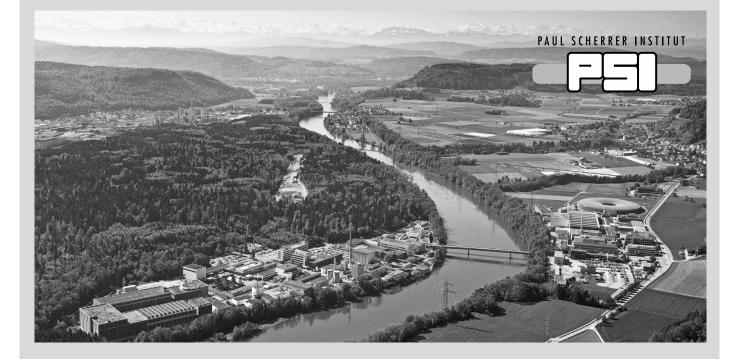
Program and Abstracts

Tuesday, April 5th 2022 29th edition







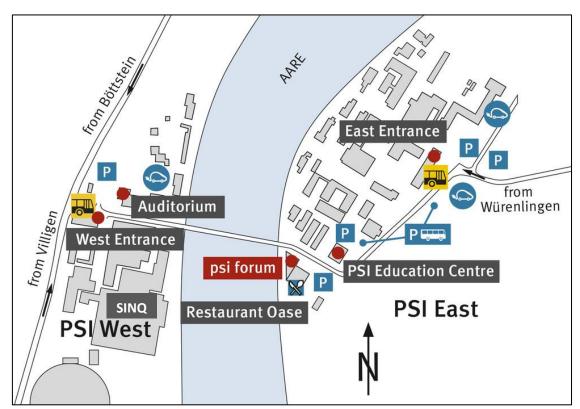
Paul Scherrer Institute

Forschungsstrasse 111, 5232 Villigen

Workshop, coffee break and poster session: PSI West, Building WHGA - Auditorium. Google maps link.

Lunch: PSI East, Restaurant OASE, Building OKAA.

SINQ visit: PSI West, Building WNLA.



Plan of the PSI campus.



Entrance of the WHGA building/Auditorium.



Program

| | 09:00 | Registration and coffee* | | | | |
|-----------|-------|--|---|--|--|--|
| | 09:30 | Plenary talk** | | | | |
| | | Fabrice Cousin | Small Angle Neutron scattering and contrast variation: a unique tool for probing soft matter systems | | | |
| | 10:30 | Coffee and Poster Session | | | | |
| Session 1 | 11:00 | Qiyao Sun | Polymer Induced Liquid Crystal Phase Behavior of Cellulose Nanocrystal Dispersions | | | |
| | 11:15 | Stéphane Bernhard | Supramolecular Reinforcement of Polymer–Nanoparticle Hydrogels for Modular Materials Design | | | |
| | 11:30 | Boyang Zhou | pNIPAM microgel deswelling and suspension structure in crowded suspensions studied with SANS | | | |
| | 11:45 | Chuen-Ru Li | Selectively permeable viscoelastic composite microcapsules | | | |
| | 12:00 | Lukas Heuberger | Polymeric Giant Unilamellar Vesicles for High-Throughput Screening | | | |
| | 12:15 | Kostas Parkatzidis | Transformer-Induced Metamorphosis of Polymeric Nanoparticle Shape at Room Temperature | | | |
| | 12:30 | Leonard Krupnik | Illuminating the structure of iron carbohydrates in complex biological environments | | | |
| | 12:45 | Lunch at OASE and Poster Session | | | | |
| - | 14:00 | Eleonora Secchi | The role of eDNA in the formation of biofilm streamers | | | |
| | 14:15 | Tom de Geus | A theory for the statistics of slip at a frictional interface: unifying rate-and-state and depinning approaches | | | |
| | 14:30 | Nicolas Bain | Surface tension and the strain-dependent topography of soft solids | | | |
| Session 2 | 14:45 | Carla Fernandez-Rico | Spinodal Decomposition in Elastic Matrices | | | |
| | 15:00 | Kata Dorbic | Synthesis of polymeric particles with multiple lobes | | | |
| | 15:15 | François Lavergne | Hallmarks of intermittent rearrangements in creep of liquid foams | | | |
| | 15:30 | Coffee and Poster Session | | | | |
| | 16:00 | Soft Matter Research at SINQ/PSI, Final remarks & Poster Prize | | | | |
| | 16:30 | | SINQ visit | | | |

* At your arrival, please hang your poster on the available poster stands.

** All talks will take place in the Auditorium. Contributed talks are expected to last 12 minutes with 3 minutes of questions.



Plenary Talk:

Small Angle Neutron scattering and contrast variation: A unique tool for probing soft matter systems

Fabrice Cousin

Laboratoire Léon Brillouin, CEA-Saclay, 91191 Gif sur Yvette, France

Soft Matter deals with systems made of individual building blocks (e g colloidal nanoparticles, polymers, surfactants,) whose characteristic sizes lay in the 0.1–10 nm range. In such systems, the delicate balance of interactions (of the order of k_BT) can lead to the formation of large self-assembled complex architectures. Understanding the underlying mechanisms of their self-assembly is then the key to control and tune their very specific properties at the nanometer scale (1-100 nm). In this framework, the neutron scattering techniques combined with H/D isotopic labeling are a unique tool to characterize the systems at the relevant spatial scales of the systems owing to the possibilities provided by contrast variation methods. Such "contrast variations" methods are usually declined with two philosophies: (i) to create some contrasts in binary systems where it does not exist, e g by deuteration, for instance in polymer melts or (ii) to adjust the contrast of a component of a ternary system to those of another in order to "match" it, simplifying the system to a two-components one from neutron point of view.

In this lecture, I will illustrate how such such contrast variation methods can be applied to probe soft matter in bulk systems by Small Angle Neuton Scattering (SANS) on three representative systems of soft matter. First, I will show how it can be used in bulk solution on colloidal suspensions complexes polyelectrolyte and proteins of opposite charges. I will even show that contrast-variation can be used on 4-composent systems when the system is craftily designed with respect to neutron contrast. Second, I will show how it can be used on nanocomposites made of polymeric melts reinforced by nanoparticles [2]. This will allow me to show how SAXS and SANS can be used in a very complementary way. Finally, if time permits, I will show that SANS can also be successfully used to probe interfaces when contrast conditions are smartly chosen. This will be illustrated by an example on Pickering emulsion stabilized by cellulose nanocrystals [3].

 ^[1] Cousin *et al*, Langmuir, 2005, *21(21)*, 9675-9688. Gummel *et al*, *J. Phys. Chem. B*, *2006*, *110(49)*, 24837-24846; Gummel *et al*, J. Am. Chem. Soc., 2007, *129(18)*, 5806-5807; Gummel *et al*, Macromolecules, 2008, *41(8)*, 2898-2907, Gummel *et al*, 2008, *4*, 1653–1664.
 [2] Robbes *et al*, Macromolecules, 2010, *43(13)*, 5785–5796; Robbes *et al*, Macromolecules, 2011, *44(22)*, 8858–8865; Robbes *et al*, Soft Matter, *8*, 3407-3418; Robbes *et al*, Macromolecules, 2012, *45*, 9220–9231; Robbes *et al*, Macromolecules, 2018, *51 (6)*, 2216–2226; Robbes *et al*, Macromolecules, 2022, *submitted*.

