Programme

Annual Meeting 2023, Tuesday 23 May

Start time	End time	Title of contribution	Speaker first name	Speaker family name	Start time	End time	Title of contribution	Speaker first name	Speaker family name
08:45	09:00	Opening remarks					Opening remarks		
09:00	10:00	The paradoxical material properties of biological soft matter	Gijsje	Koenderink			The paradoxical material properties of biological soft matter	Gijsje	Koenderink
10:00	10:30	Cofee break							
10:30	10:50	Janus helices: From fully attractive to hard helices	Laura	Dal Compare	10:30	10:50	In situ investigation of nanoparticle formation using a batch reactor and in-house SAXS/WAXS	Manuel	Wilke
10:50	11:10	Cellulase and betaglucosidase co-adsorbed into mesoporous silica nanoparticles: a nanostructured	Giulio	Pota	10:50	11:10	Sizing multimodal suspensions with differential dynamic microscopy	Wilson	Poon
11:10	11:30	Impact of the substrate on the phase transitions properties in supported lipid bilayers	Nicolo	Tormena	11:10	11:30	Passive Microrheology of Supramolecular Polymer and Gelatin Hydrogel at High ? Pressure	Nikolaos	Bourker
11:30	11:50	Can Polymer Helicity Affect Topological Chirality of Polymer Knots?	Jan	Rothörl	11:30	11:50	Coupling of Microfluidics and Dynamic Light Scattering	Luis	Torquato
11:50	12:10	Amino acid characteristics in protein native state structures	Tatjana	Skrbic	11:50	12:10	Systematic parametrization of non-Markovian dissipative thermostats for coarse-grained molecular simulations with accurate dynamics	Viktor	Klippenstein
12:10	12:40	Hydrogel Membranes for Selective Filtration	Sixtine	de Chateauneuf-Randon	12:10	12:30	Measuring the viscoelastic properties of microscopic soft particles using time-dependent Capillary Micromechanics	Kalpit	Bakal
12:40	14:00	Lunch break			12:30	14:00	Lunch break		
14:00	15:00	Memory of shear in soft jammed materials	Veronique	Trappe			Memory of shear in soft jammed materials	Veronique	Trappe
15:00	15:20	MXenes-stabilized emulsions: interfacial viscoelastic properties	Benedetta	Attaianese	15:00	15:20	Understanding Enhanced Rotational Dynamics of Active Probes in Rod Suspensions	Joost	de Graaf
15:20	15:40	Cellular Automata Modeling Reveals cell tissues evolution dynamics	Carmine	Schiavone	15:20	15:40	Active vesicles: from complex dynamic shapes to motility	Dmitry	Fedosov
15:40	16:00	Chain-length-dependent relaxation dynamics in poly(methyl acrylate)	Jiaxin	Zhao	15:40	16:00	Self-steering and responsive active particles	Rajendra Singh	Negi
16:00	16:20	Follow Up of UHMWPE Rheological Properties Under Ultra-Fast Magnetic Hyperthermia Sintering	Mathieu	Salse	16:00	16:20	Self-propelled particles in an alignment field	Sameh	Othman
16:20	16:50	Coffee break							
16:50	17:20	Transforming sustainable plant proteins into lubricants by microgelation	Ben	Kew	16:50	17:10	Targeted delivery of thrombolytic proteins using multifunctional nanovesicles derived from red blood cell membranes	Nicole	Henry
17:20	17:40	Towards mechanistic understanding of biofilms: understanding the transport phenomena, kinetics and rheology of biofilm formation, functioning and morphology.	Vince	Engelborghs					
17:40	19:00	Posters and networking							
18:00	20:00	Network Coordination Committee (NCC)							
20:00		Dinner							

SoftComp
SOFT MATTER COMPOSITES

EUSMI

Annual Meeting 2023, Wednesday 24 May

Start time	End time	Title of contribution	Speaker first name	Speaker family name	Start time	End time	Title of contribution	Speaker first name	Speaker family name
09:00	10:00	Some recent progress on filler structure and interfacial layer dynamics of polymer nanocomposites	Julian	Oberdisse			Some recent progress on filler structure and interfacial layer dynamics of polymer nanocomposites	Julian	Oberdisse
10:00	10:30	Cofee break							
10:30	10:50	Characterisation of the destabilisation of saliva filaments during phonation by a model experiment	Christian	Ligoure	10:30	10:50	Flow-Switched Bistability in a Colloidal Gel with Non-Brownian Grains	John	Royer
10:50	11:10	Inducing irreversible strain hardening and alignment during collagen gelation	Pavlik	Lettinga	10:50	11:10	Binary mixture of hard and soft colloids with tuneable interactions	Fabien	Dutertre
11:10	11:30	Protein phase behavior in electric fields	Debes	Ray	11:10	11:30	Drying Drops of Colloidal Suspensions	Matteo	Milani
11:30	11:50	A DNA Origami Fiducial for Accurate Multidimensional Atomic Force Microscopy Imaging	Pauline	Kolbeck	11:30	11:50	Hydrodynamic Lubrication in Colloidal Gels	Kim William	Torre
11:50	12:10	Modelling Biomolecular Interactions of Protein Solutions	Marco	Polimeni	11:50	12:10	Sustainable Formulations: Cellulose Based Colloid-nematic Gels	Orlaith	Skelton
12:10	12:30	Planar Confined Water Organisation in Lipid Bilayer Stacks of Phosphatidylcholine and Phosphatidylethanolamine	Gerome	Vancuylenberg	12:10	12:30	Solvents effect on Particle contact and Rheological behaviour in Jamming suspensions	Anh Vu	Nguyen Le
12:30	14:00	Lunch break							
14:00	15:00	Everything flows? but how? A quest for the microscopic origin of yielding	Stefano	Aime			Everything flows? but how? A quest for the microscopic origin of yielding	Stefano	Aime
15:00	15:20	Neutron scattering and reflectivity to study foams in a brand new multi-scale experiment	Julien	Lamolinairie	15:00	15:20	Solvation Shell Thermodynamics of Extended Hydrophobic Solutes	Madhusmita	Tripathy
15:20	15:40	Measuring the interaction between small colloidal particles using optical tweezers	Chi	Zhang	15:20	15:40	Dilute surfactant solutions by using a pharmaceutical salt: equilibrium characteristic lengths & strain hardening in start-up flow	Rossana	Pasquino
15:40	16:00	Solving inverse design problem with enumeration-selection strategy	Vladimir	Baulin	15:40	16:00	The evolution of equilibrium NaPSS / DTAB supramolecular structure in dilute aqueous solution with increasing surfactant binding	Bence	Fehér
16:00	16:30	Coffee break							
16:30	16:50	Linear, Star, Comb and Ring Crystallizable Multiblock Copolymers Investigated by Molecular Dynamics Simulations	Guilhem	Baeza	16:30	16:50	Nonlinear shear rheology of unentangled melts and solutions	Salvatore	Costanzo
16:50	17:10	How to unravel and quantify the heterogeneous structure of silicone rubbers by swelling, NMR and DMA analysis	Xavier	Morelle	16:50	17:10	Stimuli responsive 3D bioprinted in vitro alveolar models	Ane	Urigoitia Asua
17:10	17:30	Structure and dynamics of a 1,4-Polybutadiene melt in confinement: A molecular dynamics simulation	Lama	Tannoury	17:10	17:30	Constraining effects on polymer chain relaxation in crosslinked supramolecular dual networks	Jasper	Feng
18:00	20:00	Network Governing Board (NGB)							
20:00		Dinner							

Annual Meeting 2023, Thursday 25 May

Start time	End time	Title of contribution	Speaker first name	Speaker family name	Start time	End time	Title of contribution	Speaker first name	Speaker family name
09:00	10:00	Dynamics and structure of metallo-supramolecular networks: The importance of the interplay between entanglements, supramolecular dynamics and phase separation	Evelyne	van Ruymbeke			Dynamics and structure of metallo-supramolecular networks: The importance of the interplay between entanglements, supramolecular dynamics and phase separation	Evelyne	van Ruymbeke
10:00	10:30	Cofee break							
10:30	10:50	Effective Potentials, Phase Behavior and Viscoelastic Behavior of Reversible Polymer Gels	Angel	Moreno	10:30	10:50	alpha-synuclein binding to model membranes: effect of composition, solution condition and external stimuli	Marco	Fornasier
10:50	11:10	High frequency dynamics of hydrogels studied by DWS microrheology	Tetsuharu	Narita	10:50	11:10	?-Synuclein - lipid membrane interactions depends on membrane charge and lipid:protein ratio	Alexandra	Andersson
11:10	11:30	Microrheology of dense solutions of DNA	Jenny	Harnett	11:10	11:30	SLE3S ? water system: a linear rheological characterization	Rosalia	Ferraro
11:30	11:50	Copolymeric templates for plasmonic substrates fabrication	Jacek	Jenczyk	11:30	11:50	Creating Microstructures through Controlled Wrinkling	Jens	Elgeti
11:50	12:10	Photon correlation imaging of polymer network fracture	Nicholas	Orr	11:50	12:10	Engineered proteins toward an all-protein bioelectronic platform	Maxence	Fernandez
12:10	12:30	Synthesis of multi-responsive supramolecular PNIPAM microgels	Antoine	Brezault					
12:30	14:00	Lunch break							
14:00	15:00	Active ring melts and topological glasses	Jan	Smrek			Active ring melts and topological glasses	Jan	Smrek
15:00	15:20	Specific ion effects on amino acid dissociation equilibria	Varun	Mandalaparthy	15:00	15:20	Synthesis and characterization of structurally colored silica foams via colloidal templating	Kalpana	Manne
15:20	15:40	Tuning the dimensionality of supramolecular materials through the design of peptide-protein co-assemblies	Laura	Perez-Chirinos	15:20	15:40	Smart-hybrid multifunctional bioinks for a 3D printed pulmonary artery model	Uxue	Aizarna Lopetegui
15:40	16:00	Microfluidic flow of vesicle prototissues : A model for cell tissues	Majid	Layachi	15:40	16:00	Electrostatics in PNIPAm-based microgels: from two-step deswelling to polyelectrolyte adsorption	Rajam	Elancheliyan
16:00	16:20	Lipid ordering and fluidity of colloid supported lipid bilayers	Levena	Gascoigne	16:00	16:20	Effect of charge on the stabilization of water-in-water emulsions by thermosensitive bishydrophilic microgels	Do Nhu Trang	Nguyen
16:20	16:50	Coffee break							
16:50	17:10	Closing remarks: Future vision of the SoftComp Consortium							
17:10	18:00	Posters and networking							
20:00		Conference Dinner							

Collection of Abstracts

Plenary Talks

Auditorium

Tue. 23 May 09:00-10:00	Gijsje Koenderink	The paradoxical material properties of biological soft matter
Tue. 23 May 14:00-15:00	Veronique Trappe	Memory of shear in soft jammed materials
Wed. 24 May 09:00-10:00	Julian Oberdisse	Some recent progress on filler structure and interfacial layer dynamics of polymer nanocomposites
Wed. 24 May 14:00-15:00	Stefano Aime	Everything flows? but how? A quest for the microscopic origin of yielding
Thu. 25 May 09:00-10:00	Evelyne van Ruymbeke	Dynamics and structure of metallo-supramolecular networks: The importance of the interplay between entanglements, supramolecular dynamics and phase separation
Thu. 25 May 14:00-15:00	Jan Smrek	Active ring melts and topological glasses

The paradoxical material properties of living matter

Gijsje Koenderink
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Cells and tissues are dynamic but also need to withstand large mechanical loads. This paradoxical mechanical behavior is governed by fibrous protein scaffolds known as the cytoskeleton and the extracellular matrix. It is still poorly understood how these biopolymer networks can combine mechanical strength with the ability to dynamically adapt their structure and mechanics. I will summarize our recent findings obtained via quantitative measurements on synthetic cells reconstituted from purified biological constituents. I will focus on the role of mechanical crosstalk between the four cytoskeletal networks in the cell: actin filaments, microtubules, intermediate filaments and septins. These four filamentous systems contribute different structural and dynamical properties, enabling specific cellular functions. I will highlight our recent efforts to biochemically reconstitute their interplay, which allows us to connect the collective mechanical properties of cytoskeletal networks to the underlying molecular interactions, which involve cytoskeletal crosslinkers, motors, and the plasma membrane.

Memory of shear in soft jammed materials

V. Trappe[1]; H.A. Vinutha[2], M. Marchand[1], M. Caggioni[3], V.V. Vasisht[4], E. Del Gado[2]
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Shearing jammed suspensions of soft particles results in heterogeneous and correlated dynamics leading to stress heterogeneities. To assess the role of such complex dynamics in encoding memory of shear into the system, we perform shear cessation tests in simulation and experiments. These tests consist of stopping the shear once the stress reaches a constant value, and measuring the stress relaxation upon shear cessation. Consistent with previous work we find that the preshear-rates set the time scales of stress-relaxation at early times, which is correlated with a ballistic-like motion, reminiscent of the non-affine short-time particle dynamics observed during shear. An investigation of the correlations of the short-time non-affine displacement fluctuations observed just before and after shear cessation reveals remarkable similarities in the dynamical correlations observed in both regimes. This indicates that the spatially heterogeneous dynamics during shear imprints stress-inhomogeneities that in turn drive spatially heterogeneous dynamics upon shear cessation. Beyond the short-time behavior, we find that the long-time relaxation towards a residual stress is connected to the evolution of local stiffness. Our findings suggest that steady-state shear is a process through which a memory of the imposed shear rate and of the distribution of local yield stresses is built into the material, a memory that can then be effectively read out in a shear cessation test.

Some recent progress on filler structure and interfacial layer dynamics of polymer nanocomposites

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The physics and in particular macroscopic properties of polymer nanocomposites (PNCs) depend in a crucial way on the microscopic state of the filler nanoparticles (NPs) and the polymer. In particular mechanical properties are strongly affected by percolation of hard phases, which may be NP networks, or dynamically modified (i.e. hardened) polymer regions, or combinations of both. In this talk, we will review some recent progress in small-angle scattering associated with simulations to study particle dispersions, and broadband dielectric spectroscopy (BDS) to investigate polymer dynamics at the NP interface.

Nanoparticles used in industrial applications may be very polydisperse, and form agglomerates of complex geometry [1]. The conceptual difficulty of their analysis goes hand in hand with their superior performances. We will present one of the first self-consistent models of their structure based on a combination of electron microscopy with scattering [2]. We did not realize it back then, but this approach was the first based on a correlation hole analysis [3], which is a measure of the strength of interaction between particles or small aggregates, and thus the local concentration. In collaboration with Vera Bocharova and Alexei Sokolov [4,5], we then moved to an in-depth characterization of the dynamic state of the polymer using BDS in strongly attractive model systems. Here the combination of structural analysis based on scattering, with a careful look on interparticle distances, with BDS turned out to allow for a better quantitative determination of the thickness of the interfacial layer. The experimental system under scrutiny is a surface-modified PNC (C_8 or C_{18} silane grafting), where the NP structure and the interfacial layer dynamics can be followed simultaneously as a function of grafting density and particle content. The strongest dynamical slow-down in the polymer is found for unmodified NPs, while grafting weakens this effect progressively. The combination of all three techniques enables a unique measurement of the true thickness of the interfacial layer, which is ca. 5 nm. Finally, the comparison between longer (C_{18}) and shorter (C_8) grafts provides unprecedented insight into the efficacy and tunability of surface modification. It is shown that C_8-grafting allows for a more progressive tuning, which goes beyond a pure mass effect.

If time allows, we will present a highly speculative and non-conclusive analysis of a problem encountered in the scattering analysis of the above system: sometimes there is no structure factor (S=1), even at high particle concentrations [6]. Any ideas are welcome!

References

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[6] A.C. Genix and J. Oberdisse, submitted (on the occasion of the 50th birthday of D11)

Everything flows… but how? A quest for the microscopic origin of yielding

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Everything flows: that's where rheology comes from. Yet, the flow of solid matter can be more complex than that of a simple liquid. Or can it? Soft glassy materials such as those that populate our fridge may take forever to spontaneously spread on our toast, and luckily this process can be helped by mechanical stress, and/or heat. Is spreading butter any similar to melting it? Surprisingly, or maybe unsurprisingly, it turns out that what is so common in our daily experience is based on profound science that is not yet fully understood.

In this talk I will discuss experiments in which we investigate the microscopic signature of mechanical yielding in various soft materials, by simultaneously measuring their mechanical response and microscopic dynamics. I will show that these dynamics change qualitatively upon yielding, and that this change can be described by an Ising-like model formally identical to that describing thermodynamic phase changes in real gases. I will build upon this analogy to propose a unified state diagram for the yielding transition of soft colloids, and will discuss potential implications of this unified description.

Dynamics and structure of metallo-supramolecular networks: The importance of the interplay between entanglements, supramolecular dynamics and phase separation

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Understanding and tailoring the viscoelastic response of polymer melts or concentrated solutions from the knowledge of their molecular structure (architecture) represents a formidable challenge and remains an important field of soft matter research. In order to further study the dynamics of these samples, we have developed a general coarse-grained approach based on the tube model, that we are now using as a tool to investigate the viscoelastic properties of complex, entangled polymer architectures.

In the present work, we extend this approach to investigate the dynamics of reversible polymer networks created through the metal-ligand association of entangled building blocks bearing terpyridine ligands. These building blocks are telechelic linear or star polymers, or polymer chains bearing stickers along their backbone. By varying their topology, their lengths, their chemistries, and the stickers density, a large variety of rheological properties can be obtained. In particular, while the nature of the metal ions used to create the metal-ligand associations largely influences the lifetime of a supramolecular interactions, we show that the dynamics of the reversible networks can also be largely modulated by playing with the possible cooperative effect of the stickers, with the ratio between entanglements and stickers density, as well as with the ratio between their association and disentanglement times [1].

As these physical networks present structural changes in the long term, double networks are then made either by promoting the phase separation of the metal-ligand complexes in order to reinforce the sample [2], or by mixing the metallo-supramolecular networks with a very stable dynamic covalent network (DCN) [3]. We show how adjusting the dynamics of the weaker network is a key process to govern the viscoelastic response, creep properties and shape recovery properties of the slower network.

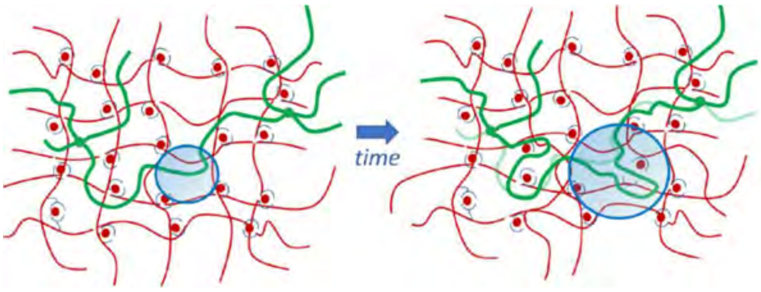

Figure 1: *Constraint Release Rouse relaxation of the dynamic covalent network (in green) due to the relaxation of the metallosupramolecular network (in red). With time, the bis-complexes dissociate and associate many times, allowing the DCN to explore a larger space (represented by the blob). [3]*

References

[1] Y Li, C Pyromali, F Zhuge, CA Fustin, JF Gohy, D Vlassopoulos, E. van Ruymbeke, *Journal of Rheology*, **2022** 66 (6), 1203-1220, DOI: https://doi.org/10.1122/8.0000418

[2] S Ghiassinejad, K Mortensen, M Rostamitabar, J Malineni, CA Fustin, E. van Ruymbeke, *Macromolecules* **2021** 54 (13), 6400-6416, DOI: https://doi.org/10.1021/acs.macromol.1c00373

[3] R Lyons, L Hammer, A André, CA Fustin, R Nicolaÿ, E Van Ruymbeke, *Journal of Rheology,* **2022** 66 (6), 1349-1364, DOI: https://doi.org/10.1122/8.0000473

Active ring melts and topological glasses

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I will talk about computational investigation of dense polymeric systems where the topology of the polymer chains governs the material properties in- and out-of-equilibrium.

A prominent example of such a system is the melt of nonconcatenated and unknotted ring polymers, which has been fascinating for a number of reasons. For example, the equilibrium state has the same mean conformational properties as the (linear) chromosomes of higher eukaryotes [1] and the system exhibits interesting rheological behavior: close to equilibrium a power-law stress relaxation with the absence of a rubbery plateau, but also a strong extensional viscosity thickening. It turns out that all these effects are the consequence of the topological constraints of different kinds.

Besides the constraints of no linking and no knots, the rings can restrict each other by threading - a ring entering anothers ring opening [2]. It has been a long-standing conjecture that the threadings (topological in nature) of sufficiently long rings can form a hierarchical percolating network that would impede the mutual rings' motion to the extent of a glassy state (aka the topological glass conjecture) [3]. Despite the efforts, such a state has not been directly observed in simulations or experiments, maybe due to the insufficient threading in equilibrium at the accessible ring lengths. But can we manipulate the threadings to generate a topological glass or tune the response at will?

Using externally driven or active blocks (modelled as a stronger-than-thermal fluctuations) on the polymers, we can alter the ring dynamics and shift the prevalence of certain threading entanglements to generate a novel type of glass. This Active Topological Glass [4, 5] differs from ordinary polymeric glasses in many properties and exhibits the counter-intuitive behavior of a slow-down as a consequence of the energy input.

The opposite dynamic behavior can be achieved for equilibrium rings with torsional stiffness. The competition of the torsion and bending generates supercoiled conformations that reduce the threadings, and linear entanglements, thereby exhibiting a speed-up [6].

References

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Young Scientists Session 1

Tuesday 23 May 10:30 – 12:40

Auditorium

Janus helices: From fully attractive to hard helices

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The phase diagram of hard helices [1, 2] differs from its hard spherocylinders [3] and hard cylinders rods [4] counterpart for the presence of additional phases stemming from the chiral nature as well as the specific shape of the helices. Using extensive numerical simulations, we study the addition of a short-range attraction to a fraction of the sites forming the hard helices, ranging from fully attractive to a single-site attraction. Different temperature regimes exist for different fractions of the attractive sites, as assessed in terms of the relative Boyle temperatures, that are found rather insensitive to the shape of the helical particle, at a variance of the hard helices case. In the present study, we focus on the weakly attractive regime, where the reduced temperatures range from 1 to 0.1 well above the corresponding Boyle temperature, and on slender helices. In the case of fully attractive helices, we observe only a minor change in the phase behavior with respect to its hard helices counterpart, in qualitative agreement with past results on attractive rods [5]. In the opposite limit of a single attractive site, we observe a marked tendency to the formation of micelles competing with the formation of thermotropic liquid crystal phases at moderately low temperatures. Also, the Janus case, where half of the beads are attractive and half are repulsive, does not seem to play a peculiar role, at variance to the spherical [6] and dumbbell [7] counterparts. Perspectives for future directions are then outlined on the basis of these results.

References

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Cellulase and β-glucosidase co-adsorbed into mesoporous silica nanoparticles: a nanostructured biocatalyst for cellulose hydrolysis

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Cellulose hydrolysis might not result in high glucose yealds. Indeed, the process is catalyzed by cellulase enzyme group, which contains reduced amount of β-glucosidase (BG) [1]. BG is accountable for the hydrolysis of disaccharide cellobiose, which acts as inhibitor for the other two enzymes namely endoglucanase and exoglucanase, contributing to keep the glucose production low. To address this issue, β-glucosidase and cellulase were easy co-immobilized by adsorption on wrinkled mesoporous silica nanoparticles (WSNs) with radial and hierarchical open pore structure [2]. The proteins were simultaneously and sequentially immobilized into WSNs in order to optimize the synergy between cellulase and BG for the hydrolysis of cellulose extracted from *Eriobotrya japonica* leaves. Simultaneous co-immobilization resulted to provide the best biocatalyst. In this case, 20% yield of immobilization and enzyme load of 100 mg/g of support were achieved. 85% of initial cellulose was converted to glucose in 24 h whereas the activity was 72 μmol/min·g, almost the same value as the one exhibited by the enzyme mixture in the free form. Operational stability measurements assessed 83% of the initial yield of reaction after 9 cycles of reuse (Fig. 1A). Moreover, it had better stability than the free enzyme mixture in a wide range of temperatures, preserving 72% of the initial yield of reaction up to 90°C (Fig. 1B).

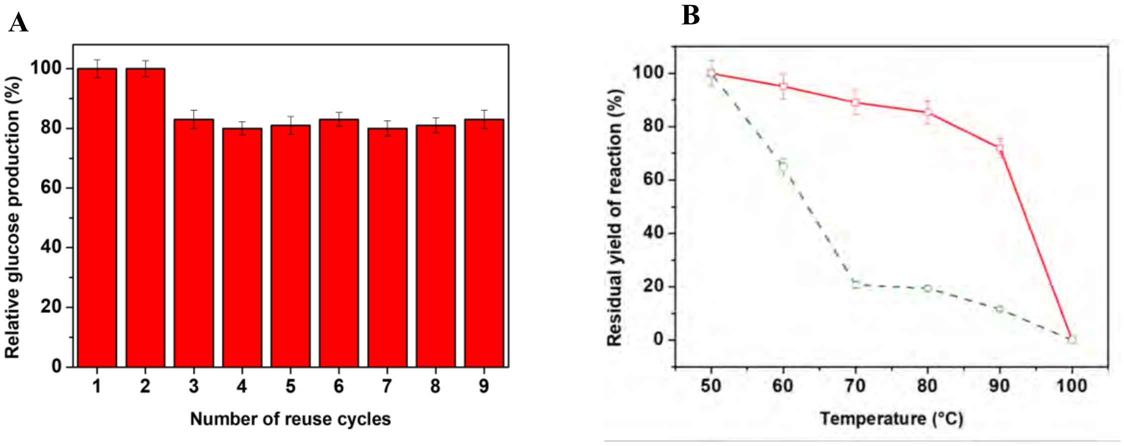

Figure 1. Relative glucose production up to 9 reaction cycles (A). Residual yield of reaction evaluated in 50-100 °C temperature range.

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Impact of the substrate on the phase transitions properties in supported lipid bilayers

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Bacterial membranes play a crucial role in the survival of the organism, from providing a physical barrier with the surroundings, to controlling membrane trafficking, shape changes and growth, and underpinning drugs resistance. Membranes are self-assembled structures, comprising a phospholipid bilayer where proteins and sugars are embedded. The activity of the proteins and their response to external stimuli depends on the biophysical properties of the lipid bilayer such as thickness, elasticity, and molecular mobility (1). Additionally, bacterial membranes are always in close contact with various structural filaments such as cytoskeleton tubules or peptidoglycan chains which can all influence the movement of macromolecules in the bilayer. E Coli is a routinely used as a platform to investigate fundamental biological questions about the function of membrane proteins (2) and it is also heavily used in biotechnology, making it a key bacterial system.

Here, we create and test a minimal model system for E. coli's inner membrane, focusing on the membrane's mechanical properties. Our model system contains three types of lipids that replicates the main aspects of E Coli's lipidomic, and their relative proportion is adjusted to mimic the transition temperature of native E Coli membranes, as used in research. The goal is to subsequently use this system to investigate the propagation of mechanical energy within the membrane, for example due to protein activity.

Using a combination of atomic force microscopy (AFM) and differential scanning calorimetry (DSC), we comparatively track the phase transition kinetics of our model E. coli membrane, comparing it when supported and unsupported. The results show that only part of the kinetics depends on the cooling/heating, with the main influence coming from contact with a support in AFM experiments. The presence of a contacting substrates not only shifts the transition temperature dramatically, it can also arrest the transition and induce a global re-arrangement of the lipid species. The result is a phase transition that partially follows classical nucleation on short timescales (<1h) but moves on to a spinodal decomposition on the longer term.

Our work highlights the importance of external membrane contacts to control the composition and biophysical properties of bacterial membranes.

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Can Polymer Helicity Affect Topological Chirality of Polymer Knots?

