

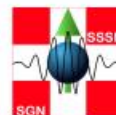
2nd FRENCH-SWISS MEETING
SANS FOR SOFT MATTER

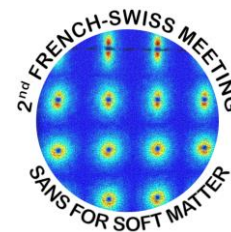
24th - 25th January 2024
Paul Scherrer Institute PSI
Villigen, Switzerland

Liquids, colloids, surfactants, polymers, foams, gels,
granulars, liquid crystals, emulsions, capsules,
proteins, biological materials, food, pharma,
cosmetics, and more!

Invited guests

Prof. Andrea Scotti, Malmö University, Malmö
Dr Jean-Paul Chapel, CRPP, Bordeaux
Dr. Isabelle Capron, INRAE, Nantes
Prof. Harm-Anton Klok, EPFL, Lausanne
Prof. Peter Fischer, ETH, Zurich
Dr. Pierre Bauduin, ICSM, Marcoule





2nd French-Swiss Meeting: SANS for Soft Matter

Day 1: 24.01.2024

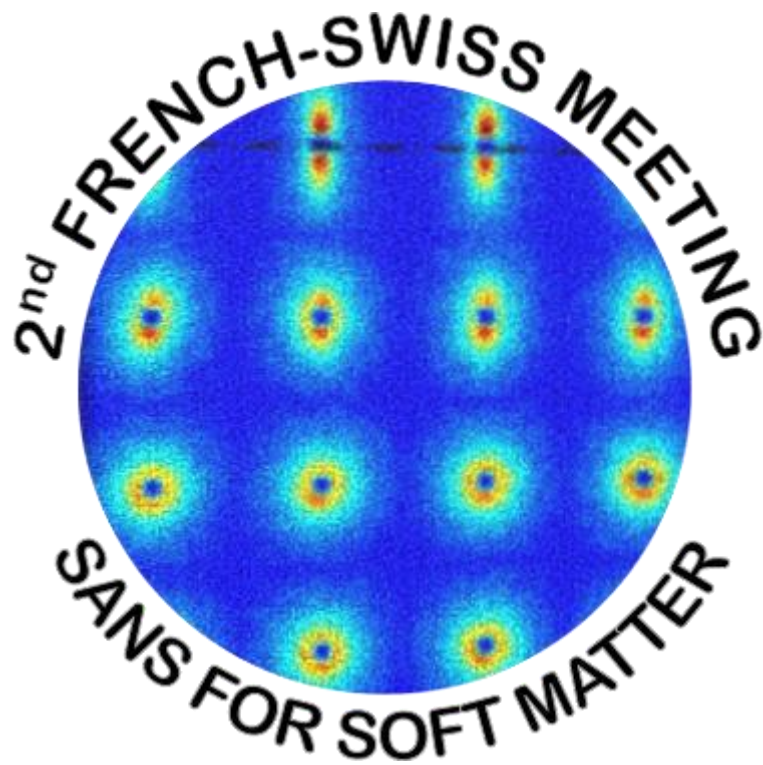
Time	Session	Title	Speaker
11:00	Registration at the Auditorium		
12:00	Lunch at OASE		
13:30	Opening	Welcome to PSI	Michel Kenzelmann (PSI)
13:50	Keynote 1	Particle softness probed by small-angle scattering	Prof. Andrea Scotti, Malmö University
14:25	Talk 1	Oppositely-charged microgels in crowded environment, a SANS with contrast variation study	A. Petrunin
14:45	Talk 2	Counterion cloud percolation induced spontaneous deswelling of pNIPAM microgels investigated via Small-angle neutron scattering (SANS)	A. Zhou
15:05	Talk 3	Exploring Soft Matter with Advanced Sample Environments	L. Chiappisi
15:25	Talk 4	Moisture-dependent swelling in nanocellulose foams investigated with small angle neutron scattering	E. Nocerino
15:45	Coffee break		
16:15	Keynote 2	Macromolecular assembly in slow motion - Dialysis under a neutron beam	Dr. Jean-Paul Chapel, CRPP, Bordeaux
16:50	Talk 5	Iron-carbohydrate Complexes treating Iron Anaemia: understanding the Nano-structure and Protein Interactions using Microfluidic-SAXS and SANS	L. Krupnik
17:10	Talk 6	Decorating tunable structures with PEG	M. Almeida
17:30	Talk 7	Surfactant-induced gelation of oxidised cellulose nanofibrils dispersions: using contrast-variation studies to unravel the micelles-fibrils interactions.	J. Schmitt
17:50	Keynote 3	Probing an oil-water interface stabilized by colloidal Cellulosic particles	Dr. Isabelle Capron, INRAE, Nantes
18:25		SANS-LLB at PSI: keeping up with the soft matter community needs	A. Chennevière
18:35	Poster session, Cheese & wine dinner		

Day 2: 25.01.2024

Time	Session	Title	Speaker
09:00	Opening	Welcome	
09:05	Keynote 4	Characterizing Soft Polymer Materials in the Bulk and at Interfaces with Neutrons	Prof. Harm-Anton Klok, EPFL, Lausanne
09:40	Talk 8	Unravelling the role of amphiphilic polymer conetwork structure in silicone hydrogel contact lens properties	O. Sandre
10:00	Talk 9	Interdiffusion of water in waterborne polymer latex films	D. Saha
10:20	Coffee break		
10:50	Keynote 5	Structure and rheology of stimuli responsive nanocellulose interfacial layers	Prof. Peter Fischer, ETH, Zurich
11:25	Talk 10	Study the mechanisms of the fibrous structure formation in plant-based meat analogues (PBMA) via in situ small angle neutron scattering	T. Guan
11:45	Talk 11	Study of functionalised polymeric micelles through Small Angle Scattering	A. Unnikrishnan
12:05	Keynote 6	Nanometric-sized ions: Emerging Players in Soft Matter - The Decisive Role of Combining Neutron and X-ray Scattering	Dr. Pierre Bauduin, ICSM, Marcoule
12:40	Closing	Poster prize	
13:00	Lunch at OASE		
14:30	Guided visit at SINQ and SANS-LLB		

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ORAL PRESENTATIONS

Particle softness probed by small-angle scattering

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Suspensions of colloids have been used as models for atomic systems to tackle fundamental questions on the equilibrium phase behaviour and flow properties of materials. In contrast to hard spheres, microgels allow us to study the role of the softness and compressibility of an individual particle on the macroscopic properties of the suspension. However, the fact that microgels can change both shape and volume makes the understanding of the role of softness complicated. Here, I will show how we have combined small-angle x-ray and neutron scattering with contrast variation, together with computer simulation, to tackle this problem and show how isotropic deswelling and faceting play a key role in microgel suspensions.

Oppositely-charged microgels in crowded environment, a SANS with contrast variation study

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Microgel suspensions are colloidal dispersions of submicron-sized polymeric gels that swell in a good solvent. They are soft and responsive particles that are perfect for the creation of “smart” materials and for studies of crystallization or glass transition. Due to their softness, microgels deswell, deform or interpenetrate their neighbours at concentrations close to or above close packing. Recently, using small-angle neutron scattering (SANS) with contrast variation, we have shown that the dominance of deswelling or deformation in suspensions of ionic microgels is controlled by their charge state and the charge state of the surrounding microgels [1].

