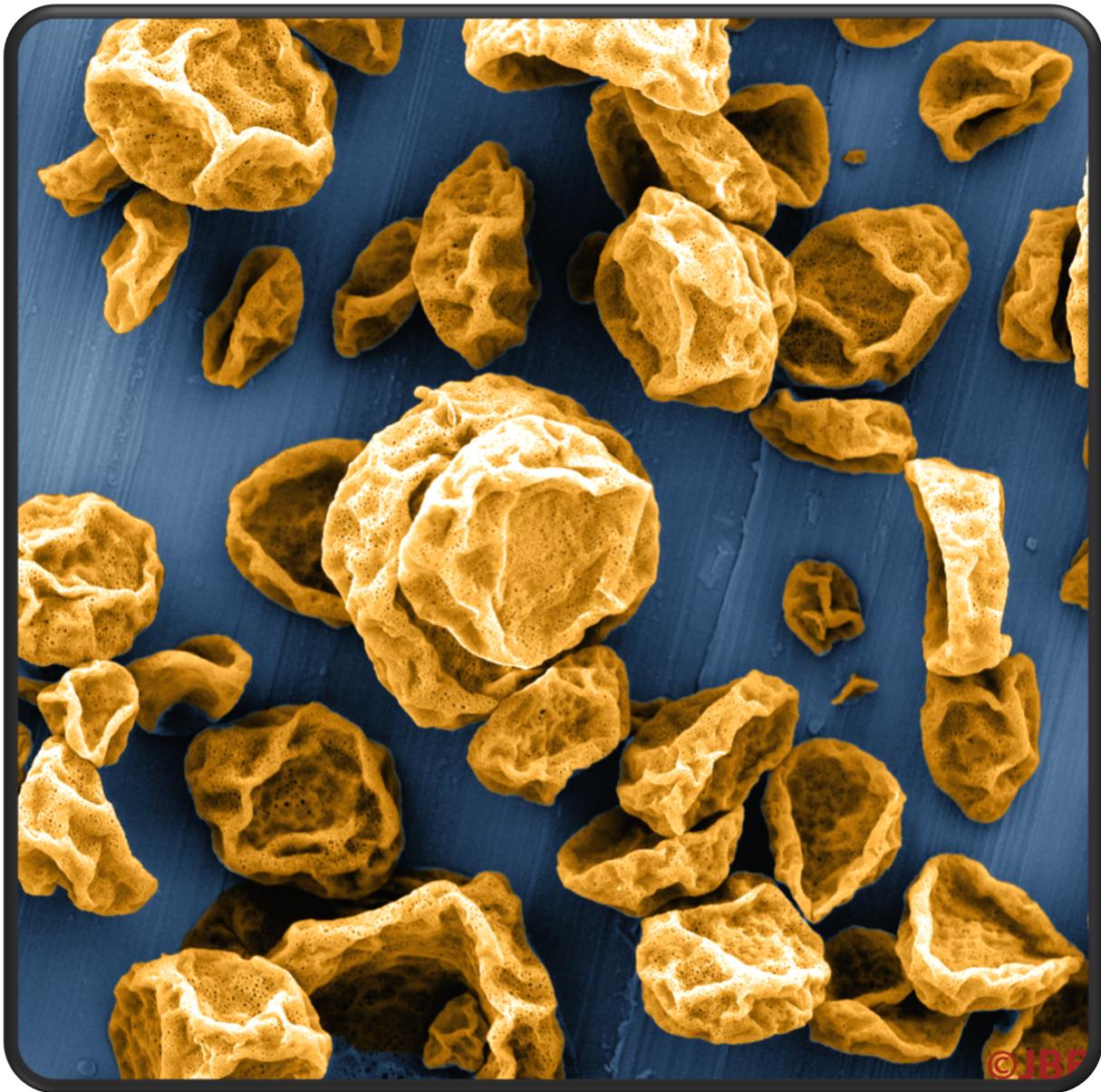


Swiss Soft Days

NESTLÉ RESEARCH

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SEM image of wrinkled cellulose colloids
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25th Edition

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En transport public depuis Lausanne, prendre le métro ligne M2 direction Les Croisettes ensuite le bus 64 pour le Chalet-à-Gobet, arrêt Chalet-à-Matthey.

Program

Salle Pasteur

09:00 Registration and Coffee

09:55 Welcome

10:00-10:45 Keynote 1
Microstructure engineering in foods:
from physics to innovation and back
(Prof. Erik van der Linden)

13:15-14:00 Keynote 2
Nanoscale Engineering of the Structure and
unctionality of Fat and Oleogel Systems
(Prof. Alejandro G. Marangoni)

Short talks:

10:45-10:50: Lázló Forró (EPFL)

10:50-10:55: Shabnam Tarvirdipour (ETH/Basel)

10:55-11:00: Valeria Zoni (U. Fribourg)

Session 2:

14:00-14:20 : Dorothee Kurz (ETH)

14:20-14:40 : Ahmad Moghimikheirabadi (ETH)

14:40-15:00 : Johann Nuck (U. Geneva)

15:00-15:20 : Emanuele Petretto (U. Fribourg)

11:00-11:20 Coffee

15:20-16:00 Poster Session + Coffee

Session 1:

11:20-11:40 : Jan Dedic (EPFL)

11:40-12:00 : Kristina Jajcevic (U. Geneva)

12:00-12:30 Introduction to Idea Competition

Session 3:

16:00-16:20 : Reza Ghanbar (AMI)

16:20-16:40 : Nick Jaensson (ETH)

16:40-17:00 : Yiping Cao (ETH)

17:00-17:20 : Mirela Malekovic (AMI)

17:20-17:40 : Vittoria Chimisso (U. Basel)

12:30-13:15 Lunch + Coffee

17:40-18:10 Tour through the Nestlé facilities



Invited Lecture 1

Microstructure engineering in foods: from physics to innovation and back

Erik van der Linden

*Physics and Physical Chemistry of Foods, Dept. Agrotechnology and Food Science, Wageningen University,
Wageningen, The Netherlands*

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The presentation will survey examples of the role of physics in understanding the formation and properties of microstructures in food and how this understanding can fuel innovations, and, reversely, how innovative ideas lead to exploring novel microstructures with concomitant new understanding of the physics of formation and properties of microstructures in food. The examples cover proteins, fats and carbohydrates as molecular ingredients, and microstructures of fibrillar, planar or spherical shape.