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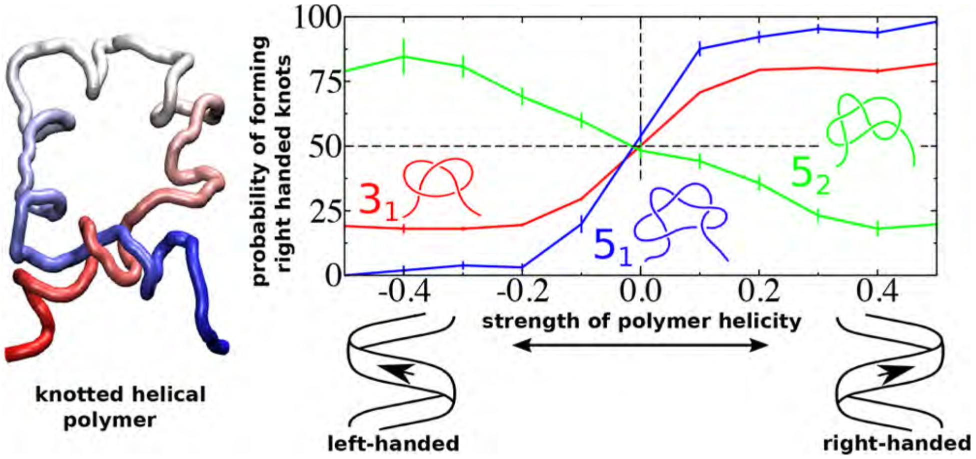
We investigate the effect of helicity in isolated polymers on the topological chirality of their knots with computer simulations. Polymers are described by generic worm-like chains (WLC), where helical conformations are promoted by chiral coupling between segments that are neighbors along the chain contour. The sign and magnitude of the coupling coefficient u determine the sense and strength of helicity. The corrugation of the helix is adjusted via the radius R of a spherical, hard excluded volume around each WLC segment. Open and compact helices are, respectively, obtained for R that is either zero or smaller than the length of the WLC bond, and R that is a few times larger than the bond length. We use a Monte Carlo algorithm to sample polymer conformations for different values of u, spanning the range from achiral polymers to chains with well-developed helices. Monitoring the average helix torsion and fluctuations of chiral order as a function of u, for two very different chain lengths, demonstrates that the coil-helix transition in this model is not a phase transition but a crossover. Statistical analysis of conformations forming the simplest chiral knots, 3_1, 5_1, and 5_2, demonstrates that topological mirror symmetry is broken – knots formed by helices with given sense prefer one handedness over the other. For the 3_1 and 5_1 knots positive helical sense favors positive handedness. Intriguingly, an opposite trend is observed for 5_2 knots, where positive helical sense promotes negative handedness. We argue that this special coupling between helicity and topological chirality stems from a generic mechanism: conformations where some of the knot crossings are found in "braids" formed by two tightly interwoven sections of the polymer.



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Amino acid characteristics in protein native state structures

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Proteins are chain molecules made up of twenty naturally occuring amino acid types. The set of amino acid side chains span a range of geometrical shapes, physical sizes, as well as chemical properties. We analyze experimental data on amino acid identity and side chain orientations with respect to the protein backbone in more than 4000 high-resolution protein native state structures. We consider the magnitude and direction of protrusion along with a simplified chemical attribute captured by a hydrophobic scale. The geometrical, physical, and chemical properties of the side chains are simultaneously studied using principal component analysis to infer the consensus propensity to harmoniously substitute one amino acid with another in protein sequences, while preserving the native state structure. This propensity also indicates the destabilization potential of a point mutation to the native state fold. We benchmark our results against mutational studies reported in the literature.

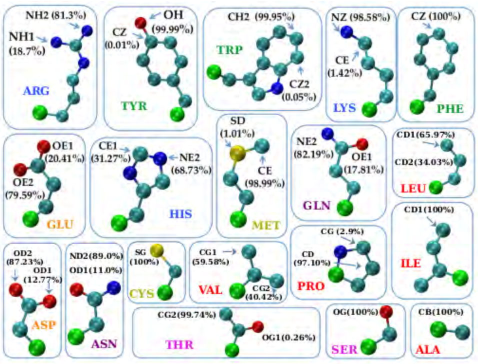

Figure 1: *Twenty amino acid types naturally occuring in proteins: side chain atoms that protrude 'maximally' from the protein backbone are indicated, along with the frequency with which that occurs.*

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Hydrogel Membranes for Selective Filtration

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[2] *Université Paris Est Créteil, Institut Chimie de Matériaux Paris Est, Thiais, France*
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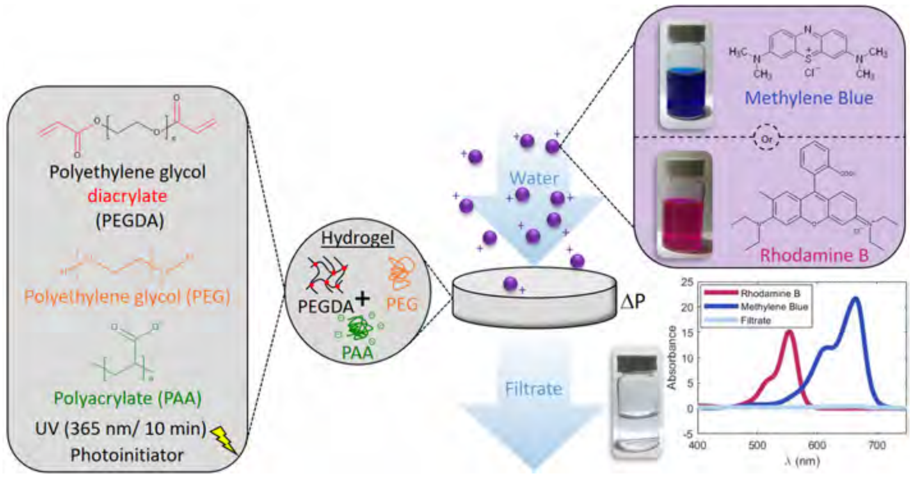

Hydrogels are networks of polymer molecules bound together by covalent bonds. While the diffusive transport of molecules in hydrogels has been well studied in the context of drug delivery, the hydrodynamic transport of water, molecules, and particles in hydrogels in the context of filtration has been barely studied.

Recently our group has synthesized macroporous hydrogels based on the UV cross-linking of polyethylene glycol diacrylate (PEGDA) in water, a mechanically resistant hydrogel. To control the permeability of PEGDA hydrogels we showed that crosslinking PEGDA in the presence of free polyethylene glycol (PEG) chains dramatically increases water permeability by several orders of magnitude [1]. We found that these PEG chains do remain trapped in the matrix and provide nanometric defects that control the permeation of nanoparticles.

In this work, our goal is to use the fact that these free chains remain trapped in the matrix to functionalize the hydrogels. Hence we replace the free PEG chains with electrostatically charged polymers like polyacrylate (PAA). This allows us to obtain selective membranes able of adsorbing or repulsing solutes. As a proof of concept, we chose to filter a positively charged dye (Methylene Blue) and a zwitterionic one (Rhodamine B). This selectivity can be reversed by protonation of the PAA due to an acidification of the pH. Furthermore, we designed a similar membrane capable of making hydrogen bonds with a small acidic molecule to retain it.

This approach will allow the design of new hydrogels for water treatment or the separation of molecules of pharmaceutical interest.

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New methods and techniques for soft matter 1

Tuesday 23 May 10:30 – 12:30

Sala Polveri

In situ investigation of nanoparticle formation using a batch reactor and in-house SAXS/WAXS

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In the last decades, nanoparticles have been of great interest due to their unique properties, technical applications, and potential use in medical diagnostics. [1,2] For comprehensive industrial use, reproducible size-controlled synthesis is crucial and therefore a better understanding of the formation mechanisms is needed. In most of the current *in situ* methods the synthesis is either performed directly inside a capillary or samples are pumped from a batch into a capillary to produce high-quality data (SAXS, WAXS, Uv/Vis). [3,4] Thanks to these attempts important findings could be revealed, like non-classical nucleation and growth mechanisms. [5]

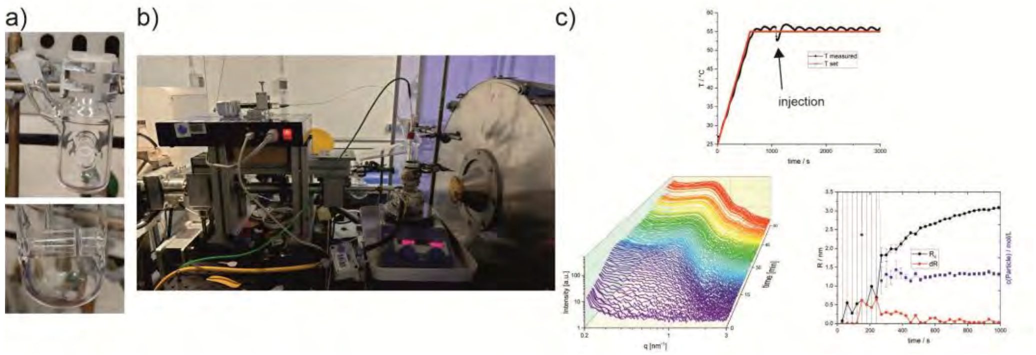

Figure 1: *a) Custom-made batch reactor with glass channels for data acquisition, b) in situ setup with reactor applied at our SAXS, with resistance heating element, temperature sensor, and syringe pump for hot injection, and c)* ***up*** *Temperature development during the reaction,* ***down left*** *Waterfall plots of gained SAXS curves,* ***downright*** *plot of the refinement results for particle size, polydispersity, and particle concentration.*

However, the used capillary setups are not close to real-life synthesis conditions. Additionally, they have their limitations when it comes to high temperatures and hot injection reactions. In our case the reaction is done in a custom-made batch reactor, heated with a resistance heating element (Figure 1). The temperature can be controlled from the outside up to 400°C. Via an automated syringe pump, additional chemicals can be added during the reaction. With our lab X-ray source we are able to measure SAXS and WAXS simultaneously. As examples we will show data for FeO_x nanoparticles from thermal decomposition reactions and for Au nanoparticles from hot injection syntheses. [6]

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Sizing multimodal suspensions with differential dynamic microscopy

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Differential dynamic microscopy (DDM) can be used to extract mean particle size from videos of suspensions. However, many suspensions have multimodal particle size distributions (PSDs), for which this is not a sufficient description. After clarifying how different particle sizes contribute to the signal in DDM, we show that standard DDM analysis can extract the mean sizes of two populations in a bimodal suspension given prior knowledge of the sample's bimodality. Further, the use of the CONTIN algorithm obviates the need for such prior knowledge. Finally, we show that by selectively analysing portions of the DDM images, we can size a trimodal suspension where the large particles would otherwise dominate the signal, again without prior knowledge of the trimodality.

Passive Microrheology of Supramolecular Polymer and Gelatin Hydrogel at High – Pressure

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3 Forschungszentrum Jülich, Institute of Complex Systems (ICS-3), 52425 Jülich, Germany

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We demonstrate passive microrheology in single (Dynamic light scattering, DLS) and multiple scattering limit (Diffusing Wave Spectroscopy, DWS) at High-Pressures. Two different high pressure light scattering cells were used, using N_2 gas (or hydraulic oil) as pressure transmitted medium. The linear viscoelastic properties of i) hydrogen-bonding motif 2,4-bis(2-ethylhexylureido)toluene (EHUT) in apolar solvents and ii) pig-gelatin hydrogels at elevated pressures (up to 120 MPa) are extracted by means of passive microrheology. EHUT self-assembles into supramolecular structures (tubes and filaments) in dodecane and cyclohexane. The analysis of the microrheological data while varying the pressure at different temperatures for a given concentration yields a temperature–pressure diagram that reveals the stabilization of the tube phase at high pressures [1]. Depending on concentration, the application of pressure in the tube regime leads to a transition from viscous (unentangled) to viscoelastic (partially entangled or well-entangled) solution. For well-entangled, long tubes, the extent of the plateau regime (ratio of high- to low-moduli crossover frequencies) increases with pressure. The collective information from these observations is summarized in a temperature–pressure state diagram[2]. The effects of high pressure on gelatin gelation have not been much studied. Using passive microrheology we are able to monitor sol and gel states and their evolution and to detect the sol-gel transition under a broad range of pressure and temperature. We observe that the isothermal gelation process speeds up with increased applied pressure and we evaluate a 0.04 K/MPa shift of the gelation mechanism which is in agreement with the effect of HP on the the helix-coil transition in collagen. We also report time-dependence of sol viscosities and gels elastic modulus at different pressures and temperatures [3].

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Coupling of Microfluidics and Dynamic Light Scattering

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Dynamic light scattering (DLS) is a ubiquitous technique in soft matter due to its accessibility and ease in characterising the size of structures and their diffusion coefficients in solution. Here, we present a DLS setup based on a fibre optic arrangement coupled to microfluidic and capillary devices [1], to enable spatio-temporal examination, over vast parameter spaces, of soft matter structures and their dependence on salt, pH, temperature, etc. Theoretically, this is a challenging endeavour, requiring the decoupling of particle Brownian motion from the flow profile [2], the shear gradient tensor of the flow, and Doppler shifts [3-5]. By careful design and engineering of the setup, we can neglect both shear and Doppler shift contributions to the autocorrelation function and, by utilising experimental data of model particles, we construct regions in the flow velocity-hydrodynamic radius parameter space of 'approaches to data analysis', namely quiescent, transit, deviations, and breakdown, in order of increasing analytical difficulty (Fig. 1).

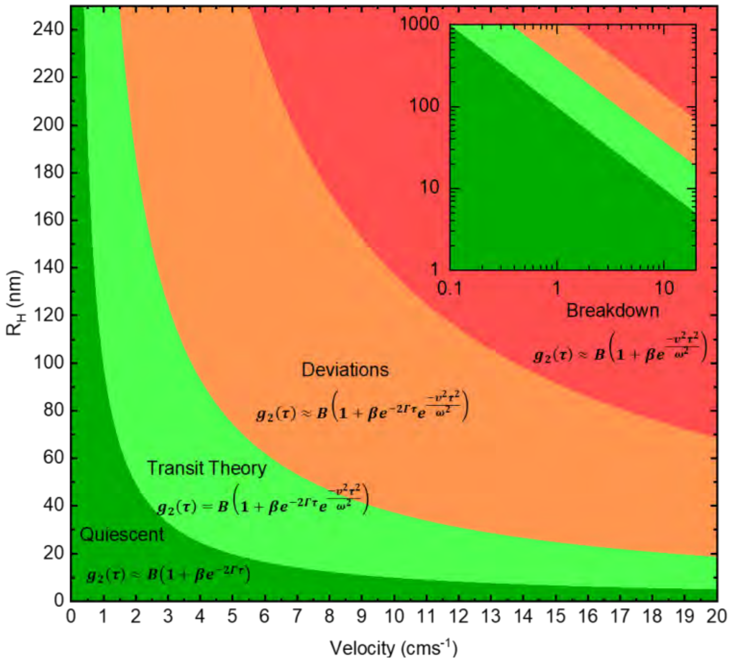

Figure 1: *Regions of data analysis approaches to DLS measurements carried out under flow. For Quiescent, the flow can be assumed to be negligible. Transit theory, where Brownian and transit contributions can be separated [2]. Deviations, where the particle size will decrease with flow velocity. Breakdown, where a DLS measurement will give only the decorrelation due to flow.*

Finally, we show how this setup can be implemented into various other techniques such as microfluidics and microscopy for the mechanistic investigation of model time-varying physical and chemical processes (e.g. reactions, emulsifications, complex-formation, physical changes, etc) to elucidate fundamental laws governing the interaction of various soft matter systems with changes in their environment and interactins with other substances.

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Systematic parametrization of non-Markovian dissipative thermostats for coarse-grained molecular simulations with accurate dynamics

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In Hamiltonian molecular dynamics (MD) simulations, coarse-grained models generally show a speed-up of dynamics. The Mori-Zwanzig theory, in principle, allows to derive an exact equation of motion for chosen coarse-grained degrees of freedom based on the dynamics of an underlying fine-grained reference system.[1] In simple cases, an accurate linear non-Markovian generalized Langevin equation (GLE) can be derived to describe dynamic properties. The simultaneous representation of structural and dynamic properties in particle-based models poses a more complicated problem, e.g. due to the non-linearity of the exact coarse-grained equation of motion. In practice, approximations have to be made to model complex systems. A prominent approach is to start from a conservative coarse-grained force-field and to extend the standard Newtonian equation of motion used in molecular simulation with a dissipative thermostat based on Markovian or non-Markovian variants of a GLE.

In the simplest version, the GLE-thermostat is isotropic and the friction is linear in the particles momenta. I will demonstrate how such thermostats can be parameterized[2, 3] to model colloids (Asakura–Oosawa model) and molecular liquids. I will further discuss the interplay of conservative and dissipative interactions in representing dynamic properties.

References

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Measuring the viscoelastic properties of microscopic soft particles using time-dependent Capillary Micromechanics

Kalpit J. Bakal [1], Hans M. Wyss[1]
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Capillary Micromechanics [1] is a method that enables measurement of the elastic properties of soft, microscopic objects such as biological cells or hydrogels. The method employs a tapered capillary with a tip diameter smaller than the particle size. Consequently, as a suspension of particles is flown through such a capillary, a single particle becomes trapped, blocking further flow. By measuring the change in volume and shape as a function of the applied pressure, both the compressive and shear elastic modulus of the particle can be extracted.

Here we show a semi-automated implementation of Capillary Micromechanics, where, once a particle is trapped in the tapering section of the capillary, the process of pressure regulation and image acquisition is automated. This has improved the repeatability of the measurements and the ease of operation. Moreover, the semi-automation has enabled us to conduct time-dependent stress-controlled tests analogous to a creep test and oscillatory test known from conventional rheometry. For the creep test, we apply an instantaneous increase in pressure, as shown in the insert of figure 1(b). By measuring the resultant time-dependent volumetric strain, as shown in figure 1(b), we can extract the time-dependent response of the particle, which depends on the inherent viscoelastic properties of the particles, but also on poroelastic effects, which are strongly dependent on the particle volume [2]. We validate and test our new approach through experiments on microscopic polyacrylamide (PAAm) hydrogel particles fabricated in-house.

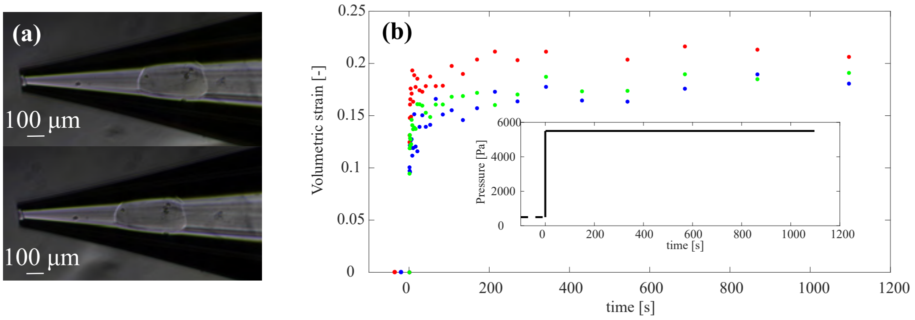

Figure 1: *(a) Microscope images particles in creep test; top: initial state at ($t = 0$), and bottom: final state at $t = 1100$ s. (b) Volumetric strain as a function of time for 3 different PAAm particles (blue symbols: particle in (a)). Insert: Pressure as a function of time.*

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Young Scientists Session 2

Tuesday 23 May 15:00 – 16:20

Auditorium

MXenes-stabilized emulsions: interfacial viscoelastic properties

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Leveraging particles-stabilized emulsions as a template to build stable 3-dimensional structures is an interesting technique to process a wide range of nanomaterials (e.g. ceramic materials, proteins, carbon-based nanoparticles) [1]. The presence of particles at the liquid-liquid interface yields the formation of a strong interfacial network that lowers the interfacial tension and confers elasticity to the interface. In this context, bidimensional particles such as MXenes represent interesting candidates for assembling stable interfacial networks. MXene flakes have hydrophilic electronegative terminal groups that allow the formation of stable colloidal suspensions in water. The hydrophilicity of MXenes can be tuned by dissolving ligands with complementary functionalization in the oil phase to interact with the nanosheets at the interface thereby creating an elastic interface [2], as shown in the figure below.

Currently, little is known about the mechanical properties of MXene nanosheets at the water-oil interface and their relationship with the emulsion stability (e.g. droplet deformation, droplet breakup, coalescence). Therefore, this project focuses on investigating the viscoelastic properties of MXenes at water-oil interfaces. Mxene nanosheets were synthesized by the MILD etching method followed by a delamination step to obtain monolayer flakes [3]. The produced flakes are dispersed in water, while a positively charged organic ligand is added to the oil phase for promoting interfacial assembly. Finally, the interfacial viscoelastic response of MXenes-covered interfaces is investigated under different conditions (nanosheets concentration, type of ligand, oil phase) using the oscillating pendant drop method for dilatational deformation measurements and the double-wall ring method for shear deformation measurements.

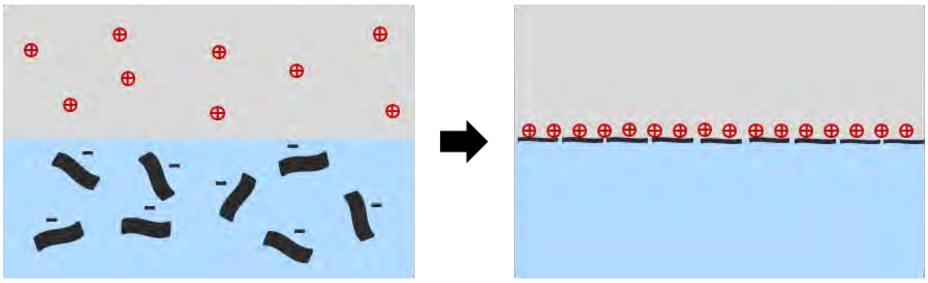

Figure 1: *Schematic of the interfacial assembly mechanism of MXene nanosheets in combination with a cationic surfactant.*

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Cellular Automata Modeling Reveals cell tissues evolution dynamics

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Metastasis, the leading cause of death in cancer patients, is induced by migration of tumor cells. Despite its relevance, the mechanistic basis of this phenomenon remains elusive[1]. Recent years have seen an increase in the use of in silico models to study complex biological processes due to their cost and time efficiency[2]. In this study, we developed a Cellular Automata (CA) model that simulates the dynamic evolution of cell tissues to investigate the migration and invasion of cancer cells. The model characterizes the physical environment as a discrete lattice of elements where each element is in a defined state that changes according to a set of rules depending on cellular activity. The main physiological phenomena considered are cell motility and proliferation, that can be affected by external environment depending on chemical and mechanical stimuli. The model was validated using in vitro data from Wound Healing experiments. An extended numerical experimentation identified the most sensitive physiological parameter governing the wound healing process. To study tumor growth and invasiveness, an hybrid model was developed, coupling CA lattice with continuous partial differential equations (PDEs) able to simulate external stimuli. In particular chemical stimuli (chemotaxis) was accounted modeling nutrient gradients from blood vessels. Mechanical stimuli (mechano-transduction) was accounted modeling the influence of shear stress on cell aggregates. The hybrid model was used to investigate the effects of glucose concentration on tumor growth and invasiveness. Global and local sensitivity analyses revealed that cell duplication speed and adhesion force between cells were the most significant contributors to tumor growth, while chemotaxis was the primary driver of tumor invasiveness. Overall, in silico models present a powerful tool to study the dynamic evolution of multicellular systems, including tissue engineering and cancer invasion. The results of this study can provide insights into the mechanisms behind tumor growth and invasion and aid in the development of new pharmacological strategies.

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Chain-length-dependent relaxation dynamics in poly(methyl acrylate)

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Glassy polymers are important materials for construction, coatings, optical components and functional membranes. However, glass formation in polymers is still poorly understood due to the complexity introduced by chain connectivity and chain flexibility.[1] Here, we address this by investigating the chain-length-dependent glass transition and associated relaxation dynamics in a model polymer – poly(methyl acrylate) (PMA).

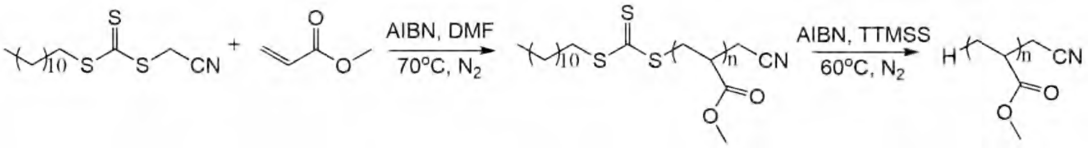

Figure 1: *Scheme of PMA RAFT polymerization and alkyl trithiocarbonate end-group removal.*

We synthesize PMAs using reversible addition-fragmentation chain-transfer (RAFT) polymerization [2] and determine the chain-length-dependent relaxation dynamics both with and without the chain transfer agent alkyl (dodecyl) end-group. We present a wide range of experimental data from broadband dielectric spectroscopy and calorimetry. We observe the presence of three molecular relaxations: the structural α-relaxation and two secondary (β and γ) relaxations; the β-relaxation in PMA is very weak and has often been overlooked in earlier studies. For long-chain PMA in the glass, the two secondary relaxations show activation enthalpies of $\sim$100 and 34 kJ/mol, respectively. We characterise the detailed molecular weight dependence of the three observed relaxations, and the glass transition temperature, T_g, both with and without the additional alkyl end-tail. We also demonstrate that PMA shows decoupling between ion conductivity and the α-relaxation, even though the decoupling is less dramatic than that observed for other highly fragile polymers such as poly(methyl methacrylate) and polycarbonate.[3]

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Follow Up of UHMWPE Rheological Properties Under Ultra-Fast Magnetic Hyperthermia Sintering

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Ultra-High Molecular Weight Polyethylene (UHMWPE) has been increasingly used in research and industry over the last decade, particularly for bio-engineering, coating and sport-oriented applications. Its extremely high molar mass (M>1 Mg mol-1) confers it remarkable impact strength, wear resistance and a rather good chemical resistance [1]. On the other hand, its high viscosity in the molten state prevents the utilization of classic polymer processing methods (extrusion, injection …), obliging manufacturers to use sintering-oriented techniques, i.e. interfaces welding through re-entanglement and co-crystallization [2]. Toward this idea, magneto-responsive UHMWPE-iron nanocomposites have been prepared following two sintering methods. One method involves the simultaneous application of pressure and temperature rise ($T>T_m$) on a blend of ca. 3%vol of Fe nanoparticles (Fe-n) with a highly crystalline micrometre sized UHMWPE powder. The other process uses a powder densification step via the application of a pressure below the melting point, followed by a temperature rise through magnetic hysteresis under a high frequency magnetic field (855 kHz, 5 mT). Using an innovative rheological set-up, coupling a PEEK plate-plate geometry with an induction heating system and an IR camera, we followed-up the nanocomposites thermomechanical behaviour during their sintering. The Fe-n act as a filler, a magnetic stimulus receptor and as a polymer state probe (see Figure 1).

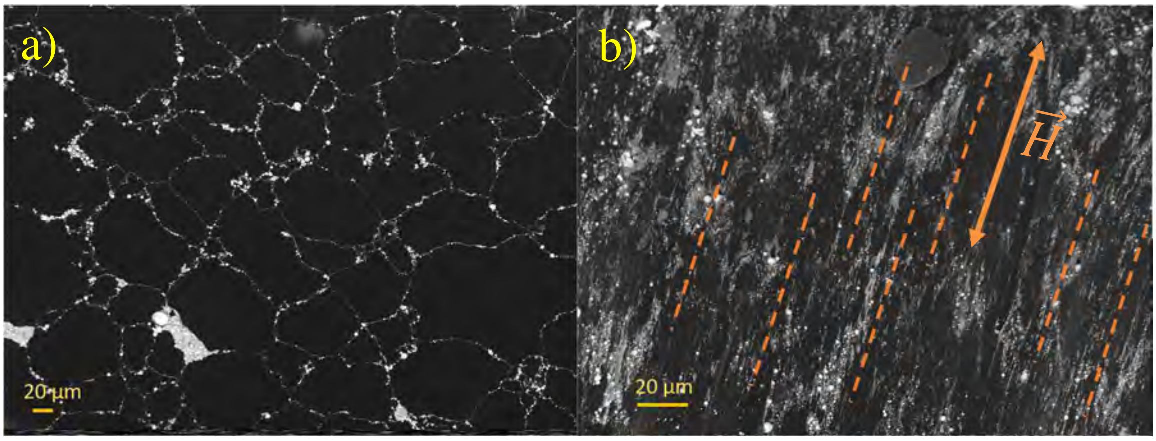

Figure 1: *SEM micrographs of a) conductive heating and b) induction heating sintered nanocomposites*.

The main interest of using in situ rheology magnetic hyperthermia sintering resides in the possibility to track rapid conformation changes of the UHMWPE molecules, likely to clarify the mechanism of "melting explosion" predicted by de Gennes in 1995, allowing the diffusion and re-entanglement of the UHMWPE chains in about 10 minutes instead of the ca. 2h needed according to classical reptation mechanisms. Coupled with mechanical tests performed near and above the melting point, microstructure analysis (SEM, tomography), comparing the two shaping methods, but also adding modelling data (molecular dynamics), these observations can allow us to establish the microstructure-properties links as well as provide explanations of the fundamental mechanisms behind sintering.

