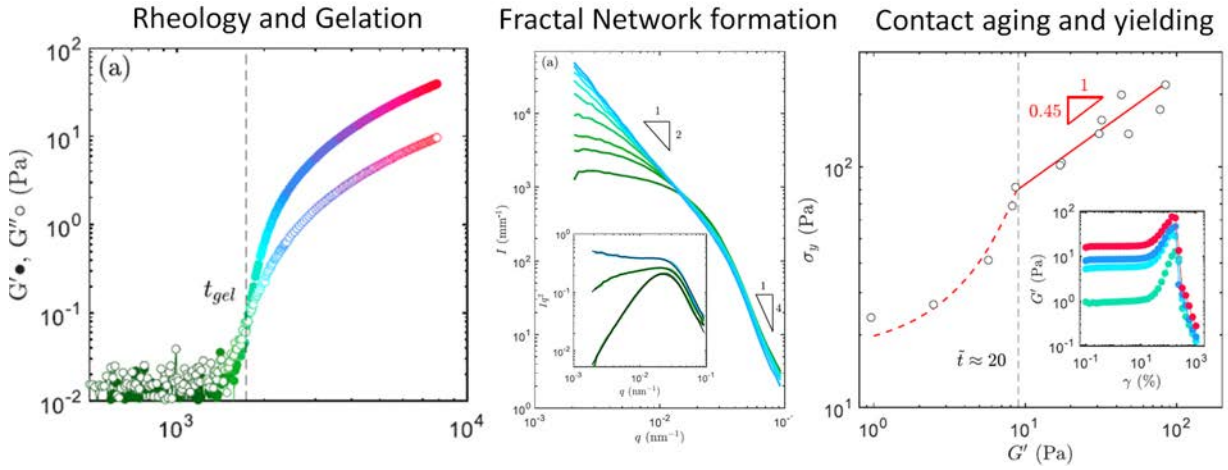
In the limit of strong particle interactions and low volume fraction, colloidal suspensions form gels, whose elasticity arises from the stress-bearing capacity of the particle network. In many "real-life" gel systems, the interparticle interaction energy is of the order of the thermal energy and bonds have a finite lifetime. Consequently, weak colloidal gels show time dependent properties, term as "aging", and attributed to structural rearrangements as the structure explores deeper energy minima. Macroscopically, the shear modulus is usually found to increase with time after gelation, along with the maximum relaxation time probed by dynamic light scattering. Recently, it was shown that a change of interparticle interactions with time could also lead to aging without structural changes. It evidences that the time-dependent properties of colloidal gels can have different origins and require systematic characterization to draw a general picture.

Enzymatic milk gels are natural colloidal gels formed through the destabilization of "casein micelles", a colloidal structure composed of proteins and minerals. After gel formation, the mechanical properties of the gel readily evolve, an essential feature for the early phases of cheese manufacture. From microscopy observations, it was postulated that aging proceeds through both structural rearrangement and particle sintering. In this study, we use time-resolved mechanical spectroscopy to investigate the time evolving viscoelastic properties of enzymatic milk gels in the linear regime.

First, using a combination of rheology and scattering experiments we show that then structural rearrangements are hindered by topological constrains, aging proceeds by contact aging solely, resulting in an increase of the moduli without changes in the mechanical spectrum signature.



Polyethylene glycol-based polymer bottlebrushes: Synthesis, stability and anti-fouling properties

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Biocompatible coatings are essential tools to promote an optimal environment for implant integration, to the controlled release of drugs, to regulate the permeability of molecules and to control the settling and accumulation of biological matter in diverse fields. The flexibility and ability to mimic natural tissues have raised the interest in using polymeric coatings in advanced functional substrates [1]. Among different architectures available for such coatings, polymer brushes have been widely exploited. These films combine the endless possibilities of polymer with different architectures to the development of surface modification techniques enabling the functionalization of a variety of surfaces [2]. Such versatility of chemical composition, thickness, adaptive physicochemical properties and surface density provide a toolbox to obtain polymer brushes with the desired characteristics.

Polyethylene glycol-based brushes have been at the forefront of biological applications and nanomedicine due to their non-specific anti-fouling properties, low toxicity, wide availability, and use history in medicine and drug delivery materials [3]. In this work, a surface-initiated activator regenerated by electron transfer atom transfer radical polymerization (ARGET ATRP)[4] was used to synthesize bottlebrushes of polyethylene glycol methyl ether methacrylate monomers (PEGMA) varying the number of ethylene oxide repeating units. The optimization of synthesis conditions was conducted and the brushes' characterization was performed by ellipsometry and atomic force microscope (AFM). Aiming the potential application in a medical device, different anchoring strategies have been employed to enhance the coating stability [5, 6]. PEGMA brushes anti-fouling properties were probed by quartz crystal microbalance with dissipation (QCM-D). The results pointed to an efficient prevention of bovine serum albumin adsorption in physiological conditions.

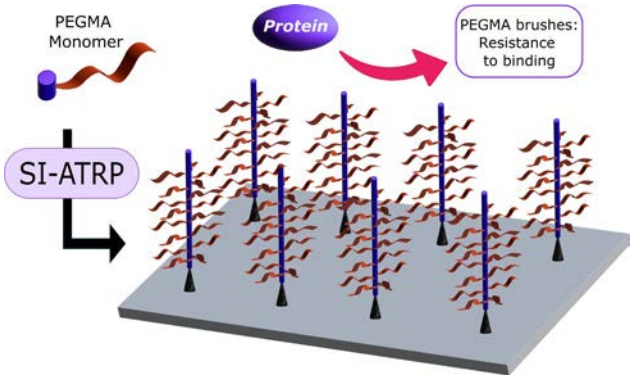

Figure 1: Representation of PEGMA bottlebrushes synthesized by surface-initiated atom transfer radical polymerization (SI-ATRP) from silicon oxide substrates.

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Insight on the myoglobulin interaction with lipid bilayers within sponge phases using polarized neutron reflectometry

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Lipid nanoparticles (LNPs) are dispersions of liquid crystalline phases [1,2] and feature different structure and curvature of the aqueous lipid interface, including inverse bicontinuous cubic (Q_2), sponge phase (L_3), or inverse hexagonal (H_2) structure depending on the lipid composition [1-3]. In previous work, we have characterised the encapsulation of several industrially relevant proteins: aspartic protease (34kDa, used in cheese production), β-galactosidase (456kDa, used for lactose free dairy products), and sugar beet phytoglobin (potential iron supplement replacement) into lipid sponge phases [4-7]. Here, the interaction between the protein and lipids is protein specific and can strongly affect both the structure and dynamics of the lipid nanoparticles. In the present study we focus on the hem-protein-lipid interaction with lipid bilayers, which is key for understanding the encapsulation of the iron binding hem-protein, such as myoglobin and phytoglobin, in the sponge phase. This type of hem-bound iron can be used to treat anaemia instead of iron in organic salts which is conventionally used. Encapsulation is needed to prevent unwanted proteolytic and redox reactions. We have used sponge phase LNPs with diglycerolmonooleate (DGMO), glycerolmonooleate (GMO) and Polysorbate 80 (P80) as well as LNPs where DGMO was partially replaced with Dioleoylglycerophosphocholine (DOPC) to form well defined lipid bilayers mimicing the lipid interface inside the sponge phase. To enhance the contrast and reduce the need of additional solvent contrasts we used silicon substrates with a switchable magnetic contrast layer (MCL) during polarised neutron reflectometry (PNR) [8]. These substrates consisted of 10 nm Fe layer capped with 100 nm SiO_2 layer to protect the Fe layer against corrosion and gave excellent response to the spin state of the neutrons. The formed lipid bilayers had a very high coverage of about 90%, which allowed studies of the interaction of the protein with the lipid interface. The results show that myoglobulin interacts so strongly with the lipid bilayer that it was mostly removed from the substrate. The presence of DOPC increased the stability of the bilayer that remains intact with very low amounts of protein attached.

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Electrostatic interaction between lipid layers : beyond Poisson-Boltzmann theory

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Lipid bilayers play key roles in biology, where phospholipid bilayers act as walls for cells and cellular organelles and also as matrices for membrane proteins. Most of the lipids constituting the cellular membrane are neutral or charged phospholipids. External leaflet contains zwiterrionic phospholipids like phosphatidylcholine (PC), whereas the internal leaflet is rich in aminophospholipids like phosphatidylserine (PS). The asymmetry of lipids distribution is an essential component of any living cell. Interactions between membranes are also fascinating for the physicists. Indeed, the phospholipid bilayers are two-dimensional model systems exhibiting a wide range of properties combining different length and time scales [1]. Because they are soft matter systems, both structure and fluctuations properties are strongly correlated. More specifically, interactions between charged surfaces raise a lot of fundamental questions. Many theoretical and numerical studies [2] have been done showing the limits of the Poisson-Boltzmann theory. The presence of charges can dramatically change the interactions between the surfaces, leading to
condensation of ions onto the membranes, or to attraction between close likely-charged surfaces.

We investigate the interaction between highly charged lipid bilayers in presence of monovalent ions [3]. Neutron and x-ray reflectivity experiments show that the water layer between like-charged bilayers is significantly thinner than for zwitterionic lipids, demonstrating the existence of counter-intuitive electrostatic attractive interaction between them. This can be explained by correlations between counterions beyond the classical Poisson-Boltzmann theory of electrostatics, in the Strong Coupling limit. Our results show the limit of the strong coupling continuous theory in highly-confined geometry and are in agreement with a decrease of the water dielectric constant.

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Spontaneous formation of a cushioned lipid membrane? What we have learned

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When exposing a supported lipid bilayer (SLB) to a solution containing the histidine-rich intrinsically disordered peptide Histatin 5 (Hst5), we observed the spontaneous formation of a cushion below the bilayer. [1] The formation is dependent on a number of conditions, for example, the charge of the lipid bilayer, the solid substrate, as well as the ionic strength of the system. Since this discovery, the work has continued to understand which properties of Hst5 responsible for this effect, the ability to translocate the lipid bilayer without leaving persisting deformations in the bilayer. The properties investigated so far has been the number of histidines in the sequence as well as the length of the peptide. Hst5 contains seven histidines, an amino acid known to charge titrate, therefore, variants of Hst5 with fewer histidines in the sequence was designed. [2] The size of the peptide could also be of importance for translocation, therefore, a peptide with half the sequence of Hst5, as well as double the sequence of Hst5 have been investigated. Quartz Crystal Microbalance with Dissipation Monitoring (QCM-D) and Nuetrom Reflectometry (NR) have been used to study the peptide-bilayer interaction. These measurements have been complemented with characterization of the Hst5 variants with Small Angle X-Ray Scattering (SAXS), Circular Dichroism (CD), as well as Molecular Dynamics simulations (MD).

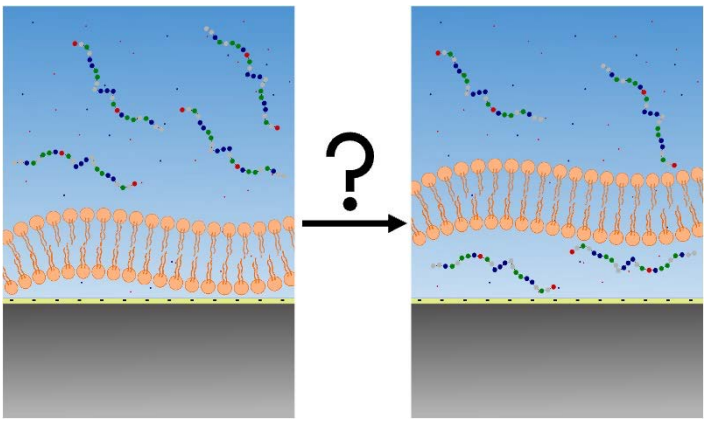

Figure 1: Schematic representation of the interaction of Hst5 and the negatively charged SLB.

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Orthotropic organization of a cellulose nanocrystal suspension realized via the combined action of frontal ultrafiltration and ultrasound as revealed by *in situ* SAXS, SALS and dichroism.

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Cellulose nanocrystals (CNCs) are particularly attractive crystalline nanoparticles for the design of new bio-based materials with enhanced mechanical, optical (iridescence) or barrier (oxygen or water) properties. One important challenge for reaching these specific functional properties is to control the orientation and organization of the materials during their processing, in a wide spatial scale and with controlled external fields with the best possible efficiency.
Recently, we were able to evidence the ability of the ultrafiltration processes to develop well-defined layered structures of CNCs [1-2]. Furthermore, we discovered by using ultrasound waves, it was possible to align the CNCs along the wave propagation direction [3].
In this work, an original combined frontal ultrafiltration (FU) and ultrasound (US) set-up compatible with in situ SAXS, SALS and dichroism observations has allowed revealing for the first time a multilayer orthotropic structuring of CNC suspensions, that mimics the organization of articular cartilage: a first layer composed of CNCs having their director aligned parallel to the horizontal membrane surface, a second intermediate isotropic layer, and a third layer of CNCs with their director vertically oriented along the direction of US wave propagation direction (Figure 1).
We have interpreted our observations, in particular the length scales and time scales involved in the spectacular alignment of the CNCs along the ultrasonic wave propagation direction in terms of Rayleigh acoustic streaming initiated by the viscous attenuation of the acoustic waves generated by the vibrating blade. These results open the way for developing novel orthotropic biomaterials with tunable structured cellulosic organizations for tissue engineering applications.

