

SEM image of wrinkled cellulose colloids © Johannes Bergmann

# Swiss Soft Days

27th Edition

#### FORMULA

The Swiss Soft Days is a one-day workshop taking place 2 times per year where around 20 speakers give short talks (~15 minutes) to introduce their research activities in a way specifically designed for a heterogeneous public. Besides well established scientific figures, the workshops are aimed at emerging researchers, especially assistant professors, post-docs and PhD students. The short duration of the talks and the frequency of the meetings are meant to develop active, rapidly up-to-date communications and cover various interdisciplinary areas of research.

8.6.2021

# Program

12h00 Platform opening

12h20 Welcome

12h30: Session 1 – Active and responsive materials

Steven van Kesteren, ETHZ: Responsive colloidal molecules as internally-controlled microswimmers with multi-state dynamics

**Elena Sesé Sansa**, EPFL: Emergent phase behavior of active Brownian disks in the presence of different alignment interaction symmetries

Boyang Zhou, PSI: Direct measurements of the pNipam Microgel Counter-ion Cloud via Small Angle Neutron Scattering

Alexandre Torzynski, ETHZ: Growing Polymer Brushes from Lipid Membranes

13h50: Break (5min)

13h55: Keynote 1

Saad Bhamla, Georgia Tech: Tangled Worm Blobs: Living polymers that inspire collective robotics

14h40: Break (20min)

15h00: short talks

Fotis Christakopoulos, ETHZ: Melting kinetics, ultradrawability and microstructure of nascent ultra-high molecular weight polyethylene powder

Martin Hofmann, ETHZ: Intensification of emulsification of high viscosity ratio systems by fractal mixers

Javier Diaz Branas, EPFL: Active anisotropic particles in block copolymer melts

Neda Iranpour, Empa: In-situ studies of selfassembled gold nanoparticles in biological environments

Steffen Geisel, ETHZ: Mechanical and Structural Analysis of Channel Networks in Bacterial Biofilms

15h25: Break (5min)

15h30: <u>Session 2</u> – Soft matter under deformation

Manolis Chatzigiannakis, ETHZ: Dynamic stabilisation of draining thin liquid films consisting of polymer solutions

Hamed Almohammadi, ETHZ: Flow-induced orderorder transitions in amyloid fibril liquid crystalline tactoids

**Dominic Gerber**, ETHZ: What happens when a soft material freezes?

#### 16h30: Poster (40 min)

#### 17h10: Session 3 - Electrical and optical effects

Livius Muff, AMI: Exploiting phase transitions in Polymer Bilayer Actuators

Trevor Kalkus, AMI: Soft Power Sources Inspired by Strongly Electric Fishes

Alba Sicher, ETHZ: Structural color from solid-state polymerization-induced phase separation

Maximilian Ritter, ETHZ: Wood Membranes Incorporating Stimuli-Responsive Fluorescent Dyes

18h30: Break (5min)

#### 18h35: Keynote 2

Patrick S. Doyle, MIT: The Polymer Physics of Kinetoplasts: 2D Catenated Polymers

#### 19h20: Break (20min)

19h40 Session 4 – Microfluidics

Giovanni Savorana, ETHZ: A microfluidic platform for characterizing the structure and rheology of biofilm streamers

Ariane Stucki, ETHZ: Triggered reagent delivery in double emulsions using encapsulated lipid vesicles

Marco Rocca, IBM: In situ polymerization in a microfluidic chip

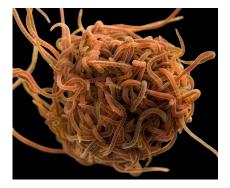
20h40: Final remarks

# **Keynote Talks**



# Tangled Worm Blobs: Living polymers that inspire collective robotics

Saad Bhamla Georgia Institute of Technology



#### **INTRODUCTION**

In this talk, I will describe our recent discovery of a new entangled active matter system composed of aquatic blackworms (*Lumbriculus variegatus*). Thousands of worms tangle together with their long, slender, and flexible bodies to make a three-dimensional, soft, and shapeshifting "blob." The blob behaves as a living material capable of mitigating damage and assault from environmental stresses through dynamic shape transformations as well as exhibit emergent locomotion for thermotaxis (survival) or for foraging. I will share our current understanding why these worms form blobs from a biophysical perspective, how active polymer physics models can help reveal the trade-offs in phase separation and emergent locomotion, and finally, how we apply robophysical swarming robot blobs to uncover rules of entangled active matter collectives. In the end, I will share some unpublished recent discoveries of marvellous new behaviours in this seemingly mundane blob of squishy worms.

#### REFERENCES

Ozkan-Aydin, Yasemin, Daniel I. Goldman, and M. Saad Bhamla. "Collective dynamics in entangled worm and robot blobs." Proceedings of the National Academy of Sciences 118.6 (2021

# The Polymer Physics of Kinetoplasts: 2D Catenated Polymers

Patrick S. Doyle<sup>1,2</sup>

<sup>1</sup>Massachusetts Institute of Technology. <sup>2</sup>Singapore-MIT Alliance for Research and Technology

**INTRODUCTION:** There is considerable interest in the materials community in molecules which are more topologically complex than the canonical linear polymer. Two-dimensional polymers are of particular interest as it is anticipated that their properties are significant different than their linear counterparts. While there has been recent progress made in the synthesis of novel 2D polymers, there is significantly less progress in understanding their polymer physics due to a lack of model systems. For the past 2 decades, linear double-stranded DNA has proven to be a model system to study linear polymers at the single molecule level. Recently, my group proposed the kinetoplast as a model system for studying 2D-catenated polymers. A kinetoplast is a planar network of topologically interlocked circular DNA and bears resemblance to chain mail armor. The kinetoplast is among the most complex mitochondrial genomes found in nature, and its unique structure has been a topic of interest in the field of cell biology, but it has yet to be explored from a polymer physics perspective. The kinetoplast topology is a subset of the more general Olympic gels. In this talk, I will discuss our recent work in single molecule studies of kinetoplasts [1-4].

METHODS: We study kinetoplasts from the mitochondria of the trypanosomatid Crithidia fasciculata (TopoGEN) containing approximately 5000 minicircles (~2.5 kbp) and 25 maxicircles (~ 40 kbp). Each minicircle is topologically linked (catenated) to three other minicircles on average and the maxicircles threaded through the minicircle network. Although the repeat units of minicircles are not covalently bonded in the network, each minicircle has a fully stretched length of approximately 5 Kuhn lengths and can be treated as an effective bond in a coarse-grained model of a 2D polymer. We stain the molecules with the fluorescent dye YOYO-1 and image the molecules using fluorescence microscopy. Molecules are observed both in bulk, and also in custom-built microfluidic devices.