^[3] Cherhal et al, Biomacromolecules, 2016, 17(2), 496–502; Haouache et al, Biomacromolecules, 2022, submitted.

Polymer Induced Liquid Crystal Phase Behavior of Cellulose Nanocrystal Dispersions

<u>Qiyao Sun</u>, Viviane Lutz-Bueno, Jiangtao Zhou, Ye Yuan, and Peter Fischer

1 Institute of Food, Nutrition and Health, ETH Zurich, 8092 Zurich, Switzerland; 2 Paul Scherrer Institute, 5232 Villigen PSI, Switzerland

Cellulose nanocrystal (CNC) is a promising bio-based material that has attracted significant attention in the fabrication of functional hybrid materials. The rod-like shape and negative surface charge of CNCs enable their rich colloidal behavior, such as a liquid crystalline phase and hydrogel formation that can be mediated by different additives. [1,2]

This study investigates the effect of depletion-induced attraction with the presence of non-absorbing polyethelene glycol (PEG) of different molecular weights in CNC aqueous dispersions, where the polymer molecules deplete the space around particles, apply osmotic pressure and drive the phase transition. Polarized light microscopy (PLM), rheology, small angle X-ray scattering (SAXS) and atomic force microscopy (AFM) are used to characterize the phase behavior over a time period of a month. In our results, pure CNC dispersion shows three typical liquid crystal shear rheology regimes and cholesteric self-assembly behavior. Tactoid nucleation, growth and coalescence are observed microscopically, and eventually the dispersion presents macroscopic phase separation, and these structural developments are confirmed by the evolution of scattering correlation peaks. PEG with lower molecular weight induces weak at- tractive depletion forces. Tactoid growth is limited, and the whole system turns into fully nematic phase macroscopically. With PEG of higher molecular weight, attractive depletion force becomes predominant, thus CNC self-assembly is inhibited and a nematic hydrogel formation is triggered, accompanied by significantly enhanced mechanical strength. Overall, we demonstrate that depletion induced attraction forces by the addition of PEG enables precise tuning of CNC self-assembly and phase behavior with controllable mechanical strength and optical activity. These findings deepen our fundamental understanding of cellulose nanocrystal and advance its application in colloidal systems and nanomaterials.

Parker RM et al. The self-assembly of cellulose nanocrystals: Hierarchical design of visual appearance. Advanced Materials (2018).
 Bertsch P et al. Ion-induced formation of nanocrystalline cellulose colloidal glasses containing nematic domains. Langmuir (2019).



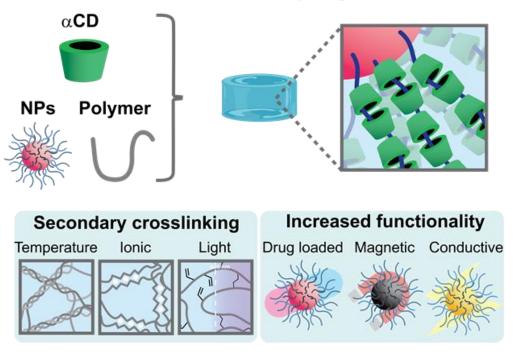
Supramolecular Reinforcement of Polymer–Nanoparticle Hydrogels for Modular Materials Design

Stéphane Bernhard, Giovanni Bovone, Elia A. Guzzi, Tim Weber, Dalia Dranseikiene, and Mark W. Tibbitt

Department of Mechanical and Process Engineering, ETH Zurich

Injectable hydrogels are increasingly used in the biomedical field for their shear thinning and selfhealing properties. Polymer–nanoparticle (PNP) hydrogels are a class of injectable nanocomposite hydrogels based on physical interactions between polymers and nanoparticles. (1) Such hydrogels have been used as drug delivery platform or bioink for additive manufacturing. (2-3) Current formulations of PNP hydrogels are however, based on specific interactions between particular polymers and nanoparticles. The restriction in building blocks choices limit the range of mechanical properties, functionalities, and possible applications.

In this work, we reinforced PNP hydrogels using a simple supramolecular motif through the addition of α cyclodextrin (α CD). (4) Polypseudorotaxane formation between α CD and PEGylated nanoparticles significantly enhanced the material mechanical properties. Additionally, the supramolecular motif enabled the decoupling of the mechanical properties from the hydrogel building blocks enabling modular hydrogel formation using various structural components from a library of biocompatible polymers and PEGylated nanoparticles. Using α CD, a variety of biopolymer with secondary cross-linking were employed for the design of bioinks. Cell laden scaffolds were printed in complex 3D scaffolds. Biocompatible hydrogels were designed as drug delivery platform for the release of small and macro molecules. Finally using PEGylated gold or PEGylated iron nanoparticles conductive and magnetic materials were obtained.



Supramolecular hydrogel

(1) Bernhard et al., Chimia 2019, 73, 1034.

- (2) Appel et al., Nat.Commun. 2015, 6, 6295.
- (3) Guzzi et al., Small **2019**, 15, 1905421.

⁽⁴⁾ Bovone, G., Guzzi, E. A., Bernhard, et al., Advanced Materials 2021. 2106941.



pNIPAM microgel deswelling and suspension structure in crowded suspensions studied with SANS

Boyang Zhou [1], Urs Gasser [1], Alberto Fernandez-Nieves [2,3]

[1] Laboratory for Neutron Scattering and Imaging, Paul Scherrer Institute. [2] Catalan Institution for Research and Advanced Studies (ICREA). [3] School of Physics, Georgia Institute of Technology.

Microgels are formed by cross-linked polymer networks that exist in and reversibly change between a swollen and collapsed state in response to the changes in external conditions. In particular, due to their compressibility, soft particles exhibit a phase behavior that is more complex than their hard-particulate counterparts. As a result, there is no generally accepted model for their interactions and overall phase behavior at both dilute and concentrated conditions. The importance of particle softness was highlighted by the spontaneous deswelling of large particles in bidisperse suspensions of pNIPAM microgels in water at high concentrations [1]. This deswelling was found to be triggered, above a critical concentration ζ_c , by a sharp increase of the suspension osmotic pressure set by counterions originating from charged groups in the periphery of the microgel [2]. $\zeta = \frac{N_{\text{tot}}V_{\text{sw}}}{V_{\text{tot}}}$ is the generalized volume fraction calculated with the particle's swollen radius. Recently, we have directly measured the configuration of the counterion cloud using Small-Angle Neutron scattering (SANS) with contrast variation. The results indicate the presence of a counterion cloud that is electrostatically bound to the initiators' SO_3^- groups remaining close to the microgel surface. At high concentrations, the counter-ion cloud starts to percolate, and due to entropic reasons, some ions overcome the electrostatic attraction and contribute to the suspension osmotic pressure. When this pressure becomes larger than the particle bulk modulus, the particle is isotropically compressed [2,3]. To investigate the critical concentration for microgel suspension with different sizes, we prepared microgel suspensions with particle radius of ~80nm, 90nm and 100nm from $\zeta = \frac{N_{\text{tot}}V_{\text{sw}}}{V_{\text{tot}}} \approx 0.1$ to 1.2. The measurements were done via SANS, where we find that the microgels with radius ~80nm, 90nm and 100nm retain their swollen size until reaching $\zeta_{\text{c}} \approx 0.3, 0.4, 0.45$ respectively. At ζ_c , we believe that particles are effectively in direct contact, with the counterion cloud width as part of the radius, meaning that the limit of effective suspension volume fraction $\phi_{\text{eff}} = \zeta \left(\frac{R(\zeta) + \sigma_{ic}}{R_{\text{sw}}}\right)^3 = 1$ is reached. Different from ζ , this the true subscripts ζ is the true subscript. is reached. Different from ζ , ϕ is the true volume fraction calculated with $R(\zeta)$, where $R(\zeta)$ is the radius extracted from the fitting at each ζ , R_{sw} is the particle swollen radius and σ_{ic} is the counterion cloud width. Consequently, we can calculate σ_{ic} with this limit. Our results for σ_{ic} are in a good agreement with a prior estimate from the bidisperse pNIPAM suspension [2,3]. It is crucial to know the configuration of the cloud to understand the effect of the counterion cloud towards the spontaneous deswelling behavior, as σ_{ic} is an important input for calculating the particle radial charge density and particle electrostatic potential. Reassuringly, we have found that even at the highest ζ , the true volume fraction is still below the random close packing density, $\phi = 0.64$, and the fuzzy sphere model is still sufficient to describe the data. Therefore, we believe the particles are not physically in direct contact and they still maintain a spherical shape; this supports our model for microgel deswelling triggered by the percolation of counterion clouds and the associated increase in osmotic pressure [2,3]. Our results stress the importance of the microgel softness and counterion effect for developing a more systematic understanding of pNIPAM microgels and other soft and deformable colloids at high concentrations and for formulating a model for the phase behavior of microgels that takes spontaneous