Invited Lecture 2

Nanoscale Engineering of the Structure and Functionality of Fat and Oleogel Systems

Alejandro G. Marangoni

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Fats and oils are extremely useful natural products which are widely used in foods, cosmetics and industrial applications. As the concern for the environment and health grows, consumers are demanding more natural, green and sustainable materials in everyday consumer products. Fats and oils are complex multicomponent mixtures of triacylglycerol molecular species. The nature of these molecular species are a function of both fatty acid composition and distribution within the TAG molecule. The purpose of this talk is to discuss the structure of fats and oils, from constituent TAG molecules to the crystals they form. Upon crystallization, TAG molecules form lamellae (shown in blue), which stack to form a highly asymmetric nanoplatelet with about ~8 TAG lamella (Figure 1)¹. We have been able to engineer the thickness of these nanoplatelets by using specific surfactants and affecting the surface energy and surface nucleation

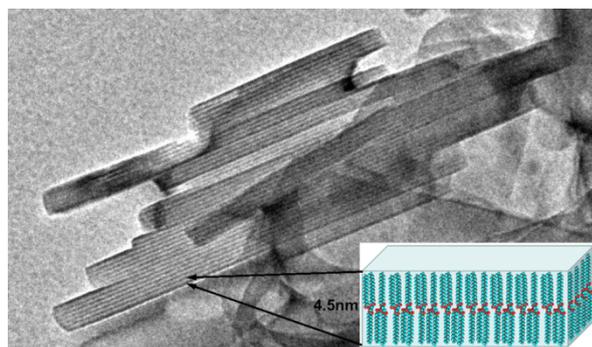


Figure X: Cross-sectional view of a TAG nanoplatelet showing epitaxial molecular packing in the [001] direction

behavior of TAGs on these crystalline nanoplatelets². These nanoplatelets rapidly aggregate into colloidal structures of differing morphologies and size depending on external fields and concentration, forming networks which are responsible for the binding of oil, water vapour barrier properties, and mechanical properties of the fat. Our work has focused on developing and understanding of the functionality of fats from a structural perspective. Early work focused on the quantification of structure using small deformation rheological techniques. More recent work has focused on the use of scattering methods, in particular Ultra-Small Angle X-ray Scattering at synchrotron facilities to quantify atomic scale structure to mesoscale structure simultaneously, in a non-destructive fashion³. Increasing public concerns over excessive saturated and *trans* fat intake from manufactured food products has led to the search for alternative strategies to structure liquid oils into

semisolid fats without addition of large amounts of unhealthy *trans* and saturated fats. Surfactant-like small molecules have been shown to self-assemble into long fibrils, effectively causing oil gelation at concentrations as low as 0.5%. Phytosterols, ceramides, waxes and 12-hydroxystearic acid have been shown to be effective organogelators. Liquid oils can also be structured by microencapsulation within multilamellar vesicles, with walls composed of monoglyceride hydrates in the alpha-gel state. The surface potential of these monoglyceride vesicles is then adjusted so as to maximize inter-vesicle interactions and the formation of a cellular solid with oil-filled cells. These monoglyceride gels have recently been proven to have excellent functional characteristics in baking applications as well as for omega-3 oil stabilization. High-molecular weight polymers such as ethylcellulose have also been successfully used by our group to gel oil in the absence of water. This development of a polymer-stabilized organogel is very promising since these polymers are widely available and are food-grade. The development of a new way to make fat exploiting the self-assembly properties of food-grade molecules is at hand⁴. A final perspective of future challenges will be offered.

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Short Talks

*Life is short,
speak fast*



Electron spin resonance (ESR) as a tool to monitor the antioxidant activity in food

Andrzej Sienkiewicz and László Forró
École polytechnique fédérale de Lausanne (EPFL), Lausanne, Switzerland.
ADS Resonances

Abstract

Reactive oxygen species (ROS) and their counterparts, antioxidants, play a central role in oxidation mechanisms occurring in food production and storage [1]. ROS is a collective term that refers to oxygen-based free radicals, such as superoxide anion ($O_2^{\bullet-}$), hydroxyl (HO^{\bullet}), peroxy (ROO^{\bullet}), and alkoxy (RO^{\bullet}) radicals. Electron spin resonance (ESR) is a method of choice for the detection and quantification of various types of ROS, as well as for monitoring the antioxidant activity in a wide range of chemical and bio-chemical processes [2,3]. In this context, ESR has been proposed as a simple and efficient spectroscopic tool to gather insight into oxidation processes and antioxidant activity in foods at different stages of their production and storage.

This talk will present examples of the ESR-based tests oriented towards quantification of the antioxidant activity in two types of grapes: white seedless (hereinafter ‘white’) and pink Muscatel (hereinafter ‘red’). To this end, we use a popular spin-probe, 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPOL) [4], as a paramagnetic target for the antioxidant species, which are present in freshly-prepared grape juices (containing no preservatives). Specifically, we show that the kinetic decay curves of the ESR signal of 50 μ M TEMPOL are definitely faster for the ‘red’ grape juice than the ‘white’ one (on a timescale of \sim 30 min). This observation points to a stronger antioxidant content in ‘red’ grapes and corroborates with published reports indicating higher concentrations of flavonoid-type antioxidants, such as resveratrol, stilbenes, quercetins, catechins, *etc.*, in ‘red’ grapes as compared to ‘white’ ones [5].

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Self-assembly of Peptide Nanoparticles for Efficient and Safe DNA Delivery

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[1] Department of Chemistry, University of Basel, [2] Department of Biosystems Science and Engineering, ETH Zurich

Abstract

The delivery of nucleic acids as therapeutic agents to the site of pathogenesis has considerable potential in the treatment of many diseases. While viral delivery systems dominate in clinical applications, safety concerns led to the emergence of non-viral vectors. However, non-viral methods generally suffer from a low delivery efficiency. To sidestep this limitation and bridge the gap between non-viral delivery systems that exist for antisense oligonucleotides (AOS) and those that transfer entire genes, we developed a purely peptidic delivery system that is able to entrap DNA larger than the average ASO. For this purpose, we designed an amphiphilic peptide (HR)3gT comprising a hydrophilic domain prone to undergo electrostatic interactions with DNA cargo, and a hydrophobic domain at a ratio that promotes the self-assembly into micellar nanostructures. Purified (HR)3gT peptide was tested for its ability to self-assemble into nanoparticles and entrap single- and double-stranded DNA (ssDNA/dsDNA) of 22 and 100 nucleotide length. The (HR)3gT peptide vector offers several advantages over other non-viral delivery systems including the precursor peptide H3gT(1). A particle size between 100 to 180 nm supporting a rapid and efficient cellular uptake, no adverse effects on HeLa cell viability, and long-term structural stability at 4°C distinguish the (HR)3gT peptide delivery system. Furthermore, at 37°C the multicompartamental organization of the (HR)3gT disassembles which should facilitate DNA release. Our data unravel a unique non-viral strategy for DNA delivery that sets the stage for developing amphiphilic peptide nanoparticles as candidates for future systemic gene delivery.