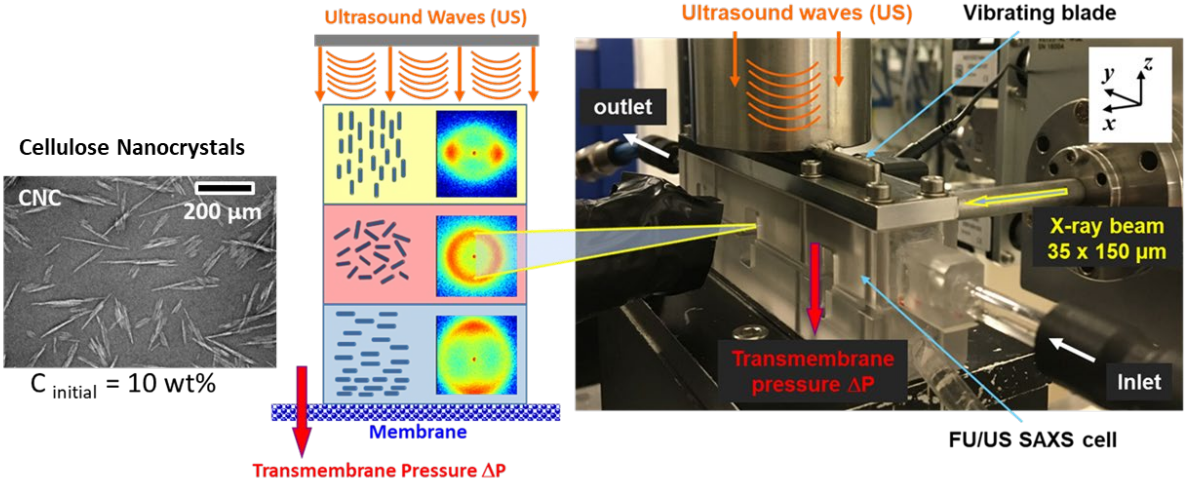

Figure 1: *in situ* SAXS experiment during combined frontal ultrafiltration and ultrasound processes revealing the multilayer orthotropic structuring of CNC suspensions, that mimics the organization of articular cartilage.

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Salt-induced temperature dependent liquid-liquid phase separations in protein solutions

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Multivalent saltions can induce a rich phase behavior in protein solutions (Figure 1a)[1]. Next to cluster formation [2], liquid-liquid phase separation (LLPS) can also be induced. This LLPS is temperature-dependent, which implies an easily accessible control parameter. By investigating different protein – salt combinations, we can draw, on the one hand, system-independent conclusions such as universal scaling laws. On the other hand, we are able to determine salt-specific properties such as different interaction strengths of the ions.
Within these systems, we have performed systematic studies exploiting several control parameters such as protein and salt concentration [2,3], temperature [2], isotope effects [4] and pressure [5]. To investigate the static and dynamic properties of the mixture as well as the dilute and dense phases of the LLPS, we have used various methods such as microscopy, temperature-dependent UV-Vis measurements, light scattering, small angle scattering, XPCS and QENS.

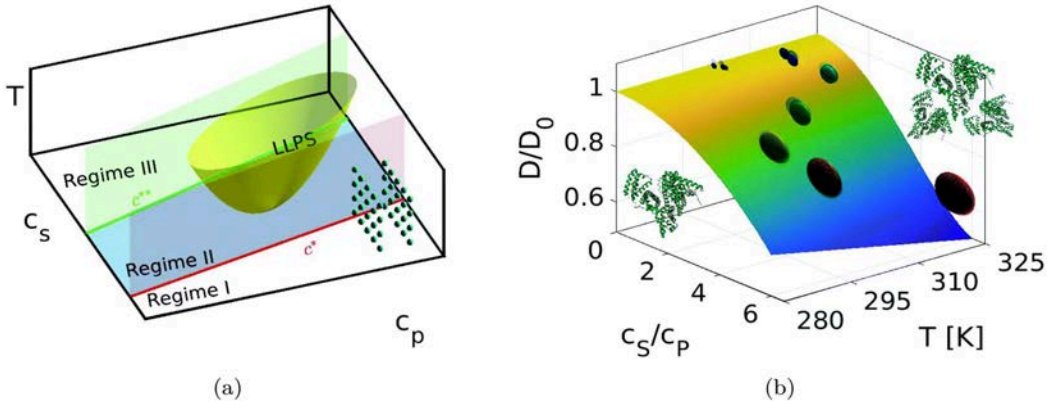

Figure 1: Left: Schematic phase diagram of a solution with negatively charged proteins in the presence of trivalent salts. The temperature dependence is indicated in the third dimension. Right: At a given temperature, the diffusion coefficient of BSA in a solution containing salt normalized by the one in salt free solution is independent from the protein concentration and only depends on the number of salt ions per protein. With increasing temperature, the salt-induced clustering is becoming stronger and the diffusion coefficient is decreasing.

Recently, systematic pressure variations [5] allowed us to investigate the pressure dependence of the clusters observed previously with QENS in Regime I (Figure 1b) [2]. We observe a pressure-induced increase of the diffusion coefficient, indicating a shift of the averaged cluster radius to smaller values.
With our latest QENS measurements [6], we were able to investigate the microscopic dynamic properties of the onset of LLPS, to separate the contributions to the scattering signal from the dense and dilute phases and to compare these contributions to the scattering signal obtained from the individual phase-separated samples.

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Polypeptide/surfactant films: three-dimensional structure control

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Polyelectrolyte/surfactant (P/S) mixtures have been extensively studied because of their use in everyday life products and their application in materials science. Over the last decade a number of protocols have been developed to create nanostructured films for use in a range of applications including tissue engineering and drug delivery. We have recently developed a methodology to create P/S films at the air/water interface by spreading a small aliquot of P/S aggregates formed in the bulk of an aqueous mixture [1]. The resulting films have a higher surface excess than those formed by adsorbing bulk complexes, thus providing environmental and economic advantages through the use of water as the spreading solvent.

We have turned recently to focus on the use of polypeptides as being generally biocompatible materials [2]. Our work demonstrate reversible 2D:3D control on a Langmuir trough of poly-L-lysine/sodium dodecyl sulfate (PLL/SDS) films and precise control of the formation of extended structures (ESs) and their coverage (see Figure). The use of the Langmuir trough in combination with ellipsometry, Brewster angle microscopy and neutron reflectometry (NR) allowed us to elucidate the compositional and structural changes taking place.

We go on to compare the structure and morphology of films from PLL/SDS mixtures, which adopt bulk β-sheet conformations, with films from poly-L-arginine (PLA)/SDS mixtures, which correspondingly adopt α-helices. Our working hypothesis was that differences in bulk secondary structures may translate into different properties of films that have ESs. Indeed, it is shown that specific polypeptide/surfactant interactions can be exploited to tune the resulting structures and morphologies of spread films.

With such unprecedented control and tuning of these film properties demonstrated, this research opens possibilities in the future to design new, efficient, biocompatible and/or biodegradable films with tailored properties for specific applications, e.g., in tissue engineering, biosensors and antimicrobial coatings.

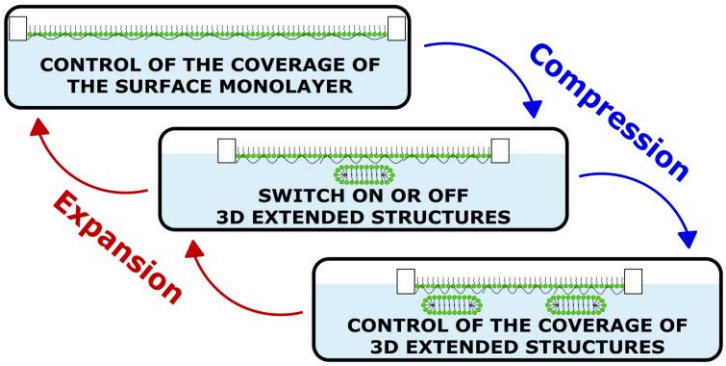

Figure: Schematic illustration showing control over the monolayer coverage, formation of ESs and their coverage.

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«Structure and dynamics of protein-nanoplastic complexes»

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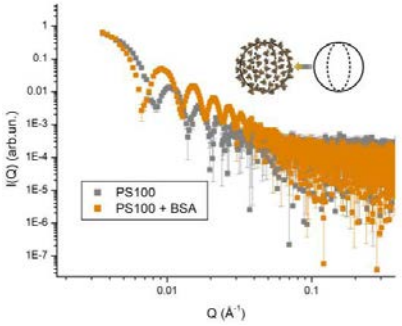
Anthropogenic pollution releases large amounts of plastics in aquatic environments. This includes plastic fragments reduced to sub-micrometre sizes, so-called nanoplastics, produced either upon machining or due to weathering effects [1,2]. This nanoscale fractions are actively investigated to assess their toxic potential [3-5]. One aspect crucial to the physiological effects and to the destiny of nanoplastics in organisms is the formation of a so called « protein corona », which modulates their interfacial properties. This talk summarizes findings on the structure and dynamics of the protein corona on polystyrene nanoplastic models of increasing complexity.



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Multi-scale diffusion in therapeutic monoclonal antibody solutions

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Monoclonal antibodies (mAbs) are relevant for therapeutic applications due to their specificity and versatility. One of the current pharmaceutical challenges concerns mAb formulation for subcutaneous injection, which is becoming the preferred delivery route due to its improved convenience compared to other parenteral administration methods.
Since volumes < 2mL are better tolerated in the subcutaneous space, highly concentrated mAb formulations are needed to achieve significant therapeutic effects, potentially leading to high viscosities and altered drug injectability. The main challenge is therefore to keep their viscosity below 15-20 mPa·s [1] without compromising the solution stability.
Since the understanding of macroscopic viscosity requires an in-depth knowledge on protein multi-scale diffusion, mutual interactions and aggregation [2,3], we employ high-resolution neutron spectroscopy techniques to investigate 9 different mAbs of IgG1/IgG4 subtypes in aqueous solution as a function of protein concentration and temperature. The synergy between quasi-elastic neutron scattering (QENS) and neutron spin-echo (NSE) spectroscopy allows us to probe short-time self- and collective diffusion of the different mAbs, to observe their different clustering behaviours and to access their internal dynamics [4,5,6,7] (Figs. 1,2). QENS data are treated using established analysis frameworks and are interpreted using colloid physics models [4,7]. Polyclonal antibody solutions are measured as a reference [8].

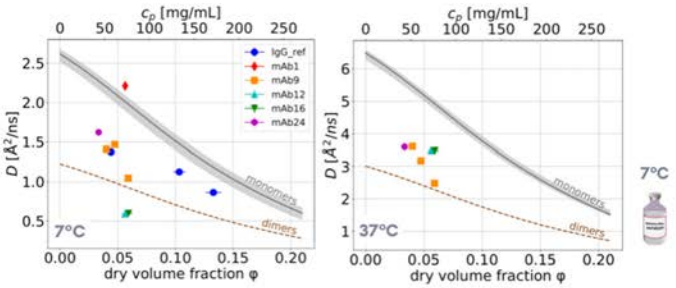

Fig. 1: Apparent self-diffusion coefficients D (symbols, obtained from global fits of QENS data collected on IN16b) of the mAbs and polyclonal IgG *vs* protein dry volume fraction φ (lower) and concentration c_p (upper x-axis) in solution at T=280 K (left) and T=310 K (right). Grey solid lines and shaded areas denote the value of D_{theo} for monomers averaged on all mAb structures and two other IgG crystal structures, obtained using a colloid physics hard-sphere model. Dashed brown lines are the approximated dimer curves obtained by rescaling the monomer ones by the dilute limit $D_{theo}(0)$ of the dimeric immunoglobulin structure 2QTJ. Symbols below the monomer lines corroborate the presence of clusters due to their larger hydrodynamic size. However, the clusters are mainly dimers or formed by few monomers and they dissociate with T increasing from storage to body temperature.

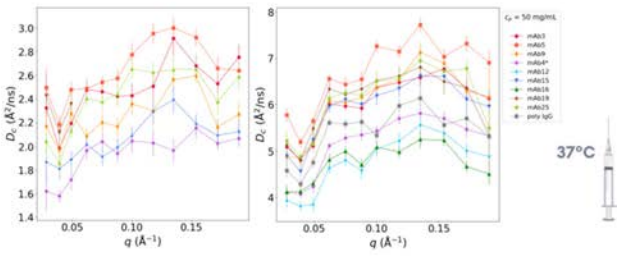

Fig. 2: Effective collective diffusion coefficient D_c (symbols, obtained from a cumulant fit of the NSE data collected on IN15) of the mAbs and polyclonal IgG *vs* momentum transfer q, in solution at T = 280 K (left) and T = 310 K (right). Coloured solid lines between symbols are guides to the eye. For this experiment, all the mAbs were measured at the same nominal protein concentration, of 50 mg/mL. The formulation buffer is the same as the one used in the QENS experiment, namely the 20 mM His-HCl in D_2O at pH 6.0.

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NR determination of the structural profile of asymmetric myelin membranes and their interaction mechanism with Myelin Basic Protein (MBP)

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Myelin, an asymmetric multilamellar membrane enveloping axons, comprises alternating extracellular and cytoplasmic leaflets[1]. Structural alterations in the myelin sheath, particularly demyelination, are indicative of various inflammatory neurological disorders, such as Multiple Sclerosis (MS)[2]. Experimental autoimmune encephalomyelitis (EAE) serves as a recognized animal model for MS, characterized by significant changes in the overall myelin lipid composition[3]. Previous studies have reported an approximate asymmetric lipid composition in both native and EAE leaflets[4].

This study focuses on generating flat asymmetric myelin membranes, suitable for Neutron Reflectometry (NR) analysis. Employing the Langmuir-Blodgett and Langmuir-Schaeffer techniques, we successfully adsorbed asymmetric bilayers onto wafers at PSCM facilities.

According to our results, the subtle compositional difference between cytoplasmic and extracellular leaflets results in a minimal disparity in Scattering Length Density (SLD) when using non-deuterated lipids. Conversely, employing deuterated lipids, specifically d45-cholesterol, enables clear detection of asymmetric bilayers (Figure 1). Solvent fractions indicate a reasonably acceptable percentage of bilayer coverage on silicon wafers.

Upon the addition of Myelin Basic Protein (MBP), the results demonstrate preferential adhesion to the cytoplasmic leaflet, replicating in-vivo observations. MBP exhibits reduced thickness when binding to EAE myelin compared to native myelin, offering valuable insights into the protein-membrane interaction dynamics.

