# Swiss Soft Days

23rd Edition

Zürich, 28.9.2018

# How to get there:

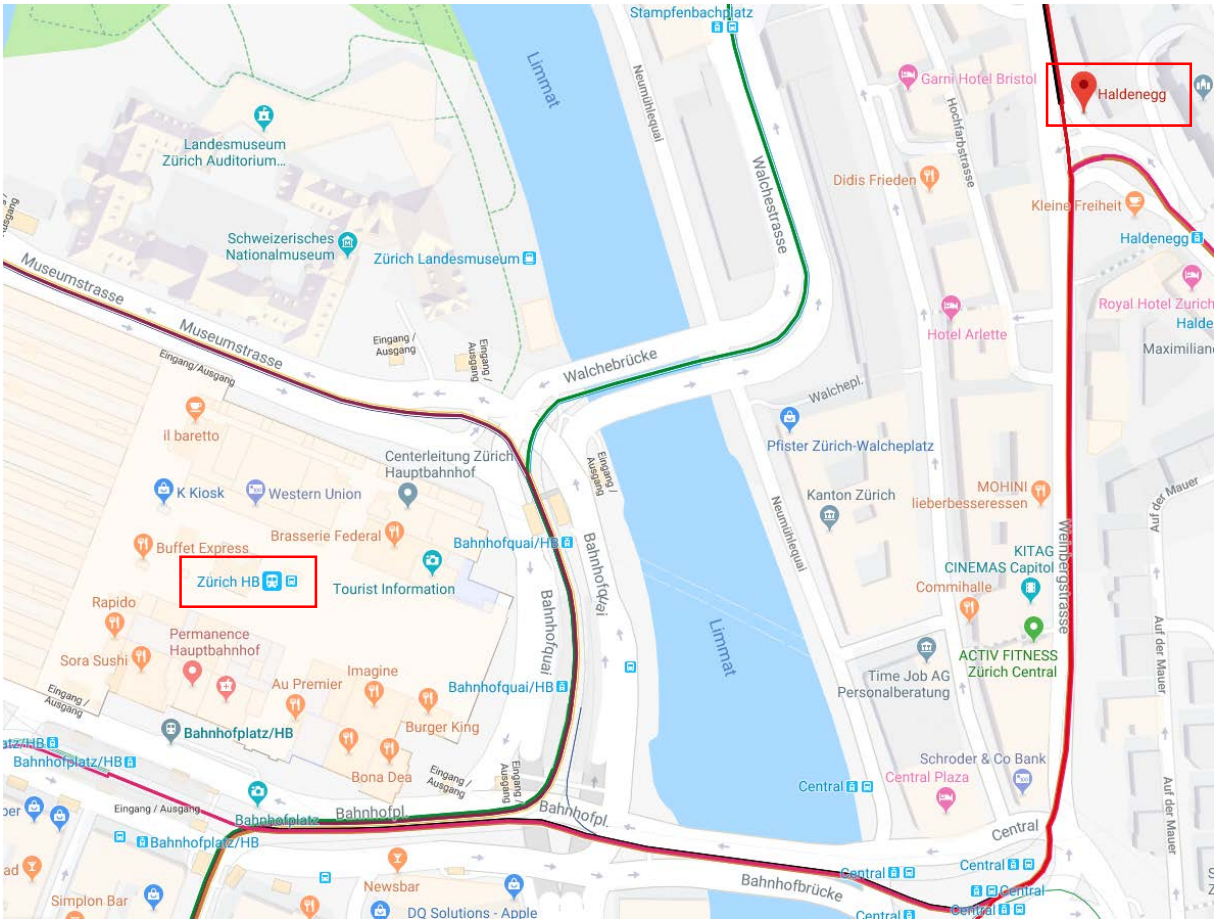
Welcome to the 23rd edition of the Swiss Soft Days!

The conference venue is in the building HCI on the **Hönggerberg Campus of ETH in Zurich**. Welcome coffee and registration takes place in the G-floor foyer.

**Address**
ETH Zürich, Campus Hönggerberg
Vladimir-Prelog-Weg 1-5 / 10
8093 Zürich
Switzerland

Overview of campus Hönggerberg. The venue is marked with a red circle and the arrows show the path from the bus station to the building.


Details on arriving on ETH Hönggerberg can be found on the next page.




The most convenient way of transportation between Zurich center and the campus Hönggerberg, is to use the ETH shuttle bus.

The shuttle bus departs from the station “Zürich Haldenegg” four times per hour (xx:07, xx:17, xx:37, xx:57) and takes you directly to ETH Hönggerberg. The station “Zürich Haldenegg” is within 600 m of Zurich main station and can be reached by various trams (see map above).

Once arrived at the station ETH Hönggerberg, the HCI building is quite close to the bus station. You can enter the building via the “Fusion Coffee” Cafeteria and the elevators are straight ahead. The registration and welcome coffee takes place right in front of the elevator entrance on G floor.

If you have any questions do not hesitate to contact us at swisssoftdays@ethz.ch.

Have a happy meeting!

The organizers,
Doha Abdelrahman, Kilian Dietrich, Damian Renggli

Other possibilities are:

- Tram 7 / 14 / 10 to Milchbuck and Bus 69 to ETH Hönggerberg.
- Tram 11 to Bucheggplatz and Bus 69 to ETH Hönggerberg
- Tram 13 to Meierhofplatz and Bus 80 to ETH Hönggerberg.

For more details, please refer to

- www.sbb.ch
- www.zvv.ch

or visit www.ethz.ch/en/campus/access/zurich-region/hoenggerberg.html.

*HCI building:*

# Program

## HCI G

09:00-10:00 Registration / Welcome Coffee

## HCI J 3

10:00-10:45 Understanding Food Oral Breakdown to Guide Food Structure Design
(Dr. Benjamin Le Révérend)

**Short talks:**

10:45-10:50: Chatzigiannakis (ETH)

10:50-10:55: Demirörs (ETH)

10:55-11:00: Stoop (Univeristy of Barcelona)

11:00-11:05: Testa (ETH)

11:05-11:10: Wehr (University of Basel)

11:10-12:00 Poster Session + Coffee

**Session 1:**

12:00-12:20 Talk 1: Barabé (Nestlé)

12:20-12:40 Talk 2: Pioli (ETH)

12:40-13:00 Talk 3: Woigk (ETH)

13:00-14:00 Lunch + Coffee

## HCI G 7

14:00-14:45 Pasta – the processing secrets and challenges of a great food
(Dr. Andreas M. Kratzer)

**Session 2:**

14:45-15:05 Talk 4: Kopp (ETH)

15:05-15:25 Talk 5: Colombo (ETH)

15:25-15:45 Talk 6: Gantenbein (ETH)

15:45-16:15 Poster Session + Coffee

**Session 3:**

16:15-16:35 Talk 7: Cao (University of Geneva)

16:35-16:55 Talk 8: Grigolato (ETH)

16:55-17:15 Talk 9: Küffner (ETH)

17:15-17:35 Talk 10: Wyss (ETH)

17:35-17:55 Talk 11: Zoni (University of Fribourg)

17:55-19:00 Poster Session + Apéro

# Invited Lecture 1

## Understanding Food Oral Breakdown to Guide Food Structure Design

Benjamin Le Révérend, Christopher J. Pipe and Christoph Hartmann

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### INTRODUCTION:

During food structure processing in mouth, multiple physico-chemical processes occur leading to the sensing of taste, aroma and texture stimuli, which in turn may induce specific processing patterns. Ultimately, a time-dependent dynamic sensory perception is created with every bite and depends on the initial characteristics of the ingested food. This opens opportunities for design of sensory experiences in indulgent categories and the reduction of public health sensitive nutrients using innovative product architectures.

### METHODS:

Research approaches include psychophysics and psychorheology compared with analytical and numerical solutions of PDEs describing transport phenomena in the oral cavity as well as biomimetic setups mimicking oral cavity perception processes at lab scale.

### RESULTS:

Concerning taste perception, we demonstrate how mass transfer processes are involved in taste signaling at several length and time scales. Saltiness perception scales with the low shear viscosity of polymer solution in agreement with a simple extension of the Chilton-Colburn analogy [1] to link a bulk oral cavity convection dominated domain, and the thin salivary film at the tongue surface, proposed to be diffusion dominated (see Fig. 1).

$$h \propto \eta^{-1/6} \qquad (1)$$

This is also supported by classical dimensional analytical approach showing that a time-dependent delivery of taste concentration patterns to the oral cavity can be employed to enhance taste perception, which we validated experimentally in a separate set of studies.

Concerning texture perception, we hypothesize that sensory perception of liquids viscosity can be mediated by the fluid structure interaction between fluid and filiform papillae at the surface of the tongue. Filiform papillae have the ability to bend leading to a deformation $\delta$ linked with the stress generated around the papilla and thus by the fluid rheological properties [2].

$$\delta \propto \eta U / H \qquad (2)$$

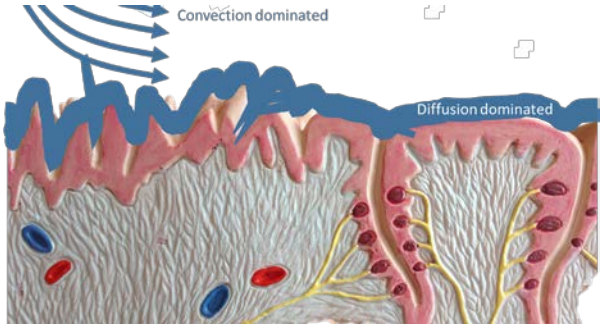


*Fig. 1: A conceptual advection-diffusion model of taste perception [1].*

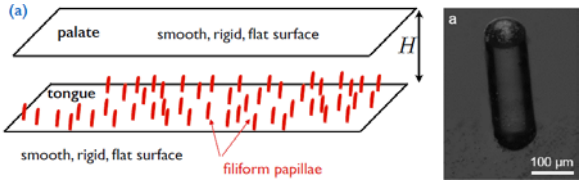


*Fig. 2: Conceptual and experimental simplification of filiform papillae structures [2].*

### ACKOWLEDGEMENTS:

Béatrice Aubert, Anthony Lima, Jean-Baptiste Thomazo from Nestlé contributed to the collection of the data. Eric Lauga (U. Cambridge), Alexis Prevost and Elie Wandersman (Sorbonne U.) contributed to this research during collaborations with Nestlé Research.

### References:

[1] Aubert, Lima and Le Révérend, **Food Hydrocolloids** (2016), Dufauret, Lima, Le Révérend and Wooster, **Food Hydrocolloids** (2018)

[2] Lauga, Pipe and Le Révérend, **Frontiers in Physics** (2016), Thomazo, Pastenes, Pipe, Le Révérend, Wandersman, Prevost (in preparation)

# Invited Lecture 2

## Pasta – the Processing Secrets and Challenges of a Great Food

Andreas Kratzer

*Bühler Group, Switzerland*

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# Short Talks

# Dynamics of beer thin liquid films: Implications for foam stability

E.Chatzigiannakis, A.Alicke, J.Vermant

*Soft Materials Group, ETH Zürich, Zürich, Switzerland.*

**INTRODUCTION:** Thin liquid film (TLF) dynamics is considered to be the governing factor when it comes to foam stability. When two bubbles come into close proximity a TLF is usually formed between them, which gradually drains. The drainage process and, consecutively, the stability of TLFs has been found to depend heavily on the mechanical properties of the interface. For example, beer foam stability is believed to be enhanced by the formation of a rigid protein film at the $CO_2$/liquid interface that hinders Ostwald ripening and coalescence[1]. Although the addition of certain proteins during the brewing process is common industrial practice, the mechanism by which they act still remains unclear.

**METHODS:** The drainage of four different commercial beer foam TLFs was evaluated using newly developed variation of the thin film balance technique coupled with interferometry[2]. The influence that the surface tension, bulk and interfacial rheological properties have on TLF stability was assessed by pendant drop tensiometry, double-wall ring interfacial rheometry and bulk viscosity measurements.

**RESULTS:** The surface tension and the viscosity of all five beers did not show large variations. However, their drainage behaviour differed significantly. Increased film stability, highly heterogeneous film thicknesses and lower thinning rates were observed for the beers of higher quality. Comparison between the experimental drainage curves and the predictions of the non-dimensional form of the Reynolds model[3] indicates that the interfaces are highly stress-carrying.