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Active and living soft matter 1

Tuesday 23 May 15:00 – 16:20

Sala Polveri

Understanding Enhanced Rotational Dynamics of Active Probes in Rod Suspensions

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Synthetic active particles (APs) have received considerable interest for biomedical applications and as model systems for non-equilibrium dynamics. However, because an AP's motion strongly depends on the properties of the surrounding liquid, it can additionally serve as a microrheological probe for the properties of the surrounding medium [1,2]. APs in Newtonian media have been studied in great detail, but much less is known when these particles move in complex fluids. Such a fluid's nonlinear rheological properties can lead to a drastically enhanced rotational diffusion (ERD) coefficient [1-3].

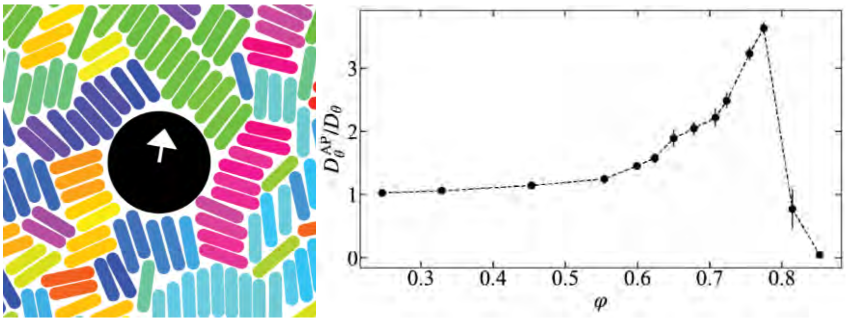

Figure 1: *(left) Snapshot of an active probe in our simulation study; colors indicate rod orientation. (right) The associated ERD as a function of rod area fraction.*

In this presentation, we study the motion of an AP in a polydisperse quasi-2D suspension of colloidal rods, see Fig. 1 for a simulation snapshot. Compared to previous studies [1,2], wherein we embedded APs in a spherical colloid suspension, the use of rods allows us to unlock a new mode of fast, local structural dynamics. This dynamics enabled a comprehensive understanding of the mechanism underlying ERD. Combining simulations and experiment, we conclude that minute microstructural fluctuations of rods in near contact with the AP, together with the probe's active motion, generate a fluctuating torque on the AP eventually leading to ERD [4]. These fluctuations can be connected to a local stress relaxation, which may be used in the continuum formalism that was proposed [1,3,5] to capture ERD. Our work thus unifies the previously disjoint continuum and particle-based descriptions for this phenomenon. Beyond the rheological characterization abilities of APs, our findings are important to understand the dynamics of microorganisms in their natural (typically viscoelastic) habitat.

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Active vesicles: from complex dynamic shapes to motility

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Biological cells are fascinating micromachines capable of moving and performing various tasks. Simple engineered cell-mimicking systems help us not only in learning about their natural counterparts, but also in designing soft-matter microrobots capable of performing cell-like and beyond-nature activities. One interesting model is an active vesicle which combines a soft membrane with enclosed self-propelled particles (SPPs) [1,2]. Due to the forces exerted by SPPs on the membrane, this system exhibits a variety of different non-equilibrium shapes with tether-like protrusions and highly branched, dendritic structures (see Figure 1). However, this system does not seem to exhibit a directed motility. An alteration to the system design through the attachment of active particles to the membrane from outside leads to the generation of directed motion. We will discuss the behaviour of active vesicles and physical mechanisms involved. Furthermore, possible strategies for their motility control will be suggested.

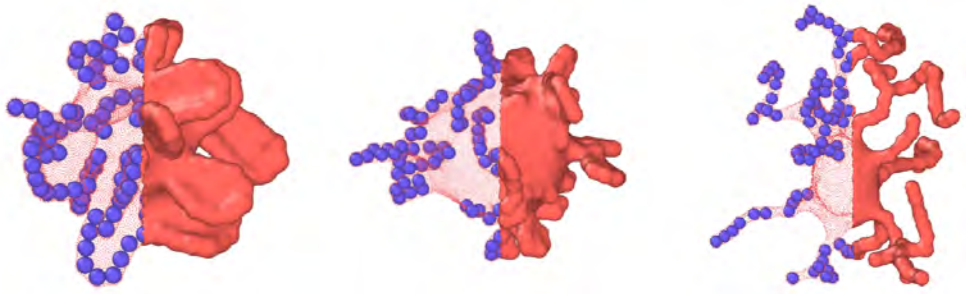

Figure 1: *Shapes of active vesicles filled with adhesive self-propelled particles for the volume fraction of* $\varphi = 0.04$*. From left to right, the activity strength of particles is increased. Particle structures change from membrane-wrapped ring-like arrangements (left) to membrane-wrapped (branched) tubular aggregates (left), as the propulsion is increased. The left half of the membrane is made transparent in all snapshots, so that the arrangement of active particles is visible.*

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Self-steering and responsive active particles

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Group formation and collective motion in form of swarms or flocks is hallmark of living systems across different length scale. The behaviour often emerges without central control and is govern by the response of individual to the action of other group members. Important features of such systems are active non-equilibrium behavior, non-reciprocal interactions, information processing, and self-steering [1, 2]. In our model of intelligent active Brownian particles (iABPs), the particles can react to information about the position and orientation of neighboring particles, obtained through directed visual and isotropic perception, respectively, by adjusting its propulsion direction. The strength of polar alignment and maneuverability of visual signal determines the dynamics and structure of the system. Several non-equilibrium structures like worms, millings, closed packed and dispersed cluster are obtain at different parameter set [3]. Here closed packed cluster are usually immobile, while worms and millings are mobile with high velocity correlation.

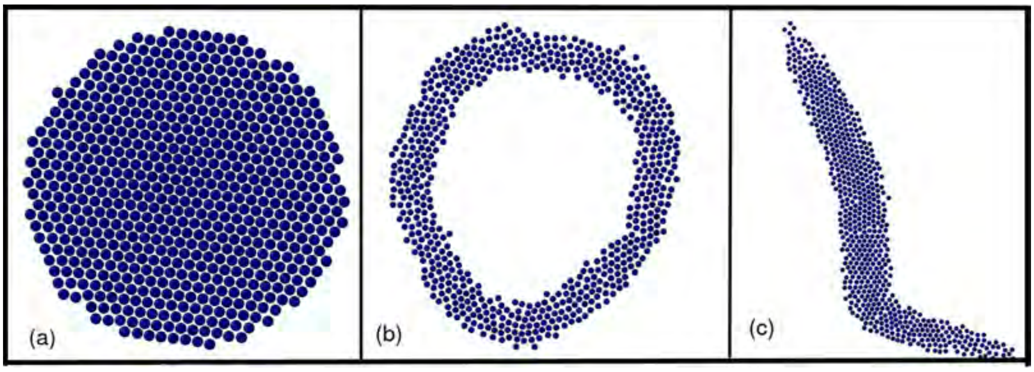

Figure 1: *Snapshots of different phases (a) closed-packed, (b) milling, and(c) elongated worm.*

The strength of polar alignment and maneuverability of visual signal determines the dynamics and structure of the system. As the strength of polar alignment increased compared to visual maneuverability, elongated worms-like structures dominates over closed packed structures. Our results help to understand the collective behavior of cognitive self-propelled particles, like animal herds and micro-robotic swarms.

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Self-propelled particles in an alignment field

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Self-propelled particles display an intriguing collective behavior, with many potential applications in biomedicine, robotics, and material science. Here, we study numerically self-propelled particles that mutually repel each other. The particles also possess dipole moments aligned with the directions of their self-propulsion [1]. In such a system, motility-induced phase separation causes the emergence of gas-liquid phase coexistence [2]. We investigate the phase behavior and the dynamics of this system in a homogeneous alignment field. We show that an increased strength of the alignment field shifts the onset of the two-phase coexistence to higher Péclet numbers and higher packing fractions of the particles. Thus, with increasing field strength, the two-phase region in the phase diagram shrinks. Furthermore, we examine the system's dynamics after quenching from a one-phase state to a two-phase state [3]. At finite field strength, the interfaces between the gas and liquid phase align with the alignment field, see Fig. 1. Our analysis uncovers a significant impact of an alignment field on the system's dynamics and phase behavior.

(a)

(b)

t = 0 t = 5.5 t = 500

Figure 1: Phase separation after quenching a system of self-propelled particles into the two-phase region. Snapshots of the system at various times after the quenche, for the alignment field strengths (a) $\tilde{B} = 0$ at the critical packing fraction $\phi = 0.60$ at $\mathrm{Pe} = 138$ and (b) $\tilde{B} = 2$ at $\phi = 0.63$ at $\mathrm{Pe} = 221$. The time t is given in MD time and the system size is $512\sigma \times 512\sigma$.

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Young Scientists Session 3

Tuesday 23 May 16:50 – 17:40

Auditorium

Transforming sustainable plant proteins into lubricants by microgelation

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Due to the increasing strain on planetary resources, increased low carbon plant-based foods are crucial for sustainable food development. Over a third of human-generated greenhouse gas emissions come from food, with animal-based foods accounting for almost twice as much (57%) as plant-based foods (29%). Therefore, shifting towards plant-based proteins is considered a key strategy for achieving the UN's sustainability goals in the food sector.

However, plant proteins face functional and in particular sensory challenges. Even in success, products are often masked by adding unhealthy amounts of salt, sugar or fat which is not a viable solution. Firstly, this study characterised the tribology, rheology and adsorption (Quartz crystal microbalance dissipation) behaviour of a number of sustainable future proteins (Pea, potato, insect and lupin protein powders) at low and high concentration (5-15 wt% protein). It was found plants suffer from high friction coefficients, particularly at high concentration.

Secondly, to alleviate frictional issues new microgelled plant proteins were created by thermally crosslinking the proteins at 80 °C for 30 minutes to form gels, followed by shearing and homogenisation. These particles were characterised using atomic force microscopy (AFM) and dynamic light scattering (DLS) with tribology performance compared to that of native and 20 wt% oil-in-water emulsion using new 3D printed biomimetic tongue. Strikingly the microgels were an order of magnitude lower in friction compared to native protein of same protein concentration, with similar friction coefficient values to that of the oil-in-water emulsion when introduced between 3D biomimetic tongue-like surfaces owing to their adsorption properties and effective viscosities. Additionally, these particles were highly soluble, proving that sustainable protein microgels can facilitate the incorporation of alternative proteins, as well as functional fat mimetics, without causing any negative mouthfeel effects.

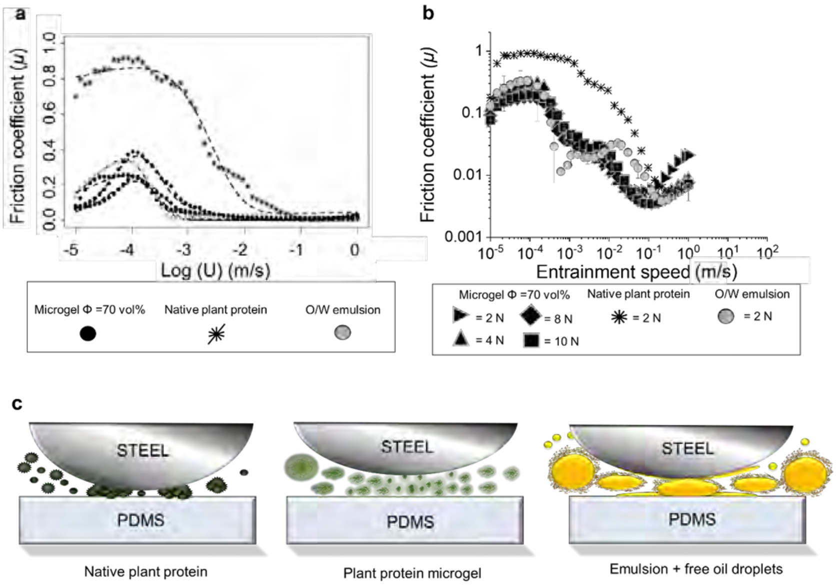

Figure 1: *Mechanism of the effective lubrication of plant based microgel particles. A)theoretical modelling of lubrication b) load dependancey of microgels vs native and 20:80 O/W emulsion c) Schematic illustration of microgel performance*

Towards mechanistic understanding of biofilms: understanding the transport phenomena, kinetics and rheology of biofilm formation, functioning and morphology.

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Biofilms are bacterial communities of cells enclosed in a self-produced matrix of extracellular polymeric substances. In many applications, biofilms are undesired, causing issues in wound healing [1], food production [2], medical treatments [3] and industrial fouling [4]. However, biofilms are of growing interest as a positive instrument in biotechnical applications [5] including bioremediation, biofertilization and energy production. From an engineering perspective, it is intriguing to see how the bacterial colonies are capable of shaping their surroundings to provide protection from external influences (mechanical and chemical stress). At the same time, and despite these protective properties, the biofilm needs to be structured such that bacteria can move during its formation and nutrients can reach the bacteria.

In this paper we demonstrate how to gain a mechanistic understanding of the internal functioning and morphology of biofilms. We demonstrate how to examine the hierarchical porous structure of the biofilm using confocal microscopy in combination with a variety of dyes selective for different components of the biofilm matrix. Using this palette of dyes, information is obtained about the relative amounts of the components of the biofilm matrix. Additionally, image processing algorithms are used to quantify the hierarchical porous structure of the biofilm by calculating values such as the porosity, tortuosity and lacunarity, and to monitor the volume of biofilm over time (growth kinetics). To determine the rheological properties of biofilms and how these evolve over time, active particle microrheology is used to identify local heterogeneities. From this mechano-spectroscopical response of the different hierarchical structures identified with confocal imaging, the mesh sizes of the polymer matrices are determined. Finally, combining the above obtained insights with fluorescence recovery after photobleaching [6] measurements enables an understanding of the diffusion kinetics inside the different identified regions of the biofilm.

Combined with simulations and experiments with genetic mutants, this allows to obtain information about the different transport processes (diffusion, advection) occurring inside the biofilm, their relative importance, and the effect of bacterial motility on these transport processes.

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Active and living soft matter 2

Tuesday 23 May 16:50 – 17:10

Sala Polveri

Targeted delivery of thrombolytic proteins using multifunctional nanovesicles derived from red blood cell membranes

N. Henry, Y. Huang, I. Salles-Crawley, M. Emerson, C. Longstaff, R. Chen
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Designing drug delivery systems that reach their target is crucial for their success. By utilizing naturally derived materials instead of synthetic, there is a higher probability that the particles will be able to reach their target. The nanoparticles can reach a higher level of complexity using a top-down approach, unattainable using a bottom up approach. Making a drug delivery platform using isolated red blood cell membranes as a starting material, increases the likelihood it will inherit properties of the original source, such as, long circulation time, biocompatibility and biodegradability. Most synthetic systems taking inspiration from nature, however, this work directly leverages the enhanced evolution that cells in the body have gone through to achieve a highly engineered system.

Cardiovascular diseases are the leading cause of death worldwide (Ritchie et al., 2018). Currently, there is only one Food and Drug Administration approved treatment for acute ischemic stroke; tissue plasminogen activator (tPA) (Marshall, 2015). tPA has been a significant advance in the treatment of clots. Unfortunately, tPA has several limitations that reduce the potential of this therapeutic: short half-life and unwanted bleeding due to a lack of specificity (Marshall, 2015). To increase the therapeutic index of tPA, clots can be specifically targeted through activated platelets. During activation, platelets change their conformation and several integrins are activated. The most abundant upregulated integrin is αIIbβ3 (Posch et al., 2013). Studies have shown that the peptide cyclic arginine glycine aspartic acid (cRGD) can bind to αIIbβ3, on the surface of activated platelets (Srinivasan et al., 2010). The structure of cRGD and the wide and flexible binding site of αIIbβ3 integrins leads to a higher binding affinity between the two (Pfaff et al., 1994). Therefore, when designing a thrombolytic system, incorporating cRGD could produce a clot targeting system. Clot specific thrombolytic nanoparticles can be produced by loading tPA into red blood cell derived vesicles (RBCVs) and functionalizing cRGD on the surface. Specific binding to activated platelets was observed using confocal microscopy and flow cytometry for cRGD-RBCVs. tPA loaded RBCVs with and without cRGD present showed fibrinolysis and thrombolysis in static models. Preliminary results also showed comparable thrombolysis for free tPA and RBCVs with and without cRGD under physiological flow conditions. The presence of cRGD showed an enhanced targeting of thrombi. These results suggest that a clot specific naturally derived nanoparticle could be produced and selectively delivery tPA to blood clots.

Biophysics and biomechanics 1

Wednesday 24 May 10:30 – 12:30

Auditorium

Characterisation of the destabilisation of saliva filaments during phonation by a model experiment

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Recent research on the transmission of SARS-Cov-2 has highlighted the crucial role played by aerosols. However, the behaviour (transport, infectivity) of the virus once inhaled by a potential host is not yet known. We are interested here in the production of droplets during phonation[1,2] using a model experiment in which we study the destabilisation of a saliva filament with and without wind. The filaments are created by a violent elongation of a few milliseconds to simulate the opening of the lips during speech. The airflow (wind created) mimics the airflow exhaled by phonation. The same experiments are performed for comparison on Newtonian solutions (glycerol + water) and aqueous solutions of Poly-oxyethylene, with viscosities comparable to those of saliva. Using a high-speed camera and image analysis techniques, the destabilisation of these three types of filaments with and without air flow is studied quantitatively. A simplified analytical model to explain the shape of a saliva filament subjected to an air flow is presented.

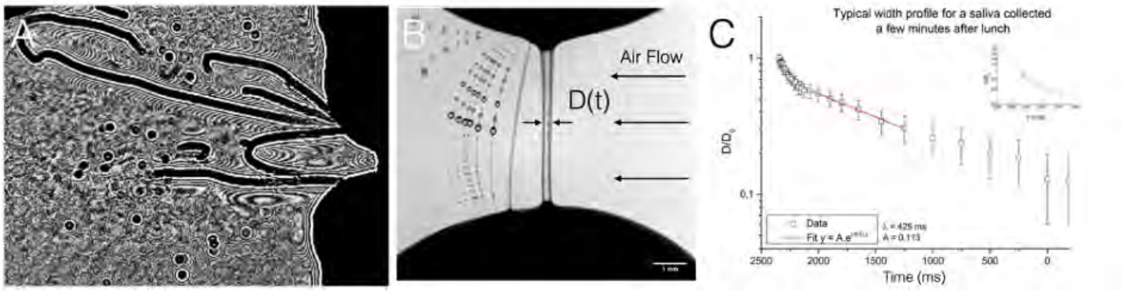

Figure 1: *A) Hologram of filaments production and deformation, with atomization producing droplets at the lips. The fringes bear the information of the 3D scene: both position and size of the filament and drops. (B) Saliva filament (stretched in less than 2 ms) thinning over a fraction of a second under a constant air flow 0.9 m/s. (C) Thinning dynamics is initially exponential and its fit gives the relaxation time of saliva which depends strongly on the moment of the day, e.g. before or after lunch..*

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Inducing irreversible strain hardening and alignment during collagen gelation

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Collagen is one of the main building blocks of the mammalian extracellular matrix, due to its ability to form tough structures with a wide variety of non-linear mechanical properties allowing it to support multiple tissue types. The mechanical properties of collagen gels have been extensively studied under static conditions, however, in nature gelation will mostly take place in the presence of flow. Here we show how the modulus and the alignment of the fibrillar collagen hydrogel can be tuned by applying a stress-ramp at a well-defined moment during gelation, following up on our earlier study [1]. Where the first stress block induces most of the final strain, sequential, increases in stress cause the modulus to rapidly increase. This effect is more pronounced when gelation takes place at 37 °C, where due to relatively rapid kinetics a dense network of thin filaments is formed, than at 27 °C, where slower kinetics result in the formation of an open network with thick bundles. Contrary to the modulus, the increase in alignment is more pronounced for the samples formed at lower temperatures. Thus, we not only produce tough gels with alignment, but also provide insight into in vivo collagen structure formation.

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Protein phase behavior in electric fields

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The structural and dynamical properties of protein solutions are governed by intermolecular and hydrodynamic interactions. If the interactions are sufficiently attractive, proteins are prone to crystallize [1], phase separate [2] or aggregate [3]. These condensation processes are relevant in diverse fields ranging from structural and cell biology to pharmaceutical industry and food processing. If, in addition, an external electric field is applied, the conformation, structure, dynamics, and stability of proteins can be altered through a combination of electrophoresis and electrostatic interactions [3,4]. Subsequently, this can affect the protein function and lead to potential applications, e.g., in protein crystallography and protein separation [3,4]. For example, lysozyme with antagonistic salt interactions was recently found to exhibits localized motions under a low AC electric field [5].

In the present work, we systematically study the effects of electric fields on the collective behavior of proteins. Lysozyme in the presence of sodium thiocyanate is used as a model system. Solutions with various protein and salt concentrations are exposed to low-strength AC electric fields. The collective behavior of the protein solutions and their response to the electric field are followed in-situ by time-resolved polarized optical microscopy. The information derived from the microscopy images helps to understand to which extent protein phase behavior can be modulated by electric fields. Our preliminary results suggest that electric fields can significantly alter the structure and dynamics of the protein solutions and also affects phase transition kinetics. The effect depends on the frequency and strength of the field as well as on the protein and salt concentrations.

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A DNA Origami Fiducial for Accurate Multidimensional Atomic Force Microscopy Imaging

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Atomic force microscopy (AFM) is a powerful tool for imaging biomolecules, macromolecular complexes, and nanoparticles with nanometer resolution. However, AFM images are distorted by the shape of the tip used. These distortions can be corrected if the tip shape can be determined by scanning a sample with features sharper than the tip and higher than the object of interest. Here, we present a 3D DNA origami structure as a fiducial for AFM tip reconstruction and image correction. Our fiducial is stable under a wide range of conditions and features sharp steps at different heights, allowing reliable tip reconstruction using only ten fiducials. Since the fiducial structure is made of DNA origami, it is easily co-deposited with biological and non-biological samples. Additionally, it achieves higher accuracy for the apex of the tip than polycrystalline samples, and significantly improves the accuracy of the lateral dimensions determined from the images of DNA origami, protein-DNA complexes, and silica nanoparticles [1]. We anticipate that this approach will be applicable to various areas of study within and beyond bionanotechnology, paving the way for multidimensional AFM tip reconstruction and image correction. For example, we are currently using our fiducial structure to study the stiffness of multilayer DNA origami with the ultimate goal of establishing a stiffness standard for biomolecules, their complexes, and various other types of nanostructures.

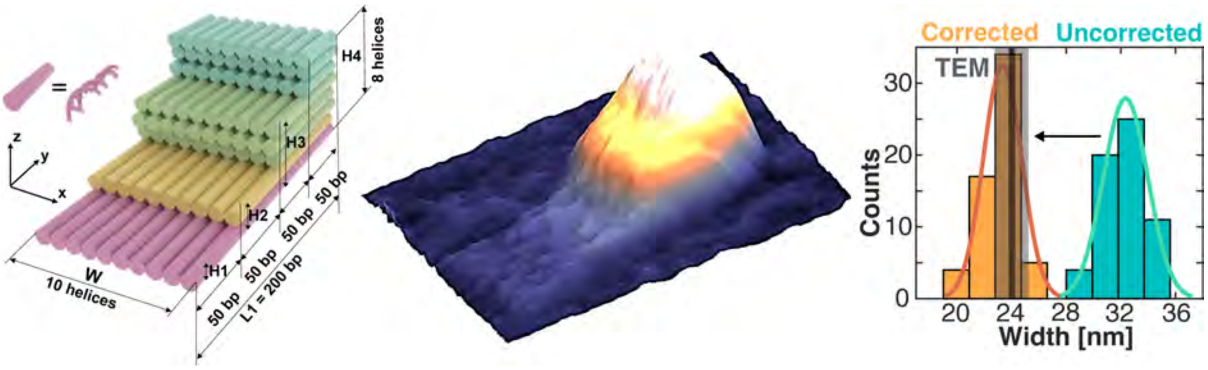

Figure 1: *Design of the DNA origami fiducial structure, 3D-AFM visualization, and finite tip size correction using the fiducial.*

Reference

[1] Pauline J. Kolbeck, Mihir Dass, Irina V. Martynenko, Relinde J. A. van Dijk-Moes, Kelly J. H. Brouwer, Alfons van Blaaderen, Willem Vanderlinden, Tim Liedl, and Jan Lipfert, *Nano Letters,* **2023** 23 (4), 1236-1243, DOI: 10.1021/acs.nanolett.2c04299

Modelling Biomolecular Interactions of Protein Solutions

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Nowadays, therapeutic proteins such as monoclonal antibodies (mAbs) represent an important tool for the treatment of numerous diseases such as cancer, autoimmune disorders, and viral infections. An example is the anti-SARS-CoV-2 mAbs recently authorized by the Food and Drug Administration (FDA) to be used for the treatment of COVID-19 symptoms, but more than one hundred of mAbs have been already approved in the last 35 years and many more are under investigation. However, developing therapeutic mAbs is not an easy task. Phenomena like protein aggregation and self-assembly, high viscosity, and opalescence, can give rise to problems when trying to achieve stable and low-viscosity formulations and cause immune responses in patients treated with them. Studying the best formulation conditions either with lab experiments and/or computer simulations is then of crucial importance. The investigation of protein solutions with computer simulations often requires strategies and models able to reduce their complexity while maintaining their peculiarity. Developing computational models that are easy to handle becomes essential if one wishes to perform mAb studies in the high-concentration regime. This is due to the enormous number of interactions that need to be accounted for while dealing with such big molecules. Our work focuses on developing new strategies that can be used to predict the effective structure factor of a mAb solution with a lower computational effort. Based on the information obtained from all-atom and amino-acid level simulations, we have developed more coarse-grained bead models (Fig. 1) which have the advantage of reproducing the properties of interest while being computationally much easier to handle. Further, as they allow for many-body simulations with much more molecules at the same time, they can be used to explore conditions not accessible with a less coarse-grained model and perform effective comparisons with experimental data in order to test our current models for protein-protein interactions and their role in phase behavior and self-assembly.

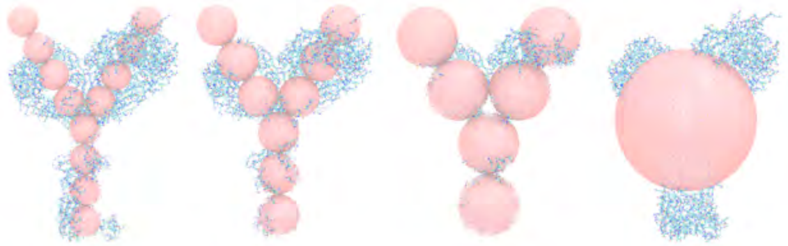

Figure 1: *Beads models in comparison with an all-atom mAb representation.*

Planar Confined Water Organisation in Lipid Bilayer Stacks of Phosphatidylcholine and Phosphatidylethanolamine

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Phospholipid-based liposomes are abundantly studied in biomembrane research and used in numerous medical and biotechnological applications. Despite our great knowledge on membrane nanostructure and its mechanical properties under various environmental conditions, there is still a lack of understanding on interfacial lipid-water interactions. In this work, we have investigated the nature of the confined water layer for L-α-phosphatidylcholine (egg-PC), 1,2-dioleoyl-*sn*-glycero-3-phosphocholine (DOPC), 1,2-dimyristoyl-*sn*-glycerol-3-phosphatidyl-choline (DMPC) and 1,2-dimyristoyl-*sn*-glycero-3-phospho-ethanolamine (DMPE) in the fluid lamellar phase of multilamellar vesicles. We are proposing a new model for describing three different water regions, which have been characterised, using a combination of small angle X-ray scattering (SAXS) and densitometry. The three regions concern (i) 'the headgroup water', (ii) 'perturbed water' near the membrane interface and (iii) a core layer of 'free water' (unperturbed water). The behaviour of all three layers is discussed as a function of temperature, concerning influences of chain saturation and headgroup type. While the overall water layer and perturbed water layer thickness increase with temperature, the free water layer displays the opposite trend for PCs, and in PEs is completely absent. Furthermore, an estimate of the temperature dependent headgroup orientation is given for both, PCs and PEs. The newly presented structural data deduced from the three-water region model will be useful for future refined molecular dynamics simulations and allow a better theoretical understanding of the attractive van der Waals force between adjacent membranes.

