# Swiss Soft Days

## 24th edition
## Fribourg 22.03.2019

Adolphe Merkle Institute, University of Fribourg
Chemin des Verdiers 4, 1700 Fribourg

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Anton Paar

Local organizers: Véronique Trappe
Stefano Vanni

# PROGRAM

| **09.30-10.00** | **Registration / Coffee** | |
|---|---|---|
| 10.00-10.05 | Welcome | |
| 10.05-10.50<br>invited | Isa<br>(ETHZ) | Controlling active Brownian motion by feedback |
| *Chair: Gregor Trefalt (U Geneva)* | | |
| 10.50-11.00 | Schwemmer<br>(IBM) | High-resolution multi-channel nanoparticle separation utilizing rocked Brownian motors |
| 11.00-11.10 | Secchi<br>(ETHZ) | Fluid flow and motility control initial bacterial colonization on curved surfaces |
| 11.10-11.20 | Spanke<br>(ETHZ) | Dynamics of membrane wrapping of microparticles |
| 11.20-11.30 | Ong<br>(EPFL) | Selectively-permeable double emulsions |
| 11.30-11.40 | Drücker<br>(ETHZ & U Bern) | Engineering of microfluidic devices to unravel small molecule and pore-forming toxin interactions on biomembranes |
| 11.40-11.50 | Vutukuri<br>(ETHZ) | Artificial astrocytes: self-propelled particles in lipid vesicles |
| 11.50-12.00 | Belluati<br>(U Basel) | A nanotechnological approach to synthetic biology: cascade reactions in polymeric compartments |
| 12.00-12.10 | Steinmetz<br>(U Fribourg) | Investigation of nanoparticle presence in cellular environments via stimuli-induced heating |
| 12.10-12.15 | Renggli<br>(ETHZ) | Announcement<br>Swiss Soft Days edition 25 |
| **12.10-13.15** | **Lunch (Pavillon Vert)** | |
| 13.15-14.00<br>invited | Roux<br>(U Geneva) | Endosomal membrane tension controls escrt-iii-dependent intra-lumenal vesicle formation |
| *Chair: Frank Scheffold (U Fribourg)* | | |
| 14.00-14.10 | Arosio<br>(ETHZ) | Protein phase separation: from biology towards new protein materials |
| 14.10-14.20 | Pilo-Pais<br>(U Fribourg) | DNA-mediated self-assembly of plasmonic structures |
| 14.20-14.30 | Fennouri<br>(U Fribourg) | Artificial membrane attack complex through DNA-guided self-assembly of pore-forming peptides: biological nanopores with programmable diameter |
| 14.30-14.40 | Jajcevic<br>(U Geneva) | Lipid nanotubes as template for gold nanowire fabrication |

| | | |
|---|---|---|
| 14.40-14.50 | Bertsch (ETHZ) | Injectable biocompatible hydrogels from cellulose nanocrystals for locally targeted sustained drug release |
| 14.50-15.00 | Rigo (U Basel) | Co-immobilization of polymersomes and micelles |
| **15.00-15.30** | **Coffee** | |
| *Chair: Ahmet Demirörs (ETHZ)* | | |
| 15.30-15.40 | Shang (ETHZ) | Assessing numerical methods for molecular and particle simulation |
| 15.40-15.50 | Marco-Dufort (ETHZ) | Rheology of boronic ester-based dynamic covalent hydrogels |
| 15.50-16.00 | Gasser (PSI) | Spontaneous deswelling of microgels controlled by counterion clouds |
| 16.00-16.10 | Bayles (ETHZ) | Anomalous solute diffusivity in ionic liquids and iongels: label-free visualization and physical origins |
| 16.10-16.20 | Galli (U Geneva) | Surfactant mediated particle aggregation in nonpolar solvent |
| 16.20-16.30 | Panzarasa (ETHZ) | Controlling self-assembly in the time-domain by means of complex chemical dynamics |
| 16.30-16.40 | Ardham (U Fribourg) | Droplet induced deformations of solid surfaces |
| **16.40 - …….** | **Apero (Pavillon Vert)** | |

## INVITED CONTRIBUTION

### Controlling Active Brownian Motion by Feedback

Lucio Isa

Laboratory for Interfaces, Soft Matter and Assembly, Department of Materials,
ETH Zurich

Active Brownian Particles (ABPs) are colloidal objects capable of harvesting energy and converting it into directed propulsion by virtue of their internal asymmetry. In particular, they move ballistically at short times, with a propulsion velocity dependent on the available "fuel", and diffusively at longer times, when rotational diffusion effectively randomizes the propulsion direction. If control over active trajectories by modulating the speed has already been established, the counterpart, where characteristic reorientation times are controlled, presents more challenges. Naturally, rotational diffusivity is set by temperature and by the geometry of the particle, leaving very little room for modulation. In this talk, I will show two different strategies to control ABPs by modulating rotational diffusivity using feedback. I will first show that we can realize ABPs with internal feedback. By composing active particle clusters comprising thermo-responsive colloids, we can achieve objects that reconfigure and adapt their geometry, and therefore their rotational diffusivity, depending on local temperature changes, e.g. achieved by light absorption. I will then describe the case of active magnetic particles with external feedback. By applying randomly oriented magnetic fields, we can effectively impose rotational diffusivities decoupled from the bath temperature. Moreover, by using real-time tracking of the particle position, we realize landscapes of spatially-varying rotational diffusion with dramatic consequences on particle dynamics. These results indicate that different kinds of feedback open new avenues to control ABPs towards the vision of realizing autonomous micro-devices.

**High-resolution multi-channel nanoparticle separation utilizing rocked Brownian motors**

Christian Schwemmer, Francesca Ruggeri, Xiaoyu Ma, and Armin Knoll

IBM Research – Zurich

Nature uses fascinating machines called molecular motors to achieve intracellular directed transport of molecules (1). The discovery of their working principle in the 1990s inspired the invention of so called Brownian motors, which utilize molecular Brownian motion. In detail, the two main ingredients of a Brownian motor are an asymmetric energy landscape and an external unbiased zero-mean driving force to bring the system out of equilibrium. Our implementation defines a ratchet shaped energy landscape (2,3) provided by electrostatic interactions in weak electrolytes between charged gold nanoparticles of 60 nm to 100 nm diameter and the like charged surfaces of a patterned nanofluidic slit (4). To power the motor, we apply a zero-mean AC electric field across the slit which induces an electro-osmotic flow and thus a driving force on the particles. We observed average drift speeds of up to 50 $\mu$m/s for 60 nm gold spheres. As discovered by Bartussek et al., the motor exhibits an Arrhenius-like dependence of the particle current on the amplitude of the energy barriers which is a promising feature for nanoparticle separation (5).
Exploiting this property, we developed a Brownian motor for fast and highly selective nanoparticle sorting based on a ratchet shaped energy landscape with steadily increasing amplitude of the single teeth. The device separates gold spheres of nominally 80 nm and 100 nm diameter along its y-coordinate into up to 30 subpopulations with nominally <2 nm sensitivity in particle diameter. By switching the applied field to the x-direction, the separated populations are subsequently transported to compartments for collection. Thus, scalable continuous multi-channel particle separation is within reach. Due to the electrostatic origin of the interaction energy we expect that the method also works for small molecules, such as 60 bp DNA or charged proteins (e.g. prothymosin α, starmaker-like protein). Moreover, the flow-less directed transport and the potential to fabricate complex energy landscapes from a single lithographic step paves the way for unique separation and accumulation devices with high dynamic range and the capability of analyzing complex mixtures.