In the present study, we use the same methodology to investigate how a few negatively-charged microgels behave in crowded environments of positively-charged ones (and vice versa). To do so, we measure the form factors of a few negatively-charged protonated microgels in the matrix of positively-charged deuterated microgels, which are contrast-matched by the solvent. The structure factors of the same suspensions are measured using small-angle X-ray scattering (SAXS), where the contrast of protonated and deuterated microgels is equal.

We find strong deswelling of the negatively-charged microgels already far below close packing, which indicates that electrostatic interactions and free counter-ions determine the response to crowding in this case. Furthermore, we observe progressive deformation (faceting) of the negatively-charged microgels with increasing packing fraction, but significantly earlier than has been reported for neutral or like-charged microgel suspensions. Overall, the results are consistent with formation of complexes or aggregates of oppositely-charged microgels, which become progressively compacted by crowding. This study is of high relevance for understanding the structure and properties of electrostatically-driven soft supracolloidal structures, like colloidal gels, colloidal molecules and many other.

[1] Petrunin et al., “Self-Healing of Charged Microgels in Neutral and Charged Environments.” *Langmuir* (2023).

Counterion cloud percolation induced spontaneous deswelling of pNIPAM microgels investigated via Small-angle neutron scattering (SANS)

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Microgels are colloidal stimuli sensitive, cross-linked polymer networks, which are a good model system for soft colloids. As a result of their compressibility and deformability, soft colloids have a higher degree of freedom than hard colloids and, as a consequence, their phase behavior and interaction are not well understood, especially at high concentrations. Although pNIPAM is an uncharged polymer, pNIPAM microgels are peripherally charged due to charges remaining from the ionic initiator used in the microgel synthesis. The corresponding counterion cloud has been found to play a crucial role for the observed spontaneous deswelling behavior at high concentrations; particles deswell before reaching random closing packing, ϕ_{rcp} , due to the raising suspension osmotic pressure induced by free counterions exploring the suspension volume. In this work, we have studied microgels with a crosslink density of 2.0 mol% in suspensions with effective volume fractions from $\zeta = 0.02$ to $\zeta = 1$ at 18°C. Additionally, we replace the counterions with either Na^+ or NH_4^+ via dialysis, which allows obtaining the cloud form factor using SANS with contrast variation. These measurements confirm that the counterion cloud indeed locates at the particle surface, and both cloud radius, R_{ic} , and width, σ_{ic} , can be determined using a spherical-shell model. Interestingly, the microgels remain at their swollen size at relatively low concentration, and shrink above a critical concentration ζ_c . Their inter-microgel distance d follows the behavior $d \approx \zeta^{-1/3}$, indicating that the deswelling is isotropic without the direct interaction of microgels. We use the effective particle radius $R_{eff} = R_{SANS} + \sigma_{ic}$ including the counterion cloud to assess the role of the counterions for deswelling. Indeed we find that $\phi_{eff} = 1$ at ζ_c , indicating that all space between microgels is occupied by counterions such that the osmotic pressure increases and the microgels isotropically deswell. This supports the theory of spontaneous deswelling induced by the percolation of the counterion clouds. Our results stress the importance of including counterion effects for a comprehensive understanding of microgels at high concentrations and for formulating new models for their phase behavior that take spontaneous deswelling at high concentrations into account.

In addition, SANS with contrast variation utilizing different ion species has proven to be robust for determine the characteristics of the very dilute counterion cloud, which can be potentially applied for the studies of other charged systems, such as other microgels, polymers, or micelles.

Exploring Soft Matter with Advanced Sample Environments

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The neutron scattering facilities worldwide constantly replace or upgrade their instrumental suite to provide the scientific community with unprecedented capabilities. Progresses all-along a neutron scattering beamline, from the improved production and optics to more sensitive detectors, allow nowadays experiments which were unthinkable until some time ago. However, not less relevant are the strong progresses which have been made with sample environments, allowing samples to be probed under extreme conditions, with high throughput or under in-operando or in-vivo conditions.

Herein, we provide an overview of some of the recent sample environment developments achieved at the ILL for the small-angle scattering machines in the domain of soft condensed matter. By showcasing different experimental studies, we provide an overview of the following setups:

- A recently developed foam column, entirely made in quartz and integrating optical prisms and electrodes, allows to probe liquid foams with small-angle neutron scattering, mesoscopic photography and electrical conductivity. The setup, associated with a fully consistent analysis, allows to characterize the relevant aspects of a liquid foam structure: liquid content, plateau border size and specific area, bubble size distribution, and thin film thickness and specific area.
- Controlling the humidity in a system allows for a precise control of the water chemical potential in the system. Accordingly, it is an excellent tool to probe the role of water and the swelling behaviour of colloidal systems. A new setup has been developed, in which saturated vapours of D₂O, H₂O and an optional additional liquid are mixed with dry nitrogen or an additional gas. The setup precisely tunes the humid content in the system and allows to perform contrast variation experiments in humidity-controlled environments. The potential of the setup is showcased using the examples of time-resolved swelling of historic woods.
- Hydrostatic pressure is a fundamental thermodynamic parameter that profoundly influences the physicochemical properties of colloidal systems, making it a powerful tool for investigating their structural or self-organization properties. Herein, we will present the high-pressure cells optimized for small-angle neutron scattering and neutron spin-echo. The setup allows also to perform time-resolved pressure-jump experiments with time resolution of few tens of milliseconds.

In summary, recent development in sample environment allow to address challenging scientific questions in very different domains of soft condensed matter and to exploit to a maximum the neutron scattering instruments.

Moisture-dependent swelling in nanocellulose foams investigated with small angle neutron scattering

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Cellulose nanomaterials had a substantial impact on the technological advancement of sustainable materials that could replace the currently used energy-intensive and fossil-based ones in various applications, including thermal super-insulation of built infrastructures. Nonetheless, cellulose is hygroscopic and, when considering cellulose based nano-materials, the influence of water is even more puzzling because of the non-trivial behavior of fluids in nano-confined environments. The complex interaction of nanocellulose with moisture will inevitably affect the nanomaterials performance in realistic applications. The aim of this study is to gain fundamental understanding of the water-cellulose interactions by probing the structural evolution of nanocellulose foams at different relative humidity conditions with SANS. In particular, we characterized the morphology of the fibrils and their organization in bundles at the nanometer scale, as a function of water uptake.