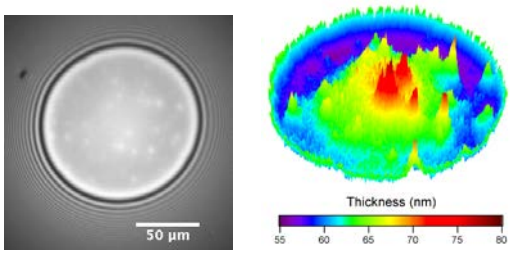


*Fig. 1: (left) Microinterferometry image of a beer (Pilsner Urquell) thin liquid film just before rupture, and (right) its 3D thickness map*

**DISCUSSION & CONCLUSIONS:** Enhanced film stability was attributed to the formation of a stable viscoelastic layer by the protein aggregates, which greatly decelerates the drainage of the corresponding TLFs. More experiments are currently underway in order to determine the exact mechanism of stabilization of beer TLFs.

**REFERENCES:**

[1] Bamforth C.W.; **2004**; J Inst Brew*;* 110(4):259.

[2] Beltramo P.J. et al.; **2016**; Soft Matter; 12(19):4324.

[3] Reynolds O.; 1**886**; Philos Tran R Soc Lond; 177:157

# Electric Field Assembly of Colloidal Superstructures

Ahmet F. Demirörs

*ETH Zürich, Complex Materials, Zürich, Switzerland.*

**INTRODUCTION:** The assembly of materials from building blocks have been in the core of wide range of applications from catalysis to photonics and electronics. External fields such as electric fields enable the control of the interactions between building blocks via induced-dipoles[1,2]. Dipolar interactions were used so far to obtain one dimensional chain assemblies or to change the order of the three dimensional lattice from closed-packed to non-close-packed structures. However, they were never used to create more complex building blocks from binary mixtures of simple spherical ones. Here we demonstrate a novel approach of self-assembly enabling the formation of regular axially-symmetric clusters, array of colloidal assemblies as per design of posts, and hierarchical complex assemblies by using posts and dipolar interactions or combining them. Regulating the polarization of the particles from positive to negative by applying an alternating electric field allows us to control the inter-particle interactions from attractive to repulsive at the poles or equator of the particles. Therefore, such particle-particle interactions enable the switch between Saturn-ring-like and candle-flame-like axially-symmetric assemblies.

**RESULTS:** Figure 1 demonstrates an example of how electric fields are used to trap and finally unload the particles, while using magnetic forces for transport of the cluster.

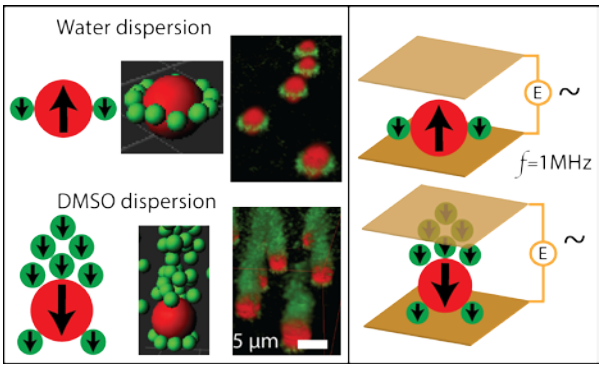


*Fig. 1: Assemblies of particles in different suspensions, namely in water(above) and DMSO (below).*

**REFERENCES:**

1. Demirörs, A. F., Courty, D., Libanori, R. & Studart, A. R. Periodically microstructured composite films made by electric- and magnetic-directed colloidal assembly. Proc. Natl. Acad. Sci. 113, 4623–4628 (2016).

2. Demirörs, A. F., Eichenseher, F., Loessner, M. J. & Studart, A. R. Colloidal shuttles for programmable cargo transport. Nat. Commun. 8, 1872 (2017).

**ACKNOWLEDGEMENTS:** AFD is grateful for the financial support from the Swiss National Science Foundation (PZ00P2_148040).

# Clogging and Jamming in Colloidal Monolayers Driven Through a Random Obstacle Landscape

R. L.Stoop, P.Tierno

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We investigate clogging and jamming of colloidal microspheres driven through a random array of obstacles by external magnetic fields. Monodisperse paramagnetic polysterene particles are diluted in water and dispersed above the surface of a ferrite garnet film (FGF) produced by a liquid phase epitaxy process[1]. These ferrimagnetic films depict a periodic stripe pattern of magnetic domains with alternating up/down magnetization perpendicular to the film surface, Fig. 1a. The magnetic substrate generates a periodic magnetic potential in which particles are confined. Using external magnetic fields, we translate the potential and particles at constant speed, investigating their flow behavior through the system of obstacles, Fig. 1b. The obstacles are realized by immobilizing non-magnetic silica spheres on the FGF surface prior to the measurements. We find a global Faster-Is-Slower effect, which means that the overall particle speed decreases for increasing driving force, due to the formation of cloggs. The Faster-Is-Slower effect is strongest at intermediate obstacle densities and minimal for high and low densities.

Furthermore, via tuning the particle-particle interactions with the external field, we find that attractive interactions can enhance the transport through the disordered landscape, suggesting an efficient method to minimize clogging and jamming of colloidal particles.

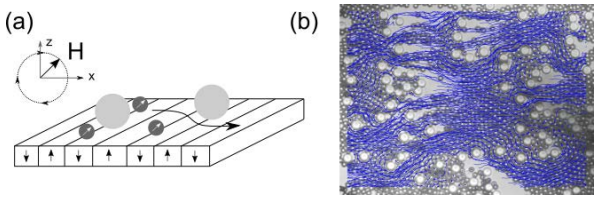


*Fig. 1 (a) Schematic of the FGF and particles. (b) Micrograph of obstacle array (bright, large particles) and mobile magnetic particles (dark, small particles). In blue their trajectories for a selected time interval.*

**REFERENCES:** [1] P. Tierno et al. Phys. Chem. Chem. Phys. 11, 9615 (2016).

# Mechanical Properties of Active Coacervate Microdroplets

Andrea Testa[1], Yingjie Xiang[2], Robert W. Style[1] and Eric R. Dufresne[1]

[1] *Laboratory of Soft and Living Materials, ETH Zürich, Zürich, Switzerland.*

[2] *Jacobs-Wagner Lab, Yale University, West Haven, USA.*

**SUMMARY:**

Out of equilibrium, active materials are capable of interesting functions such as the ability to perform work, being self-healing and adaptive, and being able to move. In living systems, the excess energy needed for performing these actions is typically provided by the decomposition of a chemical fuel in a plethora of different reactions. In particular, it has been shown[1] that bacteria can change the viscosity of the cytoplasm (and in turn the diffusion of the different components) in function of their metabolic state, hinting at the possibility that activity can influence the mechanical properties of materials.

Inspired by these studies, in this research we devised a system composed of coacervate microdroplets, widely regarded to be relevant as protocells and membraneless organelles models, containing an artificial enzyme (gold nanoparticles) and we envision to study the influence of a chemical fuel (hydrogen peroxide) on the mechanical properties.

The effect of the energy injection given by the fuel consumption into the catalytic microdroplets will conceivably give new insights on how the activity can influence the properties of matter and how this can be used to design a new class of out of equilibrium, active materials.

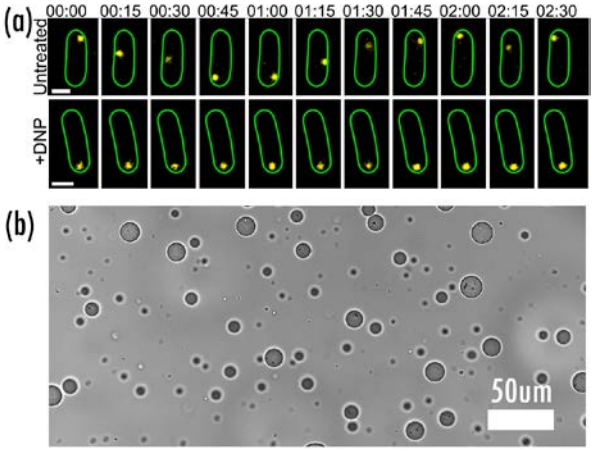


*Fig. 1: (a) Motion of a fluorescent tracker into a bacterium with (up) and without (bottom) metabolic activity[1]. (b) System of coacervate microdroplets*

**REFERENCES:**

[1]Parry, B. R., et al. (2014). *The bacterial cytoplasm has glass-like properties and is fluidized by metabolic activity*. ***Cell,*** *156*(1–2), 183–194.

[2]Li, M., Huang, et al (2014). *Synthetic cellularity based on non-lipid micro-compartments and protocell models*. ***Current Opinion in Chemical Biology****, 22*, 1–11.

# Microwave-Assisted Synthesis of PDMS-*b*-PMOXA as Amphiphilic Diblock Copolymer

R. Wehr, D. Daubian, J. Gaitzsch, W. Meier

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**INTRODUCTION:** Amphiphilic block copolymers have shown to perform defined self-assembly into distinct morphologies in aqueous dispersions. From those, vesicles are of particular interest for biomedical applications due to their aqueous cavity and ability to encapsulate cargo.[1] A prominent example of a suitable biocompatible block copolymer is poly(dimethyl siloxane)-*block*-poly(2-methyl-2-oxazoline) (PDMS-*b*-PMOXA). However, its synthesis is time-consuming (reaction times up to three days) and challenging as it contains highly reactive intermediates (e. g. triflates).[2] Here we present an alternative way of synthesizing a PDMS-*b*-PMOXA diblock copolymer that shows improvements regarding the reaction time, control and reproducibility.

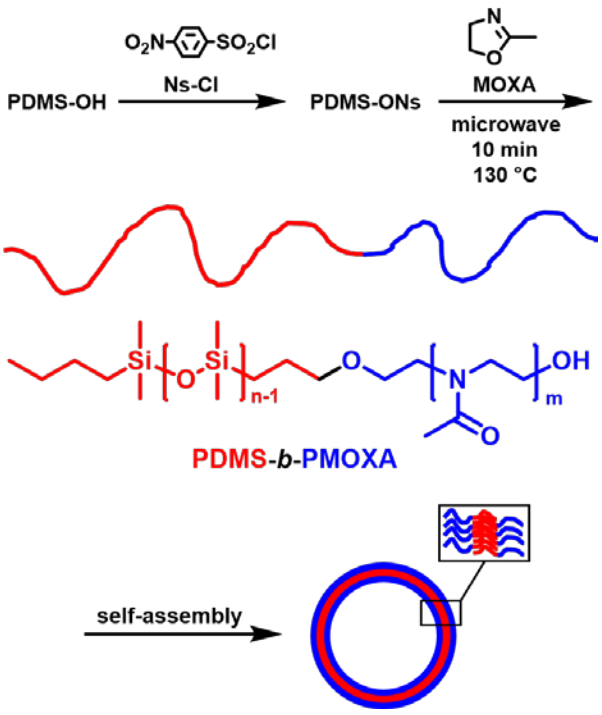


*Fig. 1: Protocol for the microwave-assisted synthesis of PDMS-b-PMOXA diblock copolymers and schematic representation of their self-assembly into polymersomes.*

**METHODS:** Starting from a commercially available monocarbinol-functionalized PDMS homopolymer we activated the terminal hydroxy group by deprotonation and addition of nosyl chloride (Ns-Cl). The following cationic ring-opening polymerization of 2-methyl-2-oxazoline was performed in a microwave-based reaction.

**RESULTS:** The microwave-assisted polymerization led to the formation of PDMS-*b*-PMOXA diblock copolymers. NMR and GPC studies revealed that besides the copolymer also non-reacted PDMS was present in the reaction mixture. Additionally, PMOXA homopolymers were formed to some extent. After purification by extraction and precipitation, a batch of pure PDMS-*b*-PMOXA was obtained.

**DISCUSSION & CONCLUSIONS:** This microwave-assisted synthesis benefits from a highly controlled and reproducible polymerization with massively reduced reaction times of only 10 minutes. The obtained amphiphilic diblock copolymers consisting of a hydrophobic PDMS block and a hydrophilic PMOXA block are promising candidates to perform self-assembly and to serve as nanoreactors or drug delivery systems in biomedical applications.[3]

**REFERENCES:**

[1] J. Gaitzsch, X. Huang, B. Voit; **2016**; *Chem. Rev.*; 116:1053–1093.