(1) Hänggi et al., Rev. Mod. Phys, **81**, 387, (2009)
(2) Skaug et al., Science, **359**, 1505, (2018)
(3) Schwemmer et al., Phys. Rev. Lett, **121**, 104102, (2018)
(4) Krishnan et al., Nature, **467**, 692, (2010)
(5) Bartussek et al., Europhys. Lett., **28**, 459, (1994)

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**Fluid flow and motility control initial bacterial colonization on curved surfaces**

Eleonora Secchi

Department of Civil, Environmental and Geomatic Engineering, ETH Zürich

The vast majority of microorganisms are exposed to fluid flow, whether in natural environments, the human body, or artificial systems. However, despite the pervasive

occurrence and implications of a fluid dynamic environment, its influence on the transport and attachment of bacteria to surfaces1–3 remains poorly understood, especially in complex geometries that best describe real systems. We will show that fluid flow and surface geometry greatly influence transport and surface colonization by swimming microorganisms such as *Pseudomonas aeruginosa* and *Escherichia coli*4. Using a combination of microfluidic experiments and numerical modelling, we will demonstrate that flow preferentially promotes bacterial attachment on specific regions of curved surfaces, i.e., on the leeward side of isolated cylindrical pillars and directly after the apexes of regular and randomly corrugated surfaces. Colonization is tightly linked to bacterial motility, which increases the attachment rates by two orders of magnitude compared to the case of non-motile bacteria or passive particles. Moreover, for relatively low flow rates (i.e., for fluid velocities not greater than 10 times the swimming speed of bacteria) a simple scaling law for the pillar capture efficiency is found, which means that the density of adhered bacteria is independent of the size of the pillar. In contrast, for high flow rates, the behavior of motile bacteria is equivalent to that of passive particles, for which the attachment rate per unit surface decreases with increasing pillar dimensions. Taken together, these results underscore the importance of fluid flow in governing bacterial colonization and biofilm formation under common environmental conditions, with significant ecological, industrial, and clinical implications.

(1) Rusconi, R., Guasto, J. S. & Stocker, R. Bacterial transport suppressed by fluid shear. *Nat. Phys.* **10,** 2–7 (2014).
(2) Peruzzo, P., Defina, A., Nepf, H. M. & Stocker, R. Capillary interception of floating particles by surface-piercing vegetation. *Phys. Rev. Lett.* **111,** 164501 (2013).
(3) Lecuyer, S. *et al.* Shear stress increases the residence time of adhesion of Pseudomonas aeruginosa. *Biophys. J.* **100,** 341–350 (2011).
(4) Secchi, E. *et al*., paper in preparation

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**Dynamics of Membrane Wrapping of Microparticles**

Hendrik Th. Spanke [1], Claire François-Martin [1], Robert Style [1], Eric Dufresne [1], Manuel Eisentraut [2], Holger Kress [2]

[1] Department of Materials, ETH Zürich

[2] Fakultät I - Mathematik, Physik und Informatik, Universität Bayreuth, Germany

Biological membranes partition eukaryotic cells into different compartments, each of which having its own function and integrity. Moreover, some organelles are characterized by very complex membrane shapes, which seem to confer to them, at least partly, their function. The regulation of biological membrane geometries is therefore crucial.
In vivo, proteins are most probably the main actors of membrane deformation. The underlying physical mechanisms of protein-membrane interactions are not comprehensively understood. 3D membrane geometries can be observed in protein-free systems as well. As the result of the adsorption of particles for example (1,2). The adsorption of inert particles could thus enable reproduction of the essential physics of membrane deformation by bound proteins. Many numerical and simulation works have

predicted how particles behave when adsorbed to membranes (3,4). However, corresponding experimental data is lacking.

We observe experimentally how micron sized particles bind and subsequently are enveloped by lipid membranes. The lipid membranes are characterized by a bending rigidity $\kappa_b$ and a membrane tension $\sigma$, which is near zero in our experiments. The polystyrene particles used experience an adhering force introduced by depletion interactions. Both the adhesion energy and particle size can be varied continuously in our system without changing the underlying composition. Due to depletion interactions being used, the experimental system is also independent of the choice of particle material or specific lipid composition of the membrane. We observe the extent of wrapping of the particle over time and see the particle being taken up and effectively recoiling over a distance of one particle radius.

(1) Dietrich *et al.*, J Phys II **7**, 1651 (1997)
(2) Yu and Granick, JACS **131**, 14158 (2009)
(3) Deserno, PRE **69**, 031903 (2004)
(4) Bahrami, Advances in Colloid and Interface Science 208 (2014), 214-224

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**Selectively-permeable double emulsions**

Irvine Lian Hao Ong, Esther Amstad

Institute of Materials, EPF Lausanne

Selective permeability of cell membranes facilitates active transport of essential molecules upon appropriate stimulation, and this is a fundamental function that ensures viability of cells. Double emulsions mimic such an architecture in that two miscible fluids are separated by an immiscible shell. Despite the apparent immiscibility between the fluids, molecules that are for practical purposes immiscible in the shell are transported across it.(1,2) In this talk, I will demonstrate how this transport can be controlled using newly developed end-functionalised surfactants that impart a pH-responsive release/retention behaviour to the double emulsions. These surfactants can be used to repetitively and controllably load and unload double emulsions, thereby opening up new possibilities to controllably initiate chemical reactions within picoliter-sized reaction vessels.

(1) P. Gruner, B. Riechers, B. Semin, J. Lim, A. Johnston, K. Short, J. C. Baret, Nat. Commun., 2016, 7, 10392.
(2) J.-W. Janiesch, M. Weiss, G. Kannenberg, J. Hannabuss, T. Surrey, I. Platzman, J. P. Spatz, Anal. Chem. 2015, 87, 2063–2067.

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**Engineering of microfluidic devices to unravel small molecule and pore-forming toxin interactions on biomembranes**

Patrick Drücker [1,2], Ioan Iacovache [3], Simon Bachler [1], Benoît Zuber [3], Eduard B. Babiychuk [2], Annette Draeger [2], Petra S. Dittrich [1]

[1] Department of Biosystems Science and Engineering, ETH Zurich
[2] Department of Cell Biology, Institute of Anatomy, University of Bern
[3] Laboratory of Experimental Morphology, Institute of Anatomy, University of Bern

Microfluidic devices gained high attention due to their advantage to analyse reactions and membrane binding in small, controllable compartments. Recently, a microfluidic trapping device was prepared, that allowed trapping of individual giant vesicles in sealed micro-compartments (1). Operated via pressure-control, circular valves allowed trapping of vesicles and subsequent exchange of the surrounding medium to guarantee precise incubation with analytes. Another mayor advantage is their transparency for optical light, which makes them ideal for live-analysis via confocal laser scanning microscopy and transmission light microscopy. This design was modified to enhance capture efficacy by adding further trapping-pods into the chambers. Thereby we could demonstrate perforation and lipid-domain specific binding of vesicle membranes by the pore-forming toxin pneumolysin (PLY), which is secreted from *Streptococcus pneumonia* during a bacterial invasion (2). Herein, we will demonstrate the advantages and application of microfluidic devices for the analysis of membrane-interactions on unilamellar and multilamellar giant vesicle membrane models and living cells. Interestingly, cholesterol dependent pore-forming toxins could disintegrate multilamellar membranes in a hitherto unseen manner. By membrane deformation and expansion of the outer layer on giant vesicles, PLY could disrupt the barrier integrity and induce a layer-by-layer peeling event, which allowed the quantification of layers (3).

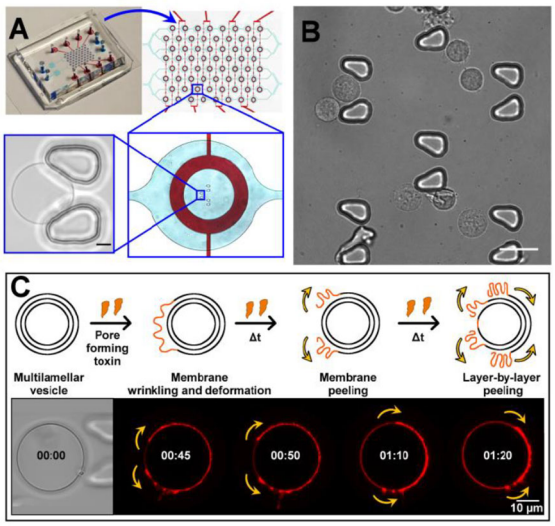


**Fig. 1: Design and application of microfluidic trapping devices.**
**A:** Two-layer microfluidic device with two parallel arrays of trap chambers. Fluid layer (blue) red layer pressure control. Scale = 5 µm.
**B:** Trapping of U937 cells. Scale = 20 µm.
**C:** PLY-induced Layer-by-layer peeling of giant vesicles. Scale = 10 µm.

(1) Robinson et al., Biomicrofluidics **2013**, *7* (4), 044105.
(2) Drücker et al., Biophys. Acta, Mol. Cell. Biol. Lipids **2018**, *1863*, 795-805.
(3) Drücker et al., **2019**, *submitted*.