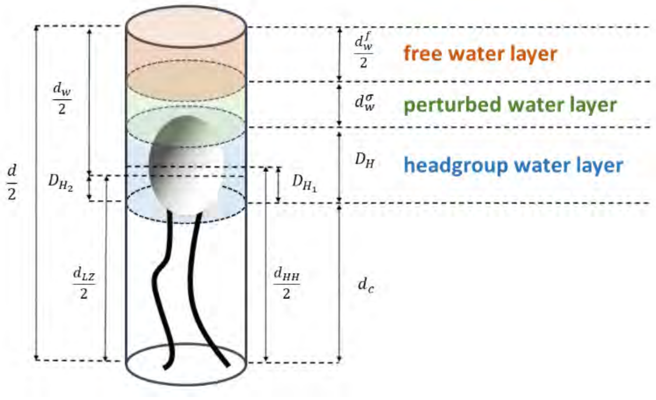

Figure 1: The three-water region model. A simplified lipid model is depicted in grey together with the distinct water layers associated with (i) headgroup, (ii) perturbed and (iii) free waters

Particulate materials, gels and pastes

Wednesday 24 May 10:30 – 12:30

Sala Polveri

Flow-Switched Bistability in a Colloidal Gel with Non-Brownian Grains

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We show that mixing a colloidal gel with larger, non-Brownian grains generates novel flow-switched bistability. Using a combination of confocal microscopy and rheology, we find that prolonged moderate shear results in liquefaction by collapsing the gel into disjoint globules, whereas fast shear gives rise to a yield-stress gel with granular inclusions upon flow cessation. This bistability requires the granular inclusions, as un-filled colloidal gels may coarsen under shear but do not completely phase separation. We find this same phenomena in a variety of model systems with differing particle and fluid compositions, suggesting this behavior is generic, and map out the state behavior varying an array of suspension properties.

Our findings present a new entry to toolkit of smart, field-responsive materials by offering a ‘mechanorheological material’ that can be reversibly switched between stable solid and liquid states by stress and accumulated strain. The shear-driven phase separation that underlies this bistability could also wreak havoc in industrial processes if not anticipated (eg. degrading conductivity in a cathode paste). Understanding this phenomena is therefor crucial for both enabling novel applications and preventing processing mishaps.

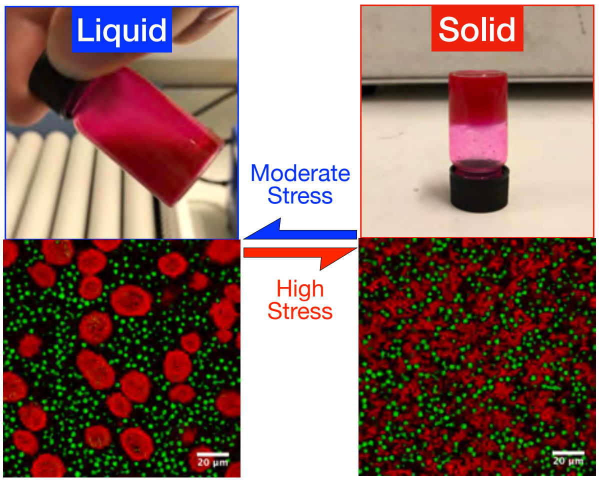

Figure 1: *Shear-switched bistability between solid and liquid states in a colloidal gel (small attractive spheres, red) with granular inclusions (large repulsive spheres, green) (adapted from [1])* .

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Binary mixture of hard and soft colloids with tuneable interactions

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Industrial and academic researchers have granted a lot of attention to mixture of hard and soft colloids[1] by means of the impact of their softness on rheological properties and phase diagrams. In this work, we broaden these knowledges by studying the implication of an innovative binary mixture where attractive interactions are modulated, not by depletion effect, but by the use of a patchy co-monomer.

To do so, we derived a well-known nanocomposites system[2,3] of polyacrylamide matrix containing silica particles to a colloidal scale of hard and soft colloids. Our system consists of an aqueous solution where the soft colloids are synthesized polyacrylamide microgels and the hard ones are silica nanoparticles.

Our goals are to study the impact of attractive interactions, brought in the microgel by the use of a patchy co-monomer, onto the flow properties, the structure and the phase diagram of the mixture. In the presentation, we will firstly introduce how we tuned the softness and size of our polyacrylamide microgels depending on the synthesis process. Then, we will show the implication the attractive interaction on the colloidal glass transition, the phase diagram and the structure of the binary mixture.

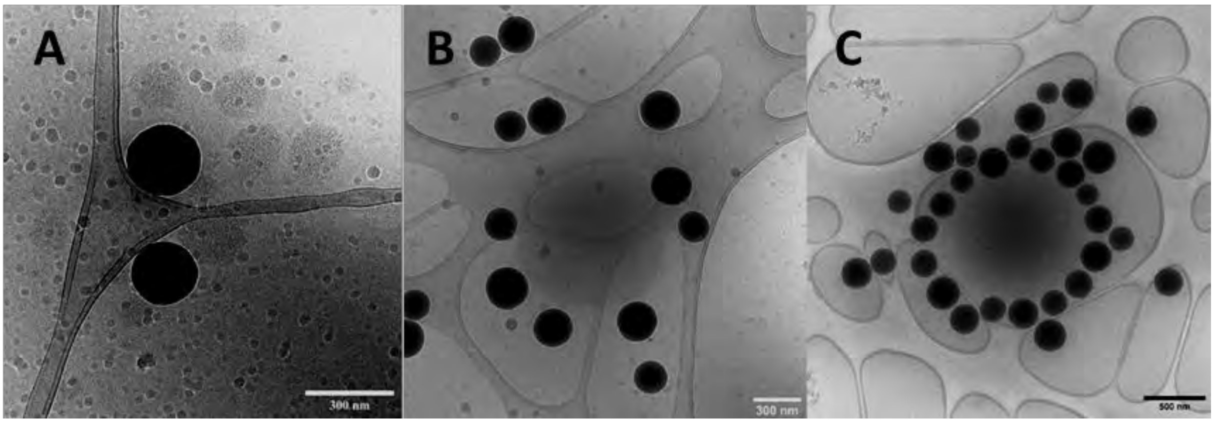

Figure 1: *Cryo-TEM micrographs of binary suspension of silica particles and microgels with 0, 5 and 10 % of sticky monomer, from A to C, in dilute conditions.*

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Drying Drops of Colloidal Suspensions

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The slow evaporation of drops of colloidal suspensions plays a key role in numerous contexts, such as, virus survival in aerosols, production of powdered milk and preparation of functional supraparticles for applications like catalysis, photonics, or sensing[1]. Depending on the evaporation speed, quantified by a Peclet number Pe, the NPs may remain homogeneously distributed or accumulate at the periphery of the drop, forming a dense shell, may undergo a double shape instability.

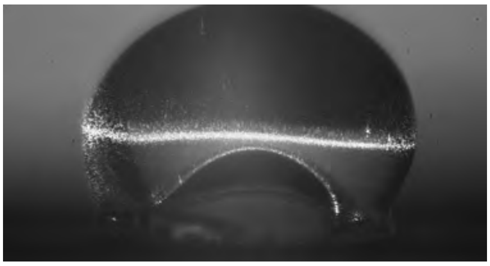

Figure 1: *Image of a drop of nanoparticle suspension undergoing a shape instability. The drop diameter is 4 mm. A laser beam propagating along a drop diameter forms a characteristic speckle image, whose time evolution allows for measuring the suspension dynamics*

Previous works, done only on fast evaporating drops ($Pe \geq 1000$), proposed that the buckling is caused by particles aggregation, with the particles permanently aggregated forming a rigid porous solid[2].To date, however, no experiments could directly test this scenario applies for drops drying at low evaporation rate ($Pe \leq 100$). To answer this question, we have developed a custom multispeckle light scattering setup to measure, with spatial and temporal resolution, the microscopic dynamics of colloids confined in a drop. Interestingly, we find that, the colloids in the drop undergo two consecutive state transitions, each of them associated to a macroscopic shape instability. The first instability is characterized by an invagination of the drop, which is induced by the colloids forming a dense shell, that undergoes a dynamic glass transition dye to their high microscopic relaxation time. Subsequently, the NPs irreversibly aggregate, leading an abrupt macroscopic fracture of the drop. This phenomenon is depicted by a state diagram that shows a unified picture for data gathered at different evaporation rates, relating the microscopic dynamics of colloids confined in the drop and the macroscopic shape instability of the drying drops.

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Hydrodynamic Lubrication in Colloidal Gels

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Colloidal gels are self-assembled networks of solid particles suspended in a liquid medium. They are widely used in everyday products and technologies, but their out-of-equilibrium nature makes it difficult to predict and control their structure. Hydrodynamic interactions — which are dissipative forces mediated by the liquid solvent — may affect the structure of non-equilibrium systems, leading to debates on their role in the formation and aging of colloidal gels.

The current understanding is that the structural evolution of a gel is slowed down or sped up (depending on the volume fraction) by far-field hydrodynamic interactions. However, the emergent and aging gel network is the same when compared at equal 'structural time' [1]. The impact of near-field lubrication interactions remains poorly understood. As the interactions that lead to gelation are typically short ranged, they could compete with short-ranged forces driving formation.

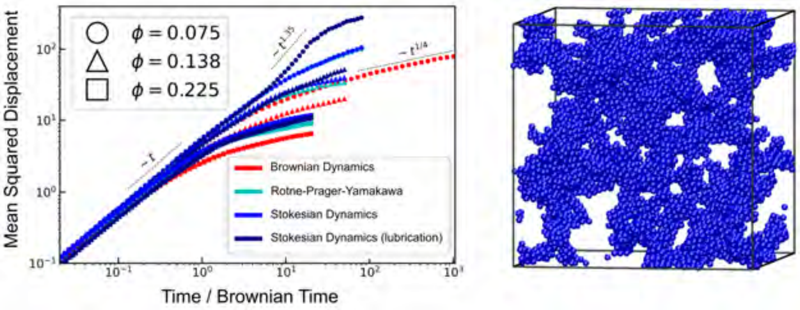

Figure 1: *(left) Mean Squared Displacement averaged over all colloids in the simulation box, for different volume fractions and hydrodynamic models used. (right) Snapshot of a gel configuration.*

Here, we investigate how various approximations to modeling hydrodynamic interactions impact colloidal gels. We considered single-body (Brownian Dynamics), pairwise (Rotne-Prager-Yamakawa), many-body (Stokesian Dynamics), and lubrication-corrected many-body interactions [2]. The dynamics of gel formation is sensitive to the exact nature of the approximation that is used. However, the steady-state structure is relatively unaffected, except when lubrication interactions are included. Counterintuitively, we also find that the effect of lubrication is to accelerate the aging of the gel. Both elements can be explained by lubrication interactions facilitating local rearrangements, which we will explain in detail.

Our findings provide a solid foundation for the future study of colloidal gels subjected to external stimuli. We anticipate that despite their computational cost, accounting for lubrication interactions in the study of colloidal gels is crucial to accurately describe their dynamics.

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Sustainable Formulations: Cellulose Based Colloid-nematic Gels

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Stiff, yet highly thinning, viscoelastic gels can be formed upon mixing colloids with homeotropic (normal) alignment into a nematic liquid crystalline medium. This is due to the entangled network of defect lines that percolate throughout the sample. Cellulose nematic phases can be created from biorenewable ingredients obtained from wood and seaweed.

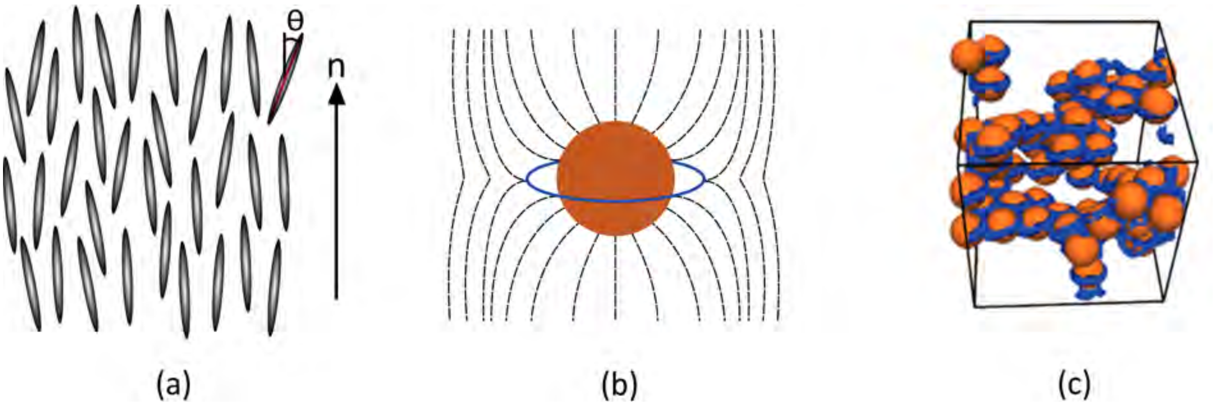

Figure 1: *(a) Nematic liquid crystal phase where n is the director and θ is the angle the rod makes with the director. (b) Saturn ring disclination where rod shaped particles have homeotropic (normal) anchoring to the surface of the colloid. (c) A configuration with percolated defect lines at ϕ=16%, where blue ribbons are defects, and orange spheres are particles [1].*

In this work, the rheological properties of the colloid-nematic composite are explored. While the nematogen concentration has little to no effect on the composite, we show that rheological properties are greatly impacted by colloid volume fraction. We also show broad linear viscoelastic regions, suggesting high stability of the composite gels.

References

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Solvents' effect on Particle contact and Rheological behaviour in Jamming suspensions

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The behaviour of suspensions of hard spheres in a Newtonian fluid may seem simple, but it is actually quite complex and not well understood. Many recent studies (cf. this recent review [1]) have emphasized the importance of interparticle contact forces in these behaviours.

In our work [2], we demonstrate that when the same polystyrene particles are immersed in different Newtonian solvents, they exhibit different behaviours at both the microscopic and macroscopic levels.

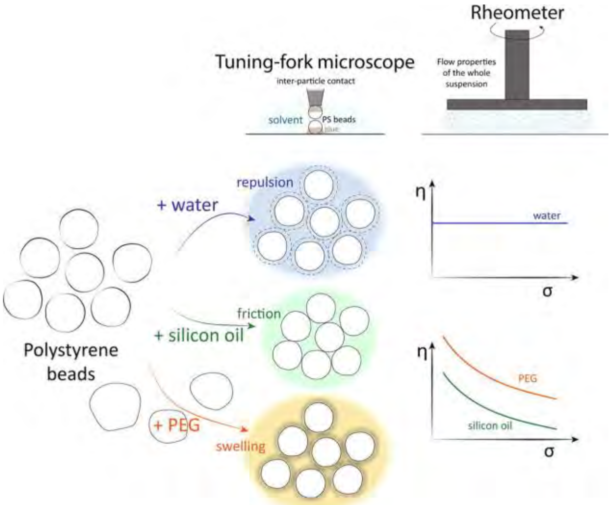

Figure 1: *The same polystyrene beads, when immersed in three types of solvent, exhibit three types of particle contact and three rheological behaviour [2].*

By conducting interparticle force measurements and rheological measurements in each solvent, we show how the details of the pairwise particle interactions affect the macroscopic behaviour. We found that the rheological properties of the suspensions, which are made up of the same particles, depend on the nature of the solvent, including the shear thinning, shear thickening, and jamming solid fraction value. We also identified several mechanisms at the particle scale that contribute to these behaviours, such as the swelling of polymeric particles in an organic solvent, the role of colloidal repulsive forces and inertia in water solutions, and the variation of the friction coefficient with load in silicone oils.

Our study provides new quantitative data for testing micromechanical models and simulations and emphasizes the need to systematically characterize interparticle normal and tangential forces when studying a given suspension of hard spheres in a Newtonian fluid.

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New methods and techniques for soft matter 2

Wednesday 24 May 15:00 – 16:00

Auditorium

Neutron scattering and reflectivity to study foams in a brand new multi-scale experiment

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[2] *Institut de Chimie Séparative de Marcoule, Marcoule, France*
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Liquid foams are non-equilibrium multi-scale soft structures for which the stability is still difficult to predict. In order to better understand the physicochemical factors that affect the aging of foams at different length scales, a new columnar device was developed. It enables simultaneous data collection from a small-angle neutron scattering (SANS) diffractometer, from an optical camera, and from an electrical conductivity meter. The volume of the foam, its liquid fraction, and the radius of the foam bubbles as a function of time (obtained by image analysis and conductivity processing) are macroscopic information, necessary for foam lifetime characterization but not sufficient. SANS analysis is known to provide useful information at the nano-scale, on the structure of the inter-bubble film or the surfactant self-assemblies trapped within the foam [1, 2]. However, to extract this information over a large structural range, we have for the first time performed a quantitative analysis - in absolute scale - of the scattering data [3].

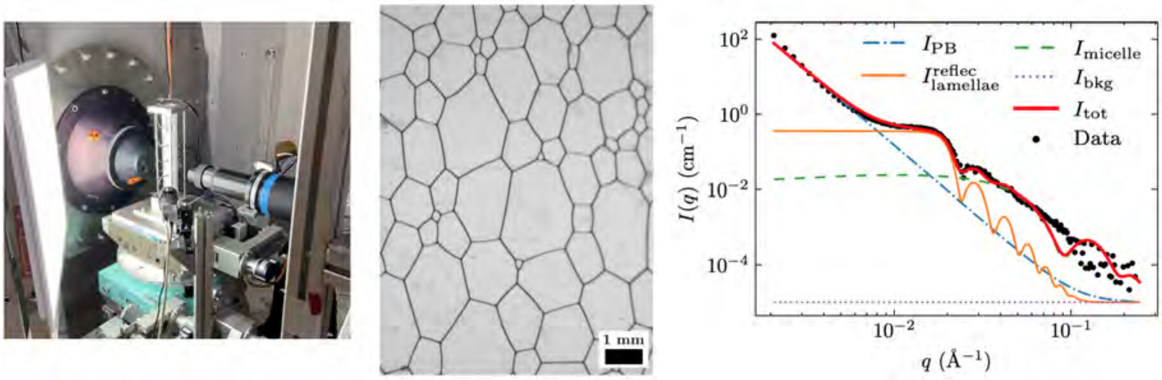

Figure 1: *Left: Picture of the multi-scale setup. Middle: Picture of a foam obtained at 65 min. Right: Various contributions of the total scattering fit (red curve) to adjust SANS data from the foam shown in the middle picture : from Plateau Borders, from micelles, from lamellae.*

The analysis of nano- and macroscopic information obtained simultaneously for foams stabilized from a mixture of the nonionic alkylether BrijO10 surfactant and of the sodium dodecyl sulfate (SDS) anionic surfactant enabled us to better understand the underlying mechanisms involved in the stability of liquid foams.

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Measuring the interaction between small colloidal particles using optical tweezers

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Pair interaction between colloidal particles can be measured using the technique of optical tweezers [1,2]. Essentially, this technique involves using the optical forces of a trapping laser to bring two particles close together, while digital microscopy is used to obtain the distribution of the interparticle distance. If the forces induced by the trapping laser (such as optical binding) are well understood, the pair interaction can be extracted. However, when dealing with laser induced forces, especially when the particle size is comparable to the laser wavelength, this can be difficult. In addition, accurately locating particles can be challenging due to their apparent size under the microscope being larger than their actual size. When two small particles are near contact, their images overlap [3,4], leading to ill-defined particle position. In this presentation, we will address these technical obstacles.

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Solving inverse design problem with enumeration-selection strategy

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The challenges of designing efficient patterns, adapting complex molecules to external conditions, and finding the structure of molecules with an affinity for specific targets are examples of difficult to solve problems of inverse design problems or inverse search for molecule structure. Nature has provided inspiration for solving these problems through evolution strategies based on the selection of successful adaptations and heritable traits over generations. To create new adaptable materials, the concept of adaptive chemistry has been proposed, which aims to synthesize self-adapting molecules that can fit into their environment.

A computational method has been proposed [1] that uses massive parallelization on modern GPUs to perform an efficient exhaustive search, solving the inverse problem by repeatedly solving the direct problem in the mean field approximation. This method can be applied to a wide range of design problems in soft matter, where adaptive behavior in multi-parameter space in response to environmental conditions leads to non-trivial patterns or molecule architectures and compositions. It can also be combined with machine learning or other optimization techniques to explore the parameter space more efficiently. Examples of such problems include finding a copolymer composition that allows the polymer to translocate through a lipid membrane at a minimal time or a copolymer sequence that maximizes the polymer load in a micelle defined by radial core-shell potentials. Additionally, hydrogen bonding can be used as a pathway of adaptation to the environment through reversible links, and branching of molecules can be adjusted to external fields to provide molecules with annealed topology that can be flexibly changed by changing external conditions.

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Polymers and responsive networks 1

Wednesday 24 May 15:00 – 16:00

Sala Polveri

Solvation Shell Thermodynamics of Extended Hydrophobic Solutes

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Interfacial solvent density fluctuations play an important role in hydrophobic effects, which regulate the functional characteristics of a wide variety of soft matter systems [1]. Small hydrophobic solutes are hydrated without disrupting the hydrogen bonded water network around them. In contrast, the inability of water molecules to maintain their hydrogen bonded network around extended interfaces leads to enhanced density fluctuations near large non-polar solutes, which make their hydration shells susceptible to small perturbations [2]. This crossover between the small and large length scale regimes has crucial implications in the folding/unfolding of proteins and responsive polymers. Cosolutes can either enhance or quench the interfacial solvent density fluctuations [3] and thereby regulate the hydration behavior of non-polar solutes, which results from their preferential accumulation or depletion on the solute surface.

To understand the molecular mechanisms and driving factors behind these observations, we employ atomistic computer simulation to investigate the solvation behavior of molecular solutes. We use an extended hydrophobic solute as a model system to quantify the density fluctuations in the solute's hydration shell in pure water. On strengthening the solute–water repulsive interaction, we observe a hydrophobic length scale transition in the compressibility of the hydration shell [4]. Further, we investigate the effect of two adsorbing cosolutes: urea and methanol on the interfacial density fluctuations [5], whose mode of action is found to be strongly coupled to their hydration behavior. We found preferential accumulation of urea to quench the density fluctuations around the extended solute, leading to a decrease in the compressibility of the solvation shell. In contrast, methanol accumulation enhances the density fluctuations, leading to an increase in the compressibility. To isolate the dominant interactions that lead to these contrasting effects, we are currently exploring the energetics of the solute solvation shells. The observations from this simple model can be discussed in the context of cosolute induced swelling and collapse of polymers in aqueous solutions.

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Dilute surfactant solutions by using a pharmaceutical salt: equilibrium characteristic lengths & strain hardening in start-up flow

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Surfactant solutions containing Cetylpyridinium Chloride (CPyCl), a classical ionic surfactant, and Sodium Diclofenac (Diclo), a non-steroidal, anti-inflammatory drug, were investigated in a wide range of compositions using rheology and Cryo-EM. Solutions were made at three different concentrations of CPyCl, i.e. 5.0, 16.7 and 33.0 mM. The ratio between the salt and the surfactant concentrations, R=CPyCl/Diclo, was within the range $0.4<R<1.4$. Linear viscoelastic rheology was performed at 25°C using a stress controlled DHR-2 Rheometer (TA instruments), equipped with sandblasted 40 mm diameter parallel plates, a Peltier system to control the temperature, and a solvent trap to avoid evaporation. The use of dilute solutions allowed to examine their microstructure via cryo-EM imaging, e.g. avoiding high density of micelles. High-resolution images of vitrified specimens were recorded with a Glacios FEG electron microscope (Thermo Fisher) at 200 kV.

By following the zero-frequency viscosity evolution as a function of Diclo content, it was possible to identify various regions, characterized by a completely different rheological response. By matching the frequency sweep data and the cryo-EM images, we were able to connect these regions to specific morphological transitions: from spherical micelles to very long and entangled wormlike micelles, to branched networks and eventually well-defined vesicles.

For some systems, we were able to measure the entire spectrum of relaxation times, including the shortest characteristic Rouse time at high frequencies, usually reached only by Diffusive Wave Spectroscopy. This allowed for the evaluation of some important microstructural parameters, such as entanglement, contour, and persistence lengths, taking advantage of available models.

For the more entangled systems, the transient behaviour in shear flow was investigated through startup measurements, performed at different shear rates, covering a wide range of Weissenberg (Wi) numbers. The long-time part of these tests allowed to build up the flow curves for each sample.

During the transient regime, some samples show flow instabilities and strain hardening phenomena at $Wi>1$, a phenomenon already detected before on surfactant solutions. Other solutions do not show the same features, behaving like ordinary linear polymers in fast shear flows, i.e. exhibiting pronounced overshoots followed by tiny undershoots of the transient shear viscosity, before approaching the steady state. A possible mechanism for the onset of flow singularities is suggested and discussed.

The evolution of equilibrium NaPSS / DTAB supramolecular structure in dilute aqueous solution with increasing surfactant binding

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In the past decades comprehensive research has been carried out in order to understand the behaviour of complexes of oppositely charged polymer polyelectrolytes and surfactants (P/S). A general feature of P/S system is that they self-assemble into supramolecular structures above a certain surfactant concentration, the critical aggregation concentration (cac). There are several studies aiming at describing the structural and phase properties of P/S systems. In the literature, two main topics have been investigated: i), the structure of the precipitate in the equilibrium two-phase region, and ii) the structural evolution of the complexes as a function of the polymer/surfactant ratio. In the phase-separation region, examples of hexagonal, lamellar, and cubic structure have been identified. At the same time, there is little information about the structure of the complexes in the one-phase region and only a few studies have been published dealing with the effect of surfactant concentration on the morphology of P/S aggregates. Despite that one of the most investigated P/S systems is the dodecyl trimethylammonium bromide (DTAB)/ sodium polystyrene sulfonate (NaPSS) mixture, structural information about this system is practically not available in the literature. In our study we prepared several 17 kDa NaPSS/DTAB samples with increasing DTAB and constant NaPSS concentrations in the equilibrium one-phase region and we also prepared stoichiometric NaPSS/DTAB precipitate. Since in the recent decades, it has been clearly shown that the high charge density P/S mixtures are prone for formation of kinetically arrested non-equilibrium aggregates, we used a novel sample preparation method to facilitate the formation of the equilibrium non-aggregated P/S complexes in the entire investigated surfactant concentration range. We measured the binding isotherm and simultaneously, we performed small-angle X-ray scattering measurements and performed data modelling with least-square fitting method on absolute scale. We showed that by increasing the binding ratio the formed complexes exhibit an elongated to spherical transition which ends with well-defined precipitate with hexagonally closed packed structure with spherical particles at the crystal lattice points. We also showed that the addition of indifferent electrolyte (NaCl) changes the structural behavior of the system and yields amorphous structure. Summarizing, we have now connected the binding isotherm to the evolution of the structural features of complexes in the equilibrium one phase region and to the structure of the phase separated stoichiometric precipitate.

Heterogeneous polymeric systems and nano-composites

Wednesday 24 May 16:30 – 17:30

Auditorium

Linear, Star, Comb and Ring Crystallizable Multiblock Copolymers Investigated by Molecular Dynamics Simulations

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We use coarse-grained molecular dynamics simulations to study the impact of the chain topology on the structure, thermal and mechanical properties of crystallizable multiblock copolymers. We investigate linear, star, comb and ring topologies for which we vary in a systematic way the content in crystallizable units through the length of the so-called "hard-segments" while keeping the overall molecular weight constant. Through the establishment of a master-curve, our results emphasize that the crystallization temperature is driven by the hard-segment length, regardless of the chain topology and the fraction of crystallizable units in the material. The analysis of the resulting crystallites (hard-segments clusters) nevertheless reveals major structural differences. While ring molecules (and comb ones to a lesser extent) tend to form a high number of small and well-distributed crystallites, linear and star architectures result in much coarser clusters from 12% of crystallizable units. This trend is further enhanced for higher hard-segment contents until ca. 20% where ring molecules start to form worm-like clusters. The shear modulus at rest is systematically computed by following the Green-Kubo method, which demonstrates the role of i) the average cluster's size and ii) the network connectivity [1]. Beyond contributing to the understanding of the structure-properties relationship of thermoplastic elastomers, the peculiar nature of the molecules investigated in this work also extends the fundamental knowledge of polymer crystallization.