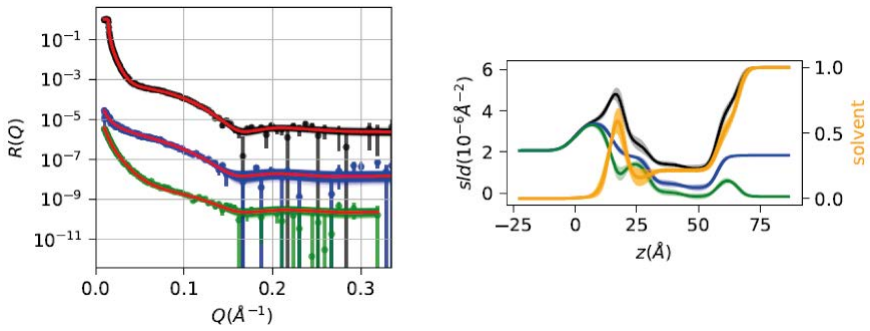

Figure 1: (left) Reflectivity curves for an asymmetric bilayer with d45-Cho in one of the leaflets. It was measured at three different contrasts: D2O buffer (black), SiMW (blue) and H2O (green). (Right) Electron density profiles for the supported membranes at three contrasts and solvent fraction curve (yellow).

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Simultaneous Interfacial Rheology and Neutron Reflectometry studies of interfacial films

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Fluid interfaces with adsorbed substances are present in many systems in nature and industrial processes. Such interfaces often have a complex structural configuration which confers them the capability to withstand deformations [1]. Consequently, they have been the object of study in recent decades both from a structural and rheological point of view. To date, there have been limited examples of simultaneous measurements of the interfacial rheology and the structure of complex fluid interfaces. This aspect holds particular significance, considering the challenge of comparing independently conducted structural and rheological experiments, where reproducing identical experimental conditions, such as temperature and/or concentration, is difficult. Specifically, there is great interest in the study of Langmuir monolayers of fatty acids and phospholipids which appear in many biophysical processes. This work focuses on the development, building, and exploitation of an interfacial shear rheometer, with DWR geometry [2], to be used on the neutron horizontal reflectometer FIGARO at Institut Laue-Langevin (ILL). Consequently, the instrument allows for simultaneous measurements of neutron reflectometry and interfacial rheology. In particular, a DWR probe 3D printed in titanium has been commissioned for the Anton Paar MCR702e Space rheometer available at the PSCM, and a suitable shear channel with annular geometry (machined in PTFE) has been designed and built to be used in the Langmuir trough. Notably, an improved Flow Field-Based data analysis [3] software package has been developed to properly subtract bulk phases contribution, taking into account non-linear velocity profiles. The performance of the new instrument is illustrated with a study of the isothermal compression of C19 fatty acid Langmuir monolayers (FALMs). Additionally, Brewster Angle Microscopy (BAM) has been used to observe the formation of structures above the micron scale at the interface. The studies carried out attempt to shed light on the mechanism of loss of molecules observed in condensed phases at high interfacial pressures in monolayers of fatty acids from a dynamic and structural point of view.

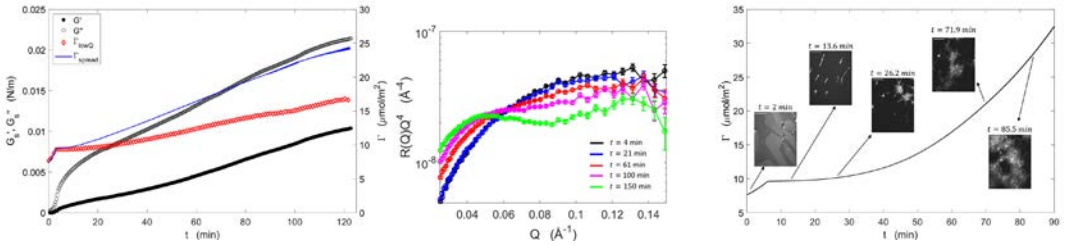

Figure 1: (a) Evolution of the interfacial shear dynamic moduli (G_s' and G_s'') and the deuterated C19 (d37) fatty acid surface excess concentration, Γ, obtained by neutron reflectometry and the apparent one obtained by the amount of spread material. (b) Neutron reflectivity curves at different times. (c) BAM images showing the formation of structures at the interface.

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Between tribology and soft matter: understanding the fundamentals of Organic Friction Modifiers behaviour

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Organic Friction Modifiers (OFMs) are a class of lubricant additives of surfactant-like structure built of polar head and nonpolar hydrocarbon chain with at least 12 carbon atoms. As OFMs do not contain sulphur and/or phosphorus like widely used anti-wear additives ZDDPs (zinc dialkyl dithiophosphates) that are related to poisoning of car catalytic converters, they are believed to be a more sustainable solution. Despite the first use of OFMs 100 years ago, their fundamental behaviour and contribution in friction reduction is not very well understood. It is believed that OFMs form **reversed micelles** in nonpolar solvents like base oils and adsorb to the fretted surfaces as **monolayers**[1]. Experimental studies include different tribotests, and more fundamental approach has been incorporated in molecular dynamics (MD) simulations. The latter suggest that OFMs adsorb to the surface as clusters of reversed micelles, contradictory to the monolayer model[2]. Still, there is no sufficient experimental data that can confirm the simulated results.

Friction is a complex phenomenon; therefore, fundamental changes of OFM molecules and micelles under temperature, shear and pressure are studied to explain the main factor of the beneficial friction reduction. Soft matter issues are often neglected in tribological studies, leaving a substantial gap to be addressed.

By combination of synchrotron scattering techniques with laboratory techniques, structure-performance relations can be obtained. Wide- and small-angle X-ray scattering give an insight into OFMs and base oil structure from atomic to mesoscopic level. Laboratory techniques complement structural data by *e.g.* tribological performance, bulk modulus[3], dynamic light scattering, and others, which emphasise the importance of initiatives like Partnership for Soft Condensed Matter in the work of large-scale facilities.

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Structural changes in lipid monolayers induced by synapsin and vesicles investigated X-ray reflectivity and GID
PSCM User Meeting 2024

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Neurotransmitter release happens upon fusion of synaptic vesicles (SVs), which carry the neurotransmitter, with the presynaptic membrane. SVs act as the trafficking organelles and are clustered in pools to facilitate the rapid release of neurotransmitters into the synaptic cleft. While the process of SV fusion mediated by SNARE complexes is well understood, the influence of the vesicle pool and its mediating protein, synapsin, on the membrane-vesicle interaction is less clear. Previous X-ray reflectivity (XRR) measurements have focused on the interaction of synaptic vesicles with a target membrane [1]. Here, we extend the measurements to include synapsin and calcium at varying concentrations. To compare the data with a model system of reduced complexity, we perform measurements using liposomes in the place of SVs.

To this end, we have carried out XRR and grazing incidence diffraction (GID) experiments on lipid monolayers at controlled surface pressures in a Langmuir trough at ID10 (ESRF). Preliminary experiments were carried out with a Langmuir-Blodgett trough at the PSCM to investigate the pressure-area isotherms of various sample compositions, revealing optimal experimental parameters. The interaction between monolayer and SVs is measured in the monolayer plane by GID measurements, allowing the measurement of lipid molecule tilt angles. Density profiles modelled to fit the XRR data additionally reveal changes in the structure along the third dimension. We hypothesise that synapsin protein has a stiffening influence on the monolayer and also strengthens the interaction between monolayer and SVs, thus highlighting the importance of the protein not only to the clustering of SVs but potentially to the docking process as well.

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Structural and thermodynamic variations occurring during protein denaturation – PSCM User Meeting 2024

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Proteins are biomolecules which in any cases adopt a well-defined structure directly correlated with their function. When they are submitted to conditions far from their native environment, they unfold and lose their functionality. Denaturation under heat conditions is a well-established fact, and widely used for instance for pasteurization. In many cases, the process leads to aggregation and is irreversible. Much less known is that cold temperatures can also lead to denaturation[1], which is thought to be generally reversible. Therefore, the driving mechanisms underlining the two processes are different. The most limiting difficulty when studying cold denaturation is that for most proteins it occurs at temperatures below the freezing point of water, therefore prohibiting many experimental techniques for their study.
Here we will present different biophysical techniques as DSC, FT-IR and UV/Vis spectroscopy which give access by different means to information about the effects of hot and cold denaturation. As an example, we show in figure 1 DSC measurements on a sample in a hydrated powder from subzero to high temperatures permitting to extract thermodynamic quantities changing at the transition temperatures. This information will be compared to what we see with FT-IR and UV/Vis spectroscopy.

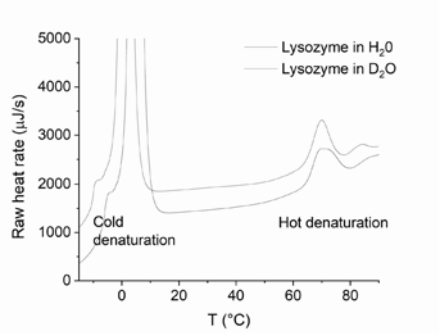

Figure 1: Heat flow measurements around the cold and hot denaturation temperature on hydrated powder samples.

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Unfolding and refolding of Albumin induced by a time-programmable dissipative pH-jump

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Simple reagents can be employed to control the pH of a water solution as a function of time, generating dissipative pH jumps whose amplitude and duration can be tuned. This represents a strategy to control pH-dependent properties as a function of time without additional intervention. Nitroacetic acid (NAA), an activated carboxylic acid able to undergo base catalysed decarboxylation, can be used as a chemical fuel to achieve pH_{high} - pH_{low} - pH_{high} sequences, exploited to drive the operation of host-guest systems and DNA based molecular devices [1,2]. We show how this strategy works to induce and monitor with fluorescence and synchrotron small-angle X-ray scattering (SAXS) the pH-dependent conformational variations of Human Serum Albumin (HSA), in a complementary way to the time-dependent acidification obtained by slow hydrolysis of glucono-*d*-lactone [3,4]. Starting from the protein in its native form, we employed NAA to achieve a fast acidification of the solution with consequent denaturation of the protein, followed by a time-tunable slow raising of the pH without additional intervention, which enables a full protein refolding. This method allows a whole conformational cycle (from native form to acid open form, and then to native again) and a verification of the extent and reversibility of the protein structural transition in different conditions. It could be applied to formulate pH-dependent drug encapsulation and release protocols using albumin as a safe and versatile macromolecular carrier.

Keywords: human serum albumin; acid unfolding; protein refolding, nitroacetic acid; decarboxylation; dissipative pH jump; SAXS; fluorescence.

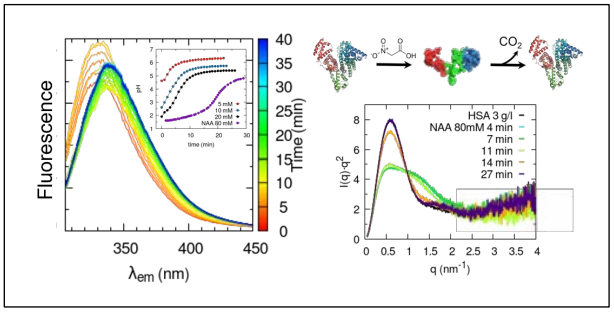

Figure1. *Intrinsic fluorescence of HSA as a function of time during the time programmable pH jump with NAA 20 mM, showing recovery after initial blue shift; in the inset, the pH variation over time obtained with different NAA concentrations is shown. Pictorial view of an unfolding-refolding experiment triggered by the NAA time-dependent decarboxylation. SAXS data in the form of Kratky plot collected for albumin showing time-dependent refolding to native state.*

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Phase behaviour of cotton-derived cellulose nanocrystal suspensions in water and in the presence of salts

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Using polarization imaging, particle-tracking microrheology, and small angle X-ray scattering, we show how the phase behaviour of cellulose nanocrystal (CNC) suspensions obtained from cotton is highly sensitive to ionic strength, anionic surface functional groups and the cationic counterion. Sulfated CNCs separated macroscopically into an isotropic and a nematic phase at 4 wt%, while phase separation of CNCs containing both functional groups takes place at significantly higher concentrations of CNCs. Carboxylated-only CNCs form a gel instead of a nematic phase, which could be due to enhanced attractive interactions between carboxylate groups or due to higher charge density. The isotropic-nematic binodal point of sulfated CNCs shifts to higher concentrations with increasing ionic strength owing to charge screening. At sufficiently high (10 mM) ionic strength, sulfated CNC suspensions also formed birefringent gels, whereas suspensions of CNCs bearing both functional groups remained liquid up to CNC concentrations of 18 wt%. The gelation was more prevalent in the presence of weakly hydrated counterions such as K^+ and Cs^+. Addition of hydrophobic quaternary ammonium ions to sulfated CNC suspensions resulted in a significant upshift in the isotropic-nematic binodal point, however, it did not cause gelation at CNC concentrations below 12 wt%. Thus, repulsive hydration force generated in the presence of strongly hydrated counterions was found to promote chiral nematic self-assembly of CNCs and to prevent gelation, whereas attractive entropy-driven interactions in the presence of hydrophobic ions inhibited the isotropic-nematic phase transition.

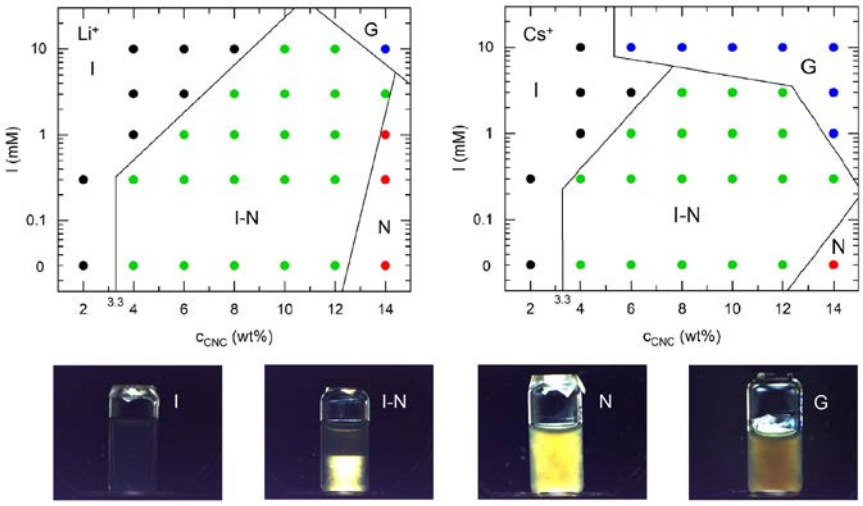

Figure 1. Phase diagrams of sulfated CNC suspensions in the presence of LiCl (left) and CsCl (right) as a function of CNC concentration and ionic strength: I: isotropic suspension; I-N: biphasic suspension; N: nematic suspension; G: birefringent gel; isotropic-nematic binodal point in water = 3.3 wt%

New Insights on the Molecular Structure of Tear Film Lipids Revealed by Surface X-ray Scattering – PSCM User Meeting 2024

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The tear film lipid layer (TFLL) is the outermost layer of human ocular fluid and is crucial in maintaining the surface tension and moderating the evaporation rate of tear fluid. There is still much to learn about this complex membrane, particularly about the functions of the individual lipid classes that make up this fluid. We have selected key lipids from the principal classes identified in the TFLL and have studied thin films of these lipids using surface x-ray scattering. Grazing Incidence X-ray Diffraction (GIXD) and X-ray Reflectivity (XRR) techniques were employed to yield quantitative insights on the lattice distances, molecular tilt angles, layer thicknesses and film density profiles. A Langmuir trough environment allowed us to measure at close to physiological conditions. These insights are then contrasted with previous work on the composition of human meibum.