[2] S. Lörcher, W. Meier; **2017**; *Eur. Polym. J.*; 88:575–585.

[3] C. Palivan, R.Goers, A. Najer, X. Zhang, A. Car, W. Meier; **2016**; *Chem. Soc. Rev.*; 45:377–411.

**ACKNOWLEDGEMENTS:** The SNSF is acknowledged for financial support.

# Talks

# Sedimentation rate of non Brownian inclusions in networks of rod like particles

B. Barabé[1,2], D Z. Gunes[1], M P. Lettinga[2]

[1] *Nestlé Research Centre, Route du Jorat 57, 1000 Lausanne 26, Switzerland.*
[2] *Institute for Complex Systems-3, Forschungszentrum Juelich, D-52425 Juelich, Germany.*

**INTRODUCTION:** Paste like products are omnipresent in foodstuff, building and geological material. Their solid like properties enable them to bear their own mass and those of fillers, that may be added to increase the overall elastic properties of those viscoelastic systems.

Successive shearing events may decrease, or even suppress, particle-bearing properties[1]. This may be the case when shearing the gel irreversibly changes its structure. Such effects are not desirable for consumer products, in which fillers should stay homogeneous in solution during process and shelf life.

For this reason, model systems are sought in order to understand better the recovery of gel macrorheological properties in the presence of inclusion(s). Yield stress fluids composed of anisotropic subunits, efficiently trap beads at low volume fractions. A model colloidal system of repulsive colloidal rod-like fd virus and Pf1 bacteriophages was studied[2].

Homogeneous dispersed large non-Brownian inclusions were suspended in solutions of fd virus or Pf1 bacteriophages. The aim was to determine whether conditions for which beads were trapped in solutions could be found, hinting at the existence of a yield stress. A further goal was to investigate whether for some set of conditions, the system of inclusions in the virus suspensions is stable enough at rest to be used for shear experiments.

**METHODS:**

The viruses were suspended in a 20 mM Tris buffer, at range of concentrations below the transition to the nematic, aligned, phase. PS beads of 10 $\mu$m diameter and low density were purchased from Polysciences Inc. The PS beads were suspended in the virus's dispersions at a volume fraction of $\varphi_I$=0.07 % such that interparticle interactions can be neglected. The samples were loaded in rectangular capillaries (path length: 200 $\mu$m, width: 2 mm), and sedimentation was imaged using a horizontal microscope. The bead's sedimentation motion was tracked the python version of a code due to Weeks and Crocker.

**RESULTS:** The sedimentation rate of inclusions was investigated as a function of fd virus length, concentration and the solvent density.
In order to put in perspective these experimental results, we used the Stokes terminal speed predictions with a modified viscous term to account for concentration effects.
We noticed discrepancies between experiment and theory, validated by the study of inclusion sedimentation in a suspension of longer rods.
Furthermore, we compared the experimental data for the two rod length and showed that the decreasing trend is similar after rescaling with the overlap concentration.

**REFERENCES:**

[1] Emady, H. et al., J. Rheol., 57, 1761 (2013)

[2] M. P. Lettinga et al, EPL, 71 692 (2005)

**ACKNOWLEDGEMENTS:**.

The ICS-3 group is acknowledged for discussion on the fd virus system. The PGI-JCNS-TA workshop is acknowledged for making parts of the experimental setup.

# Capillary deposition of microorganisms in a microfluidic channel for the study of cells in spatially controlled environments

R.Pioli[1], E.Secchi[1], M.A.Fernandez-Rodriguez[2], Laura Alvarez-Frances[2], L.Isa[2], R.Stocker[1]

[1] *ETH Zürich, Department of Civil, Environmental and Geomatic Engineering, Zürich, Switzerland.*
[2] *ETH Zürich, Department of Materials, Zürich, Switzerland.*

**INTRODUCTION:** Controlled and precise deposition of microorganisms into defined spatial arrangements would offer unique and innovative possibilities for the study of microbial physiology and interactions. Full control over the geometrical arrangement is highly desirable because of the crucial importance of distances in microbe-microbe interactions, arising from their dependence on the propagation of chemical signals. Coupling accurate spatial patterning and full control over environmental conditions would provide a powerful and versatile platform for single-cell studies in microbial ecology

**METHODS:** We develop a microfluidic platform to perform sCAPA[1,2] (sequential capillarity-assisted particle assembly), a capillary deposition technique originally developed to create regular arrays of inert particles[3], in a closed channel. Our technology exploits the capillary forces resulting from the controlled motion of an evaporating droplet inside a microfluidic channel over a microfabricated substrate bearing an array of traps to trap individual microorganisms.

**RESULTS:** The microfluidic sCAPA has been applied to the preparation of different arrangements of colloidal particles and microorganisms. First, we calibrated the technique depositing spherical colloidal particles of 2 µm and 1 µm in diameter. Several sequential depositions have been done, obtaining desired sequences of particles. We deposited *Escherichia Coli* bacteria with single depositions, resulting in traps with just one trapped bacterium for the 500 nm deep traps, and in completely filled traps for the 1 µm deep traps. In addition, the sequential deposition of bacteria and colloids together has been performed. The spacing and relative position of individual microorganisms is controlled by the spacing and relative position of the traps, which can be adjusted with extreme accuracy during the microfabrication process of the template. Sequential depositions allow the generation of the desired spatial layout of single or multiple microorganisms. The geometry and composition are decoupled and can be independently be controlled: the shape of the trap defines the geometry of the final microbial arrangement, while the filling sequence determines its composition.

(a) (b)


*Fig. 1: (a) Sketch illustrating a side view section of a single deposition of colloidal particles. (b) SEM image of Escherichia Coli wild type trapped in PDMS traps. The lateral dimensions of the traps are 2 µm by 4µm, and the depth is 1 µm.*

**DISCUSSION & CONCLUSIONS:** We successfully calibrated the microfluidic sCAPA with colloidal particles and tested it on bacteria. We have shown that the coupling of sCAPA and microfluidics technology allows both geometric patterning of bacterial cells and precise control of environmental conditions, and thus opens a window into physiology of single microbes and ecology of microbe-microbe interactions.

**REFERENCES:** [1] Ni, S., Leeman, J., Wolf, H. & Isa, L., *Faraday Discuss.* **181,**225-242 (2014).

[2] Isa, L., Kumar, K., Muller, M., Grolig, J., *ACS Nano* **4,** 5665-5670 (2010)

[3] Ni, S., Leeman, J., Buttinoni, I., Isa, L. & Wolf, H., *Sci. Adv*, **2,** e1501779 e1501779 (2016)

**ACKNOWLEDGEMENTS:** ES thanks ETH Postdoctoral Fellowship and RP thanks ETH Research Grant for funding their research.

# Hierarchical damping of natural fibre composites

W. Woigk, K. Masania, S. Gantenbein, A.R. Studart

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**INTRODUCTION:** The dynamic behaviour of materials is of interest when the damping of structural vibrations is important. The ability to suppress vibrations has a significant influence on the component's performance, acting acceleration forces and service life. Viscoelastic materials capable of transforming kinetic into thermal energy are favourable damping materials. Lightweight engineering materials such as aluminium and fibre-reinforced plastics generally have high specific stiffness but suffer from poor damping [1,2]. Conversely, biological materials such as seashells and wood exhibit both high stiffness and damping due to hierarchical structuring of their reinforcements embedded in highly viscoelastic matrices. Biological composites combine mutually exclusive properties. By adapting the design guidelines from two natural systems, i.e. seashells and wood, we are able to design novel bio-inspired composites composed of hierarchically assembled stiff and soft phases that allow for simultaneous high stiffness and damping.

**METHODS:**

Nacre-inspired composites (NIC) are produced with $Al_2O_3$ (RonaFlair) platelets which were previously surface-functionalised with super-paramagnetic iron oxide nanoparticles (SPIONs) [3] to allow for magnetic alignment. Those platelets were introduced into uncured low-viscosity polymer matrix systems. Optionally a low magnetic field was applied to align the platelets in the matrix during cure [4].

Hierarchical natural fibre-reinforced plastics (hFFRP) were manufactured by placing natural fibre fabrics followed by an extrusion of the matrix onto the preform using a modified print head on an Ultimaker2+. The resin contained optionally various contents of $Al_2O_3$ platelets, whereas the extruded amount was controlled to account for a fibre volume fraction of 50%. The pre-infiltrated fibre stack was placed in a closed mould and the composite created in a compression-RTM process.

Dynamical Mechanical Analysis (DMA) in the form of frequency and amplitude sweeps was carried out in three-point bending to determine the viscoelastic material properties: E', E'' and tan (δ), where $E'' = E' \cdot \tan(\delta)$.

**RESULTS:** Fig. 1 (a) and (b) show the morphologies of the composites when introducing 20 vol% of platelets and aligning them in-plane and 7.5 vol% of initial matrix content in combination with natural flax fibres, respectively.

Fig. 1 (c) and (d) show the developments of the loss moduli dependent on the platelet volume content for NIC and hFFRP. An increase in loss modulus was measured for the NIC, which can be accurately described by a tension-shear chain model [2].

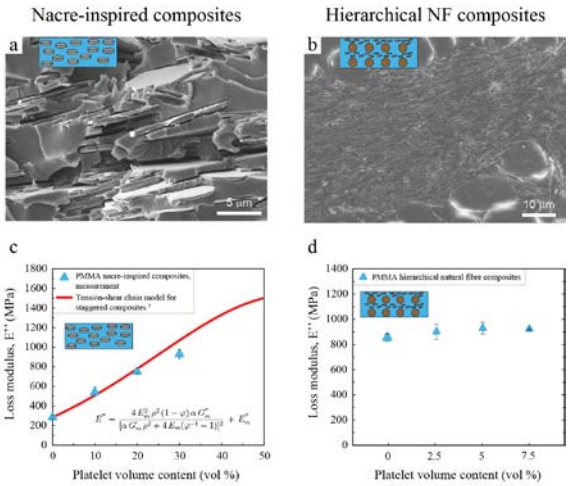


*Fig. 1: Morphology of (a) NIC and (b) hFFRP, Loss modulus of (c) NIC and (d) hFFRP as a function of $Al_2O_3$ platelet matrix volume content*

**DISCUSSION & CONCLUSIONS:** We show the enhancement of the damping figure of merit with increasing platelet volume content in the nacre-inspired composites, whereas the overall loss modulus can be significantly increased when introducing flax fibres. The platelet and flax fibre reinforced composites have a figure of merit similar to biological composites such as bone and wood. With the implementation of such materials, engineers will be able to design composite components that perform dynamically better and are less susceptible to vibrational failure.

**REFERENCES:**

[1] R.S. Lakes, Comp. Mat, 2002.
[2] P. Zhang et al., Mech. Phys. Solids, 2015.
[3] M. Grossman et al., Adv. Mat., 2017.
[4] R. Libanori et al., Appl. Mater. Interfaces, 2013.

**ACKNOWLEDGEMENTS:** GRS-077/15, SCCER Mobility Capacity Area A3, FHNW - IKT

# Microfluidic diffusion analysis of the size distribution and micro-rheological properties of protein solutions at high concentrations

M.R.G. Kopp, A. Villois, U. Capasso Palmiero P. Arosio
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**INTRODUCTION:** The size distribution and rheological properties of dispersions of biocolloids are essential quality attributes for a variety of industrial applications, including pharmaceutical, food, and cosmetic products. For instance, the biophysical properties of therapeutic proteins, which represent an important class of drugs in the pharmaceutical market, are important for their safety and efficacy. Many successful methods have been developed to measure these two fundamental properties, yet encounter a variety of analytical challenges, such as a low throughput, limited amounts of sample available, sample perturbations during the analysis, and narrow dynamic range of sizes probed by an individual technique, especially in the nanometre range. Biases in such measurements can also result from sample heterogeneity in terms of biomolecules sizes and concentrations. In this context, microfluidic technology offers a series of attractive features based on the different physics occurring at the micron scale with respect to the bulk.

**METHODS:** In this work, a microfluidic diffusion-sizing platform is applied to analyse protein sizes and interactions in high concentration samples directly in the solution state with minimal perturbation of the sample. The same device can be used to probe for sample viscosity at zero-shear, by monitoring the increase in the measured apparent radius of tracer nanoparticles of known sizes.