**RESULTS:** In bulk solution, we find that the kinetoplasts adopt the conformation of a cup-shaped sheet with  $\sim$ 5 mm diameter and  $\sim$ 3 mm thickness (Fig. 1). We observe a range of shapes in a given population of kinetoplasts at equilibrium, attributable to the kinetoplasts being extracted at different stages of the replication cycle and the

unique connectivities of the underlying structures. Unlike linear DNA in a good solvent, the 2Dcatenated system maintains a highly extended conformation with small fluctuations about the equilibrium conformation. In the context of 2D polymers, this appears to be the flat phase.

We next studied the role of slitlike confinement on the conformation of the kinetoplasts. It is well known that linear polymers exhibit markedly different properties in confined geometries than in bulk. We find that the in-plane size of kinetoplasts increases with degree of confinement, akin to the slitlike confinement of linear DNA. The change in kinetoplast size with channel height is consistent with the scaling prediction from a Flory-type approach for a 2D polymer. Unexpectedly, with an increase in extent of confinement, the kinetoplasts appear to unfold and take on more uniform circular shapes, in contrast to the broad range of conformations observed for kinetoplasts in bulk.

We will also discuss the deformation of kinetoplasts in planar elongational fields where we observe stagewise conformational changes at large strains.

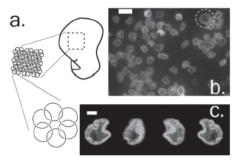
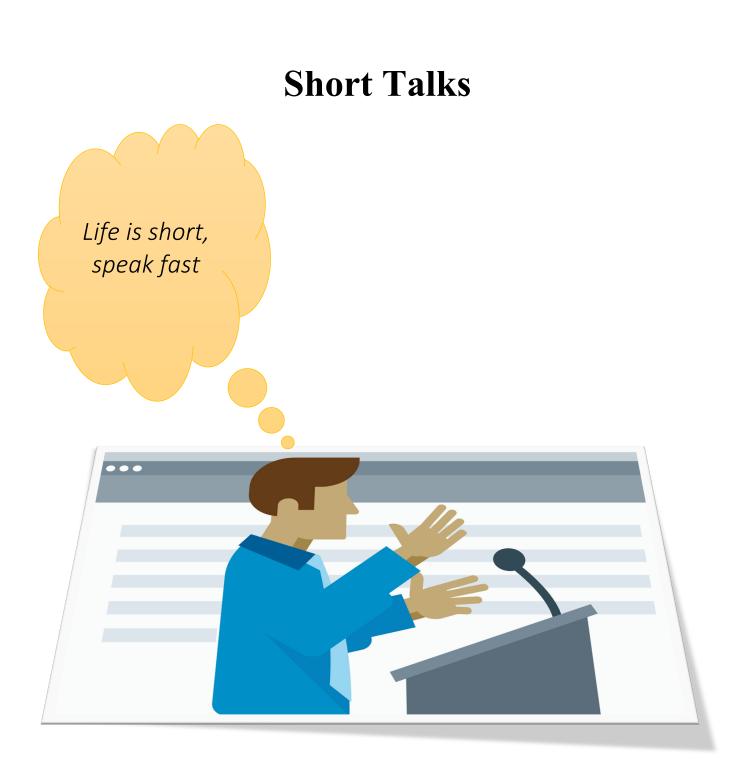


Fig. 1: (a) Schematic diagram of a kinetoplast molecule. (b) Fluorescence microscopy image of an ensemble of kinetoplasts in solution. Scale bar: 10 mm.(c) Confocal image of a single kinetoplast viewed at 4 different angles. Scale bar: 2mm.

**REFERENCES:** [1] Klotz, Soh and Doyle, *PNAS* 2020, [2] Soh, Khorshid, Al Sulaiman, and Doyle, *Macromolecules* 2020, [3] Soh and Doyle, *ACS Macro Letters* 2020, [4] Soh and Doyle, *submitted*.

ACKNOWLEDGEMENTS: Funding for this work was provided by the National Science Foundation grant CBET-1936696. Data presented are from experiments performed by Alex Klotz, Beatrice Soh, Ahmed Khorshid, Dana Al Sulaiman, and Indresh Yadav.



# Melting kinetics, ultra-drawability and microstructure of nascent ultra-high molecular weight polyethylene powder

<u>Fotis Christakopoulos</u><sup>[1]</sup>, Enrico M. Troisi<sup>[2]</sup>, Alla S. Sologubenko<sup>[3]</sup>, Nic. Friederichs<sup>[2]</sup>, Laura Stricker<sup>[1]</sup>, Theo A. Tervoort<sup>[1]</sup>

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#### Abstract

For the production of high-performance polyethylene fibers and tapes by ultra-drawing, using solid-state processing of disentangled nascent ultra-high molecular weight polyethylene (UHMWPE), the maximum draw ratio is an important design parameter, as it determines the maximum degree of chain alignment and, therewith, the properties of the final product. It would, therefore, be advantageous to have a fast scanning method to estimate the maximum drawability of reactor powders.

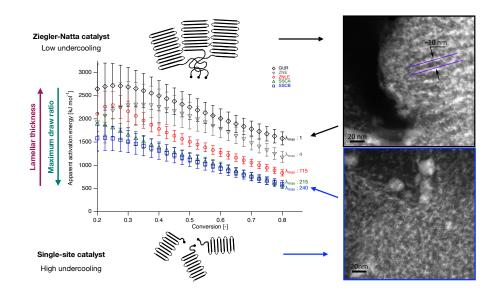
In the present work, the melting behavior of nascent ultra-high molecular weight polyethylene (UHMWPE) reactor powder is studied by differential scanning calorimetry, followed by isoconversional analysis to evaluate the apparent activation energy barrier of melting for the different UHMWPE grades of different level of disentanglement.

Powder samples are solid-sate processed into tapes at elevated temperature. Ultra-drawing of these tapes at the optimum drawing temperature allowed for the evaluation of the maximum draw ratio ( $\lambda_{max}$ ) that is determined by the entanglement density.

The morphology of the lamellar structure of the nascent powder was studied by small-angle X-ray scattering and by scanning transmission electron microscopy analyses.

A correlation between the melting kinetics, the microstructure and the maximum draw ratio was observed for all grades, suggesting that the apparent activation energy of melting can be used as a screening method to estimate the maximum draw ratio.

The effect of molecular weight on the melting kinetics and microstructure is also discussed.