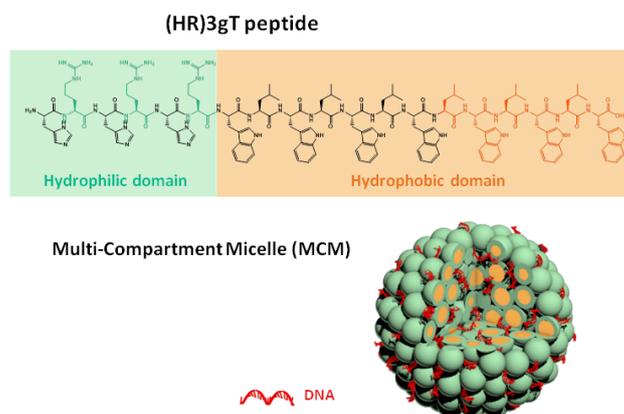


Fig 1: The (HR)3gT peptide consists of a hydrophilic and hydrophobic domain based on the core of H3gT peptide (represented in black) and schematic representation of nanoparticle assembly into MCM in the presence of DNA.

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The physical chemistry of lipid droplet biogenesis

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²Ecole Normale Supérieure, Laboratoire de Physique Statistique, Paris (France).

Abstract

Lipid droplets (LDs) are intracellular organelles that serve as the main cellular site of metabolic energy storage. Besides their metabolic functions, LDs also play a central role in numerous pathological processes, including lipotoxicity, cancer development, endoplasmic reticulum (ER) stress and viral attack¹. Despite the multiple functions of LDs in the cell, a basic understanding of their molecular properties is still missing, mostly because of their unique structure: a core of neutral lipids, such as triacylglycerols and steryl esters, surrounded by a single monolayer of phospholipids, that makes them, in essence, intracellular oil emulsions². Furthermore, little is known about the formation process of this organelles, that occurs in the ER. Here we present our results on the molecular mechanism of LD biogenesis using both existing and newly-developed methodologies based on molecular dynamics (MD) simulations and *in vivo* experiments. Using these approaches, we could identify the relevant parameters driving the spontaneous phase separation between triglycerides and phospholipids, leading to the formation of oil lenses in the ER bilayer.

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Talks

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



Investigating cyclodextrin-liposome interactions with vibrational sum-frequency scattering

Jan Dedic, Sylvie Roke

Laboratory for Fundamental BioPhotonics (LBP), Institute of Bioengineering (IBI), Institute of Materials Science (IMX), School of Engineering (STI), and Lausanne Centre for Ultrafast Science (LACUS), EPF Lausanne

Abstract

The behavior of lipid membranes is determined by the interactions of the constituent lipids with each other and with the outside environment. However, accessing this molecular-level information in small unilamellar vesicles is experimentally challenging. Vibrational sum-frequency scattering (VSFS) is a promising optical technique developed in our lab for probing the molecular structure colloidal interfaces in a label-free and surface-specific manner (1, 2). In this talk, I will present a study on the interaction of lipid vesicles with methyl- β -cyclodextrin (CD), a cyclic oligosaccharide with industrial and scientific applications (3). Our results show that CD does not simply adsorb to the surface of vesicles, but profoundly disturbs the structure of the lipid membrane over a period of hours and days. The structural changes in the membrane are observed starting from an unprecedented low CD/lipid ratio and persist even after washing out the CD. The VSFS spectra indicate that the membrane structure is perturbed at the level of the lipid headgroups as well as the acyl chains. Moreover, the observed CD-membrane interaction is headgroup-specific, with a strong preference for PS and PG headgroups over PC and PA. These findings indicate that VSFS could be a powerful technique for studying the interaction of a wide variety of molecules with lipid vesicles.

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Carbon nanomaterials fabricated with lipid nanotube templates

Kristina Jajcevic, Kaori Sugihara

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Abstract

Carbon nanomaterials have recently attracted a great deal of attention in the semiconductor industry due to their unique electrical, optical, thermal, mechanical, and chemical properties. Thus, carbon nanomaterials have gained importance in biology for applications such as biosensors and drug delivery. There is a growing interest in the use of self-assembled bioorganic templates in the fabrication of such one-dimensional carbon nanostructures.

The lipid 1,2-dioleoyl-sn-glycero-3-phosphoethanolamine (DOPE) which is the main component of bacterial cell membranes is known to self-assemble into single-wall synthetic lipid nanotubes (LNTs) on polyelectrolyte-functionalized surfaces. [1-4] We have demonstrated a high-throughput approach to transform these LNTs into surface attached carbon nanostructures through pyrolysis. First, biotin-tagged DOPE LNTs are formed from lipid blocks in inverted hexagonal phase adsorbed on polymer-coated surfaces upon application of shear force and cross-linked by chemical fixation. [5] Samples were dried and treated with high temperature under inert atmosphere to form connected carbon nanostructures. The created carbon nanostructures were characterized by transmission electron microscopy, atomic force microscopy and electrical measurements. The method is advantageous because the small size of LNTs enables the fabrication of surface attached mesh-like nanostructures with a higher throughput without using expensive electron beam lithography. The approach can further be combined with single LNT patterning with a micromanipulator to create distinct patterns instead of random networks. [3]

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A Microfluidic Study on Biofilm and Preferential Flow Path Formation in Porous Media

Dorothee Luise Kurz ^[1,2], Eleonora Secchi ^[1], Vicente Fernandez ^[1], Roman Stocker ^[1] and Joaquin Jimenez-Martinez ^[1,2]

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Abstract

In environmental (bioremediation and ecology) and industrial (chemical engineering) applications, it is of growing importance to understand the interplay between hydrodynamics and biofilm formation processes. The mosaic of regions of high and low fluid flow velocity found in porous media permits microorganism a free swimming lifestyle and to form surface-attached communities known as biofilms. The biofilm matrix is mainly formed of extra-polymeric substances (EPS), which are composed predominantly of polysaccharides, glycoconjugates and proteins. When characterizing this biofilm as a material, it could be considered as an “active” hydrogel. The growth of biofilms influences pore geometries by clogging them, and thus redirecting the flow, which in turn affects biofilm development and mass transport. Besides clogging of pore spaces, time varying preferential flow paths can be formed. We study these phenomena with a model microorganism, *Bacillus subtilis*, ubiquitous in soil and commonly used in biotechnology for enzyme production, in porous media analogues created in microfluidic devices to obtain a mechanistic understanding of the interplay between hydrodynamics and biofilm development at the microscale.