**Artificial Astrocytes: Self-propelled Particles in Lipid Vesicles**

Hanumantha Rao Vutukuri, Jan Vermant
Soft Materials, Department of Materials, ETH Zürich

Biological cells actively respond to external stimuli, extend protrusions to explore their environment, and experience metabolic fluctuations. Artificial soft matter systems, which mimic various features of biological systems, can help us to understand an abundance of complex cellular phenomena. One of the prominent questions in synthetic biology is whether such soft artificial systems with high local forces, mimicking biological cells, can be engineered. Here, we present a minimal experimental model system consisting of self-propelled Janus particles in giant unilamellar lipid vesicles, to study certain features of cellular shape transformations induce by highly localized forces. We demonstrate that the propulsion force of a single particle as small as ~ 0.1 pN is already strong enough to induce a plethora of vesicle shapes and fluctuations, ranging from quasispherical shapes with active fluctuations to astrocyte-like structures. Moreover, the analysis of membrane fluctuations shows a strong deviation from the Helfrich model elucidating the specific role of active non-equilibrium processes. The minimalistic biomimetic system described here could provide insights into dramatic shape changes in cells, i.e., cell budding, and endo- and exocytosis.

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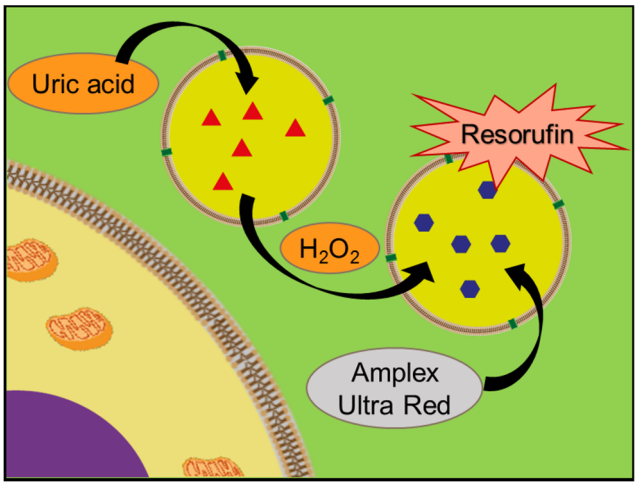
**A nanotechnological approach to synthetic biology: cascade reactions in polymeric compartments**

Andrea Belluati, Sagana Thamboo, Ioana Craciun, Juan Liu, Cornelia G. Palivan

Chemistry Department, Universität Basel

Compartmentalization plays a fundamental role in biology: the spatiotemporal segregation of biochemical processes, both within the cell and between cells, allows a fine control of optimal reaction conditions, kinetics and overall protection from external environment. Much like phospholipids, amphiphilic block copolymers can self-assemble into spherical vesicles resembling cells, which can host a variety of enzymes and thus perform several specific reactions, with applications mainly in biomedicine and biosensing.[1]
Using more than a single enzyme in an interconnected, cascading system means that nanometre-sized objects start to behave as simple enzymatic networks, achieving complex responses depending on the polymer-enzyme assembly. In addition, the biocompatibility of the chosen poly(2-methyloxazoline)-*block*-poly(dimethylsiloxane)-*block*-poly(2-methyloxazoline) (PMOXA-PDMS-PMOXA) polymer means that cells can be phenotypically modified by assisting their native metabolism or outright expanding their environmental response.[2] The ever-growing complexity of nanometric catalytic assemblies leads them to behave dynamically and, in turn, to interact with living matter.




(1) Belluati, A.; Craciun, I.; Meyer, C. E.; Rigo, S.; Palivan, C. G. Enzymatic Reactions in Polymeric Compartments: Nanotechnology Meets Nature. *Curr. Opin. Biotechnol.* **2019**, *60*, 53–62. https://doi.org/10.1016/j.copbio.2018.12.011.

(2) Belluati, A.; Craciun, I.; Liu, J.; Palivan, C. G. Nanoscale Enzymatic Compartments in Tandem Support Cascade Reactions in Vitro. *Biomacromolecules* **2018**, *19* (10), 4023–4033. https://doi.org/10.1021/acs.biomac.8b01019.

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**Investigation of nanoparticle presence in cellular environments via stimuli-induced heating**

Lukas Steinmetz [1], Joel Bourquin [1], Christoph Geers [1], Patricia Taladriz-Blanco [1], Mathias Bonmarin [2], Sandor Balog [1], Barbara Rothen-Rutishauser [1], Alke Petri-Fink [1,3]

[1] Adolphe Merkle Institute, University of Fribourg
[2] Institute of Computational Physics, Zurich University of Applied Sciences,
[3] Chemistry Department, University of Fribourg

The detection and characterisation of nanomaterials in analytically complex environments are prominent research interests in nanotechnology. Applied methods must be capable of analyzing nanoparticles (NPs) with various sizes, shapes and chemical compositions. When those NPs are e.g. exposed to a cellular environment they will likely be associated and uptaken by cells, which significantly complicates the characterisation of such NPs. Common techniques to investigate NP-cell interactions include for example inductively coupled plasma mass spectrometry (ICP-MS), electron microscopy (EM) or laser scanning microscopy (LSM). However, all these methods have their limitations, e.g. time-consuming sample preparation and measurements or sample destruction (1).
Therefore, new complementary approaches are being developed. Lock-in thermography (LIT) is a sensitive infrared imaging technique, which is commonly used to test composites and electronic components (e.g. solar panels) (2). The method allows analysis of stimuli-responsive samples by applying a specific trigger to excite NPs, which results in the generation of heat. Due to the flexibility of the method, various trigger signals can be employed, such as light or alternating magnetic fields (3). Furthermore, sample

preparation is straight-forward, as solid as well as liquid samples can be investigated without any pre-treatment. Additionally, LIT is a non-destructive technique and samples can be analysed within minutes.

We used LIT to stimulate plasmonic gold nanoparticles (Au NPs) and multiwalled carbon nanotubes (MWCNTs), which we exposed to different cell types for 24 hours. Homogeneous light of a specific wavelength was applied to excite these nanomaterials. As cells do not produce any heat under the employed conditions, the detected signal originates purely from the NPs. The result is a 2D heat map, which allows quantifying the produced heat with respect to the applied light intensity. As such, we gain insights in the degree of NP-cell association over the course of 24 hours, as an increase of heat generation directly relates to enhanced NP uptake and association.

To confirm the association and uptake of NP into cells, we used transmission electron microscopy (TEM) and darkfield optical microscopy with high resolution hyperspectral imaging for nano-scale imaging and analysis. We were able to resolve time-dependent differences in NP-cell association for different Au NPs and MWCNT sizes as well as cell types. For example, J774A.1 macrophages associate significantly more NPs than endothelial cells and continuously uptake NPs over 24 hours, whereas endothelial cells saturate after around 16 hours.

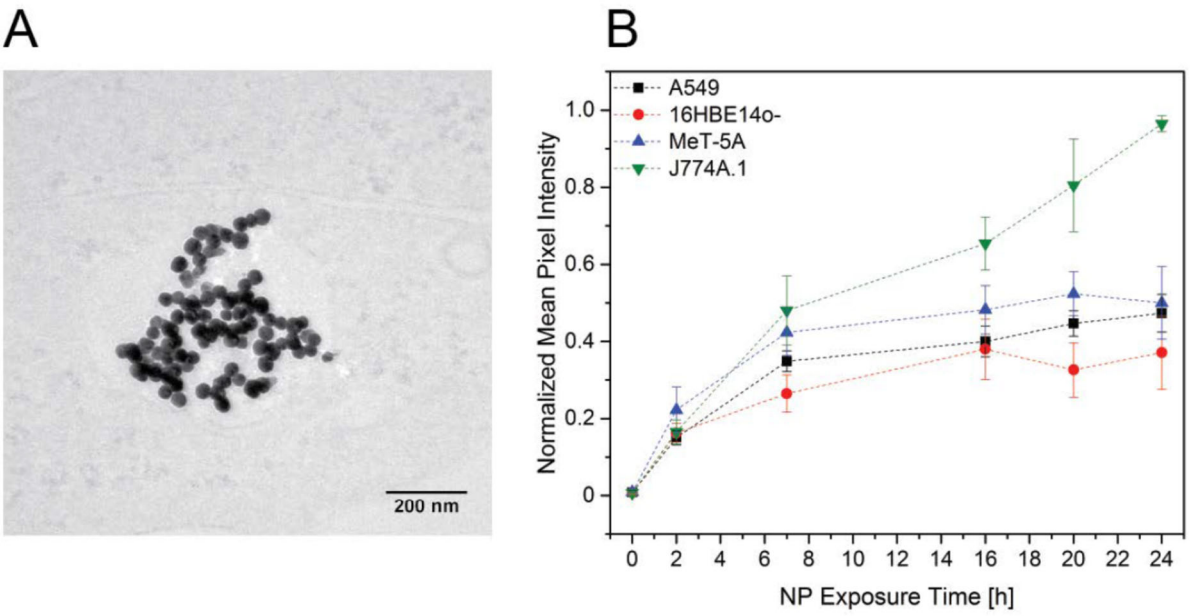


**Figure 1.** (A) TEM micrograph of 45 nm Au NPs in A549 cells. (B) NP association trends over 24 hours in different cell types measured by lock-in thermography.