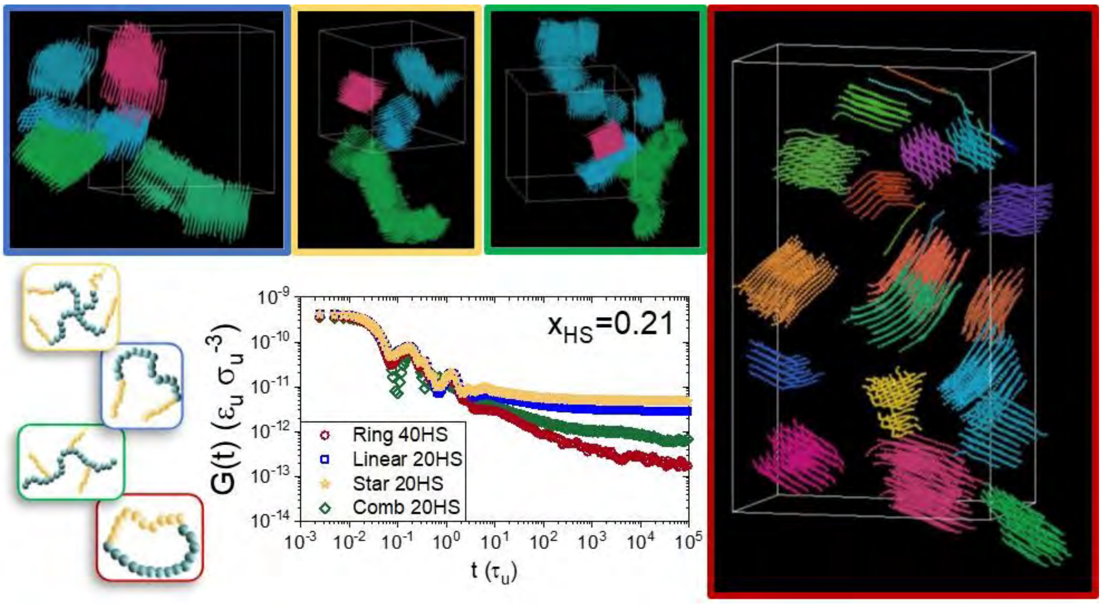

Figure 1: *Snapshots of simulation boxes containing Linear, Star, Comb and Ring block copolymers (from left to right) and corresponding shear modulus calculated from the Green-Kubo method.*

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How to unravel and quantify the heterogeneous structure of silicone rubbers by swelling, NMR and DMA analysis

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When characterizing elastomers, a common approach consists in first measuring the crosslink density by classical macroscopic techniques such as equilibrium swelling in a good solvent or mechanical measurements at small strains. In complement to these macroscopic methods, a time-domain proton NMR method has been more recently proposed to characterize the crosslink density, based on the so-called double-quantum (DQ) detection. This more local technique gives access to details about the network architecture which are difficult, if not impossible, to elucidate by macroscopic techniques, such as the quantitative amount of non-elastically active chains (so-called 'network defects') or the relative contributions of trapped entanglements and chemical crosslinks. Besides, time-domain proton NMR also provides a simple way to characterize the dynamics at the scale of monomers, based on the fact that rigid domains have NMR relaxation times orders of magnitude shorter than mobile domains, one can define a fraction of rigid polymer chains present in the elastomeric network.

Here we combine several techniques to characterize the crosslink density of commercial silicone materials. The approach is motivated by the fact that combined classical macroscopic methods (*i.e.* swelling and mechanical response) do not give coherent results. More specifically, different molar masses between crosslinks (*Mc)* are obtained when analyzed under the usually made hypothesis that the materials are homogeneous at the macroscopic scale. Instead, we show that obtaining different *Mc* through complementary experimental techniques demonstrates that the systems are heterogeneous, and that the results can be nicely rationalized as a heterogeneous network, when combined and correlated to the results of NMR measurements.

This approach sheds new light on the complex network architecture of silicone rubbers and more generally provides a rather simple protocol to verify and quantify the heterogeneous nature of elastomers which formulation is often not precisely known.

Structure and dynamics of a 1,4-Polybutadiene melt in confinement: A molecular dynamics simulation

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The study of the structure and dynamics of polymers confined by solid surfaces, e.g. [1, 2, 3], enhances our knowledge about the properties of composite materials. The topic has been a desired area of study given the development of its applications. In such systems, the macromolecules are responsible for the general performance of the whole system. Therefore, understanding the effect of the confinement on the structure and dynamics of polymers is crucial for the advancement of the field.

It has been shown that conformations and dynamics of polymer melts confined to thin films and flat surfaces as well as cylindrical pores are altered in comparison with the bulk. The change in properties depends on several factors including but not limited to the geometry of confinement. In our research, we study the effects of both the nanoscopic confinement and curvature on the dynamics and properties of a chemically realistic united atom model of a 1,4-Polybutadiene (PBD) melt using Molecular Dynamics (MD) simulations. Therefore, we divide our work into two systems: one with a PBD melt confined in a cylindrical pore [4] and the other with a PBD melt surrounding a cylindrical nano-rod. In both systems, the effects induced by the confinement on the melt's structure and dynamics on several scales are examined and compared.

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Polymers and responsive networks 2

Wednesday 24 May 16:30 – 17:30

Sala Polveri

Nonlinear shear rheology of unentangled melts and solutions

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The comprehension of the nonlinear shear rheology of entangled polymers with different molecular architectures attracted substantial efforts from researchers in the past decades. As a result, many experimental and theoretical studies are now available on the topic, and entangled polymer dynamics are fairly understood for a variety of polymer structures.

Conversely, less attention was devoted to unentangled systems. For example, until recently, few experimental studies were available in the literature on unentangled melts and solutions, and they were mainly concerned with linear architectures [1].

The last few years, however, witnessed a renewed interest towards unentangled polymers. Several studies were performed on unentangled or marginally entangled linear and branched melts and solutions [2, 3, 4]. They revealed interesting rheological features, especially for solutions, where deviations from Cox-Merz rule were found at high shear rates, and shear strain hardening was also observed.

This work presents an experimental investigation of the nonlinear shear flow of unentangled melts with linear and star architectures, highlighting differences and similarities in the nonlinear behaviour. Furthermore, it presents the rheological features of unentangled solutions made of long chains dissolved in different oligomeric matrix. The effect of the oligomer on the shear hardening is also examined.

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Stimuli responsive 3D bioprinted in vitro alveolar models

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Our aim is to develop a realistic 3D-printed lung model, consisting of hybrid functional biomaterials that can provide different functionalities. The model is focused on the air-blood interface of the lung, which will be obtained by printing a net-like structure by Stereolithography (SLA) printing. The photopolymerizable ink is composed of vinyl caprolactam (VCL), which is a thermoresponsive monomer [1], polyethylene glycol diacrylate (PEGDA), which acts as a crosslinker and provides flexibility [2], ionic monomers that provide a positive charge to interact with the negatively charged cell membrane, and a photoinitiator (lithium phenyl-2,4,6-trimethylbenzoylphosphinate, LAP). The temperature of the polymer and surrounding matrix can be altered with an external stimulus. This will generate an expansion-contraction response on the material, generated by the VCL when the temperature varies between above and below the Lower Critical Solution Temperature (LCST) [1]. The expansion and contraction movements are aimed to mimic the native environment of the alveoli when the breathing occurs. Therefore, the material needs to be flexible and provide mechanical strength[3]. The characterization of the inks include printability tests, swelling, determination of rheological properties, mechanical tests and degradability tests. Additionally, another type of ink including the most abundant cell types in the alveoli, which are type I and II pneumocytes, as well as endothelial cells [4] embedded in a decellularized lung extracellular matrix (lung dECM) to be combined with the SLA-printed material is considered. The development of this novel hybrid pulmonary model opens new opportunities to provide ideal platform to better understand the causes behind different pulmonary diseases and perform drug screening studies.

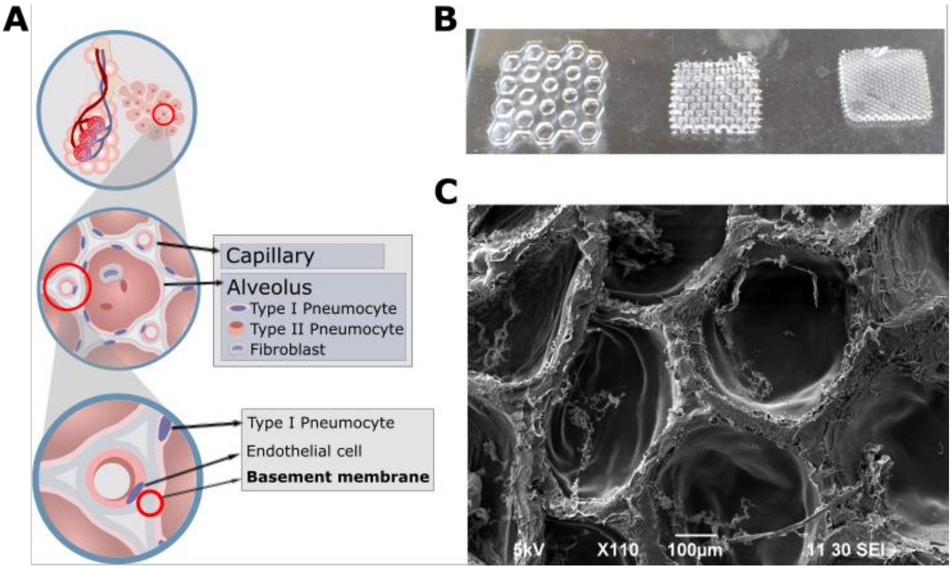

Figure 1. Initial approach for SLA printing the air-blood barrier of the lung. (**A**) Illustration showing a schematic organization of the alveoli. (**B**) Photograph of SLA-printed scaffolds with a honeycomb shape, consisting of VCL, PEGDA and LAP. The designs were printed at different scales. (**C**) SEM micrograph of lyophilized scaffold (smallest scale printed), showing the hexagon-shaped structures.

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Constraining effects on polymer chain relaxation in crosslinked supramolecular dual networks

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Polymer networks containing transient physical and permanent chemical cross-links exhibit unique mechanical properties due to the intrinsic reassociating ability of supramolecular functional groups. s. In this study, we investigated the rheology, dielectric spectroscopy, stress-strain behavior and dynamic mechanical analysis of networks based on long polybutylene oxide (PBO) branches functionalized with randomly placed thymine (thy) side groups (Fig. 1 left). A transient network was formed by proportionally mixing this matrix with short non-entangled linear 1,3,5-diaminotriazine (DAT) head-tail modified PBO chains. This transient polymer network was further cross-linked to a dual network via a thiol-ene click reaction to form static covalent bonds. In PBO, the similarity in polarity between the PBO matrix and the thy-DAT functional group ensures that molecular chain motion is not affected by segregation [1]. The results of this study reveal the presence of two distinct plateaux in the shear modulus of the transient network, which are attributed to the contribution of entanglement and hydrogen bonding. The complex Young's modulus also exhibits two plateaux in the dual network sample. Dielectric relaxation spectroscopy was employed in combination with rheology to quantitatively analyze the relaxation processes of the interconnected polymers and the strength of the thy-DAT bonding interactions. The macroscopic behavior of the system was successfully described using the Dobrynin-Konkolowicz model [2], which accounts for the network strain rate-dependent bond lifetime. In the case of the dual network system, the binding time of the chemical bond was prolonged and a higher activation energy was observed, likely due to the physical link preventing the movement of the long chain.

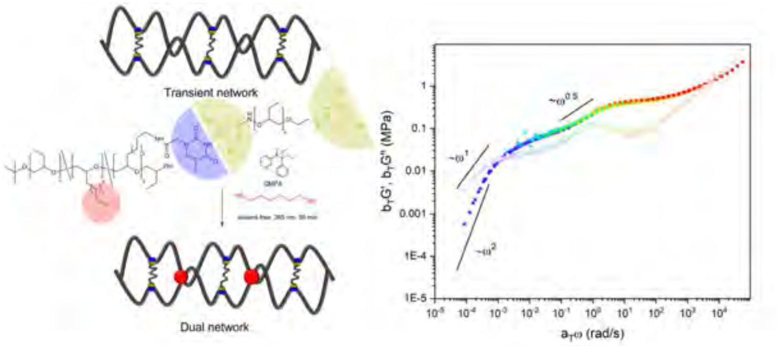

Figure 1: *Left: Schematic representation of the synthesis of transient network and dual network. Right : rheology master curve of transient network*

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Polymers and responsive networks 3

Thursday 25 May10:30 – 12:30

Auditorium

Effective Potentials, Phase Behavior and Viscoelastic Behavior of Reversible Polymer Gels

Angel J. Moreno [1,2]; Mariarita Paciolla [1], Mounika Gosika [1], Christos N. Likos [3]
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We present a global picture of the thermodynamic and dynamic properties of a gel-forming system of polymers with reversible bonds. By means of MD simulations we investigate a generic bead-spring model and characterize the properties of the dynamic network as a function of the sequence of reactive sites in the polymer. Moreover we study the effect of introducing two types (A,B) of reactive sites (orthogonal chemistry) and their distribution (mixture of pure-A and pure-B chains, mixture of A-B chains with complementary compositions, and one-component systems of A-B chains with identical compositions). The molecular conformations in the crowded solution are weakly perturbed with respect to high dilution, even far above the overlap concentration, in clear contrast to the collapse from self-avoiding to random walk behavior experienced by linear chains with no bonds. This result suggests that the validity of the effective (mean-force) potential between the molecular centers-of-mass can extend far above the overlap concentration and many-body interactions essentially contribute as a flat energy landscape. Effective interactions are systematically derived through force integration methods. To assess their validity, we compare correlations in all-monomer simulations of crowded solutions with those of ultrasoft particles interacting through the effective potential. Very good agreement is found even far above the overlap concentration, extending the validity of the effective fluid approach much further than usual. Mean-field DFT and simulations of the effective fluid predict demixing in binary systems of orthogonal components, which is confirmed by simulations of the real all-monomer system. No interpenetration of the two dynamic networks is found, and they instead demix. However, interpenetrated networks are stable in mixtures of A-B chains with complementary sequences even for very low fractions of the minority species. Finally, we investigate dynamic properties of one-component solutions of A-B chains with different activation energies for the bonds. Varying the A/B fraction and the sequence of reactive sites (random vs. diblock) becomes a powerful approach to fine-tuning the viscoelastic behavior, allowing to simultaneously slow down and speed up the stress relaxation in different frequency windows and to obtain a non-monotonic viscoelastic response of the polymer network.

High frequency dynamics of hydrogels studied by DWS microrheology

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Rheological responses of a chemically crosslinked gel are characterized by an elastic plateau at which G’ is higher than G’’ observed at low frequency accessible by shear rheometry. The value of the plateau modulus is correlated with the mesh size of the gel. At higher frequency, the rheological responses of the network at the length scale smaller than the mesh size should be observed, while systematic measurements and analyses are rarely reported. In this work we characterized high frequency dynamic properties of a model chemical hydrogel using high frequency microrheology based on diffusing-wave spectroscopy (DWS), with the aid of the existing theory of polymer dynamics in solution [1]. Poly(vinyl alcohol) (PVA) hydrogels crosslinked by glutaraldehyde were prepared at varied polymer concentration and crosslinker concentrations. Polystyrene nanoparticles (size: $2R = 500$ nm) were used as probes for DWS measurements. A laboratory-made DWS setup was used. From the autocorrelation function, mean-square displacement (MSD) was calculated. By using the generalized Stokes-Einstein relation (GSER), complex modulus of the gel was determined.

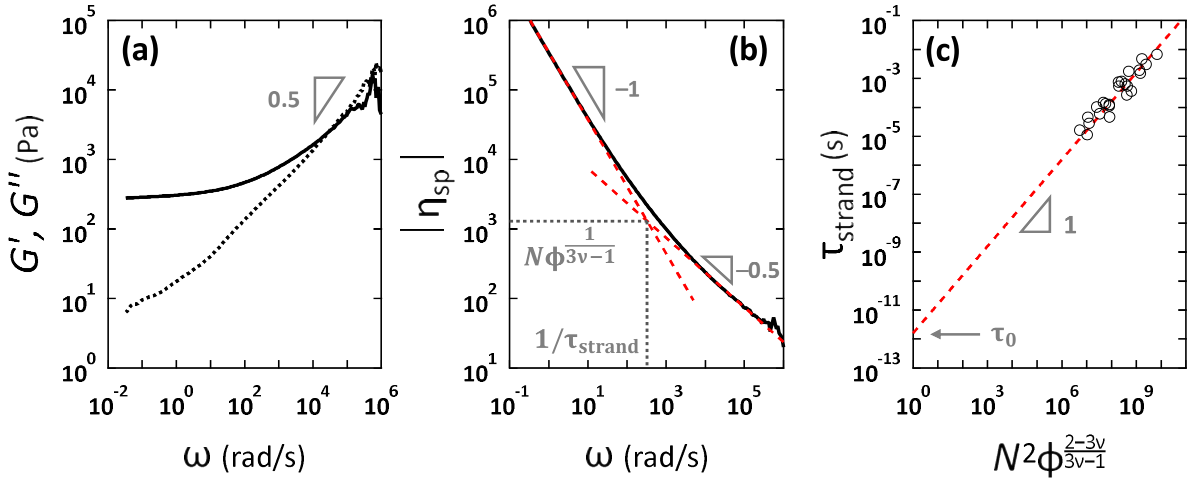

Figure 1: *(a) dynamic moduli and (b) absolute specific viscosity of a PVA chemical gel as a function of angular frequency. (c) Determination of Kuhn segment relaxation time* τ_0 *from the scaling of Rouse relaxation time of the strand.*

We found that at high frequency, microrheologically measured G' and G'' exhibit a power-law behavior $G' \sim G'' \sim \omega^{0.5}$ (Fig.1a). We attribute this dynamic mode to the Rouse mode of strand between crosslinks made of correlation blobs in semi-dilute condition in a good solvent [1]. We propose an accurate method to determine the longest Rouse relaxation time of the strand τ_{strand} and the number of correlation blobs in it $N\phi^{1/(3\nu-1)}$, from the specific viscosity of the gel exhibiting crossover from elastic plateau (with a slope of −1) to Rouse mode (slope of −0.5) (Fig.1b). From the scaling of the Rouse time, we determined the monomer relaxation time τ_0 thus the Kuhn segment size b (Fig.1c) We found $b = 0.36$ nm, which is reasonably close to a literature value (0.6 nm, determined by AFM force spectroscopy) [2].

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Microrheology of dense solutions of DNA

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The field of DNA-based materials is rapidly growing, and holds great promise for the development of novel materials with unique properties and applications. These materials exhibit complex rheological behaviours that are strongly dependent on the topology and concentration of DNA, as well as the surrounding environment. During this presentation, I will discuss research that delves into the influence of all three factors on DNA-based fluids.

First, I will report microrheology data investigating the correlation between cation concentration and the viscoelastic behaviours of DNA fluids. I will discuss the effects of monovalent and divalent cations on the rheology of entangled solutions of lambda DNA. Through this research, I will demonstrate how these molecules can hybridise, and form long-lived concatenamers with a timescale that depends on salt concentration.

In the second part of my talk, I will discuss how varying DNA topology can influence rheology. More specifically, I am using DNA origami, a technique pioneered by Paul Rothemund [1] to design polymer topologies which simultaneously display both linear and circular architectures, assuming "tadpole"-like shapes (see AFM images in Fig 1). Motivated by recent simulations [2], I aim to characterise the fluid viscoelastic behaviour and identify the presence of threadings, which will dramatically slow down the polymer dynamics compared with their topologically simpler counterparts.

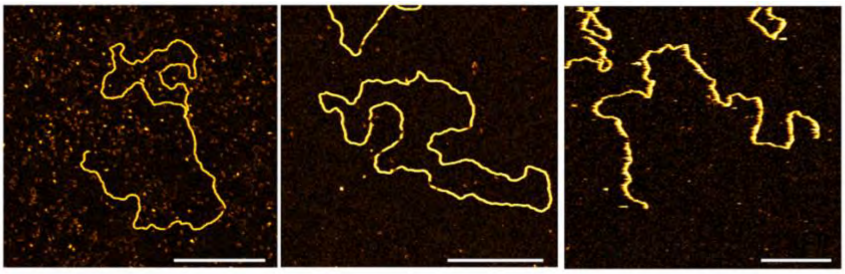

Figure 1: *AFM of varying DNA origami topologies. Scale bar is 300nm.*

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Copolymeric templates for plasmonic substrates fabrication

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Gain control over metalic nanostructures assembly remains an important challenge in nanotechnology. Well developed top-down strategies (i.e. photolithography, electron-beam lithography) do provide great structural control, however they become increasingly time-consuming and expensive when it comes to nanoscopic structural motifs reaching the size down to ~100 nm and below. Therefore, an alternative bottom-up solutions, involving self-assembling systems are being intensively explored. Development of commonly available and reliable technology of this kind would accelerate the progress made in photonics, plasmonics and allow entering the field of new generation of optical devices based on metasurfaces.

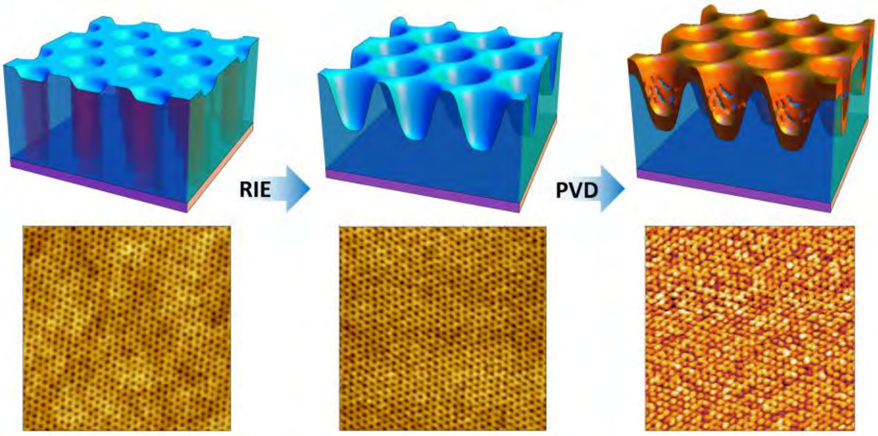

Figure 1: *Substrate preparation strategy: i) copolymer matrix fabrication, ii) Reactive Ion Etching, iii) Physical Vapour Deposition of Au layer. bottom) AFM images of PS-PEO copolymer based matrix.*

In order to fabricate well ordered gold nanostructures we employed block copolymer lithography combined with electron-beam physical vapour deposition. Initially, the poly(styrene-b-ethylene oxide) PS-PEO thin film was spincasted onto thermally reconstructed sapphire substrate and subsequently solvent vapour annealed to get the long-range order of hexagonaly arranged cylindrical domains, oriented perpendicular with respect to the film surface. Afterwards, the reactive ion etching was applied to modify the polymer film surface. Finally, a thin gold layer was deposited using the ultra-high vacuum electron beam evaporation system. Obtained substrates were examined in terms of surface enhanced Raman spectroscopy. Model analyte (thiophenol) was used to monitor the impact of surface topography on signal amplification.

Ackowledgements

The studies were performed within the LaSensA project carried out under the National Science Centre of Poland, project No. 2020/02/Y/ST5/00086 and National Centre for Research and Development under grant NanoHEART DWM/WPC2/285/2020.

Photon correlation imaging of polymer network fracture

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Network-forming materials are ubiquitous and appear in industrial products such as tires, food and cosmetics as well as composing the cytoskeleton within the cells of living organisms. They are lightweight and display properties such as optical transparency and reversible deformability up to large strains. However, microscopic mechanisms protecting a network against macroscopic fracture and the processes that control crack growth are still poorly understood. A deeper understanding is needed to fully exploit the potential of polymer networks in advanced and novel material design. To this end, we adapt photon correlation imaging [1] (PCI) to reveal the microscopic rearrangements within poly(ethyl acrylate) networks [2] during deformation by extension and fracture (see figure 1).

PCI creates a time-resolved macroscopic map (field of view of several mm) of the microscopic movements (on the order of 1 μm) induced by the applied strain preceding fracture. We find that, in our nearly transparent samples, surface scattering dominates the PCI signal, obscuring bulk rearrangements. To address this issue, we first minimise surface scattering by immersing the sample in a pool filled with refractive index matching glycerol, where the geometry of the pool walls is carefully designed to avoid reflections. Furthermore, the pool design allows PCI to be performed at both high (176°) and low (4°) angles simultaneously to measure rearrangements of the polymer network on length scales of 200 nm and 5 μm, respectively. Second, we introduce melamine formaldehyde nanoparticles to the polymer networks to increase the scattering from the bulk. Preliminary measurements reveal non-affine contributions even at low strain, well within the linear regime. We will continue by investigating the role that network architecture, such as interpenetrated multiple networks [3,4], has in the dynamic response of the network and the resultant resistance to fracture.

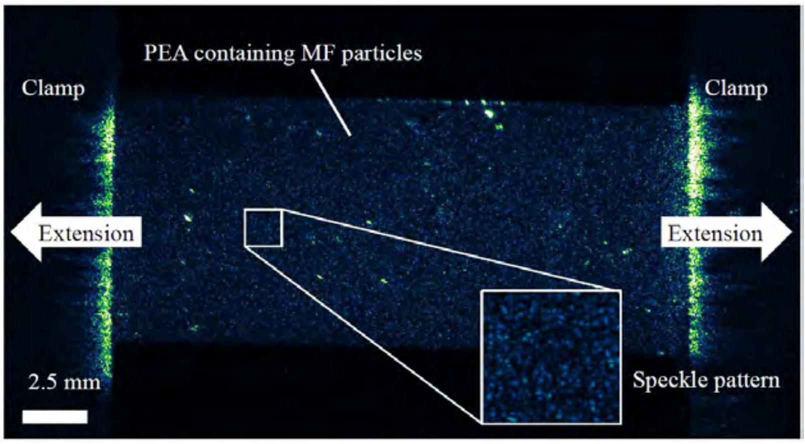

Figure 1: *Photon correlation imaging speckle image of a poly(ethyl acrylate) (PEA) network containing melamine formaldehyde nanoparticles (MF) which enchance bulk light scattering. The sample is subjected to deformation (uniaxial extension) by two clamps, one either side of the sample. PCI is performed by correlating the rearrangements of the speckle pattern over time and space.*

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Synthesis of multi-responsive supramolecular PNIPAM microgels

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Stimuli responsive microgels are of great interest not only in fundamental research but also increasingly mentioned in a broad range of applications [1]. To endow the microgels with pH or ionic strength response, NIPAM is often copolymerized with various functional comonomers in aqueous solution [2]. Nevertheless, authors rarely focus on the crosslinker to synthesize stimuli responsive microgels [3]. In this study, we synthesize multi-responsive supramolecular PNIPAM microgels by simply replacing the commonly used N,N'-methylenebis(acrylamide) by a home-made metallosupramolecular crosslinker. For the first time, this supramolecular crosslinker is based on a coordination complex which plays a multiple role (Figure 1). Indeed, the crosslinkers not only maintain a coherent structure by linking the PNIPAM chains together but also allow microgels stimulation. For instance, the synthesized supramolecular microgels show temperature responsive properties as expected from PNIPAM-based objects, but also exhibit salt responsiveness and degradable properties benefiting from the supramolecular crosslinker. In addition, we tailor both the size of the microgels and the SC/NIPAM molar ratio by using sodium dodecyl sulfate (SDS) in the synthesis. Note that the SC content is easily measured by spectroscopy thanks to a characteristic absorption band of the complex. Besides, by combining SEM pictures and light scattering measurements we can demonstrate the core-shell like structure of these new supramolecular microgels. Finally, such well controlled multi-responsive microgels could be relevant to stabilize smart emulsions or to perform drug delivery.