Experiments were performed in carefully designed porous geometries under different flow rates. The devices were exposed to a flow of nutrient broth after being seeded with bacteria, and over a period of 48 hours. Biofilm growth was continuously imaged using phase-contrast microscopy.

The rate of biofilm growth is influenced by both hydraulic and geometric parameters of the porous medium. For the same porous geometry, the initiation of biofilm formation and the definition of preferential flow paths occurs earlier in time with increasing flow rate. The preferential paths for fluid flow through the biofilm show an intermittent opening and closing behavior, intermittent bioclogging. Preferential flow paths are characterized by the opening-closing frequency and the channel width on the pore scale. Besides the impact of flow rate and geometry of the porous medium, this intermittent behavior is also controlled by the biofilms' rheological properties, which enable it to accommodate flow and pressure differences. The results shed light on the mechanisms involved in biofilm formation, clogging and its impact on the hydraulic properties of porous media.

Surface rheology of triblock copolymer stabilized interfaces: a molecular dynamics study

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[1] *Polymer Physics, Department of Materials, ETH Zürich*

[2] *School of Mathematical, Physical and Computational Sciences, University of Reading, UK*

[3] *Food Physics Group, Wageningen University, The Netherlands*

Abstract

We present here the results of extensive molecular dynamics (MD) simulations on structure and surface rheology of model symmetric triblock copolymers spread at an explicit liquid-vapor interface. The effect of polymer architecture on static and dynamic interfacial properties is investigated through considering two kinds of triblock copolymers with different degrees of hydrophobicity. The results of equilibrium MD simulations reveal that the more hydrophilic triblock copolymer imparts a higher surface pressure to the interface at a given surface concentration and takes a conformation with a larger radius of gyration at the interface. Nonequilibrium MD (NEMD) simulations were performed to obtain surface rheology data and quantities describing the interfacial microstructure in both linear and nonlinear regimes. Large amplitude oscillatory dilatation (LAOD) tests show that both interfaces exhibit strain softening at high strain amplitudes. However, intracycle nonlinearity analysis of a single Lissajous curve shows an apparent strain hardening in extension, a paradox which we pointed out in our recent experimental work (1). Parametric plots of parallel and normal components of gyration tensor with respect to the interface plane, as a function of dilatational strain reveal that these two structural variables vary completely out of phase; while the former increases in extension towards its maximum, the latter decreases and reaches its minimum. The results of the present research render possible a test of the theoretical frameworks which link interfacial rheological data to the surface microstructure, and provide physical insights to interpret experimental data obtained from surface rheological measurements.

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How to visualise forces: Peptides interacting with a mechanosensitive polymer

J. Nuck, K. Sugihara

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Abstract

Opening mechanosensitive ion channels, cellular virus infection and killing bacteria by antimicrobial peptides, all involve an application of forces to the cell membranes. Characterization techniques such as giant unilamellar vesicle aspiration and force spectroscopy are able to extract information about the surface tension and binding forces respectively. However, until now there is no possibility to measure the local molecular forces in lipid bilayer. Therefore, the goal of this project is to develop a calibrated fluorescence probe for mapping forces in cell membranes by the mechanosensitive polymer polydiacetylene (PDA).

PDA is a popular mechanosensitive polymer, used as chromic and fluorescence biosensors for the detection of ions, ligands, bacteria and peptides. The current center of debate is the molecular mechanism of the PDA activation by these ligands, where how these biomolecules alter the PDA structure and thus change its optical properties are left unexplored. In this work, to clarify the mechanism of the PDA activation by peptides, we investigated the interaction between PDA and an antimicrobial peptide from bee venom, melittin, by fluorescence and atomic force microscopy. These microscopy techniques provide spatio-temporal resolution in contrast to the traditional spectroscopy technique used in previous works, which revealed unique interaction kinetics between the peptides and PDA. Our new approach lets us furthermore observe the phase transition of the PDA domains induced by peptides and compare it to classic differential scanning calorimetry technique.(1) Understanding the peptide-PDA interaction mechanism is the first step to engineer this material for the use as a peptide force sensor.

References

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Development of a coarse grained model for nanoparticles simulation

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Abstract

Monolayer-protected gold nanoparticles (Au-NPs) have been thoroughly studied for their simple synthesis and tunable size. As a result of their nanometer scales, NPs are characterized by an extremely high surface-to-volume ratio, and NPs in solution tend to agglomerate in order to minimize the surface energy affecting the rapid settling of the suspension. Electrostatic repulsion and steric stabilization are the fundamental effects through which colloidal suspensions can be stabilized.(1)

Molecular Dynamics (MD) simulations have emerged as a promising computational approach to investigate the physicochemical properties of NPs, and, in particular, their interactions with biological structures.(2)

In this contest, we are developing a coarse-grained (CG) molecular model based on the Shinoda, DeVane and Klein (SDK) force field for surfactants. In this model, the potential function for nonbonded interaction in SDK force field is fitted on experimental data such as density and surface tension since these properties are significant in molecular self-assembly.(3)

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The impact of molecular partitioning and partial equilibration on the estimation of diffusion coefficients from release experiments

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[‡]Present: Department of Theoretical Condensed Matter Physics, Universidad Autónoma de Madrid, Spain