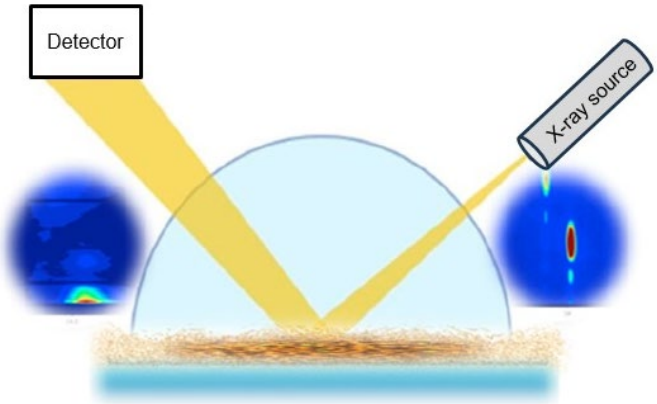

Figure 1: an artistic impression of the experimental setup.

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Poster Abstracts

«Small-angle X-ray scattering of human haemoglobin mixed with PEG additives of different sizes and concentrations»

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Polyethylene glycols (PEGs) are popular polymers for protein precipitation in protein crystallography due to their non-toxicity and the availability of a wide variety of sizes and modifications on the market. PEG additives have been shown to have opposing effects on various protein structures. Initially, PEGs were considered to be protein-neutral molecules that could cause exclude-volume effects on proteins [1]. More recent spectroscopic studies have shown that PEGs can interact with proteins, sometimes forming complexes and, for certain proteins, significantly altering the tertiary and secondary structures [2]. In the present study, we investigate the effect of PEG600, PEG2000, and PEG4000 on the hydration structure of human haemoglobin (Hb) at neutral pH and different PEG concentrations using the small-angle X-ray scattering (SAXS) technique. We established that a short-chain PEG600 at low concentrations has a stabilizing effect on the Hb molecule without noticeable changes in its structure. 5% of PEG2000 and PEG4000 slightly reduce the size of hydrated Hb with an almost unchanged radius of gyration. The addition of 10% of PEG2000 resulted in the interaction of the PEG molecules with Hb to form a complex without distorting the protein spatial structure. The obtained data provide a better understanding of the interaction of PEG with human haemoglobin and complement previous knowledge of polymer-protein interactions.

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«Nanostructural characterisation of glycosylated protein biomarkers interaction with lipid bilayer membranes: basis for biosensor development– PSCM User Meeting 2024»

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Plasma proteins are often used as biomarkers for severe pathologies including cancers and autoimmune diseases since they provide a circulating representation of the body conditions. The study and understanding of protein-lipid interactions is of great importance, especially to optimise the sensitivity and reliability of biosensing techniques to identify protein biomarkers, in particular when present in their glycosylated forms which are currently challenging to recognise with current methods [1].

In the project we investigated at nanostructural level the interaction of glycosylated protein biomarkers with biologically relevant lipid bilayer membranes using scattering techniques, particularly to identify how different lipids and glycosylation can affect this interaction to build a potential biosensor that is aimed for early detection of scarce biomarkers in blood samples. The glycosylated proteins of interest for the study are soluble vascular-endothelial cadherin (sVE) and alpha-fetoprotein, two clinical biomarkers found in the blood for vascular abnormalities and liver cancer detection respectively [2,3,4]. To better discriminate the effect of glycosylation, the interaction behavior of these proteins is compared with results on a non-glycosylated protein, BSA.

NR results, together with QCM-D complementary data, showed significant changes in the lipid bilayer after the injection of glycosylated proteins, alpha-fetoprotein and sVE, while smaller changes were reported in presence of non-glycosylated protein, BSA. We highlighted that the kinetic has an important role for the interaction and we proved that the interaction behavior is influenced by the lipid composition of the system as well as the degree of glycosylation in the protein. In fact, glycosylated proteins interact faster and stronger with lipidic moieties most probably due to hydrogen bondings. With an anionic lipid in the composition the bilayer is disrupted faster in the presence of glycosylated proteins, while for the bilayer containing a cationic lipid the model that seems to describe the interaction most appropriately is the one considering not only the adsorption of the protein on the bilayer, but a partial incorporation of the protein in the outer head region of the bilayer. In addition, we found interesting results comparing the interaction behavior of native non-glycosylated BSA and glycated BSA.

Thanks to the study and glycosylation chemistry, it was possible to set the basis for the development of a lipid-based protein-biosensor in collaboration with the industrial partner of this project (Surgical Diagnostics Pty Ltd).

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Protein Crystallization induced by multivalent salts

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The comprehension of crystallization pathways is of great interest for the growth of protein crystals which can be used for protein structure determination. A possibility to trigger different crystallization pathways is the addition of multivalent salt ions to the protein solution.
To understand the structure and dynamics of the crystallization process, we have investigated the protein crystallization in a time-resolved fashion with QCM-D [1], microscopy [2,3], small angle scattering [3,4], DLS (Figure 1), neutron backscattering and neutron spin echo [4,5].
We present an overview of the different studies including salt-induced changes in the crystal structure,classical (monotonous) and non-classical crystallization pathways as well as influences of the sample environment on the crystallization process.
In addition, influences of the isotope effect and the dependence on the localization within the phase diagram are discussed.

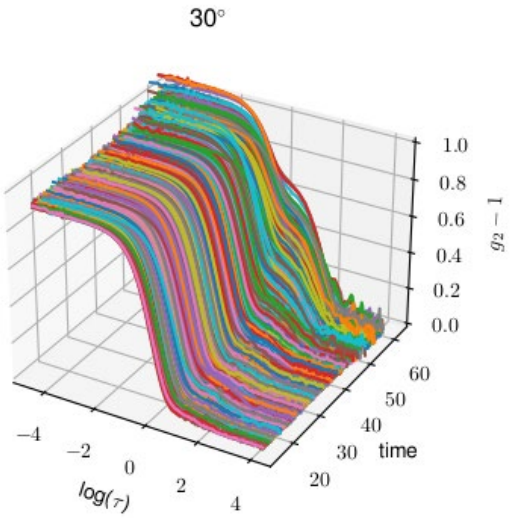

Figure 1: Time-dependent DLS data of a salt-induced crystallizing HSA solution. A clear formation of an additional shoulder is visible, indicating changes in the long time collective diffusive properties during the crystallization process.

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«Polymer-surfactant interaction: connection between confinement and bulk»

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Interaction between polymer and surfactant is of great interest both for applied and fundamental research. Specifically, the connection between the interaction in bulk and behaviour of complexes in proximity to the surface is extremely important for applications in cosmetics and other areas [1]. In this work we study the relationship between structure of thin films of polymer-surfactant complexes and their interactions in water solution using Small-Angle X-ray Scattering (SAXS) and X-ray Reflectivity (XRR). In this work we investigated interaction between poly(maleic acid-co-butyl ether) with C12-amine oxide surfactant and hydrophobically modified poly(vinylpyrrolidone) with sodium dodecyl sulphate. We have found the formation of multilayer structures in confined state, while no pre-organized layered structures were discovered in the bulk solution, contrary to the findings of Micciulla et al[2]. SAXS data suggests the formation of pearl-necklace structure, with polymer chain wrapped around core-shell surfactant micelles (Figure 1, left). Increase in polymer concentration leads to a tighter wrapping of micelles with polymer chain, manifested in the increased density of the shell region. Such arrangement provides an opportunity to form an organized structure on the surface, in which polymer matrix allows for reorganisation of surfactant into layered structure upon in increase in humidity, observed by X-ray reflectivity (Figure 1, right). Notably, we have obtained important results on the structure of polymer-surfactant complexes in confinement, which are highly tunable and present in wide variety of compositions. This provides an opportunity to fabricate nanostructured films where surfactant is retained in the polymer matrix, providing an opportunity for further developments of durable antimicrobic coatings.

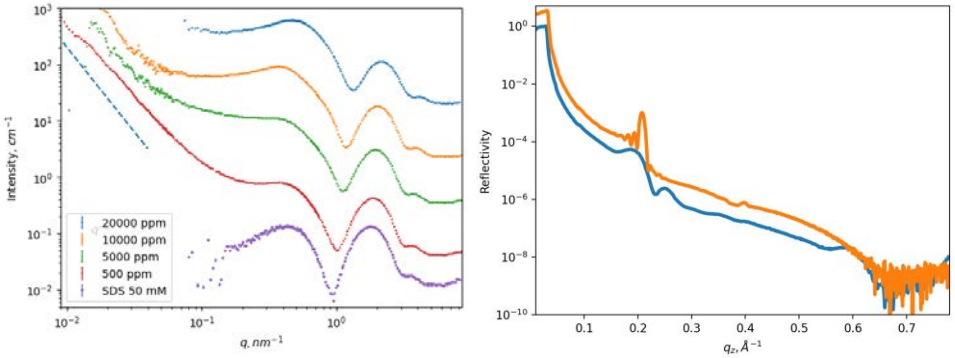

Figure 1: Left: SASX curves for complexes with different polymer concentrations. Right: Reflectivity profiles before (blue) and after (orange) exposure to humidity.

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Development of Sample Cells for the Investigation of Solid-Liquid Interfaces

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The new design of sample cells for the investigation of solid-liquid interfaces by neutron reflection is currently under development for the ESTIA & FREIA reflectometers at the European Spallation Source (ESS), see Fig 1. The design has evolved from earlier work [1] to allow smaller sample volumes and faster flow rates. Use of standardized components and a modular design allows a wide range of experiments that include horizontal & vertical reflectometry geometries as well as grazing incidence scattering. Various flow arrangements to fill and replenish the liquid in the cell as well as continuous stirring are also possible. A seven cell sample changer is also under development for automation of measurements and precision control of solution mixing for contrast matching.

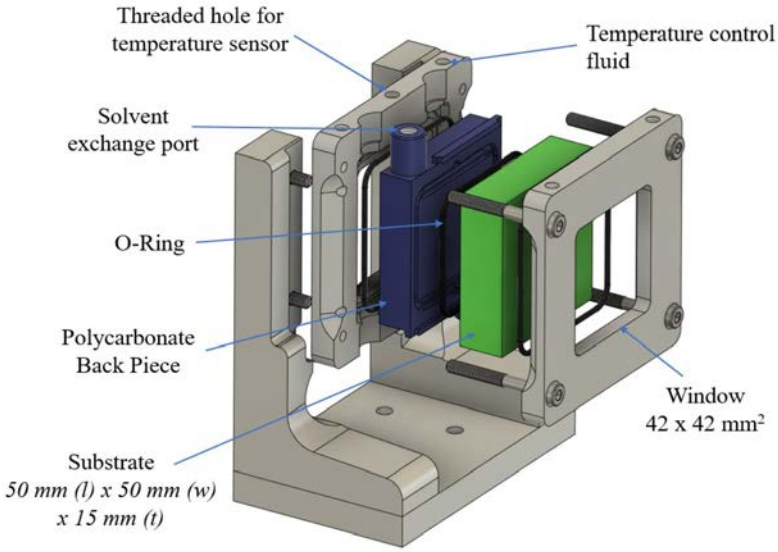

Figure 1: Model of solid-liquid sample cell showing the relationship and order of assembly of its various parts.

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« Role of tacticity and density effect on the glass transition dynamics under 1D confinement – PSCM User Meeting 2024»

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Spatial configuration impacts the properties of soft matter under geometrical nanoconfinement, which is crucial for developing materials with desired properties and functions. Also, knowledge about the sensitivity of polymer materials to density changes is essential because it will allow for a better understanding prediction of the effects caused by confined geometries.

In this talk, our main aim was to show how tacticity influences the glass transition dynamics under high-pressure and geometrical nanoconfinement. Our findings reveal that the dynamics of syndiotactic and isotactic PMMA thin films are affected by density effects and the interaction between the sample and the supporting substrate. Segmental relaxation of syndiotactic PMMA is less modification by compression compared to isotactic stereoisomers. Therefore, both stereoisomers will be differently sensitive to density changes induced by spatial constraints. The segmental dynamics of isotactic and synditactic PMMA thin films have also been investigated. This research contributes to a comprehensive understanding of how pressure, confinement, and molecular structure collectively influence the dynamic behaviour of polymers in confined geometry.

Pair Distribution Function analysis of fine effects in supported Pd and Pt nanoparticles catalysts during activation in liquid phase

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Keywords: Nanoparticles, PDF, time-resolved, liquid environment

Pd and Pt heterogeneous catalysts are widely used in hydrogenation reactions for the synthesis of fine and bulk chemicals, which are often conducted in liquid phase. Since the active phases are commonly deposited as oxides on a non-reducible support [1-2] we seek to study how the catalyst activation procedure affects the reducibility of the oxide phase and the properties of the supported nanoparticles, and how these correlate with the catalyst behaviour during hydrogenation. We carried out experiments in liquid phase at various temperatures, at different nature and concentrations of the reducing agent, and in three solvents to isolate the kinetics and dynamics of the reduction of the oxide phases (PdO, PtO) and the formation of metallic (Pd, Pt) and hydride (PdH, PtH) phases.