deswelling at high concentrations into account.

^[1] A. St. John Iyer and L.A. Lyon, Chem. Int. Ed. 48, 4562-4566 (2009)

^[2] A. Scotti, U. Gasser, E.S. Herman, M. Pelaez-Fernandez, J. Han, A. Menzel, L.A. Lyon and A.Fernandez-Nieves, Proceedings of the National Academy of Sciences 113, 5576 (2016).

^[3] U.Gasser, A. Scotti, and A. Fernandex-Nieves, Physical Review E99, 042602 (2019).

Selectively permeable viscoelastic composite microcapsules

Chuen-Ru Li, Pavel Kalinin, Esther Amstad

Institute of material science, EPF Lausanne

Microcapsules with a selectively permeable shell are attractive containers for sensing, drug delivery and synthetic cells. Despite the wide application range, it remains a challenge to develop mechanically stable microcompartments that are capable of repetitively and selectively uptake and release the cargo. One possibility to design capsules whose permeability can be dynamically changed is the use of ionically crosslinked polymers as shell materials. Inspired by the adhesive properties of the mussel byssus, we are developing surfactants that are functionalized with chelators such that they can be reversibly crosslinked with appropriate ions or nanoparticles.

Microcapsules are fabricated from water-oil-water double emulsions that are stabilized with appropriate surfactants. To convert drops into capsules, surfactants located in proximity to the liquid-liquid interfaces are crosslinked with metal oxide nanoparticles. The resulting capsules have a pH-selective permeability to low molecular weight substances and resist osmotic stresses. The release of reagents can be repetitively triggered by cycling the pH. This platform opens up new possibilities to tune the permeability with the choice of nanoparticles and repetitively release reagents with a good temporal control.

Polymeric Giant Unilamellar Vesicles for High-Throughput Screening

Lukas Heuberger, Elena C. dos Santos, and Cornelia G. Palivan

Department of Chemistry, University of Basel

Biological systems use compartmentalization strategies to generate microenvironments with controlled biochemical compositions. These environments serve as a protective method from undesired influences from outside of the compartment and to keep diffusing elements in proximity.(1) Giant unilamellar vesicles (GUVs) are micrometer-sized vesicles that are applied in this context based on their size similarity to cells.(2) Amphiphilic block copolymers can be synthesized with a wide range of compositions, block ratios, and functionalization and serve as excellent alternatives to lipids for vesicle formation.(3) Double emulsion microfluidics can produce GUVs at high-throughput. The modularity and design of this system facilitates the formation of monodisperse GUVs with controllable inner, polymer membrane, and membrane functionalization.(4) Employing high-throughput methodologies, GUVs can be applied for screening assays. By adjusting the inner composition, enzymatic cascades, smaller vesicles, organelles and entire living organisms can be encapsulated within GUVs.

In the presented work, GUVs were produced using the di- and triblock copolymer PDMS-*b*-PMOXA/PMOXA-*b*-PDMS-*b*-PMOXA. Thanks to their size being comparable to cells, GUVs can be screened using flow cytometry. Using these techniques, tens of thousands of GUVs can be analyzed, making them a convenient alternative to w/o/w double emulsions. This allows for their applications as microreactors or cellular models. This approach shows the versatility of double emulsion templated polymer GUVs for studying compartmentalized biological systems, deepening the insights into fundamental biological processes.

⁽¹⁾ Roodbeen, R.; Van Hest, J. C. M. Synthetic Cells and Organelles: Compartmentalization Strategies. *BioEssays* **2009**, *31* (12), 1299–1308. https://doi.org/10.1002/bies.200900106.

⁽²⁾ dos Santos, E. C.; Angelini, A.; Hürlimann, D.; Meier, W.; Palivan, C. G. Giant Polymer Compartments for Confined Reactions. *Chemistry* **2020**, *2* (2), 470–489. https://doi.org/10.3390/chemistry2020028.

⁽³⁾ dos Santos, E. C.; Belluati, A.; Necula, D.; Scherrer, D.; Meyer, C. E.; Wehr, R. P.; Lörtscher, E.; Palivan, C. G.; Meier, W. Combinatorial Strategy for Studying Biochemical Pathways in Double Emulsion Templated Cell-Sized Compartments. *Adv. Mater.* **2020**, *32* (48), 2004804. https://doi.org/10.1002/adma.202004804.

⁽⁴⁾ Itel, F.; Chami, M.; Najer, A.; Lörcher, S.; Wu, D.; Dinu, I. A.; Meier, W. Molecular Organization and Dynamics in Polymersome Membranes: A Lateral Diffusion Study. *Macromolecules* **2014**, *47* (21), 7588–7596. https://doi.org/10.1021/ma5015403.



Transformer-Induced Metamorphosis of Polymeric Nanoparticle Shape at Room Temperature

<u>Kostas Parkatzidis</u>,¹ Nghia P Truong,^{1,3} Manon Rolland,₁ Viviane Lutz-Bueno,² Emily H Pilkington,³ Raffaele Mezzenga,^{1,2} Athina Anastasaki¹

[1] Department of Materials, ETH Zürich; [2] Department of Health Sciences and Technology, ETH Zürich; [3] Monash Institute of Pharmaceutical Sciences, Monash University, Australia.