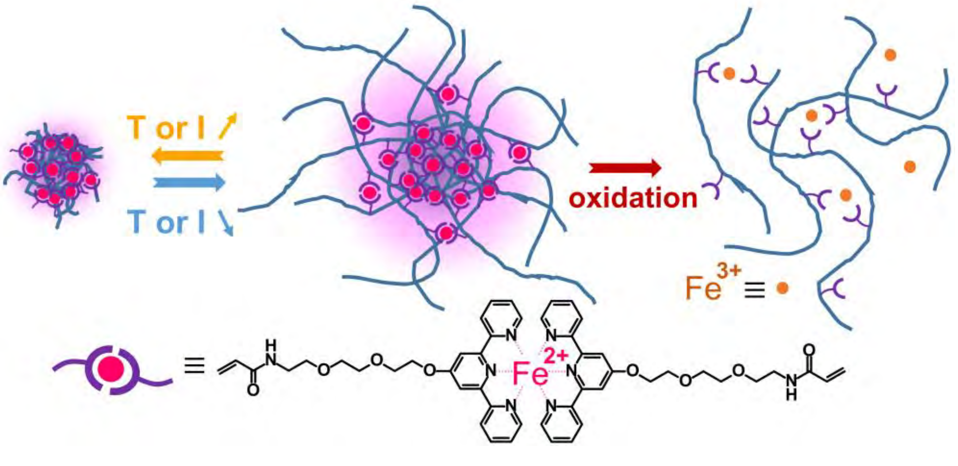

Figure 1: *Temperature behaviour, salt responsiveness, and degradable properties of new PNIPAM supramolecular microgels.*

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Interfaces and surface-active matter

Thursday 25 May10:30 – 12:10

Sala Polveri

α-synuclein binding to model membranes: effect of composition, solution condition and external *stimuli*

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The amyloidogenic α–synuclein (αSyn) can aggregate *in vivo* forming the so-called Lewis bodies, which are hallmarks of Parkison's disease. The behavior of the protein in healthy condition is still debated [1-2], but it is believed to mediate cell communication in its monomeric [1]. To investigate on the parameters that may regulate the interactions with lipid membranes, the adsorption behavior of αSyn to supported lipid bilayers (SLBs) and vesicles was studied varying the lipid composition and the solution conditions (e.g. pH and ionic strength). Fluorescently labelled membranes composed of the zwitterionic POPC and the negatively charged DOPS and GM1 (10 mol % in both cases) were formed as model systems. Fluorescence microscopy experiments highlighted that protein adsorption is strongly related to pH and ionic strength, but similar results were obtained for DOPS and GM1 bilayers in terms of protein concentration. The protein yields a layer which is mostly immobile for GM1 bilayers at the different solution conditions, whereas it is more mobile for DOPS containing SLBs at pH 5.5. The same lipid compositions were tested in solution using fluorescence correlation spectroscopy, studying the affinity of αSyn for GM1 and DOPS vesicles at different lipid to protein ratios. Finally, a custom micropipette setup coupled with the fluorescence microscope was used to study how cycles of negative and positive pressure could affect the aggregation of the protein on the SLBs. Physiological pH and high ionic strength led to an irreversible aggregation of the protein, whereas the accumulation was reversible at pH 5.5, pointing to the electrostatic nature of the αSyn aggregation. These results suggest key molecular parameters in αSyn binding and aggregation, which may help to understand the behavior of the protein *in vivo* on more complex membranes.

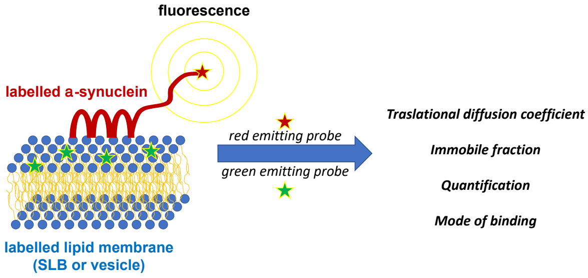

Figure 1: Schematic representation of the qualitative and quantitative information of the protein-lipid system.

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α-Synuclein - lipid membrane interactions depends on membrane charge and lipid:protein ratio

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α-Synuclein is an intrinsically disordered pre-synaptic protein known to interact with lipid membranes. During the neurodegenerative pathway of Parkinsons' disease, the protein starts to misfold and co-aggregates with lipids. However, neither the degenerative pathway, nor the function of the protein in the healthy body is fully understood yet. To understand the function of the protein in a healthy body, it is vital to study the binding dynamics of the protein-membrane interaction, and how membrane properties affect the protein-membrane interaction. This work has studied the protein adsorption onto supported lipid bilayers (SLBs) and small unilamellar vesicles (SUVs) containing an increasing amount of negatively charged lipids using fluorescence microscopy and Circular Dichroism spectroscopy. The results showed that the membranes need to contain at least 5% anionic lipids for binding to occur. The amount of bound α-Synuclein increased steadily with anionic lipid content in the range 5% to 20% after which it levelled out at a density of approximaetly 5000 molecules/μm^2 for SLBs. Comparing α-Synuclein adsorption to SLBs and SUVs, the SUVs were saturated with protein at a 5 times lower lipid:protein ratio. This result suggest that there is a higher number of proteins bound to SUVs for a certain membrane area, indicating binding with shorter amino acid sequence on SUVs (Figure 1A). Further investigation of the binding modes and dynamics showed that in a system with a high lipid:potein ratio, binding of single proteins to SUVs were detected for up to a few seconds. However, for low lipid:protein ratios, the SUVs were saturated with protein and there was an exchange between the bound and the free states. When washing away non-bound proteins, bound proteins remained bound longer, which suggests that in an excess of protein there is competitive binding which increases the exchange rate (Figure 1B). Overall, the results suggest that the binding of the protein is a rather complex system where the dynamics depends on membrane properties and lipid:protein ratio.

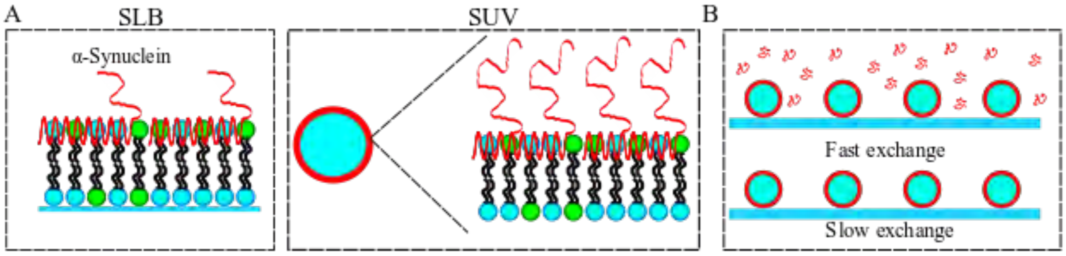

Figure 1: *(A) SUVs are saturated at lower lipid:protein ratios than SLBs, indicating that α-Synuclein is bound with a longer amino acid sequence to SLBs. (B) The exchange rate depends on the lipid:protien ratio.*

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SLE$_3$S – water system: a linear rheological characterization

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Surfactants are amphiphilic molecules fundamental for an extremely wide range of applications.

Due to their complex molecular structure, surfactant-water systems show different morphologies as function of concentration, establishing a complex phase diagram, also as function of temperature. A detailed investigation of the rheological behaviour of surfactant water system is of strategic importance for a variety of industrial application. Despite this interest a rheological phase diagram of these system is missing.

The main goal of this work is to fill this gap in the knowledge, providing a systematic rheological characterization of one of the most used anionic surfactants, Sodium Lauryl Ether Sulphate (SLE$_3$S), to quantify the influence of two key parameters, concentration and temperature.

In this paper, in order to identify different textures of the water-based mixture and to obtain macroscopic qualitative information on sample structure, optical anisotropy properties of each phase are observed by using Polarized Light Microscopy.

Four phases with different texture are identified: micellar, hexagonal, cubic and lamellar, all showing a shear-thinning behaviour. A special attention is paid to the cubic phase which exist only in a narrow concentration range and, for this reason, is not easy to identify. Consequently, cubic phase is often poorly characterized [1], despite being related to most of the difficulties faced in industrial processes, due to a dramatic increment in rheological parameters respect to the neighbouring phases.

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Creating Microstructures through Controlled Wrinkling

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Wrinkling patterns, the buckling patterns that form after relaxation when a stretched elastic film is connected to an elastic substrate, have been studied widely in the Soft Matter community[1], and used to explain a variety of phenomena - from crumpled apples to the folding of the brain cortex[2]. Recently, we discovered that brain-folds can be better explained, when cortical thickness inhomogeneities are taken into account [4]. Similarly, inhomogeneities in a stretched surface can be used to control wrinkling patterns [5].

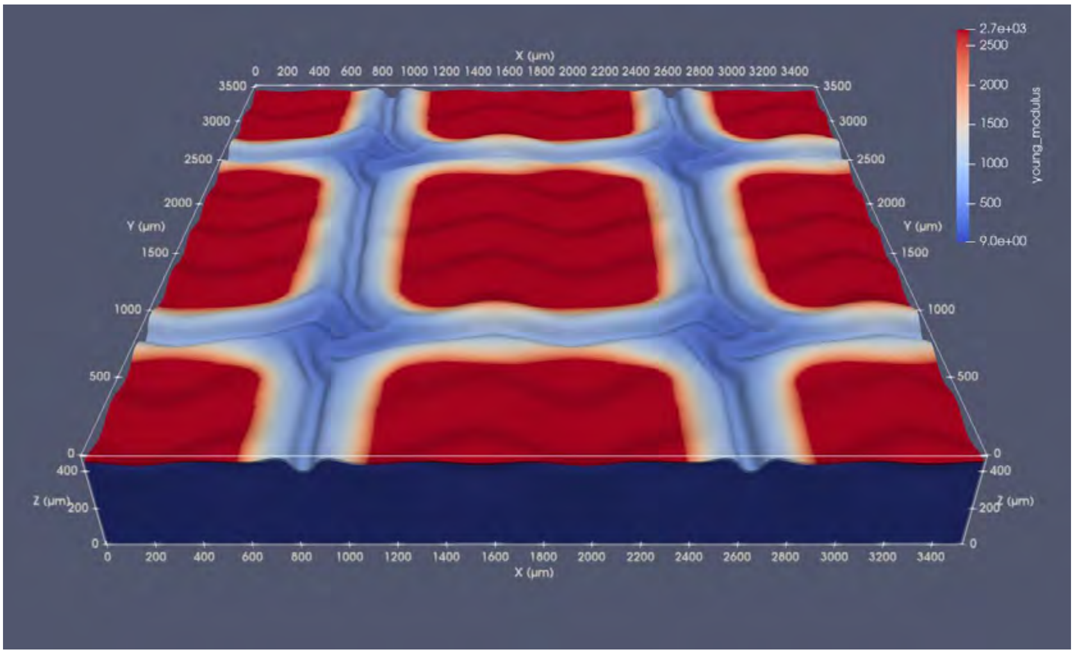

Figure 1: *Simulation snapshot of channel structures as used for a minimal microfluidic chip created by hardening the surface of a stretched PDMS.*

We use computer simulations and experiments to exploit this idea to create controlled three dimensional microstructures. PDMS substrates are stretched, masked, and than treated in a UV Ozone Cleaner. Thanks to the Mask, we can control the type of emerging structure, such as nobs or channels. Recently, we managed to create a simplistic microfluidic chip, see Fig. 1.

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[4] Patent PCT/EP2021/065763

Engineered proteins toward an all-protein bioelectronic platform

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In the context of the booming demand for green and flexible electronics, proteins present appealing biocompatibility and mechanical properties. Considered to be molecular insulators for a long time, proteins in fact present remarkable structural features and benefit from the rich chemistry of amino acids, which make them able to support the conduction of charges from the nano- to the millimeter scale.[1] However, the main difficulty for their application in real-life bioelectronic devices stems from the limited mechanical properties and chemical stability observed in highly conductivity systems. In this work, we propose the use of designed consensus tetratricopeptide repeat (CTPR) proteins as novel engineered material for bioelectronics. CTPR are highly tunable repeat proteins with self-assembly properties that have been used for the development of sophisticated ordered functional materials.[2] CTPR proteins have already been demonstrated to be able to support current conduction, particularly when templating conductive elements.[3,4] However, for efficient application of these protein-based systems in bioelectronics it is needed to enhance their ionic and electronic conduction by new design strategies. For improved ionic conductivity, the proteins have been generated based increased content in ionizable amino acids that behave as nearby proton hopping sites. For enhanced electronic conductivity, an increase in aromatic content was achieved through tryptophane substitutions to generate an extended array of neighboring redox centers for electron hopping.

Impedance spectroscopy measurements on interdigitated electrodes allowed us to dissect the conduction features of protein thin films, while their potential in electrical double-layer capacitors was evaluated by cyclic voltammetry. On one hand, an increase in ionic conductivity was observed because of the increased content in acidic residues. On the other hand, CTPR-based films used in supercapacitor devices showed their ability to isolate the two electrodes and to allow the diffusion of ions, resulting in quadratic capacitive responses. This multidisciplinary work paves the way for the use of CTPR proteins in conductive inks and electrolytes for printed electronics and flexible supercapacitors.

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Biophysics and biomechanics 2

Thursday 25 May15:00 – 16:20

Auditorium

Specific ion effects on amino acid dissociation equilibria

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Proteins are important biological macromolecules whose stability and function are affected by a range of physiological factors such as the pH and ionic strength of the solution. The identity of the ions in solution is important since different ions affect protein stability in qualitatively different ways, explained by the well-known Hofmeister series.[1] In general, salts are expected to reduce the pKa of amino acids in solution by screening the charge of the deprotonated state. However, the magnitude of this effect may be altered by changes in the properties of the ions.[2]

In this study, we utilize Constant pH MD simulations[3] to study the pH-dependent behavior of the amino acid Aspartic acid (Asp) in the presence of salts. We calculate the pKa of Asp in the presence of salt and to interrogate Hofmeister effects, we systematically vary the radius of the ions (σ in the Lennard-Jones (LJ) potential) while keeping the charge (q) and interaction strength (ϵ in the LJ potential) fixed. This has the effect of altering charge density, allowing us to study strongly and weakly hydrated ions. An increase in the anion size leads to a monotonic decrease in the pKa of Asp while changes in the cation size lead to non-monotonic trends. In particular, the cation effects are sharply peaked, resembling an inverted volcano plot.[4] This effect may be understood in context of the Law of Matching Water Affinity (LMWA) which states that binding is optimal when the cation and the deprotonated Asp have similar hydration free energies.

Overall, our study contributes new insight into Hofmeister effects on the stability of proteins as a consequence of variable protonation states of amino acids.

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Tuning the dimensionality of supramolecular materials through the design of peptide-protein co-assemblies.

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Peptide-based supramolecular assemblies have been widely studied for their inherent ability to self-organization, making them useful for applications in nanotechnology.[1] Combining these structures with other molecules opens a new perspective for the design of complex functional materials.[2] Here, we aim to build complex architectures combining a versatile engineered protein, which has potential applications in bioelectronics and nanotechnology, with self-assembled fibers.[3] For this purpose, the protein is modified to incorporate one or two peptides in one or both termini, respectively. This modification will drive the co-assembly with the fibers, resulting in one-dimensional co-assemblies when the protein has one peptide, and an extended network on a second dimension when the protein has two peptides, acting as a fiber cross-linker. The material design was carried out by screening peptide sequences using molecular dynamics (MD) simulations to optimize their co- assembly with the engineered proteins. The resulting architectures were experimentally characterized to prove the change in dimensionality with the number of peptides linked to the protein. The combination of the experimental and computational techniques provided a better understanding of each component in the system, facilitating further rational functional modifications. Therefore, versatile hybrid materials have been created using biocompatible building blocks without introducing any artificial chemical groups or bonds. These materials can be customized to suit specific needs in the fields of bioelectronics and biomedicine.

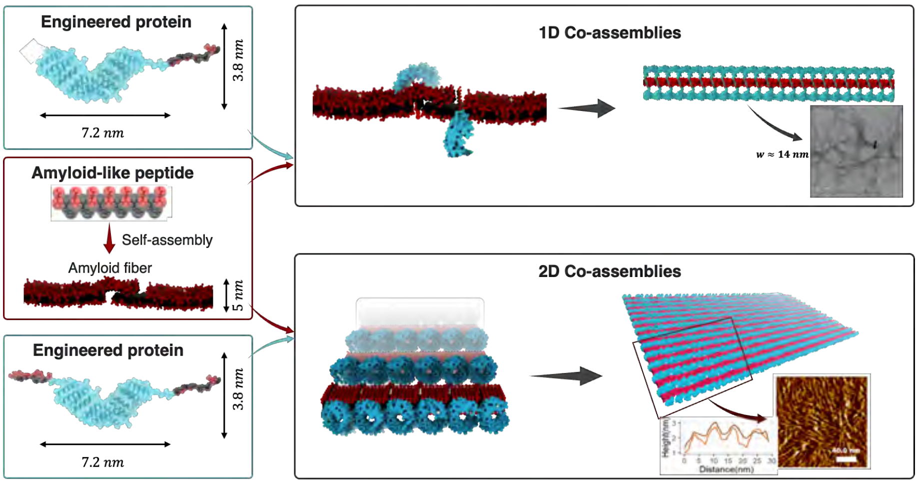

Figure 1: *Rational design of 1-Dimensional (1D) and 2-Dimensional (2D) hybrid materials.* Amyloid fibers co-assemble with modified proteins, with one or two peptides incorporated in one or both termini, resulting in 1D or 2D hybrid materials.

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Microfluidic flow of vesicle prototissues : A model for cell tissues

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Synthetic biomimetic prototissues with reduced complexity can facilitate the understanding of intricate biological processes, by allowing the role of specific physical or chemical mechanisms to be isolated. The aim of the present work is to provide a rheological description of vesicle prototissues as a biomimetic model for the flow of cellular tissues, which can be relevant for the mechanical comprehension of embryogenesis or tumor metastasis. Prototissue were obtained by the controlled assembly of Giant Unilamellar Vesicles (GUVs) mediated by the biotin-streptavidin pair or complementary DNA-strands, using a simple assembly protocol. Prototissues were mechanically probed in a "pipette-aspiration" inspired microfluidic chip, under controlled pressure conditions [1]. We quantified the rheological response of the prototissue to a creep experiment and we described the viscoelastic behavior observed with a modified Maxwell model. Moreover, flow velocimetry and fluorescence quantification provided the monitoring of phenomena occurring at the meso scale such as tissue reorganization and vesicle-vesicle rearrangement.

Figure 1: *Epi-fluorescence microscopy image of the aspiration of a vesicle prototissue in a microfluidic chip*

This rheological tool enables the simultaneous study at two different length scales making a bridge between the global viscoelastic response of the whole prototissue and the adhesion properties between the individual vesicles. Designed for vesicle prototissue assays, it can be translated to the study of embryonic tissues, thus allowing a deeper comprehension by comparing the two tissular systems. This parallel can help giving valuable insights into the complex phenomena at the tissue scale observed during morphogenesis.

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Lipid ordering and fluidity of colloid supported lipid bilayers

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Colloid-supported lipid bilayers (CSLB) are artificial lipid membranes that are stabilized by a solid substrate (Fig 1A). They are widely used as model systems for studying lipid membrane fundamentals and self-assembly processes. One of the attractive features of CSLBs is the dynamic and tunable characteristic of the surrounding lipid membrane. Additives such as poly(ethylene glycol) (PEG), fluorescent probes, and DNA linkers can be easily incorporated into the surface without chemical modification. Incorporating polymers such as PEG to achieve colloidal stability must be done with care. The appealing signature features of CSLBs is their ability to switch between a fluid-like and solid-like state and should not be compromised. In this work, we study effect of PEG insertion on the membrane fluidity and packing order of a fluid (DOPC) and gel (DPPC) membrane.

We investigated the effect of poly(ethylene glycol) (PEG) bearing lipids inserted within the membrane for colloidal stability (Fig 1B).[1] We found that up to 5 mol% of PEG could be incorporated into either membrane without any pronounced effects on ordering or fluidity. However, the fluidity of the DOPC membrane was markedly decelerated upon incorporating 10 mol% of either PEG types. From this work we conclude that the amount of incorporated PEG stabilizer, not the chemical nature of the lipid anchor, should be tuned carefully to achieve sufficient colloidal stability without compromising the membrane dynamics.

Our fundamental work on CSLBs dynamics offers guidance for the experimental design of cell mimics and functionalized lipid bilayers used for self-assembly process.

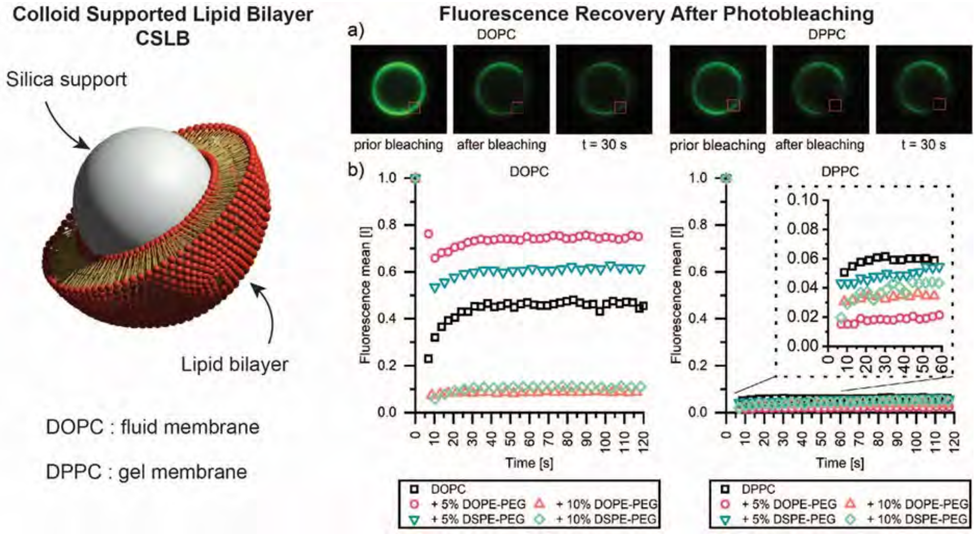

Figure 1: *Left; Scheme of colloid supported lipid bilayer. Right; FRAP recovery curves for DOPC and DPPC membranes with 0,5 and 10% PEG incorporated.*

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Polymers and responsive networks 4

Thursday 25 May15:00 – 16:20

Sala Polveri

Synthesis and characterization of structurally colored silica foams via colloidal templating

Kalpana Manne,[1] Sofia Magkiriadou, [1] Pavel Yazghur, [1] Ahmet Demirörs, [1] Frank Scheffold[1]
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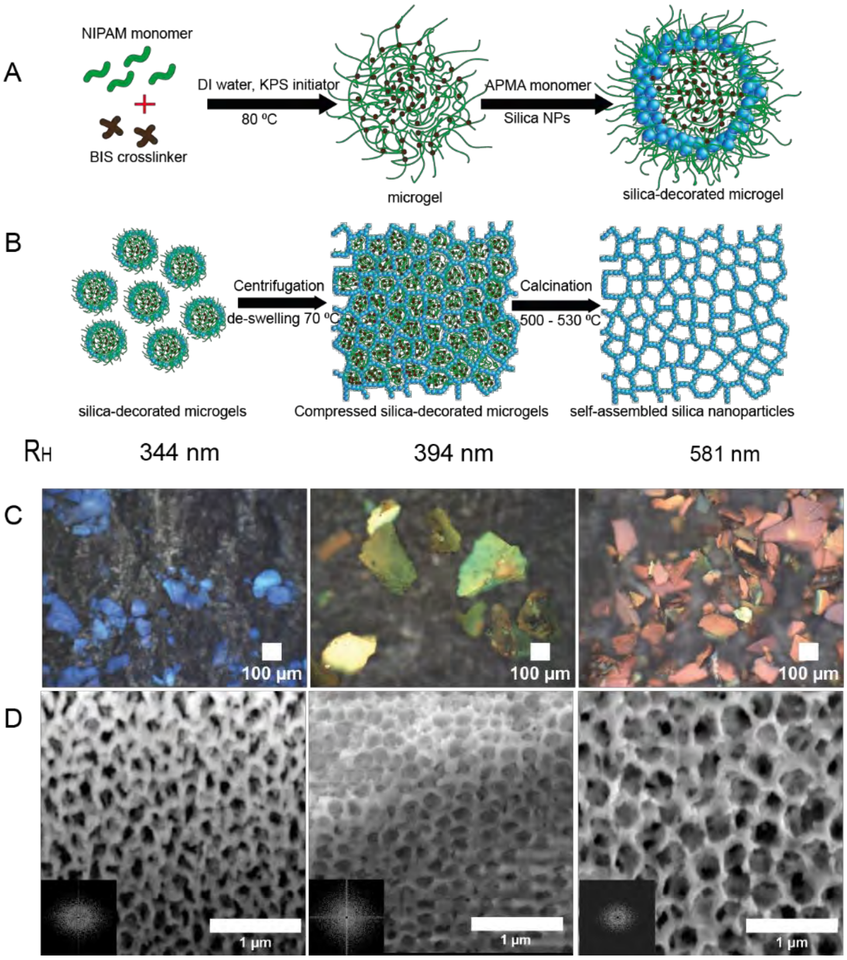
Foams are widely used in various fields such as food, acoustics, and cosmetics, making them an important class of materials in chemistry. While some foams are colored using chemical pigments, nature offers another method of coloration through structural correlations of dielectric materials at the nanoscale. These so-called 'structural colors' are non-fading and more environmentally friendly than pigment-based colors. To mimic nature's structural coloration and take advantage of its benefits, researchers are exploring top-down and bottom-up approaches to create these structures.In this study, we present a method of fabricating solid silica dry foams with structural colors using colloidal templating. Our approach involves densely packed microgel particles that are decorated with silica nanoparticles. By compressing and shrinking the microgel particles, we can tune their morphology, resulting in faceted particles with tetrahedral geometries that are favorable for their optical response potentially leading to bright colors. This faceting behavior sets microgels apart from hard-sphere particles, which cannot be compressed.We obtain inverse structures by burning the organic polymer, leaving behind silica networks, as we have previously demonstrated. Here, we focus on the synthesis of structurally colored foams and their optical and structural characterization. The resulting foams exhibit brilliant structural colors that are tunable by varying the size and shape of the microgel particles. Our study offers insights into the creation of novel materials with structural colors using colloidal templating.



A) Synthesis schematic of silica-decorated microgels. B) Illustration of silica foams fabrication from silica-decorated microgel particles. C) Optical micrographs of structurally colored silica foams captured in reflection mode optical microscopy, bright field, 10X/0.25 NA. The corresponding hydrodynamic radii of the particles are shown above Panel C. D) Cross-sectional scanning electron micrographs of the above foams show porous silica networks (bright region is silica and dark region is air). The color red-shifts with increase in the pore size. Power spectra shown in insets.

Hybrid multifunctional bioinks for a 3D printed pulmonary artery model

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The combination of biomaterials with living cells can be exploited to generate 3D printable bioinks for the fabrication of complex *in vitro* models replicating the natural vascular tissue microenvironment. [1,2] Novel bioinks based on hybrid multifunctional formulations have been developed for the development of a multi-layered pulmonary artery model through 3D bioprinting. An elastic external layer, and an extracellular matrix-derived bioink as the internal layer have been developed. Different 3D printing techniques and the use of a variety of materials have been evaluated for formulating the external layer. The cell-containing bioinks are prepared by embedding primary smooth muscle cells (SMC) in a decellularized extracellular matrix-based formulation and endothelial cells suspended in cell media. After assessing the chemical and mechanical properties, printability, homogeneity, and biocompatibility of the materials, 3D bioprinting has been used to build the vascular tissue *in vitr*o model. The suitability of 3D printing for processing hybrid and diverse multicomponent materials for the fabrication of arterial multilayer 3D model, resembling native tissues and microenvironments, has been verified.

