



14. ZSIGMONDY COLLOQUIUM

of the German Colloid Society

at the

**Max Planck Institute for Polymer Research,
Mainz, Germany**

9 – 11 April 2018

Table of contents

Patrons / Exhibitors	2
Program	3
General information	7
Invited lectures	9
Talks – overview	12
Posters – overview	15
Talk abstracts	17
Poster abstracts	54
Social program	93
Conference dinner	95
Organizers	96
Imprint	96

Patrons / Exhibitors



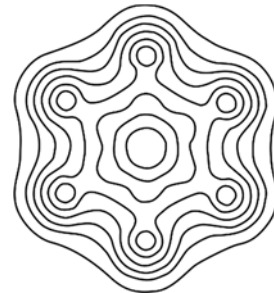
Anton Paar



**Boehringer
Ingelheim**



EVONIK
POWER TO CREATE



FCI
FONDS DER
CHEMISCHEN
INDUSTRIE

LubISS



Lubricant **I**mpregnated **S**lippery **S**urfaces

Park

SYSTEMS



14th Zsigmondy-Colloquium

April 9 - 11, 2018

Monday, April 9, 2018

11:30 **Registration and coffee**

12:30 **Welcome**

12:40 **Prof. Dr. Stefan Weber** Watching Ions Move: Scanning Probe Microscopy on Perovskite Solar Cells

13:40 Schlicke Li+-Doping of polyelectrolyte multilayers for enhanced ionic conductivity

13:55 **Break**

14:15 Stuckert Mapping diffusion and sedimentation in model colloids with tailored shapes

14:30 Botin Super-heterodyne Doppler light scattering under multiple scattering conditions

14:45 Bretz Characterization of non-ergodic systems through advanced light scattering

15:00 Bley Hierarchical design optimizes transparency and haze factor of holey metal films

15:15 **Break**

15:35 Turnhoff Investigations of the internal structure of hollow charged microgels by SANS

15:50 Wiehemeier Core-shell microgels in suspension: Swelling behaviour observed by FTIR spectroscopy

16:05 Jans Highly positively charged amine functionalized core-shell microgels

16:20	Strzelczyk	Study of temperature switchable adhesion between ligands and receptors by soft colloidal probe
-------	------------	--

16:40	Poster Session	
-------	----------------	--

19:30	End	
-------	-----	--

Tuesday, April 10, 2018

08:55	Welcome	
-------	---------	--

09:00	Baumli	Emulsion-based lubricant replenishment strategies for lubricant-impregnated slippery surfaces under flow
-------	--------	--

09:15	Nath	A viscous tweezer
-------	------	-------------------

09:30	Sadullah	Modeling droplet dynamics on liquid infused surfaces
-------	----------	--

09:45	Shiri	Dewetting of liquid two-layer films
-------	-------	-------------------------------------

10:00	Break	
-------	-------	--

10:30	Prof. Shlomo Magdassi	From Gutenberg Bible to 4D printing
-------	-----------------------	-------------------------------------

11:30	Backes	Hybrid gold nanoparticles with conductive polymer ligands
-------	--------	---

11:45	Ferrarotto	Formation of silver nanoparticles in spherical polyelectrolyte brushes and encapsulation in silica
-------	------------	--

12:00	Poster session and coffee	
-------	---------------------------	--

13:00	Lunch	
-------	-------	--

14:00	Satarifard	Nanodroplets at interfaces and membranes: Line tension effects
-------	------------	--

14:15	Rostami	Merging drops with unstable wetting films
-------	---------	---

14:30	Gurumurthy	Spontaneous rise of rivulets in square capillaries
-------	------------	--

14:45	Yao	Dynamics of capillary imbibition of poly(ethylene oxide) melts in nanoporous alumina
-------	-----	--

15:00	Break	
-------	-------	--

15:20	Lehnfeld	Influence of buffer pH and composition on wettability of modified surfaces
-------	----------	--

15:35	Herrles	Sand and rain erosion testing of structured and modified Titanium surfaces
15:50	Schermer	Deep eutectic solvents to remove rust and limescale from sur
16:05	Break	
16:25	Werner	PFA-PEG particles: A colloidal model system for the investigation of phase diagrams of PEGylated drug carrier systems
16:40	Schütz	Effect of source on the properties and behavior of cellulose nanocrystal suspensions
16:55	Voigtländer	Surface modification of self-assembled nanotubes from amino acid amphiphiles in solution
17:10	Break	
18:00	Social Event	
19:30	Dinner	

Wednesday, April 11, 2018

08:40	Welcome	
08:45	Frey	Modulation of STAT3-mediated tumor-associated tolerance mechanisms using IL-2 functionalized hydroxyethyl starch (HES) nanocapsules
09:00	Goonoo	Enhancing the physico-chemical and biological performances of synthetic polymers via blending with natural polymers
09:15	Siewert	mRNA drug-nanoparticles: Polymer and liposomes – study by SANS and DLS
09:30	Töpel	Microgel arrays for regulation of cell motility and adhesion
09:45	Break	
10:05	Marschelke	Insights into the immobilization of enzymes onto hybrid hairy particles for interfacial catalysis
10:20	Brilmayer	The influence of chain architecture on polyelectrolyte functionalized mesopore accessibility
10:35	Xu	A near-infrared and temperature-responsive nanoreactor based on core-shell polydopamine@PNIPAm microgel

10:50	Wagner	Temperature-dependent energy-transfer in colloidal dispersions
11:05	Break	
11:25	Grosskopf	Shear-induced transformation of polymer-rich lamellar phases to micron sized vesicles
11:40	Steck	Gelled lyotropic liquid crystals: visual, rheological and thermal phase studies
11:55	Zhan	Study on Interactions between Surfactant, Polymer and Dye in Solution and at Interfaces
12:10	Lunch	
13:10	End	

General information

Badges

Please wear your name badge throughout the conference, in particular for the coffee and lunch breaks. In case you have lost your badge, please report at the conference registration desk.

Certificate of Attendance

A certificate of attendance will be issued upon request at the conference registration desk.

Cloakroom

A cloakroom is located next to the registration area. During the opening hours of the conference registration desk, you can deposit your coats and luggage here.

Events

Social event, Tuesday, April 10 at 18:00

Option 1: Carnival Museum (<http://www.mainzer-fastnachtsmuseum.de/>)

Meeting point: Proviant-Magazin (Westeingang - <http://www.proviant-magazin.de/>), Neue Universitätsstr. 2, Mainz.

Option 2: Sightseeing tour of the city in GERMAN

Meeting point: Domininformation (Cathedral info point -

<https://mainzerdom.bistummainz.de/dominformation-neu/>) – Marktportal, Markt 10, 55116 Mainz

Option 3: Sightseeing tour of the city in ENGLISH

Meeting point: Domininformation (Cathedral info point -

<https://mainzerdom.bistummainz.de/dominformation-neu/>) – Marktportal, Markt 10, 55116 Mainz

Conference dinner, Tuesday, April 10 at 19:30 in the Proviantamt, Schillerstraße 11a, Mainz

Internet

You can log yourself to the Eduroam network. Alternatively, there will be free Wireless LAN available at the conference venue during the conference.

The network-ID is: Conference

The password is: smdco2018

Mobile Phones

Participants are kindly requested to keep their mobile phones silent in the conference rooms during sessions.

*PLEASE NOTE: Filming and photography of talks or posters are not allowed during the conference.

Oral Presentation

You can bring your own computer (Mac users must supply their own VGA adaptor) or a USB memory stick. It is required that speakers test their presentation in the lecture hall before the session starts. The time slot for your presentation includes discussion time. The time for a keynote lecture is 45 + 15 min. Contributed lectures are 12 + 3 min.

Photographs taken during the 14th Zsigmondy Colloquium

Pictures and videos taken during the 14th Zsigmondy Colloquium might be used in the Intranet and Internet as well as for news coverage. Should you disagree with the use of your picture, please contact: info@mpip-mainz.mpg.de for your picture to be removed.

Poster Presentation

The poster areas are located in the foyer of the Staudinger lecture room. Fixing materials will be provided.

Please mount your poster starting from the first coffee break (Monday, April 9 ~11:30).

Remove your poster at the latest on Tuesday, April 10 ~17:00.

Public transport

From the main station, take tramline no. 51 or 53 to reach the Max Planck Institute for Polymer Research. The journey should take about 10 minutes.

Fares

Single fare tickets can be bought at a vending machine or from the driver. A one-way ticket costs 2.80 Euros. You can find more information about the fares at [Mainzer Verkehrsgesellschaft](http://www.mainzer-verkehrsgesellschaft.de).

If you arrive at Mainz central station with a RMV or RNN ticket, no extra ticket is needed to reach the institute. The same applies, if you have a long distance train ticket with the addition "Mainz+City": no need to pay for the public transportation ride directly preceding or following your train journey.

Tramlines no. 51 and 53 (direction Lerchenberg/Hindemithstraße)

Tram no. 51 departs from platform A, tram no. 53 from platform L. Get off at the stop "Hochschule Mainz". The institute can be reached after a two-minute walk across Koblenzer Straße into Ackermannweg.

Invited lectures

Invited Lecture - Stefan Weber

Watching Ions Move: Scanning Probe Microscopy on Perovskite Solar Cells

Stefan Weber

Max Planck Institute for Polymer Research
Mainz, Germany



Abstract:

Perovskite solar cells have electrified the solar cell research community with astonishing performance and surprising material properties. Very efficient ($>20\%$) devices with perovskite layers of low defect density can be prepared by cheap and simple solution based processes at moderate temperatures ($<150^{\circ}\text{C}$). For commercializing this technology, a stable and reliable operation has to be ensured. In perovskite solar cells, however, the output power is strongly influenced by the history of the device in terms of bias voltage (causing hysteresis) or illumination (known as light soaking effect). The underlying process is assumed to be the slow migration of ionic charges within the perovskite layer.

In my presentation I will demonstrate how scanning probe microscopy can help understanding these processes. Using a method called Kelvin probe force microscopy, we were able to follow the vertical charge distribution in the active perovskite layer of an operating device. In particular, we found that the hysteretic behavior is caused by a thin dipole at the anode interface. The electric field generated by mobile ions in the perovskite layer only plays a minor role. This finding is contrary to the common assumption that homogeneously distributed ions in the perovskite layer are the main cause for hysteresis and adds important pieces of information for a thorough understanding of hysteresis in perovskite solar cells.

About Stefan Weber

Stefan Weber studied Physics at the University of Konstanz. Already as an undergrad student he started to work with an SFM in the group of Prof. Leiderer. For his diploma thesis under the supervision of Prof. Dr. Johannes Boneberg he studied the interaction of gold nanoparticles with pulsed laser light.

In his PhD thesis in the group of Prof. Hans-Jürgen Butt/Dr. Rüdiger Berger at the Max Planck Institute for Polymer Research (MPI-P), Mainz, he used and developed electrical scanning force microscopy methods for the investigation of organic optoelectronic materials. The project was embedded in the

international research training group (IRTG) "Self-organizing materials for optoelectronics" - a joint graduate school between University and MPI-P in Mainz and the Seoul National University (SNU) and Hannam University Daejeon in South Korea. In 2009 and 2010 he spent 6 months at SNU in the groups of Prof. Kookheon Char and Prof. Changhee Lee. In 2010 he received a joint doctoral degree from Mainz University and SNU.

In 2011 he went to University College Dublin as a Feodor Lynen Fellow (Alexander von Humboldt Foundation). Together with Prof. Brian Rodriguez and Prof. Suzi Jarvis he developed a new method for mapping surface potentials in liquid electrolytes. Here, he could demonstrate that atomic scale imaging is possible even in very viscous media.

In 2012 he became a project leader in the Physics of Interfaces group in the department of Prof. Hans-Jürgen Butt at the Max Planck Institute for Polymer Research (MPI-P), Mainz. In 2015 he was appointed as a junior professor in the Physics department of Mainz University.

Invited Lecture - Shlomo Magdassi

From Gutenberg Bible to 4D printing

Shlomo Magdassi

Chair, Institute of Chemistry

The Hebrew University of Jerusalem

Jerusalem 91904, Israel

Magdassi@mail.huji.ac.il



Abstract:

Functional printing brings additional performance of printed patterns, beyond the conventional graphic output. The synthesis and formulations of nanoparticles and inks will be presented, with their utilization in printed devices, responsive and 3D objects. New approaches for achieving silver, copper and carbon nanotubes electrical circuits for printed electronics will be presented, as well as new materials and processes for 3D and 4D printing. Utilization of 3D and 4D printing technologies for fabrication of objects composed of ceramics, shape memory polymers, elastomers and hydrogels will be demonstrated, for applications such as soft robotics, drug delivery systems, responsive connectors and Internet of Things (IoT), dynamic jewelry and medical devices.

About Shlomo Magdassi

Shlomo Magdassi is a professor of chemistry, at the Casali Center for Applied Chemistry, the Institute of Chemistry and the Center for Nanoscience and Nanotechnology at the Hebrew University of Jerusalem, Israel. Prof. Magdassi holds the Enrique Berman Chair in Solar Energy. His research focuses on colloid science, and in particular on formation, formulation and applications of novel micro and nanoparticles. These particles can be used as active components in functional inks and coating, for example light absorbing particles for solar energy devices, and metal nanoparticles and CNTs for 2D and 3D printing. He is the editor of three books, among them "The chemistry of inkjet inks". In addition to his scientific publications, he also has various inventions on applications of colloids in industrial products. Based on these inventions, some commercial activities evolved leading to worldwide sales and establishing new companies.