# Stretch, fold, and break: Intensification of emulsification of high viscosity ratio systems by fractal mixers

<u>Martin Hofmann</u>, Alexandra V. Bayles, Jan Vermant Department of Materials, ETH Zürich, Zurich, Switzerland

#### Abstract

During emulsification process design, the bulk and interfacial rheology of the target formulation must be carefully considered. Formulations with high viscosity ratios and/or finite interfacial elasticity are particularly challenging to emulsify, as conventional drop-breakup methods consume significant energy and provide limited control over polydispersity. Here, we develop a two-stage process that produces monodisperse emulsions from high viscosity ratio constituents. In the first stage, a custom static mixer generates co-flowing layers of alternate phases, and progressively thins layers until they rupture, thus forming a high-internal phase emulsion. The interfacial properties and flow conditions that promote stable fractal multiplication are discussed. In the second stage, extensional flow elements refine the polydispersity. We demonstrate the utility of this novel process by producing remarkably monodisperse polyisobutylene-in-water emulsions with an energy efficiency that is orders of magnitude higher than classical emulsification methods. The moderate throughputs achieved show promise for upscaling and intensification in industrial applications.

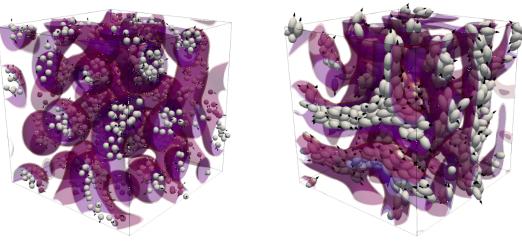
# Active anisotropic particles in block copolymer melts

Javier Diaz, Ignacio Pagonabarraga CECAM, EPF Lausanne

### Abstract

Block copolymer (BCP) melts have been widely used to template the position of colloidal nanoparticles (NPs) in the nanoscale, due to their ability to self-assemble into periodic ordered structures (1). Furthermore, chemically complex and anisotropic NPs have been shown to exhibit a rich phase behaviour when trapped at fluid-fluid interfaces or in the bulk (2,3). The interplay between the BCP intrinsic ordering and the NP alignment and collective behaviour can offer novel self-assembly mechanisms to achieve ordered structures.

In this work we study the role of self-propulsion and anisotropy in colloidal NPs dispersed in a BCP matrix. The BCP is shown to act as a template in the low-activity regime, with NPs displaying a strong alignment within the BCP domains. Self-propelling disks are shown undergo motility-induced phase separation mediated by the BCP properties, under soft confinement. 3D anisotropic active particles can self-propel along BCP domains, modifying the matrix.



(a) Active Nanospheres

(b) Active Nanoellipses

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- (2) Großmann R., Aranson I. S., Peruani F. Nature comm 2020
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### In-situ studies of self-assembled gold nanoparticles in biological environments

Neda Iranpour [1,3,4], Marianne Liebi [1,2], Quy Ong [5], Peter Wick [3], Antonia Neels [1,4]

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 [3] Laboratory of Particles-Biology Interactions, Empa, Swiss Federal Laboratories for Materials Science and Technology

[4] Department of Chemistry, University of Fribourg

[5] Laboratory of supramolecular nanomaterials and interfaces, EPFL University

#### Abstract

Self-assembled gold nanoparticles (NPs) or gold superlattices in colloidal suspensions can enhance single NPs properties and lead to a wide range of applications such as diagnostic tools in medicine. Polymer grafting, particularly PEGylating, is commonly used in functionalizing gold NPs and driving their assembly in solutions with higher ionic strength (IS). The salt ions deplete in the PEG brushes on the NPs surface and generate an osmotic pressure gradient between the PEG shell and the salt solution. The self-assembly into an ordered three-dimensional (3D) arrangement is ensured by partnering nearest-neighbors to minimize the surface tension gradient at the boundary between the PEG shell, and the high IS environment (1,2).

Our research introduces SAXS (3) as a unique characterization method to study 3D self-assembled gold NPs in biological solutions in real-time and physiological conditions. PEGylated 5nm gold NPs are introduced in saline solution (NaCl 0.9% w/v) and human serum albumin (HSA). NPs in saline solution assemble in a very stable 3D ordered arrangement. This ordering is even maintained in the presence of HSA. The HSA molecules, which present a similar size as the gold NPs, create defects by penetrating the 3D NPs ordered arrangement and, consequently, expanding the NP-NP distance.

#### References

(1) Assembling and ordering polymer-grafted nanoparticles in three dimensions. Nanoscale 2017, 9 (25), 8710-8715

(2) Nanoparticle Superlattices: The Roles of Soft Ligands. Adv Sci (Weinh) 2018, 5 (1), 1700179.

(3) New approach for time-resolved and dynamic investigations on nanoparticles agglomeration. Nano Research 2020, volume 13, pages2847–2856.

### Mechanical and Structural Analysis of Channel Networks in Bacterial Biofilms

<u>Steffen Geisel</u> [1,3], Eleonora Secchi [2,3], Jan Vermant [1] [1] Laboratory of Soft Materials, ETH Zurich [2] Stockerlab ETH Zurich [3] bioM<sup>2</sup> ETH Zurich

#### Abstract

Bacterial biofilms are formed by communities of microorganisms that are encased by a matrix consisting of self-produced, hydrated extracellular polymeric substances. Biofilm formation is observed in a large variety of microorganisms and provides a protected mode of growth. Recent advances show that biofilms are structurally complex, dynamic systems that exhibit different morphologies depending on the environmental conditions.[1] In certain growth conditions, large three-dimensional structures, which can be defined as channels, are found within biofilms. These channels show low resistance to liquid flow and therefore enable transport by advection.[2] Recent works identify the role of interfacial energy and mechanical instabilities as driving forces during biofilm morphogenesis[3], but the exact mechanism of channel formation is still unclear. Our work represents a step towards understanding the physical process of channel formation within a microbial biofilm.

We study how the adhesion of the biofilm matrix to the substrate influences the formation of channels inside *Pseudomonas aeruginosa* biofilms grown under flow in microfluidic devices. We perform confocal laser scanning microscopy to examine the structure of the biofilm during growth as a function of substrate surface energy. Our results show that biomass production and its adhesion to the substrate control a mechanical buckling instability, which triggers the formation of folds and wrinkles. These three-dimensional structures can be identified as hollow channels in which bacterial movement is greatly facilitated and which rapidly increases the effective volume occupied by the biofilm. Combining methods and concepts from biology and material science sheds light on the physical process of channel formation inside bacterial biofilm grown in flow and enables us to predict and control the biofilm morphology.