Macromolecular assembly in slow motion - Dialysis under a neutron beam

J. P Chapel

Paul Pascal Research Center (CRPP) – CNRS/University of Bordeaux (France)

How easy is it to self-assemble/co-assemble colloids and macromolecules? A central question for academic and industrial laboratories, where formulation is a key step. Micelles, vesicles, polymersomes, lipid membranes and polyelectrolyte complexes are just some of the assembled structures formed by amphiphilic or oppositely charged macromolecules. Most of the time, these objects are assembled under non-equilibrium conditions and are therefore not the most thermodynamically stable, but the fastest-forming, with morphologies (and final properties) that are highly dependent on the formulation pathway followed. *Can we then slow down the intimate contact between these building blocks enough to observe the most stable structures and follow the various stages of their formation?* In this presentation, I will use selected examples to illustrate an innovative experimental protocol developed in collaboration with ILL's D22 team (L. Porcar) using dialysis under a neutron (or light) beam. This setup allows water to diffuse slowly into a mixture containing a miscible solvent (THF or salt water), making it possible to monitor *in situ* the desalting of polyelectrolytes, the formation of polyelectrolyte complexes or the self-assembly of amphiphilic block copolymers under quasi-equilibrium conditions. This approach offers numerous possibilities for observing and better understanding the organization of other supramolecular or macromolecular systems controlled by selective solvent diffusion or any other molecular entity capable of triggering assembly, including acids or bases, ions, H-bonding agents or small-molecule ligands. It is now part of the D22 environment sample.

Iron-carbohydrate Complexes treating Iron Anaemia: understanding the Nano-structure and Protein Interactions using Microfluidic-SAXS and SANS

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Intravenous iron-carbohydrate complexes are widely used nanoparticles to treat iron deficiency anaemia, which is associated with illnesses such as chronic kidney disease and inflammatory bowel disease [1]. A variety of clinical and biological in-vivo studies on these products (e.g. ferric carboxymaltose and iron sucrose) are available [2,3]; however, their undergoing structural changes during the early stages of entering the human bloodstream, referred to as biotransformation, are not fully understood. Using a combination of cryo-STEM, SAXS and SANS we investigated the core-shell structure of these complexes and how it is affected by interactions with serum proteins.

Our SAXS and SANS experiments indicate the presence of nanoparticle clusters with a diffusely bound carbohydrate layer for iron sucrose and a strongly bound carbohydrate shell for ferric carboxymaltose. Both cluster structures further agglomerate into larger NP-protein domains upon addition of human serum albumin or fibrinogen. The onset of this agglomeration process could be pinpointed at 10 min by combining microfluidics with both SAXS and SANS. With this approach, we are able to understand the early interactions of iron-carbohydrate complexes in a dynamic and highly biological environment mimicking physiological biotransformation to better predict clinical outcomes.

[1] J. Rottembourg, et al., *Nephrology Dialysis Transplantation*, 2011, 26(10), 3262-3267.

[2] L. Krupnik, et al., *European Journal of Pharmaceutical Sciences* 188 (2023): 106521.

[3] N. Nikravesh, et al., *Nanomedicine: Nanotechnology, Biology and Medicine*, 2020, 26, 102178.

Decorating tunable structures with PEG

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To target a particular organ effectively, hydrophobic and hydrophilic drugs often require transport within nanoparticles, such as vesicles. A common approach to improve their compatibility with biological systems and increase their stealthiness involves decorating them with poly(ethylene glycol) (PEG) on the surface. This process is commonly called “pegylation.”

In this presentation, I will show a strategy to obtain long pegylated tubes or vesicles as nanocarriers, which could transit onto micelles above 37°C. We use a fatty acid, 12-hydroxy stearic acid (HSA), obtained from castor oil. In presence of a counter ion, HSA is able to self-assemble in micrometric multilamellar tubes at low temperature, or in nanometric micelles at high temperature. This transition can be tuned with the nature and the ratio of the counter ion in solution [1]. Such solution of HSA would be doped by telechelic PEG. Which is obtained by grafting fatty acids on each extremity by a Steglich esterification, to enable their insertion in HSA self-assemblies.

Structures of such complex systems have been studied by Small Angle Neutron Scattering (SANS), using contrast variation method to elucidate either the structure of HSA self-assembly or of polymer conformation. This system enables us to build a large variety of different thermosensitive pegylated nanocarriers that goes from vesicles (Figure 1A) to multilamellar tubes (Figure 1B) and to micelles at high temperature (Figure 1C).

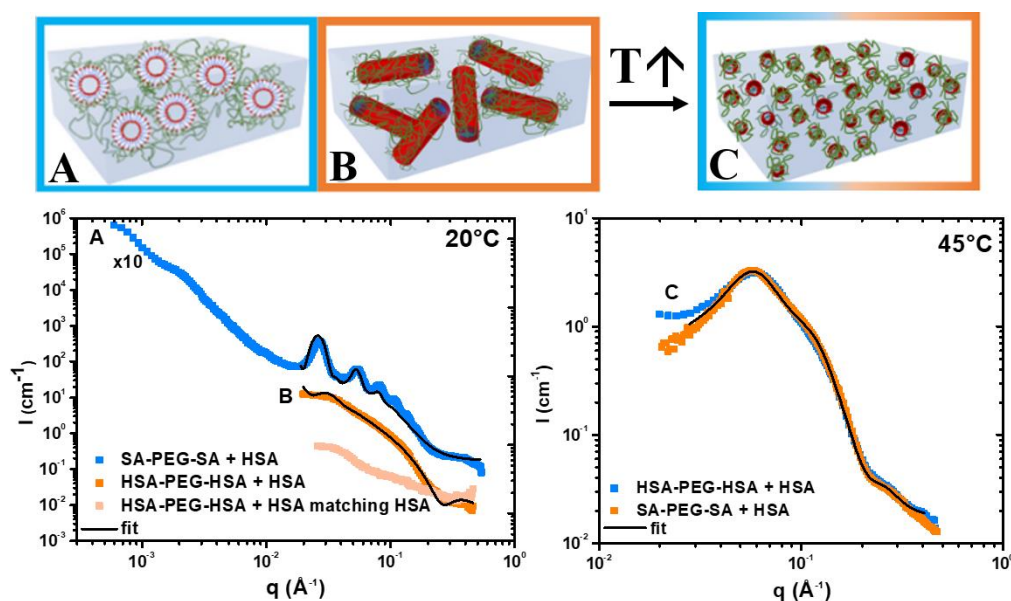


Figure 1 Left: structure at 20 °C. Top panel: sketches of the vesicles with PEG chains represented in green lines. Sketches of multilamellar tubes with PEG chains represented in green lines. Bottom panel: SANS intensity profiles PEG grafted HSA + HSA mixture in orange, PEG grafted HSA + HSA mixture in the solvent that matches HSA and pure PEG in beige, PEG grafted SA (stearic acid) + HSA mixture in blue. Right: Structure at 45 °C. Top panel: sketches of the micelles with PEG chains represented in green lines. Bottom panel: SANS intensity profiles PEG grafted HSA + HSA mixture in blue. SANS intensity profiles PEG grafted SA + HSA mixture in blue.

[1] Fameau, A. L., et al. (2017). Langmuir, 33(45), 12943-12951.