At the ESRF beamline ID15A we used High-Energy X-Ray Diffraction (HE-XRD) and Pair Distribution Function Analysis (PDF) to quantify hydride, metallic, and oxide phases in both average and local structure, and thus separate long-range from short-range structural effects overcoming the complications of investigating a heterogeneous catalyst in a liquid environment through total scattering: parasitic signals, competing side reactions and thermodynamic limitations involving the solvent.

In the case of Pd nanoparticles (size ~ 2.4 nm) PDF was used to follow the consumption of PdO upon reduction, the subsequent formation of metallic Pd and the nucleation of a bulk Pd hydride phase with a time resolution of 1s. Analysing the ΔPDF on this timescale (Fig.1A) allowed us to determine the kinetics of formation of metallic Pd and Pd hydrides. By testing various reducing agents at different concentration in three different solvents we observed different kinetics, suggesting a different extent of reducing ability. Fast-scanning XAS measurements performed on X10DA at Swiss Light Source independently confirmed the reliability of the PDF data timescale. FT-EXAFS and MCR analysis confirmed what PDF highlighted: the formation of PdH does not start until all of the PdO has been reduced to Pd (Fig.1B).

As to Pt nanoparticles, deposited clusters only consist of 55 atoms (size ~ 1.4 nm) dramatically reducing the scattering amplitude with respect to the Pd case. Modulated Excitation – Phase Sensitive Detection [3] proved necessary to isolate the Pt scattering contribution, and thus to observe just the fraction of atoms that respond to the repeated pulsing of solutions. Modulated Excitation-PDF on fully hydrogenated Pt nanoparticles with cycles of Ar- and H_2-saturated solvent could detect the reversible reconstruction of the NPs due to the formation of surface hydrides detached from the support. This subtle effect was anticipated by DFT [4] but never experimentally observed before. Both these cases show how PDF can be successfully used to investigate fine structural effects in metal nanoparticles under actual working conditions in a liquid environment, which make it challenging for total scattering experiments.

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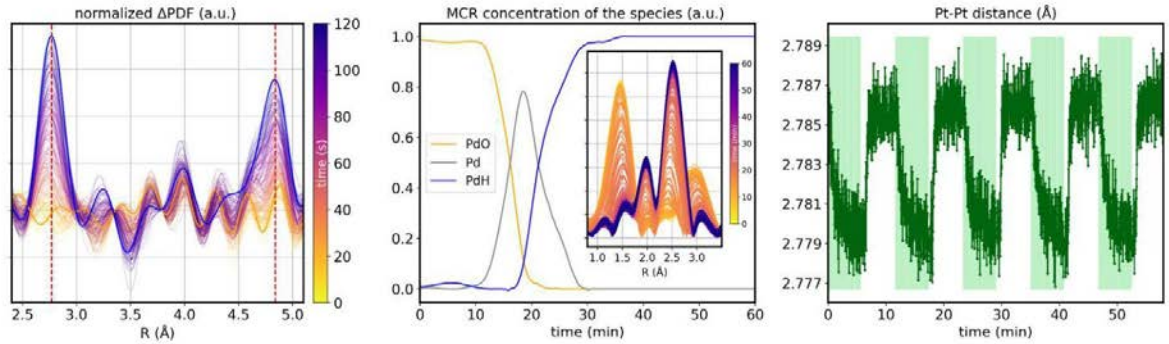
Figure 1. (A) fast acquisition ΔPDF of the reduction of PdO in HCOONa (10mM in H_2O), Pd-Pd distances in red; (B) MCR concentrations of quick-XAS data collected in the same conditions, time-resolved FT-EXAFS data in the inset; (C) reversible evolution of Pt-Pt distance during a M.E. experiment with Ar (light green) and H_2 (white) in cyclohexane.



XPCS in bunch mode: XPCS-echo and wide timescale measurements

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With the emergence of 4th generation synchrotrons, X-ray Photon Correlation Spectroscopy (XPCS) has improved both in terms of the available coherent photon flux and speckle contrast [Chevremont2024]. Together with fast photon counting pixel array detectors, this technique has become more attractive for the investigation of a broad range of systems [Narayanan2023]. However, one of the main limitations of XPCS measurements is the sample degradation by the X-ray beam and resulting beam-induced dynamics [Chushkin2022]. Yet another bottleneck when performing XPCS at a high frame rate for a long time is the time and memory needed to process the data, which scale quadratically with the number of frames.

To address these issues, a novel acquisition scheme has been developed at the TRUSAXS Instrument (beamline ID02), ESRF. This new scheme has been termed as “time resolved” or “bunch mode” XPCS. It involves acquiring frames at the highest frame rate according to the lowest lag time to be measured only when needed and thus exposure of the sample to the beam is minimized. Bunches of frames are acquired, spaced by variable dead time where the fast beam shutter remains closed and the sample unexposed to X-ray beam. The autocorrelation functions are still calculated by performing the correlation between all the frames, and reconstructing the two-time correlation function (TTCF) before averaging.

In this work, the application of the bunch mode XPCS is demonstrated on samples (colloidal gels formed by short-range attraction between particles) whose correlation functions span over several orders of magnitude in lag time. Another interesting application is for XPCS-echo, where the acquisition is synchronized with an oscillatory motion of the sample imposed by a rheometer [Pham2004]. In this experiment, the detector frames are acquired on each oscillation period and echoes in the autocorrelation function [g2(q,t)] appear each time the sample returns to the initial position. The envelope of echoes measured corresponds to the decay of the autocorrelation function due to the intrinsic dynamics in the sample. For fully reversible motion, the envelope strictly corresponds to the autocorrelation function of the sample at rest. On the other hand, an acceleration of the decorrelation occurs when the sample yields with increasing amplitude of deformation. The XPCS-echo then provides an elegant way to measure the intrinsic dynamics within the sample, discriminating the Doppler shifts caused by the shear.

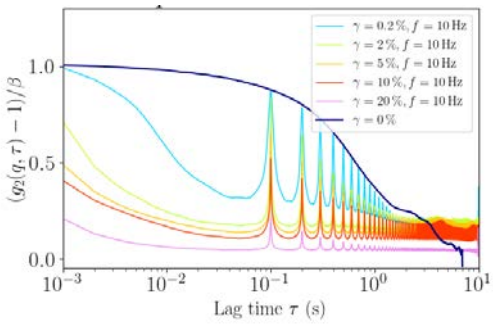

Figure 1: Measurements of XPCS-echo and normal autocorrelation functions of a dense colloidal suspension of PMMA particles (size ~ 800 nm) in cis-decalin subjected to oscillatory shear of varying amplitudes at a frequency of 10 Hz.

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Air-liquid-interface assisted formation of self-assembled monolayer of 2D nanoparticles

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The Langmuir method is widely recognized for its ability to facilitate the controlled formation of monolayers composed of organic amphiphilic molecules, followed by their transfer onto solid substrates. This technique has found extensive application in the scientific exploration of new materials and has gained significant traction in the coatings industry. Recently, there has been a growing interest in leveraging the Langmuir method for the creation of monolayers with complex architecture comprising ordered nanoparticles derived from colloidal media. Successfully applying the Langmuir method in this context represents a promising avenue for the controlled generation of both mono- and multi-layer nanoparticles, holding substantial potential across various high-tech applications.

Two water-based colloidal systems were selected for investigation. The first system focused on two-dimensional MXene $Ti_3C_2T_x$ (T = O; OH) nanosheets, with their hydrophilicity manipulated by adjusting the ionization level of carboxylic acid groups through pH reduction of the media [1]. The second system examined magnetic monodomain $SrFe_{12}O_{19}$ nanoplatelets (MNPs) stabilized by a positive charge in an aqueous solution [2].

A series of experiments conducted at the ID10 beamline (ESRF) and PSCM laboratories showcased the application of the Langmuir method for the first time in preparing monolayers of MXenes and $SrFe_{12}O_{19}$ MNPs. Various methods for forming monolayers from aqueous solutions of two-dimensional nanoparticles, both with and without surfactants, were thoroughly investigated. A comprehensive set of techniques, including X-ray Reflectometry/Grazing-Incidence-Diffraction/Langmuir method, Langmuir method/Brewster-Engle Microscope, Scanning Electron Microscopy, and Atomic-Force Microscopy, among others, were employed for meticulous investigation and characterization.

Spontaneous assembly of MXene layers into monolayer films at water-air interface is observed both in basic and acidic suspensions. Direct assembly of 1.5 nm thick $Ti_3C_2T_x$ monolayer appears at liquid-air interface at pH~8 and lower, while anion coordination of MXene flakes with formation of Br_{aq}-/$Ti_3C_2T_x$/subphase interface occurs from the acidic medium. Formed layer provides surface tension over 40 mN/m and can be readily transferred onto solid substrates by conventional LB approach or modified by surfactants for further transfer of composite films.

The phenomenon of self-assembly of a densely packed monolayer of magnetic nonsurfactant nanoplatelets at the air-liquid interface has been found due to two mechanisms. In the first case, the appearance of MNPs occurs on a pure liquid surface due to particle diffusion, minimisation of the surface energy of the interface, and requires considerable time for the formation of a continuous layer. In the second case, the organization of a monolayer of MNPs occurs under an oppositely charged Langmuir surfactant monolayer and can be formed within half an hour. The solid monolayer of nanoplates created in both cases with a thickness of 5 nm and an area more than to several square centimeters can be transferred to a flat substrate by the Langmuir-Schaefer method for subsequent use. The possibility to occur the underlying layers of MNPs oriented parallel to the surface was demonstrated in subsequent experiments at the P03 beamline of the PETRA III synchrotron (DESY, Hamburg, Germany).

This achievement holds significant implications for advancing the field of nanotechnology and opens new possibilities for a range of innovative high-tech applications.

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«Understanding molecular interactions at the hair surface – a cosmetic perspective»

Serena Cozzolino[1], Mark Rutland[1,2], Alexei Vorobiev[3,4], Philipp Gutfreund[3], Andrew Greaves[5], Gustavo S. Luengo[5]

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The outermost surface of the hair fibre is made up of a lipid layer, the main component of which is the 18-MEA molecule (18-methyl eicosanoic acid) [1,2]. The density of 18-MEA molecules decreases along a fibre from the root to the tip due to chemical and physical "damages" leading to surface changes in terms of tribology and hydrophobicity [3]. This means that the interaction properties of the hair can be very different depending on a number of conditions [4]. A detailed knowledge of how lipid composition, density and distribution affect molecular adsorption from complex systems, such as those found in hair care formulations, is still lacking. This is principally due to the difficulty of directly studying the hair surface. Greater knowledge is crucial for the cosmetic industry to design formulations with improved properties using more sustainable ingredients. The aim of this project is to produce hair mimetic surfaces and to study the adsorption of single model molecules as well as complex mixtures. Hair biomimetic surfaces are obtained by self-assembly on gold of suitable alkylthiols, pure or in mixtures. The study uses mainly neutron reflectometry (NR) since it offers the possibility of contrast variation by deuteration, which is useful to characterize hierarchical adsorption. Preliminary measurements were obtained with straight, branched or charged alkylthiols, and studying how the structure of these molecules affect the adsorption of an anionic surfactant alone or mixed with a natural polymer (chitosan). The first results show that the protocol is adapted to understand the different behavior of surfaces (tribologically different with varied hydrophobicity to better understand the role of lipids). In general, important knowledge on the influence of the structure of the hair surface on the type of molecular interaction with more complex biopolymers is being attained which should ultimately lead to more eco-friendly hair care formulations.

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$CsPbI_3$ *black phase* stabilization probed by in-situ XAFS

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The push to commercialize perovskite solar cells is driving the development of new more materials and more affordable and scalable production methods. The $CsPbI_3$ system is emerging as a favoured candidate for a top absorber material, owing to the solar-compatible bandgap (1.7 eV) of its γ phase, also known as *black phase*. Such a solar-friendly *phase* is stable only at high temperatures, but it becomes metastable under ambient conditions (RT), with times varying between a few minutes and some tens of minutes, depending on environmental conditions. Such instability severely hinders the progress of solar cells based on $CsPbI_3$ while understanding the origin of such instability is primarily important for applications and challenging from a fundamental point of view.

It has been discovered that thermal annealing $CsPbI_3$ under oxidizing atmosphere extends the stability of the γ-*phase* at RT but the origin of such trend is unclear. Here we are addressing the question of the γ-$CsPbI_3$ stability using XAFS[1] to study in situ the evolution of local structure and electronic states of Pb, I and Cs in $CsPbI_3$ samples that were first heated (350 °C) and then cooled to room temperature, in an inert (He) or oxygen atmosphere (Air). The Pb-XANES spectra of pristine and annealed samples depict no relevant changes in shape or position excluding sizable modifications of average Pb oxidation state. On the contrary changes induced by the thermal treatment are evident in the EXAFS region resulting different for sample annealed in air or under inert atmosphere (Fig. 1). The quantitative analysis demonstrates the sharpening of Pb-I shell in the *black phase*, and the effect is larger for sample annealed under oxygen atmosphere demonstrating the role of oxygen in promoting the gamma phase stabilization.[2]

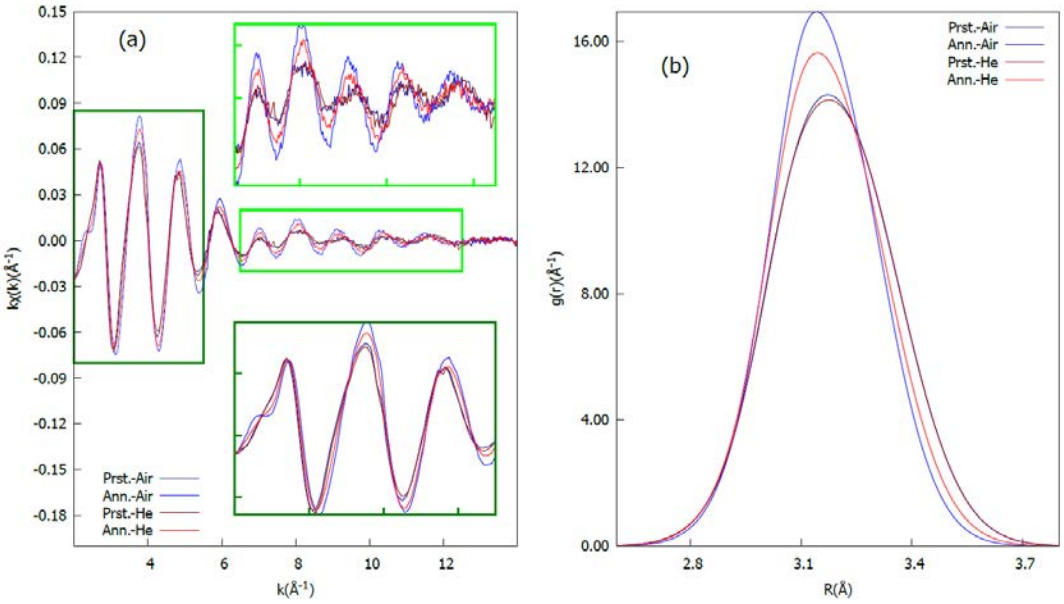

Figure 1 The EXAFs spectra of pristine (Prst.-) and annealed (Ann.-) samples under inert (He) and oxidizing (Air) atmosphere, differences being highlighted in the top and bottom inserts. The Pb-I Pair Distribution functions calculated from the refined structural parameters (b) highlight the structural differences.