- [1] Flemming et al., The perfect slime. IWA Publishing, London, 2017
- [2] Asally et al., PNAS, 109(46):18891–18896, 2012
- [3] Yan et al., *eLife* 2019;8:e43920, 2019

# Talks

The essence of science is not to make simple things complicated, but to make complicated things simple - Stanley P. Gudder



# Responsive colloidal molecules as internally-controlled microswimmers with multi-state dynamics

<u>Steven van Kesteren</u>, Laura Alvarez, and Lucio Isa Laboratory for Soft Materials and Interfaces, D-MATL, ETH Zürich

#### Abstract

Active colloids are propelled micro-scale objects that serve as model systems for biological microscopic swimmers. The ability of microswimmers to autonomously sense and adapt to their environment is widespread throughout nature, and synthetic analogues are key in the development of micro-scale robotics. However, synthetic microswimmers lack any autonomous self-regulation and typically rely on external feedback schemes to control their motion. Here, we show the fabrication of colloidal molecules with soft and hard components, which serve as internally controlled microswimmers propelled by induced-charge electrophoresis. These colloidal molecules are purpose-built clusters of PNIPAM-co-AAC thermoresponsive microgels using sequential capillary assembly(1) which allows an unprecedented control over the geometry and composition. Clusters with multiple microgels exhibit multi-state motilities controlled by temperature. We rationalize the different motilities of these states by temperature-induced changes in shape and dielectric properties(2). Hereby, we demonstrate a rich class responsive microswimmers with properties akin to simple soft-robotics. In the future, additional components in our synthetic microswimmers could provide them with different responses and interparticle communication schemes to potentially reach "nature-like" sensing and collective motion.

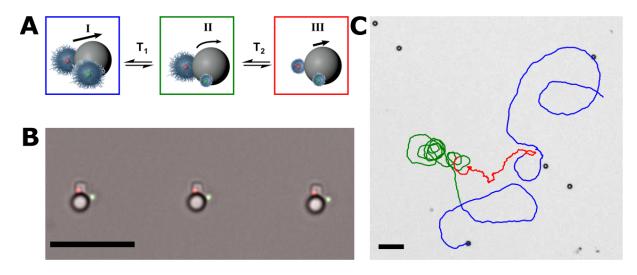


Figure 1. A. Schematic of multi-state responsive microswimmer. B) Composite brightfield-fluorescence micrograph colloidal molecules C. Example trajectory of a microswimmer switching between state I (blue), state II (green), state III (red). (scale bars are 10 µm)

#### References

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# Emergent phase behavior of active Brownian disks in the presence of different alignment interaction symmetries

<u>E. Sesé-Sansa</u> [1], D. Levis [2,3], I. Pagonabarraga [1,2,3] [1] CECAM Centre Européen de Calcul Atomique et Moléculaire, EPF Lausanne [2] Departament de Física de la Matèria Condensada, Universitat de Barcelona, Spain [3] UBICS University of Barcelona Institute of Complex Systems, Universitat de Barcelona, Spain

#### Abstract

We study the phase behavior of Active Brownian Particles (ABP) moving in two-spatial dimensions and interacting through volume exclusion and local alignment. The interplay between steric effects and velocity alignment has recently led to a number of studies (1-4). Usually, this question is addressed by studying self-propelled elongated particles that align upon collisions due to their anisotropic shape. Here, we tackle the problem from a different perspective and study a system of isotropic active Brownian disks with an explicit velocity alignment torque. Our model allows us to investigate different types of symmetries in the alignment rule by independently controlling activity and local torques. Specifically, we analyze polar (5) and nematic (6) alignment and show that their different symmetries lead to different scenarios in the emergent collective behavior of active Brownian disks. We combine particle-based simulations with a mean-field theoretical model to quantify the impact that these different velocity alignment interactions have on the so-called motility-induced phase separation (MIPS) (7,8), in the regime of weak alignment interaction, i.e. below the onset of global orientational order.

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- (2) Jayaram A., Fischer A. and Speck T., *Phys. Rev. E* 101, 022602 (2020)
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# Direct measurements of the pNipam Microgel Counter-ion Cloud via Small Angle Neutron Scattering

Boyang Zhou [1,2], Urs Gasser [1], Alberto Fernandez-Nieves [3,4]
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#### Abstract

Microgels are formed by cross-linked polymer networks. Due to their stimuli-sensitive nature, their responsiveness towards changes in external conditions such as temperature, pH, pressure and concentration lets microgels reversibly change between a swollen and collapsed state. Their responsiveness also makes them interesting for applications and a good model system for soft colloids. Unlike hard colloids, soft colloids like microgels are not well understood, especially at high concentrations because of the complex interplay of internal and colloidal degrees of freedom, which is not present in hard colloids. In this study, we use pNipam microgels that have an uncharged polymer network and low critical solution temperature close to room temperature. However, due to the initiator used during synthesis, pNipam microgels carry charged groups and counter-ions at the periphery, which we have found to play a crucial role for the observed spontaneous deswelling behavior at high concentrations; the counter-ion clouds percolate at high concentration and cause the suspension osmotic pressure to increase [1,2]. When the osmotic pressure exceeds the bulk modulus, deswelling occurs. This deswelling mechanism can also resolve point defects that would otherwise hinder the crystallization in the case of a hard-incompressible particle suspension.[3,4] Importantly, our theory for microgel deswelling relates the particle softness and surface charges with the phase behavior. We present the first direct measurements of the counter-ion cloud via small angle neutron scattering (SANS). Note that the form factor can be decomposed as  $P(q)=F_p^2(q)+2F_p(q)F_c(q)+F_c^2(q)$ , where  $F_p^2(q)$  and  $F_c^2(q)$  are the form factor of the pNIPAM polymer and the counter-ion cloud, respectively. We prepare one suspension with Na<sup>+</sup> ions and another with NH4<sup>+</sup> ions via dialysis and use the scattering-length-density difference between Na<sup>+</sup> and NH4<sup>+</sup> to obtain a signal from the counterion cloud. The difference of their form factors at dilute situation is given by the cross term  $2F_p(q)[F_{NH4}^+(q)-F_{Na}^+(q)]$ , which gives detailed information on the configuration of the counterions and charged groups. By using this method, we are able to detect the signal of the cloud, even though the concentration of the counter-ions is very low. Our results show the counter-ion clouds are indeed located at the particle periphery, which corroborates our theory. The findings are crucial for developing a more systematic understanding of 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.

#### References

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# **Growing Polymer Brushes from Lipid Membranes**

<u>A. L. Torzynski</u> [1], M. Romio [2], G. Panzarasa [3], E. M. Benetti [2], E. R. Dufresne [1] [1] Lab. of Soft and Living Materials, Dept. of Materials, ETH Zürich [2] Lab. For Surface Science and Technology, Dept. of Mat., ETH Zürich [3] Wood Materials Science Lab., Institute for Building Materials, ETH Zürich

#### Abstract

Polymers anchored by one end to a deformable membrane are known to deform said membrane, on a scale that varies with the surface coverage and the chain length (1). With lipid membranes, the effect can lead to dramatic shape changes, experimentally observed for both model vesicles (2) and actual cell membranes (3). To study this effect, we develop a polymerisation initiator able to incorporate into a lipid bilayer, and use aqueous ARGET ATRP to grow polymer chains from model lipid membranes.