Surfactant-induced gelation of oxidised cellulose nanofibrils dispersions: using contrast-variation studies to unravel the micelles-fibrils interactions

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Cellulose, as the most abundant natural polymer, is extensively studied in the formulation of new biodegradable materials, as it is biocompatible and environmentally friendly [1]. The TEMPO oxidation procedure yields negatively-charged nanofibrils (labelled OCNF for oxidised cellulose nanofibrils) with an elliptical cross-section of ca. 5nm and a length ≥ 100 nm that we previously studied in SAXS.[2] OCNF can be easily dispersed in water and thanks to their biocompatibility be used as rheological modifiers for healthcare products. Notably, hydrogels can be formed in solution by tuning the concentration of OCNF, the addition of salt or the presence of surfactants. The latter is a common component of personal or home care formulations (such as creams or shampoo), it is hence of crucial interest to study the influence of surfactants on OCNF dispersions. In this work, we studied OCNF suspensions in presence of four different surfactants, all presenting the same hydrophobic carbon tail but different headgroups: hexaethylene glycol mono-n-dodecyl ether (C12EO6, nonionic), sodium dodecyl sulfate (SDS, anionic), cocamidopropyl betaine (CapB, zwitterionic), and dodecyltrimethylammonium bromide (DTAB, cationic). We compared the structural information obtained from SANS studies with the rheological properties of the dispersions.

Contrast variation SANS studies using deuterated version of C12EO6 or SDS, or by varying the D2O/H2O ratio of the suspensions (with CapB), allowed focusing only on the structural properties of OCNF or surfactant micelles. For C12EO6, we showed that, in the concentration range studied (above the CMC), both OCNF and micelles are present in solution. Although the nanofibrils are concentrated thanks to an excluded volume effect observed in SANS, the rheological properties of the suspensions are not affected. Addition of SDS or CapB induces gelation for surfactant concentrations superior to the critical micellar concentration (CMC). SANS results show that attractive interactions between OCNF arise in the presence of micelles from these anionic or zwitterionic surfactants, hinting at depletion attraction as the main mechanism of gelation. Finally, addition of small amounts of DTAB (below the CMC) allows forming a tough gel by adsorbing onto the OCNF surface, decreasing their overall surface charge and possibly creating hydrophobic patches that favours aggregation [3].

[1] D. Klemm et al., *Angew. Chem. Int. Ed. Engl.*44 (22), 3358 (2005)

[2] J. Schmitt et al., *Phys. Chem. Chem. Phys.*20 (23), 16012 (2018)

[3] J. Schmitt et al., *J. Chem. Phys.*158 (3), 034901 (2023)

Probing an oil-water interface stabilized by colloidal Cellulosic particles

I. Capron

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Nanocelluloses constitute elementary bricks that are used to design cellulose-based materials with notably mechanical, optical, sustainable and interfacial properties. Cellulose nanocrystals (CNCs) are rod-like parallelepiped nanoparticles that, despite being considered hydrophilic, adsorb efficiently at oil–water interfaces and enable to produce highly stable emulsions armored by a layer of solid particles, forming the so-called Pickering emulsions [1]. These CNC-stabilized emulsions have raised a strong interest for further applications but their exact anchoring at the interface required combining several techniques to obtain a refined description of their structure.

In this presentation, I will show how the use of various contrast variations small angle neutron scattering enabled to describe the stabilization of Pickering emulsions, probing the interface. I will notably compare the organization of two crystalline kinds of CNCs once adsorbed on the surface of oil droplets. SANS revealed a clear change in orientation at the interface between the native CNC-I and mercerized CNC-II. The evolution of the thickness of the nanolayer adsorbed with concentration showed a face-on for CNC-I and edge-on for CNC-II [2]. SANS gave experimental results that were confirmed by molecular dynamics simulation in a spontaneous and irreversible way.

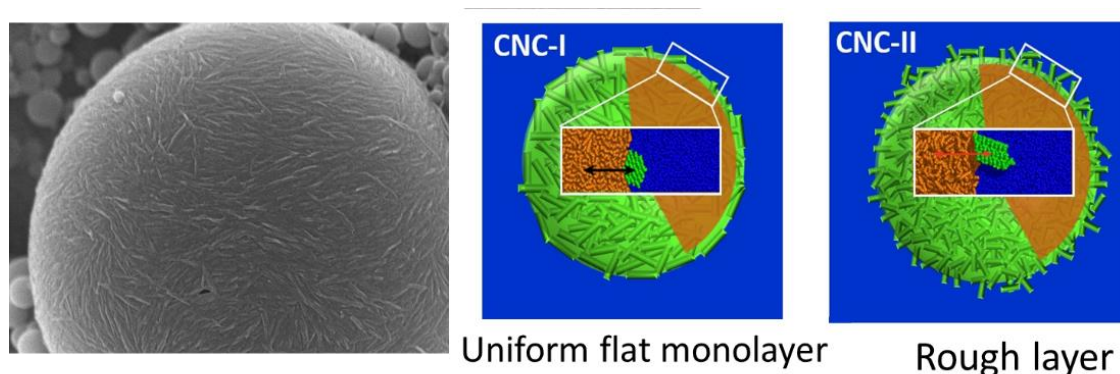


Figure 2. Left: SEM picture of CNC-stabilized Pickering emulsions. Right: CNC-I and CNC-II schematic structures of emulsions. CNC are in green, oil in orange, and water in blue. The inset shows a snapshot from MD simulations.

[1] F Cherhal et al. *Biomacromolecules*, 2016, 17(2), 496-502

[2] S. Haouache et al. *Biomacromolecules*, 2022, 23(9), 3517–3524.

Characterizing Soft Polymer Materials in the Bulk and at Interfaces with Neutrons

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Solvent-swollen crosslinked polymer networks and surface-grafted thin polymer films are attractive materials that possess a range of interesting properties. Unraveling the molecular and nanoscale structure – property relations that govern the characteristics of these materials systems, however, is a challenge. Crosslinked polymer networks, for example, typically feature molecular-level and larger length scale heterogeneities. Surface grafting of polymers results in thin polymer films with a complex nanoscale structure that is characterized, amongst others, by a non-uniform segment density profile. Neutron-based characterization methods are powerful tools that can help to more accurately study these systems. This presentation will highlight examples of experiments that were done to study the structure of polymer gels prepared by crosslinking of 4-arm-star-shaped poly(ethylene glycol) precursors as well of thin polymer films, also referred to as polymer brushes, obtained via surface-initiated polymerization.