Abstract

The present work addresses the effect of partial equilibration and molecular partitioning on the interpretation of release experiments. In this regard, it is shown how release profiles and the values of extracted transport parameters are affected by the time protocol chosen for sample collection by considering a series of experiments where the latter is systematically varied. Caffeine is investigated as a main model drug due to its similar affinity for water and lipids, while monolinolein-based lipid cubic phases are chosen as host matrices due to their wide employment in release studies. Our findings point to a progressive decline in diffusion rate upon increasing the time step, i.e. the gap in time between two consecutive pick-ups, which is a signature of increasing equilibration of caffeine concentration between the lipidic mesophase and the water phase. Furthermore, the amount of released molecules at the first pickup displays negligible changes for large time steps, indicating complete equilibration in such cases. A model is introduced based on Fick's diffusion which goes beyond the assumption of perfect-sink conditions, a common feature of the typical theoretical approaches hitherto developed. The model is shown to account quantitatively for the experimental data, and is subsequently employed to clarify the interplay of the adopted release protocol with the various transport parameters in determining the final outcome of the release process. Particularly, two additional molecular drugs are considered, namely glucose and proflavine, which are respectively more hydrophilic and hydrophobic than caffeine, thus allowing elucidating the role of molecular partitioning.

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Acknowledges support from Japan Society of Promotion of Science.

Dynamics of thin liquid films: Implications for beer foam stability

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[2] Polymer Technology Group, Department of Mechanical Engineering, TU Eindhoven, the Netherlands

Abstract

Beer foam stability is believed to be enhanced by a rigid protein-stabilized thin liquid film (TLF) formed between two neighboring CO₂ bubbles. Such a film is expected to hinder drainage, coalescence and even Ostwald ripening (1), which are the main foam destabilization mechanisms. Although the synthesis or addition of certain proteins during the brewing process is common industrial practice, the mechanism by which they act still remains unclear. We present a combined experimental-numerical study to unravel the mechanisms by which beer foam can be stabilized.

The thin film drainage of three commercial beers was evaluated experimentally using a newly developed variation of the thin film balance technique coupled with interferometry (2). The influence of surface tension, particle size, bulk and interfacial rheological properties on TLF stability was assessed by Wilhelmy-plate tensiometry, dynamic light scattering, double-wall ring interfacial rheometry and bulk viscosity measurements. The surface tension and the bulk viscosity of the different beers did not show large variations. However, their drainage behavior differed significantly. Increased film stability, highly heterogeneous film thicknesses and slower thinning rates were observed for the beers of higher fermentation. Although the comparison between the experimental drainage curves and the predictions of the Reynolds model (3) indicates that the interfaces are highly stress-carrying, the mechanism of stabilization was found to differ. For two of the beers, it was observed that the drainage time increases with the interfacial shear viscoelasticity, while the most stable one was stabilized through Marangoni stresses.

These effects were investigated in more detail by performing simulations using the finite element method, which solves the full set of flow- and transport equations. It is shown that film drainage can be delayed by orders of magnitude, as compared to clean surfaces, by two distinct mechanisms: 1) an inhomogeneous surfactant distribution, leading to Marangoni stresses and 2) surface viscosity effects, possibly including anisotropic surface stresses. If both of the mechanisms are present, a non-trivial coupling is observed, which was systematically investigated.

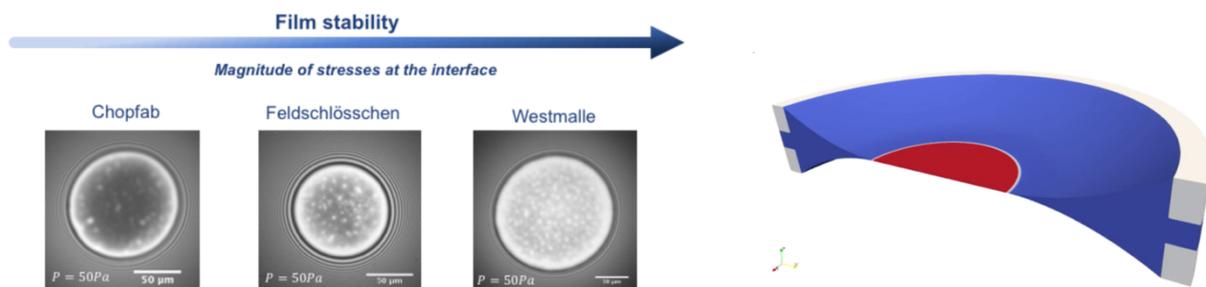


Figure 1. Left: Microinterferometry images of the films of the studied beers and right: FEM simulation of the drainage of a thin liquid film. The color indicates the pressure.

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Food protein amyloid fibril gels: from fundamental to applications

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Abstract

Amyloid fibrils have evolved from pathological materials implicated in neurodegenerative diseases to efficient templates for last-generation functional materials (1). Due to their high intrinsic stiffness and extreme aspect ratio, amyloid fibril gels can serve as ideal building blocks for material design and synthesis, especially for those derived from food proteins since they are non-toxic, agriculturally sustainable, inexpensive, etc. Yet, how the elasticity of amyloid fibril gels is ruled by intrinsic and extrinsic factors, is still not clearly understood. Moreover, in these gels, stiffness is generally not paired by toughness, and their fragile nature hinders significantly their widespread application. To answer these questions, two model food protein amyloid fibril gels, made from beta-lactoglobulin and lysozyme, were investigated from fundamental to applications. It was found that the elasticity of fibril gels can be described by combining the affine thermal model of network elasticity with the DLVO theory of electrostatically charged colloids (2). The mechanical properties of amyloid networks can also be improved by coating fibrils with silica or constructing double networks (3). The better understanding of amyloid fibril gels will boost the development of functional materials and spark novel food applications.

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Rapid assembly of sol-gel manufactured distributed Bragg reflectors

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Abstract

Distributed Bragg Reflectors (DBRs) are one-dimensional (1D) multi-layered structures whose morphology enables display of interesting optical features, e.g. a high reflectance or resistance to colour fading. The manufacturing of these seemingly simple alternating configurations usually requires exquisite precision. Most industrial techniques only allow deposition of “compact” metal oxides thin films in a vacuum atmosphere. Here, we present a spin-coating deposition technique, which gives us good control over thin film thickness and material composition. We assemble optical multilayers by breaking the multilayers into minimally repeating segments of carefully designed tri-layers to shorten the manufacturing time and reduce the number of possible defects. Usage of a sacrificial material enables release of high concentration of “flakes” into the compatible solvent. With solvent evaporation, tri-layers start to stack together and a high-quality DBR with any desired number of layers is achieved. The resulting materials can be used as proof-of-concept materials, e.g. for gas sensors.