Talks – overview

Monday, April 9, 2018				
I-1	12:40	13:40	Stefan Weber	
O-1	13:40	13:55	Schlicke	Li+-Doping of polyelectrolyte multilayers for enhanced ionic conductivity
O-2	14:15	14:30	Stuckert	Mapping diffusion and sedimentation in model colloids with tailored shapes
O-3	14:30	14:45	Botin	Super-heterodyne Doppler light scattering under multiple scattering conditions
O-4	14:45	15:00	Bretz	Characterization of non-ergodic systems through advanced light scattering
O-5	15:00	15:15	Bley	Hierarchical design optimizes transparency and haze factor of holey metal films
O-6	15:35	15:50	Turnhoff	Investigations of the internal structure of hollow charged microgels by SANS
O-7	15:50	16:05	Wiehemeier	Core-shell microgels in suspension: Swelling behaviour observed by FTIR spectroscopy
O-8	16:05	16:20	Jans	Highly positively charged amine functionalized core-shell microgels
O-9	16:20	16:35	Strzelczyk	Study of temperature switchable adhesion between ligands and receptors by soft colloidal probe
Tuesday, April 10, 2018				
O-10	09:00	09:15	Baumli	Emulsion-based lubricant replenishment strategies for lubricant-impregnated slippery surfaces under flow

O-11	09:15	09:30	Nath	A viscous tweezer
O-12	09:30	09:45	Sadullah	Modeling droplet dynamics on liquid infused surfaces
O-13	09:45	10:00	Shiri	Dewetting of liquid two-layer films
I-2	10:30	11:30	Shlomo Magdassi	
O-14	11:30	11:45	Backes	Hybrid gold nanoparticles with conductive polymer ligands
O-15	11:45	12:00	Ferrarotto	Formation of silver nanoparticles in spherical polyelectrolyte brushes and encapsulation in silica
O-16	14:00	14:15	Satarifard	Nanodroplets at interfaces and membranes: Line tension effects
O-17	14:15	14:30	Rostami	Merging drops with unstable wetting films
O-18	14:30	14:45	Gurumurthy	Spontaneous rise of rivulets in square capillaries
O-19	14:45	15:00	Yao	Dynamics of capillary imbibition of poly(ethylene oxide) melts in nanoporous alumina
O-20	15:20	15:35	Lehnfeld	Influence of buffer pH and composition on wettability of modified surfaces
O-21	15:35	15:50	Herrles	Sand and rain erosion testing of structured and modified Titanium surfaces
O-22	15:50	16:05	Schermer	Deep eutectic solvents to remove rust and limescale from surfaces
O-23	16:25	16:40	Werner	PFA-PEG particles: A colloidal model system for the investigation of phase diagrams of PEGylated drug carrier systems
O-24	16:40	16:55	Schütz	Effect of source on the properties and behavior of cellulose nanocrystal suspensions
O-25	16:55	17:10	Voigtländer	Surface modification of self-assembled nanotubes from amino acid amphiphiles in solution

Wednesday, April 11, 2018				
O-26	08:45	09:00	Frey	Modulation of STAT3-mediated tumor-associated tolerance mechanisms using IL-2 functionalized hydroxyethyl starch (HES) nanocapsules
O-27	09:00	09:15	Goonoo	Enhancing the physico-chemical and biological performances of synthetic polymers via blending with natural polymers
O-28	09:15	09:30	Siewert	mRNA drug-nanoparticles: Polymer and liposomes – study by SANS and DLS
O-29	09:30	09:45	Töpel	Microgel arrays for regulation of cell motility and adhesion
O-30	10:05	10:20	Marschelke	Insights into the immobilization of enzymes onto hybrid hairy particles for interfacial catalysis
O-31	10:20	10:35	Brilmayer	The influence of chain architecture on polyelectrolyte functionalized mesopore accessibility
O-32	10:35	10:50	Xu	A near-infrared and temperature-responsive nanoreactor based on core-shell polydopamine@PNIPAm microgel
O-33	10:50	11:05	Wagner	Temperature-dependent energy-transfer in colloidal dispersions
O-34	11:25	11:40	Grosskopf	Shear-induced transformation of polymer-rich lamellar phases to micron sized vesicles
O-35	11:40	11:55	Steck	Gelled lyotropic liquid crystals: visual, rheological and thermal phase studies
O-36	11:55	12:10	Zhan	Study on interactions between surfactant, polymer and dye in solution and at interfaces

Posters – overview

Chen	Droplet impact dynamics on solid surfaces: bubble entrapment and high speed jet
Chiera	Investigation of reaction parameters in one-step surfactant-free emulsion polymerization reactions
Choi	Thermo-responsive polymer brush-coated titanium to control bacterial biofilm colonization for enhanced biocompatibility
Dabrowski	Biodegradable monodisperse polymer foams
Dirksen	Smart membranes by electron beam cross-linking of copolymer microgels
Galvan	Ionic liquid-infused nanostructures as repellent surfaces
Heidt	Evaluation of interfacial free energy of charged colloidal crystals
Hu	Directing supraparticles architecture by controlled evaporation and dewetting of magnetic nanoparticle suspensions on superamphiphobic surfaces
Khalil	Gradually controlled wetting properties and its influence on ionic transport in mesoporous silica thin films
Koch	Finetuning the properties of styrene-based porous polymers via emulsion templating
Laroche	Ice adhesion test data for ice-phobic and durability testing of lubricant impregnated slippery surfaces
Nawroth	Targeting drug-nanoparticles: Liposomes and polymer - study by SANS and DLS
Nickel	Synthesis of anisotropic hollow microgels
Niu	Formation of a transient amorphous solid in low density aqueous charged sphere suspensions
Paul	Microgel surfaces for temperature-enhanced adhesion of proteins and bacteria
Peng	Gelled non-toxic bicontinuous microemulsions: a phase behavior study
Ponomareva	Spectroscopic investigation of periodic plasmonic superstructures
Raguzin	Synthesis of colloidal BaTiO ₃ nanoparticles with paramagnetic properties

Raju	Pickering janus emulsions stabilized by magnetic nanoparticles
Rommel	Dissipative disassembly of colloidal microgel crystals driven by a coupled cyclic reaction network
Saal	The drop adhesion force instrument
Schmidt	Interaction of well-ordered paramagnetic chains through a PDMS polymer matrix
Schröer	Polyethylene glycol-based microgels for selective inhibition of pathogens
Schwarzer	Design of functional heterogeneous particle-based surfaces with controlled ice nucleation and adhesion
Thijssen	Active nematics in confinement
Thill	Surface properties of deposits composed of casein micelles
Uebbing	mRNA-lipoplexes for controlled delivery in personalized cancer vaccines
Uebel	Sulfur-based polymer nanocolloids
van Duinen	The influence of a temperature-responsive polymer brush on the Brownian motion of a microbead
Vercillo	Analysis and modelling of icing of engines' air intake protection grid structures
Wang	Creation of submicron patterns by using microcontact printing for plasmonic templates
Wong	Durable transparent superhydrophobic surfaces via sprayable interpenetrated polymer networks
Xie	Unlimited reconfiguring surface functions using visible-light-controlled metal-ligand coordination
Zhao	Mechanical property of water-air interface in superhydrophobic nanopores
Zimmermann	Patchy silica particles via micro contact printing

Talk abstracts

Li⁺-Doping of Polyelectrolyte Multilayers for Enhanced Ionic Conductivity

Jannis Schlicke¹, Cornelia Cramer¹, Monika Schönhoff¹

¹ Institute of Physical Chemistry, University of Münster, Corrensstraße 28/30, Münster 48149, Germany

Our work studies the effect of a pH-driven Li⁺-doping approach (Fig. 1a)) on the conductivity of polyelectrolyte multilayers (PEMs) containing poly(acrylic acid) (PAA). This approach involves the postpreparational treatment of PEMs in LiCl solutions at increased pH when compared to the pH of preparation. The goal is to compensate the resulting negative excess charge due to the deprotonation of PAA by the incorporation of Li⁺ ions.

The deprotonation of PAA inside poly(diallyldimethylammonium) (PDADMA)/PAA multilayers is successfully observed via *in-situ* Attenuated Total Reflection-FTIR (ATR-FTIR) studies during the doping process. The deprotonation is only seen for the treatments in LiCl solutions and does not occur in the case of pure water, which suggests Li⁺ ion uptake. Additional *in-situ* Dissipative Quartz Crystal Microbalance (QCM-D) experiments reveal slow equilibration processes lasting for up to 5 d, which involve losses in mass coverage.

Impedance spectroscopy studies are conducted according to a routine established by Akgöl *et al.*[1]. The DC conductivities, which were measured at 54 %RH, increase from $(12 \pm 1) \cdot 10^{-9}$ S/cm for as-prepared samples (pH 4) to $(7 \pm 1) \cdot 10^{-7}$ S/cm for samples treated in 0.1 M LiCl solutions at pH 7. A significant increase in the conductivity due to postpreparational treatments was hereby successfully proven (see Fig. 1).

Currently, ongoing studies investigate, to which extent the conductivity enhancement can be attributed to Li⁺ ions as charge carriers, or to possibly enhanced hydration accompanied by increased proton mobilities.

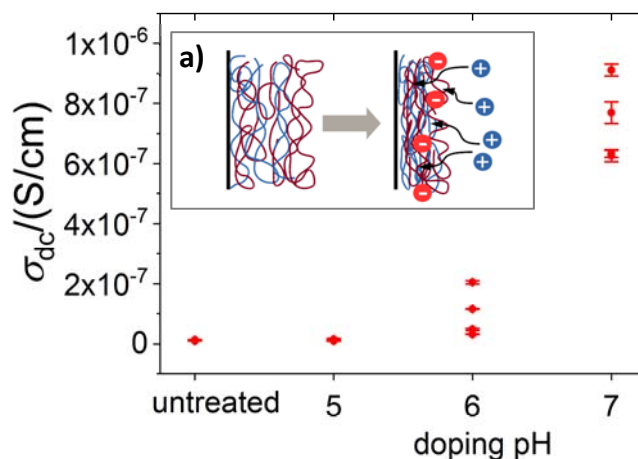


Figure 1. DC conductivity of (PDADMA/PAA)₅₀ PEMs prepared at pH 4 and treated in 0.1 M LiCl solutions at different pH values. Multiple samples were prepared for each pH. The error bars represent deviations determined for each sample, respectively. **a)** Scheme of the pH-driven approach of doping in LiCl solutions based on the generation of negative excess charges inside the PEM.

[1] Y. Akgöl, C. Hofmann, Y. Karatas, C. Cramer, H.-D. Wiemhöfer, M. Schönhoff, *The Journal of Physical Chemistry B* **2007**, 111, 8532-8539.

Mapping diffusion and sedimentation in model colloids with tailored shapes

Rouven Stuckert¹, Simone Plüsch¹, David McDonogh¹ and Alexander Wittemann¹

¹ Colloid Chemistry, University of Konstanz, Universitätsstraße 10, 78464 Konstanz, Germany.

Building on previous work [1], we present a comprehensive study of the diffusion and sedimentation of clusters of spherical nanoparticles. Cluster preparation is accomplished by assembling polystyrene particles on evaporating emulsion droplets [2]. This results in supracolloids that exhibit well defined configurations that are governed by their number of constituent particles. Sorting into uniform cluster fractions is achieved through centrifugation of the cluster mixture in a density gradient.

The rotational and translational diffusion of the clusters is investigated by polarized and depolarized dynamic light scattering. Sedimentation coefficients are elucidated by differential centrifugal sedimentation. The experimental results are compared to data obtained via a hydrodynamic bead-shell model suitable to describe diffusion and sedimentation of particles with arbitrary shapes [3]. The experimental data is in excellent agreement with predictions from hydrodynamic modelling.

The diffusion and sedimentation of particles with defined anisotropic shapes play an important role in assembling 3D colloidal crystals, paving the way for improved photonic materials. The variety of investigated shapes shows the robustness of our approach and provides a complete picture of the hydrodynamic behavior of complex particles.

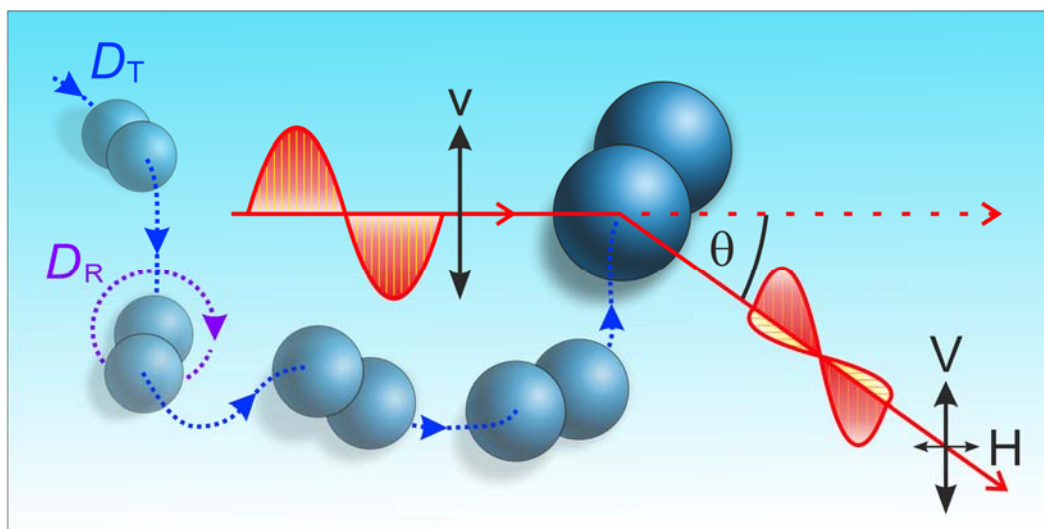


Figure 1. Mapping the diffusion of a dimer cluster by depolarized dynamic light scattering.

[1] M Hoffmann, CS Wagner, L Harnau, A Wittemann, *ACS Nano* **3** (2009), 3326.

[2] CS Wagner, A Wittemann, *Macromol. Rapid Commun.* **34** (2013), 1798.

[3] J García de la Torre, G del Rio Echenique, A Ortega, *J. Phys. Chem.* **111** (2007), 955.

Acknowledgement: The authors acknowledge funding from the DFG via SFB1214/A10.

Super-heterodyne Doppler Light Scattering under Multiple Scattering Conditions

D. Botin¹, Ludmilla Mapa Marota¹, Christopher Wittenberg¹, Holger Schweinfurth¹ and Thomas Palberg¹

¹ Institute of Physics, JGU Mainz, Germany

Multiple scattering (MS) is a plague to dynamic light scattering studies intended to cover broad ranges of particle concentrations. We here report a novel empirical correction scheme for multiple scattering (MS) in Super-Heterodyne Doppler-Velocimetry. We find that due to detection volume and angle restriction in our home-build low angle reference beam configuration, MS is of moderate intensity even at sample transmission as low as 40% (Fig.1). The remaining MS signal is excellently approximated as a Lorentzian and can be subtracted from the raw power spectra. From the noise and MS corrected spectra of charged sphere suspensions subjected to DC electric fields we can infer the electro-kinetic properties of particles and cell walls. We further use our scheme for measurements of the self-diffusion coefficients in fluid-like ordered samples in the absence or presence of shear, as well as in polycrystalline samples during crystallization and coarsening. We discuss the scope and limits of our approach as well as possible future applications [1].