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Hierarchical self-assembly of surfactants and cyclodextrins: from inclusion complexes to responsive supramolecular aggregates

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Cyclodextrins (CD) are cyclic oligosaccharides formed by α-(1-4)-D-glucopyranoses linked units, conferring unique shape and a cavity. Such characteristics provide them particular physicochemical properties and the ability to form host-guest complexes. Cyclodextrin-surfactant inclusion complexes are an attractive research field due to the availability, diversity of surfactants and the tendency to self-organize into highly ordered structures [1]. Among many surfactants, polyoxyethylene alkyl carboxylic acids ($C_iE_jCH_2COOH$) are interesting guests candidates to integrate these systems because of their pH and thermo-responsiveness properties [2]. In the last years, a multi-level assembly involving complex building blocks ordering has raised strong interest in many scientific areas. In a delicate balance of forces, the lattice self-assembly of inclusion complexes produces rigid and complex structures relying on directional intermolecular interactions between the CDs [3]. One of many challenges is controlling and directing such self-assembly process to obtain the desired structures linked to their function-oriented potential.

A thermodynamic and structural approach is used to characterize the formation of inclusion complexes in aqueous solution of α-CD and β-CD with $C_{12}E_5CH_2COOH$ and $C_{12}E_{10}CH_2COOH$. The thermodynamics of inclusion complexation was studied by densitometry and isothermal titration calorimetry (ITC), and a comprehensive structural investigation was conducted by small-angle neutron scattering (SANS), differential scanning calorimetry (DSC) and microscopy. The complexes' spontaneous formation and their assembly as building blocks of large supramolecular aggregates with rich structural behavior was verified. The number of ethylene oxide units and CDs features demonstrated to play an important role in the formation and topology of the novel aggregates. The remarkable dependence of the structures on the mixing ratio, concentration of the components, the pH and temperature allowed to fine-tune the structures and, therefore, to control the self-assembly process. The formation of well-layered structures exhibited long-range order, forming multilayered hollow cylinders in the concentrated systems with ionized surfactant, at high pH, and, rhomboidal crystalline plates in nonionic systems, at low pH [4].

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The new “biology, deuteration, chemistry and soft matter” group at ILL

F. Gabel[1]

[1]ILL Grenoble

I will present the newly founded “Biology, deuteration, chemistry and soft matter” group which encompasses the ILL part of the PSCM and chemistry laboratories, as well as the ILL deuteration and lipid laboratories (D-lab and L-lab). An overview of associated personnel, equipment and lab spaces will be provided. The current state of the proposal/access system and interactions with the user community will be presented. Ideas for future interactions and collaborations with the PSCM users and ILL/ESRF staff, and, more broadly, the Partnership for Structural Biology (PSB) and the local Grenoble community will be open for discussion.

«3D Printing of Light Sensitive Biopolymers for Soft Robotics – PSCM User Meeting 2024»

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[1] Institute of Chemistry and Chemical Technology, Faculty of Natural Sciences and Technology, Riga Technical University, P. Valdena Str. 3, Riga, LV-1048.

This research focuses on the exploration of sustainable bio-based alternatives for commonly used traditional elastomeric polymers such as silicones and acrylates in soft robotics applications.
We report the soft biopolymers and ionogels synthesized from functionalized vegetable oils, ionic liquids, and nanocellulose components. The stereolithography and light-assisted direct ink writing of the developed biobased inks can be used to print different structures. The of developed biopolymers shows perspective electromechanical sensor-actuator possibilities. Electrically conductive biocomposite resins using blends of vegetable oil acrylate and single-walled carbon nanotubes (0-1 wt%) are also developed and applied as electrodes for the 3D printed actuator demonstrator.
Finally, a fully 3D-printed soft-robotic actuator, containing up to 70% of biopolymer components, with performance comparable to that of commonly used petroleum-based alternatives is demonstrated.

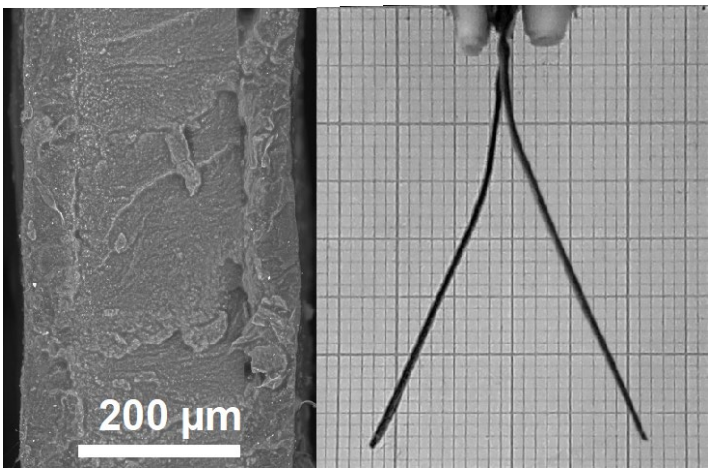

Figure 1: 3D printed soft membrane structure and demonstrator actuation.

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Attractive carbon black dispersions: structural and mechanical responses to shear

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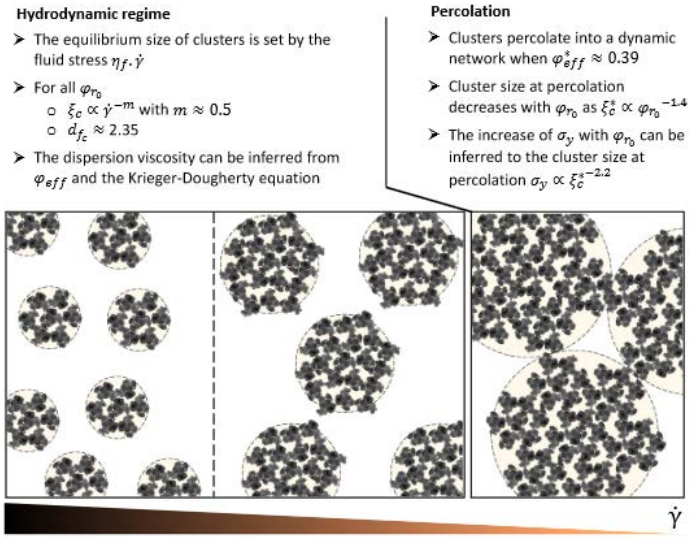
The rheological behavior of colloidal dispersions is of paramount importance in a wide range of applications, including construction materials, energy storage systems and food industry products. These dispersions consistently exhibit non-Newtonian behaviors, a consequence of intricate interplays involving colloids morphology, volume fraction, and inter-particle forces. Understanding how colloids structure under flow remains a challenge, particularly in the presence of attractive forces leading to clusters formation. In this study, we adopt a synergistic approach, combining rheology with ultra small-angle X-ray scattering (USAXS), to probe the flow-induced structural transformations of attractive carbon black (CB) dispersions and their effects on the viscosity. In practice, flow curve tests were conducted on CB suspensions in oil with volume fractions ranging from 0.6 to 4.1 %. Our key findings can be summarized as follow.

First, in the hydrodynamic regime at high shear rate, CB particles are structured into fractal clusters, which size conforms to a power law of the shear rate, with the breaking constant m = 0.5. Second, drawing insights from the fractal structure of clusters, we compute an effective volume fraction and find that microstructural models adeptly account for the hydrodynamic stress contributions. For each volume fraction, we identify a critical shear rate at which the clusters percolate to form a dynamical network, that sets the lower bound of the hydrodynamic limit. Third, we show that under fast transient shear, the apparent yield stress measured at low shear rates inherits its properties from this percolation point.



Summary:
Here, we try to understand the dynamics as well as structuration of microemulsions in ternary systems without any added surfactants using tools like Small Angle Xray Scattering (SAXS), Small Angle Neutron Scattering (SANS), Neutron Spin Echo and NMR.

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Surfactant-free microemulsions: how molecular dynamic reflects nano-structuration

MALAYIL KALATHIL Firoz, Marie PLAZANET, Ingo HOFFMANN, Sylvain PRÉVOST, Thomas ZEMB & Christiane ALBA-SIMIONESCO

Abstract:
Mixtures of simple molecules may lead to complex systems with unforeseen properties of particular interest such as reactivity or solubility. This is the case of aqueous solutions of alcohol and oil, typically found in all kind of liquors, cosmetics or solvents for liquid-liquid extraction.
The archetypical case of this family is the ternary mixture of water, ethanol and octanol. Its phase diagram presents a biphasic region with a critical point (Upper Solution Critical Temperature) close to which a strong nanostructuration of the liquid can be observed. In the biphasic region, this emulsion was termed **Ouzo effect**, following the greek beverage, commonly observed when the 40% alcohol liquor is quickly diluted with water. In the monophasic state, a 'pre-Ouzo' region has also been evidenced [1], extending between identified frontiers around the critical point (see Fig. 1, [2]). The structuration is also characterized by a structure factor presenting an Ornstein-Zernike behaviour, indicating the presence of aggregates of the order of 100 molecules similar to a micro-emulsion formed by a ternary water-poor mixture of octanol and ethanol and water, surrounded by a surface excess of ethanol that is immersed in a binary water-ethanol solution saturated with a low quantity of octanol.
In this system, we investigated, using QENS and various isotopic mixtures, the relaxation dynamic of each component along different composition lines crossing the phase diagram. The evolution of the diffusion coefficient is measured over a wave vector ranging from ~0.05 $Å^{-1}$ to 0.6 $Å^{-1}$, bridging the scale from characteristic droplet size to molecular distances, i.e. from collective to individual dynamics.
The recent study of Octanol-ethanol-water ternary using SAXS at ESRF ID02 could be helpful in further understanding the system.
We will show how the dynamics also reflect the (nano)structural organisation.

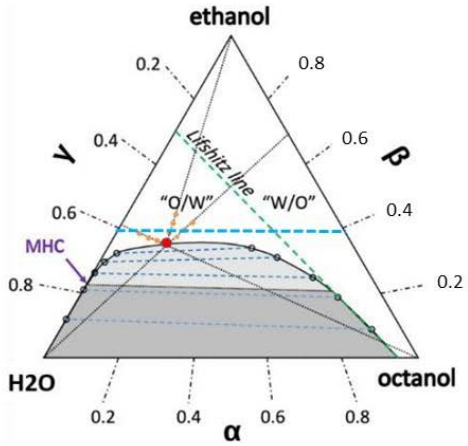

Fig. 1: phase diagramm (wt.%) of the ternary mixture octanol/ethanol/water. The binary region is colored in grey; the Lifshitz line delimitates the onset of structural organisation; the minimum hydrotrope concentration (MHC) indicates the minimum quantity of ethanol required to form a monophasic solution as soon as octanol is added to water; the dynamics was investigated along the blue dotted line.

Orientational ordering and assembly of silica-nickel Janus particles in a magnetic field.

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The orientation ordering and assembly behavior of silica-nickel Janus particles (JPs) in an external magnetic field ($\vec{B}$) were probed by ultra small-angle X-ray scattering (USAXS). Even in a weak applied field, the net magnetic moments of individual particles aligned in the direction of the field as indicated by the anisotropy in the recorded USAXS patterns[1]. At higher fields, the magnetic forces led to chain-like configurations of particles as indicated by an additional feature in the USAXS pattern. A theoretical framework is provided for the quantitative interpretation of the observed anisotropic scattering diagrams and the corresponding degree of orientation. No anisotropy was detected when the magnetic field was applied along the beam direction, which is also replicated by the model.

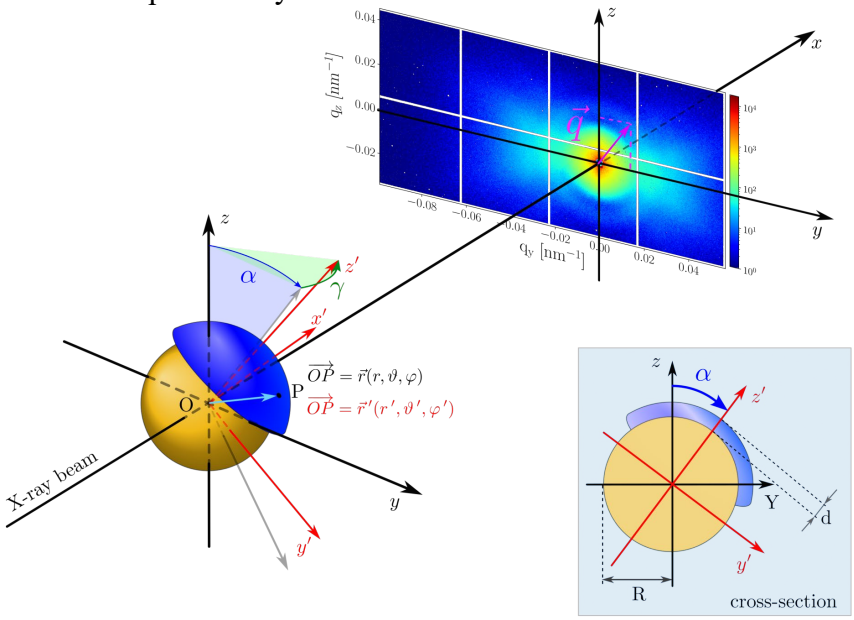

Figure 1: A schematic representation of a JP and the scattering geometry involved in the calculation. The axis of the particle is rotated with respect to the x and z axes.