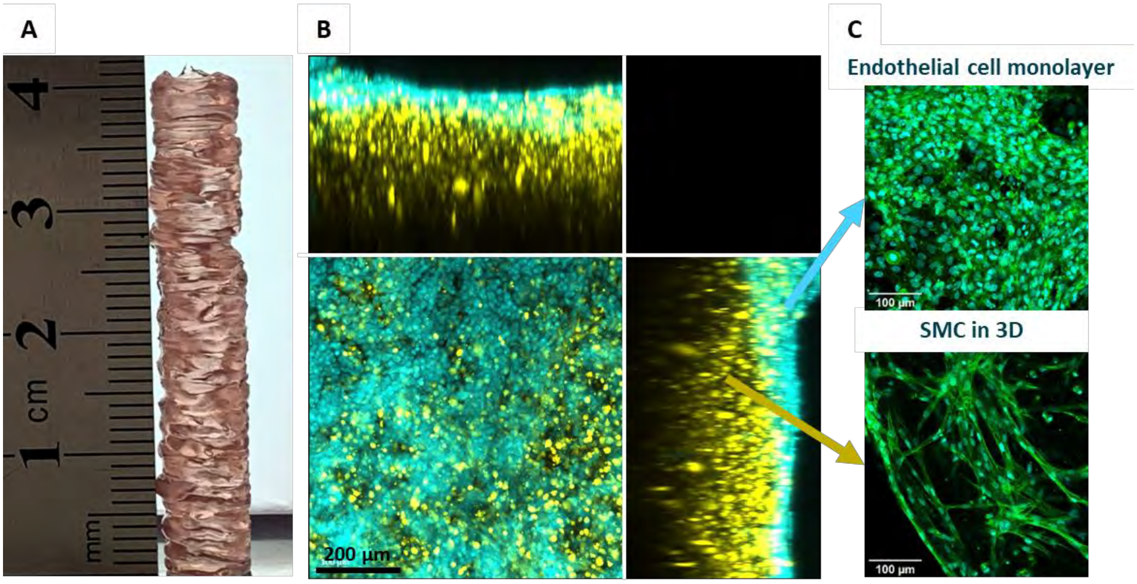

Figure 1. *Photograph of 3D printed cylinder of elastic extaernal layer bioink (**A**). Confocal fluorescence imaging of living cells (**B**) in the 3D printed model composed of SMCs (yellow) and endothelial cells (cyan). Actin and DAPI staining of the endothelial cell monolayer (left) and SMCs embedded in 3D.*

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Electrostatics in PNIPAm-based microgels: from two-step deswelling to polyelectrolyte adsorption

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Since their first synthesis PNIPAm microgels showed intriguing electrostatic properties due to the presence of the ionic initiator used to promote chain polymerization. A drastic increase of microgel electrophoretic mobility is systematically reported for temperature larger than the volume phase transition (VPT) temperature T_c as a consequence of the large increase of their charge density due to the particle collapse. This has raised many questions on the role played by electrostatics on the VPT itself, and on the adsorbing power and the flow properties of PNIPAm microgels when they are co-suspended with other charged species. Here we will summarize our recent findings in this field, showing first that PNIPAm microgel VPT is radically influenced by the residual charge born by these colloids [1, 2]: VPT always occurs in a two-step fashion, with the outer corona collapsing at temperatures larger than those marking the collapse of the inner core. Such a feature is general for this class of colloids, and it is amplified by the addition of charged co-monomers [2], such as acrylic acid.
The charge densification occurring above the VPT is also responsible for a large enhancement of the adsorption of oppositely charged species and we show that PNIPAm microgels have a "double-faced" electrostatic behavior [3]. Their low charge density at $T<T_c$ makes them nearly neutral colloids staying stable even when they are co-suspended with a highly concentrated oppositely charged polyelectrolytes (PEs) or nanoparticles, while they show typical features of charged colloids at high temperatures ($T>T_c$), with a large overcharging and a reentrant condensation characterizing their stability in presence of PEs or NPs bearing an opposite charge. Finally, we show that this phenomenology has also an important impact on concentrated suspensions of collapsed anionic PNIPAm microgels forming volume-spanning gel network, whose elasticity is first largely enhanced when the charge borne by the microgels is compensated by cationic PEs and then decreased by the onset of a large microgel charge overcompensation [4]. Strikingly, we find that also anionic PEs can be at least partially embedded in or adsorbed onto collapsed anionic microgels, causing an increase of the net charge of the so-formed complex and the melting of the original gel. Our study put forward the crucial role of electrostatics in thermosensitive microgels, unveiling an exciting new way to tailor the flow of soft colloids and highlighting a largely unexplored path to engineer soft colloidal mixtures.

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Effect of charge on the stabilization of water-in-water emulsions by thermosensitive bishydrophilic microgels

Do-Nhu-Trang Nguyen[1], Léa Waldman[2], Valérie Ravaine[2], Taco Nicolai[1], Lazhar Benyahia[1]
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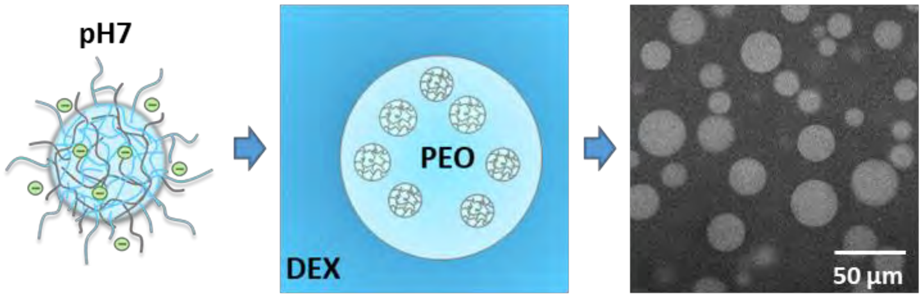
Water-in-water (W/W) emulsions are defined as mixtures of two immiscible polymer solutions, which tend to separate to form two distinct phases [1]. These emulsions cannot be stabilized by molecular surfactants, but can in some cases be stabilized by particles [2]. In recent studies, the bis-hydrophilic microgels of dextran (Dex) grafted with poly(N-isopropylacrylamide) (pNIPAM) gave promising initial results on the stability of W/W emulsions [3]. Their ability to stabilize is based on their respective affinity for each phase. In addition, the thermosensitivity of pNIPAM has an important effect on the stability [4]. Based on these particles, the aim of this study is to evaluate the effect of charge on the stabilization of W/W emulsions, formed by Dex and poly(ethyleneoxide) (PEO). To this end, acrylic acid groups were used to incorporated into neutral microgels during the synthesis. The charge density of the microgels could be modified by varying the pH or adding salt. The stability of the emulsion was assessed by using a centrifuge combined with turbidity measurement at room temperature and at 50°C. The structure of the emulsion was determined by a confocal laser scanning microscopy (CLSM). It is found that the presence of charge units rendered the stability of emulsion pH and salt sensitive, in addition to the thermosensitivity already observed for the neutral microgels. In particular, the equivalent neutral microgels stabilized the POE/Dex emulsion only at high temperature, whereas the charged microgels stabilized this emulsion both at low and high temperatures if more than 20 mM NaCl was added. The strong effect of temperature on the stabilization of P/D emulsion was also recovered with the charged microgels at low pH, but the emulsion destabilized after increasing the pH, in the absence of salt. It is clear that introducing a small amount of acidic units can be useful to control and manipulate the stability of W/W emulsions.



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Posters

Tuesday 23 May17:40 – 19:00

Thursday 25 May17:10 – 18:00

Multiplexed microfluidic setup for analysing emulsification and removal of triglycerides with surfactant solutions

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We demonstrate experimental approaches that will aid in predictively designing surfactant formulations of greater efficiency and sustainability, leading to a reduction in water and energy consumption and a lower environmental footprint. We examine the emulsification ability of model surfactants and mixtures, employing representative complex hydrophobic films, namely blends of triglycerides. We utilise microfluidic techniques, able to control the thermal and flow fields and quantify the removal process using a combination of experimental probes and process conditions.

We study the removal of triglycerides in a single microfluidic channel and then introduce ways to incorporate multiple channels in a single microfluidic setup, that is, multiplexing. Multiplexing in microfluidics enables multiple, comparative experiments, simultaneously within a small chip. We demonstrate that the microfluidic chip can incorporate tens and hundreds of channels in a single chip and then comparatively study the removal of triglycerides by varying the surfactant formulations in different channels. The model hydrophobic substrate, a combination of three triglycerides that mimics tallow, is deposited within microfluidic channels by capillary flow technique. The multiplexed setup consists of multiple outputs attached to reservoirs of surfactant solutions and a single input connected to a pump, where the single pump is pulling the solution, and between the input and output cleaning occurs in channels. Different pressure conditions were experimented with to realize a uniform flow in different branches of the multiplexed setup. This experimental setup enables efficient screen surfactant's molecular structure, mixture, and concentration for specific water hardness and process temperature, by varying a single parameter at a time and only utilising a small amount of materials.

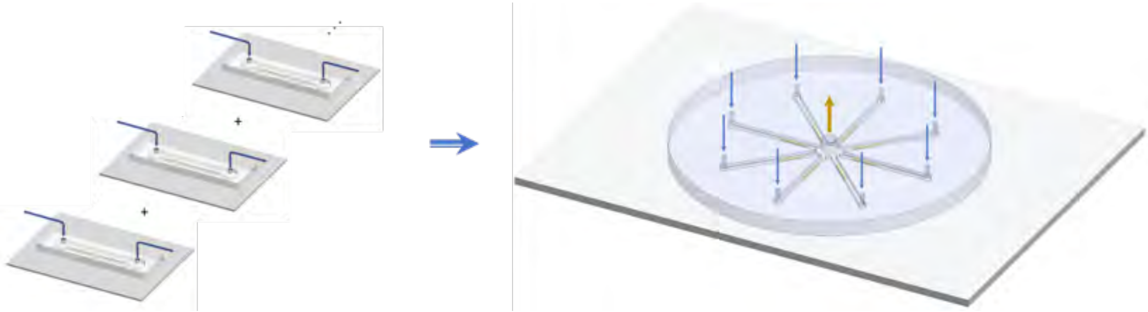

Figure 1: *Illustration of the multiplexed microfluidic chip that incorporates parallel channels in a single chip with multiple inlets and a single outlet. Different surfactant solutions flow in individual channels to efficiently screen the formulations for the removal of triglycerides from the substrate.*

On-chip observation of single-cellular biomechanics to monitor the progressive stages of cancer development and disease

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Characterised by the level of deformation under a particular given stress, cellular elasticity is a key differentiator between different cell types, with this heterogeneous cellular signature dependent on the ever-changing subcellular structures in each cell-division cycle, as well as their progressive disease states[1]. For accurate multivariate analysis of single-cell deformation between disease states, a high-throughput approach is required[2]. This hydrodynamic deformation of cells can be achieved through microfluidic-based methods, which have been demonstrated to detect stages of cancer development[2-4]. Characterised as “soft” when compared to healthy cells, diseased cells show increasing deformability towards cancer progression[5], allowing utilisation of this technique for possible identification of dysplastic cells, which may be undetected during current diagnostic methods.

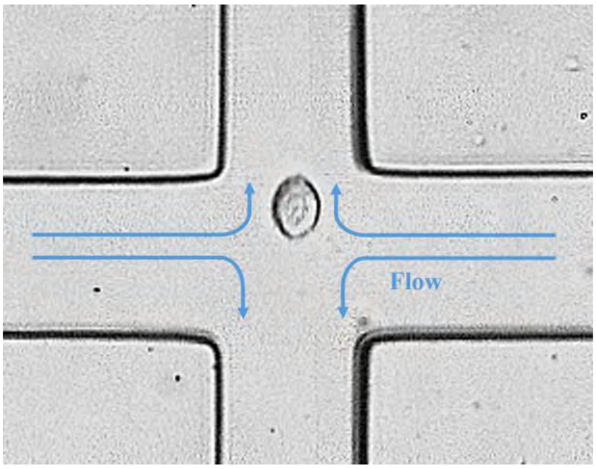

Figure 1: *A single non-dysplastic Barrett’s oesophagus cell deforming at the stagnation point of an extensional flow device.*

Barrett’s oesophagus is a pre-cancerous condition for oesophageal adenocarcinoma, with <1% of patients developing cancer for reasons unknown. Whilst cancer progression is currently monitored through healthy, non/low-grade dysplasia, and high grade dysplasia to cancer, each individual stage of dysplasia is hard to identify through traditional histopathology alone[6]. Through single-cell microfluidic deformation (Figure 1), we have characterised each stage of cancer progression using convolutional neural networks, demonstrating how features from deformed single-cell images can be used for classification with a 99% classification accuracy. This work not only allows identification of patients who are high-risk, but also presents a possible non-invasive diagnostic method for further aiding future diagnosis.

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Evolution and comparison of the physicochemical properties of new GMO-based contrast agents modified with Gd-chelating lipids

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Magnetic Resonance Imaging (MRI) is an advanced method that provides more accurate images compared to other diagnostic modalities. However, it is often necessary to use a contrast agent (CA) that, by interacting with water molecules in its close vicinity, will provide contrast enhancement in the region of the application, which in turn will increase the diagnostic value of the obtained image. Over the past four decades, many CAs have been developed for use in clinical practice, and some have already been withdrawn for safety reasons [1]. Currently, a particular focus is on obtaining high-relaxivity, Gd-based magnetic resonance imaging CAs of high biocompatibility. These may ensure lower dosing, which is especially important in view of the current safety concerns of Gd-based CAs [2]. Lipid nanoparticle-based CAs with embedded Gd-chelating lipids are considered to provide high-resolution and sensitivity MR imaging [3].

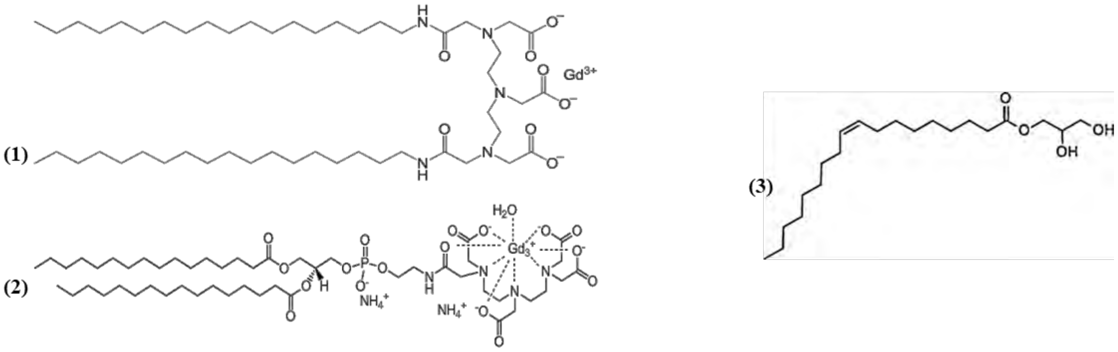

Figure 1: Chemical structures of Gd-chelating lipids: (1) DTPA-BSA (Gd), (2) DPPE-DTPA (Gd); and (3) GMO

The aim of the research was to develop novel MRI CAs based on GMO (glyceryl monooleate) lipid nanoparticles loaded with Gd-chelating lipids. Here we investigated systems with two different high molecular weight Gd-chelating lipids: DTPA-BSA (Gd) and DPPE-DTPA (Gd). The effect of the lipid type on the physicochemical properties of obtained nanoparticles and finally MRI contrasting properties were studied. The relaxation times measurements and MR imaging results indicated that more efficient was system GMO/DTPA-BSA (Gd). Thus, it could be concluded that this type of lipid-based nanoparticles could be a very promising type of CAs, which due to its other advantageous properties could be used for the development of systems combining diagnostics and therapy functionalities.

Acknowledgments

The work was supported by the research grant Sonata Bis 2016/22/E/ST/00458 from the National Science Centre and DWM/WPC2/285/2020 funded by the National Centre for Research and Development

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Liquid-Liquid Phase Separation of the Myelin Basic Protein

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The myelin basic protein (MBP) is a key player when it comes to the formation of tight membrane wrapping around vertebrate's nerve cells [1]. In physiological conditions, MBP is acting as a glue that stacks multiple myelin layers to build up an insulating sheath which covers axons. To accomplish this task, MBP undergoes a so-called Liquid-Liquid Phase Separation (LLPS) - a property which has recently attracted wide attention in the biological and biophysical community. In a LLPS, two liquid phases with different protein concentrations and physio-chemical properties coexist. Damaged integrity of human MBP and the consequent lack of LLPS capability often results in neurodegenerative diseases such as, for instance, Multiple Sclerosis.

Although the importance of its ability to perform a LLPS is already known, the kinetics of MBP's phase separation are not well studied yet. Hence, we focus on investigations that follow the formation of liquid-like MBP droplets which can be observed when suitable conditions are applied. To examine both the nucleation and the growth of those µm-sized condensates, we combine imaging techniques and (neutron) scattering experiments: Confocal microscopy of labelled MBP has confirmed the phase separation and provided information about the droplet size distribution. These finding we compared to Small Angle Neutron Scattering (SANS) experiments. Microfluidic experiments where combined with high-speed camera imaging in order to obtain details about the nucleation kinetics. Complementary, a stopped flow setup was used for Time Resolved (TR-SANS) experiments to support the previous results and to determine the growing droplet size within low second to early minute time-scale *in situ*. For long term droplet growth, Dynamic Light Scattering (DLS) yielded a $t^{1/3}$-dependent growth which indicates Ostwald ripening as dominating mechanism.

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Functionalized Cellulose Nanocrystals as nanomechanical antimicrobials

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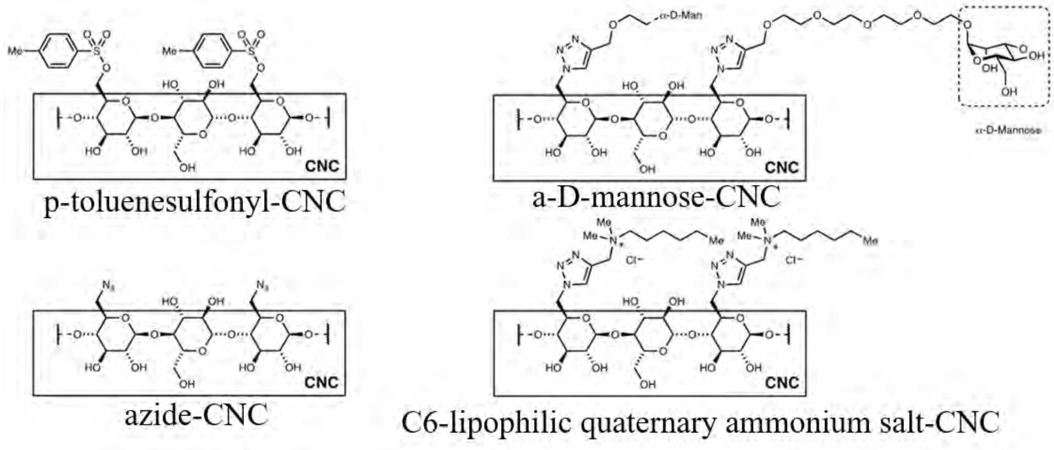
The upsurge of antimicrobial resistance (AMR) has become one of the greatest and most urgent global risks to human and animal health nowadays, which may severely impact future human development. Mechano-bactericidal action of nanostructured materials constitutes a novel path to overcome such threat[1]. In this sense, cellulose nanocrystals (CNCs) can be a promising candidate[2] depending on their geometry and surface ligands as a potential antimicrobial agent, which mechanism consists of selectively binding to bacteria and mechanically disrupting their cell membrane leading to their elimination. The aims of this work were to evaluate the antimicrobial effect of aqueous suspensions of functionalized CNCs against *Escherichia coli* ATCC 25922 (Gram-negative) and *Staphylococcus aureus* ATCC 12600 (Gram-positive) bacteria, and to study their possible toxicity on the J774A.1 murine macrophage cell line. The CNCs (Nano Crystalline Cellulose NCC™, CelluForce) were functionalized through the addition of specific ligands: p-toluenesulfonyl-CNC, azide-CNC, a-D-mannose-CNC, and C6-lipophilic quaternary ammonium salt-CNC (Figure 1), and 1% wt suspensions were prepared in MilliQ water. The antimicrobial activity of these samples was assessed on planktonic bacterial cells through the determination of Minimum Inhibitory Concentration by broth dilution method and calculating the viable cells by counting the CFU /mL, while measuring of inhibition growth halos was assayed on LB Agar plates. Antibiotics Ampicillin and Vancomycin were used as positive controls for antimicrobial activity against *E. coli* and *S. aureus*, respectively. Additionally, quantification of the enzyme Lactate dehydrogenase (LDH) on J774A.1 murine macrophages was performed as a measurement of cell death, linked to the toxicity of the samples to this eukaryotic cell model.



p-toluenesulfonyl-CNC

a-D-mannose-CNC

azide-CNC

C6-lipophilic quaternary ammonium salt-CNC

Fig.1. *Functionalized CNC samples.*

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Using many-body dissipative particle dynamics to predict the properties of surfactant systems

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Dissipative particle dynamics (DPD) is a coarse-grained simulation method, which can be used to study soft matter systems which require long simulation times and length scales, i.e. well beyond those accessible to molecular dynamics. However, a disadvantage of DPD is that the bead density of a system is roughly constant across a domain, leading to an inability to simulate vapour-liquid interfaces. This led to the development of many-body dissipative particle dynamics (MDPD), which allows density to vary across a system, allowing surface tensions to be calculated and improving the description of interfaces in soft matter systems. However, because of coarse graining, the parameters used in calculating force are not directly related to the molecular scale; therefore, one requires a parameterization to map beads to real systems.

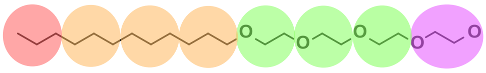

Figure 1: *Surfactant molecules (e.g. C12E4) are coarse-grained into 'beads'.*

In this work, we present a new parameterization scheme for MDPD simulations based on experimental surface tensions, densities and chemical potentials. The parameterization is tested via application to various mixtures and surfactant solutions, and by comparison with experimental studies. We perform an in-depth study of nonionic polyoxyethylene alkyl ether surfactants, as well as zwitterionic surfactant lauryldimethylamine oxide, at the air/water interface. In particular, the influence of the number of ethylene oxide units in polyoxyethylene alkyl ether surfactants is investigated.

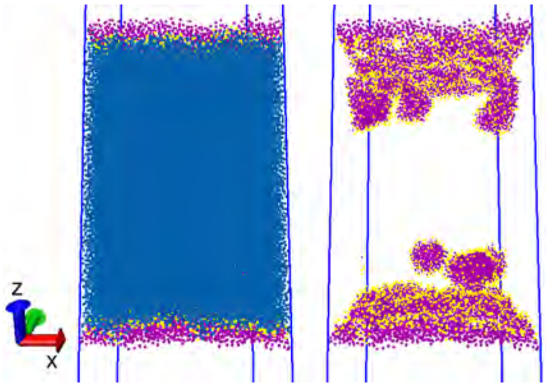

Figure 2: *Overpacked surfactants at an air/water interface will be removed into the bulk to form micelles.*

We show that our scheme correctly predicts surface tension as a function of surface coverage, together with surface phase transitions. Aspects of behaviour which are difficult to study experimentally, such as conformation and packing, are studied in detail, providing insight into the nature of water-surfactant interfaces. Additionally, key properties of micellar systems (such as CMC, aggregation number, micelle shape etc.) can be readily determined.

Understanding dispersions of insoluble particles in non-aqueous media

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Non-aqueous dispersions are utilised in a vast range of applications such as paints, coatings, drilling fluids and also confectionary products. Controlling the dispersion of solid particles in less polar media such as oils is challenging, particularly when the particle is hydrophilic in nature. Although techniques such as emulsification and surface modification have been demonstrated as effective methods to prepare such non-aqueous dispersions, direct dispersal of such particles into non-polar media remains a difficult task. This work has set out to evaluate physical techniques to aid the dispersion of hydrophilic particles in various oil phases and to gain a mechanistic understanding of this behaviour. The behaviour of silica nanoparticles (primary particle size ca. 20 nm) with different degrees of covalent hydrophobic surface modification (35% to 70% silanol content relative to that of unmodified silica) was studied using rheological techniques. Silica particles considered to be hydrophilic (more than 50% of the particle surface is unmodified) formed structured aggregates even at very low (< 1 vol.%) volume fractions, that was more marked the more non-polar the oil. However, pre-wetting these more hydrophilic particles with ethanol, a higher polarity solvent, led to an order of magnitude reduction in the viscosity and elastic moduli, presumably due to hindering of network formation. Addition of certain food-grade oil-soluble dispersants such as triacetin also aided dispersion of the more hydrophilic particles at low volume fractions (< 2 vol.%) in hydrophobic oils. There is potential to apply these findings to promote the dispersion of more complex hydrophilic particles in a range of complex oily phases.

Investigating silk fibroin and cellulose interactions at differing length scales

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Silk fibroin and cellulose are two commonly available polymers capable of forming composites with numerous desirable properties including: biocompatibility, high mechanical performance, biodegradability, and others. Using ionic liquid solvent systems to overcome 'raw' material insolubility, previous research has indicated silk fibroin and cellulose can blend at a molecular level and form regenerated films with superior properties to pure cellulose or silk samples[1]. Natural raw fabrics of these molecules utilise hierarchical secondary structures which contribute to material properties far in excess of regenerated films. For example, silk films are often brittle while silk fibres are strong and stretchy[2].

By utilising partial dissolution, we retain secondary structures while forming a strong and highly compatible matrix to bond silk and cotton fabrics into a single biocomposite. This requires a deep understanding of polymer and polymer blend behaviours at different lengthscales and interfaces to control this procedure adequately. This study investigates and provides quantitative data about the properties of novel cellulose/silk fibroin materials, in so presenting a new class of self-reinforcing hybrid biocomposites. Anisotropic reinforced hybrid composites were seen to achieve material properties comparable to those of all-cellulose composites with a Young's Modulus, ultimate strength, and elongation at break of 2.11 ± 0.05 GPa, 31.1 ± 0.6 MPa, and 3.0 ± 0.2 % respectively.

Investigations into different polymer systems with differing lengthscales of reinforcement enables understanding of these systems. Fully dissolved and regenerated films, films reinforced with isotropic fibres, and laminates reinforced with anisotropic woven textiles are compared. Samples were characterised by wide angle X-ray scattering, optical microscopy, tensile testing, thermal characterisation, and infrared spectroscopy to indicate material behaviours and morphology.

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Thermoplastic liquid crystal elastomers for 3D-printing

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Stimuli-responsive and active materials that show a mechanical response to external stimuli have potential in novel actuators, e.g., in soft robotics or sensing. Especially liquid crystal elastomers (LCEs) offer programmable shape morphing in response to various triggers, e.g., temperature, light, and electric fields. The shape change directly depends on the inner structure, determined by the domain and crosslinking topology that conventionally is fixed in the preparation process. [1, 2] In 3D-printing, suitable mesogenic oligomers are extruded using heat-assisted direct-ink writing (HOT-DIW) and crosslinked using UV-curing at the printing nozzle. [3] Unfortunately, most of these materials suffer from high operation and stimulation temperatures. Our strategy is to develop a thermoplastic liquid crystal elastomer based on ionomeric physical crosslinks that can be reshaped and remodeled repeatedly. The reversibility of ionomer-based crosslinks is useful, e.g., in thermoplastic or even self-healing elastomers. [4]

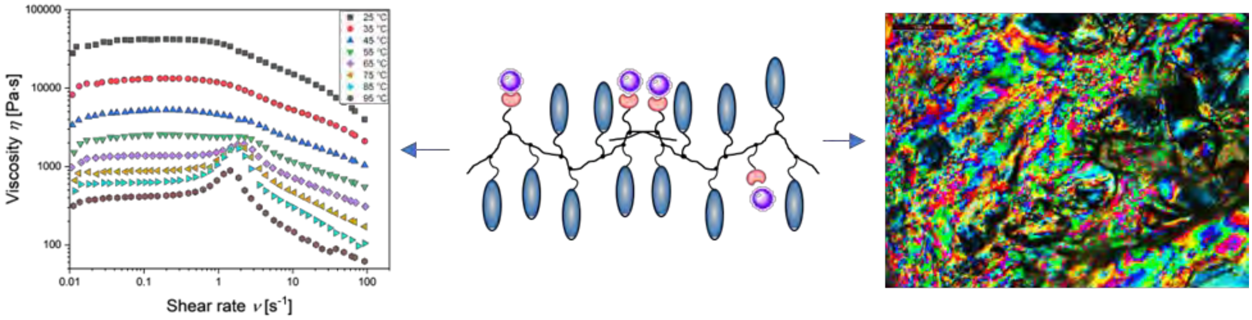

Figure 1: *Schematic view of a liquid crystal ionomer, mechanical properties and nematic order*

For this, polysiloxane-based liquid crystal ionomers are developed that contain nematic side chains and up to 15 % of carboxylate ionic groups. Properties of these materials can be tailored with the molar mass of the PHMS backbone and the grafting degree with the liquid crystal as well as the acid. Neutralization using different transition metal acetates leads to physically crosslinked networks and elastomeric behavior. We present data on the control of the tailored polymers, measured by NMR, GPC and IR, as well as data on the mechanical and thermal behavior by rheology and differential scanning calorimetry (DSC). The shown properties a promising starting points for the development of thermoplastic liquid crystal elastomers.