**RESULTS:** The technique is based on the measurement of several diffusion profiles under laminar flow (Fig. 1A). [1] The shape of these profiles contains information about the diffusion coefficients. The contribution of each species in the sample can be deconvoluted by fitting these profiles to a combination of simulated profiles (Fig. 1B), yielding number-average distributions. Based on this principle, a stressed antibody solution could be measured, revealing the presence of both monomeric species and aggregates, which could not be resolved by dynamic light scattering. The size distribution of monomeric solutions of proteins at concentrations as high as 150 mg/mL could be measured, eventually leading to the detection of protein complexes formation. Finally, we show that the same platform can be applied to measure viscosity-scaling effects in crowded environments by probing the Brownian motion of several tracers with different sizes. Such tracers experience a shift from the microviscosity to the macroviscosity of the sample at a critical probe size that is equal to the characteristic dimension of the main components of the dispersions.

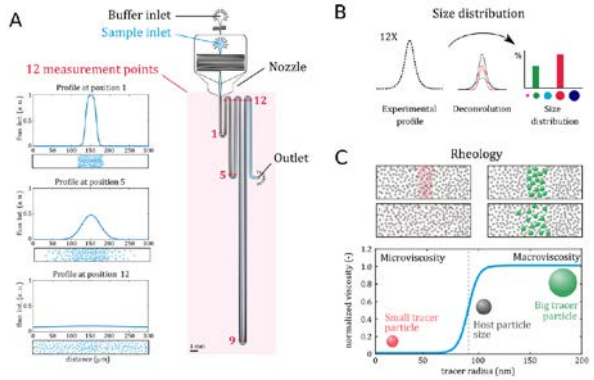


*Fig. 1: (A) Schematic drawing of the microfluidic diffusion device and of the evolution of the diffusion profiles along the channel. (B) The distribution of diffusion coefficients is evaluated by fitting the experimental profiles with a suitable combination of simulated profiles extracted from a library. (C) Probing formulation rheological properties by measuring the diffusion coefficients of standard tracer particles. Depending on the relative size of the tracer and the main component of the sample mixtures, the tracers can sample the microviscosity or the macroviscosity of the solution.*

**DISCUSSION & CONCLUSIONS:** Overall, this platform represents an attractive tool for the analysis of sizes and interactions of proteins in both diluted and high-concentration solutions during development, manufacturing, and formulation.

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# High speed confocal imaging of sheared colloidal gels

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**INTRODUCTION:** Colloidal gels represent an interesting family of soft materials. Despite the wide range of possible technological applications, the microstructural details underlying their typical solid-to-liquid transitions upon shear remain poorly understood, therefore posing challenges for industrial formulations. This stems from their hierarchical, strongly heterogeneous structure, lying at the roots of their bulk mechanical properties. The rheology of colloidal gels is very sensitive to the applied flow history and typically shows a complex behaviour including a yield stress and thixotropy. Dramatic changes in mechanical properties may well result from subtle, highly localized microstructural changes, which are impossible to resolve using scattering experiments.

**METHODS:** The experimental approach relies on the quantitative study of the gel microstructure using high-speed confocal microscopy. Microscopic studies under flow are performed using a stress-controlled rheometer with a home-made shear cell for counter-rotation of the lower plate, allowing single particles to be located and tracked for long times at the stagnation plane. The stress is directly measured, so that the link between microscopic observations and nonlinear rheology can be established.

The fast image acquisition (up to 1000 fps in plane) and the enhanced resolution (2x with respect to a normal confocal microscope) of our setup are ideal to study the nonlinear rheology of intermediate to low volume fraction gels, with field of views larger than typically possible.

**RESULTS AND DISCUSSION:** A model depletion colloidal gel was used. It consists of PMMA particles with a steric stabilizing layer of polyhydroxystearic acid, suspended in a density and refractive index matching solvent mixture, to which monodisperse PS was added. Structural rearrangements under shear are readily observed with our setup. At low shear rates, the gel structure coarsens and larger voids are created. At increasingly higher rates, the gel undergoes structural breakdown and eventually flowing aggregates are obtained. The microstructure in this flowing state is anisotropic, with a preferential orientation of microstructural features in the vorticity direction of flow. A direct link can be established with the flow curve of such materials, which behave as Herschel-Bulkley yield stress fluids

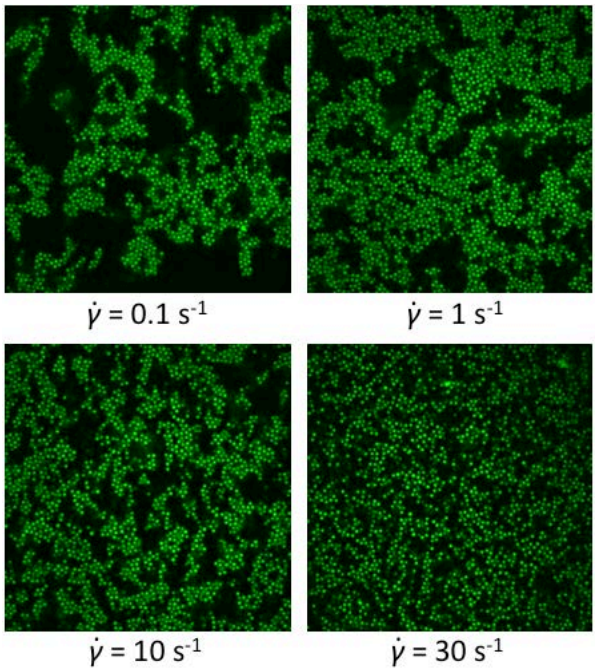


*Fig. 1: Snapshots of a model depletion colloidal gel under flow at different shear rates. The particles are 1 μm large, while the field of view is 100 μm wide*

**ACKNOWLEDGEMENTS:** this work is supported by the Swiss National Science Foundation, project number 157147.

# Three-Dimensional Printing of Hierarchical Liquid Crystal Polymer Structures

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**INTRODUCTION:** Fused deposition modelling is a technique that makes it possible to produce complex parts. However, the available polymers are relatively weak and thus methods have been developed to incorporate fibres, such as glass or carbon, into the print path. This increase in mechanical properties comes at the price of recyclability and ease of processing. It is well known that liquid crystal polymers (LCPs) can be aligned along shear and elongational stress fields [1] and that those fibres can be used to create monolithic composites [2]. These recyclable structures exhibit high stiffness and strength but are limited to simple geometries and orientations. Here, we combine the shaping freedom of3D Printing and LCPs to create complex structures with excellent mechanical properties

**METHODS:** Thermotropic LCPs form nematic liquid crystalline domains when melted. These domains can be aligned in the FDM nozzle along the extrusion direction. After exiting the nozzle, solidification stops the thermal reorientation of the molecules due to the cessation of flow resulting in a skin-core morphology.

Tensile samples with varying print line orientation and layer heights were tested before and after annealing. Thermal annealing below the $T_m$ of the material leads to a solid-state transesterification of the polymer and increased strength.

**RESULTS:** The maximal Young's modulus and strength were achieved when printing parallel (0°) to the loading direction (17 GPa stiffness and 400 MPa strength). The dependence of the modulus on the print direction can successfully be predicted using a classical laminate theory approach. Annealing leads to an increase in the strength for perpendicular (90°) sample, due to cross-linking between the individual filaments.

It is possible to adapt the local material architecture to the specific loading conditions that are applied to the part by designing the filament deposition direction during 3D printing. We demonstrated this capability by printing two OHT laminate architectures with either straight unidirectional print lines or bioinspired directional print lines, that resemble the fibre orientations in wood knots, and compare those result to the isotropic case *(Fig. 1).*

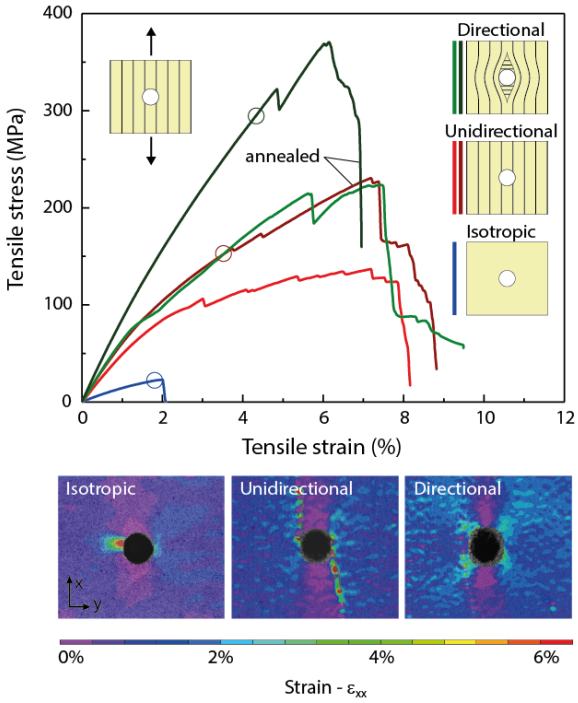


*Fig. 1: Comparison between two different print line geometries for an open hole tension samples and an isotropic reference. The bioinspired directional printed sample distributes load better than the simple unidirectionally printed specimen, which leads to improved stiffness and strength (Reproduced from [3]).*

**DISCUSSION & CONCLUSIONS:** We show 3D printed objects with stress-adapted print line architecture with mechanical properties that are much stronger than state-of-the-art 3D printed polymers and rival the highest performance lightweight materials using a readily available polymer and a commercial desktop printer. Thus, the technology is expected to be a game-changer in several structural, biomedical and energy-harvesting applications, where lightweight materials are used to reduce fuel consumption

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[2] R. Schaller et al. **2016**; *Comp. Part A; 81:296-304*

[3] S. Gantenbein et al. **2018**; *Nature; 561:226-230*

**ACKNOWLEDGEMENTS:** SCCER - Capacity Area A3, ETH Foundation grant SP-MaP 01-15, SNSF Project 200021_156011 and consolidator grant BSCGIO_157696

# Heteroaggregation of oppositely charged particles in the presence of multivalent ions

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**INTRODUCTION:** Particle aggregation is an important process in many systems and phenomena, such as wastewater treatment and paper making. The classical Derjaguin, Landau, Verwey, and Overbeek (DLVO) theory states that the aggregation of particles induced by increasing the salt concentration follows the mechanism of slow and fast aggregation regimes [1]. The transition between these two regimes occurs at a certain concentration, referred to as the critical coagulation concentration (CCC). Particle aggregation can be categorized into homoaggregation and heteroaggregation due to the identity of particles involved. Homoaggregation between the same particles has been well-studied. Researchers already have a reasonably good understanding of homoaggregation by proposing Schulze–Hardy rule [2] and inverse Schulze–Hardy rule [3]. However, heteroaggregation involving particles with different size and property is understood to a much lesser extent. In the present work, absolute heteroaggregation rate constants in the presence of multivalent ions were studied by time-resolved dynamic light scattering for the first time [4].

**METHODS:** Time-resolved multi-angle dynamic light scattering was used to measure stability ratios and rate coefficients for heteroaggregation between amidine latex (AL) and sulfate latex (SL) particles in electrolytes containing multivalent ions. These results were completed with measurements of stability ratios and rate coefficients for homoaggregation and the determination of electrokinetic potentials (ζ-potentials).

**RESULTS:** Two patterns for heteroaggregation between two types of oppositely charged particles were observed. The classical pattern features fast aggregation under all conditions. This pattern is characteristic of oppositely charged particles, and in the present system occurs in solutions containing ions of low valence. The novel pattern shows an intermediate region of slow heteroaggregation. This region occurs, when one of the particles undergoes a charge reversal, which can be induced by addition of multivalent ions of higher valence.