(1) B. Michen, C. Geers, D. Vanhecke, C. Endes, B. Rothen-Rutishauser, S. Balog, A. Petri-Fink, Scientific Reports, 5 (2015) 9793-9799

(2) S. Huth, O. Breitenstein, A. Huber, D. Dantz, U. Lambert, F. Altmann, Solid State Phenomena, Vol. 82-84 (2002) 741-746

(3) C. A. Monnier, M. Lattuada, D. Burnand, J. C. Martinez-Garcia, A. M. Hirt, B. Rothen-Rutishauser, M. Bonmarin, A. Petri-Fink, Nanoscale, 8 (2015) 13321-13332

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## Lunch Break

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## INVITED CONTRIBUTION

### Endosomal membrane tension controls escrt-iii-dependent intra-lumenal vesicle formation

Vincent Mercier [1], Jorge Larios [1,2], Guillaume Molinard [1], Antoine Goujon [3], Adai Colom [1,2], Stefan Matile [2,3], Jean Gruenberg [1,2], Aurélien Roux [1,2]

[1] Department of Biochemistry, University of Geneva
[2] National Center of Competence in Research Chemical Biology, University of Geneva
[3] Department of Organic Chemistry, University of Geneva

Downregulated receptors and other membrane proteins are sorted into intralumenal vesicles (ILVs), which are formed in endosomes and delivered to lysosomes, where they are degraded together with their cargo. The ESCRT-III complex is the major membrane remodelling complex that drives ILV formation on endosomal membranes. Here, we made use of a new fluorescent membrane tension probe to show that ESCRT-III subunits are recruited onto endosomal membranes when membrane tension is reduced. We find that tension-dependent recruitment is associated with ESCRT-III polymerization and membrane deformation in vitro, and correlates with increased ILVs formation in ESCRT-III decorated endosomes in vivo. Finally, we find that endosomal membrane tension decreases when ILV formation is triggered by EGF under physiological conditions. These results indicate that membrane tension is a major regulator of ILV formation, and support the notion that reduced membrane tension facilitates membrane remodelling in all ESCRT-III mediated reactions.

**Protein phase transition: from biology towards new protein materials**

M. Linsenmeier, A.M. Küffner, L. Faltova, M. Hondele, K. Weis, P. Arosio

Department of Chemistry and Applied Biosciences, ETH Zurich

Increasing evidence demonstrates that cellular organelles can form via phase separation of proteins and nucleic acids. Yet, the molecular mechanisms that govern the dynamics of these membrane-less compartments remain largely elusive. Here, we analyze the microscopic processes underlying the phase separation of the DEAD-box protein ATPase Dhh1, which is strongly associated with the formation of processing bodies (P-bodies) in yeast. We show that binding to ATP triggers the reversible formation of protein-rich droplets, while RNA promotes phase separation and maintains the protein dense phase in the liquid state. These results reveal molecular mechanisms that cells have plausibly developed to accurately control the reversible assembly and the biophysical properties of P-bodies. Moreover, we demonstrate the possibility to mimic these mechanisms and induce similar behaviours in synthetic proteins by conjugating low complexity domains to soluble globular regions. We show that these biologically derived molecular adhesives enable the self-assembly of these proteins into supramolecular architectures via a multistep process. This multistep pathway involves an initial liquid−liquid phase transition, which creates protein-rich droplets that mature into protein aggregates over time. These protein aggregates consist of permeable structures that maintain activity and release active soluble proteins. We further demonstrate that this feature, together with the dynamic state of the initial dense liquid phase, allows one to directly assemble different globular domains within the same architecture, thereby enabling the generation of both static multifunctional biomaterials and dynamic microscale bioreactors.

(1) Faltova L., Küffner A. et al, "Multifunctional Protein Materials and Microreactors using Low Complexity Domains as Molecular Adhesives", ACS Nano, 2018, 12, 9991-9999

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**DNA-mediated Self-assembly of Plasmonic Structures**

Mauricio Pilo-Pais, Mathias Lakatos, Guillermo Acuna
Department of Physics, University of Fribourg

DNA can be used as a pre-programmable tool to fabricate metallic nanoparticles assemblies with a desired arrangement, nanometer spacing gaps, and tunable plasmon resonances. The structures are tailored to have unique optical properties such as custom-tuned hot spots for Surface Enhanced Raman (SERS) and fluorescence spectroscopy (1). More recently, we have shown the feasibility of using the DNA origami technique to fabricate plasmonic cavities with small mode volumes, able to achieve strong coupling between plasmons and molecular excitons (2). In this talk, I will discuss our assembly strategies toward assembling DNA-mediated hybrid structures which incorporate multiple components such as gold and silver nanoparticles, molecular excitons, and individual colloidal quantum dots (3). The design flexibility and the parallel assembly of DNA templates are ideal for combining photonic nanocomponents for optical applications.

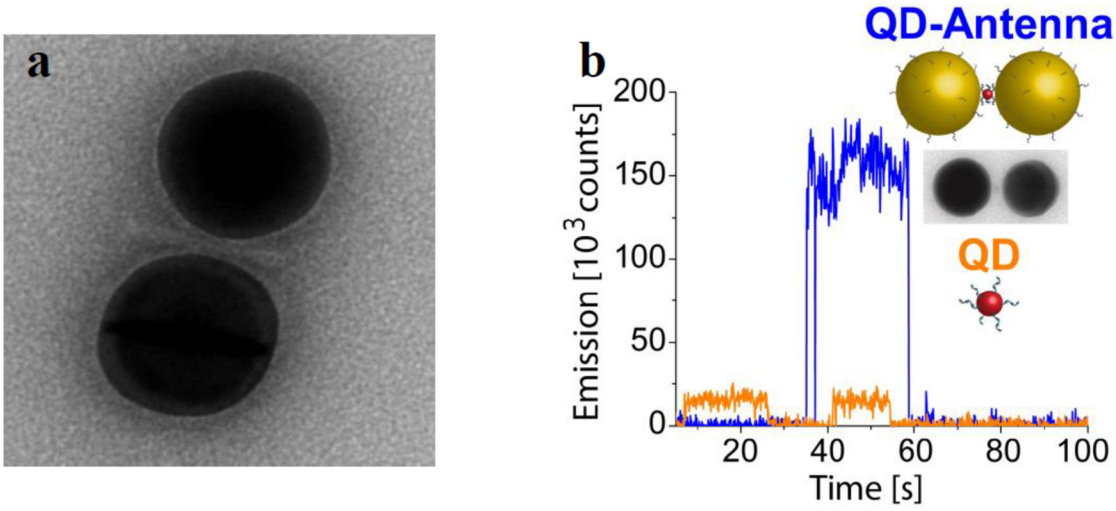


**Figure:** Examples of DNA self-assembled nanoantennas using **a)** a DNA-origami template and **b)** nanocomponents functionalized with complementary DNA sequences. In the latter, an individual QD is positioned between two metallic NPs resulting on enhanced fluorescence emission in respect to individual QDs.