Effect of Bivalent Cation on Swelling Behavior of Anionic Microgels

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Abstract

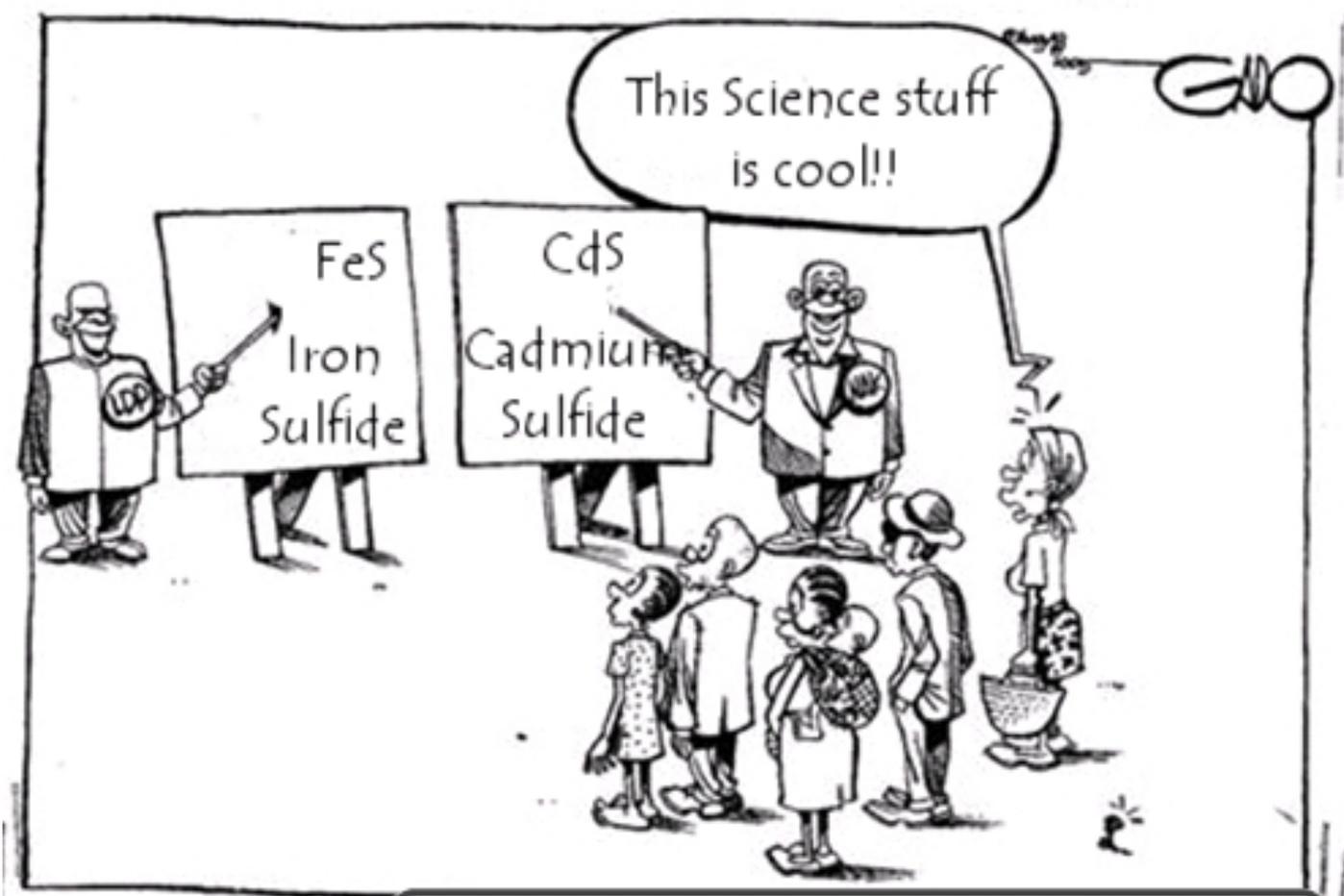
«Smart» microgels are strong candidates for applications as sensors, waste water purification, drug delivery systems and could serve as thickeners and emulsion stabilizers in the food and cosmetic industry. [1] Their peculiar softness and porosity play a fundamental role in the uptake and release of a guest, which can be released on demand upon the addition of an external trigger such as temperature, pH or light. Hence, studies on their capability of uptake and controlled release of small molecules, proteins and polyelectrolytes are widely available. [2] However, the same application potential as sequestrants and release systems has scarcely been investigated on bivalent ions such as Ca^{2+} .

Biocompatible anionic vinyl caprolactam (VCL) based microgels were designed to carry carboxy groups in different amounts in order to fine-tune their temperature, pH and bivalent ion responsiveness. [3] The gels were fully characterized in their chemical composition, morphology and temperature depend size *via* NMR, potentiometric titration, TEM and DLS. Their behavior towards Ca^{2+} as representative ion was investigated. Their responsiveness towards Ca^{2+} was measured *via* DLS and SLS, in terms of gel collapse range, thermal and ion stability. The amount of bivalent ion uptake and pH triggered release was quantified *via* ion chromatography. The dynamics of binding were also measured, which might play a fundamental role for future applications in synthetic biology.

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Posters



Silica-Silica Interactions in Multivalent Coion Solutions

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Abstract

Interactions between charged particles determine the behavior of colloidal systems. Particle interactions in the presence of monovalent salt solutions are very well studied. Recently, experimental data for systems containing multivalent counterions is also becoming increasingly more available. On the other hand for systems where the multivalent ion is a *coion* much less data is available. Here we present direct force measurements between charged silica particles in the presence of multivalent anions. In such solutions multivalent ion has the same sign of charge as the silica surface and the multivalent ions are thus coions. We systematically vary the concentration and the valence of the coions and study their effects on the double-layer interactions. Surprisingly, in contrast to textbook knowledge, which states that screened electrostatic forces are exponential, here we show that the double-layer forces in the presence of multivalent coions are non-exponential. This non-exponential behavior is caused by the expulsion of the multivalent coions from the slit between the two surfaces. The diffuse-layer potentials and regulation properties of silica surfaces are extracted from the DLVO fits. The surface properties in multivalent coion solutions collapse to a master curve when plotted as a function of the monovalent counterion concentration (1). Similar non-exponential behavior was observed in systems containing negatively charged electrolytes, which represent highly-charged coions (2).