Controlled polymerizations have enabled the synthesis of a wide range of amphiphilic block copolymers which can form nanostructured materials with different shapes exhibiting distinct properties and performance.¹ Despite the importance of shape, current strategies that allow for the efficient morphological transformation are limited in polymer scope, often alter the chemical structure, operate at high temperatures, and can be fairly tedious and time-consuming. Herein we present a rapid and versatile morphological transformation strategy which operates at ambient temperature and without impairing the chemical structure of the resulting morphologies. By simply adding a small amount of a molecular transformer (i.e. small organic molecule) in an aqueous solution of polymeric nanoparticles, a rapid evolution to the next high-ordered morphology was observed within seconds, yielding a range of nanoparticles morphology from the same starting material. Significantly, this approach can be applied to nanoparticles produced by disparate block copolymers (i.e. with different cores and coronae) obtained by various synthesis techniques, including emulsion polymerization, polymerization-induced self-assembly and traditional solution self-assembly.²

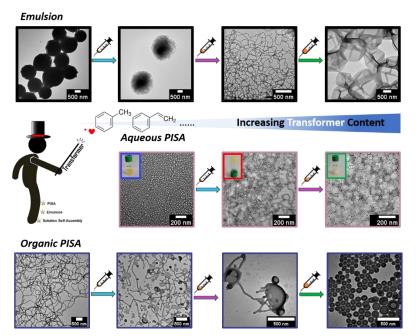


Figure 1: Transformer-Induced Metamorphosis of Polymeric Nanoparticle Shape at Room Temperature: application in nanoparticles obtained via emulsion polymerization, aqueous PISA and organic PISA

(1) K. Parkatzidis, H. S. Wang, N. P. Truong and A. Anastasaki, Chem, 2020, 6, 1575–1588

(2) K. Parkatzidis, N. P. Truong, M. Rolland, V. Lutz-Bueno, E. H. Pilkington, R. Mezzenga and A. Anastasaki, *Angew.Chem.*, **2022**, 134, e2021134

Illuminating the structure of iron carbohydrates in complex biological environments

Leonard Krupnik [1,3], Neda Iranpour Anaraki [1,3], Marianne Liebi [4,6], Jonathan Avaro [1], Joachim

Kohlbrecher [5], Peter Wick [3], Antonia Neels [1,2]

[1] Center for X-ray Analytics, Empa St. Gallen; [2] Department of Chemistry, University of Fribourg; [3] Laboratory for Particles-Biology Interactions, Empa St. Gallen; [4] Structure and Mechanics of Advanced Materials, PSI Paul Scherrer Institute; [5] Laboratory for Neutron Scattering, PSI Paul Scherrer Institute; [6] Laboratory for X-ray characterization of materials, École Polytechnique Fédérale de Lausanne

Intravenous iron carbohydrate nanoparticles are widely used nanomedicines to treat iron deficiency anaemia, which is associated with illnesses such as chronic kidney disease and inflammatory bowel disease (1,2). A variety of clinical and biological studies on these products (ferric carboxymaltose and iron sucrose) are available (3); however, there is little knowledge on their undergoing structural changes during the early stages of entering the human bloodstream. Using a combination of SAXS and SANS, we investigated how physico-chemical parameters of iron carbohydrates were influenced by interaction with proteins or cells in the plasma. Hereby, SAXS and WAXS was used to study the iron core, and was complemented by SANS to investigate the much weaker scattering signature of the carbohydrate shell. By coupling SAXS with a microfluidic mixing system, we also looked at the structural changes dynamically and in real-time. Our SAXS experiments indicated changes in particle size and shape of the iron core of ferric carboxymaltose once diluted in a biological buffer. SANS measurements also enabled calculation of the thickness of its carbohydrate shell. First experiments on interactions of iron sucrose with human serum albumin suggested aggregation after only 1h of incubation time. With this approach, we may be able to correlate physicochemical parameters of iron carbohydrates with their behavior in biological environments for better prediction of clinical outcomes.

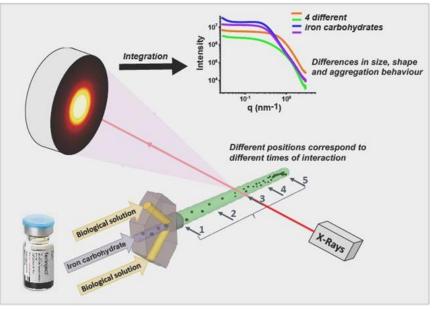


Figure 1: Investigating the structure of iron carbohydrates via SAXS combined with microfluidics.

(1) Praschberger, Monika, et al. "Iron sucrose and ferric carboxymaltose: no correlation between physicochemical stability and biological activity." Biometals 28.1 (2015): 35-50.

(2) Cançado, Rodolfo Delfini, and Manuel Muñoz. "Intravenous iron therapy: how far have we come?" Revista brasileira de hematologia e hemoterapia 33 (2011): 461-469.

(3) Rottembourg, Jacques, et al. "Do two intravenous iron sucrose preparations have the same efficacy?" Nephrology Dialysis Transplantation 26.10 (2011): 3262-3267.



The role of eDNA in the formation of biofilm streamers

Giovanni Savorana¹, Eleonora Secchi¹

¹ Institute of Environmental Engineering, ETH Zürich, Zürich, 8093, Switzerland

Across many different habitats, bacteria are often found as sessile communities embedded in a self-secreted matrix of extracellular polymeric substances (EPS). The biofilm matrix enhances bacterial resistance to harsh environmental conditions and antimicrobial treatments, and hinders our ability to remove biofilms in medical and industrial applications. Nevertheless, little is known about how environmental features shape its microstructure and chemical composition.

Here, we show that a laminar flow of a diluted suspension of *Pseudomonas aeruginosa* PA14 and PA01 around a pillar can trigger the formation of suspended filamentous biofilm structures known as streamers. The biochemical composition and the viscoelastic nature of the EPS play a key role in determining the streamers' structure and rheology. In particular, we have shown for the first time that the ionic interaction between extracellular DNA (eDNA) and the polysaccharide Pel determines the structure and the rheology of biofilm streamers. eDNA is essential for the formation of the streamers and their structural stability, while Pel affects their rheological properties. In particular, increasing the concentration of Pel stiffens the biofilm filament. Furthermore, the Pel-induced stiffening of the eDNA network allows an analogy to be drawn for the first time between biofilms and double-network gels. Finally, we could promote streamers formation by adding suble-thal concentration of an antibiotic commonly used to treat *P. aeruginosa* infections.

A theory for the statistics of slip at a frictional interface: unifying rate-and-state and depinning approaches

Tom de Geus and Matthieu Wyart

Physics institute, EPFL, Switzerland

Slip at a frictional interface occurs via intermittent events. Understanding how these events are nucleated, can propagate or instead spontaneously stop remains a challenge, central to earthquake science and tribology. In the absence of disorder, rate-and-state approaches predict a diverging nucleation length [1] at some stress σ^* beyond which cracks can propagate [1,2].

Here we argue that disorder is a relevant perturbation to this description. We justify why the distribution of slip contains two parts (Fig. 1a): a power law corresponding to 'avalanches' (e.g. Fig. 1e), and a narrow distribution of system-spanning fracture events (corresponding to macroscopic stress drops in a stick-slip cycle in Fig. 1b). We derive novel scaling relations for both objects, including a relation between the stress drop and the spatial extension of a slip event (involving the interface's roughness exponent ζ , illustrated in Fig. 1e). We compute the cut-off length beyond which avalanches cannot be stopped by disorder, leading to a systemspanning fracture, and successfully test these predictions in a minimal model of frictional interfaces [3].

Our results underline that the mere presence of inertia can lead velocity weaking that is well fitted by the classical rate-and-state constitutive law (Fig. 1c, solid blue curve). During slip events, the unstable interface is stabilized by having to accelerate the surrounding bulk [2,4], resulting in an effective flow curve that displays a minimum at a stress σ_c (Fig. 1c, dashed green curve). We argue theoretically that $\sigma_c = \sigma^*$, implying that rate-and-state approaches capture the critical stress affecting the slip statistics.