As a first step into this project, we use quartz crystal microbalance with dissipation monitoring (QCM-D) to observe the polymerisation of N-isopropylacrylamide (NIPAM) from a supported bilayer, and study the influence of monomer and initiator concentrations.

#### References

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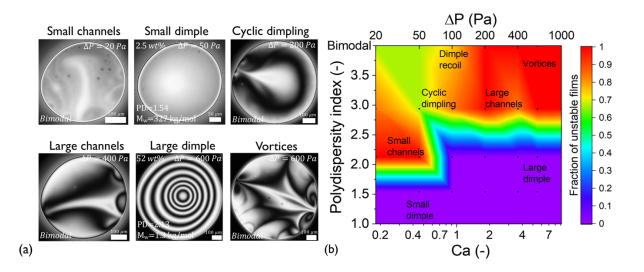
(3) Physical Principles of Membrane Shape Regulation by the Glycocalyx. Shurer et al., Cell, 2019.

# Dynamic stabilisation of draining thin liquid films consisting of polymer solutions

Emmanouil Chatzigiannakis and Jan Vermant Materials Department, ETH Zürich

#### Abstract

The hydrodynamic drainage and rupture of polymer solutions was investigated using a dynamic thin film balance (1). The polymeric nature of the dissolved molecules leads to significant resistance to the deformation of the thin liquid films. The influence of concentration, molecular weight, and molecular weight distribution of the dissolved polymer on the lifetime of the films was systematically examined under varying hydrodynamic conditions. Depending on the value of the capillary number and the degree of confinement, different stabilisation mechanisms are observed. For low capillary numbers, the lifetime of the films was the highest for the highly concentrated, narrowly-distributed, low molecular weight polymers. In contrast, at high capillary numbers, the flow-induced concentration differences in the film resulted in lateral osmotic stresses, which caused a dynamic stabilisation of the films. Phenomena such as cyclic dimple formation, vortices, and dimple recoil were observed. The factors which lead to enhanced lifetime of the films as a consequence of these flow instabilities can be used to either stabilise foams or, conversely, prevent foam formation (2).



#### References

(a) Microinterferometric images of polymer films of different PDIs. (b) State diagram describing the propensity for asymmetric drainage as a function of Ca and  $\Delta P$  for films containing polymer of different PDIs. (1) Chatzigiannakis, E., Veenstra, P., Ten Bosch, D., & Vermant, J. (2020). Mimicking coalescence using a

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(2) Chatzigiannakis, E., & Vermant, J. (2021). Dynamic stabilisation during the drainage of thin film polymer solutions. *Soft Matter*. Advance article

### Flow-induced order-order transitions in amyloid fibril liquid crystalline tactoids

<u>Hamed Almohammadi</u> [1], Massimo Bagnani [1], Raffaele Mezzenga [1,2] [1] Department of Health Sciences and Technology, ETH Zurich [2] Department of Materials, ETH Zurich

#### Abstract

Liquid crystalline droplets, also known as tactoids, forming by nucleation and growth within the phase diagram region where isotropic and nematic phases coexist, challenge our understanding of liquid crystals under confinement due to anisotropic surface boundaries at vanishingly small interfacial tension, resulting in complex, non-spherical shapes. Little is known about their dynamical properties, since they are mostly studied under quiescent, quasi-equilibrium conditions. Here we show that different classes of amyloid based nematic and cholesteric tactoids undergo order–order transitions by flow-induced deformations of their shape. Tactoids align under extensional flow, undergoing extreme deformation into highly elongated prolate shapes, with the cholesteric pitch decreasing as an inverse power-law of the tactoids aspect ratio. Free energy functional theory and experimental measurements are combined to rationalize the critical elongation above which the director-field configuration of tactoids transforms from bipolar and uniaxial cholesteric to homogenous and to debate on the thermodynamic nature of these transitions.

### What happens when a soft material freezes?

<u>Dominic Gerber</u>, Eric R. Dufresne and Robert W. Style Department of Materials, Soft and Living Materials, ETH Zürich, Switzerland

#### Abstract

The freezing of soft matter is a common occurrence, for instance in the freezing of food for preservation, in cryo-SEM, or when soil freezes in the winter, leading to destructive frost heave. This invariably causes damage to the samples but, surprisingly, this damage process is still not at all well understood. Indeed, although freezing damage is commonly attributed to the expansion of water during freezing, experiments suggests that this actually plays only a minor role. In fact, porous materials soaked in benzene (which contracts upon freezing) show similar levels of damage to the same, water-soaked materials upon freezing. Instead, a different mechanism called cryosuction is the culprit.

To better understand cryosuction we study the forces around ice crystals in our experimental setup. We measure the solidification-induced stresses with Traction Force Microscopy (TFM). I will describe how this process allows us to measure the stresses around growing ice crystals with a spatial resolution at the micron scale. This technique reveals how the freezing stresses are typically extremely localised, explaining their large propensity for causing damage.

# **Exploiting phase transitions in Polymer Bilayer Actuators**

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#### Abstract

Very much like in nature, biomimetic soft robotic systems depend on mechanical morphing or adaptive functional materials to execute a variety of elaborated tasks like gripping or locomotion. Stimuli responsive polymers used in such systems can reversibly change their density, shape, stiffness, porosity or hardness as a response to a range of stimuli. Temperature is a frequently used stimulus that can be applied through radiation, oscillating magnetic fields, or Joule heating. Recently we reported<sup>1</sup> a novel type of temperature responsive bending actuator with integrated Joule heater, which relies on the anisotropic thermal expansion across the bilayer for actuation. The thermal expansion was maximized by exploiting the discontinuous volumetric change associated with the first-order phase transition, allowing for a large dimensional change within a narrow temperature range (25-65 °C). A segmented polyurethane elastomer was used as phase changing material. This polymer features a crystallizable hard segment with hydrogen bonding sites acting as physical cross-links to prevent melting above the transition temperature of the crystalline soft segment, responsible for the large discontinuous thermal expansion. While the previously reported system relied on a polyester soft segment for actuation, it was possible to achieve an order of magnitude larger thermal expansion across the melt transition by switching to a polyether soft segment with more applicable crystallization behavior. This segmented polyurethane features a higher degree of crystallization and a sharper thermal transition resulting in larger bilayer deflection and faster recovery. To fabricate bilayer bending actuators, this new high-thermal-expansion polyether-based polyurethane was joined with a polyimide film, additionally a thin Joule heating electrode, patterned via photolithography, was sandwiched between the two layers to enable electro-thermal control. To improve the actuator performance a finite element model was created to simulate the behavior of bilayer bending actuators in action. With this modelling approach, the mechanical properties, geometrical factors and thermal transport issues of bilayer bending actuators were investigated and subsequently tuned to optimize application specific operations necessary for integration into complex soft robotic systems. Given a specific soft robotic application, this model can furthermore expedite the identification of material property requirements to facilitate the material selection or allow a synthesis-on-demand approach.