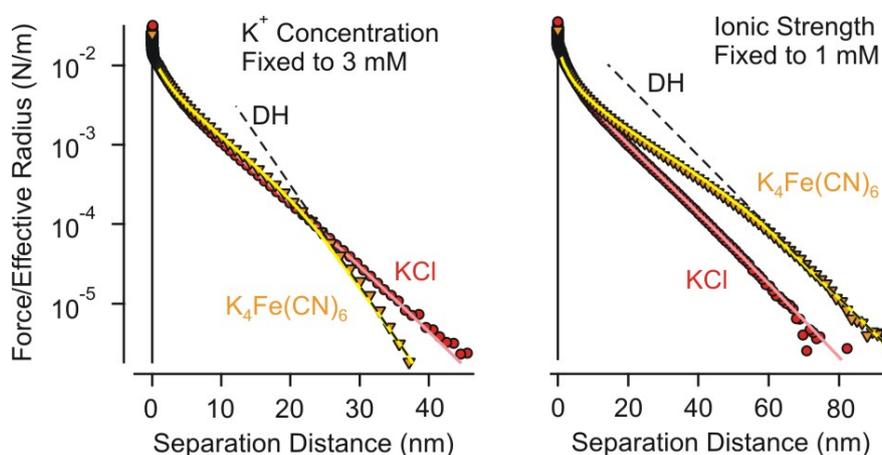


Figure: Comparison of forces in the presence of fourvalent and monovalent coions at (a) fixed potassium concentration and at (b) fixed ionic strength.

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Melting behaviour and ultra-drawability of nascent UHMWPE powder

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Abstract

The melting behavior of nascent ultra-high molecular weight polyethylene (UHMWPE) powder has recently received considerable attention (1). It was shown that the elevated first melting peak is due to superheating of the nascent UHMWPE powder (1-3). The anomalous superheating effect, which is not observed in melt-crystallized UHMWPE, is thought to be due to the special morphology of nascent powder resulting in a high crystallinity and a low degree of entanglement. This special nascent (also called “virgin”) morphology can be achieved by polymerization at relatively mild conditions or by using unsupported single-site catalysts. In both cases, the as-polymerized polymer chain is thought to crystallize before it can entangle with its neighbors.

Reliable characterization methods for the degree of disentanglement are key to steer catalyst selection and polymerization conditions in order to speed up research. The currently used methods include drawability, which is a semi-quantitative method as the drawability is influenced by other factors apart from the level of disentanglement, such as powder morphology, compaction stage and deformation rate and temperature during drawing. Another way of analyzing the nascent powders in term of degree of disentanglement could be through thermal characterization. It is known that nascent polymer materials depict strong superheating and it has been proposed that this correlates with the state of entanglement.

Rastogi et al. have observed that UHMWPE reactor powders show slow melting when annealed below the melting temperature (1). By annealing the powder below the melting point for different annealing times, they found that the higher the level of disentanglement, the faster the complete melting of the powder that is achieved. It is thus believed that the time required for melting upon annealing is related to the level of disentanglement. This hints to different melting kinetics, dependent on the amount of entanglements in the nascent powder

The objective of the current study is to evaluate the level of disentanglement of nascent UHMWPE powder by investigating the kinetics of nascent UHMWPE crystal melting by differential scanning calorimetry (DSC), evaluated in the framework of isoconversional kinetic analysis. Isoconversional analysis is a relatively new method for analyzing thermally stimulated processes such as crystallization and melting (4).

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Detection and characterization of nanoliter-sized droplets by Impedance Spectroscopy

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Abstract

Parkinson's disease (PD) and Alzheimer's disease (AD) represent big medical challenges which modern medicine has to face with, nowadays. Due to the increase of life expectancy of older population, the number of people in the world suffering from dementia is expected to reach 75 million, by 2030, and 131 million, by 2050 (1). The economic impact on public health is not secondary and represents, each year, an investment of hundreds of billions of dollars. Own to the lack of understanding the causes of these neurodegenerative conditions (2), the existing solutions provided by medicine only alleviate the symptoms. Brain microdialysis is a powerful tool for research in Neuroscience and pharmacokinetics monitoring that enables to get a better understanding of the chemical processes taking place in the brain. The analysis of nanoliter-sized droplets, constituted of cerebral extracellular fluid (ECF), coupled with mass spectroscopy techniques, allows to retrieve the concentration of neurotransmitters in time, thus studying drug effects or the mechanisms behind neurodegeneration. The final goal of this project is to realize a biocompatible neural probe able, ultimately, to electrically and optically stimulate the brain (e.g. photobiomodulation), collect and store samples from the substantia nigra, as droplets, and analyze the evolution of neurotransmitter concentrations, in time. A big focus is provided to the nanodroplets detection and characterization, through the fabrication of Pt-Ti (Platinum-Titanium) microelectrodes at the CMI (Center of MicroNanotechnology) facilities of EPFL. An electrochemical model derived for the electrodes is presented, the critical design parameters are discussed and compared with respect to the experimental results, derived through impedance spectroscopy measurements. The correlation of the nanodroplet size (nl range) and differential capacitance signal retrieved is demonstrated. Finally, in order to detect and count in time the number of nanodroplets in the channel, the employment of a lock-in amplifier set-up is presented: the differential capacitance peak and the transient time over the electrode show a correlation with respect to the volume and the flow rate of the nanodroplet. The hope of this work is to have contributed to one part of an ambitious project, which might change in future the perspectives of Neuroscience.

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Investigating MAPbBr₃ Perovskite Solar Cells through Interfacial Passivation Using Ultrathin Polymeric Films

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Abstract

Perovskite solar cells based on MAPbBr₃ received less attention due to their high bandgaps that are unsuited for high-performance solar cells. However, if realized, high open-circuit voltages (V_{oc}) offer considerable opportunities for different applications such as water splitting and the pathway to an all-perovskite multijunction device that urgently requires wide band gap perovskite with high V_{oc} .

Thus, investigating the reasons why high voltage with adequate output power have not been achieved is an underexplored part in perovskite research.