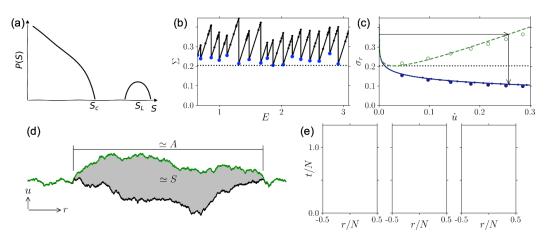


Figure 2. (a) We denote *S* the integrated slip and the duration of slip events. The distribution P(S) consists of two parts. First, there is a power-law distribution cut-off beyond some characteristic value S_c , i.e. $P_a(S) = S^{-\tau}f(S/S_c)$ where *f* is a rapidly decreasing function of its argument. We call the associated events 'avalanches' and denote by A_c their maximal characteristic spatial extension. Second, there are system-spanning events of extension $A \approx L$, where *L* is the system size, whose characteristic magnitude we denote by S_L . (b) Using inertial dynamics and disorder only, our minimal mesoscopic model predicts stick-slip: in macroscopic drops in the stress Σ , punctuated by strain *E* intervals during which no macroscopic slip occurs. (c) Driven at finite rate, but also in slip events, our model predicts velocity weakening: the stress inside a slipping region σ_r decreases as a function of slip rate \dot{u} (blue line). During a growing event, the weaking is stabilised by having to accelerate the bulk. The effective flow curve, in green, shows a minimum at σ_c . (d) At σ_c , disorder results in avalanches that result in a roughness (the slip *u* is plotted as a function of space *r*). (e) Event map of representative large avalanches. A point is placed in time *t* vs space *r* for each yield event (black for yielding in positive direction and blue for yielding in negative direction).

- [1] E. A. Brener, M. Aldam, F. Barras, J. F. Molinari, and E. Bouchbinder, Physical Review Letters **121**, 234302 (2018).
- [2] G. Zheng and J. R. Rice, Bulletin of the Seismological Society of America 88, 1466 (1998).
- [3] T. W. J. de Geus, M. Popović, W. Ji, A. Rosso, and M. Wyart, PNAS **116**, 23977 (2019).
- [4] F. Barras, M. Aldam, T. Roch, E. A. Brener, E. Bouchbinder, and J.-F. Molinari, Physical Review X 9, 041043 (2019).

Surface tension and the strain-dependent topography of soft solids

N. Bain, K. Smith-Mannschott, S. Heyden, R.W. Style, E.R. Dufresne

Department of Materials, ETH Zürich

Despite its importance in any adhesion and wetting phenomena, there is a fundamental property that is not yet understood in soft solids: surface elasticity. Also called the Shuttleworth effect, surface elasticity can be boiled down to one question. Does stretching the surface of a soft solid change its surface tension? In 2017, Xu et. al (1) designed an experiment in which the opening angle of a wetting ridge was a proxy to evidence a dramatic increase of surface tension with stretch. In 2019, however, Masurel et al. (2) claimed that the coupling between nonlinear mechanics and the singular nature of the wetting ridge suffice to explain the behavior of the opening angle observed by Xu et al, without invoking the Shuttleworth effect. The question, therefore, remains open. This presentation will focus on an experimental setup with no geometric singularity, that leaves no doubt on the existence or absence of surface elasticity in soft solids, hopefully closing this long-lasting controversy.

(1) Q. Xu, K. E. Jensen, R. Boltyanskiy, R. Sarfati, R. W. Style, and E. R. Dufresne, Nature communications 8, 1 (2017). (2) R. Masurel, M. Roché, L. Limat, I. Ionescu, and J. Dervaux, Physical Review Letters 122, 248004 (2019).



Spinodal Decomposition in Elastic Matrices

Carla Fernandez-Rico, Sai Tianqi, Robert Style, and Eric Dufresne

Department of Materials, ETH Zurich

Phase separation is a ubiquitous process and finds applications in a variety of biological, organic, and inorganic systems (1). Nature has evolved the ability to control phase separation to both regulate cellular processes and make composite materials with outstanding mechanical and optical properties. Striking examples of the latter are the feathers of many bird species, which show fascinating structural colours and are thought to result from an exquisite control of their phase-separated microstructures (2). By contrast, it is much harder for material scientists to arrest and control phase separation in synthetic materials with such a high level of precision at these length scales (3). In this work, we demonstrate the control over spinodal decomposition processes at the microscale by using elastic polymer matrices. Our system consists of a silicone gel immersed in a liquid at high temperatures. Phase separation is subsequently triggered by reducing the temperature of the system (4). This simple yet robust method, allows us to tune the length scale our spinodal structures via controlling the mechanical properties of the polymer network. By using optical microscopy, we unveil the structure and phase diagram of our system at different compositions. Finally, we also demonstrate the polymerization of the resulting structures which leads to polymer composites with promising optical and mechanical properties.

- (1) Perry, SL, et al, "Phase separation: Bridging Polymer Physics and Biology". Current Opinion in Colloid and Interface Science, (2019)
- (2) Dufresne, E, et al, "Self-assembly of amorphous biophotonic nanostructures by phase separation". Soft Matter, (2009).
- (3) Fernandez-Rico, C., et al, "Putting the Squeeze on Phase Separation". JACS Au, (2021).
- (4) Style, R., et al, "Liquid-Liquid Phase Separation in an Elastic Network", PRX (2018).



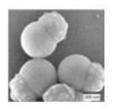
Synthesis of polymeric particles with multiple lobes

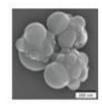
Kata Dorbic, Marco Lattuada

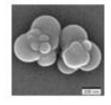
Department of Chemistry, University of Fribourg

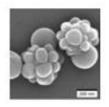
The formation of particles with multiple lobes has been the focus of several investigations, because of their potential applications as colloidal molecules. Such particles can be used as building blocks in the processes of self-assembly, or they can be used as carriers of different substances because each lobe can be different from the others in the same entity. In the production of multi-lobed particles, it is important to develop protocols that are reproducible and robust, with good yield, and where it is easy to recover the particles at the end of the synthesis.

If one wants to form non-spherical particles, the interfacial tension that drives a particle to adopt a spherical shape must be overcome. Here will be shown how this can be achieved by using a method based on multiple swelling and polymerization steps, starting from simple polystyrene colloids. By combining hydrolyzed 3-(trimethoxysilyl)propyl methacrylate with styrene, with the possibility of introducing a crosslinker, we have been able to induce phase separation. This allowed us to create multi-lobed particles whose morphology changes with the quantity and ratio of monomers.









Hallmarks of intermittent rearrangements in creep of liquid foams

François A. Lavergne and Véronique Trappe

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Liquid foams are soft jammed materials that constantly reconfigure due to coarsening-induced intermittent bubble rearrangements. Under a small applied stress, rearrangements lead to a slow power-law creep deformation at early times, which is followed by a constant creep rate at long time, reminiscent of normal viscous fluids. Here, we use optical microscopy to identify the rearrangements involved in these two regimes. We find that at short timescales, newly rearranged zones appear in different regions of the sample, with volumes distributed according to the same power-law as the creep rate. At the crossover to viscous relaxation timescales, rearrangements start occurring mostly in previously rearranged zones, while about 50% of the total volume still remains unchanged. As we find that the power-law strain is recovered when the stress is released, we conclude that the early-time rearrangement dynamics correlates with reversible contributions to creep, while the recurrence of events at the same location relates to dissipation.