Unravelling the role of amphiphilic polymer conetwork structure in silicone hydrogel contact lens properties

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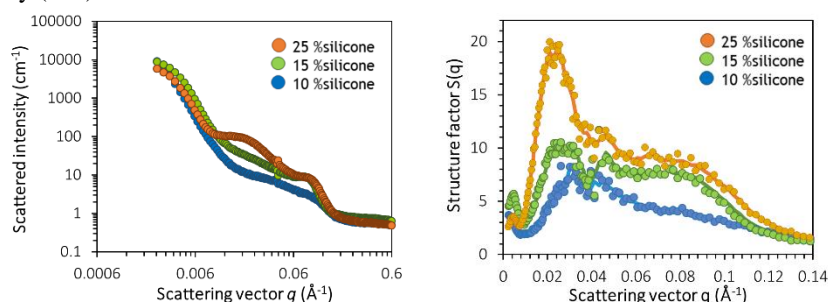
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Contact lenses are biomedical devices that correct ocular defects such as astigmatism, myopia, hypermetropia, and presbyopia. Based on their composition they can be classified as rigid, soft and hybrid [1]. Within soft contact lenses we can find silicone hydrogel contact lenses which are composed of amphiphilic polymer co-networks (APCN) mixing (meth)acrylic and vinyl polymer hydrogels with a silicone network [2]. Together they form an interpenetrated network (IPN) of silicone and hydrophilic chains [1,3,4]. The main advantage of silicone hydrogels is that they show higher oxygen permeability than classical hydrogels due to the mobility and low cohesive energy of Si-O groups [5-8]. In general, contact lenses should provide, good vision, comfort, and they should be able to allow an appropriate corneal metabolism. All these features depend on the optical (transparency, refractive index), chemical (water content and oxygen permeability) [3] and mechanical (modulus) [9] properties of the contact lenses. The goal of this investigation is to use a bifunctional hyperbranched polyglycerol (HPG-AI) [10] as a crosslinker to obtain silicone hydrogel contact lenses. Contact lenses with different concentrations of crosslinkers and silicones were prepared by cast molding and characterized by a polarographic method, gravimetric analysis, and UV-vis spectroscopy to determine the oxygen permeability, equilibrium water content (EWC) and transparency (T%).



With the aim to study the structure-property relationship, a series of contact lenses (both dry and saturated with either 100% D₂O or 22% D₂O : 78% H₂O mixture matching the hydrophilic components) were analyzed by small angle neutron and synchrotron X-ray scattering. The SANS, SAXS and WAXS curves were analyzed qualitatively and quantitatively. For example, samples with identical monomers and crosslinkers yet varying silicone contents were compared in the swollen and dry states for the total contrast condition. We interpret the curves as typical of a composite of silicone domains embedded in the hydrophilic matrix. By analogy with silica-polymer composites in literature [11], we estimated the intraparticular structure factor $S(q)$ that displays two peaks correspond to domains at increasing mean distances with higher concentrations of silicone, in accordance with the decay of the oxygen permeability at higher silicone amounts. Additionally, swelling kinetics were carried out for selected contact lenses by following the time evolution of the scattering curve along hydration, from which water diffusion coefficients within the network were deduced. Our aim is to measure other features such as the values of the two mesh sizes of the APCN structure for all the samples studied (more than 120 in total) and to correlate them with the macroscopic properties of the lens formulations (transparency, O₂ permeability and elastic modulus).

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Interdiffusion of water in waterborne polymer latex Films

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Waterborne latex films, obtained from the dispersion of latex particles are of particular interest due to the non-content of volatile organic compounds (VOC), often mandatory under environmental legislation [1]. However, abrupt water penetration inside the films restricting their lifespan and deteriorating the shining of the coating. In order to prepare efficient and solvent-free coatings with the low glass-transition temperature ($T_g < \text{the drying temperature}$) but with higher mechanical strength, we have integrated hydrophilic layers (Acrylic acid/Poly(acrylamide)) around the hydrophobic cores (mixture of Methyl methacrylate and Butyl acrylate) and also hard shell around the soft core in the latex film. Latex particles with different morphology (hairy layer variants and core-shell particles) have been synthesized using emulsion polymerization. Polymer latex films have been prepared in the next step by evaporating water in a climate chamber at temperature 25°C. The structure formation of polymer latex films in the dry state (crystallinity) and in re-swelled state (change in crystallinity and whitening or blushing) have been studied to propose a recipe for the reparation of efficient latex coatings. The SANS study shows FCC-like structure formation by the latex film, which become more organized with the inclusion of the that the hydrophilic shell. On the other hand, the inclusion of hard shell protects the latex films from water whitening and provides additional mechanical strength.

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Structure and rheology of stimuli responsive nanocellulose interfacial layers

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The use of particles such as nanocelluloses, i.e. cellulose nanocrystals (CNC) and nanofibrils (CNF) received increasing attention for the Pickering stabilization of fluid interfaces [1]. The adsorption of nanocellulose and nanocellulose-protein composites at oil-water or air-water interfaces facilitates the formation of stable and biocompatible emulsions and foams but depends heavily on the particles' surface properties. In this contribution, we review the structure of differently designed adsorption layers by neutron reflectivity and interfacial rheology measurements as a function of physico-chemical boundaries conditions (pH, salts, oils, enzymes) [2, 3], surface properties of the cellulose crystals (natural, methylation, esterification) [4, 5], and protein or polysaccharide addition [6]. Native unmodified CNC (hydrophilic, negatively charged, and anisotropic nanoparticles) showed negligible viscoelasticity that could be increased by charge screening due to a shift from repulsive to attractive CNC interactions. Methylated CNCs formed dense monolayers with higher dynamic moduli compared to native CNCs and could be thermo-gelled into multilayers. The esterified CNCs formed aggregated clusters at the interface, resulting in a Maxwellian frequency behavior with distinctive relaxation times, a rarely observed phenomenon for interfacial layers. Scattering length density profiles obtained from neutron reflectivity measurements are used to elucidate the thickness and roughness of the adsorption layer, and in case of nanocellulose-protein composites, their spatial composition. Supported by in vivo digestion experiments in humans we rationalize the design principles of nanocellulose-stabilized emulsions and foams for food and drug delivery vehicles [7-9].

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Study the mechanisms of the fibrous structure formation in plant-based meat analogues (PBMA) via in situ small angle neutron scattering

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Current unsustainable meat consumption makes a growing number of meat consumers turn to PBMA. To facilitate the transition towards a plant-based diet with its health and environmental benefits, the demand for an accurate reproduction of meat-like structure, texture and mouthfeel in PBMA is pressing. High Moisture Extrusion Cooking (HMEC) is one of the methods to produce PBMA. During HMEC, mixtures of plant proteins, dietary fiber and fat undergo heat- and flowinduced denaturation and subsequent plastification and texturization. The key to reproduce meatlike structures are the plastification and texturization which take place in a cooling die attached to the end of the extruder. However, the “black-box” characteristics of the extrusion process make understanding this process difficult. In addition, most studies are based on either raw materials or end products, and to our knowledge, there is no study available which describe the texturization process in the cooling die. Therefore, we have performed in situ Small Angle Neutron Scattering at SANS-I beamline at SINQ with a customized cooling die. It has three neutron-transparent ‘windows’ which allow neutron beam to pass to shed light on the plastification and texturization mechanisms throughout the entire cooling process during extrusion. Contrast variation via solvent deuteration was applied to determine the contribution of the different components. We found the fibrous structure in macro-scale did not assemble from nano-scale. Fractal nanogel of 40 nm which is consist of proteins with radius of gyration of 4.5 nm were found instead. Hypothesis about the arrangement of the nanogel was proposed as the possible mechanism. Our results contribute to a detailed insight into PBMA structuring and thereby help pave the way towards a more sustainable nutrition.