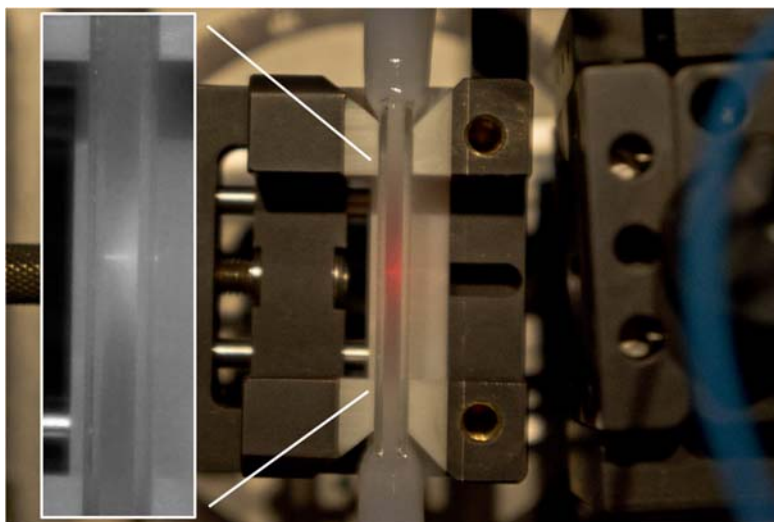


Figure 1. Optical appearance of a multiply scattering suspension in a rectangular cell with transmittance 40%, illuminated by a He-Ne laser from the left. Insert shows the intensity distribution in the multiple scattering cone.

[1] D. Botin et al. *J. Chem. Phys.* **146** (2017), 204904

Acknowledgement: Financial support of the DFG (SPP 1726 and Pa459/18) as well as of Interne Forschungsförderung, JGU is gratefully acknowledged. L.M.M. further gratefully acknowledges financial support by the DAAD IAESTE program.

Characterization of non-ergodic systems through advanced light scattering

Coline Bretz¹, Andrea Vaccaro¹, Mathias Reufer¹, and Andreas C. Voelker¹

¹ LS Instruments, Fribourg, Switzerland, <http://www.lsinstruments.ch>

Much of the research interest in the field of soft matter focuses on studying slow relaxation processes in systems that are close to a phase transition or are dynamically arrested. Gels, glasses and aging soft materials are example of such systems. In some cases, accessing dynamic properties in time scales of seconds or even minutes is crucial.

A method that allows for studying slowly relaxing systems is to perform many dynamic light scattering (DLS) measurements, providing a series of time averaged correlation functions. Between each measurement the sample is rotated such that a different speckle is observed. The measurements are then summed to provide the ensemble average [1]. Additionally, when working with concentrated samples, which is frequently the case for non-ergodic samples, the suppression of multiple scattering is required to obtain meaningful results. This is achieved through 3D modulated cross-correlation [2,3], where two temporally separated light scattering experiments are performed at the same scattering vector on the same sample volume in order to extract only the single scattering information common to both.

In this work, we present modulated 3D static and dynamic light scattering measurements on Polystyrene particles suspended in a transparent gel matrix. Through a sample goniometer, we rotate the sample to record a subsection of the configuration phase space. We then average over many sub-ensembles to capture the full phase space.

We demonstrate that to follow slowly relaxing or fully arrested systems, modulated 3D cross-correlation combined with a sample goniometer is a very powerful experimental tool that can record information not accessible by traditional approaches.

[1] P.N. Pusey and W. Van Megen, *“Dynamic light scattering by non-ergodic media”*, Physica A 157 (1989)

[2] Patent EP2365313 A1

[3] Ian D. Block and Frank Scheffold, *“Modulated 3D cross-correlation light scattering: Improving turbid sample characterization”*, Rev. Sci. Instrum. 81, 123107 (2010).

Hierarchical design optimizes transparency and haze factor of holey metal films

Karina Bley¹, Johannes Semmler², Marcel Rey¹, Chunjing Zhao¹, Nemanja Martić¹, Robin N. Klupp Taylor^{1,3}, Michael Stingl², Nicolas Vogel^{1,3}

¹ Institute of Particle Technology, Friedrich-Alexander-Universität Erlangen-Nürnberg, Erlangen, Germany

² Applied Mathematics 2, Friedrich-Alexander-Universität Erlangen-Nürnberg, Erlangen, Germany

³ Interdisciplinary Center of Functional Particle Systems, Friedrich-Alexander-Universität Erlangen-Nürnberg, Erlangen, Germany

Colloidal lithography is a key feature to fabricate thin metal coatings with regularly arranged nanoholes [1]. These nanohole arrays find application for instance as optically transparent electron conductive coatings and serve as ideal model structures to study the relation between optoelectronic properties and structural design. An important but less systematically studied property of transparent conductors is the amount of scattered light passing through the coating, described by the haze factor. We investigated systematically the influence of structural parameters of metal nanohole array coatings on the optical performance. The transmission, transparency and haze factor are highly dependent on each other and cannot be controlled individually. Generally, the percolation threshold sets an upper limit for the transparency of such metal nanohole array coatings. Here, we propose a new fabrication method to optimize the optoelectronic properties and maximize the transparency up to 84%. A hierarchical design of metal micro/nanohole arrays combines precisely controlled and highly regular features at two length scales and simultaneously provides low haze factors. Further, finite elements and ray optic computer simulations are in close agreement with the experimental results. They reveal that the reduced haze factor results from a drastic decrease of grating efficiency in the hierarchical films [2].

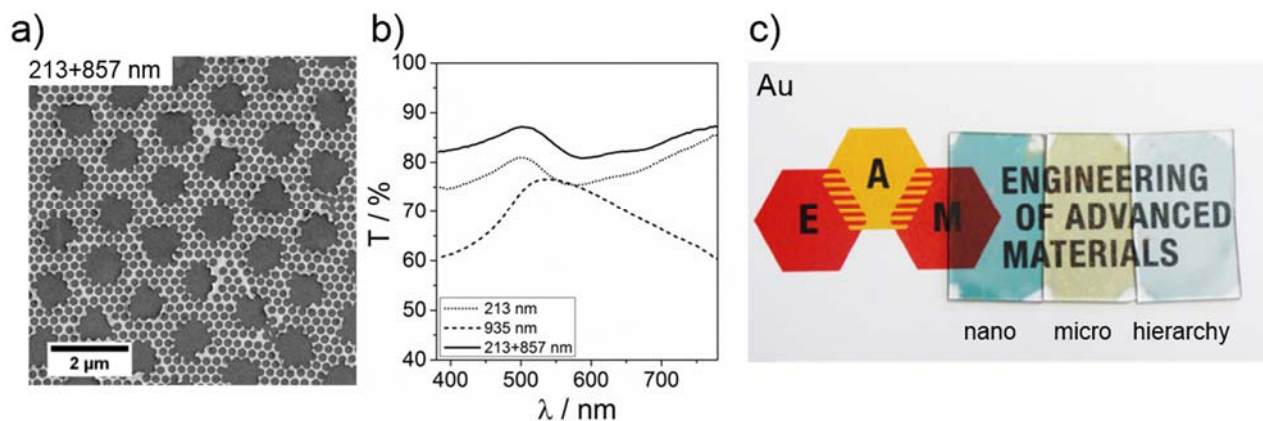


Figure 1. Optimized optical performance of hierarchical gold micro/nanohole arrays. 15 nm gold film with small hole diameter $D_{\text{small}} = 213$ nm (periodicity: $a = 245$ nm; ratio $D/a = 0.87$) and large holes with $D_{\text{large}} = 857$ nm (periodicity: $a = 1500$ nm). (a) scanning electron micrograph of the regular micro/nanohole structure, (b) transmission spectra of small (dotted line), large (dashed line) and hierarchical array (compact line), (c) photograph single hole size nano-, microhole, and hierarchical micro/nanohole array coating.

[1] K. Cheng, *Nanotechnology* **2012**, 23, 425303.

[2] K. Bley, *Adv. Funct. Mater.* **2018**, 1706965.

Acknowledgement: The authors acknowledge co-funding of the Deutsche Forschungsgemeinschaft (DFG) through the Cluster of Excellence “Engineering of Advanced Materials” and BASF SE.

Investigations of the internal structure of hollow charged microgels by SANS

Sarah K. Turnhoff¹, Andrea Scotti¹, and Walter Richtering¹

¹ Institute of Physical Chemistry, RWTH Aachen University, 52056 Aachen, Germany

Hollow microgels have the potential to meet one of the key challenges in biomedical research: The design of nano-carriers allowing for triggered uptake, storage and release of drugs [1]. Small-angle neutron scattering (SANS) was already used to study the internal structure of hollow doubly temperature-sensitive microgels. Based on the temperature-dependent swelling behavior of poly(*N*-isopropylacrylamide) (PNIPAM) based microgels, the size of the void changes when changing the temperature [2]. Introduction of charges into the polymeric network improves the swelling properties of microgels due to the repulsion of similar charges and the increased osmotic pressure within the gel network [3].

In this work, we address the synthesis of hollow charged microgels and the investigation of their properties as a function of charge density and ionic strength of the solvent. NIPAM is copolymerized with dimethylitaconate (DMI) onto sacrificial silica cores in a seed and feed precipitation polymerization. Sodium hydroxide is used to etch the silica and to saponify the DMI to itaconic acid introducing negative charges into the shell. Potentiometric titrations, electrophoretic mobility and different scattering techniques are used to analyze the pH-dependent behavior of charge density and microgel size. Furthermore, SANS is used to prove the persistence of the void below and above the volume phase transition temperature (Fig. 1). Additionally, the suppression of the temperature-sensitive collapse of the shell due to the presence of charges is demonstrated.

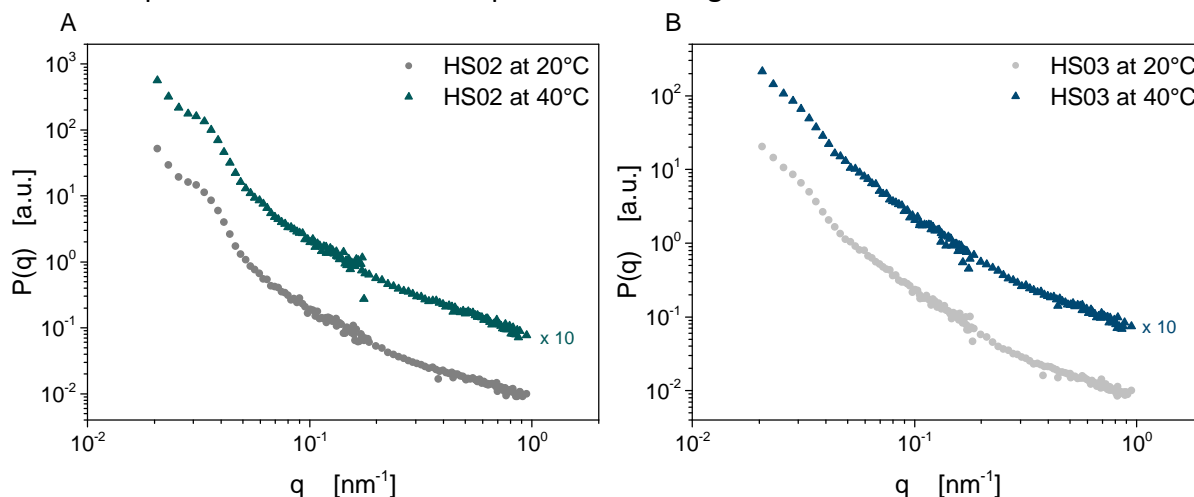


Figure 1. (A) SANS form factor for the hollow microgel HS02, with a DMI content of 10 mol% at two different temperatures below and above the VPTT at pH 9 and 10 mM ionic strength. Data are shifted up for clarity. (B) SANS form factor for the hollow microgel HS03 with a DMI content of 25 mol% at two different temperatures below and above the VPTT at pH 9 and 10 mM ionic strength. Data are shifted up for clarity.

[1] W. Richtering et al., *Nanomedicine* **11** (2016), 2879.

[2] A. J. Schmid et al., *Scientific Reports* **6** (2016), 22736.

[3] A. Pich et al., *“Chemical Design of Responsive Microgels”*, (Springer Berlin Heidelberg, 2010).

Acknowledgement: The authors acknowledge funding from the German Research Foundation (DFG) within the SFB 985 (Functional Microgels and Microgel Systems). Andrea Scotti thanks the Alexander von Humboldt Foundation for financial support.

Core-Shell Microgels in Suspension: Swelling Behaviour Observed by FTIR Spectroscopy

Lars Wiehemeier, Marian Cors, Oliver Wrede, Thomas Hellweg, Tilman Kottke

Physical and Biophysical Chemistry, Bielefeld University, Bielefeld, Germany

Stimuli-responsive microgels are promising candidates for applications like drug delivery, matrixes for catalysts, nanoactuators and smart surface coatings. To tailor the response, the architecture is of vital importance: While statistical copolymer microgels based on *N*-isopropylmethacrylamide (NiPMAM) and *N*-*n*-propylacrylamide (NnPAM) show a cooperative phase transition at a certain temperature [1], a linear response of the hydrodynamic radius measured by photon correlation spectroscopy (PCS) is observed for core-shell microgel particles (Fig. 1, c) [2].

FTIR spectroscopy is a sensitive method to investigate the molecular hydration in the microgel network [3]. In this work we investigate the swelling behavior of various microgels in H₂O by temperature dependent measurement of the NH-vibration. The phase transition determined by FTIR spectroscopy in homopolymer and statistical copolymer microgels based on NiPMAM and NnPAM is in accordance with results from PCS. However, measurements of core-shell particles show a broadening and shift of the respective phase transition temperatures indicating an interaction of core and shell polymers on a molecular level.

In conclusion, FTIR spectroscopy is a convenient approach to investigate the whole particle, with a special focus on the internal structure, whereas PCS is limited to the diffusion properties dominated by the particle shell.