(1) M. Pilo-Pais, G. P. Acuna, P. Tinnefeld, and T. Liedl. *MRS Bull.,* **2017**, 42, 936.
(2) E.-M. Roller, C. Argyropoulos, A. Högele, T. Liedl, and M. Pilo-Pais. *Nano Lett.,* **2016**, 16, 5962.
(3) Francesca Nicoli, Tao Zhang, Kristina Hübner, Boyuan Jin, Florian Selbach, Guillermo Acuna, Christos Argyropoulos, Tim Liedl, and Mauricio Pilo-Pais. *Small,* **2019**, 1804418.

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**Artificial membrane attack complex through DNA-guided self-assembly of pore-forming peptides: biological nanopores with programmable diameter**

Aziz Fennouri [1], Jonathan List [1], Julie Ducrey [1], Laura Pascual [1], Jessica Dupasquier [1], Viktorija Sukyte [1], Frederick Bertani [1], Sandra Rodriguez Gonzalo [1], Simon F. Mayer [1], Jerry Yang [2], and Michael Mayer [1]

[1] Adolphe Merkle Institute, University of Fribourg
[2] Department of Chemistry and Biochemistry, University of California, San Diego, USA

The membrane attack complex (MAC) of the complement system is an essential part of the innate mammalian immune response. Invasion of a host by a pathogen triggers a proteolytic cascade leading to the activation of various proteins that assemble on the pathogen cell membrane and form a transmembrane channel. These large MAC pores induce osmotic lysis of the pathogen cell. Targeted cell killing applications would benefit from such large pores than insert upon programmable signals.
Here, we developed DNA-templated assemblies of pore-forming peptides to large and defined pores, which insert into membranes in response to stimuli, to mimic the function

of the MAC. To this end, we covalently linked a nucleic acid to an antimicrobial peptide, Ceratotoxin A (CtxA). This CtxA-nucleic acid conjugate hybridizes to complementary DNA template structures possessing multiple hybridization sites, which define the number of peptide monomers involved in pore formation. A simple DNA strand allowed templating tetra-, hexa-, octa- or dodecameric assemblies, while rigid DNA origami structures further increased the assembly size and made it possible to template up to 40 peptide-DNA monomers. We observed direct incorporation of these templated assemblies into planar lipid bilayer membranes as opposed to sequential peptide association and dissociation typically seen with native CtxA. These DNA-templated peptides assemblies also killed cancer cells at 30-fold lower total peptide concentrations compared to native CtxA.
The modularity of this design allowed us to functionalize the construct with hydrophobic or receptor-binding moieties. This straightforward modification increased the affinity of the construct for the membrane, without modifying the peptide's amino acid sequence. Folic acid-modified constructs, for instance, exhibited a 10-fold greater cytotoxicity than non-specific peptide assemblies. Ultimately, employing DNA-based recognition mechanisms or biomolecular targets such as cancer-derived microRNAs may make it possible to trigger templated pore formation for targeted killing of pathogenic cells.

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**Lipid nanotubes as template for gold nanowire fabrication**

Kristina Jajcevic, Kaori Sugihara

Department of Physical Chemistry, University of Geneva

The fabrication of conductive nanostructures is the key technology in semiconductor industry and has gained importance in biology for applications such as biosensors and drug delivery. There is a growing interest in the use of lipid nanotubes (LNTs) as templates in the fabrication of one-dimensional nanostructures such as gold nanowires.
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 LNTs on polyelectrolyte-functionalized surfaces. We have demonstrated a high-throughput approach to fabricate gold nanowires on surfaces with a LNT template. First, biotin-tagged DOPE LNTs are formed from lipid blocks in inverted hexagonal phase adsorbed on polymer-coated surfaces upon application of shear force. Streptavidin-coated gold nanoparticles were then attached to the biotin-tagged LNTs and gold nanoparticle-encapsulated LNTs were cross-linked by chemical fixation (1). Samples were dried and particles were connected through electroless gold metal plating to form gold nanowires. The created nanowires 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 solid 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.

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**Injectable biocompatible hydrogels from cellulose nanocrystals for locally targeted sustained drug release**

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Nanocrystalline cellulose (NCC) is a biological nanoparticle that has attracted attention for potential biomedical applications. Due to its surface charge, NCC phase behavior and rheology can be controlled by targeted salt addition, e.g. NCC hydrogels may be obtained by sufficient charge screening [1]. NCC hydrogels have a yield stress, are shear-thinning, and reform after flow, allowing their application as injectable self-healing hydrogels [1,2]. Their rheology allow flow for subcutaneous or intramuscular injection. In-situ, they rebuild their gel structure and form natural extracellular matrix mimetics. The hydrogels may further be loaded with drugs, growth factors, or living cells for controlled release applications and regenerative medicine [3].

In our current work [4], we loaded NCC hydrogels with three model drugs (bovine serum albumin (BSA), tetracycline (TC), doxorubicin (DOX)) and examined in-vitro drug release kinetics into physiological saline at pH 7.4 and simulated gastric juice at pH 2 and 37°C. Drug diffusion coefficients D were calculated from the initial linear release. All three model drugs revealed first order release kinetics, although diffusion and release rates varied from days to weeks, underlining the importance on drug-NCC or solvent interactions (see Fig. 1). The charged protein BSA was not released into simulated gastric juice (pH 2) due to charge inversion and complexation with NCC, potentially allowing gastric administration with pH-triggered release in the duodenum.

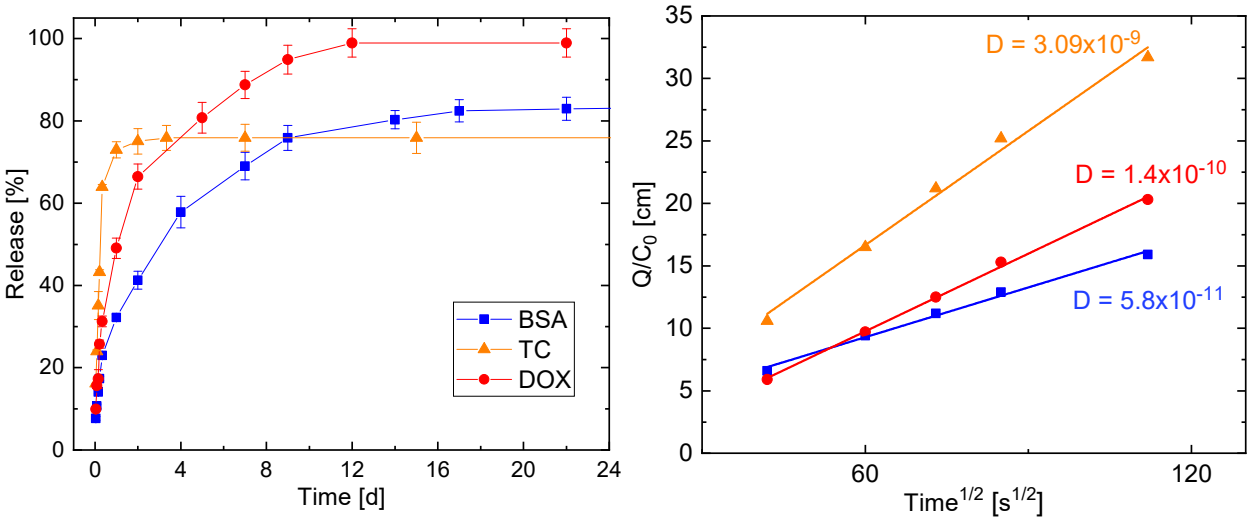


**Figure 1** left: Release rates of model drugs into physiological saline from 3 wt% NCC hydrogels (30 mM NaCl) at 37°C. Right: Respective diffusion coefficients calculated from initial release rates.

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**Co-immobilization of polymersomes and micelles**

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Amphiphilic block-copolymers are the main building blocks of self-assembled polymeric micro- and nanostructures, such as polymersomes or micelles. To engineer, improve, and optimize safe biomedical surfaces, the bio-orthogonal and catalyst free strain promoted Azide-Alkyne click (SPAAC)[1] reaction is promising for the immobilization of such soft, polymeric nanostructures that can protect and release an active agent when needed.[2] Here we present the immobilization of nanostructures as well as the co-immobilization of two different types of nanostructures through SPAAC and a thiol-ene click reactions.[3, 4]

METHODS: Poly(2-methyloxazoline)-*block*-poly(dimethylsil-oxane)-*block*-poly(2-methyloxazoline) (PMOXA-*b*-PDMS-*b*-PMOXA) based polymersomes with different ratios of azide terminated polymers were prepared by thin film rehydration and characterized by transmission electron microscopy (TEM), dynamic light scattering (DLS) and fluorescence correlation spectroscopy (FCS).