Study of functionalised polymeric micelles through Small Angle Scattering

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PolyIon Complex (PIC) micelles are well appreciated structures in the synthesis of functionalized ordered mesoporous materials (2-50 nm pore diameter, having applications in a range of domains including catalysis and medicine), due to the controlled micellisation and their role as both templating and functionalising agent. They are formed by the electrostatic complexation between a double hydrophilic block copolymer (DHBC), presenting one neutral block and one charged block, with an oppositely-charged polyelectrolyte. Their micellisation is controlled by physico-chemical parameters, such as pH variation. In presence of silica, a hybrid material is obtained where PIC micelles act as template, before freeing the porosity by dismantling the micelles via pH change. While the polyelectrolyte can be thus recovered, the DHBC remains at the surface of the pores, giving a functional material whose functional groups depends on the charged block chosen for the DHBC. To extend the range of applications of such materials, it is hence of prime importance to design novel DHBC and assess their capacity to form PIC micelles in solution in presence of a carefully-chosen polyelectrolyte.

We synthesised two new DHBC with amine groups in the charged block for CO₂ capture: P(APEO)m-b-P(AEMA)n, made of a poly (ethyleneoxidepolyacrylate) (PAPEO) neutral block and a positively charged aminoethyl methacrylate block (PAEMA) and, P(APEO)m-b-P(AA/NH₂)n, fabricated using the same neutral block and a partially amidated poly (acrylic acid) block (9% amidation). The latter was obtained via modification (amidation) of acrylic acid block of the copolymer using ethylene diamine. Both DHBC were found to form micelles in presence of Poly (acrylic acid) PAA or Poly (styrene sulfonate) PSS for P(APEO)m-b-P(AEMA)n and Oligochitosan (OC2500) for P(APEO)m-b- P(AA/NH₂)n.

PIC micelles developed using the above copolymers, were characterised using Dynamic and Static light scattering (DLS/SLS) along with Small Angle Scattering (SANS/SAXS). The preliminary characterization using DLS at pH 5, indicated that PAPEO21-b-PAEMA21 along with PAA (2.1 kD), and PSS (1 kD) as polyelectrolyte, form structures with hydrodynamic radius $R_h=43.6\pm 0.6$ nm, and 32.0 ± 0.6 nm respectively. On the other side, P(APEO)-b-P(AA/NH₂) (9% amidation) with OC2500 form micelles with R_h and R_g values of 11.5 ± 1.3 and 53.4 ± 1.5 nm respectively, which indicate the formation of elongated objects ($R_g/R_h=4.64\pm 0.65$). The shape and structure of the PIC micelles can be precisely acquired employing Small-Angle X-ray Scattering (SAXS) and Small-Angle Neutron Scattering (SANS). SANS can allow to look into the hydration of the shell more precisely (in X-ray, both core and corona have SLDs close to the solvent). SANS (D22, ILL) and SAXS (Swing, Soleil) measurements, primarily focusing on the inter-micellar scattering, confirmed that P(APEO)21-b- P(AEMA)21 form typically spherical PIC micelles, while P(APEO)m-b-P(AA/NH₂)n (9% amidation) form stable elongated structures. The patterns were not only fitted using the Guinier approximation, allowing to obtain similar gyration radii than in SLS, but also using spherical and cylindrical models for P(APEO)m-b-P(AEMA)n and P(APEO)m-b-P(AA/NH₂)n based micelles respectively. P(APEO)21-b-P(AEMA)21 micelles with PAA 2.1 kD and PSS were found at 19.3 ± 1 nm and 12.8 ± 1 nm radius respectively, while P(APEO)m-b-P(AA/NH₂)n (9% amidation) build elongated micelles of radius 4.8 ± 0.2 nm and ≥ 20 nm length. By varying the type of polyelectrolyte or the block length of the DHBC used, we can hence tailor the size and shape of the micelles to adjust them for the synthesis of functionalised materials.

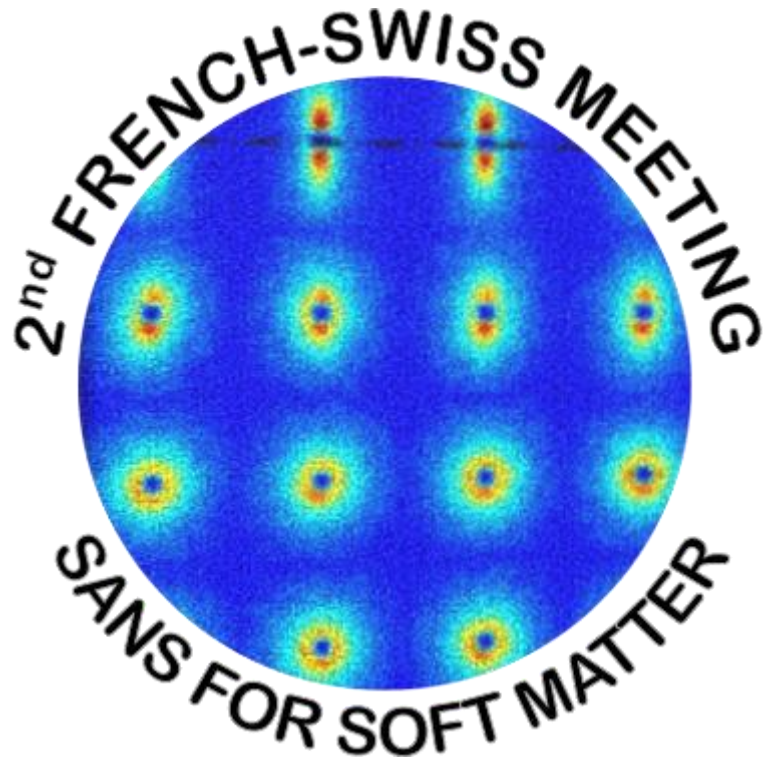
Nanometric-sized ions: Emerging Players in Soft Matter - The Decisive Role of Combining Neutron and X-ray Scattering

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Nanometric ionic species (nano-ions), such as polyoxometalates (POMs) or (metal-) boron clusters, are at the frontier between ions and charged colloids. Their large size and low charge density, compared to conventional ions, result in a unique behavior known as "super-chaotropicity". This behavior leads to a strong affinity for organic molecules, causing nano-ions to adsorb at neutral hydrophilic interfaces and exert influence on their stability. Nano-ions enable both stabilization and destabilization of colloidal systems through non-specific interactions, including electrostatics, hydrophobic and super-chaotropic effects.

In this contribution, I will highlight the critical role of complementary neutron and X-ray scattering techniques in studying the profound effects of nano-ions on soft matter systems. Examples will be presented illustrating the impact of nano-ions on self-assembly or disassembly processes, phase transitions in surfactant systems, and the solubilization of hydrophobic compounds. The super-chaotropic behavior of nano-ions presents significant opportunities in diverse fields, including biology, separation science, catalysis, and the design of nanostructured hybrid materials.



POSTERS

Therapeutic lipid nanoassemblies in a biomimetic medium: transformation, fate and interactions

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For two decades, pharmaceutical industries have developed a growing interest towards nanoparticles (NPs). The combination of pharmaceutical activity and nanoscale formulation offers many advantages such as better targeting and reduced toxicity of the drug, improvement of the pharmacokinetic to cite a few. However, the limited knowledge regarding some of their physicochemical characteristics following their administration in the body poses a barrier to their safe use. Despite the abundance of publications in the field over the past years, only a limited number of nanoparticles have received marketing authorization [1].