Multicomponent nanotextured membranes deposited onto a biocompatible solid support

Maryame Bina, Agata Krywko-Cendrowska, Wolfgang Meier, Cornelia Palivan

Department of Chemistry, University of Basel

Nanotextured surfaces are widely found in nature and display versatile properties such as antibiofouling or enhanced adhesion. On the biochemical level, the cellular membrane is a great example of a textured surface where regions enriched in specific phospholipids enable or prevent membrane protein insertion or signalling pathways. Artificial model membranes are typically reproduced using naturally occurring phospholipids, amphiphilic block copolymers, or their mixtures. While separation into domains occurs in membranes composed of lipids and diblock copolymers, it has not been achieved for fully synthetic planar membranes. Here, we show how a nanotextured membrane using a mixture of properly chosen synthetic amphiphilic block copolymers is obtained. We determine that intrinsic properties of the polymers as well as their molar ratio affect the morphology of the membranes and the size of the domains. Our approach opens new possibilities for the development of multifunctional patterned surfaces with nanoscale texture for various biomedical technologies, such as biosensing or unveiling critical biochemical pathways.

Frustrated frustules: geometric frustration in diatom frustules

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Diatoms are single-celled organisms with a cell wall made of silica, called the frustule. Even though their elaborate patterns have fascinated scientists for years, little is known about the biological and physical mechanisms underlying their organization. In this work, we take a top-down approach and examine the micron-scale organization of diatoms from the *Coscinodiscus* family. We find two competing tendencies of organization, which appear to be controlled by distinct biological pathways. On one hand, micron-scale pores organize locally on a triangular lattice. On the other, lattice vectors tend to point globally toward a center of symmetry. This competition results in a frustrated triangular lattice, populated with geometrically necessary defects whose density increases near the center.

Nanocellulose and lysozyme based antimicrobial wound dressing mediated by surface charge

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Novel antimicrobial treatment to combat chronic wounds and the growing number of antibiotic-resistant bacteria is needed.^{[1],[2]} Positively charged lysozyme amyloids (LA) have been shown to provide strong antimicrobial activity through electrostatic interactions with the bacteria cell walls and membranes.^[3] In this work, the goal was to integrate the LA into a functional wound dressing while optimizing physical properties, such as high strength and swelling behavior to improve the liquid management of the wound. To achieve set properties a bio-based layered hydrogel out of cellulose nanofibrils, sodium alginate, and LA was created with a vacuum filtration system and ionic cross-linking. The antimicrobial activity against S. aureus was assessed with different methods to mimic the situation of a wound dressing on an infected wound. The presence of the LA-layer led to a reduction of 10⁹ CFU S. aureus (complete removal) if the sample was stored in milliQ-water (mQ) before the experiments. If the material was stored in PBS the antimicrobial effect was lost. We were able to link the antimicrobial effect to the surface zeta potential. While the ions present in PBS screened the charges of the LA layer (zeta potential 0.4 mV), the storage in mQ resulted in zeta potentials of 5.8 mV. Additionally, the elastic modulus of 10⁵ Pa through rheological investigations was measured. Reaching favorable mechanical properties and swelling behavior would qualify the material for its use as a wound dressing. However, the hypothesized antimicrobial activity would be absent under physiological conditions found in wounds due to the charge screening of the positively charged groups of the LA layer.

[3] Kummer, N., Wu, T., De France, K. J., Zuber, F., Ren, Q., Fischer, P., Silvia Campioni & Nyström, G. (2021). Self-Assembly Pathways and Antimicrobial Properties of Lysozyme in Dierent Aggregation States. Biomacromolecules, 22(10), 4327-4336

^[1] Yazdanpanah, L., Nasiri, M., & Adarvishi, S. (2015). Literature review on the management of diabetic foot ulcer. World journal of diabetes, 6(1), 37.

^[2] Dadgostar, P. (2019). Antimicrobial resistance: implications and costs. Infection and drug resistance, 12, 3903

Transmembrane protein-mediated loading of synthetic compartments

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Compartmentalization, a prerequisite for the spatiotemporal control of biochemical pathways in cells, is an emerging concept in designing new materials for medical and technological applications. Synthetic nanoand micro-compartments (NCs, MCs) with their chemical versatility and superior stability provide the basis for developing catalytic compartments, artificial organelles or cell mimics furnished with specific biomolecules [1]. However, a higher compartment loading efficiency and better permeability of the synthetic membrane remain hurdles that need to be overcome to increase the efficacy of *in situ* reactions. This interdisciplinary project aims to develop next-generation functional synthetic compartments whose composition is modulated by specific transmembrane proteins that deliver or selectively let molecules pass to the interior and test their activity *in vitro*. By inserting specific membrane proteins into the membrane of synthetic compartments, we plan to deliver protein cargo to the compartment interior or to allow a specific molecular flow across the membrane [2][3].

[1] Einfalt et al. Nat. Comm., 2018, 9, 1127, DOI: 10.1038/s41467-018-03560-x

[2] Kammerer & Benoit, Trends Biochem. Sci. 2014, 39, 517-526, DOI: 10.1016/j.tibs.2014.08.009

^[3] Murphy, Toxins 2011, 3, 294-308, DOI: 10.3390/toxins3030294

Designing catalytic nanocompartments for inverting glucuronidation

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Glucuronidation, one of the main processes of metabolism is the conjugation of endogenous or exogenous molecules with glucuronic acid. Glucuronic acid leads to the formation of water soluble derivatives which can then be excreted and eliminated from the body (1). In the case of therapeutic compounds, when this process takes place rapidly, their half-lives become shorter and their therapeutic effects wear off quickly. To overcome this limitation, higher doses of therapeutic compounds are administered which can lead to drug abuse or even addiction (2). In our study, catalytic nanocompartments (GUS_CNCs) were made from PMOXA₁₀*b*-PDMS₂₅ block copolymer and β-glucuronidase (GUS), the enzyme responsible for cleaving the glucuronide moiety was encapsulated inside the polymerosomes. In addition, the polymer membrane was permeabilized with melittin, a pore-forming peptide. Then, resorufin-glucuronide was given to the GUS_CNCs solution and subsequent resorufin production in the surrounding environment proved GUS_CNCs catalytic activity. The promising results of inverting glucuronidation with catalytic nanocompartments offers them as a potential nanosystem that can produce pharmacologically active compounds locally and on demand.

(1) L. A. Stanley, in *Pharmacognosy: Fundamentals, Applications and Strategy*, eds. S. Badal and R. Delgoda, Academic Press, 1st edn., 2017, pp. 527–545.
(2) B. Sproule, B. Brands, S. Li and L. Catz-Biro, *Can. Fam. Physician*, 2009, **55**, 68–69.

Note: Prof. Dr. Wolfgang P. Meier passed away on January 2022.