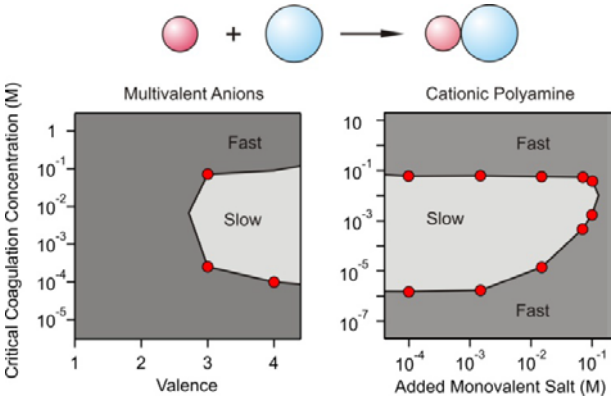


*Fig. 1: Stability maps featuring the dependence of the critical coagulation concentrations (CCCs) on the valence of the multivalent anions (left) and the aliphatic amine N6 on the concentration of the added monovalent salt (right).*

**DISCUSSION & CONCLUSIONS:** These intermediate regions of slow heteroaggregation resemble the ones observed for homoaggregation, which are systematically wider for heteroaggregation than for homoaggregation. This difference is related to the different magnitudes of surface charge densities near the charge reversal point. In addition, stability ratios and CCCs for heteroaggregation are very sensitive to the boundary conditions entering the calculations of double layer forces, especially where one of the particles is close to the charge reversal point.

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[3] T. Cao; I. Szilagyi; Oncsik T; M. Borkovec; G. Trefalt; **2015**; *Langmuir;* 31 : 6610.

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**ACKNOWLEDGEMENTS:** This work was supported by the Swiss National Science Foundation and the University of Geneva. TS acknowledges support from Japan Society of Promotion of Science.

# Synergistic Effects of Shear Flow and Solid-Liquid Interfaces on Protein Stability and Aggregation

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**INTRODUCTION:** Undesired aggregation of therapeutic protein formulations constitutes a severe drawback for the biopharmaceutical industry, since protein aggregates have been linked to *in vivo* immunogenic reactions and compromise the safety and potency of biotherapeutics. Different types of hydrodynamic stresses, present along the biotherapeutics manufacturing chain [1], have been suggested to be critical in triggering the aggregation of proteins. In parallel to hydrodynamic strains alone, the presence of interfaces is known to have a crucial influence on flow-induced protein aggregation [2]. While air-liquid interfaces have been extensively discussed, relatively little is known about solid-liquid interfaces and their interplay with fluid flow. In the present work, we investigated flow-induced protein aggregation in the absence of air-water interfaces and in the presence of controlled solid-liquid interfaces [3].

**METHODS:** A model IgG1 immunoglobulin and human insulin were employed for the study. The experimental setup used consisted of two syringes, connected by either a tubing (Fig.1A) or a microfluidic device, between which the protein solution was shuttled. The amount of protein aggregation occurred was determined through centrifugation of the aggregates and measure of the supernatant concentration via spectrophotometer measurements.

**RESULTS:** With fixed solid-liquid interfaces, the dependence of protein aggregation on parameters like shear rate, shear and protein concentration was investigated. The application of extremely high shear rates by means of a microfluidic device induced only modest increases in the amount of protein aggregation detected. When keeping fixed the hydrodynamic experimental parameters, instead, the controlled change of the solid-liquid interfaces to which protein solutions were exposed resulted in dramatic changes in the aggregation outcomes (Fig.1,2).

**DISCUSSION & CONCLUSIONS:** The pivotal role of the synergy between fluid flow and solid-liquid interfaces is confirmed by several aggregation tests. The data sets associated to two distinct experimental assays, differing only in the nature of the solid-liquid interface, strikingly predict opposite stability behaviours for a same protein formulation. Our results point towards the ubiquitous existence of complex and non-negligible protein-surface interactions that influence the microscopic mechanisms leading to protein aggregation, while hydrodynamic stresses *per se* are shown to be of limited relevance.

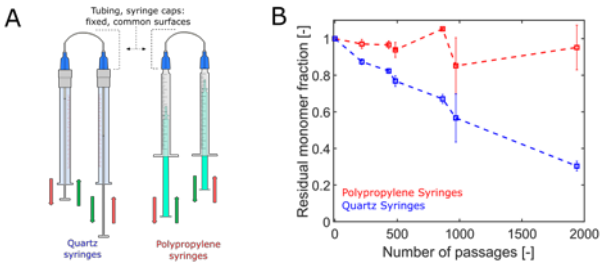


*Figure 1: Differences induced in the model IgG1 aggregation by changes in the solid-liquid interface. **A**: experimental setups employed. **B**: the corresponding residual monomer fractions computed from the aggregation assay*

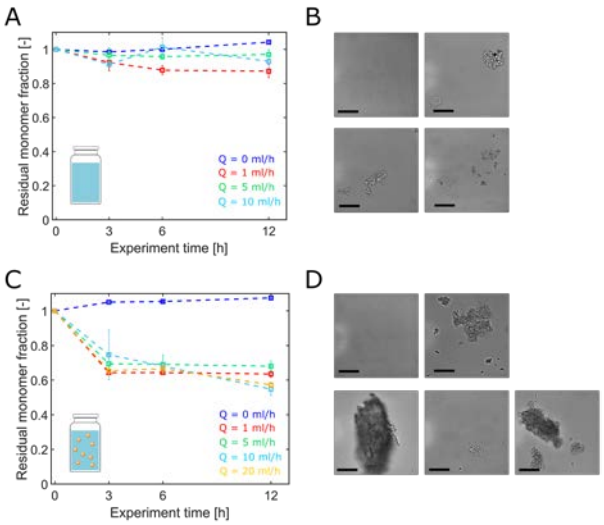


*Figure 2: Differences induced in human insulin aggregation in the absence (**A**,**B**) and presence (**C**,**D**) of hydrophobic nanoparticles.*

**REFERENCES:**

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# Multifunctional Protein Materials and Microreactors using Low Complexity Domains as Molecular Adhesives

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[1] *Department of Chemistry and Applied Biosciences, Institute for Chemical and Bioengineering, ETH Zürich, Switzerland.*

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**INTRODUCTION:** Recent findings indicate that a class of disordered amino acid sequences promotes functional phase transition of biomolecules in nature. Such sequences consist of low complexity domains (LCDs) of a few amino acids. In this work, we exploit these sequences by conjugating them to soluble globular domains to develop molecular adhesives that enable sensitive, controlled self-assembly of these proteins into supramolecular architectures, including both dynamic, protein-rich droplets and hardened particles. We further demonstrate that these features allow us to direct assemble different globular domains within the same architecture, thereby enabling the generation of both static multifunctional biomaterials and dynamic microscale bioreactors.

**METHODS:** Chimera proteins were expressed in an *E.Coli* host and subsequently purified by ion metal affinity column and gel filtration. Purity of product was assessed by SDS-PAGE gel electrophoresis and size exclusion chromatography coupled with a multi angle light scattering detector.

Phase separation at multiple pH, ionic strength values were assessed via bright field optical microscopy and epi-fluorescent microscopy. Permeability of liquid and solidified droplets were determined via Thioflavin T diffusion and staining into and out of the respective structures. Activity of protein rich phases and solidified droplets were assessed using a commercial enzyme activity assay.

**RESULTS:** By conjugation with LCDs obtained from biological phase separating systems, we were able to induce liquid-liquid phase separation of highly soluble globular proteins, namely Adenylate Kinase (AK) and Green Fluorescent Protein (GFP). We observed that the formation of the protein-rich liquid droplets was followed by maturation into solidified particles that under some conditions maintained their spherical shape. We were able to show that both the liquid droplets and the hardened particles are permeable to organic molecules, which can diffuse into and out of the respective structures. In addition, mixing of two different globular domains with the same LCDs resulted in homogenous, protein rich, microscale droplets, which retained the activity of both globular domains even in the solidified state, effectively creating homogenous, microscale reactors (Fig. 1).

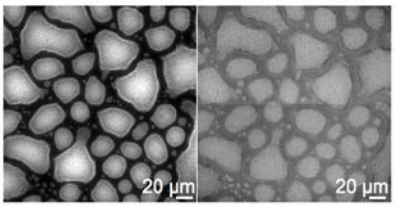


*Fig. 1: Epi-fluorescence microscopy images of solidified homogenously dispersed droplets containing AK-LCD2 and GFP-LCD2 at GFP emission (left) and fluorescence product of AK catalysed reactions (right).*

**DISCUSSION & CONCLUSIONS:** We have demonstrated that the conjugation of globular proteins with certain LCDs induces a controlled self-assembly into supramolecular structures. We have shown that this strategy can be applied to develop permeable protein materials, which retain the activity of the globular domain. Moreover, we have demonstrated that the dynamic nature of the protein-rich phase can be exploited to control the composition of the final aggregates. Furthermore, we have shown that the molecular adhesives can bring together different functionalities within the same architecture. This technology leads to the generation of both static multifunctional biomaterials and dynamic, liquid micro-scale bioreactors.

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**ACKNOWLEDGEMENTS:** We gratefully acknowledge financial support from the SNSF (grant 205321_179055), and the Novartis Foundation for Biomedical and Biological Research.

# Block Copolymer Patterning of Graphene Towards Membrane Applications

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*Soft Materials*

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**INTRODUCTION:** 2D materials, such as graphene, promise a wide variety of novel applications and devices. One interesting application is using graphene as selective membrane material due to the minimized flow resistance as a result of orifice rather than channel transport. As unpatterned graphene is not mass permeable, a method to create pores on wafer scale is required for further investigation and to unravel the full potential of 2D-based membranes.

**METHODS:** Patterning of graphene is achieved via sphere forming block copolymers (s-BCP). A thin film of s-BCP on graphene undergoes microphase separation, resulting in a porous etch mask for subsequent anisotropic patterning. A lift-off procedure enables the manufacturing of a freestanding membrane consisting of a graphene selective layer and a commercial polymer support.

**RESULTS:** The permeation characteristics of graphene-on-polymer membranes are investigated by gas and water transport measurement. The observation of high permeation rates for both, gas and liquid, in combination with a size cut-off from 30nm to 80nm indicate applications in the upper end of ultrafiltration. The high permeation is a result of the highly porous, ultrathin selective layer made from graphene, having a minimal flow impedance.

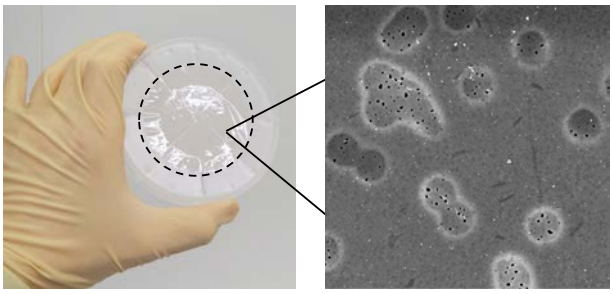

*Fig. 1: Wafer-scale graphene membrane outlined by dished circle (left). A SEM graph of the porous graphene (pores as seen as black dots) on a commercial track-etched polycarbonate support (right).*

**DISCUSSION & CONCLUSIONS:** The as-presented methods and results constitute a step towards the large-scale manufacturing of 2D membrane for filtration and separation. The challenges that need to be addressed are the minimization of leaks through process optimization, the further reliable scaling up as well as the characterization of the fouling behaviour of these membranes. Furthermore, smaller pores in such membranes would enable applications in nanofiltration (e.g. Dialysis).

**REFERENCES:** Choi et al., **2018**, submitted

**ACKNOWLEDGEMENTS:** RMW thanks LG Electronics for financial support of this work as well as Dr. Kyoungjun Choi, Karl-Philipp Schlichting and Prof. Dr. Hyung Gyu Park for their contribution to the project.

# The physical chemistry of lipid droplet biogenesis

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**INTRODUCTION:** Lipid droplets (LDs) are organelles present in every type of cell. Their main function is to store energy in the form of neutral lipids (NLs), such as triacylglycerol (TO) and cholesteryl esters (SE). While the scientific interest for these organelles has increased during the past years, little is known about the mechanisms that regulate their formation and maturation. The current model suggest that NLs are formed and stored between the two leaflets of the endoplasmic reticulum (ER). There, NLs start to aggregate into lenses that grow until LDs eventually bud off the bilayer. Our project is focused on the study of ER properties that regulates LDs formation from a molecular point of view.