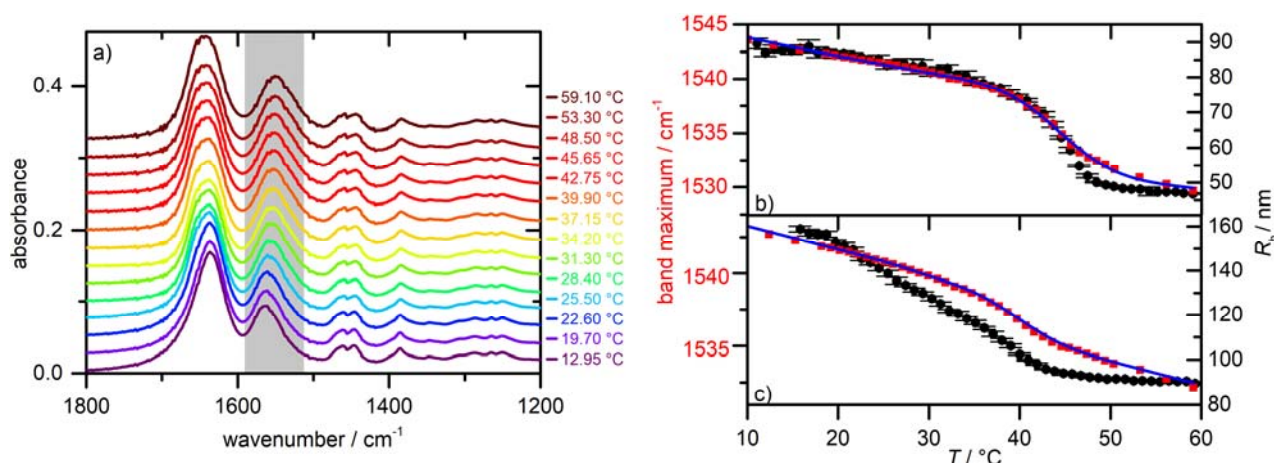


Figure 1. a) Set of temperature dependent FTIR-Spectra of an aqueous microgel suspension. b) Temperature dependent wavenumber of the NH-band (squares) in comparison to results from PCS (circles) for a NiPMAM-microgel. c) Results from a NiPMAM-core-NnPAM-shell microgel reveal that the phase transition of the whole particle is dominated by NiPMAM.

[1] B. Wedel, M. Zeiser, and T. Hellweg, *Z. Phys. Chem.*, **2012**, 226, 737–748

[2] M. Zeiser, I. Freudensprung, T. Hellweg, *Polymer*, **2012**, 53, 6096-6101

[3] M. Keerl, V. Smirnovas, R. Winter, and W. Richtering, *Macromolecules*, **2008**, 41, 6830-6836

Highly Positively Charged Amine Functionalized Core-Shell Microgels

Alexander Jans¹, Alexander J.C. Kuehne¹

¹ DWI – Leibniz Institute for Interactive Materials, Forckenbeckstraße 50, 52076 Aachen, Germany.

Microgels containing cationic moieties are widely used for drug delivery systems [1] and furthermore they can assemble to colloidal crystal structures [2]. Positive charges inside of a thermo-sensitive poly(*N*-isopropylacrylamide) (pNIPAm) microgel network change the physicochemical properties such as the volume phase transition, surface interactions and degree of swelling in a significant way. To track their behaviour by optical confocal microscopy, microgels can be marked by introducing a fluorescent solid core without significantly influencing the performance of the microgel [3]. While there are many examples of negatively charged microgels, which assemble via Coulomb interactions, highly positively charged microgels that can perform accordingly remain unavailable. Primary amines attain positive charge below their isoelectric point; however, such monomers lack sufficient incorporation rates for introduction into the microgel network [4]. To overcome this drawback, we introduce BOC-protected *N*-(3-aminopropyl)methacrylamide into the microgels shell of our composite particles. Deprotection after synthesis yields positive microgels with primary amines. We apply up to 15 wt% of the protected amine during the synthesis, yielding 4 mol% of incorporated amines. These microgels can interact with negatively charged microgels to form colloidal molecules and the primary amines enables post modification techniques for the introduction of biomedical recognition motifs (glycans and peptides) for example as scavenger units for toxins.

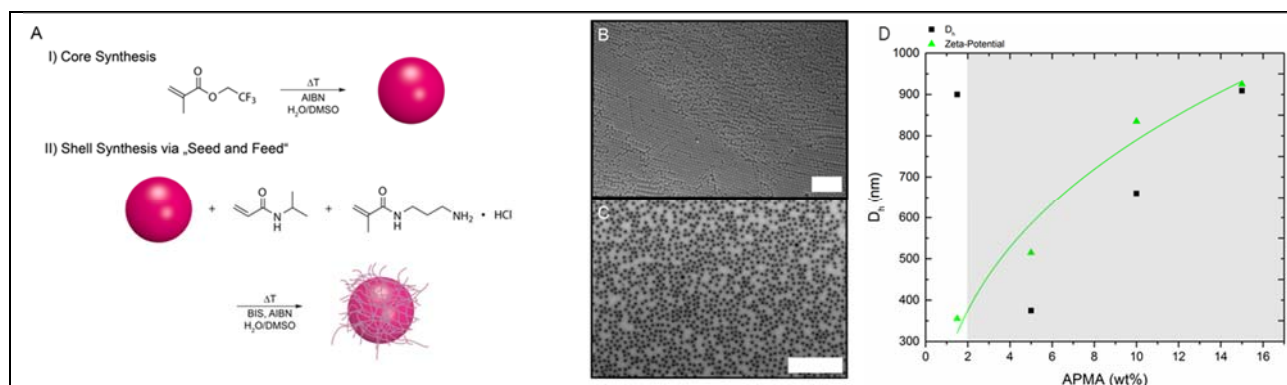


Figure 1. a) Synthesis of core and core shell microgels. Electron microscopy images of b) the prepared core and c) core-shell microgels. d) Zeta potential and hydrodynamic radius of the deprotected core-shell microgels in relation to the *N*-(3-aminopropyl)methacrylamide content. Scale bars represent 2 μm .

[1] Blackburn *et. al.*, *Bioconjugate Chem.*, 2009, **20**, 960-968.

[2] Senff H., Richter W., *J. Chem. Phys.*, 1999, **111**, 1705.

[3] Go D., Rommel D., Liao Y., Haraszti T., Sprakel J., Kuehne A. J. C., *Soft Matter*, **14**, 910-915.

[4] Hu X., Tong Z., Lyon L. A., *J. Am. Chem. Soc.*, 2010, **132** (33), 11470–11472.

Acknowledgement: The authors acknowledge support via the Deutsche Forschungsgemeinschaft DFG through the collaborative research center SFB 985 "Functional microgels and microgel systems" (project C3).

Study of temperature switchable adhesion between ligands and receptors by Soft Colloidal Probes

Alexander Strzelczyk¹, Florian Malotke¹, Melina Feldhof¹ and Stephan Schmidt¹

¹ Institute for Organic and Macromolecular Chemistry Heinrich-Heine-Universität Düsseldorf, Universitätsstraße 1, 40225 Düsseldorf, Germany

Adhesion in aqueous media is crucial for many processes in nature. Moreover, controlling adhesion in aqueous media is very important for technology, e.g. in cleaning processes or adhesive development [1]. Those interactions can be measured indirectly with methods like quartz crystal microbalance (QCM) or directly with atomic force microscopy (AFM). However, AFM is rather expensive and slow and methods like QCM merely detect the amount of adhered material but not the involved adhesion energy. Therefore, a new fast and straightforward method has been developed to measure adhesive interactions. The method utilizes soft hydrogel particles as sensors (soft colloidal probes, SCPs) which allows to determine adhesion energies by optical microscopy and evaluation with JKR model [2].

Using the SCP method adhesion energies can be measured, e.g. interactions between polymers or ligands and receptors [3]. Based on this, the temperature responsive adhesion of LCST polymers can be directly characterized with functionalized SCPs (figure 1). Additionally, functionalizing thermoresponsive polymers with ligands, e.g. carbohydrates, allows systematic investigation of switchable adhesion to receptor-functionalized surfaces, e.g. lectin functionalized glass slides. We hope that this will reveal the optimal material properties of the thermoresponsive polymer networks, e.g. swelling degree or ligand presentation, for maximized stimulus-control over specific interactions

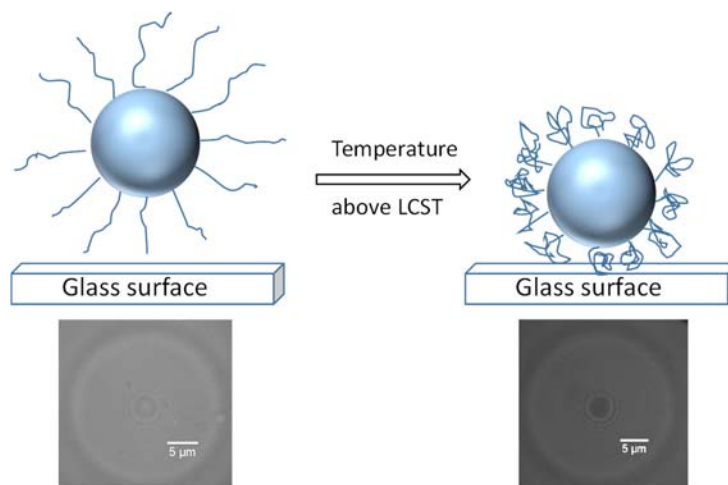


Figure 1. Behaviour of thermoresponsive polymers on colloidal probe surface and switchable adhesion to glass surface (left) below lower critical solution temperature (LCST) and (right) above LCST. The microscope images show the increase of the contact area from below (white spot) and above (dark spot) between colloidal probe and glass surface.

[1] H. G. Silverman, F. F. Roberto, *Mar. Biotechnol.* **2007**, 9 (6), 661-681.

[2] D. Pussak et al., *Soft Matter* **2012**, 8, 1664-1672.

[3] A. Strzelczyk et al., *Gels* **2017**, 3(3), 31

Acknowledgement: The authors acknowledge funding from the Henkel AG & Co KGaA.

Emulsion-based Lubricant Replenishment Strategies for Lubricant-Impregnated Slippery Surfaces under Flow

P. Baumli¹, H. Teisala¹, D. Garcia-Gonzalez², H. Bauer¹, V. Damle³, M. d'Acunzi¹, F. Geyer¹, H.-J. Butt¹, and D. Vollmer¹

¹ Max Planck Institute for Polymer Research, Department of Physics at Interfaces, Mainz, Germany.

² University of Twente, Physics of Fluids Group, Enschede, The Netherlands.

³ Arizona State University, Department of Mechanical Engineering, Tempe (AZ), United States

Lubricant-Impregnated Slippery Surfaces (LubISS) constitute of textured/porous substrates infiltrated with a chemically compatible lubricant [1]. The action of capillary forces establishes an immobilized liquid surface which keeps the lubricant in place within the texture. As a consequence, they are liquid-repellent and non-sticking surfaces. Droplets immiscible with the lubricant slide off these surfaces very easily. A formidable challenge which needs to be addressed is the problem of lubricant depletion [2, 3]. Evaporation of the lubricant, cloaking, drainage due to gravity or flow conditions causes progressive loss of lubricant which in turn destroys the functionality of the coating [4, 5]. In this work, a proof of concept for a novel approach to the formation of LubISS is introduced. We rely on the flow of emulsions through a closed water-filled flow cell containing a regular and uniform micropillar array. We observe that oil droplets transported through the channel readily attach to the tops and walls of the micropillars. Subsequently, the droplets grow in size due to the coalescence with other arriving oil droplets. Eventually, the growing droplets spread onto the bottom substrate and hence gradually fill the channel, leading to the formation of a LubISS. The influences and effects of the texture and geometry of the solid substrate, the surface chemistry, the flow conditions, the oil viscosity, the chemical nature and the filling mechanism are investigated by Laser Scanning Confocal microscopy (LSCM) and advanced image processing. Central to the successful filling of a structure is the addition of a positively charged surfactant at a concentration within the range of the point of charge reversal in order to compensate for the negative charges present on the oil droplets preventing droplet coalescence. This approach can in principle facilitate a strategy for active lubricant replenishment preventing the detrimental depletion of lubricant since starting with the empty micropillar array represents the worst-case scenario of a porous structure completely depleted of lubricant.

[1] Wong, T.-S., *et al.* *Nature* (2011), 447, 443-447

[2] Kim, J.-H., Rothstein, J. P., *Exp. Fluids* (2016), 57:81.

[3] Howell, C., *et al.*, *Chem. Mater.* (2015), 25(5), 1792-1800.

[4] Damle, V., *et al.*, *Surface Innovations*. (2016), 4(2), 102-108

[5] Wu, W., *et al.*, *Adv. Mater.* (2011), 23, H178-83

A Viscous Tweezer

Saurabh Nath^{1, 2}, Armelle Keiser^{1, 2}, Christophe Clanet^{1, 2}, and David Quéré^{1, 2}

¹ Physique et Mécanique des Milieux Hétérogènes, UMR 7636 du CNRS, ESPCI, 75005 Paris, France

² LadHyX, UMR 7646 du CNRS, École polytechnique, 91128 Palaiseau, France.

Liquid-infused surfaces (LIS) are a new class of materials, characterized primarily by their extremely low adhesion [1, 2]. Even a very viscous droplet can easily roll off a liquid-infused surface, if the surface is tilted by a few degrees. However, in this talk, we show that alongside being 'slippery', liquid infused surfaces are also 'sticky'. To investigate this, we take an elementary system comprising a water droplet placed between two horizontal LIS, infused with oils of different viscosities (Figure 1a). We find that if the upper plate is pulled with a sufficiently high velocity, the droplet completely detaches itself from the bottom plate and remains on the top (Figure 1b). Such a capture is possible only if the upper plate viscosity is greater than that of the lower plate. The captured droplet can be subsequently deposited on the lower plate by bringing it in contact and pulling the plates apart slowly. This simple system, thus demonstrates how the dynamical adhesion or 'stickiness' of liquid infused surfaces can be harnessed to create a 'viscous tweezer'. This has immense potential in terms of applications in micromanipulation and droplet transport. In this talk, we will discuss the physics of such *viscous captures* and the parameters that govern it.