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«Dynamics, kinetics and assembly of β-Casein as a model intrinsically disordered protein»

L. M. Miñarro[1,2,3], C. Beck[1,3], I. Mosca[1,3], O. Matsarskaia[1], F. Schreiber[3], T. Seydel[1]

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Intrinsically disordered proteins (IDPs) are biologically active proteins with a lack of a stable, ordered, three-dimensional structure and they constitute a crucial fraction of the proteins in a living organism. Due to its unfolded nature in its monomeric form, β-Casein belongs to this class of protein. In addition, β-Casein undergoes a reversible self-association with increasing concentration and temperature, forming protein micelles [1].

To achieve a general, comprehensive description of the static and dynamic properties of β-Casein as a model IDP in aqueous solutions, different systematic studies have been performed, using various scattering methods such as light scattering, neutron backscattering, neutron spin echo and small angle scattering.

The combination of these different techniques allows us to access the collective and self-diffusion of the protein at different timescales. The diffusive properties have been well understood for globular proteins [2], so the same models based on colloid physics have been used for an initial analysis (Figure 1).

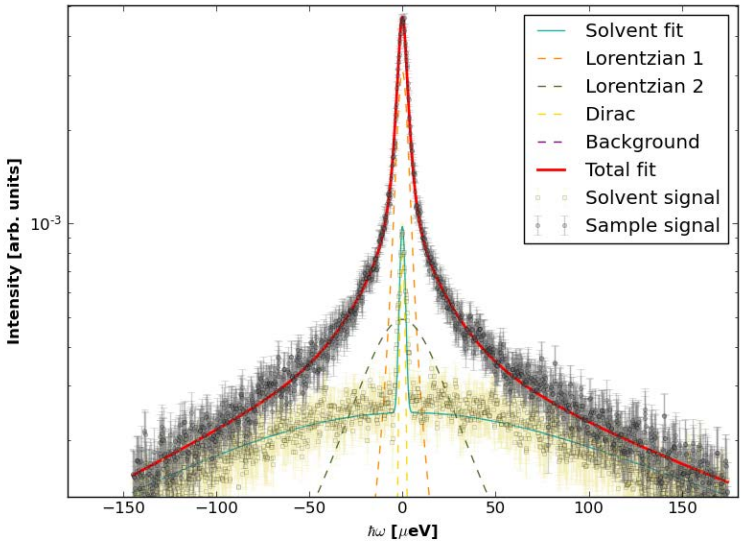

Figure 1: QENS spectra obtained from β-Casein (grey symbols) at a concentration of 100 mg/mL and from D_2O-NaPh solvent (yellow symbols), both at T = 280 K with different dynamic contributions (lines) at q = 15.7 nm^{-1}. The red and blue solid line represent the fit of the sample and of the solvent, respectively. The dashed lines correspond to the different dynamic contributions. The Dirac accounts for the sample container contribution that was not subtracted in this case, but fitted. All contributions are convolved with the resolution function.

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Imaging Biological Cells in Microflow Using a Custom-Built Beamline-Compatible Microscope

Rita Mendes Da Silva[1,2], Boram Yu[1], Mangalika Sinha[1], Daniel Fiole[2], Manfred Burghammer[2] and Sarah Köster[1]

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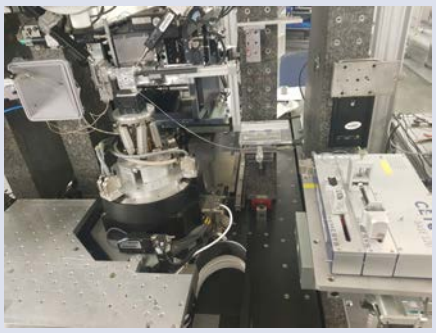
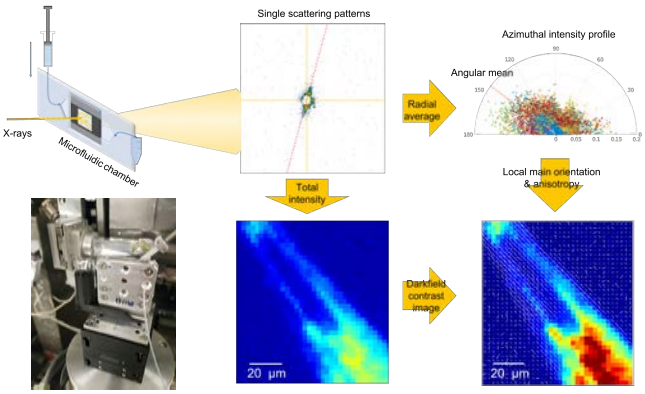


Abstract

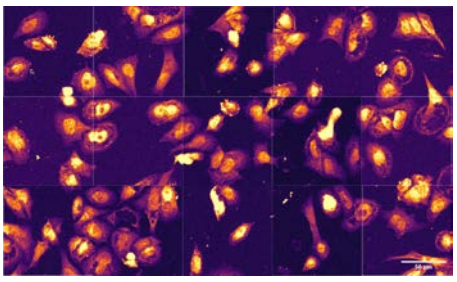
Small Angle X-ray Scattering (SAXS) is a unique technique used for imaging biological cells in a label-free approach. With the advent of high-brilliance X-ray sources and nanofocusing optics, it is possible to obtain structural information on the cellular components with sub-micron to nanometer resolution. However, due to the high photon flux, the energy deposited on the biological cells always tends to generate free radicals, which are also responsible for the structural changes in the cell [1]. It is therefore crucial to simultaneously monitor the effect of radiation damage on the cells during X-ray experiments. In this project, we aim to combine SAXS at the ESRF ID13 beamline, with simultaneous high-speed bright-field microscopy imaging of biological cells to observe the structure and structural changes caused by radiation damage. We have custom-built a reflection bright-field microscope considering the space constraints of the beamline, and demonstrated the capabilities of the setup. We find consistency in resolution and contrast between the custom-built and commercial microscope.

X-ray Nanodiffraction

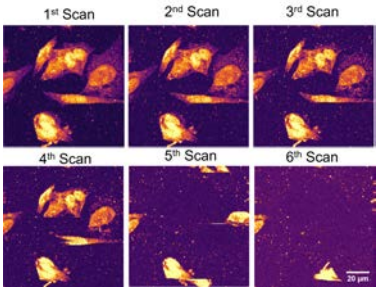


- Cells in a **microfluidic device** are raster scanned and **diffraction patterns** are recorded for each position.
- The diffraction patterns are summed to create the **darkfield image**.
- The radial average of the individual scattering pattern gives the **local orientation** and **anisotropy**.

- **X-ray experiment parameters:**
- **15 keV** photon energy; **1.10 x 10^{12}** photons/s; **2 ms** exposure time; **250 x 250 nm^2** beam size.
- **1.9 m** sample to detector distance.



- 5 x 3 X-ray scan patches of 0.5 x 0.5 µm^2 step size.
- Flow rate of **20 µl/h**.
- Nucleus and and body of the cells have a good contrast due to difference in electronic density.



- 6 sequential X-ray scans of 0.2 x 0.5 µm^2 step size.
- Flow rate of **100 µl/h**.
- Higher flow rates attenuate the effect of radiation damage compared to lower flow rates.

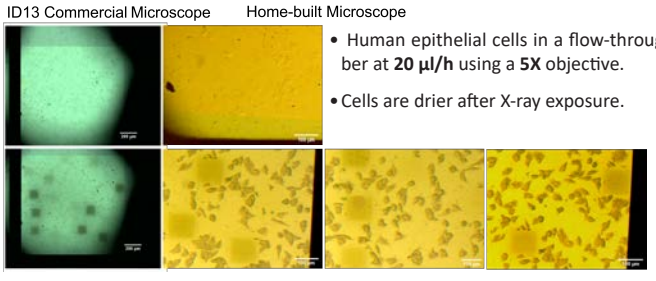
Microscope Integration & Image Comparison

Ilumination:

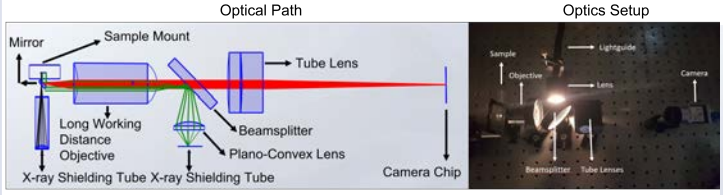
- Plano-convex lens focuses the light into the optical system.
- Beamsplitter splits the light beam to the objective.
- Light from objective is reflected by mirror to illuminate specimen.

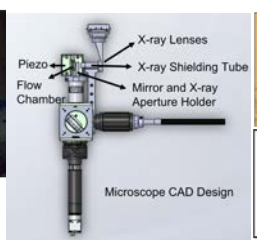
Imaging:

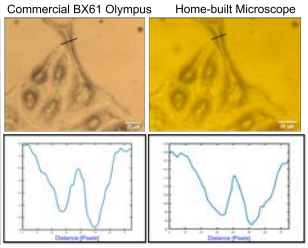
- Light reflected from specimen re-enters the objective and passes through tube lens.
- Tube lens collects and collimates the light into the camera [2,3].



- Human epithelial cells in a flow-through microfluidic chamber at **20 µl/h** using a **5X** objective.
- Cells are drier after X-ray exposure.







- Human epithelial cells with **20X** objective.
- Sharpness of signal contrast picked up in the cell is similar in the two microscopes.

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« SAXS/WAXS mapping of engineered polymers: from image to nanostructure»

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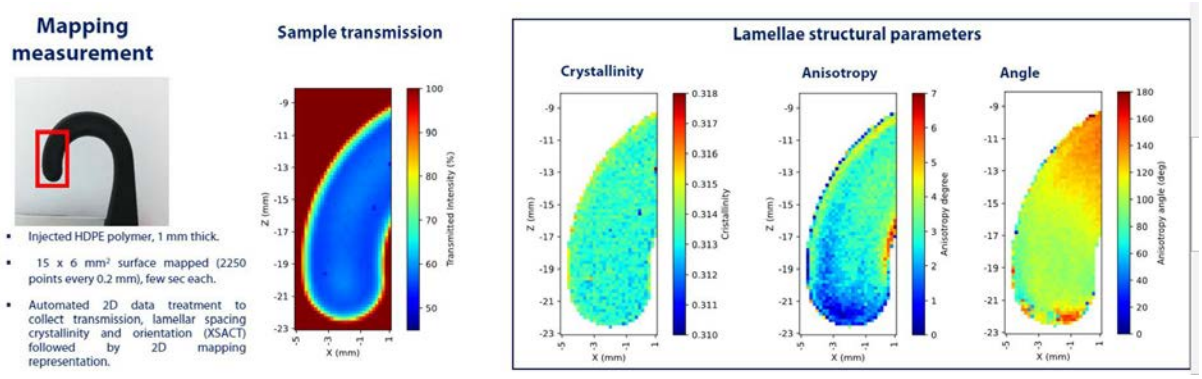
The characterization of polymer materials requires most often the combination of several techniques ranging from microcopy to elemental and mechanical methods. We present in this paper the combination of imaging and nanostructure characterization that is for the first time accessible in a practical manner at the laboratory scale. Indeed, if the mapping of polymer using micron size beam is developed since 2 decades at 3rd generation synchrotron [1], in labs such measurement were until now limited by the flux of x-ray sources, leading to either reduced area of few mm^2 of inspection or of excessive experimental times of few days. By combining short focus optic and compact collimation, we demonstrate the capability of mapping and extracting automatically, within few seconds each, at each inspected point the nanostructural parameters of the studied polymer. In the case of a typical injected HDPE, we present the crystallinity, the lamellar spacing, its degree of and the main orientation of the lamellae in the form of maps of false colors, mapping ~ 100 mm^2 within the hour range. Further, this new capability has a large potential due to its increased x-ray flux density for broader applications such as studies of transient phenomena in organo-photovoltaic films in grazing incidence or other operando measurement such as electro-polymer embedded in renewable energy harvesting components or as in microfluidics reactors enabling high throughput self-assembly in liquido. Automated data interpretation and its limits will be also discussed.



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In situ SAXS/WAXS/GISAXS Facility combined with External Fields: a single platform for the university and a springboard for access to the ESRF and ILL Large Instruments Facilities.

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The aim of this project is to provide to researchers a novel instrumentation of flexible SAXS/WAXS/GISAXS which gives access simultaneously to the scattering from the X-rays of several kind of systems submitted simultaneously to different external fields. This facility will allow to link the structural organization probed by X-rays from molecular to nanometer to micrometer length scales, to the macroscopic information coming from combined external fields solicitations. It will allow to characterize objects from a large community of researchers involved in (Soft Matter, Physics, Chemistry, Physico-Chemistry, Biology, Mechanics, Process Engineering, …) given access to a large panel of laboratories from the UGA, G-INP, CNRS, USMB, CEA, LITEN, ISTERRE, INRAE.

It will allow to study several kinds of systems from solid to soft particles, polymers, biological cells, in liquid or solid-state arrangements, in the volume of the materials or near the interfaces. The novelty of the project is to be able to apply external fields to these systems and probe in-situ the structural changes involved by the applied solicitations (shear flow, extensional flow, magnetic, electric, pressure, ultrasound, …). Time dependent changes as well as locally space position control in the sample, are also available.

The versatility of the proposed facility (Figure 1) thanks to its design, will allow to adapt in front of the X-ray beam, already existing complementary equipment (rheometer [1], microscope, Raman spectrometer probe, …), as well as original cells develop in the laboratories (shear extensional flow cell, filtration cells, ultrasound cells, magnetic, electric cells, traction cells, ….). Furthermore, this equipment has been specifically designed for a quick and reliable switch between the different complementary measurements, permitting to all the laboratories to bring their own application or theme of research in a continuous flexibility in time.

Thanks to its versatility and large community involved, this new instrument will allow to improv the knowledge on fundamental research as well as on industrial applications. This equipment will also allow the development of new cells or complementary solicitation devices, in order to acquire preliminary X-ray scattering data, and will serve as a springboard to apply for beam time allocations at ESRF and ILL.