**METHODS:** We performed coarse-grained molecular dynamics (MD) simulations, using the force field developed by Klein and coworkers[1].
All the systems were prepared through conversion of atomistic snapshots using the CG-it software (https://github.com/CG-it/) or using the software Packmol[2]. We used the software LAMMPS[3] to run all the simulations. All the systems were run using an NPT ensemble, keeping constant temperature and pressure at 310 K and 1 atm via a Nosé-Hoover thermostat and barostat. Van der Waals and electrostatic interaction were truncated at 1.5 nm. Long-range electrostatics beyond this cutoff were computed using the particle-particle-particle-mesh (PPPM) solver, with an RMS force error of $10^{-5}$ kcal $mol^{-1}$ $Å^{-1}$ and order 3. Multiple replicas of all the systems were run. The analyses were carried out using GROMACS tools[4] and TCL scripts.

**RESULTS:** Our results suggest that the formation of LDs can occur spontaneously in the cell (*Fig. 1*). Surface tension (ST) and curvature play an important role in regulating TO aggregation. Furthermore, ER lipid composition modulates LDs formation. Lipids that are known to be present at high concentrations at the site of lens formation promote the biogenesis of this organelle.

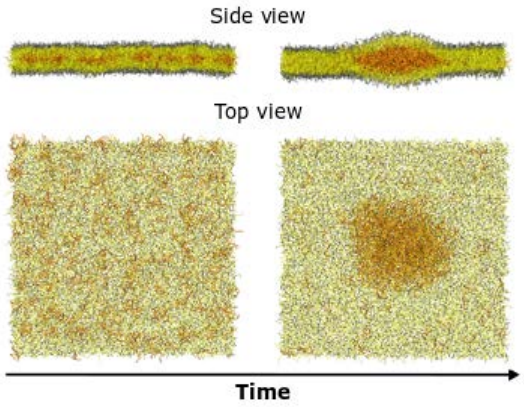


*Fig. 1: Spontaneous formation of a TO lens (orange) in a DOPC bilayer (yellow). DOPC head groups are coloured in grey.*

**REFERENCES:** 1. Shinoda et al. (2008); 2. Martinez et al. (2009); 3. Plimpton et al. (1995); 4. Abraham et al. (2016).

**ACKNOWLEDGEMENTS:** This work was supported by the Swiss National Science Foundation Grant no. 163966.

# Posters

# Compartments and cascades: a model reaction for complex nanoscale systems

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**INTRODUCTION:** Compartmentalization at the nanoscale is fundamental in nature, where the spatial segregation of biochemical reactions within cells ensures optimal conditions for regulating metabolic pathways. [1, 2] The use of synthetic membranes based on block copolymers provides versatility and biocompatibility for various applications, united with higher stability compared to liposomes. [3] Here, we present a nature-inspired approach to engineer enzymatic cascade reactions taking place between separate polymeric vesicular nanocompartments (CNC), each containing one enzyme type, uricase (UOX) and horseradish peroxidase (HRP) and acting in tandem, where uric acid is degraded by the former, resorufin is produced by the latter and with hydrogen peroxide as the linking molecule.

**METHODS:** PMOXA-*b*-PDMS-*b*-PMOXA polymersomes were formed by film rehydration, encapsulating UOX or HRP and both permeabilized by the bacterial porin OmpF. Dynamic and static light scattering (DLS/SLS) were used in concert with transmission electron microscopy (TEM) to confirm the vesicular structure of the assemblies and fluorescence correlation spectroscopy (FCS) yielded the diffusion time and total number of vesicles. BCA assay was used to quantify the encapsulated enzyme, whose activity was then compared in different setups (UV-Vis and fluorescence spectroscopy) and kinetic parameters were determined. The cascade reaction was then tested in human serum and in hyperuricemia-like conditions together with cells.

**RESULTS:** The formation of hollow vesicles was confirmed by both SLS/DLS and TEM. By comparing the same concentrations of enzymes either encapsulated or free in solution (and combinations thereof), it was possible to determine that the diffusion of substrates through OmpF is the main bottleneck of the cascade between two CNCs, until an average 1.5 μm inter-vesicle distance, where the diffusion between vesicles becomes the main limiting factor. However, the encapsulation provided high resilience against denaturing agents, temperature and protease, resilience that was further confirmed by the CNC having the same activity as the free enzymes in high-uric acid human serum. CNCs performed similarly, if not better, to free enzymes when detoxifying cell cultures from high concentrations of uric acid.

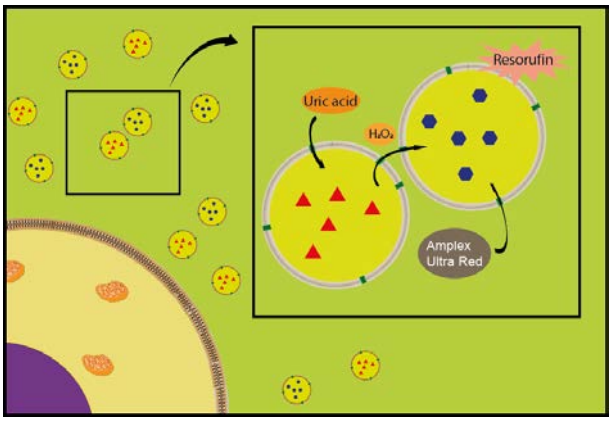


*Fig. 1: Cascade reaction of UOX-CNC (red triangles) with HRP-CNC (blue hexagons), communicating trough the membrane-integrated Outer membrane protein F OmpF (green triangles)*

**DISCUSSION & CONCLUSIONS:** As proof of concept, we successfully demonstrated communication between catalytic nanocompartments both in buffer and in biological media and measured the parameters governing this communication. Encapsulation provided protection from the external environment and could cooperate with cells to better survived toxic concentrations of uric acid.

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**ACKNOWLEDGEMENTS:** This work has been supported by the National Science Foundation. Authors would like to profoundly thank to Dr Samuel Lörcher for synthesis of the polymers.

# Solution and gel-properties of ultra-high molecular weight polyethylene in good and poor solvents

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## Abstract

Recently the gel-spinning of high-performance polyethylene (HPPE) fiber precursor from "green" solvents, such as vegetable oils, was demonstrated [1]. In comparison to the use of precursor fibers crystallized from traditional solvents, such as decalin, for a given polymer concentration, even better properties could be achieved by using precursor fibers crystallized from solvents with a remarkably poorer solvent quality.

The reasons for the improved performance were not evident and the results are questioning the established concept of the reduced entanglement density in solution being solely responsible for drawability. In this study, a systematic approach, aiming at the identification of factors affecting drawability in the gel-spinning process as a function of solvent quality, is presented. The study is divided into four parts, corresponding to four main stages of the gel-spinning process: rheological properties of the polymer solution, the gelation process, mechanical properties of the resulting gel and drawing behavior of the polymer fiber precursor. Throughout the study, measurements were performed for different polymer concentrations in good and poor solvents.

First, the linear viscoelastic behavior of polymer solutions is investigated, with a focus on differences in the molecular weight between entanglements and the zero-shear viscosity of solutions of good and poor solvents (at equal volume fraction). Second, the gelation process is analyzed using the Winter-Chambon method for near critical gels [2], addressing gelation time, gel strength and relaxation exponent in dependence of undercooling. The final gel and fiber precursor are characterized by the means of isothermal dynamic mechanical analysis in shear and compression, as well as simple uniaxial compression. Finally, the correlation of the observed properties of the gel, with the drawability of the polymer fiber precursor, will be discussed.

References

[1] Schaller, R.; Feldman, K.; Smith, P.; Tervoort, T. A., *Macromolecules* **2015**, *48*, 8877-8884.

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# Melting behaviour of nascent Polytetrafluoroethylene powder

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The melting behaviour 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, characterized by adjacent-re-entry crystallization, resulting in a high crystallinity and a low degree of entanglement. This special nascent (also called "virgin") morphology can be achieved by polymerization at low temperatures (relatively inactive catalyst surface) or by using single-site catalysts. In both cases, the as-polymerized polymer chain is thought to crystallize before it can entangle with its neighbours.

Another polymer that is known to have this specific nascent-powder morphology is polytetrafluoroethylene (PTFE). The objective of the current study is to evaluate the melting behaviour of nascent PTFE powder by differential scanning calorimetry (DSC), using isoconversional kinetic analysis, resulting in an apparent activation energy and pre-exponential factor, both as a function of conversion. It will be shown that melting of nascent PTFE powder is also dominated by superheating, even stronger than in the case of nascent UHMWPE. Specific kinetic models to describe this behaviour will be discussed.

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[2] A. Toda, M. Hikosaka, K.Yamada, "Superheating of the melting kinetics in polymer crystals: A possible nucleation mechanism", Polymer, 43 (2002), 1667-1679
[3] S. Vyazovkin, B. Yancey, K. Walker, "Nucleation -Driven Kinetics of Poly(ethylene tetrephtalate) Melting", Macromolecular Chemistry and Physics, 214 (2013) 2562-2566
[4] S. Vyazovkin, "Isoconversional Kinetics of Thermally Stimulated Processes", Springer, 2015

# Controlled microfluidic synthesis of polymeric nanoparticles for drug delivery

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**INTRODUCTION:** Drug-loaded polymeric nanoparticles (NPs) are an important class of drug delivery systems (DDS). These NPs enable the encapsulation and administration of poorly blood soluble active pharmaceutical ingredients (API). Physical parameters, such as NP size, surface charge, shape, and surface roughness influence NP biodistribution and cellular uptake[1]. In this perspective, any clinical application requires precise control over NP assembly. Further, scalable and reproducible fabrication of NPs is necessary for translation. In this work, we have engineered a system to control NP size and to better understand the underlying fundamentals of the NP formation process.

**METHODS:** Microfluidic platforms emerged for the controlled assembly of NPs[2]. Here, we have engineered a coaxial jet mixer (Fig. 1) to investigate the effect of synthesis parameters (*e.g.*, Reynolds number, polymer concentration, and solvent) on NP size. Polymeric nanoparticles were synthesized via nanoprecipitation by mixing an organic precursor solution containing the copolymer poly(ethylene glycol)-*b*-poly(lactide) (PEG-*b*-PLA) with water in the coaxial jet mixer. The NP suspensions were characterized by dynamic light scattering (DLS). Additional transmission electron microscopy (TEM) characterization was performed on selected NP populations. For each solvent, the CWC was determined by measuring the turbidity of the suspension as a function of the water content[3].

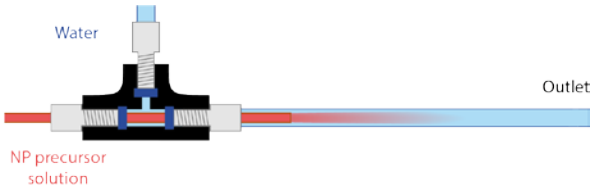


*Fig. 1: Schematic of the coaxial jet mixer utilized for nanoprecipitating polymeric nanoparticles.*

**RESULTS:** The coaxial jet mixer showed controlled nanoparticle synthesis for Reynolds numbers greater than 300 (Fig. 2). The size of $PEG_{5k}$-*b*-$PLA_{20k}$ nanoparticles was tuned between 40 and 200 nm. NP precursor solutions with different solvents showed that polymer dissolved in dimethyl sulfoxide formed the biggest nanoparticles followed by tetrahydrofuran, acetonitrile, acetone and dimethylformamide. We hypothesized that the critical water concentration (CWC) would be influential in controlling NP assembly and provide insight into the polymeric self-assembly[3]. CWC measurements of the different solvents showed a similar trend to that of the effect of solvent on NP size. The scale-up of the device showed an increase in production rate (up to 175 mg·min$^{-1}$) of more than 30 times with respect to conventional methods (~5 mg·min$^{-1}$).

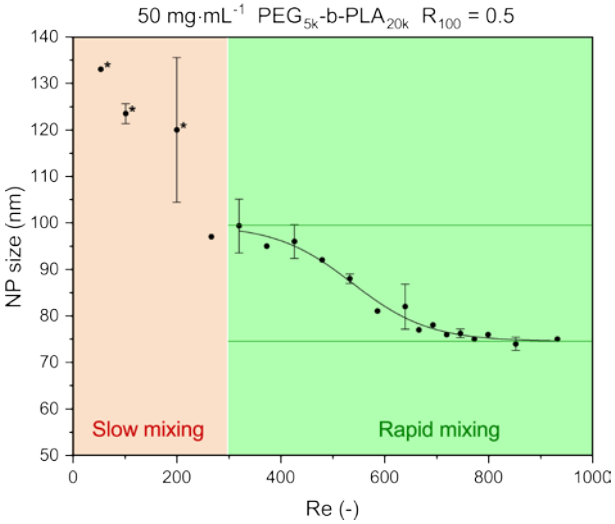


*Fig. 2: The diagram illustrates the effect of the Reynolds number on the size of $PEG_{5k}$-b-$PLA_{20k}$ NPs prepared using a coaxial jet mixer.*

**DISCUSSION & CONCLUSIONS:** These data demonstrated the ability to control and scale the synthesis of nanotherapeutics. The solvent choice influenced the nanoprecipitation process and suggested that the critical water concentration and Reynolds number are both critical physical parameters that control NP synthesis. In total, the device design provides efficient formulation engineering of polymeric drug nanocarriers while providing fundamental insight into the governing physics of polymeric nanocarrier assembly.