Interfacial carrier recombination leads to reduced carrier lifetimes and voltage loss. To address this issue and to further improve the high V_{oc} of methylammonium lead tri-bromide (MAPbBr₃) perovskite solar cells, interface passivation techniques are an important strategy. Here we demonstrate two ultrathin polymeric passivation layers consisting of PCBM and PMMA: PCBM mixture as well as PMMA that can effectively passivate defects at the perovskite/ ETL and perovskite/ HTL interfaces, respectively, where they significantly suppress interfacial recombination.

Crystallization and film-formation are key for high quality perovskite materials. Thus, perovskite crystallization was investigated with the established anti-solvent and the novel flash infrared annealing (FIRA) with and without passivation layers. This is the first demonstration of FIRA for MAPbBr₃ revealing altered film morphology and therefore a novel strategy to control the crystallization process (1-4).

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Subcompartments and triggered cytoskeleton formation in artificial cells

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Abstract

The quest for smart materials has now brought researchers to turn to cells, with the idea of mimicking the many useful features of living matter. In this regard, stimuli responsiveness is one of the most sought-after behaviours, as it allows the material to react to changes in the external environment in non-linear ways. (1) To achieve cell mimicry we devised a hybrid biological-synthetic material composed of poly(2-methyl-2-oxazoline)-*block*-poly(dimethylsiloxane)-*block*-poly(2-methyl-2-oxazoline), (PMOXA-PDMS-PMOXA) forming giant unilamellar vesicles (GUVs), encapsulating: i) smaller polymersomes; ii) reduction sensitive (poly(2-methyl-2-oxazoline)-graft(SS)-poly(ϵ -caprolactone) (PMOXA-g(SS)-PCL) nanoparticles encapsulating hydrophobic molecules; iii) proteins. Specifically, by adding the reducing agent DTT we could have either enzymatic activity or, thanks to a multi-step cascade leading to internal osmolarity changes, induce the polymerization of actin, obtaining the formation of cytoskeleton within the vesicles. We proceeded to characterize the vesicles via confocal laser microscopy and fluorescence correlation spectroscopy, showing the stimuli-responsiveness of such constructs.

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Ca-Reinforced Bioinspired Dually Crosslinked Hydrogels

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Hydrogels are among the first biomaterials expressly designed for their use in biomedicine. However, state-of-the-art applications of hydrogels are severely limited because they are typically either too soft or too brittle such that they cannot be used for load-bearing applications. Typically, conventional hydrogels have low to moderate stretchability, and fracture energy in the range of $<100 \text{ J/cm}^2$ (1). To overcome this shortcoming, dually crosslinked hydrogels encompassing covalent and ionic crosslinks have been developed in the past years(2,3). Among the large variety of ionic networks, metal-coordination chemistry has attracted great interest as a reinforcing strategy due to its implication in many biological soft and tough tissues (e.g. mussel byssus threads)(4). The combination of cations with complexing groups allows for an increase in mechanical strength while rendering the hydrogel capable of stretching to up to 5-10 times its original length. Here, we investigate the mechanical properties of biocompatible, dually crosslinked hydrogels made of poly(acrylic acid)/carboxymethyl cellulose that are ionically crosslinked with Ca^{2+} . Remarkably, we find that the E-modulus and fracture toughness both increase with increasing Ca^{2+} concentration until these properties reach a maximum value. Hence, this strategy imparts superior mechanical properties to these hydrogels, which cannot be achieved in conventional covalently crosslinked hydrogels where an increase in stiffness is usually paired with a decrease in toughness.

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Controlling the Local Composition of Hydrogels

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Many natural materials have optimized structures on different length-scales and locally varying compositions, imparting them unique mechanical properties. Inspired by nature, we are developing tools that enable the production of structured hydrogels whose conformation changes over short length scales. This is achieved using drops with well-defined sizes and compositions that are produced with microfluidics. I am working on microfluidic devices that allow control over the arrangement of the drops. These assembled drops are subsequently converted into macroscopic structured hydrogels with locally varying compositions. I will use different tools to control local conformations and show how it influences the macroscopic mechanical properties of hydrogels.

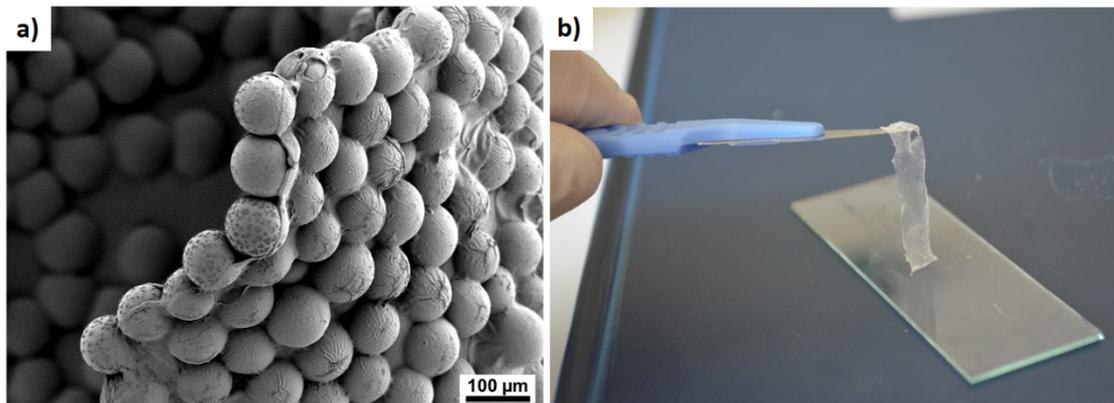


Figure: a) Composite hydrogel sheet. A monolayer of PEGDA particles is embedded into an alginate matrix, holding the sheet together. b) Macroscopic image of a composite hydrogel sheet, which is mechanically stable.

Tuneable Bio-Inspired Double Network Hydrogels

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Hydrogels with well-controlled and engineered properties are often used in biomedicine, for example for wound healing, or tissue engineering. For example, hydrogels with a very high toughness, that are well-suited soft dampers, can be fabricated by combining covalent and non-covalent bonds. However, these hydrogels are typically elastic such that they cannot be used for load-bearing applications. By contrast, nature can produce hydrogels with fine-tuned mechanical responses, that are tough and yet sufficiently strong, that they can bear load. Inspired by the marine mussel, we investigate the influence of hydrogel networks, using well-defined polymers with covalent and tuneable transient bonds, on their mechanical properties.

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