Picture series of melt-processed PEG-PU (275 μm) and polyimide (125 μm) bilayer bending actuator with an integrated copper (200 nm) Joule heater between the two layers. The anisotropic thermal contraction across the bilayer is responsible for the bent state in ambient condition. The bilayer bending actuator quickly flattens when powered (~4 W) and returns into its bent state when power is turned off.

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### Soft Power Sources Inspired by Strongly Electric Fishes

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#### Abstract

As implantable and wearable technologies become more pervasive, the development of biologically integrated technologies can benefit from power sources that are biocompatible, mechanically flexible, and able to harness energy available from the user. Although conventional batteries were not designed with these parameters in mind, strongly electric fishes, like the knifefish Electrophorus electricus (commonly known as the electric eel) and the Atlantic torpedo ray Tetronarce nobiliana, provide examples of electrical power sources that operate within biological constraints. We previously demonstrated an electric-eel-inspired soft power source that harnessed the energy from ion gradients between hydrogel compartments separated by cation- and anion-selective hydrogel membranes. By stacking a repeat sequence of these hydrogels, the system generated over 100 volts in open circuit conditions (1). Although electric eels are famous for the extremely high voltages reached by their electrical discharges (860 volts was recorded from the species *Electrophorus* voltai (2)), the Atlantic torpedo ray can generate electrical discharges with power greater than 1 kW, a 10-fold higher power output than the electric eel. Torpedo rays achieve this feat largely due to the high current of their discharges (3,4). Taking further inspiration from the morphology of the torpedo ray, we optimized the soft power source to improve its current output. A hybrid material of hydrogel-infused paper allowed for thinner and more robust components that were easily stacked in series and in parallel. This innovation, along with an optimization of salts used to generate the ion gradient, resulted in an increase in electrical power by almost two orders of magnitude compared to the original eel-inspired design. We ultimately demonstrated the ability to power a small electric device using a AA battery-sized stack of hydrogel-infused paper (5).

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# Structural color from solid-state polymerization-induced phase separation

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#### Abstract

Structural color is produced by nanostructures able to provide a variation in the material refractive index on the order of the wavelengths of visible light. These structures can cancel, deflect or reinforce specific wavelength ranges, generating a permanent, very bright, non-fading color with no need of pigments or dyes. Many natural materials display structural color, which is developed through self-assembly and phase separation [1, 2]. However, most synthetic structural colors are produced in a two-step process involving the sequential synthesis and assembly of building blocks.

Inspired by the formation through phase separation of the quasi-ordered photonic structures in the feathers of many birds [1, 3], we developed a self-limiting approach to polymerization-induced phase separation that can produce stable structures at optical length scales. The resulting composites have a blue or white color. We also demonstrate the flexibility of this approach by producing structural color in filaments and large sheets.

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### Wood Membranes Incorporating Stimuli-Responsive Fluorescent Dyes

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#### Abstract

Wood is an intrinsically sustainable and CO<sub>2</sub>-storing material, with promising applications for developing lighting materials. However, the intrinsic optical properties of wood have received only little attentional to date, and state-of-art reports of wood-based lighting applications make use of toxic quantum dots as fluorophores or impregnate the wood structure with non-biodegradable polymers to improve the matrix transparency. (1-3).

Wood membranes feature a unique combination of properties, resulting in hierarchical porous structures with high mechanical resistance. We studied how light propagates inside wood as a function of different parameters (wood species, cut direction, lignin composition). We then functionalized wood with environmentally friendly fluorescent metal-organic complexes. In addition to their strong photoluminescence, these metal-organic fluorophores are also responsive to acidic or basic gases, allowing their use as sensors of indoor pollution and air quality.

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# A microfluidic platform for characterizing the structure and rheology of biofilm streamers

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#### Abstract

In many environmental or medical settings, biofilm formation is the most successful strategy for bacterial colonization (1, 2). In the biofilm lifestyle, bacteria embed themselves in a self-secreted matrix of extracellular polymeric substances (EPS), acting as a shield against mechanical and chemical insults (3). The biofilm matrix has viscoelastic properties: it can adapt under loads, undergoing large deformations before breaking or detaching from its substrate. Due to its gel-like properties, when ambient flow is present, the EPS scaffold can take a streamlined shape, forming biofilm threads suspended in flow, called streamers (4). In many situations, the streamers architecture can enhance the harmful effects of biofilms, bridging the spaces between obstacles in the flow path (5). Despite their relevance, little is known about the structural and rheological properties of such thin biofilm filaments. Examples of open questions are how their structure and rheology are related to the EPS composition or to the physico-chemical features of the microenvironment. Investigating these relations would allow a better understanding of the mechanisms underlying biofilm resistance and would possibly lead to new removal strategies.

In this work we present a microfluidic platform that allows to grow biofilm streamers in controlled chemical and flow conditions and to characterize their structure and rheology in situ (6). We use this platform to characterize streamers formed by the opportunistic pathogen *Pseudomonas aeruginosa* PA14, a model organism for biofilm formation. By varying the composition of the biofilm matrix using mutant strains of PA14 and by applying targeted enzyme treatments, we shed light on the structural and rheological role of the different EPS components, namely extracellular DNA (eDNA) and the polysaccharide Pel. In particular, we show that eDNA is the fundamental building block of streamers, while Pel stiffens the matrix and affects their shape and rheology (7).

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# Triggered reagent delivery in double emulsions using encapsulated lipid vesicles

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#### Abstract

Microfluidic methods for the formation of single emulsion (SE) and double emulsion (DE) droplets are tools of particular interest for drug discovery or directed evolution (1-2). Such methods allow the compartmentalization of reactants at high throughput and provide a mean of retaining reactions' products for further analysis (3). However, the supply of reagents into droplets at any desired time requires complicated set-ups and reactions are therefore often limited to the compounds present at the encapsulation time.