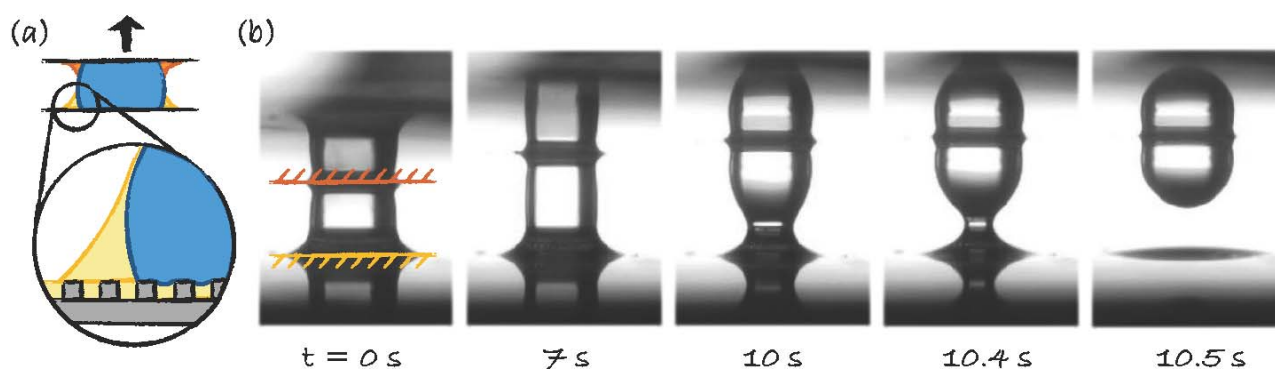


Figure 1. (a) Schematic of the experimental system: a droplet placed between two liquid-infused surfaces. The orange and yellow colours signify different oil viscosities. Zoomed in section shows oil locked in the textures rising to form a meniscus and cloaking the droplet. (b) Experimental image sequence of a 1 μL droplet being pulled up at a velocity of 30 $\mu\text{m/s}$, leading to a *viscous capture*. The oil viscosities on the upper and lower plates are 10,000 cSt and 10 cSt respectively. The red and the orange lines in the first frame mark the positions of the two plates, the droplet being in between. Outside these lines what we see are reflections of the droplet on the upper and lower plates.

[1] A Lafuma et al. Europhys. Lett. **96** (2011) 56001.

[2] T S Wong et al., Nature, **477** (2011) 443.

Acknowledgement: ITN LubISS network.

Modeling Droplet Dynamics on Liquid Infused Surfaces

Muhammad Subkhi Sadullah¹, Ciro Semprebon², and Halim Kusumaatmaja³

¹ Department of Physics, Durham University, Durham DH1 3LE, UK

² Smart Materials & Surfaces Laboratory, Faculty of Engineering & Environment, Northumbria University, Newcastle upon Tyne NE1 8ST, UK

³ Department of Physics, Durham University, Durham DH1 3LE, UK

Inspired by pitcher plants, Liquid Infused Surfaces (LIS) are constructed by infusing rough or porous materials with a lubricant, as illustrated in Fig. 1, and they have been shown to exhibit many advantageous surface properties, including self-cleaning, drag reduction, anti-icing and anti-fouling [1]. In this contribution, we demonstrate how our ternary free energy lattice Boltzmann model [2] is suitable for studying droplet dynamics on LIS [3]. First, we find that there is a rich interplay between contact line pinning and viscous dissipation at the wetting oil ridge. The effect of contact line pinning is prominent for relatively large apparent contact angle. For lower apparent contact angle, viscous dissipation at the wetting ridge is more important and hence the shape of the wetting ridge, characterised by aspect ratio, is key for determining the droplet mobility. Second, we observe that the advancing mechanism of the droplet is a combination of sliding and rolling motion, and that the amount of rolling is affected by the droplet shape and the contact area with solid. Due to the nature of the corrugated substrate, the solid contact area of the droplet decreases quickly with increasing apparent contact angle. Therefore, droplet on LIS demonstrates different rolling dynamics compared to smooth surfaces.

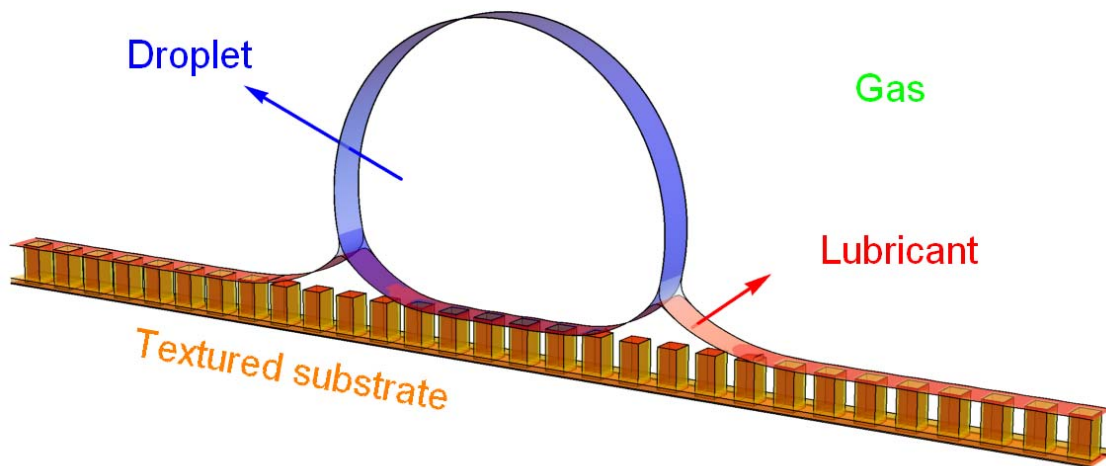


Figure 1. Illustration of LIS where a droplet is sitting on a textured substrate infused with a lubricant.

[1] C Semprebon, T Kruger, H Kusumaatmaja, *Phys. Rev. E* **93**, (2016), 033305.

[2] T S Wong et al., *Nature* **477**, (2011), 443.

[3] M S Sadullah, C Semprebon, H Kusumaatmaja, *In Preparation*.

Acknowledgement: The authors acknowledge Indonesia endowment fund for education (LPDP) as the funding body of the presenting author. The authors also thank to Dr. M. Wagner, Dr. P. Koenig and Dr. Y. Gizaw from P&G for fruitful discussions.

Dewetting of liquid two-layer films

R.Shiri¹, R. Seemann¹, D. Peschka², B. Wagner²

¹ *Experimental physics, University of Saarland, Saarbrücken, Germany.*

² *Weierstrass Institute, Mohrenstr. 39, Berlin, Germany.*

We study the dewetting of thin nanometric thin polystyrene (PS) films from liquid polymethylmethacrylate (PMMA) substrates. In order to induce dewetting the PS/PMMA samples are heated above the glass transition temperature of both polymers, where both liquids can be considered as Newtonian with comparable viscosities. After a few minutes circular holes appear in the PS film and their radii grow with time and finally coalescence leading to a set of droplets on the substrate [1-3].

The considered mechanism leading to the symmetry breaking of the initially flat film is called spinodal dewetting, which is initiated due to the growth of thermally activated surface waves. Spinodal dewetting can only take place if the second derivative of the effective interfacial potential with respect to film thickness is negative, $\varphi''(h_0) < 0$, i.e. if the long-range forces do not favor wetting, which is fulfilled in the considered system. The spinodal rupture of the liquid film results in a dewetting pattern of 'hills and gullies' with a certain preferred wavelength λ in both liquid/air and liquid/liquid interfaces leading eventually to the formation of holes after a certain time t . Interestingly, the deformation of the liquid/liquid interface is larger than that of the liquid/air interface due to the lower surface tension. According to theoretical predictions, can the deflection of both interfaces be in phase or antiphase which determines the dewetting pathway. The preferred wavelength, holes distance and deflection of interfaces contain experimentally accessible information about the underlying long range forces and evolution of the interfaces and therefore are of special interest [1,3].

In this study we experimentally measured the preferred wavelength λ and holes distance and we monitor deformation of interfaces by atomic Force Microscopy as function of PS film thickness. Using a lift off technique, we also gather information about the deformation of the liquid-liquid interface. Ultimately, the result of experimental observations will be compared with theoretical modelling.

[1] R. Seemann "*Structure formation in thin liquid films: interface forces unleashed*", ed. S. Herminghaus, K. Jacobs. Springer **490** (2007).

[2] P. Lambooy "*dewetting at liquid-liquid interface*", ed. K. C.Phelan, O. Haugg, G. Krausch. Phys. Rev. Lett (1996) 1110.

[3] R. Seemann "*Dynamics and structure formation in thin polymer melt films*", ed. S. Herminghaus, C.Neto, S. Schlagowski, D.Podzimek, R. Konrad, H.Mantz, K. Jacobs. Phys. Condens. Matter **17** (2005) 267.

Hybrid gold nanoparticles with conductive polymer ligands

Indra Backes¹, Beate Reiser¹, Lola Gonzalez-Garcia¹, David Doblas Jiménez¹, and Tobias Kraus¹

¹ INM – Leibniz Institute for New Materials, Saarbrücken, Germany

Current printed electronics are often made using inks that contain noble metal nanoparticle dispersions to exploit the good electrical properties of metals [1, 2]. Sufficient colloidal stability in dispersion is provided by bulky organic molecules that ensure steric stabilization at the expense of the electrical conductivity of the dried material. After the printing process, post-treatments are usually required in order to remove the insulating ligands and enhance conductivity. The required temperatures often exclude flexible substrates like polymer foils [3]. Here, we describe sintering-free inks that overcome this challenge.

We demonstrated that gold nanorods stabilized by water-soluble, semiconducting polymers combine high colloidal stability and electrical conductivity upon drying (Fig. 1). Inks prepared using these hybrid nanostructures exhibit high shelf-life in water and alcohols, but are not stable in unpolar organic solvents [4]. The printing of electronic systems such as multilayer devices requires to tailor ink properties, in particular viscosity and wetting behavior. Aqueous dispersions cannot fulfil the requirements for some devices, and we are developing sintering-free inks that are based on unpolar organic solvents.

We will discuss two strategies to stabilize hybrid nanoparticles in organic media. In the first approach, spherical gold nanoparticles capped by oleylamine are functionalized by a conjugated polymer ligand in a direct ligand exchange reaction. In the second, we use a two-step reaction to stabilize hybrid gold nanorods in unpolar organic solvents. First, we functionalize the gold nanorods to enable phase transfer from the aqueous to the organic phase. The intermediate gold nanorods are then modified by semiconducting polymers in a final step.

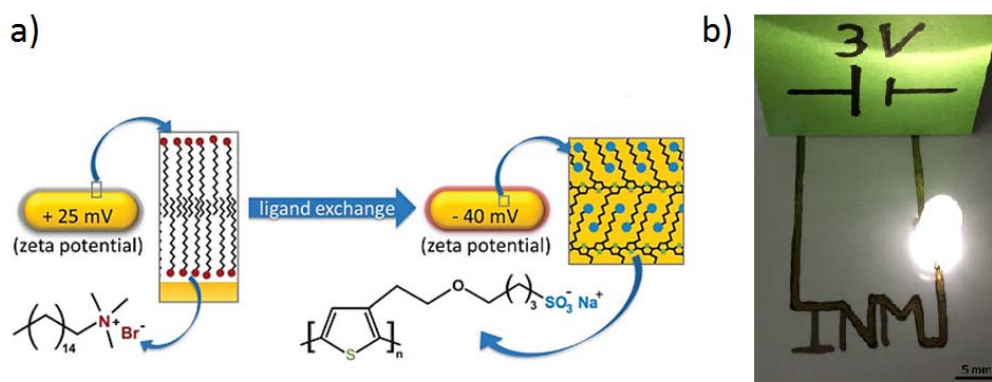


Figure 1. a) Schematic surface modification of gold nanorods with semiconducting, water-soluble polythiophene ligands. b) Circuits produced by the aqueous sintering free hybrid inks.

- [1] A. Kamyshny, *small* **10** (2014), 3515.
- [2] J. Perelaer, *J. Mater.Chem.* **20** (2010), 8446.
- [3] H. Kang, *ACS Appl. Mater.Interfaces.* **6** (2014), 1682.
- [4] B. Reiser, *Chem. Sci.* **7** (2016), 4190.

Formation of silver nanoparticles in spherical polyelectrolyte brushes and encapsulation in silica

Emmanuele Ferrarotto¹, Klaus Huber¹, and Claudia Schmidt¹

¹ Department of Chemistry, Paderborn University, Warburger Str. 100, 33098 Paderborn, Germany

Nanoparticles are of great interest for both physics and chemistry because of the wide range of applications. A large variety of metals like gold, silver and platinum as well as a large number of methods of preparation are available to tune the desired properties.

In this study we use spherical polyelectrolyte brushes (SPB) as template [1,2]. The SPB used consist of polystyrene cores upon which a large number of linear chains of polyacrylic acid is grafted. Formation of silver nanoparticles in the layer of polyacrylate chains is achieved either by photochemical reduction using UV light or by employing NaBH₄ as a chemical reducing agent. Both methods are being investigated to optimize number, density and size of the nanoparticles.

In order to protect the nanoparticle-loaded SPBs they are encapsulated in silica by applying a modified Stöber process [3]. The systems are characterized by UV/Vis spectroscopy and electron microscopy.

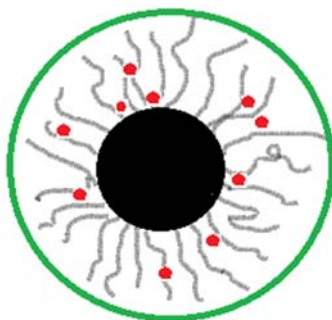


Figure 1. Schematic representation of the investigated system. Polystyrene core (black center), polyacrylic acid brushes (grey lines), nanoparticles (red dots) and silica shell (green circle)

[1] Anna Ezhova, *Specific interactions of Ag⁺ ions with linear polyacrylate chains and spherical polyacrylate brushes and Ag nanoparticle formation therein*, (Doctoral Thesis, Paderborn, 2015).

[2] X. Guo et al., *Macromolecules* **32** (1999) 6043.

[3] W. Stöber et al., *Journal of Colloid and Interface Science* **26** (1968) 62.

Acknowledgement: The authors acknowledge funding from the DFG GRK 1464 “Mikro- und Nanostrukturen in Optoelektronik und Photonik”.

Nanodroplets at interfaces and membranes: Line tension effects

Vahid Satarifard¹, Andrea Grafmueller¹, and Reinhard Lipowsky¹

¹ Theory and Bio-Systems, Max Planck Institute of Colloids and Interfaces, Potsdam, Germany.

Nanodroplets in contact with interfaces and membranes are affected by the line tension of the three-phase contact line. It is generally agreed that the magnitude of this tension is of the order of 10^{-11} N, but its sign is still a matter of debate. In addition, little is known about the wetting and nucleation behavior of nanodroplets at deformable substrates such as membranes and vesicles.

In this study, we use molecular simulations to study the effect of line tension on the behavior of nanodroplets at lipid bilayers. These nanodroplets are stable provided the interfacial tension exceeds a certain threshold value. The membrane is observed to engulf the nanodroplet, thereby forming a membrane bud, in order to reduce the area of the liquid-liquid interface. For relatively large membrane tension, the droplet-induced membrane bud has an axisymmetric shape, see Fig. 1a, which becomes, however, non-axisymmetric for low values of the membrane tension, see Fig. 1b. [1] To understand this unexpected breaking of axial symmetry, we studied the force balance along the contact line [2] from which we obtained a *negative* value of the line tension. This negative line tension provides the driving force for the non-axisymmetric bud shape.