Amyloid stabilized air-water interfaces for functional coatings

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Ultra-thin protein coatings are widely used to enhance the biocompatibility of materials and/or to introduce new functionalities. Due to their biocompatibility, antimicrobial potential and mechanical properties, bio-degradable and renewable lysozyme amyloid fibrils are interesting candidates for such coatings.(1) The term "amyloid" describes a class of protein aggregates having a fibrillar, rod-like morphology (with a diameter of ca. 2-10 nm and a length up to several micrometers) and consisting of stacks of hydrogen-bonded beta-sheet structured peptides. Such colloidal particles can be prepared *in-vitro* from lysozyme by incubating it at pH 2 and 90°C for several hours. Like all proteins, amyloid fibrils are amphiphilic and therefore surfaceactive. In our work, their interfacial behavior was exploited to produce protein foams (3D) or films (2D) inside a loop, similar to the soap films formed when blowing bubbles. Under controlled conditions of concentration, pH and ionic strength, 2D films of amyloid fibrils made from hen egg-white lysozyme were able to homogenously coat a wide range of substrate materials such as nanocellulose films, glass and metals. The coating method developed here enables a fast and simple deposition of protein nano-layers, which could be of great interest for the design of new antimicrobial biomaterials.

(1) Kummer et al. Self-Assembly Pathways and Antimicrobial Properties of Lysozyme in Different Aggregation States. Biomacromolecules 2021, 22 (10), 4327–4336.

Direct observation of amyloid fibril interaction with lipid bilayers Rebecca Sternke-Hoffmann[1], Fanni Juranyi[2], <u>Jinghui Luo[1]</u>

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Many neurodegenerative diseases, like Alzheimer's Disease, are characterized by amyloid fibril deposition, and caused by soluble amyloid oligomers assumed in many studies. The fibrils are highly heterogeneous, insoluble and weakly distributed around *in vitro* cells. However, *in vivo* forces/pressures (like cerebrospinal fluid with intracranial pressure) presumably contribute to the dispersion and fragmentation of insoluble fibrils onto cells and further the interaction with cellular membranes. It remains to be clarified how insoluble amyloid fibrils interact with cellular membranes and contribute to neurotoxicity *in vitro*.

We recently observed by using single-channel electrical recording with a probe that amyloid fibrils interact with lipid bilayers and induce the channel formation. The channels displayed instable conductance with frequent spikes at a lower voltage, but rather stable conductance at a higher voltage. Electron microscopy imaging confirmed the fibril fragmentation in lipid membranes. We proposed a potential mechanism of amyloid fibril interaction with the bilayers: the edges of amyloid fibrils undergo conformational transition whilst interacting with lipid bilayers, and then cleave from fibril to form channels in lipid bilayers. Like Hsp104, cellular membranes may act to cleave and solubilize amyloid fragments from insoluble fibrils, leading to cell hemostatic abnormalities and death. Our studies revolutionize our understanding of dynamics and toxicity of insoluble amyloid fibrils in Alzheimer's Disease and lipid-solubilized fibril may offer a stable antigen for the development of immuno-base diagnostics and therapies.

Catalytic Nanocompartments for counteracting imbalanced H2O2 in cells

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Permeabilized soft spherical catalytic nanocompartments (CNCs) with enzymes encapsulated in the core, have emerged as an elegant tool to modify metabolic signaling in cells.^{1,2} In the work presented, we developed an H₂O₂ scavenging CNC by encapsulating the hydrogen peroxide degrading enzyme lactoperoxidase (LPO) into mellitin-permeabilized PMOXA-PDMS polymersomes. CNCs were able to reduce H2O2 in bulk if their membranes were permeabilized by melittin pores that provide a passageway for the diffusion of small molecules including substrate to the confined enzyme. In addition to engineering H2O2 detoxification properties, the CNCs were modified to optimize uptake into cells and to enable detection by fluorescence. To study the scavenging potential in cells, we introduced LPO-CNCs into K562 leukemia cells transduced with a reporter system that couples the activity of NRF2, the predominant transcriptional regulator of the antioxidant response, to the expression of mCherry.^{3,4} Only cells with functional LPO-CNCs were able to scavenge H2O2 thereby decreasing Nrf2 activity. Our data support the notion that polymer-based nano-compartments offer an ideal scaffold for the development of complex cell-inspired responsive systems for applications in biosensing, catalysis, and medicine.

⁽¹⁾ Tanner, P.; Balasubramanian, V.; Palivan, C. G. Aiding Nature's Organelles: Artificial Peroxisomes Play Their Role. *Nano Lett.* **2013**, *13* (6), 2875–2883.

⁽²⁾ Maffeis, V.; Belluati, A.; Craciun, I.; Wu, D.; Novak, S.; Schoenenberger, C.-A.; Palivan, C. G. Clustering of Catalytic Nanocompartments for Enhancing an Extracellular Non-Native Cascade Reaction. *Chem. Sci.* **2021**, *12* (37), 12274–12285.

⁽³⁾ Johansson, K.; Cebula, M.; Rengby, O.; Dreij, K.; Carlström, K. E.; Sigmundsson, K.; Piehl, F.; Arnér, E. S. J. Cross Talk in HEK293 Cells Between Nrf2, HIF, and NF-KB Activities upon Challenges with Redox Therapeutics Characterized with Single-Cell Resolution. *Antioxidants & Redox Signaling* **2017**, *26* (6), 229–246.

⁽⁴⁾ Kipp, A. P.; Deubel, S.; Arnér, E. S. J.; Johansson, K. Time- and Cell-Resolved Dynamics of Redox-Sensitive Nrf2, HIF and NF-KB Activities in 3D Spheroids Enriched for Cancer Stem Cells. *Redox Biology* **2017**, *12*, 403–409.

Stress relaxations upon flow cessation in dense soft sphere

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We explore the state of dense packing of athermal soft spheres subjected to constant shear rates. Upon flow cessation, we observe that the stress relaxes to a finite residual stress. Our investigations cover both experiments and simulations, where we vary the viscosity of the continuous phase. This enables us to expose a striking difference between the transient relaxation and the final stress. While the stress relaxation process is *exclusively* determined by the shear rate applied, the residual stress depends on the *viscous stress* defined as the product of shear rate and of the continuous phase viscosity. This discrepancy suggests distinct physical origins for relaxation processes and residual stresses, an observation providing clues for a better understanding of the microscopic processes occurring during flow of soft particle dispersions.

Polymer Brush Patterns Functionalized with Molecular Beacons for DNA/RNA Sensor Applications

Maryam Moazeni, Philipp Berger & Celestino Padeste

Laboratory of Nanoscale Biology, Paul Scherrer Institute

Engineered surfaces with specific properties are increasingly needed to accurately tailor cell-surface interactions, and to develop intelligent biointerfaces for in vitro and in vivo diagnostics. Due to their chemical robustness, polymer brushes are widely used in the design of smart biomaterials suitable for clinical testing in field and laboratory settings. By introducing linkers to a brush, the properties of a surface can be controlled through specific binding of end groups, and antifouling properties may be achieved even in complex biological media. Herein, an assay is developed based on polymer brush architectures functionalized with a specific Molecular Beacon (MB) DNA probe. Patterns of polymer brushes were created on foils of poly(ethylene-co-tetra-fluoroethylene) (ETFE) activated through a metal mask using argon plasma or extreme UV radiation, yielding patterns of initiators for the subsequent graft-copolymerization of vinylpyrrolidone (VP) and glycidyl methac-rylate (GMA). The VP/GMA combination provides both hydrophilicity and epoxide functional groups, which were biotinylated and functionalized with Streptavidin and biotinylated MBs, resulting in a promising platform for fluorescence based DNA detection. In the presence of complementary DNA, the immobilized MBs undergo a conformational reorganization and a fluorescent signal is restored from the internally quenched fluorophore. As a next step towards a sensor device, the optimized MB/PB will be embedded into a microfluidics channel and coupled to a mobile-phone based fluorescence microscope used for signal detection.