Here, we present a microfluidic tool allowing for the synchronized trigger of reactions inside water-in-oilin-water DE droplets at any delayed time point (4). This method is based on two-level compartmentalization: large unilamellar lipid vesicles (LUVs) containing one of the reagents are co-encapsulated in DE droplets together with other reagents. The LUVs release their cargo by addition of sodium dodecyl sulfate (SDS) to the outer aqueous phase. The released cargo can thereby react with the other reagents present in the DE droplets. We characterize the flexibility and adaptability of this system by studying the release of a fluorescent dye and we optimize the system to perform an enzymatic assay.

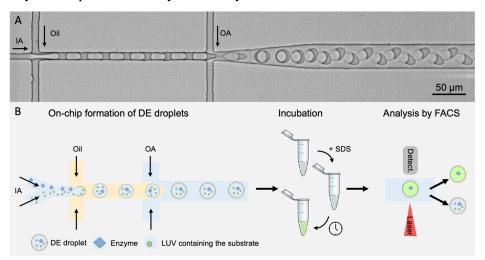


Figure: Triggered delivery in double emulsion droplets. A: Micrograph of double emulsion formation using a microfluidic chip. IA: inner aqueous phase, OA: outer aqueous phase. B: Double emulsion droplets coencapsulating the enzyme together with LUVs containing the substrate are formed on-chip. After collection of the DE droplets, SDS is added to the outer aqueous phase. SDS permeates inside the DE droplets and ruptures the LUVS which release the substrate. The product of the enzymatic assay is fluorescent and the fluorescence inside DE droplets can be analyzed by flow cytometry (FACS).

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## In situ polymerization in a microfluidic chip

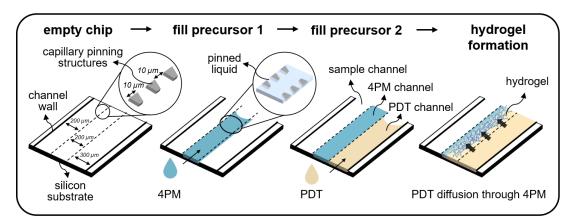
<u>Marco Rocca</u> [1,2], Maxime Dufresne [1], Marie L. Salva [2], Christof M. Niemeyer [2], Emmanuel Delamarche [1] [1] IBM Research Europe – Zurich [2] Institute of Biological Interfaces, Karlsruhe Institute of Technology, Germany

#### Abstract

Hydrogels are versatile materials used in various applications due to their unique mechanical and chemical properties. Forming hydrogels inside microfluidic chips allows to explore fundamental phenomena and implement novel applications thanks to the physics of liquids at the microscale and the small volumes required. However, forming hydrogels in specific locations of microfluidic devices remains challenging and the most common methods employ photopolymerization, which involves toxic initiators and bulky optical equipment (1). In this work, we introduce a novel approach to form hydrogels with a well-defined geometry in capillary-driven microfluidic chips by interfacial polymerization.

A PEG-based hydrogel was formed through a thiol-maleimide reaction. Precursor 1 (4-armed PEG maleimide, 4PM) and precursor 2 (PEG-dithiol, PDT) are introduced sequentially on chip with the liquid interface between both solutions being pinned by specific microfluidic structures. Precursor 2 diffuses quickly through precursor 1 and a hydrogel forms only in the area originally occupied by precursor 1 (fig. 1).

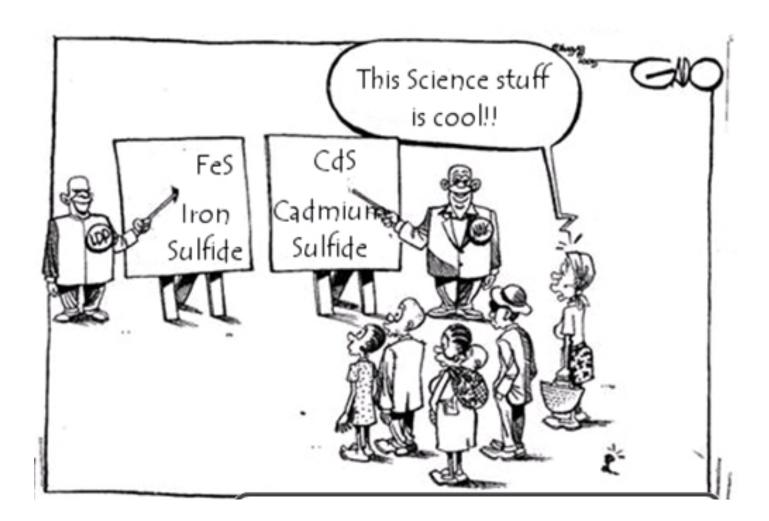
Using this method, we polymerized rectangular-shaped PEG-based hydrogels inside a sealed microfluidic chip in less than 3 minutes, using only 200 nL of precursor solutions. We could control the mesh size of the hydrogel by varying the chemical composition and the concentration of the precursor solutions and we characterized the resulting hydrogels by measuring the diffusivity of molecules with different molecular weights across it. By choosing a suitable hydrogel mesh size, large molecules such as antibodies, can be trapped inside the hydrogel, while small analytes are able to diffuse through it.



**Figure 1.** Formation of a hydrogel in situ by interfacial polymerization inside a microfluidic chip. The hydrogel precursors (4PM and PDT) are introduced sequentially into specific areas of a microfluidic chip delimited by capillary pinning structures and channel walls. PDT will diffuse through 4PM and the hydrogel will form only in the 4PM channel.

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# **Posters**



### Varying Disorder in the Photonic Structures of Longhorn Beetles

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#### Abstract

Nature's rich colour palette is based on pigmentary and structural colour resulting from the interaction of light with either absorbing pigments or transparent, nanostructured materials. Photonic nanostructures can vary in their degree of order (1,2) and are often combined with pigments to further adapt the optical appearance. Longhorn beetles display vivid colours in the UV-VIS spectral range and rely on varying degrees of disorder combined with pigments to create their complex colour patterns. The central aim of this project hence is to understand these colour variations and their origin in structural diversity, often within the same organism. Two longhorn beetles of the subfamily Lamiinae, Sulawesiella raffaelae and Sternotomis amabilis ssp. sylvia, were studied by combining optical characterization and ultrastructural analysis of the coloured scales that adorn the insects' bodies and create their vivid colour pattern. Sulawesiella raffaelae displays different extents of orientational disorder in multilayer-type structures that lead to colours ranging from orange to green to turquoise (1). In contrast, Sternotomisamabilis ssp. sylvia relies on cubic as well as amorphous photonic crystals to display an iridescent green-turquoise and an angle-independent orange colour, respectively. We show that the optical signal in this species arises from a photonic crystal that is further altered by the geometry of the scales, featuring a diffuser-like structure in the form of micrometre-scale ribs on the cortex. In both investigated beetles, the photonic structures were found to concur with pigmentary content in the scales, thus illustrating the complex interplay of structural and pigmentary colour in longhorn beetles.