We now apply our approach to simpler systems as provided by liquid lenses between two bulk phases, see Fig. 1c. In such geometry, the line tension can be measured via deviations from Neumann's triangle [3]. We use this setup to understand the parameter dependence of the line tension and of the associated force balance along the contact line.

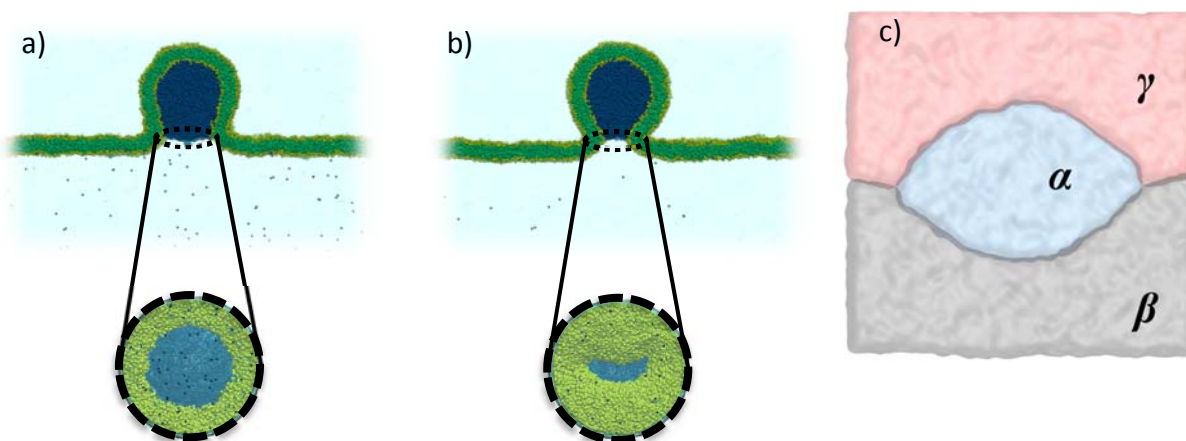


Figure 1. (a,b) Cross-section of a nanodroplet adhering to a membrane (a) under high and (b) under low mechanical tension. The membrane is axis-symmetric and non-axisymmetric in (a) and (b), respectively; and (c) Cross-section of a liquid lens α between two bulk liquid phases β and γ .

[1] V. Satarifard, A. Grafmueller, and R. Lipowsky, in preparation (2018)

[2] H. Kusumaatmaja, Y. Li, R. Dimova, and R. Lipowsky, Phys. Rev. Lett. 103 (2009), P.1

[3] P. Chen, J. Gaydos, and A. W. Neumann, Langmuir, 12, (1996)

Acknowledgement: This study was supported by the IMPRS on Multiscale Bio-Systems.

Merging drops with unstable wetting films

Peyman Rostami¹, Benedikt Straub¹, Franziska Henrich¹, and Günter K. Auernhammer^{1,2}

¹ Max Planck Institute for Polymer Research, Ackermannweg 10, D-55128 Mainz, Germany

² Leibniz Institute for Polymer Research, Hohe Straße 6, D-01169 Dresden

Fusion or merging of drops plays a key role in many different processes such as raining and coating. Due to this fact, in recent years, it has been widely studied experimentally, theoretically and numerically. Physics of fluids stipulates that after coming in contact, two drops merge to reduce interfacial energy. However the pathway might be complex [1], [2]. When two immiscible drops merge, depending on the surface and interfacial tensions, a liquid film of the drop with lower surface tension might be drawn over the surface of the other drop, i.e. the spreading coefficient can be positive. Since in most of applications like inkjet printing, two non-identical drops come to contact, studying this phenomenon has attracted a lot of attention recently.

In current study, the drops are deposited on a glass substrate via two independent syringe. We present results for pure water and cyclohexyl bromide. A high-speed camera enables us to capture the process. The flow field inside the drops is investigated by the use of tracer particles. First a water droplet is deposited on the substrate and then cyclohexyl bromide is injected as the second drop. A thin liquid film of cyclohexyl bromide covers the water droplet surface. To some extent, this behavior does not depend on the order in which the drops are placed.

In our case, these liquid films exhibit an instability that resembles the Rayleigh–Plateau instability (Fig. 1), which is responsible for breakup and atomization of liquid sheets [3]. We present a detailed study of this instability analyzing the onset of instability, the length of liquid film and characteristic wave length of instability as function of physical parameters. To measure the instability characteristics, the captured images are analyzed by ImageJ software. The results show that the instability only occurs when a cyclohexyl bromide drop comes to contact with pre-deposited water drop. If the cyclohexyl bromide drop is deposited first, no instability is observed. However the final configuration of both processes is same, the pathway is totally different.

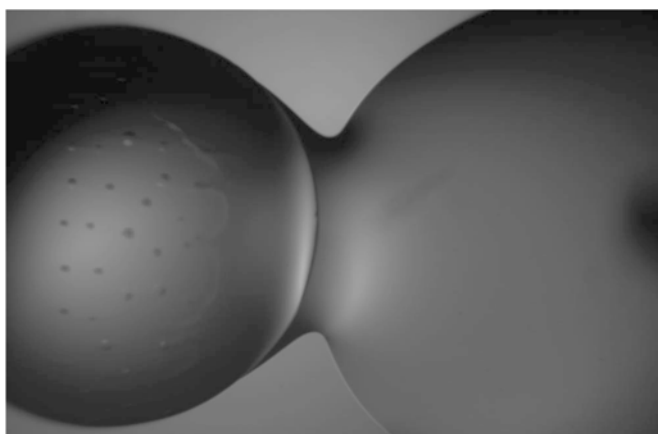


Fig. 1:

A cyclohexyl bromide drop (right) in contact to a water drop (left). A positive spreading coefficient pulls a thin film of cyclohexyl bromide over the water drop. This film however becomes unstable and disintegrates into drops.

- [1] S. Karpitschka and H. Riegler, "Noncoalescence of Sessile Drops from Different but Miscible Liquids: Hydrodynamic Analysis of the Twin Drop Contour as a Self-Stabilizing Traveling Wave," *Phys. Rev. Lett.* **109**, (2012), 066103
- [2] S. Karpitschka and H. Riegler, "Sharp transition between coalescence and non-coalescence of sessile drops," *J. Fluid Mech.* **743**, (2014).
- [3] R. Krechetnikov, "Stability of liquid sheet edges," *Phys. Fluids.* **22**, (2010), 092101.

Spontaneous Rise of Rivulets in Square Capillaries

Vignesh Thammanna Gurumurthy¹, Daniel Rettenmaier¹, Ilia V. Roisman¹, Cameron Tropea¹ and Stephen Garoff²

¹ *Institute of Fluid Mechanics and Aerodynamics, Technische Universität Darmstadt, Alarich Weiss Str. 10, 64287 Darmstadt, Germany.*

² *Department of Physics and Center for Complex Fluids Engineering, Carnegie Mellon University, Pittsburgh PA15213, USA.*

Capillary driven flows in non-circular channels/capillaries with corners are relevant in the field of microfluidics, porous media, etc. While the bulk capillary flows in the cornered capillaries are very much similar to the cylindrical capillaries, the presence of corners enhances the capillary effects resulting in the formation of rivulets rising in the corners. These rivulets are known to impact the performance of the microfluidic devices which necessitates the understanding of capillary flow in corners.

In this computational study, we investigate the capillary rise in square capillaries under gravity. The flow is modelled using Volume-of-Fluid method and the free surface is accurately tracked using adaptive mesh refinement. The influence of the parameters such as liquid viscosity, gravity, contact angle and the capillary size are investigated.

Results show that the rivulets are formed in the capillaries only when the contact angle is less than 45 degrees [1]. At long times, the rivulet grows as one-third power of time ($h \sim t^{1/3}$) as shown in the Figure. This one-third rise behaviour agrees with the existing experiments on capillary rise in corners between different geometries [2]. Finally, the growth rate of the rivulets is presented using a scaling relation which is valid for different liquids and contact angles.

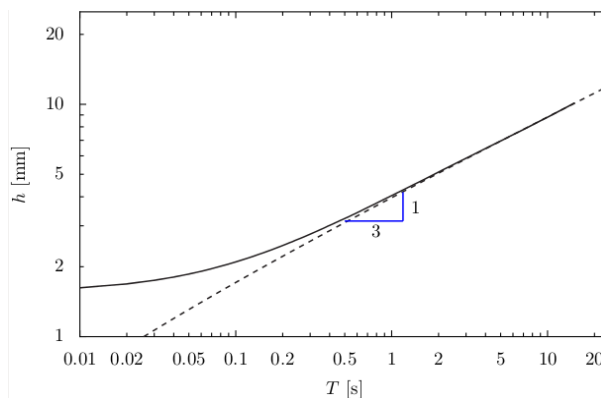


Figure 1: Temporal evolution of rivulet height for 3mm capillary at a contact angle of 30°. The dashed line is the one-third asymptotic least squares fit.

References

- [1] P Concus, R Finn, *Appl.Math.Sci* (1969).
- [2] A Ponomarenko et.al, *J.Fluid Mech* (2011).

Acknowledgement: This work has been performed in the framework of the Marie Curie Initial Training Network "Complex Wetting Phenomena" (CoWet), Grant Agreement no.607861. The authors gratefully acknowledge the computing time granted on the Lichtenberg-High Performance Computer at Technische Universität Darmstadt.

Dynamics of Capillary Imbibition of Poly(ethylene oxide) Melts in Nanoporous Alumina

Yang Yao¹, Jiajia Zhou², Masao Doi², Martin Steinhart³, Hans-Jürgen Butt¹, and George Floudas^{1, 4}

¹ Max Planck Institute for Polymer Research, D-55128 Mainz, Germany

² Center of Soft Matter Physics and Its Applications, Beihang University, 100191 Beijing, China

³ Institut für Chemie neuer Materialien, Universität Osnabrück, D-49069 Osnabrück, Germany

⁴ Department of Physics, University of Ioannina, P.O. Box 1186, 451 10 Ioannina, Greece

Understanding the behavior of polymer fluids through nanochannels is not only of fundamental interest but also important for applications in nanotechnology. Nearly hundred years ago, Lucas and Washburn derived Lucas-Washburn Equation (LWE) for Newtonian liquids penetrating a cylindrical capillary with radius R . The penetrating length is proportional to $t^{1/2}$, t is the wetting time. Herein, we investigate the penetration of a series of entangled poly(ethylene oxide) melts within nanopores of self-ordered alumina. In general, the penetration follows $\sim t^{1/2}$ behavior according to LWE. However, LWE breaks-down because of differences in the prefactor. We observe a reversal in dynamics of capillary rise with polymer molecular weight. Chains with 244 entanglements or more display a faster capillary rise than theoretically predicted. Moreover, it is the first time to our knowledge that a slower capillary rise is observed for chains with 50 or less entanglements. The reversal in imbibition can be interpreted by the competition between a polymer dead zone next to the nanopore surface and the reptation of polymer chains under a pressure gradient. Lastly, we discuss the imbibition of PEO mixtures composed from long and short chains and show that it can result to the fractionation of short/long chains.

[1] R Lucas, *Kolloid-Z.* **23** (1918), 15.

[2] E W Washburn, *Phys. Rev.* **17** (1921), 273.

[3] Y Yao, G Auernhammer, M Steinhart, H-J Butt, and G Floudas et al., *J. Chem. Phys.* **146** (2017), 203320.

[4] Y Yao, H-J Butt, J Zhou, M Doi, and G Floudas, submitted.

[5] Y Yao, H-J Butt, G Floudas, J Zhou, and M Doi, submitted.

Acknowledgement: We thank F. Henrich and Dr. S. Wooh for help during the surface tension and dynamic contact angle measurements as well as to Dr. G. Auernhammer and Dr. D. Vollmer for fruitful discussions and suggestions. We also thank A. Best and A. Hanewald for help with reflection microscopy and rheology.

Influence of buffer pH and composition on wettability of modified surfaces

Jutta Lehnfeld¹, Verena Huber¹, and Rainer Müller¹

¹ Institute of Physical and Theoretical Chemistry, University of Regensburg, Regensburg, Germany

Biomaterials have to be capable of effective tissue integration and should resist bacterial attachment [1, 2]. Those processes are strongly influenced by the physicochemical properties of the material surface [1, 3]. Thus, in this study the pH-dependent wettability of a variety of amino group-terminated surface modifications was investigated, in order to gain basic knowledge about the correlation between surface functionalizations and their properties.

For this study, silicon or silica model substrates were functionalized with organic molecules with terminal amino groups, but different structure (Fig. 1). The surface coatings were analyzed via static contact angle measurements with buffers of varying pH and composition (10 mmol L⁻¹, acetate at pH 4, phosphate at pH 6 and 7.5, carbonate at pH 9). In addition, PBS buffer (150 mmol L⁻¹, pH 7.5) was tested. Moreover, the modifications were characterized via an amino group detecting assay (sulfo-SDTB assay), IR spectroscopy and electrophoresis experiments.

In those initial contact angle measurements, the contact angle rose with increasing pH of the buffer. This can be expected because all modifications possess terminal amino groups, which are deprotonated at higher pH values. This observation was not valid for the carbonate buffer at pH 9. For this system contact angles decreased (compared to pH 7.5) for three coatings (APD, PPI-G4, PAMAM-G5), possibly indicating carbamate formation [4]. At last, the contact angles measured with PBS were considerably higher than the values at the same pH with the phosphate buffer. This effect was most pronounced for the PAMAM dendrimer coating, as the dendrimer's surface amino groups probably back-fold into the interior at higher ionic strength [5].