Surfaces were functionalized with dibenzocyclooctyne (DBCO) (scheme 1) and characterized by contact angle (CA) measurements and laser-scanning microscopy (LSM).

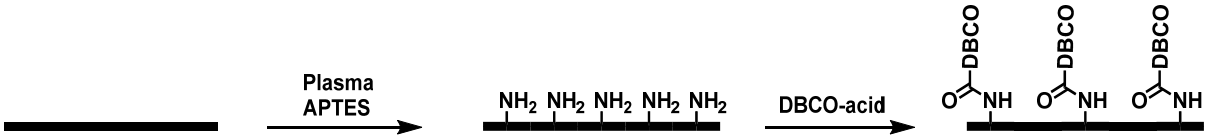


**Figure 2:** Schematic representation of the surface functionalization.

Polymersomes were immobilized and studied by laser scanning microscopy (LSM) when stained by bodipy, atomic force microscopy (AFM) and scanning electron microscopy (SEM). Furthermore, polymersomes were micro contact printed on surfaces and co-immobilized with methacrylate exposing self-assembled structures on surfaces which were bifunctionalized with DBCO and thiols.

RESULTS: Successful functionalisation of the surface with DBCO groups has been shown by an increase of surface hydrophobicity and immobilization of an azide dye, which was visualized by LSM. Polymersomes with azide groups were stable and their presence affected neither the self-assembly process nor the architecture, as characterized by DLS

and TEM. Surfaces with immobilized polymersomes were obtained after overnight reaction of the polymersomes with the surface.

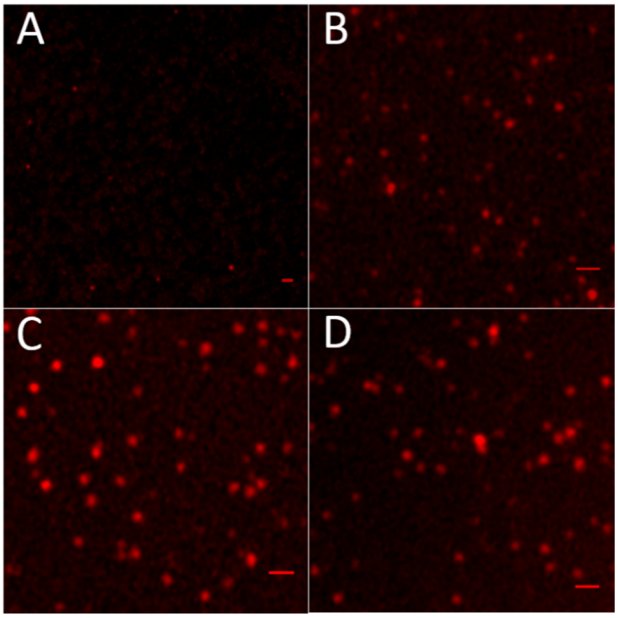


**Figure 3:** LSM images of immobilized, bodipy stained vesicles containing different ratio of $N_3$ terminated polymers A) 0% B) 0.1% C) 1% D) 10% on DBCO functionalized surfaces.

Scale bar: 1 µm.

DISCUSSION & CONCLUSIONS: The immobilization of polymersomes has been achieved by reacting overnight the DBCO functionalized surface with the azid functionalized polymersomes. Furthermore, microcontact printing polymersomes and co-immobilization of azide exposing polymersomes and methacrylate exposing micelles has been achieved.

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**Coffee Break**

**Assessing numerical methods for molecular and particle simulation**

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We discuss the design of state-of-the-art numerical methods for molecular dynamics, focusing on the demands of soft matter simulation, where the purposes include sampling and dynamics calculations both in and out of equilibrium. We discuss the characteristics of different algorithms, including their essential conservation properties, the convergence of averages, and the accuracy of numerical discretizations. Formulations of the equations of motion which are suited to both equilibrium and nonequilibrium simulation include Langevin dynamics, dissipative particle dynamics (DPD), and the more recently proposed pairwise adaptive Langevin (PAdL) method, which, like DPD but unlike Langevin dynamics, conserves momentum and better matches the relaxation rate of orientational degrees of freedom. PAdL is easy to code and suitable for a variety of problems in nonequilibrium soft matter modeling; our simulations of polymer melts indicate that this method can also provide dramatic improvements in computational efficiency. Moreover we show that PAdL gives excellent control of the relaxation rate to equilibrium. In the nonequilibrium setting, we further demonstrate that while PAdL allows the recovery of accurate shear viscosities at higher shear rates than are possible using the DPD method at identical timestep, it also outperforms Langevin dynamics in terms of stability and accuracy at higher shear rates. (1)

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**Rheology of boronic ester-based dynamic covalent hydrogels**

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Recent research in the design and engineering of polymer networks has introduced a new class of soft matter based on dynamic covalent chemistry, which combines the mechanical properties of both physically and chemically cross-linked materials [1]. Dynamic covalent networks enable the formation of responsive, mouldable, and self-healing materials, as the reversible covalent bonds in the network backbone can rearrange by breaking and reforming on experimental timescales in response to external stimuli [2]. The responsive, mouldable, and self-healing properties of reversible networks depend on the specific chemistry of the binding pairs in the cross-links as well as the design of the network topology. Application of dynamic covalent networks and gels therefore requires a robust understanding of how these factors influence each other and the emergent properties of the network. In this work, we investigated the dynamics of reversible networks by relating the macroscopic viscoelastic properties of bulk gels, as measured by dynamic mechanical

analysis, to the microscopic behaviour of the dynamic junctions, by performing studies on the small molecule binding pair interactions. Boronic ester-based hydrogels were selected as model dynamic covalent networks because their viscoelastic properties can be tuned over several orders of magnitude by tailoring the chemistry of the acid-diol binding pair using simple neighbouring effects or alternatively by changing the pH of the environment [3].

METHODS: Dynamic covalent networks were fabricated from multi-arm poly(ethylene) glycol (PEG) macromers end-functionalised with 1,2-diols or phenylboronic acid (PBA) derivatives [4]. Upon mixing equimolar amounts of acid and diol containing polymer, well-defined networks were formed that contain reversible boronic ester cross-links. As illustrated in **Figure 1a**, these can exist in the bound state (orange) or in the unbound state (red and blue). The exchange between bound and unbound is under thermodynamic control, as shown by the equilibrium dissociation constant $K_{eq}$. Quantitative measurements of $K_{eq}$ were performed using fluorescence spectroscopy during competitive binding studies between various acid-diol pairs and ARS (a diol-containing fluorescent reporter), as shown in **Figure 1b** [5]. Constant breaking and formation of the bonds enables network strand rearrangement and stress relaxation as well as the reversible transition between the gel and liquid state. The viscoelastic properties of gels formed under different environmental conditions and network topologies were characterised by dynamic mechanical analysis on a shear rheometer (Anton-Paar MCR 502) using a parallel-plate geometry (PP-20 mm). **Figure 1c** and **d** shows how plateau modulus $G_0'$ and relaxation time $\tau_r$ were estimated from frequency sweep measurements for different gels.

RESULTS AND DISCUSSION: As expected, tuning network properties, such as the number of arms, the molecular weight, or the polymer weight percent, controlled the plateau modulus but did not significantly influence the relaxation time (**Figure 1c**). On the other hand, altering the boronic ester chemistry or the environmental conditions changed the network dynamics by shifting the equilibrium constant $K_{eq}$, but did not affect significantly the plateau modulus (**Figure 1d**). However, subtler effects were observed when combining different types of cross-linkers within the same material, or when considering the effect of various buffers on network properties. Therefore, in order to better connect the experimentally determined bulk network properties determined from rheology to the underlying thermodynamics of the systems, the equilibrium constant $K_{eq}$ were evaluated for various systems. For example, it was observed that gels placed in aqueous solutions containing fructose dissolved much faster than in dextrose. This could be explained by comparing the binding affinity measurements (**Figure 1b**) of PBA and glucose ($K_{eq}$ ~ 15 $M^{-1}$) and fructose ($K_{eq}$ ~ 330 $M^{-1}$). This approach, which attempts to link the molecular dynamics of the cross-links in a reversible network to its bulk behaviour, will be used in the future to build models that connect binding pair thermodynamics to macroscale properties.