Unveiling the 3D vascular architecture of the meniscus

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The meniscus is a semicircular fibrocartilaginous tissue located between the femur and the tibia. Its characteristic shape and composition ensure the stabilisation of the knee joint, distribution of the stress load, absorption of shocks, maintenance of the articulation lubricated and nourished. Meniscus injuries are among the most common lesions in orthopedics and the vascular supply is crucial to the self-healing potential of the tissue. Indeed, in adults only tears in the outer vascularized region are capable of repair. However, so far the vascular anatomy of the meniscus has only been investigated using 2D imaging techniques (1), thus losing the complex three-dimensionality of the tissue. Therefore, this project aims to investigate the microvascular architecture of the meniscus through the use of the non-destructive X-ray imaging technique micro-CT. Analysing the entire tissue in a 3D way without physically cutting the samples allows a better understanding and a precise quantification of the vascularization.

Human and sheep healthy tissues were analysed with microCT. In CT, soft-tissue imaging quality relies on spatial resolution, i.e. the ability to distinguish two separate structures, and on contrast resolution, i.e. the ability to differentiate between objects with very similar densities as their background. Due to the low radiopacity of non-contrasted menisci, the X-ray absorption of the specimen was enhanced by either perfusing a polymerizing contrast agent in the femoral artery or soaking the meniscus in iodine contrast agent solution, thus permitting the visualization of the vascular 3D network. The specimens were analysed with micro-CT starting from the entire joint, and then scanning reducing it gradually in size to increase the applicable resolution accordingly and to maintain the spatial reference of the meniscus with its articulation. All the samples and their CT datasets were then analysed in a qualitative way creating animation and 3D models of the tissue assessed in order to analyse the CT dataset in a qualitative way and obtain a 3D model of the vascular network of the meniscus. This gain of knowledge could allow the development of new clinical treatments, e.g. vasculomorphing scaffolds, and optimal rehabilitation programs for patients based on their age, type, and position of the meniscal lesion.

(1) Arnoczky SP, Warren RF. Microvasculature of the human meniscus Am J Sports Med . 1982;10(2):90 95

Ion-mediated charge-charge interactions drive aggregation of surface-functionalized gold nanoparticles

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Monolayer-protected metal nanoparticles (NPs) are not only promising materials with a wide range of potential industrial and biological applications, but they are also a powerful tool to investigate the behavior of matter at nanoscopic scales, including the stability of dispersions and colloidal systems. This stability is dependent on a delicate balance between electrostatic and steric interactions that occur in the solution, and it is described in quantitative terms by the classic Derjaguin-Landau-Vewey-Overbeek (DLVO) theory, that posits that aggregation between NPs is driven by hydrophobic interactions and opposed by electrostatic interactions. To investigate the limits of this theory at the nanoscale, where the continuum assumptions required by the DLVO theory break down, here we investigate NP dimerization by computing the Potential of Mean Force (PMF) of this process using fully atomistic MD simulations. Serendipitously, we find that electrostatic interactions can lead to the formation of metastable NP dimers. These dimers are stabilized by complexes formed by negatively charged ligands belonging to distinct NPs that are bridged by positively charged ions present in solution. We validate our findings by collecting tomographic EM images of NPs in solution and by quantifying their radial distribution function, that shows a marked peak at interparticle distance comparable with that of MD simulations. Taken together, our results suggest that not only hydrophobic interactions, but also electro-static interactions, contribute to attraction between nano-sized charged objects at very short length scales.

direct STochastic Optical Reconstruction Microscopy (dSTORM) of soft thermoresponsive microgels

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The ability to observe at nanometer scale the microgel morphology and its response to temperature changes, opens exciting opportunities to design and precisely control the behaviour of the microgel for different applications (1). Super resolution microscopy is now an established tool used to investigate many colloidal systems and an extensively studied system because of their tuneable properties are PNIPAM microgels (2).

An important role when performing advanced microscopy experiments on such particles plays the interface where the microgels are established as they have to be fixed during the experiment. Using our home built super resolution set up equipped with a temperature controller unit, we perform dSTORM experiments to investigate how the microgels are immobilized on hydrophilic and hydrophobic interfaces. Most importantly we investigate how the particle immobilization changes when increasing the temperature above the LCST.

Super resolved images of individual microgel particles at different collapsing stages are analysed and their density profiles are obtained. The results suggest that the anchoring parts of the microgel stick to the surface as the temperature is increased. For these surfaces the experimental data and the MD simulations are in perfect agreement. Such study is quite relevant to later use this technique to investigate more complex systems along LCST, where molecules of interests can be incapsulated in the microgel network.

⁽¹⁾ Scheffold, F. Nat Commun (2020).

⁽²⁾ Conley, G. M., Nöjd, S., Braibanti, M., Schurtenberger, P., & Scheffold, F. Physicochemical and Engineering Aspects (2016).

Polymer Phase Separation under Confinement

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Phase separations are crucial for the fabrication of natural materials and their proper functions. Nature readily uses phase separations of aqueous systems to control the local composition and function of materials. However, this concept has not been used to tune the functionality of synthetic macroscopic soft materials or to combine properties that are difficult to achieve in one phase systems. The goal of this work is to exploit phase separations within aqueous systems to build hydrogel-based materials that are mechanically strong and tough and at the same time stimuli responsive. To achieve this goal, we will demonstrate how the degree of osmotic stress and its duration influence phase separations of two polymers that are confined within water-oil-water double emulsions. Further, we quench the phase separation and thereby maintain the nmsized structure by polymerizing the monomers contained in one phase using an UV-initiated radical polymerization reaction.

Understanding the Pancake-like Morphology of the Golgi Apparatus Compartments

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The Golgi Apparatus is a highly conserved membrane organelle involved in a complex cascade of protein post-translational modifications, with function being closely tied to morphology. Based on bending energy minimisation, one would expect membrane compartments of low volume-to-surface ratios, as found in the Golgi compartments (cisterna), to form a cup-like stomatocytes. In nature, however, the Golgi compartments have a flat pancake-like morphology. We investigate additional factors required for this flat pancake-like morphology. Therefore, we adhere giant unilamellar vesicles (GUVs) of varying volume-to-surface ratios to flat surfaces with varying adhesion energies. We find that by combining bending energy with adhesion, pancakelike shapes at lower volume-to-surface ratios can be achieved. However, it does not result in the ultra-flat morphology observed in the Golgi, implying that factors additional to bending and adhesion energy, such as the presence of rim stabilising proteins or lipids need to be considered.

Fabrication of Selectively Binding Microcapsules Based on Host-Guest Chemistry

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Nature can program the compositions and location of each cell, constructing tissues with various functions through a bottom-up strategy. This bottom-up strategy can be applied to soft material design and processing, customizing material properties to the specific needs of different applications by controlling the local composition on micrometer length scales. To realize this, one possible pathway is to modify the microcapsule surface with selectively binding motives such as host-guest molecules and thus enabling the self-sorting of microcapsules, potentially obtaining microcapsule assembly with controlled local compositions on the microscale. In this work, monodispersed microcapsules are produced by the coacervation between alginate (Alg) and polyethyleneimine (PEI) using microfluidics. And the permeability of the unfunctionalized microcapsules has been examined. The PEIs have been modified with host-guest pairs, β -cyclodextrin and azobenzene, which will be used to fabricate selectively binding microcapsules and construct macroscopic granular materials with well-defined local compositions.

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