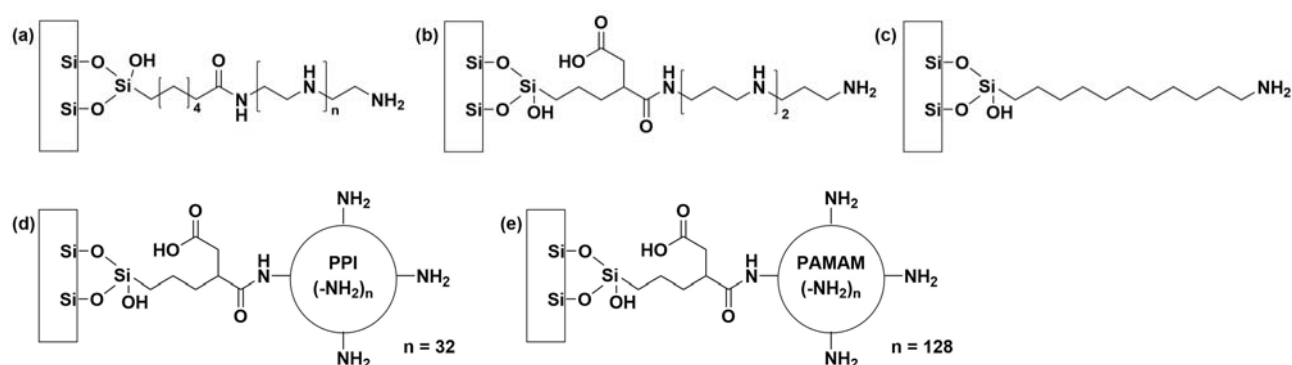


Figure 1. Overview of the surface modifications: (a) linear poly(ethylene imine) (PEI) polymer, (b) N,N'-bis(3-aminopropyl)-1,3-propanediamine (APD), an oligo(propylene imine), (c) self-assembled monolayer with terminal amino groups (SAM-NH₂), (d) poly(propylene imine) dendrimers of generation 4 (PPI-G4), or (e) polyamidoamine dendrimers of generation 5 (PAMAM-G5).

- [1] R. Müller et al., *Biomaterials* **30** (2009), 4921-4929.
- [2] J. Rychly et al., *Bio. Nano. Mat.* **14** (2013), 153-160.
- [3] N. Fauchaux et al., *Biomaterials* **25** (2004), 2721-2730.
- [4] D. E. Penny et al., *J. Chem. Soc., Faraday Trans. 1* **79** (1983), 2103-2109.
- [5] U. Boas et al., *J. Mater. Chem.* **16** (2006), 3785-3798.

Sand and rain erosion testing of structured and modified Titanium surfaces

Christian Herrles¹, Niklas Reisenauer¹, Elmar Bonaccorso¹

¹ Airbus, Central Research & Technology, Materials X, Munich, Germany

Effective boundary layer control of the air streaming around external aircraft surfaces like wings or control elements like rudder or ailerons is paramount for reducing fuel burn and emissions. To implement new hybrid laminar flow control (HLFC) systems on aircraft that are based on the suction of the boundary layer, the operability, performance, and durability of a microperforated titanium plate is investigated in laboratory scale in the frame of the “OptiHyL” project. Suction of the boundary layer through a microperforated surface element leads to a significant drag reduction and thereby to fuel saving and a reduction of CO₂ and NO_x emissions. For enabling the controlled suction of the boundary layer, the micro holes must remain open during all flight phases. To avoid the blockage of the micro holes by insects, dust, dirt, water, or ice the titanium surface was patterned with a hydrophobic/superhydrophobic nanostructure. Apart from being dirt repellent and showing low adhesion to ice, the surface pattern must withstand erosion during flight. Therefore, we tested sand and rain erosion on differently nanostructured titanium surfaces (without structure, with laser, with a galvanic process) with a hydrophobic coating on top of. Figure 1-a shows the velocity distribution of the sand particles during the sand erosion test and Figure 1-b the principle of the rain erosion test rig. Results will be discussed and possible design rules for resilient functional surface patterns will be proposed.

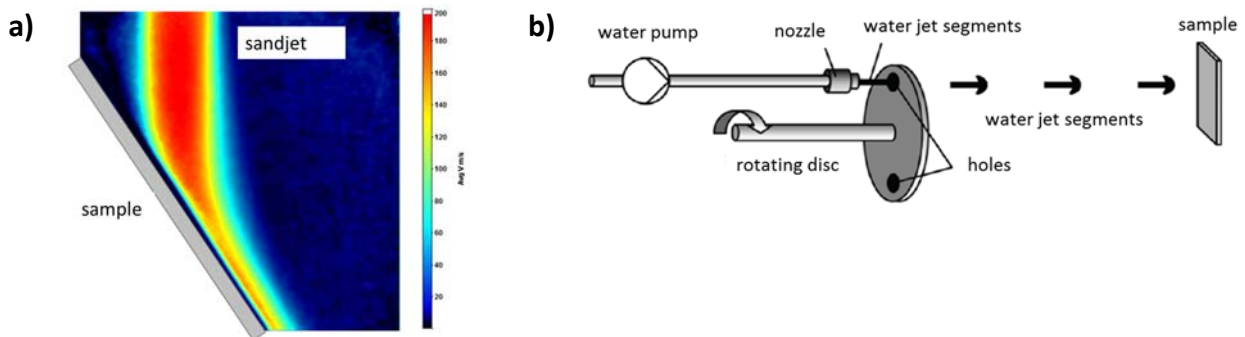


Figure 1. Sand and rain erosion test; (a): Velocity distribution of sand particles measured by particle image velocimetry (PIV); (b): principle of rain erosion testing with a segmented water jet.

Acknowledgement: The authors acknowledge B. Rico-Oller, T. Kunze and B. Krupop for structuring the samples. The presented work is framed in the German funded Project “OptiHyL” with the grant agreement No 20A1501A (LuFoV2-790-150).

Deep Eutectic Solvents to remove rust and limescale from surfaces

Franz Schermer¹, Werner Kunz¹

¹ Institute of Physical and Theoretical Chemistry, University of Regensburg, Regensburg, Germany

Limescale deposition and rusting of steel are two phenomena, which can impair the usability of machines or cause heavy damage to devices or constructions. The removal of both is therefore essential. Conventional methods include the use of highly acidic or environmentally harmful compounds, making sustainable and non-hazardous solutions a favourable alternative. Deep Eutectic Solvents (DES) have already shown to dissolve metal oxides [1,2]. When employing type III DESs, made from a quaternary ammonium salt and an hydrogen bond donor [3], they can be made from environmentally uncritical substances with negligible toxicity [4,5]. Thus, the possibility to employ DESs as rust and limescale removing agents was investigated.

For this study, DESs were prepared from choline chloride (ChCl) in combination with a selection of hydrogen bond donors. The amount of dissolved calcium carbonate (as a representation of limescale) and rust was analysed via complexometry and manganometry, respectively. The acidity of the DESs was investigated. Neutral pH was favoured as acidic compounds for the desired purposes are already widely available.

A DES made from ChCl and D-fructose showed favourable properties, being able to both dissolve calcium carbonate and rust obtained from steel samples while remaining at a mildly acidic pH value. However, the DES showed a high viscosity at room temperature when water content was below 1000 ppm. Addition of water to reduce viscosity was investigated towards its influence on the DES's ability to remove rust and limescale. Finally, a non-ionic alkyl polyglycoside surfactant was added to the DES. It was investigated, if a product that additionally removes conventional soil without sacrificing any of the other properties can be obtained. A colorimetric method was used to analyse the mixture's cleaning behaviour of dyed fats on worsted wool fabric. With added surfactant, removal of the dyed soil was achieved, while DES without surfactant did not remove fatty soil.

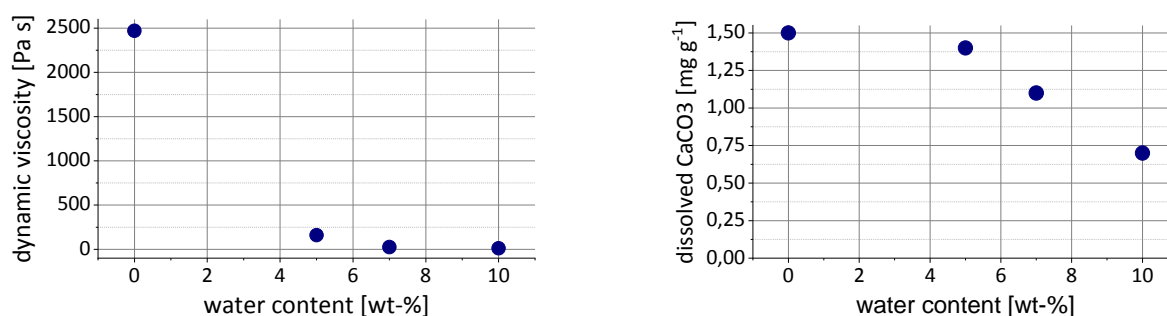


Figure 1. Left: dynamic viscosity of the DES made from ChCl and D-fructose at 25 °C with rising water content. Right: dissolved calcium carbonate in the DES with rising water content at 50 °C. The viscosity drops severely upon water addition. The CaCO₃ solubility does only start to decrease significantly at water contents higher than 5 wt-%, suggesting that the structure of the DES is broken up, causing a drastic change in its properties.

- [1] A.P. Abbott et al, *Eng. Data* **51** (2006), 1280.
- [2] E. L. Smith et al, *Chem. Rev.* **114** (2014), 11060.
- [3] A.P. Abbott et al, *Chem. Eur. J.* **13** (2007), 6495.
- [4] A.P. Abbott et al, *J. Am. Chem. Soc.* **126** (2004), 9142.
- [5] M. Hayyan et al, *Chemosphere* **90** (2013), 2193.

PFA-PEG particles: A colloidal model system for the investigation of phase diagrams of PEGylated drug carrier systems

Marcel Werner^{1,2}, Judith Ruland², Nils von Seggern¹, Moritz Tappe¹, Melanie Wernet², Gabriela Schmidt² and Eckhard Bartsch^{1,2}

¹ *Department of Macromolecular Chemistry, University of Freiburg, Freiburg im Breisgau, Germany*

² *Department of Physical Chemistry, University of Freiburg, Freiburg im Breisgau, Germany*

Pegylated particles like proteins, peptides and lipid- or polymer-based nanoparticles are known as potential drug delivery systems (DDS) or as nano drug carriers (NDC) [1,2]. Their potential as therapeutic agents for highly specific while also highly vulnerable substances leads to an increased use of PEGylated particulate materials in modern pharmaceutical technology [3]. Current research deals with e.g. completely new systems [4], shape effects [5] or the influence of the PEG density on the biocompatibility [6]. However, the phase behaviour of the DDS is not really covered. This can pose severe problems for larger therapeutic molecules with a low carrying ratio of the DDS. Due to the unknown behaviour at higher concentrations most of the DDS are administered via injection into the blood stream in high dilution. As a consequence the potency of the drug shrinks with lower carrying ratios of the DDS [2]. As a result higher concentrations or different formulations are needed but difficult to achieve without detailed knowledge of the DDS phase behaviour.

In an attempt to close this gap we synthesised a new model system, consisting of a highly fluorinated core and a sterically stabilizing PEG-shell [7]. The main advantage of this model system over standard PEG-DDS model systems [8] is that their phase behaviour can be easily investigated via light scattering by using an aqueous solvent and thereby avoiding multiple scattering effects, i.e. sample turbidity, at high concentrations. Based on a simple emulsion polymerisation technique the overall size of the particles, the thickness of the PEG-layer and even the PEG-chains of the stabilizing layer can be easily varied.

With these particles and different light scattering techniques as well as other complementary techniques such as microscopy and rheology, we gained first insights into the phase behaviour of PEGylated particles. Our findings can lead to higher concentrated carrier systems without unwanted inter particle interference and new formulations e.g. gels or cremes.

[1] F. M. Veronese and G. Pasut, DDT, 2005, **10**, 1451.

[2] T. M. Allen and P. R. Cullis, Science, 2004, **303**, 1818.

[3] K. Knop, R. Hoogenboom, D. Fischer and U. S. Schubert, Angew. Chem. Int. Ed., 2010, **49**, 6288.

[4] E. Ruiz-Hernandez, M. Hess, G. J. Melen et al., Polym. Chem., 2014, 5, 1674.

[5] Y. Li, M. Kröger and W. K. Liu, Nanoscale, 2015, 40, 16631.

[6] J. L. Perry, K. G. Reuter, M. P. Kai et al., Nano Lett., 2012, 12, 5304.

[7] D. Burger, J. Gisin and E. Bartsch, Colloids Surf. A: Physicochem. Eng. Aspects, 2014, 442, 123.

[8] A. Brindley, S. S. Davis, M. C. Davies and J. F. Watts, J. Colloid Interface Sci., 1995, 171, 150.

Acknowledgement: The financial support of the DFG through the IRTG: Soft Matter Science project C1 is gratefully acknowledged.

Effect of Source on the Properties and Behavior of Cellulose Nanocrystal Suspensions

Christina Schütz^{1, †}, Jonas Van Rie¹, Samuel Eyley¹, Alican Gençer¹, Hans van Gorp⁴, Sabine Rosenfeldt², Kyongok Kang³, Wim Thielemans¹

¹ Renewable Materials and Nanotechnology Research Group, Department of Chemical Engineering, KU Leuven, Campus Kulak Kortrijk, Etienne Sabbelaan 53, 8500 Kortrijk, Belgium

² Physical Chemistry I and Bavarian Polymer Institute, University Bayreuth, Universitätsstrasse 30, 95440 Bayreuth, Germany

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

⁴ Division of Molecular Imaging and Photonics, Department of Chemistry, KU Leuven Celestijnenlaan, 200 F, 3001 Leuven, Belgium

[†] Physics and Materials Research Unit, University of Luxembourg, 162 A Avenue de la Faïencerie, 1511 Luxembourg, Luxembourg

Cellulose being the most versatile and abundant biopolymer in nature and due to its properties that arise from the hierarchical structure, it has been used for millennia by mankind in the form of microfibers, mainly in the paper and pulp industry. However, many efforts are being directed towards retrieving even smaller cellulose constituents such as nanofibers and nanocrystals (i.e., nanocellulose), which can be used in high performance materials.¹ In order to do so, a better understanding of the behavior and interactions between these novel nanomaterials are required.^{1,2} We have investigated the effect of cellulose source on the suspension properties of cellulose nanocrystals extracted from cotton and wood sources using the exactly same preparation strategy. The structural properties revealed to be similar within the given standard deviation and prevalent polydispersity whereas other properties such as liquid crystalline phase behavior, viscosity, diffusion coefficients, and surface tension were found to differ significantly. This study shows that professedly similar cellulose nanocrystals exhibit rather differing behaviors and this presentation attempts to interpret this phenomenon.

[1] Moon et al., *Chem Soc. Rev.* **40** (2011), 3941.

[2] Lagerwall et al., *NPG Asia Mater.* **6** (2014), e80.

[3] Schütz et al., (2018), submitted.

Acknowledgement: CS thanks and the Alexander von Humboldt Foundation for financial support through a Feodor Lynen scholarship.