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**ACKNOWLEDGEMENTS:** We are thankful for the support of the Particle Technology Lab and to ScopeM for DLS and TEM measurements, respectively.

# A Rheological study of gas hydrates formed from carbon dioxide molecules

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**INTRODUCTION:** Natural gas hydrates are crystalline water-based solids formed when high-pressure and low-temperature thermodynamic conditions are attained and the water hydrogen bonds (hosts) encage and hold one or more gas molecules (guests)[1]. In this research, a high pressure cell is used to analyze rheologically the gas hydrate formation from water-in-crude oil emulsions. The viscosity behavior of the hydrate slurry is measured during the dissolution and formation process varying the shear rate and resting time. The results show relevant information in the management of hydrates.

**METHODS:** A high pressure system was utilized to supply the gas volume and pressure to make a live crude oil, that is, with light hydrocarbons. The system, illustrated in Fig. 1 is made up by the gas storage cylinder where pressurized CO2 come out until a booster, equipment that allows increasing the initial pressure established in the cylinders. After that, the pressurized gas is conducted to a serpentine pipe configuration to guarantee a constant rate of gas volume in the pressure cell. The experimental pressure is controlled and setting up in a regulating valve before entering to a measure cell. The torque applied by the rheometer measuring head is not directly transmitted to the rotor but conveyed by a non-contact, concentric magnetic coupling.

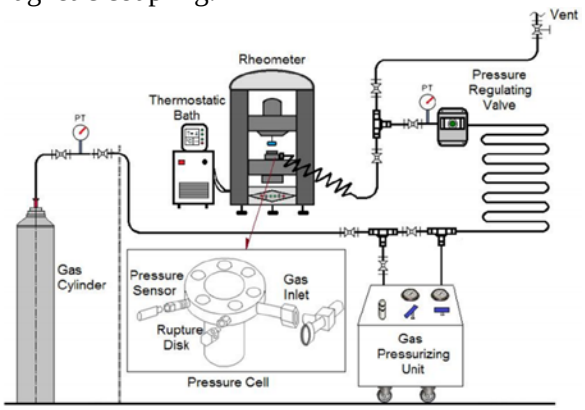


*Fig. 1: High pressure system using in the experiments.*

**RESULTS:** All our data are displayed in terms of viscosity over time. Figure 2 shows the effect of the shear rate on the induction time, and the data shown in Fig 3 are conceived to capture the ability of the reconstruction of CO2 hydrates in crude oil.

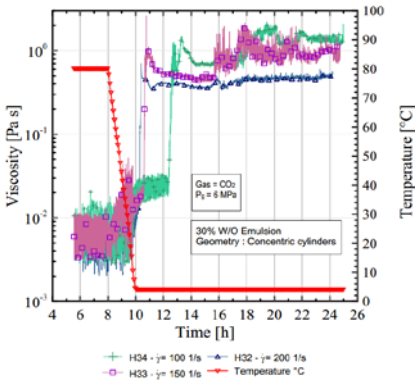


*Fig. 2: Viscosity over time for different shear rates at a fixed water fraction.*

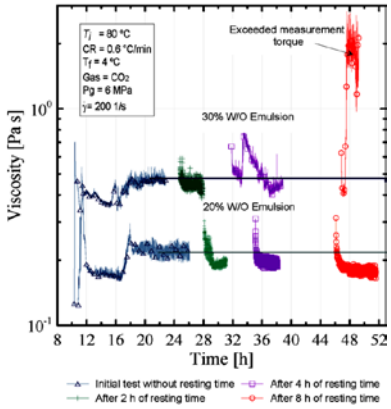


*Fig. 3: Viscosity over time at a fixed shear rate of $\dot{\gamma} = 200\ s^{-1}$ and for two water volume fractions of 30 and 20% water-in-oil.*

**DISCUSSION & CONCLUSIONS:**

- ✓ The viscosity jump represents the time of hydrate formation. Probably, this abrupt increment is due to the aggregation between hydrate crystals.
- ✓ CO2 hydrates slurries have the ability of re-built their structure after a period of rest, showing a time-dependent behavior.
- ✓ The induction time and asymptotic viscosity decreases with increasing shear rate. Which shows that the gas hydrates in the crude oil have a shear-thinning behavior.

**REFERENCES:** [1] Sloan, E. D; **2003;** Nature; 426, 353-363.

# Self-assembling behaviour of poly(ethylene oxide)-*block*-poly(butylene oxide) (PEO-*b*-PBO) in aqueous media

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**INTRODUCTION:** Block copolymers (BCPs) are well known for their potential to self-assemble into different microstructures, like vesicles, tubes, micelles and so on. That makes them interesting as nanoreactors, drug delivery systems and more.[1-2] Different BCPs consisting of poly(ethylene oxide)-*block*-poly(butylene oxide) (PEG-*b*-PBO) have been investigated depending on various block lengths. They can form vesicular structures as well as micelles depending on their hydrophilic block length. The four BCPs in this work showed various hydrophilic and hydrophobic block length ratios between 20% to 58%. Film rehydration was used as self-assembling method which was investigated by dynamic light scattering and transmission electron microscopy measurements. It was found that the BCPs (EO)45-*b*-(BO)20, (EO)25-*b*-(BO)20 and (EO)17-*b*-(BO)20 formed small, micellar structures respectively whereas (EO)8-*b*-(BO)20 showed a broader particle distribution.

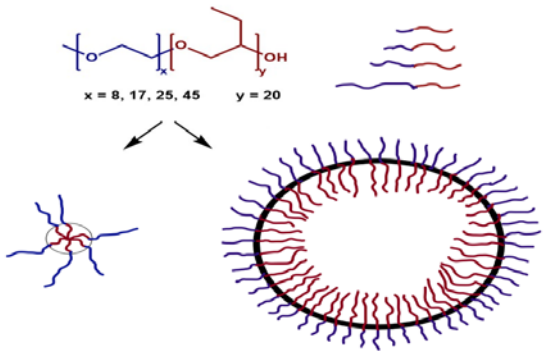


*Figure 1: Schematic representation of BCPs and their self-assembly into micelles (left) or vesicles (right).*

**References:**

[1] Jens Gaitzsch, Xin Huang, Brigitte Voit, *Chem. Rev.*, **2016**, 116, 1053-1093.
[2] M. Dionzou *et al*., *Soft Matter*, **2016**, 12, 2166-217

# Time-Controlled Self-Assembly by Clock Reactions: Chitosan Meets the Formaldehyde Clock

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Clock reactions are fascinating chemical systems, in which the formation of a product occurs abruptly after a certain time depending on the starting conditions. For this reason they have great potential for materials science applications, especially for programming the self-assembly of polymers and colloids in the time-domain.

Here we demonstrate that the formaldehyde-sulfite clock reaction, best known as "formaldehyde clock", allows the time-controlled precipitation of chitosan, a biopolymer with broad technological applications. Chitosan exhibits a pH-dependent solubility in water (pKa ≈ 6.5) and the formaldehyde clock exhibits an abrupt pH change from acidic (pH ≈ 5.5) to basic pH (≈ 10.5). By performing the formaldehyde clock in presence of chitosan, the latter is precipitated in the form of nanoparticles as soon as the "alarm" sets off *i.e.* the solution becomes alkaline.

Moreover, we show that the chemical structure of chitosan is not significantly affected by the reaction itself. Apart from demonstrating the suitability of the formaldehyde clock reaction for applications concerning biopolymers, our results may open up new possibilities for the production of chitosan particles for, e.g. controlled delivery applications.

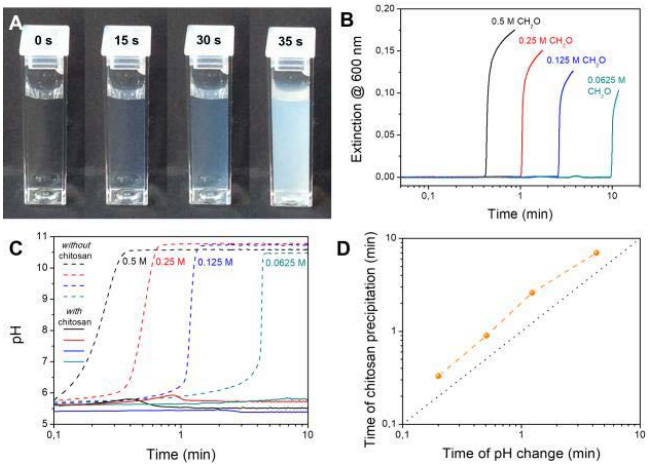


*Fig. 1: Time-controlled precipitation of chitosan. a) Movie frames showing the rapid evolution of turbidity for the chitosan-formaldehyde clock system (0.5 M CH2O). b) Turbidity plots for chitosan precipitation as a function of formaldehyde concentration. c) Evolution of pH over time for the formaldehyde clock without and with 0.1% m/v chitosan. d) Correlation between the time of chitosan precipitation and the time of sudden pH change in the absence of chitosan for identical reaction conditions. Reprinted from ref. [1].*

**REFERENCES:** 1 G. Panzarasa, A. Osypova, A. Sicher, A. Bruinink, E. R. Dufresne; **2018**; *Soft Matter*; 14:6415-6418.

# The influence of flow and geometric constraints on bacterial swimming and attachment

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**INTRODUCTION:** The vast majority of microorganisms are exposed to fluid flow, whether in natural environments, the human body, or artificial systems. Flow plays an important role in a broad variety of microbial processes, including nutrient uptake and fertilization, as well as in many industrial applications, ranging from wastewater treatment to the production of biofuels. However, despite the pervasive occurrence and implications of a fluid dynamic environment, its influence on the transport and attachment of bacteria to surfaces remains poorly investigated and understood, especially in topologically complex geometries that best describe real systems.

**METHODS:** To examine surface attachment in topologically complex geometries, we investigated the effect of laminar flow around a single pillar on motile bacteria in a microfluidics channel (Fig. 1). We developed a microfluidics platform where we could study both the effect of pillar diameter and of the local flow velocity on the transport and surface attachment of the opportunistic pathogen *Pseudomonas aeruginosa*. In order to broaden the generality of this study, we considered also corrugated surfaces.

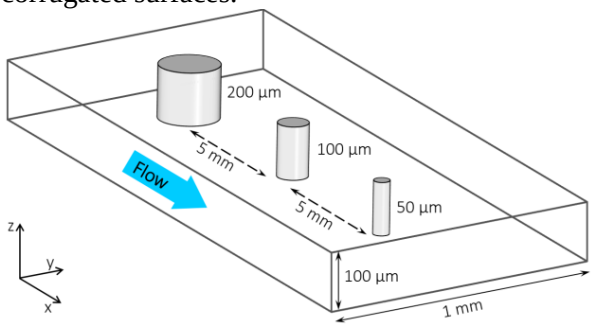


*Fig. 1: Schematic of the microchannel (with a cross-section of 100 µm×1000 µm) containing pillars of different diameter (200 µm, 100 µm and 50 µm).*

**RESULTS:** First, we present a phenomenon by which the combination of bacterial motility and shear results in a higher cell concentration near the walls of a channel and consequently in a strong enhancement of bacterial attachment to surfaces compared to quiescent conditions1. Thanks to the same mechanism, the topological features of the flow in complex geometries promote the attachment of bacteria to specific regions of the surface and shape their distribution. For example, when the imposed flow velocity is comparable to the bacterial swimming speed (45 µm/s), cells attach preferentially on the leeward side of the pillar (Fig.2) and capture events are more frequent.