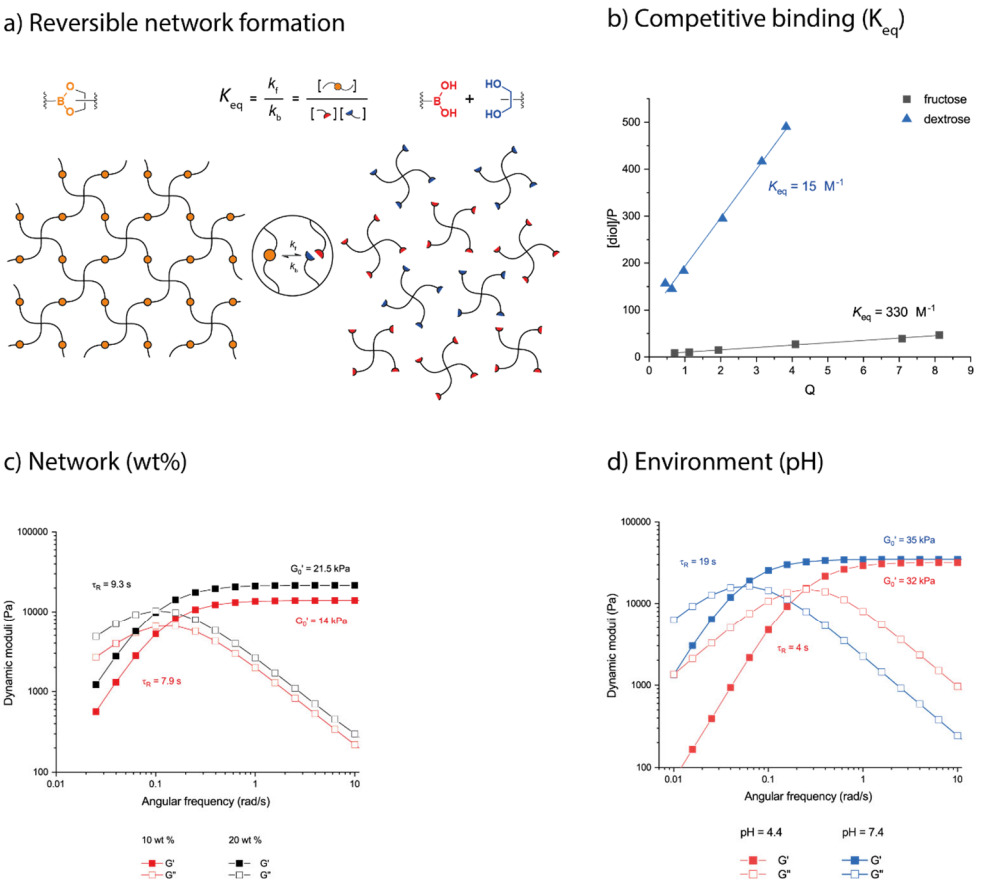


**Figure 1** a) Reversible network formation for a typical boronic ester-based hydrogel. The bound boronic ester (orange) exists in thermodynamic equilibrium with the unbound (red) and diols (blue), as shown by the equilibrium dissociation constant $K_{eq}$. b) Quantitative measurements of $K_{eq}$ were performed using fluorescence spectroscopy during competitive binding studies between various acid-diol pairs and ARS (a diol-containing fluorescent reporter). Estimates for plateau modulus $G_0'$ and relaxation time $\tau_r$ from frequency sweeps are shown for gels formed at c) different weight percentages and d) varying pH.


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ACKNOWLEDGEMENTS: This work was supported by startup funds from ETH Zürich.

**Spontaneous deswelling of microgels controlled by counterion clouds**

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INTRODUCTION: Microgels based on poly(Nisopropylacrylamide) (pNIPAM) spontaneously deswell below the critical solution temperature of 32°C when the concentration of the microgel suspension is brought above a critical value. This was first observed in bidisperse suspensions (1), where the deswelling of the large microgels was more pronounced than for the smaller but otherwise identical ones such that the polydispersity of the suspension was reduced. The same deswelling also occurs in monodisperse suspensions, and we have recently presented a model to explain the deswelling (2), which is based on charged groups and the corresponding counterions of microgels based on pNIPAM. Although pNIPAM is an uncharged polymer, charged groups are present due to the starter for the polymerization reaction. At high concentrations, the counterion clouds surrounding the microgels overlap and give rise to an increase of the suspension osmotic pressure that is not balanced by a corresponding increase of pressure inside the particles and, therefore, can trigger microgel deswelling, if the pressure difference exceeds the bulk modulus of the microgel (2). The spontaneous deswelling has direct consequences for the phase behavior of polydisperse and bidisperse microgel suspensions, where the deswelling can reduce the polydispersity of the suspension to allow for crystallization, which is suppressed due to polydispersity at low concentrations (3). Here, we present Poisson-Boltzmann calculations of the counterion clouds and small-angle neutron scattering (SANS) measurements of the form- and structure factors of pNIPAM microgels to understand the role of the counterions in more detail. Also, direct evidence of the counterion clouds has so far been missing. We present first evidence for these clouds obtained from SANS measurements.

METHODS: We have directly observed the deswelling of pNIPAM microgels in concentrated samples at fixed temperature, T~18°C, using SANS with contrast matching. Bidisperse suspensions with a small number of large particles added to a suspension of small particles as well as monodisperse suspensions have been studied. The osmotic pressure in the same samples was determined with a membrane osmometer (2). We have calculated the osmotic pressure set by the counterions using Poisson-Boltzmann calculations for the counterion cloud surrounding a charged surface. These calculations do not include deswelling. By mapping the measured osmotic pressure on the calculated pressure, we obtain an estimate for the deswelling of the microgels due to the interaction of the counterion clouds.

RESULTS & DISCUSSION: SANS measurements of the microgel size at high concentrations show that the volume fraction remains below random close packing up to effective volume fractions, $\zeta$, of about 1. This implies that deswelling occurs without direct contact between the microgels. We show that the essential aspects of the observed deswelling are captured by our Poisson-Boltzmann model of the microgels. This suggests that the deswelling is governed by the counterion clouds at least for effective volume fractions $\zeta<1$. Other contributions to the osmotic pressure relevant for microgel stability [4], i.e. polymer-solvent mixing and the elasticity of the polymer network, appear to be of lesser importance

at ζ<1. To obtain more direct evidence for the counterion clouds, we have performed SANS measurements with microgels containing either NH4+ or Na+ counterions. Although the low ion density makes such measurements difficult, we have obtained first evidence for the counterion clouds as expected in our model of pNIPAM microgels.

CONCLUSIONS: Although pNIPAM is an uncharged polymer, we find the deswelling behavior of pNIPAM microgels for concentrations up to overpacking to be governed by the counterion clouds originating from charged groups incorporated during microgel synthesis. As uncharged microgels are hard to synthesize, our results are expected to also apply for other microgels based on an uncharged polymer network.