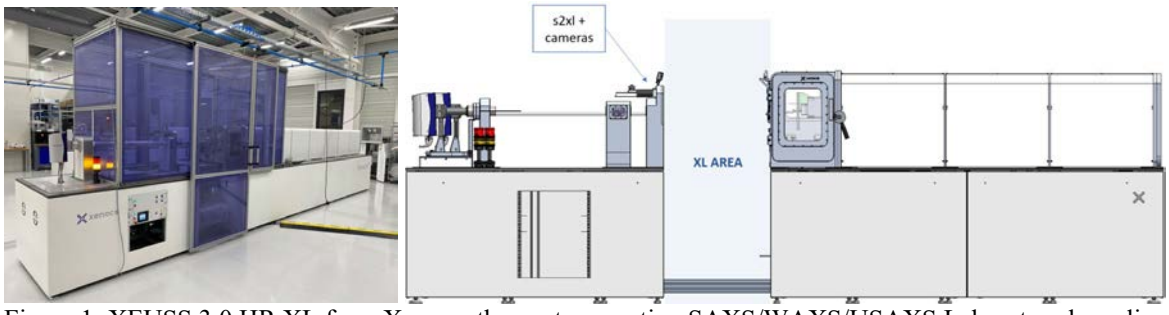

Figure 1: XEUSS 3.0 HR XL from Xenocs, the next generation SAXS/WAXS/USAXS Laboratory beamline (https://www.xenocs.com/saxs-products/saxs-equipment-xeuss/)

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« Mimicking the interface between mammalian plasma membrane and extracellular matrix: chondroitin sulphate-decorated supported lipid bilayers»

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Several vital processes, such as the interaction with pathogens or drugs, take place on the cell surface, and at the interface between the plasma membrane (PM) and the extracellular matrix (ECM). The phospholipids such as the zwitterionic phosphatidylcholine (PC), the negatively charged phosphatidylserine (PS) are among the most abundant lipids in the PM [1]. The ECM is an additional layer bound to the PM, which is composed of flexible carbohydrates and proteins and is responsible for the cell organisation within tissues. Chondroitin sulphates (CSs) are widely present in the ECM of animal cells and are composed of a disaccharide unit (i.e. glucuronic acid and galactosamine), which can be sulfonated at different positions. Mono-sulfonation at position 4 or 6 is the most common, resulting in CS-A and CS-C species, respectively. Typically, CS-A is the most abundant form in human cells, however CS-C is overexpressed in abnormal cells such as cancer cells [2]. Currently there is very few information on the structural arrangement of CS molecules onto the PM surface and how this is affected by the status of the cell, e.g. healthy cells vs cancer cells or healthy cells vs inflammation response. This project is aimed at developing supported lipid bilayers (SLB) functionalised with CS molecules to investigate the impact of the bilayer lipid composition on the structural arrangement of CS. To produce functionalised bilayers, we optimised a recently reported protocol [3], which consists in adding a modified phospholipid that bears an ammino group exposed to the bulk solvent (18:1 Dodecanylamine PE, DOPE-NH_2) to the SLB to form an amide bond with CS-C. We investigated the CS-SLBs interaction for SLBs composed of either pure PC lipids or a mixture of PC and the negatively charged PS. These systems are relevant to investigate the response of the CS layer structure to the exposure of PS lipids on the PM surface, which occurs in case of inflammation. The produced samples were characterised with quartz crystal microbalance with dissipation monitoring (QCM-D) and neutron reflectometry (NR). QCM-D measurements were performed at the PCSM lab at ILL. The presented results are the beginning of an ILL funded PhD project aimed at developing systems based on SLBs to mimic the PM-ECM interface.

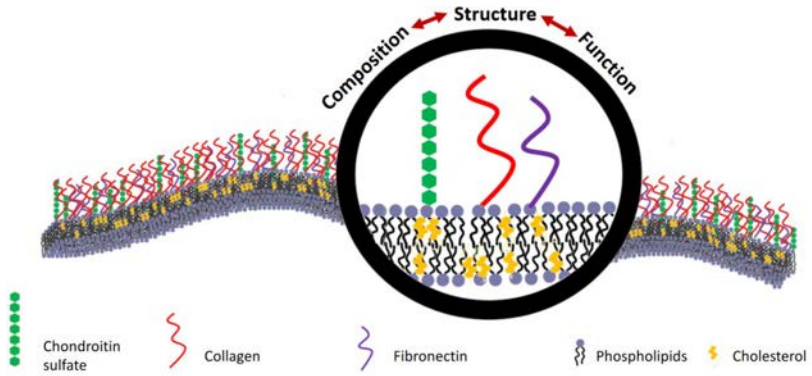

Figure 1: Schematic representation of the PM-ECM interface.

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Binding of sodium perfluorooctanoate and protein to a sapphire surface

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Perfluorinated compounds, known as PFAS, attract a lot of attention as environmental pollutants and it is important to understand their interactions with natural materials and their association in water. Small-angle x-ray scattering (SAXS) results provide details of ionic interactions and their effects on micellization. The micelles formed by the fluorocarbon amphiphiles in the presence of different counterions are highly charged and their shape changes with the different size of the hydrated ions. These will be reported briefly and compared with other studies in the literature. Neutron reflectometry has been used to study the binding of sodium perfluorooctanoate to a sapphire surface in the presence of a binding agent, *Moringa oleifera* seed protein. The protein is known to associate with different classes of materials. The protein adsorbs to the alumina surface irreversibly and is not removed by rinsing with water as seen in previous studies[1]. The amount of protein on the surface was determined to be 4.2 ± 0.5 mg m^{-2} with a very thin layer with a uniform protein concentration of volume fraction of about 55% close to the alumina surface and an exponential decay with a characteristic length of 58 ± 1 Å. The surfactant was measured at its critical micelle concentration of 18 mmol dm^{-3}. Sodium perfluorooctanoate interacts with the protein with adsorption increasing as the concentration increases. A thick uniform layer comprised of protein, perfluorooctanoate and water was formed. Further investigation using neutron reflectivity is needed to study the composition and structure of this layer and establish whether protein has been displaced after the addition of sodium perfluorooctanoate and with subsequent rinsing using different contrasts of water (D_2O and H_2O).

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Short-time transport properties of bidisperse and polydisperse suspensions of proteins confirm a colloid physics picture

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Diffusive properties of proteins are essential for transport and regulation in biological processes. Diffusion covers a wide range of time and length scales. Changes in the short time diffusion - where protein-protein collisions can be neglected - imply effects for the long time diffusion. For monodisperse solutions of proteins, several systematic studies have been performed [1-3] resulting in a comprehensive picture which is in good agreement with colloid theory, describing the temperature, size, and volume fraction dependence.

While the studies above are performed in monodisperse solutions, biological systems contain differently sized particles in the solution. This polydisperse environment influences the diffusion of individual tracers, depending on their size. Recently, the short time-diffusion of tracer proteins has been investigated in the presence of a naturally crowded environment both with quasielastic neutron backscattering and MD simulations confirming a good agreement between experiment and model [4]. The simulations as well as further studies [5] showed that the short time diffusion coefficients of the tracer particles change if the environment changes from a purely monodisperse system towards a polydisperse environment.

To investigate this effect systematically, we performed a neutron backscattering study on solutions containing the two differently sized proteins *bovine serum albumin* (BSA) and *immunoglobulin* (IgG) using the neutron backscattering spectrometer IN16b (ILL, Grenoble, France) [6]. We change both the total volume fraction as well as the fraction of BSA in the solution to probe different sample compositions. By applying advanced analysis frameworks, we are able to separate both global contributions of the different proteins from the averaged internal diffusion and from the solvent contribution. The resulting diffusion coefficients for both proteins are in quantitative agreement with the predicted deviation from the monodisperse case investigating the pure BSA or pure IgG solution.

Besides the importance of these new findings, the new analysis frameworks will open the possibility to new types of experiments, circumventing the necessity of challenging protein deuteration.

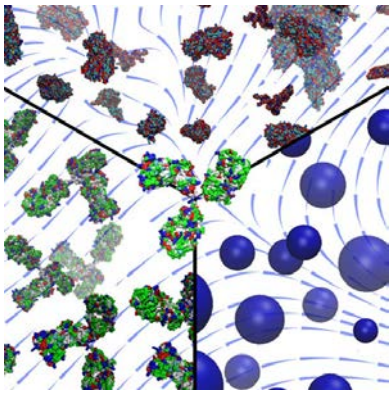

Illustration of monodisperse (bottom left) and polydisperse (top) crowding, and its simulation by polydisperse hard spheres (bottom right) [4]

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Gold nanoparticles networks in topological defects of smectic liquid crystal

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A liquid crystal (LC) is a mesophase where the molecules are free to move as in a fluid, but show a certain degree of order as in a crystal lattice. In the smectic phase, the molecules of the LC are organized in planes called "smectic layers", where the molecules are all aligned in the direction perpendicular to the planes. Under specific conditions, a thin film of smectic LC can form a pattern of flattened hemicylinders called "oily streaks" that present different kinds of topological defects (1D and 2D defects) strictly oriented along the hemicylinders direction. These defects are able to confine nanoparticles (NPs), leading to the formation of specific networks that are well oriented along the defects [1], thus interesting for the induced optical properties of NPs. With gold nanospheres, a plasmonic composite is for example created. The highly homogeneous composites necessary to allow for X-ray diffraction are prepared by spin-coating onto a substrate made of PVA rubbed by a rubbing machine that is brought to the PSCM laboratory. The use of polarized Optical Microscopy allows for a mapping of the LC thickness as a function of position with a resolution of 100 nm.

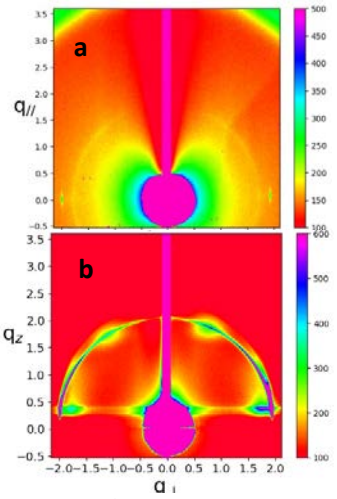

Figure 1. a) TSAXS. The circle corresponds to the disoriented (10) rod seen in transmission of the hexagonal network of NPs confined in the LC 2D defect. b) GISAXS. The two spots appearing on the semicircle indicate the presence of a 3D structure.

Using nanospheres of diameter 6nm, the coexistence of NP chains confined in the 1D defects and strictly oriented NP planar hexagonal networks in the 2D defects was revealed both by absorption measurements and by x-ray diffraction [1]. We are currently interested in using smaller gold nanospheres (2.4nm diameter) to better understand the interaction between NPs and the LC molecules. Grazing incidence Small Angle X-Ray Scattering (GISAXS) and Transmission Small Angle X-Ray Scattering (TSAXS) experiments evidence formation of different networks. At small NP concentration, the TSAXS circle (Figure1a) indicates formation of a disoriented planar hexagonal monolayer, while the signal appearing along z in GISAXS configuration at large NP concentration (Figure 1b) suggests an evolution towards a 3D network. We believe that the small NP size is responsible for their organization inside the LC. Because the size is smaller than the defect core, no interaction with the surrounding oriented LC is possible. Moreover, NP size being close to LC molecule's size, the NP organization at large NP concentration may become commensurate to the smectic layers, to create a composite NP/LC ordered system, thus modifying the LC matrix itself.

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High Pressure GISANS for soft matter systems: case study on polymer brush mixtures

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Tuning hydrostatic pressure up to moderate (P < 1000 bar) pressure values can be crucial for understanding structure-property interplay in different disciplines, including: protein treatment in food processing, biophysics of deep-sea, processing of baroplastic polymers, polymer coating technologies for artificial joints. To the best of our knowledge, the role of pressure and thermodynamic mismatch on (i) the nanostructure of more complex brush topologies such as binary brushes and on (ii) the lateral morphological characteristics of such layers in the size range 1-200 nm has so far remained elusive. We present results [1] of high pressure Grazing Incidence Small Angle Neutron Scattering (high-P GISANS) and off-specular scattering from Neutron Reflectometry acquired at the D22 and FIGARO instruments of ILL, respectively, underlining the nanoscale (Fig.1) lateral and vertical (Fig.2) morphologies of weakly and strongly segregated brush (hydrophilic) PDMAEMA and (hydrophobic) POFPMA homopolymer brushes anchored on Si substrate.

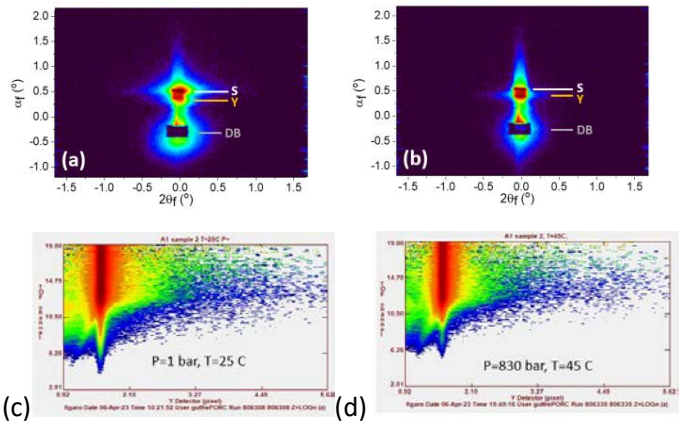

Figure 1. Panel (a)-(b): 2D GISANS images, expressed as α_f vs. $2\theta_f$, for the strongly segregated POFPMA/ PDMAEMA binary brush system, at the different settings: (a) (P = 1bar, T = 45 °C) and (b) (P = 800 bar, T = 45 °C). The direct beam (DB; grey line), the Yoneda peak (Y; orange line) and the specular peak (S; grey line) are denoted as well.

Panels (c) and (d): off-specular reflectivity maps, expressed as wavelength in Å (on the Y-axis) vs. scattering angle (2θ in degrees) on the X-axis for the strongly segregated POFPMA/ PDMAEMA binary brush system. The different (P, T) settings for each segregated system are indicated with black font in panels (a) and (b), respectively.

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