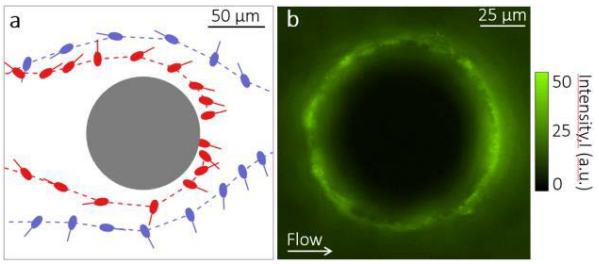


*Fig. 2: (a) Trajectories of bacteria in flow around a 100 µm pillar at a mean velocity of 150 µm/s simulated with a Langevin model. (b) Fluorescent image of PA14GFP cells attached to a 100 µm pillar after 5 hours of continuous flow of a diluted bacterial suspension at a mean velocity of 150 µm/s.*

**DISCUSSION & CONCLUSIONS:**
Thanks to a systematic experimental and numerical study, we show that the combined effect of flow past pillars of different dimensions and bacterial motility can increase the capture efficiency at imposed flow velocity compared to bacterial swimming speed. These results underscore the importance of fluid flow in triggering bacterial attachment and biofilm formation under common environmental conditions, with significant consequences in a broad range of ecological, industrial, and medical problems.

**REFERENCES:** 1Rusconi, R., Guasto, J.S. & Stocker, R.; **2014**; *Nature Communications;* 10: 212–217.

**ACKNOWLEDGEMENTS:** ES thanks ETH Postdoctoral Fellowship and SNF PRIMA Grant for funding her research.

# Structural Colour from Bio-Inspired Photonics

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Structural colours are very common in nature, where they are produced by biological nanostructures able to provide a variation in the material refractive index on the order of the wavelengths of visible light. These structures can cancel, deflect or reinforce specific wavelength intervals, generating a permanent, very bright, non-fading colour with no need of pigments or dyes.
By taking inspiration from the non-iridescent blue colours generated in the feathers of certain birds [1], which is due to the presence of phase-separated quasi-ordered photonic structures in the feather barbs, we aim to reproduce structural colours in artificial materials, where the biological components are replaced by synthetic polymers.

**REFERENCES:** [1]E. Dufresne *et al.*; **2009**; Soft Matter; 5(9), 1792-1795.

# Mechanical Properties of Giant Unilamellar Vesicles by Confocal Shape Analysis

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We present a new technique to characterize membrane tension σ, bending rigidity κ and adhesion energy density with a substrate of giant unilamellar vesicles (GUVs). The three-dimensional shape of a GUV is extracted from a confocal image stack and is subsequently fit with a shape equation containing all three parameters. The technique allows to fully characterize a vesicle from a single confocal stack without averaging over multiple vesicles of varying volumes. Results are compared to vesicle fluctuation analysis and checked for consistency. Unlike fluctuation analysis, however, the new technique is applicable well outside the low tension regime.

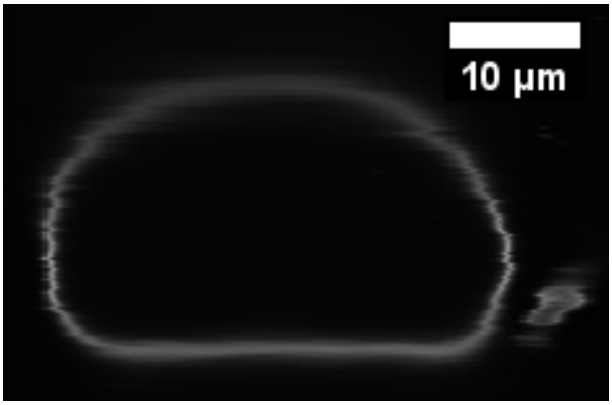


*Fig. 1: Side view of a sessile GUV made of POPC lipids. Image was taken on a confocal microscope. Each z-slice had an exposure time of 500 ms.*

# Developing Self-Assembled Peptide Nanoparticles for Safe and Efficient Gene Delivery

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**INTRODUCTION:** Gene therapy involves the delivery of exogenous nucleic acid into cells by viral or non-viral strategies [1]. Today, safer alternatives for viral vectors are under intense investigation. Among all non-viral delivery systems, peptides offer several advantages including reduced cytotoxicity and immuno-genicity along with a higher biodegradability and extensive design options [2]. In our study, we designed a new amphiphilic peptide, (RH)3gT consist of 19 amino acids that is able to self-assemble into multicompartment micelle nanostructures and condense a DNA.

**METHODS:** A Liberty Blue-Microwave peptide synthesizer (CEM, Kamp-Lintfort, Germany) was used to synthesize (RH)3gT. The synthesis was performed on a rink amide resin using standard fluorenylmethoxycarbonyl (Fmoc) solid phase peptide synthesizer chemistry and DIC/OXYMA coupling methods. (RH)3gT was analyzed by high performance liquid chromatography (HPLC) and mass spectrometry (MS). DNA loaded peptide assemblies were prepared by adding 4 µL of a 100 µM 22mer ssDNA solution to 100 µL peptide solution (1 mg/mL) and further diluting the mixture with 500 µL 35% ethanol. Dynamic light scattering (DLS), zeta potential measurements, fluorescence correlation spectroscopy (FCS), transmission electron microscope (TEM) were used to characterize the resulting self-assembled nanostructures.

**RESULTS:** (RH)3gT peptide nanoparticles and DNA-loaded (RH)3gT assemblies have a size below 200 nm (Fig. A1 and A2). TEM revealed spherical multicompartment micelles (Fig. B1 and B2). Zeta potential analysis showed a slight positive charge for (RH)3gT peptide nanoparticles which is decreased moderately after DNA entrapment (Table 1). Moreover, FCS data showed a 73% entrapment efficiency (Fig. C).

**DISCUSSION & CONCLUSIONS:** The 22-mer DNA strands were successfully entrapped inside the (RH)3gT peptide nanoparticles via electrostatic interaction with the arginine and histidine domain. Further modifications of the (RH)3gT peptide will be needed to entrap higher molecular mass single- and double stranded DNA.

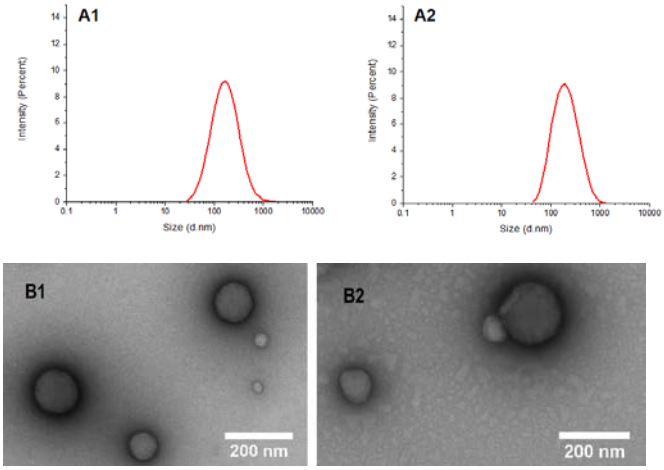


*Fig. A and B: DLS data and TEM images for (RH)3gT peptide nanoparticles (A1, B1) and DNA-loaded peptide nanoparticles (A2, B2).*

*Fig. C: FCS data for free dye, free labeled DNA and DNA-loaded peptide nanoparticles.*

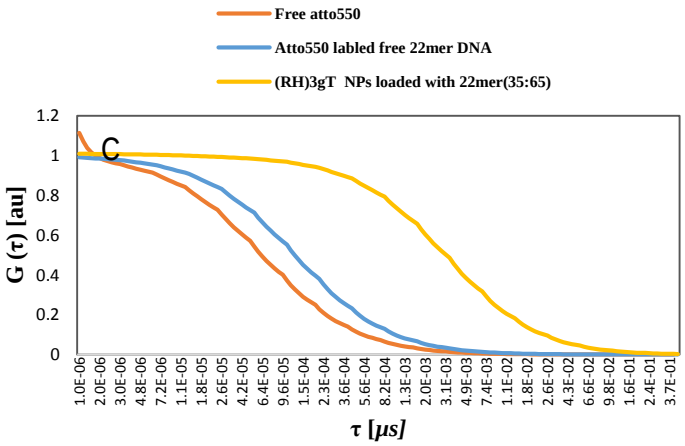


Table 1. Zeta potential of (RH)3gT peptide nanoparticles and DNA-loaded peptide nanoparticles

| | (RH)3gT | 22mer loaded (RH)3gT |
|---|---|---|
| Zeta potential (mV) | 8.02±0.48 | 4.33±0.08 |

**REFERENCES:** [1]*M. Molly E*; ***2007***; AAPS*; 9(1):E18-E29.*

[2] *S.J. Sigg, et al.*, **2016**; Biomacromolecules; *17(3): 935-945.*

# Stimuli-responsive Assemblies based on Subcompartmentalized Giant Polymersomes

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**INTRODUCTION:** Compartmentalization plays a pivotal role in the highly complex functions of eukaryotic cells. Incompatible materials are stored separately and specific metabolic activities happen in individual steps in isolated compartments which is a prerequisite of many cellular regulatory mechanisms. To attain a better understanding of the complexity of cellular multistep processes, the creation of multicompartmentalized assembly is aimed. Vesicular systems provide the simplicity and resemble the architecture of a biological cell and its organelles. Due to the lack of stability of liposomes, the use of synthetic membranes based on block copolymers with properties as biocompatibility, biodegradability and tunability provides a better solution for various applications. [1] The outer membrane of such a multicompartment is required to be semipermeable to allow passive diffusion of small molecules while the designated compartments and bigger biological elements remain inside the microenvironment. [2, 3]

**METHODS:** In an effort to form a multicompartment structure, we have encapsulated desired smaller nanostructures, such as nanoparticles, vesicles or micelles, within a larger micron-sized giant unilamellar vesicle or giant polymersome using the film rehydration method. In this perspective, we have studied a subcompartmentalized giant polymersome built-up from a fully synthetic membrane based on poly(2–methyloxazoline)–*block*–poly(dimethylsiloxane)–block–poly(2-methyloxazoline (PMOXA-*b*-PDMS-*b*-PMOXA). Additionally, this outer membrane of this giant polymersome contains another block copolymer called PDMS–block–heparin which functions as a receptor-like molecule. [4] The inner nanocompartments were prepared from PMOXA-*b*-PDMS-*b*-PMOXA / PDMS-*b*-heparin mixtures (V5, V25, M100), a reduction-sensitive graft polymer with a disulfide bond poly(2–methyloxazoline)–*graft*–poly(ε-caprolactone) (PMOXA-*g*(SS)-PCL) (NP-Graft), and (PMOXA-*b*-PCL) (NP-Control). For characterization of these multicompartments, Fluorescence correlation spectroscopy (FCS) with laser scanning microscopy (LSM) mode was used.

**RESULTS:** Our LSM measurements demonstrate that various multicompartments with sizes in the range of 4 to 50 µm can be formed using the film rehydration method. The FCS data proves the existence of the inner subcompartments and the resulting information about the hydrodynamic sizes of the respective nanostructures are similar entrapped and in bulk. The significant decrease of the number of NP-Graft in the confocal volume in the giant polymersome in presence of dithiothreitol was successfully determined by FCS measurements.

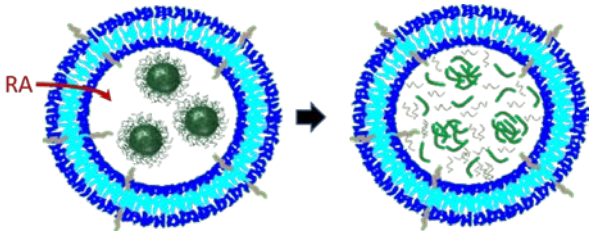


*Fig. 1: Schematic of the rupture of the subcompartments entrapped in giant polymersomes in presence of reducing agents (RA).*

**DISCUSSION & CONCLUSIONS:** As a proof of concept, we subsequently demonstrated the rupture of the reduction sensitive nanoparticles within a giant polymersome triggered by the presence of reducing agents over time.

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**ACKNOWLEDGEMENTS:** This work has been supported by the National Science Foundation. Authors would like to profoundly thank to Dalin Wu and Sven Kasper for synthesis of the polymers.

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