In this context, we propose to study a particular case of “soft” nanoparticles formed by self-assembly in water of Leu-enkephaline prodrugs using squalene (SLA). This amphiphilic nanomedicines are intended to alleviate pain in patients after intravenous administration without causing side effects [2]. Indeed, these nanoparticles constitute a great alternative to morphine since they displayed an important analgesic activity in vivo with a longer lasting effect. Moreover, it was observed that unlike morphin, they act on peripheral opioid receptors thus avoiding the central nervous system, commonly implicated in the occurrence of addiction phenomena.

The primary goal of this study is to collect quantitative data regarding the interactions of nanoparticles with blood proteins in various media mimicking the bloodstream such as Phosphate buffered saline (PBS). At a first level, we have studied the interaction of the SLA nanoparticles with BSA, the major component of the plasma using different technics (SAXS, SANS, cryoTEM, DLS, fluorescence and SRCD) [3]. The suspensions of SLA NPs in presence of BSA either in D2O or in PBS were analyzed from the nanoparticle point of view (size, concentration, swelling, colloidal stability) or from the BSA point of view (colloidal stability of BSA, complex formation between the BSA and the bioconjugate or the formation of a protein corona) [4–6]. The same approach was also followed with other types of NPs constituted of Leu-enkephalin-squalene prodrugs differing by various spacers that were introduced between squalene and Leu-Enkephalin moieties. These others NPs exhibited different surface charges and different analgesic profiles [7].

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The soft matter and chemistry support facilities at the Institut Laue-Langevin

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The Institut Laue-Langevin has been performing experiments at the cutting edge of research for more than 40 years now, in fields as varied as molecular biology, chemistry, fundamental physics, materials science and the environment. The ILL provides the scientific community with 40 high performance instruments constantly maintained at the highest state of the art.

To exploit the full potential of the high-performance instruments, a number of support facilities are available at the ILL, i.e., the deuteration laboratory, sample environment or the computing for science groups.

In this contribution, we aim at presenting the support given by the chemistry laboratories and the partnership for soft condensed matter (PSCM). The chemistry facility at the ILL manages several wet chemistry labs, as well as chemistry laboratories fully equipped to handle nano-powders. The PSCM laboratories provide approx. 30 laboratory scale equipment aimed at the characterization and preparation of samples in the domain of soft condensed matter.

Exploring Nanostructural Characteristics and Interactions of Core-Shell Upconversion Nanoparticles in Simulated Blood Environments using Small-Angle X-ray Scattering

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The interactions between nanoparticles and components of the blood may have profound consequences in their surface properties and colloidal stability, ultimately influencing their fate and therapeutic efficiency [1, 2]. Through the application of small-angle scattering techniques, our objective is to elucidate the intricate interactions between inorganic and organic nanoparticles and serum proteins. This analytical approach aims to provide comprehensive insights into the dynamic interplay of these nanomaterials with biological components, contributing to a refined understanding of their behavior in complex physiological environments.

Upconverting nanoparticles (UCNPs), which enable the use of longer-wavelength light for excitation (typically near-infrared), are promising for a wide range of biomedical applications [3-6]. Preliminary results show that UCNPs, show strong interactions with simulated blood medium, undergoing also loss of colloidal stability and aggregation [7-8]. We interpret these results in terms of specific interactions between the surface of the nanoparticles (citrate) and the charged groups of the proteins. Small-angle X-ray Scattering (SAXS) is proficiently employed as a robust analytical tool to ascertain both the average size and size polydispersity of UCNPs, offering valuable insights into their structural characteristics. Additionally, SAXS serves to elucidate the aggregation behavior of these nanoparticles, providing a comprehensive scheme of their interaction dynamics.

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Humidity response of cellulose nanofiber foams derived from upcycled cotton

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Nanocellulose has been produced from various sources during the last decade, as they are a promising building blocks to replace traditionally fossil-based materials [1]. Cellulose from wood has been one of the most common sources but recent findings promote a change in forest production. By reducing the harvesting a large impact on the climate change mitigation is predicted [2], pushing forward the need to find sustainable alternative sources for nanocellulose. From the cotton fraction of waste textiles, it is possible to obtain cellulose nanocrystals with similar characteristics as the ones produced from virgin cotton, highlighting the potential of using this residual stream to obtain high value products [3]. In this work, we investigated the humidity response of upcycled cellulose nanofiber foams using small angle x-ray scattering and x-ray tomography. Our preliminary results did not only show a better moisture resilience but the foams did also exhibit a better structural integrity compared to their wood counterpart.

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Exploring Viscoelastic Surfactant Solutions: A Review of SANS Applications in Non-Ionic and Ionic Surfactant Mixtures

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In this review, we delve into the captivating realm of wormlike micelles (WLMs), which are dynamic and elongated aggregates resulting from the self-organization of amphiphiles. These structures exhibit remarkable viscoelastic properties, akin to polymer solutions or gels, due to their entanglement into a transient network. Notably, WLMs possess the unique ability to rapidly break and reform, changing their morphology in response to subtle alterations in composition, chemical structures of amphiphiles, or external factors like temperature and pH. This inherent responsiveness opens avenues for diverse applications, particularly in biodegradable surfactant mixtures. The review emphasizes the crucial role of small-angle neutron scattering (SANS) in advancing our understanding of WLMs, providing detailed insights into their microstructure across a broad range of length scales, making it an indispensable tool for unraveling the intricacies of these dynamic aggregates

Self-association in aqueous solutions of alcohols and Amines

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Short chain alcohols, from ethanol to butanol, are known to form concentration fluctuations in their aqueous solutions. Heterocyclic amines, such as piperidine and N-methylpiperidine, also aggregate in aqueous solutions due to hydrogen bonds between hydration water molecules [1,2]. In other hydrogen bonded solvent, such as methanol, no such aggregation of amines occurs. This difference highlights the active role of water solvent in promoting the self-aggregation. In the present communication we discuss the family of solutions of pyrrolidine, piperidine, and their methylated counterparts in water and in methanol, as revealed by thermodynamic measurements as well as by direct visualization of the mesoscopic structure employing small-angle neutron scattering.

The limiting partial molar enthalpies of solutions of pyrrolidine, N-methylpyrrolidine, piperidine, and N-methylpiperidine in methanol follow closely the trend assessed from theoretically calculated molecular interaction energies. However, their behavior is markedly different in water solutions, and can be described by taking into account an empirical hydrophobic hydration term [3]. Small angle neutron scattering evidenced that the aqueous amine solutions are microheterogeneous on the nanometer length scale. Various models are considered to describe the structural arrangement of the hydrated amine molecules. The tendency of approaching phase separation increases in the order:

N-methylpiperidine < N-methylpyrrolidine < piperidine < pyrrolidine.