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Surface functionalization of hyaluronic acid-based hydrogels – a way for efficient drug delivery

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Hyaluronic acid is a biologically active glycosaminoglycan biopolymer that is primarily found in the extracellular matrix. Being nontoxic, reproducible and biodegradable, this biopolymer moreover can be characterized with unique physicochemical and biological properties, including receptor-specific binding, and the capacity to control macrophage activation through the hyaluronic acid's cell-surface receptors in order to modulate inflammatory responses. [1,2]

There are still quite a few of challenges connected with utilizing hydrogels, including the hyaluronic acid, to deliver biologics. The simple fact that water occupies up the majority of a hydrogel's volume is the first and fundamental problem. This results in a comparatively small volume to encapsulate biologics, which is a significant factor. Furthermore, the hydrophilicity of hydrogels frequently leads to burst release kinetics of biologics that are encapsulated. By adjusting the biologics to attach the hydrogel backbone or by encapsulating the biologics in an alternative form of delivery that can better control release rate. [3] Hyaluronic acid is being frequently examined to serve in medicine, pharmacy or even cosmetics industry. As explained before, there is a great need for a simple functionalization methods in order to acquire desired properties, for example appropriate hydrophobicity (for longterm and target-specific delivery of drugs), viscoelastic properties (to serve as injectable materials), thermoresponsivity (to be able to undergo a sol-gel transition by raising the temperature if a thermo-responsive moiety with a lower critical solution temperature is grafted onto it). [3,4]

In this work, we present efficient ways for hyaluronic acid functionalization in three ways in order to fain the previously explained functionalities. In this way, β-cyclodextrin-, litocholic acid-, and pNIPAM (poly(N-isopropylacrylamide))- functionalized hyaluronic acid hydrogels were prepared and characterized.

Acknowledgements

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The after drying fate of an imbedded water droplet within polydimethylsiloxane PDMS

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Due to their ample area of applications, porous polymers received a great attention from the scientific community. These materials are widely known as very good candidates for thermal and acoustic insulation. Recently, many attempts for energy saving have been developed to create a dynamic soft matter which can be alternated between porous and non-porous state.

In the present work, we report on the drying of water droplets embedded within polydimethylsiloxane (PDMS) which is composed of a pre-polymer and a crosslinker with a mixing ratio of 10:1. Using a self-made microfluidic system based on the principal of coflow, highly monodisperse emulsions (polydispersity <2%) are synthesized with different droplet radii ranging from 20μm to 300μm.

Following the crosslinking process, cavity contraction is observed upon the evaporation of the embedded droplet. By the end of drying, the droplet vanishes and two scenarios can occur. Either the cavity collapses permanently leading to drastic changes in the mechanical and optical properties, or it reopens with the same initial size.

Our statistical analysis show that, among several variables, the initial radius of a droplet as weil as the drying temperature play a primordial role to predict the behavior of a cavity. At cavity radii higher than 30μm, an opening is observed regardless of the drying temperature. At cavity radii lower than 30μm the temperature is required to be high enough (>60°C) to maintain the opening behavior. In case of small cavity and low temperature the cavity remains collapsed.

To explain this, a comparison between the strain energy within the PDMS, that tends to reopen the cavity, and the adhesion energy of the cavity walls, that tends to keep it collapsed, is considered. Using finite element simulation, we show that in case of large cavity radius ($> 30\mu$m) the strain energy overcomes the adhesion energy while the inverse is found in case of smaller cavity.

Investigations of optical absorption by liquid crystals doped by carbon nanotubes

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Beam colouring effects traversing a different light-scattering medium based on liquid crystals experimental investigations are presented. It was first time shown that the result of the beam colouring at the medium output depends on the singly forward scattered partial signals phase delays magnitudes. Colouring effects spectral investigation has been carried out using both nematic liquid crystals with carbon nanotubes and the solution of liquid crystal in a polymer matrix which was previously investigated. The non-scattered and the singly forward scattered interfering components amplitude ratio significantly affects the colour intensity in both samples. It has further been established that the spectral content of the illuminating beam strongly influences the colour of the resulting radiation. The colouring effect significant increase has been achieved due to the injection of carbon nanotubes, as well as the sensitivity of the liquid crystal to the control electric field has increased.

met.

Flexible biocompatible chitosan-based films for the development of smart electronic sensors

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The development of materials and technologies in line with the logic of circular economy appears crucial for the generation of environmentally and economically sustainable production processes [1]. In this study, we present a green, low cost and simple to implement method to produce flexible, biocompatible and biodegradable films of chitosan and chitosan-glicerol. The films consist of chitosan films obtained fish product waste trough simple and safe chemical processes. Chitosan is obtained by means of a partial deacetylation process of chitin which involves alkaline hydrolysis of the acetamide groups of chitin. Chitin is the second most abundant natural polymer in nature and plays a fundamental structural role as component of the exoskeleton of crustaceans and arthropods and of the cell walls of fungi and yeasts. Chitin extraction process involves the phases of: demineralization, deproteinization and discoloration [2]. The solvent casting production method developed using an automatic applicator yields films with highly controlled thicknesses. Atomic Force Microscopy (AFM) analysis demonstrates the high homogeneity and low roughness of the films (on the order of a nanometre). Moreover, biocompatibility and antibacterial tests proved their suitability in applications where they have to work directly in contact with the human body or foodstuffs.

By modifying the composition of the starting solutions through the addition of plasticisers or crosslinker, it is possible to finely modulate the mechanical and solubility of the composite films [3]. For example, with epidermal electronics applications in mind, it has been possible to produce insoluble films with a Young's modulus value close to that of human skin [4].

Using piezoelectric characterisation methods in Piezo Force Microscopy (PFM), a useful technique for detecting and quantifying the piezoelectric properties of the chitosan-based films produced was developed in this study [5]. This result paves the way for the potential use of the films as an active piezoelectric substrate in electromechanical sensors/ actuators and in the field of energy harversting [6].

On the basis of these observations and in view of the high capacity of the matrix to incorporate substances of different natures with excellent degrees of dispersion, homogeneity and uniformity, it is reasonable to envisage the forthcoming use of chitosan-based composite films as active or passive substrates that could be applied in the production of flexible biocompatible sensors in the smart monitoring field [7].

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Single particle tracking of heterofunctional active nanostructures in magnetic fields

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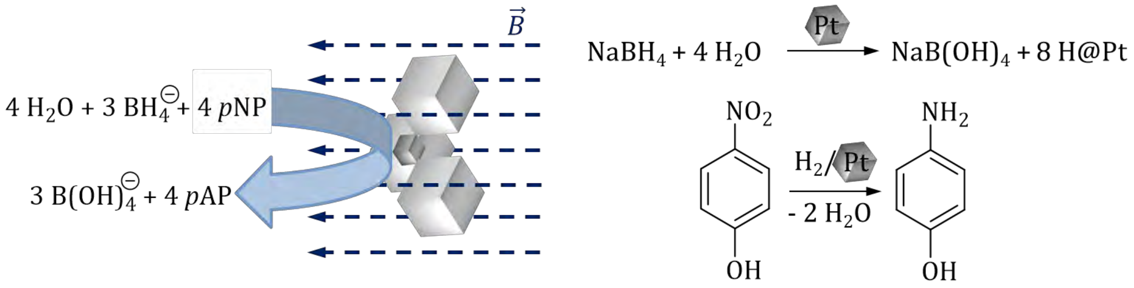
Micro- and nanomotors are small autonomous devices that are capable of performing complex tasks, powered by external forces. Chemically powered nanomotors use the catalytic decomposition of a "fuel" available in their environment. An appropriate break in symmetry is required to create an asymmetric flow field in the vicinity of the nanostructure that leads to propulsion. [1]



Scheme 1: Schematic illustration of the self-diffusiophoretic propulsion of P3.

Investigating the diffusional behaviour of a nanomotor is essential for understanding and thus optimising its design. As shown in Scheme 1, the approximately 20 nm large system of this work consists of a platinum cube that is occupied by three bigger cobalt ferrite cubes on its corners ($[CoFe_2O_4]_3@Pt$ = P3). While the Pt acts as catalyst in the reduction of *para*-nitrophenol (*p*NP) to *para*-aminophenol (*p*AP) in the presence of borohydrides, the $CoFe_2O_4$ cubes are magnetically blocked and allow for a "magnetic railing".

The main tool for the investigation of the diffusional properties of the particle system in water is Single Particle Tracking by Dark-Field Light Scattering Microscopy (SPT by DF-LSM). With this method, the motion of individual particles is recorded and tracked. Based on these data, important diffusional parameters can be calculated, such as the time-dependent mean squared displacement $MSD(t)$, the translational diffusion coefficient D and, for driven systems, the preferred directionality, the drift velocity v, the rotational relaxation time τ_R, average track lengths and many more.

We show that under optimised conditions, superdiffusion and even preferred directionality of the active particle system is observed. It is shown that the rotational relaxation time and thus the self-diffusiophoretic effect increase with stronger external magnetic fields.

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Cell motility in bacteria biofilm: An active bio soft matter approach

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Bacterial biofilm has a significant impact in many industrial and biomedical applications due to sanitay hazard and bio-fouling phenomena. Biofilm related issues were also founded abroad the International Space Station (ISS) leading to equipments loss of funtion [1].Biofilm formation and bacterial motility are influenced by a range of environmental factors, including flow and gravity[2, 3]. In this study, we proposed a methodology to quantitatively characterize bacterial motility under different laminar flow conditions, using *Pseudomonas fluorescens* AR11as a model organism. A microfluidic setup was developed based on a commercial microfluidic channel (Ibidi). We monitored sample evolution through time-lapse microscopy and bacterial motility was quantified by measuring bacterial trajectories through image analysis. Our results showed that flow has a measurable effect on bacterial motility, which can influence biofilm formation. This study provides a basis for the development of strategies for biofilm control in flow.

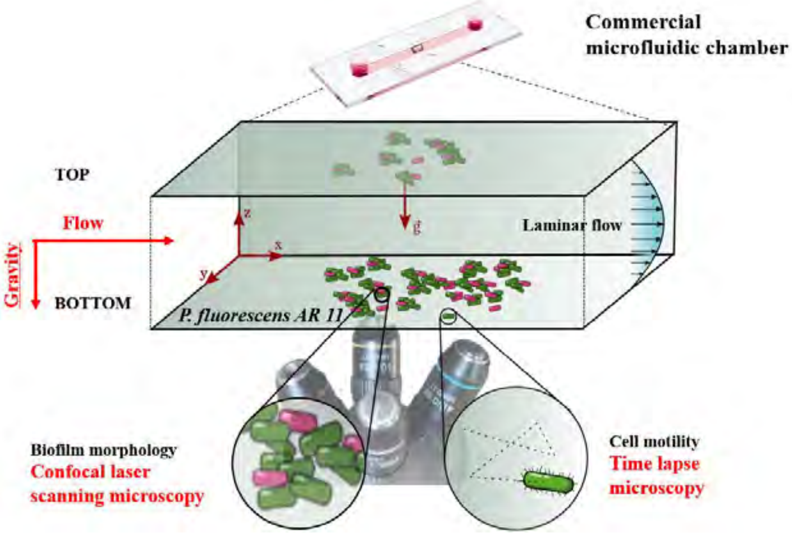

Fig.1 Schematic representation of the experimental setup.

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Manufacture of highly open macroporous cryogel beads with tunable pore size using microfluidics for cell culture

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In vitro culture is an important step for many tissue engineering strategies and for the differentiation of stem cells into patient-specific cell types. Despite great progress in the field, e. g. to produce and culture cardiomyocytes, there is still a lack in soft, elastic cell culture matrices that both can integrate with the surrounding tissue and enable the production of a large number of cells.[1] One way to achieve this goal is the synthesis of polyacrylamide cryogel beads via a droplet-based microfluidic approach. In this approach, sub-milimeter droplets of a water-based polymerisation mixture are formed and polymerized under cryoscopic conditions (cryopolymerisation), resulting in spherical beads with a highly porous structure. Due to the porosity, the beads show a large surface for cell attachment, and by populating the interconnected pores, 3D tissue structures become accessible.[2]

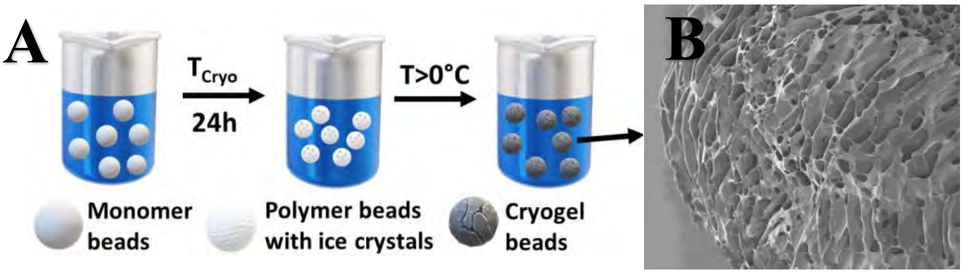

Figure 1: Schematic diagram of the copolymerization process (A) and SEM Image of the cryogel bead (B).

By changing the synthetic parameters, temperature and ionic strength, the bead production is optimized and the influence on the pore size is investigated. As a result, we found out that it is possible to finetune the pore size via three independent experimental parameters. Following this strategy, we envisage tissue matrices based on porous hydrogel beads to serve as versatile intermediates for the design and assembly of more complex tissue and organoid structures.

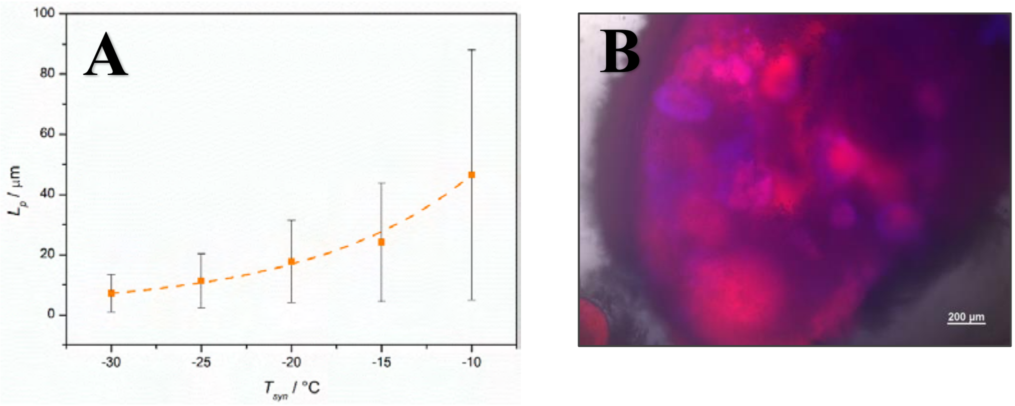

Figure 2: Pore length L_p of the cryogel beads at different T_{syn} (A) and successful cultivation of hiPSC on the surface of the cryogel bead (B).

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Long-range attraction of picolitre sessile drops

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Sessile droplets containing a binary mixture have been shown [1] to attract each other over long distances (>3x diameter) on a hydrophilic substrate if one component is both more volatile and has a greater surface tension. Our droplets were 110µm in diameter and made up of ethylene glycol and water, a mixture common to many inks. We expect this interaction may have relevance to issues found in inkjet printing, i.e. colour bleeding, non-uniform deposition. We have analysed the speed of the droplets approach and found power-law behaviour. We found that as the initial distance between the droplets is varied, that their speed of approach changes. We believe that this is due to the evaporation of the drop over the course of the interaction. We found that size of the droplets does not seem to affect their speed of approach, but initial composition does.

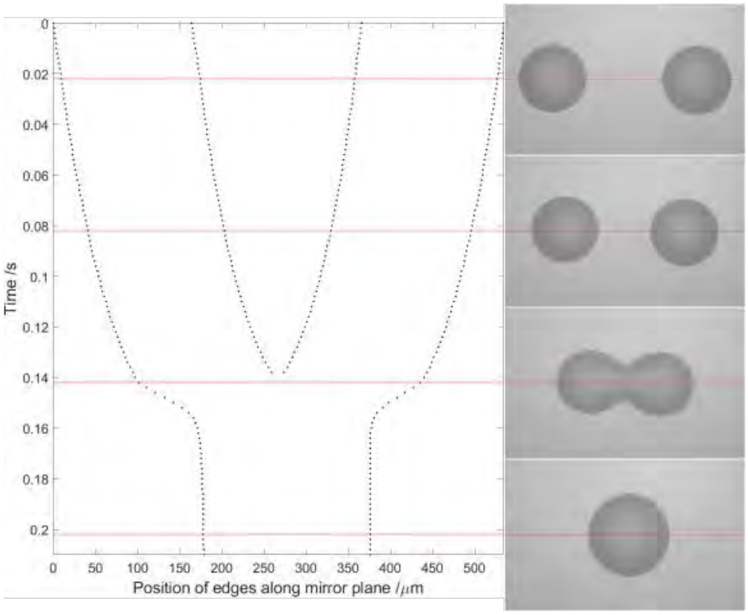

Figure 1: *Two 5.6wt% aqueous ethylene glycol drops attracting each other on a smooth hydrophilic substrate.*

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Contactless Interfacial Rheology

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Interfacial rheology is crucial for understanding material properties including the stability of Pickering-Ramsden emulsions or foams. The vast majority of measurement methods use a (macroscopic) probe directly attached to the interface. The presence of this probe can disturb the interface, and it couples to flow in the bulk phase, limiting measurement sensitivity. We have developed a contactless interfacial rheometric method to perform interfacial shear rheology on liquid/liquid interfaces without any tool attached directly to the interface [1]. This is achieved by shearing the top liquid phase and measuring the interfacial response via confocal microscopy. Using this method we have measured steady shear material parameters such as interfacial viscosities for fluid-like interfaces and interfacial elastic moduli for interfaces with solid-like behaviour. We have verified the accuracy of this method *vs* a double-wall ring geometry. Moreover, exploiting the enhanced sensitivity, achieved by having no probe attached directly to the interface, we are able to measure relatively low interfacial viscosities compared to a double-wall ring geometry. An additional advantage is the simultaneous combination of macroscopic quantitative rheometry with microscopic quantitative structural analysis. Our analysis directly visualizes how particle surface coverage and interfacial particle assembly strongly affect the interfacial response. Furthermore, we can monitor the evolution, including irreversible changes in the particle assembly, that corresponds with the rheological response to steady shear.

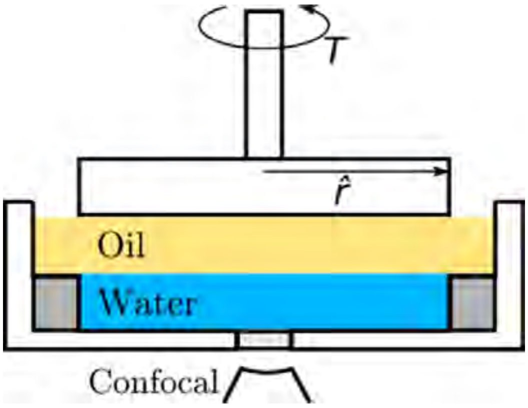

Figure 1: *(left) Schematic of set-up for contactless interfacial rheology. (right) Confocal micrograph of micron-sized interfacial particles.*

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Virucidal properties of a conical Si-substrate

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In the present work the virucidal effect of Si-nanocone array is investigated. The studied mechanical interaction relies on the Van-der-Waals forces that affect the virus‘ capcid when its surface is attracted to the Si-nanocone array. Such a virucidal action of nanostructured materials is a promising example of a multiple-use virus protecton by utilising nano-etched surfaces. For the modeling of the structural contact we use finite element method (FEM) performed by Comsol software. Geometrically, the virus is represented by a hollow sphere with 90[nm] outer and 60[nm] inner radius with structural dominance of the virus' capsid; see [1]. The Si-cones have height of 289[nm], top/bottom radii of 5[nm]/52.5[nm], respectively, and gaps between the tips of 62[nm]. The linear decrease of the thickness of the Si-cones affects the stiffness of the materal, see [2]. Thus, the lower part of the array has higher E=140[GPa] while the upper parts have lower E=60[GPa]. The attractive Van-der-Waals force is defined as sphere-sphere interaction, see [3], for the case where one of the spheres is much smaller than the other: $F_{vdw}=\pi^2\rho^2AR/6d$, where A- Hamaken constant in the order of 10^{19}[J] [3], R- the tip‘s radius of the pillars, 5[nm] and d- the distance between the surfaces of interaction. Using these parameters a Comsol simulation was built which resultsed in the following figures that describe the virus-substrate interaction.

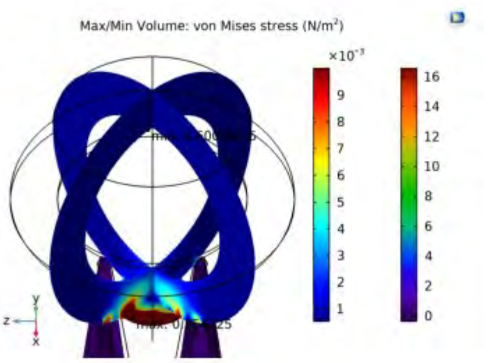

Fig.1. *Sstress distribution and stress maximum inside the virus.*

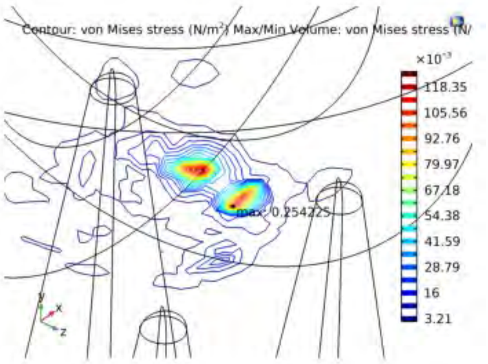

Fig.2. *Stress isolines and stress maximum along the virus surface.*

We were able to simulate nondestructive (to the virus) equilibrium that results from the VdW forces between the virus and the Si-surface. It shows a stress accumulation at the bottom part of the spherical surface of the virus‘ capsid in between the Si-pillars; see Fig.1 and Fig.2. This result prescribes the area of the capsid where the virus rupture is expected when the full scale forces are applied.

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The creation of water-in-oil Pickering emulsions for droplet-stabilized GUVs

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Emulsions are dispersions where one immiscible liquid phase is dispersed within another with an interfacial boundary. While emulsions are typically produced using surfactants, the self-assembly of nanoparticles on the emulsion interface can be used to produce Pickering emulsions. The self-assembly of the nanoparticles at the interface results from the balance between interparticle forces and the physical barrier they create at the interface. Giant unilamellar vesicles (GUVs) are spherical monolayers of lipids that form a vesicle. From a mechanical perspective, GUVs exhibit size characteristics akin to natural cells, with dimensions largely determined by the chosen method of fabrication; GUV radii span from a few microns up to just under 100 µm. [1-2] GUVs outshine other cell mimics, as lipid vesicles have a variety of physical properties that mirror the deformation response of natural cells. In this work, we use emulsion droplet stabilization to define the GUV dimensions. This work is part of a larger project to create artificial blood substitutes by using Pickering emulsions and silica nanoparticles to template droplet-stabilized giant unilamellar vesicle surfaces. A challenge in this project is to create a stable uniform Pickering emulsion with silica functionalization for droplet stabilized GUV templating.

First, to create uniform emulsion droplets, microfluidic chips were synthesized to create droplets of 10-100 µm (on the magnitude of real blood cells), dependent on the flow-focusing restriction used and the flow rate. Secondly, we have investigated preliminary nanoparticle functionalization strategies using interfacial rheology on an oscillating pendant drop tensiometer to determine interfacial elasticity, surface tension, and surface silica density to understand the physical parameters governing emulsion stability by applying a dilatational deformation. This data was also paired with complimentary light and confocal microscopy to understand better the silica localization in the system and the coalescence.

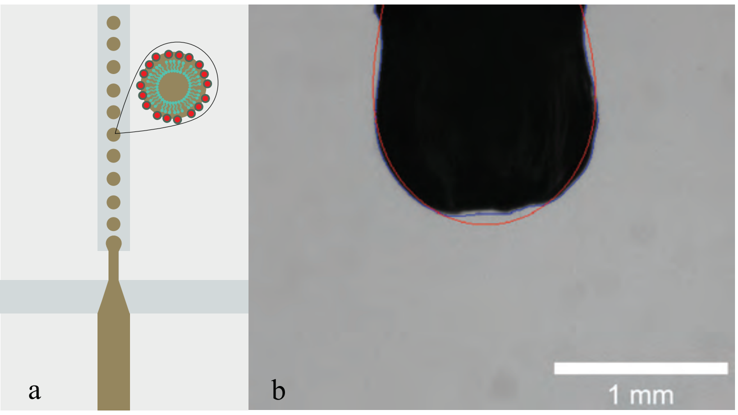

Figure 1: *a) Sketch of Microfluidic production of droplet stabilized GUVs within the water in oil Pickering emulsion. b) pendant drop measurement illustrating solidification/wrinkling of the interface with Young–Laplace fit versus actual to study interfacial properties.*

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Molecular Scope: watching macromolecular dynamic at solid-liquid interfaces at the single-chain level

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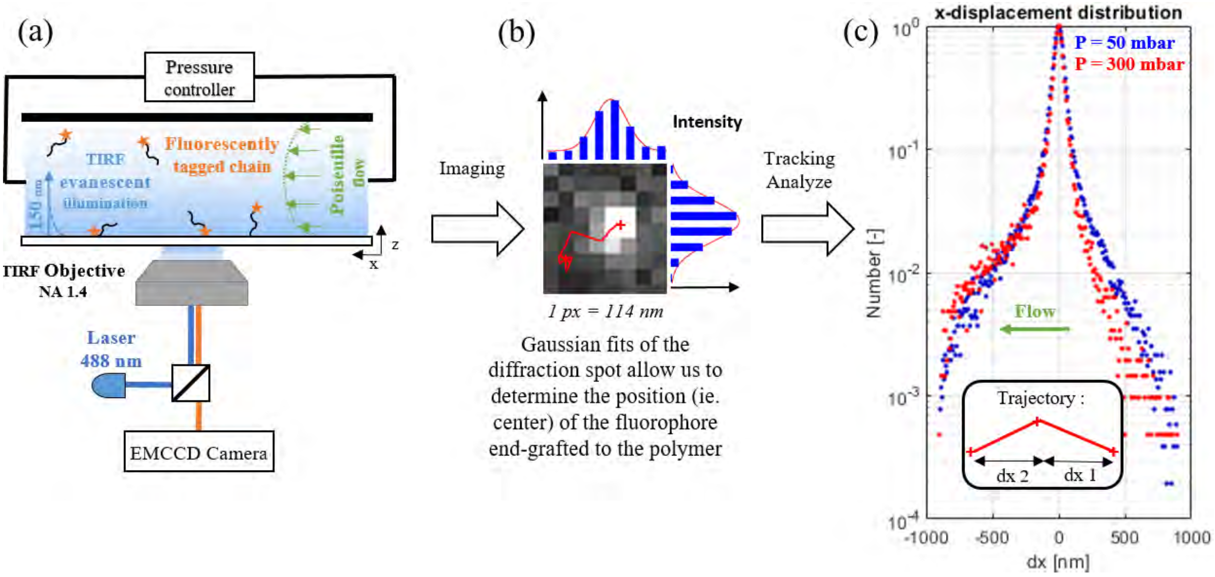
The dynamics of macromolecules at solid-liquid interfaces is key to a number of surface phenomena such as functionalization, transport in porous media or friction. In the recent years, novel single-molecule microscopy techniques based on total internal reflection fluorescence microscopy have allowed to probe the in-plane equilibrium diffusion dynamic of macromolecules at the single chain level. These experiments revealed heterogeneous surface motion characterized by periods of immobilization at the surface followed by long desorption-mediated jumps [1, 2], in strong contrast with the traditional vision of Brownian-like macromolecular diffusion at interfaces.



Gaussian fits of the diffraction spot allow us to determine the position (ie. center) of the fluorophore end-grafted to the polymer

Figure 1: *(a) Experimental set-up used to probe single-chain dynamics under flow. (b) Typical diffraction-limited spot, allowing for nanometric localization of the chain position. (c) Single-chain displacement for two distinct flow conditions*

Here, we couple microfluidics with our single-molecule set-up to bring these approaches towards out-of-equilibrium situations and probe the subtle interfacial couplings arising between flow and macromolecular transport at solid/liquid interfaces. We probe in particular the effect of solvent flow on the statistics of macromolecular interfacial trajectories in dilute solutions. Upon increasing flow rate, we observe a skewed distribution of interfacial displacements, due the symmetry-breaking effect of the convective flow. Analyzing macromolecular surface transport as a succession of transport and jumping events, we probe in detail the effect of the flow on the adsorption and near-surface transport. Comparing hydrophobic and hydrophilic surfaces, we further evidence distinct flow-induced dynamics, which we ascribe to a surprisingly strong effect of interfacial hydrodynamics on macromolecular adsorption. We expect our approach to bring a new molecular vision of macromolecular friction at solid/liquid interface.

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