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# **Polymer GUVs for Studying Compartmentalized Biological Systems**

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#### Abstract

Biological systems use compartmentalization strategies to generate microenvironments with controlled biochemical compositions. They serve as a protective method from undesired influences from outside of the compartment and to keep diffusing elements in close proximity. (1) Giant unilamellar vesicles (GUVs) are micrometer-sized vesicles that are used 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. (2) With double emulsion microfluidics, monodisperse GUVs with controllable inner, membrane, and outer composition can be produced at high throughput. (3) By adjusting the inner composition, whole enzymatic cascades, smaller vesicles, and living organisms can be encapsulated within GUVs.

In the presented work, we generate impermeable GUVs using the block copolymer PDMS-PMOXA. By inserting outer membrane porin F (ompF) (3) or the pore-forming peptide melittin into the synthetic membrane, the GUVs can be permeabilized. A subcompartmentalized system was created by encapsulating nanometer-sized polymersomes into GUVs. Furthermore, *Bacillus subtilis*, a model organism for studying biofilms, was encapsulated within GUVs. Bacteria growth and biofilm formation inside the GUV could be explored. This approach shows the versatility of double emulsion templated polymer GUVs for studying compartmentalized systems.

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# OSP, I sheared in the wrong direction! Effects of non-linear flow on orthogonal microstructural relaxation.

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#### Abstract

Performing mechanical spectroscopy of soft matter in the non-linear regime is made difficult by the complex dependence of the material on the shear history. Orthogonal superposition (OSP) rheometry permits to obtain frequency dependent measurements in non-linear flow while retaining a clear kinematics. This technique consists in superimposing a small perturbing oscillation on a steady shear flow. OSP rheometry sample the anisotropic out-of-equilibrium microstructure of the materials generated by the imposed steady shear.

Experiments were conducted on representative materials with different microstructural relaxation mechanisms. A concentrated solution of PIB in pristane and a Carbopol gel are used as samples to measure the data.

From the orthogonal data the Yamamoto relaxation spectra are extracted. Different relaxation times are recognized from prominent features in the spectra.

In particular, relaxation times for deformation, stretching of polymer chain, and convection activated motion (rotation and out-of-cage diffusion) are recognized.

From these spectra the effects of the non-linear flow on the relaxation mechanism can be observed. The characteristic features of the spectra tent to reduce in intensity and disappear as the steady shear flow get faster than the relaxation of the microstructure.

This work clearly shows a correlation between the macroscopic non-linear response of the material and the reduction in the degree of freedom of the microstructure under flow.

# Unravel the rotational properties of a squirmer in viscoelastic fluids

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#### Abstract

Microorganisms such as bacteria and algae naturally inhabit complex environments. Understanding their ubiquitous behavior in, e.g., biofilms is fundamental for medical and industrial applications. We study the rotational motion of a single swimmer in viscoelastic fluids (1) via Lattice Boltzmann (LB) simulations (2). Here, the generic squirmer model is employed and fluid viscoelasticity is achieved by added flexible polymer chains. The interplay of activity and boundary conditions between the squirmer and polymers on squirmer's rotational motion is addressed. For Reynolds number close to unity, the rotational diffusion of a pusher/puller that employs the no-split boundary condition is enhanced over an order of magnitude. This is due to the asymmetric torques generated during the heterogeneous collisions between the squirmer and polymers. However, this enhancement is about 5 times weaker when a short-range repulsion between squirmer's surface and monomers is used. By increasing system viscosity, we decrease the Reynolds number by an order of magnitude. Consequently, polymer's motility is suppressed profoundly. We find that the rotational diffusion coefficients of a pusher/neutral swimmer obtained from two boundary conditions are nearly identical. But the rotational enhancement of a puller with a no-slip boundary condition is twice stronger compared with the one exploiting short-range repulsion. This is because collisions occur mainly in the front of a puller due to its special swimming scheme. Our results can facilitate the understanding of the behavior of the microorganisms in complex systems and guide the design of microfluidic devices by harnessing these properties.

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# **Electroformation of Gold Nanoparticles in Picoliter Droplet Reactors**

Mario A. Saucedo-Espinosa,<sup>1</sup> Darius G. Rackus,<sup>1</sup> Maximilian Breitfeld<sup>1</sup> and Petra S. Dittrich<sup>1</sup> <sup>1</sup>ETH Zürich, Basel, SWITZERLAND

#### Abstract

Gold nanoparticles (AuNPs) have unique physicochemical properties and surface functionalities that make them one of the most important nanomaterials for applications in optical sensing, chemical catalysis, electrochemistry, diagnostics, and biomedicine [1]. Such unique properties, however, have a strong dependency on the size and morphology of the nanoparticles [1], which has boosted the development of novel technologies for the fabrication of AuNPs with defined sizes and shapes.

The most employed technologies for the synthesis of AuNPs rely on chemical, thermal, and electrochemical principles [2]. From these, the electrochemical process ranks as the most convenient approach, as the yield can be accurately controlled, it requires only modest equipment, and the operational costs are usually low [2]. This synthesis mode relies on the use of a gold precursor solution (e.g., HAuCl<sub>4</sub>) and two conducting surfaces serving as electrodes, where oxidation-reduction reactions take place. The nanoparticles are synthetized and deposited on the surface of the electrodes, where they form aggregates [2]. Surfactants are thus usually employed to control this colloidal aggregation, having an influence on the final particle size.

In this contribution, we demonstrate an electrochemical synthesis of AuNPs inside picoliter-sized droplet reactors. A microfluidic device with two parallel, metallic electrodes was developed. The metallic electrodes interface the droplets via two carbon-based membranes, which offer a wider electrochemical window. Droplets confined in microfluidic channels develop internal recirculation flows, which are systematically exploited to drive the synthetized nanoparticles away from the electrode surface. We prove that the use of droplets overcomes the need of surfactants, and modifies the nanoparticles nucleation and growth dynamics.

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### Subzero liquid water in lipidic mesophase nanoconfinement

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#### Abstract

Water is the most ubiquitous and essential liquid on earth and it is fundamental to the existence of life. Many biological processes take place in crowded aqueous surroundings and water in living cells can be considered as confined water(1). However, water behaves differently under confinement with respect to the nucleation mechanism and the molecular dynamics comparing to the bulk. Especially in biological systems, the role of confined water is of crucial importance though still far away from fully understood. In the talk, I will first present the crystallization and dynamics of water confined in hard media, e.g. hollow silica(2) and mesoporous silica(3). Then extend to the discussion on water under soft confining media, lipidic mesophase(4). The talk will present the cutting-edge result on water in biomimetic environment, which will shed light on the understanding of life in extreme environment.

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