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Towards Understanding the Role of ‘Softness’ in the Phase Transition Behaviour of Model Mesoscopic Soft Particles via SANS in the Metastable and Disordered Regimes

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In lieu of a quantitative, atomistic description of the structure of relativistic particles and the evolution of the emergent phenomena thereof, mesoscopically analogous and experimentally accessible colloidal suspensions provide phenomenologically versatile models to study the phase behavior of metastable and disordered glassy structures. In particular, soft particles, owing to their collapsable, deformable, and interpenetrable nature, enable physicists and material scientists to emulate and probe a more diverse range of behaviours observed for molecular systems than their hard, incompressible counterparts. Within the realm of soft colloidal suspensions explicitly, the variables of interest are particle softness, characterised by the bulk modulus k , and effective volume fraction ζ , both of which give rise to potentially complex particle-particle interaction models, which continue to remain relatively inconclusive and largely unresolved. Whereas the ‘softness’ of particles in our PNIPAM-based models of choice is tuneable by varying the degree of intraparticle crosslinking during synthesis, controlling the volume fraction in colloidal suspensions is synonymous with controlling temperature in molecular glasses. Put succinctly, we are interested in the structure of soft colloids and studying its effects on the dynamics of suspensions thereof. Although the dynamics of such materials can be better understood using techniques such as rheology and dynamic light scattering (DLS), small angle neutron scattering (SANS) is uniquely advantageous in quantitatively characterising the form and structure of colloidal particles and suspensions, respectively. Leveraging the contrast variation technique, experimentally relevant information for hydrogenated particles suspended amidst a sea of deuterated particles can be resolved for densely packed disordered systems providing us insight into the structural properties of soft colloidal suspensions correlating to their dynamical behaviours observed using other complimentary techniques. Furthermore, as a corollary of the overall objective, SANS with contrast variation can also be used to identify the mechanism suppressing crystallisation of soft colloidal suspensions in the metastable regime. The results of these investigations via SANS in the reciprocal space can also then be corroborated by real-space observations using confocal microscopy.

Effect of structure on digestion of proteins

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Although the biochemical processes of protein digestion are widely studied, the biophysical ones, like conformational changes, are more neglected, especially when resolving both time and space scales. Synchrotron radiation Small-Angle X-ray Scattering (SAXS) offers quick measurements at the resolution of tens of Å, with narrow beams. Here we present a method for efficiently monitoring the protein digestion canola proteins in a gel matrix, as a model solid-like plant protein food. Rapid scan of a capillary, allowed tracking digestion under diffusion of the enzymatic juice, for several tenth of hours. We distinguish compact, unfolded or aggregated states of proteins under different pH and enzymatic conditions. Data for compactness and size at different times and distances from the initial level of the digestive liquid fall on a master curve, evidencing the complex behavior of proteins, involving forth and back unfolding and re-compaction. This can give precious information for food and nutritional science.

At the scale of large aggregates, we mainly observe for both gels the decreasing of the size and/or number of these aggregates during digestion and the alteration of their interfaces, partly due to the loosening of the local protein network (protein unfolding and cutting).

These studies were completed by imaging experiments, allowing to explore micron scale, i.e. structure of the gels and sizes of protein aggregates (confocal and neutron imaging), and the in situ digestion processes of the gels (UV fluorescence microscopy).

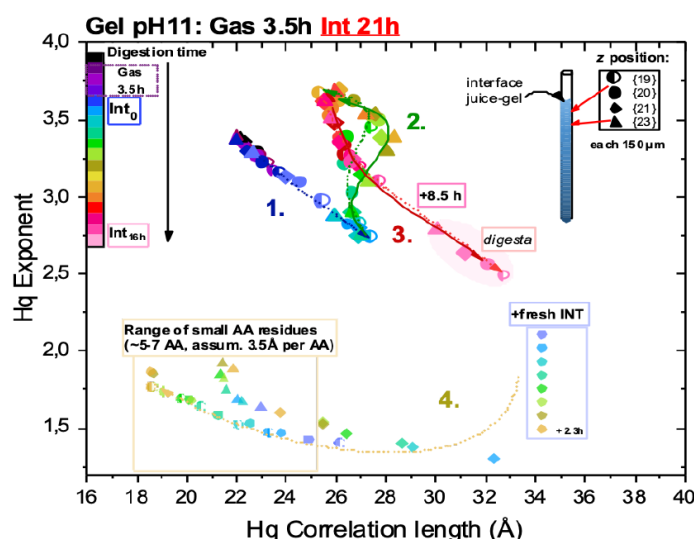


Figure 1: High q exponent of the scattering versus correlation length ξ showing successive steps (1, 2, 3, 4)

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Aqueous binary mixtures of stearic acid and its hydroxylated counterpart 12-hydroxystearic acid

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The climatic situation of the planet leads to an increase in the need for the use of environmentally friendly molecules. In this context, fatty acids are surfactants of particular interest since they can be extracted from agricultural resources. The use of an organic counterion enables their solubilization in aqueous solution at room temperature where they self-assemble into supramolecular structures.

Stearic Acid (SA), one of the most common fatty acids in nature, self-assembles in lamellar phases in water [1]. On the other hand, 12-Hydroxy-Stearic-Acid (12-HSA), self-assembles in micrometric multilamellar tubes [2] Their packing parameter are very similar, and both structures are thermo-sensitive with a transition towards spherical micelles above threshold temperatures, which are however very different from SA to HSA.

We have studied binary mixtures of these two fatty acids in order to understand the HSA's hydroxyl group contribution on the self-assemblies' structure. Our study demonstrated that a doping of SA by a few amount of 12-HSA molecules induces strong structural rearrangements whereas the reverse, i.e. doping 12-HSA by SA, almost does not change the structure. There are also diverse thermal effects when comparing the different 12-HSA/SA ratios [3]. I will show the results from SANS, microscopy, WAXS, TEM and rheology, which prove the variety of structures formed in these systems, from lamellae to rigid tubes and micelles [4].

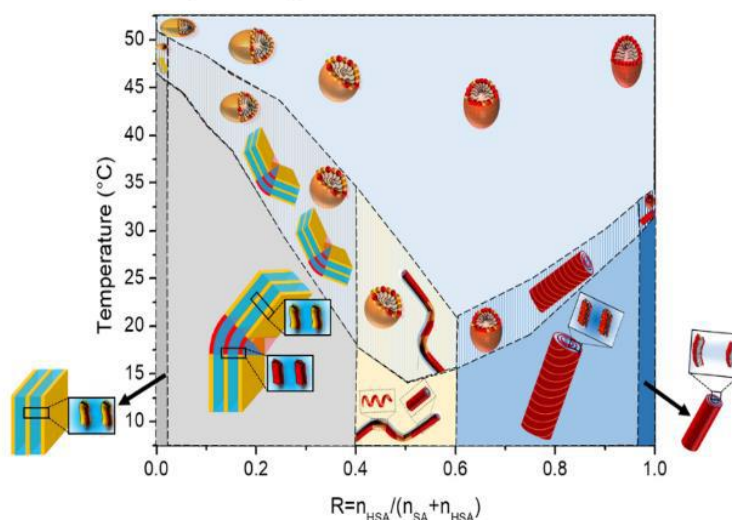


Figure 1 : Phase diagram of HSA/SA structures through R and temperature.

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