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**Anomalous solute diffusivity in ionic liquids and iongels: label-free visualization and physical origins**

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Dynamic diffusion of molecular solutes in concentrated electrolytes plays a critical role in many applications, but is notoriously challenging to measure and model. This is particularly true in the extreme case of ionic liquids (ILs), fluids composed entirely of cations and anions. Due to their superior recyclability and selectivity, ILs are poised to replace conventional industrial solvents in a number of separation and reaction processes. However, engineering solute mass transport in ILs has been hindered by a lack of methods to observe it *in operando* that would provide better fundamental insight and rational design guidelines for solute-specific IL formulation. As a result, ILs are often selected from a vast design space of ionic components on the basis of their viscosity vis-à-vis the Stokes-Einstein relation, which assumes that solutes experience the IL as a continuum fluid. To gain better mechanistic insight into transport in this class of fluids, we developed a method to visualize the spatiotemporal evolution of concentration fields using microfluidic Fabry-Perot interferometry (mFPI), enabling diffusivity measurements over an entire composition range within a single experiment. We focus on the diffusion of water, both as a model solute and ubiquitous contaminant, within alkylmethylimidazolium-halide ILs and IL-swollen poly (ethylene glycol) diacrylate gels. Notably, the Stokes-Einstein relation under predicts water diffusivities ten- to fifty-fold (1,2), indicating water does not experience these ILs as continuum liquids. Based on these measurements, together with wide-angle

X-ray scattering and pulsed-field gradient NMR measurements, we propose a new mechanistic framework in which water molecules hop between ion pairs within the IL, which acts as an immobile matrix over time scales relevant for water diffusion. In this case, diffusion is an activated process, with hops between hydrogen-bonding sites over an energetic barrier that decreases linearly with water fraction as measured by $^1$H NMR. This simple model contains the key ingredients required to accurately predict the measured trends in diffusivity—an (Arrhenius) temperature-dependence and an exponential composition-dependence—for a range of cations, anions, water contents, polymer contents and temperatures. Our results suggest a general mechanism for anomalously fast diffusion in ILs, where solutes 'hop' between binding sites more quickly than the ions re-arrange. This study reveals the consequences of a novel mechanism for solute diffusion, and offers a conceptual framework to understand, predict and design task-specific ionic liquids.

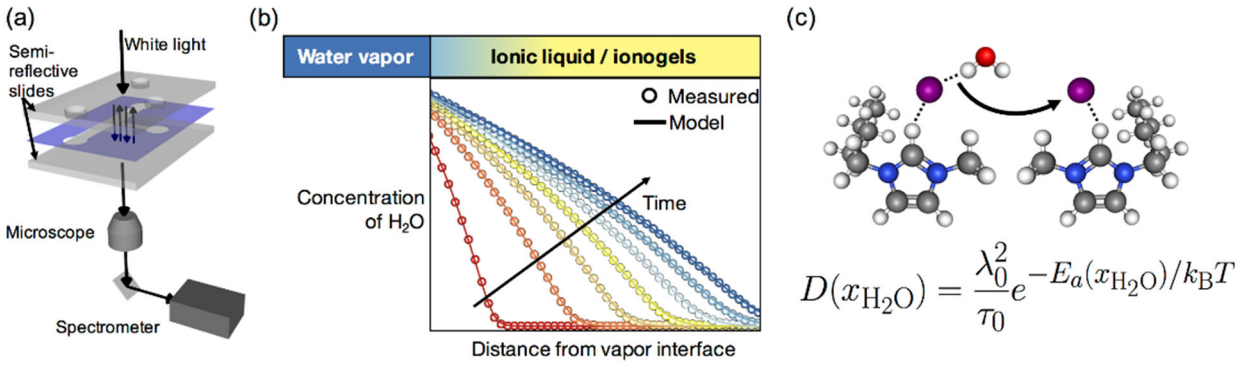


**Figure 1.** (a) Optical train of microfluidic Fabry-Perot interferometry; (b) mFPI enables label-free measurement of concentration gradient-driven diffusion; (c) Diffusion of water in ILs and ionogels is modeled as activated hops between acidic moieties.

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**Surfactant Mediated Particle Aggregation in Nonpolar Solvent**

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INTRODUCTION: The importance of colloidal systems in many different processes, both natural and man-made, has led to a great development in this field in the last century. However most of these studies focused on aqueous systems, while surfactant-mediated colloidal dispersions in non-polar media received much less attention,(1, 2) while still being central processes in many different applications (*e.g.* electrophoretic displays, airborne drug delivery systems, and toner technologies). This study aims at understanding the processes that governs colloidal dispersions in non-aqueous solvents.

METHODS: Aggregation of colloids in decane in the presence of AOT surfactant was investigated using three different methods: First of all electrophoretic mobility measurements were performed to study the particle charging behavior (Fig.1a). As a next step particle aggregation kinetics were measured by dynamic light scattering, determining the particle stability ratio for different suspensions (Fig.1b). AFM-based colloidal probe technique was used to obtain direct force measurements between silica particles in order to obtain the relevant Hamaker constant, necessary for evaluating the van der Waals attraction (Fig.1c).

RESULTS & DISCUSSION: The behavior of colloidal dispersions of three different types of particles, negatively charged silica and sulfate latex and positively charged amidine latex, were studied in AOT/decane solutions. All three particles, which are very weakly charged in absence of surfactant, show charge reversal with increasing AOT concentration. This charging behavior is consistently mirrored by the stability ratios measured by DLS. It appears from this study that the colloidal dispersion behavior can be explained by DLVO forces.

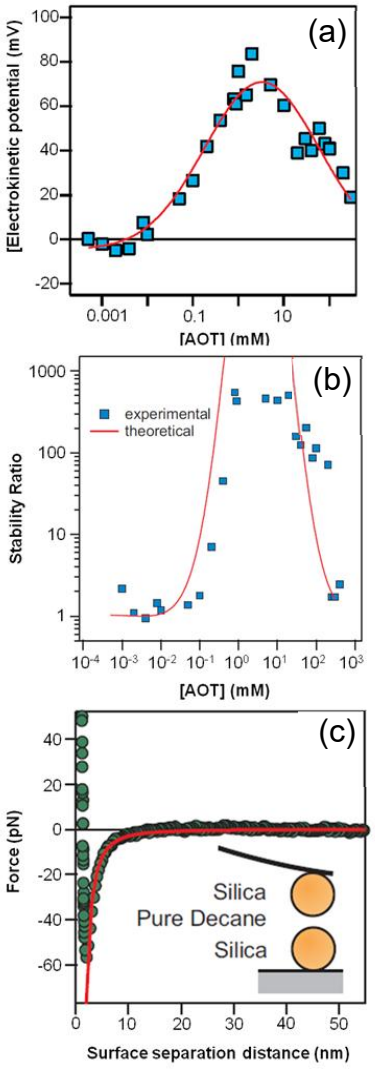


**Figure 1:** Electrokinetic potential of silica in decane as a function of AOT concentration (a), stability ratios in decane as a function of AOT concentration (b), van der Waals interaction measured between two 4 µm silica spheres measured in pure decane (c).

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**Controlling self-assembly in the time-domain by means of complex chemical dynamics**

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The ability to control self-assembly of polymers and colloids in the time domain will open new exciting perspectives for materials science, especially for the development of active, out-of-equilibrium biomimetic materials (1).

Complex chemical dynamics such as those displayed by clock reactions, systems in which product formation occurs abruptly after a tailorable induction time, are fundamental tools to achieve this goal.

Here we provide an account of the results accomplished in our laboratory by coupling different chemical clocks as *in situ* sources of stimuli (pH, redox) with molecular and macromolecular building blocks to obtain particles and gels.

We show how the formaldehyde-sulfite reaction allows the pH-driven, time-controlled precipitation of chitosan, a biopolymer with broad technological applications (2). In addition, we demonstrate how transient complexation-driven self-assembly and supramolecular gel formation can be controlled by means of clock reactions.

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**Droplet Induced Deformations of Solid Surfaces**

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Droplets exert stress on the surfaces they rest on and these surfaces deform in response. On rigid substrates the deformations are often negligible, however, on softer substrates, the deformations can play an important role. For materials with high elasto-capillary length ($\gamma/E$ >1), surface deformations can hinder the motion of the drop (1), mediate interactions between droplets separated by a distance (2) and in general can play a significant role in droplet dynamics. When a droplet is in motion, the spatial distribution of the deformations along with the relaxation dynamics of the surface determine droplet dynamics. In this contribution, we focus on the spatial distribution of the stress/deformation inside the substrate using molecular dynamics simulations. We simulate a water droplet resting on a model solid substrate at varying contact angles and substrate elastic moduli to estimate

the stresses and deformations inside the substrate. We observe that the deformations are anisotropic and are qualitatively similar to the macroscopic counterparts. The deformations are concentrated close to the contact line (CL) although they penetrate deep into the surface. Further, we noticed that the maxima in displacements at the contact line scale linearly with the elastic moduli of the surface. However, the displacements at the centre of the drop caused by the Laplace pressure do not appear to follow this simple scaling. Also, the deformations do not show any trivial scaling with the wetting parameters like, contact angle, contact surface area or the droplet radius. This contribution provides interesting insights into the spatial distribution of deformations around the CL and should motivate future studies to understand the coupling between droplet motion and surface deformation.

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