Surface Modification of Self-Assembled Nanotubes from Amino Acid Amphiphiles in Solution

Kathrin Voigtländer¹, Luba Kolik-Shmuel², Dganit Danino², Michael Gradzielski¹

¹ Institut für Chemie – Stranski-Laboratorium für Physikalische und Theoretische Chemie, Technische Universität Berlin, Berlin, Germany

² Department of Biotechnology and Food Engineering, Technion – Israel Institute of Technology, Haifa, Israel

Nanotubes with a well-defined radius can be formed by self-assembly of amino acid amphiphiles (AAAs, short synthetic peptides generated from amino acids and fatty acids). The AAA $C_{12}KC_{12}K-NH_2$ self-assembles into stable nanotubes of great length of several μm and a diameter of 70-120 nm by progressing from long thin fibers via twisted and helically coiled ribbons to nanotubes [1,2].

Such AAA nanotubes can be used as templates to produce multi-layered nanotubes. These can be produced by subsequent deposition of oppositely charged materials, e.g. polyelectrolytes, on the nanotube surface by applying the layer-by-layer (LbL) technique [3] or coating them with metals by surface reduction [4]. We coat the nanotubes using different polyelectrolytes and metals in aqueous solution and study nanotube structure and subsequent changes. By combining different techniques like scattering methods (SLS/DLS, SANS, SAXS), AFM and direct-imaging methods (cryo- and dry TEM, SEM) a comprehensive understanding of structural details of the modified nanotubes can be gained with pH and surface charge as the expected major control parameters. These modifications yield hybrid nanotubes with potentially adjustable properties rendering these systems much more versatile for employment in future applications, e.g. in delivery systems and as smart materials.

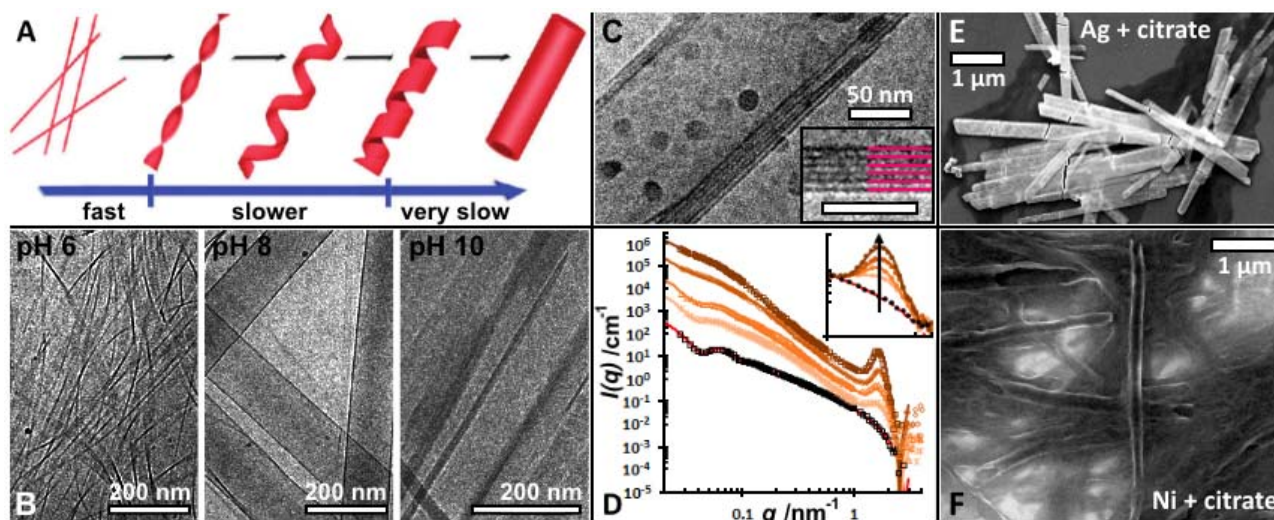


Figure 1. Self-assembly of $C_{12}KC_{12}K-NH_2$ in aqueous solution, A: Schematic illustration of self-assembly route [from 2], B: Cryo-TEM of self-assembled structures, C: Cryo-TEM of multi-layered LbL-modified nanotube, D: Neutron scattering curves of LbL-modified nanotubes, E: SEM of silver-coated nanotubes reduced with citric acid, F: SEM of nickel-coated nanotubes reduced with citric acid.

[1] L. Ziserman et al., *Phys. Rev. Lett.* **106** (2011), 238105.

[2] L. Ziserman et al., *J. Am. Chem. Soc.* **33** (2011), 2511.

[3] G. Decher and J.-D. Hong, *Makromol. Chem. Macromol. Symp.* **146** (1991), 321.

[4] M. Reches and E. Gazit, *Science* **25** (2003), 625.

Modulation of STAT3-mediated tumor-associated tolerance mechanisms using IL-2 functionalized hydroxyethyl starch (HES) nanocapsules

Marie-Luise Frey¹, Matthias P. Domogalla², Sarah Christmann¹, Svenja Morsbach¹, Kerstin Steinbrink² and Katharina Landfester¹

¹ Max-Planck-Institute for Polymer Research, 55128 Mainz, Germany

² Department of Dermatology, University Medical Center Mainz, Johannes Gutenberg-University Mainz, 55099 Mainz, Germany

Since immunotherapy has proven to be a successful method for cancer treatment, combining it with nanotechnology is the next step in modern medicine. Nonetheless, tumor-associated tolerance mechanisms are able to promote tumor growth and still represent a big challenge in anti-cancer therapies [1]. The human immune system consists of many different cell types whose regulation is extraordinarily complex. Using the cytokine IL-2, T-cells can specifically be activated and their growth and differentiation can be stimulated. Since the exact amount of IL-2 plays an important role for addressing different T-cell subsets, hydroxyethyl starch (HES)-based nanocapsules are used as carriers for a controlled delivery to the immune cells [2]. These nanocapsules with defined size are prepared in an inverse miniemulsion process and are further functionalized by introducing dibenzocyclooctyne (DBCO) groups for copper-free click chemistry. By inserting an azide group into IL-2, the protein was covalently bind to the nanocapsule surface [2]. Flow cytometry and laser scanning microscopy experiments showed increased binding and uptake of these surface modified HES-nanocapsules by human activated T-cells, which indicates that the biological activity of the cytokine can be maintained. By reducing the amount of IL-2 on the capsule surface, a dose-dependency could be shown, while in contrast, however, a dose-independent uptake by regulatory T-cells (Treg) could be highlighted. Since regulatory T-cells (Treg) are involved in STAT3-mediated tolerance mechanisms, the controlled delivery of encapsulated STAT3-inhibitors could represent one example of the intervention into such a tumor-associated tolerance mechanism.

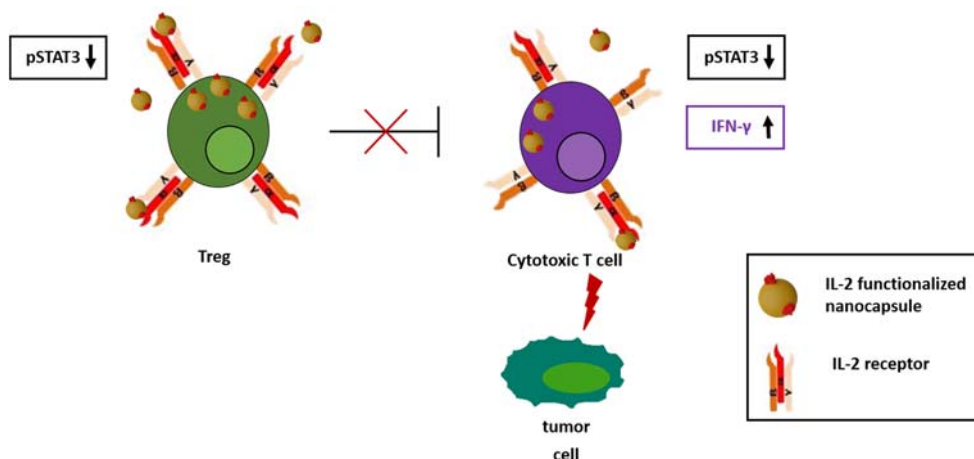


Figure 1. IL-2 functionalized nanocapsules could inhibit Treg cells and lead to tumor elimination.

[1] A. J. Adler, *Current Cancer Drug Targets* **7**, (2007), 3-14.

[2] S. U. Frick, M. P. Domogalla, G. Baier, F. R. Wurm, V. Mailänder, K. Landfester, K. Steinbrink, *ACS Nano* **10**, (2016), 9216-9226.

Acknowledgement: The authors acknowledge funding from SFB 1066 and the MPG.

Enhancing the physico-chemical and biological performances of synthetic polymers via blending with natural polymers

Nowsheen Goonoo^{1,2*}, Archana Bhaw-Luximon^{1*}, Dhanjay Jhurry¹, and Holger Schönherr^{2*}

¹ Biomaterials, Drug Delivery & Nanotechnology Unit, Centre for Biomedical and Biomaterials Research, University of Mauritius, MSIRI Building, Réduit, Mauritius

² Physical Chemistry I, Department of Chemistry and Biology & Research Center of Micro and Nanochemistry and Engineering (Cμ), University of Siegen, 57076 Siegen, Germany

A promising strategy for the fabrication of bone tissue engineering (TE) scaffolds is the use of polymer blends, which combine good mechanical properties and biodegradability e.g. of synthetic polyester on the one hand with advantageous surface properties afforded by natural biopolymers on the other hand. Amongst naturally-derived polymers, polysaccharides are interesting materials since their carbohydrate moieties interact with or are integral components of many cell adhesion molecules and matrix glycoproteins.

In this presentation, the fabrication of bone TE scaffolds consisting of blends of polysaccharides κ-carrageenan (κ-CG), fucoidan (FUC) or Aloe vera (AV) with synthetic polymer polydioxanone (PDX) as well as an in-depth evaluation of their cellular responses will be discussed. The detailed analysis of the blend nanofiber properties revealed a different degree of miscibility of the synthetic polymers and the polysaccharides leading to a different enrichment at the surface of the blend nanofibers, which in turn improved NIH3T3 fibroblast cell viability, NIH3T3 proliferation, *in vitro* biomineralization potential, human osteosarcoma (SaOS-2) cell differentiation ability. In addition, all scaffolds did not cause significant RAW264.7 macrophage inflammatory responses as evidenced by the round cell morphology (Figure 1) [1-3].

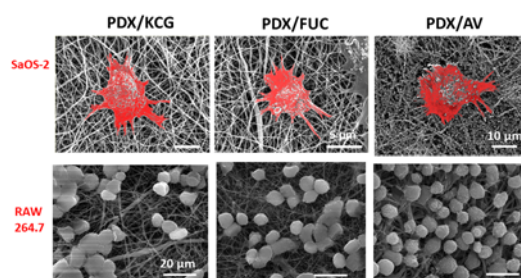


Figure 1. SEM images showing SaOS-2 and RAW 264.7 macrophage cell morphologies on PDX/KCG, PDX/FUC and PDX/AV scaffolds

[1] N. Goonoo, B. Khanbabaee, M. Steuber, A. Bhaw-Luximon, U. Jonas, U. Pietsch, D. Jhurry, H. Schönherr, *Biomacromolecules* (2017), 1563.

[2] N. Goonoo, A. Bhaw-Luximon, U. Jonas, D. Jhurry, H. Schönherr, *ACS Biomaterials Science and Engineering* (2017), 3447.

[3] N. Goonoo, A. Bhaw-Luximon, A. Fahmi, U. Jonas, S. Benard, J. Andries, D. Jhurry, H. Schönherr, submitted (2018).

Acknowledgement: The authors acknowledge funding from the Alexander von Humboldt Foundation (Georg Forster postdoc stipend to NG), the European Research Council (ERC project ASMIDIAS, Grant no. 279202), the University of Siegen and the EU INTERREG OI/POE FEDER for financial support through the NanoMauRe project.

mRNA Drug-Nanoparticles: Polymer and Liposomes - Study by SANS and DLS

Siewert C.¹, Ziller A.¹, Nogueira, S.³, Nawroth T.¹,
Haas H.³, Radulescu A.⁴, Sahin U.^{2,3}, Langguth P.¹

¹ Pharmacy and Biochemistry Inst., Pharma-Technology, Gutenberg-University, D-55099 Mainz, Germany

² Exp. Oncology, III. Med Clinics, TRON, University Medicine Gutenberg-University, D-55131 Mainz, Germany

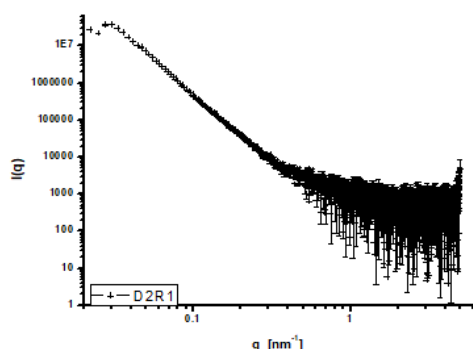
³ BioNTech AG – Individualisierte Immuntherapien, An der Goldgrube 12, D-55131 Mainz, Germany

⁴ Jülich Centre for Neutron Science JCNS at Heinz Maier-Leibnitz Zentrum MLZ, D-85748 Garching, Germany

mRNA pharmaceuticals represent a new area of therapeutics, with a large range of application, including cancer vaccination, tumour therapy and protein substitution [1-2]. For administration, formulations are required to carry messenger RNA (mRNA) to the target side. These Nano carriers bear additional excipients for the induction of genetic transfection after receptor mediated cell uptake. Such mRNA nanoparticles can be setup as polyplexes containing a polymer matrix.

In the current study mRNA containing polyplexes and basic excipients were investigated in structure by D-contrast SANS, SAXS and dynamic light scattering DLS. The bio-medical ability was demonstrated by transfection of cell cultures with luciferase mRNA nanoparticles. The polymer Diethylaminoethylen (DEAE) - Dextran formed nanoscaled poly-cationic/poly-anionic complexes with mRNA. A typical nanoparticle size of 60 - 100 nm was estimated by SANS at the JCNS, Garching, and DLS, while the absence of large aggregates was demonstrated. Due to the composition of at least two materials of different hydrogen content, structure and domains are distinguished by neutron scattering SANS with the deuterium contrast method giving us additional information in comparison to SAXS. The Dextran nanoparticles depicted SANS profiles with multiple side maxima, as it is typical for a macro-helical structure (Fig. 1 b). In contrast to SAXS measurements, main particle structure signal, side maxima, and mRNA were investigated by the solvent contrast variation technique at various H₂O/D₂O mixtures. The different D-matching points (scattering length density SLD) indicated the formation of local contact domains between polymer and mRNA. Using SANS measurements it was possible to obtain detailed structural informations for active pharmaceutical polyplexes unattainable with SAXS.

a) SAXS of DEAE-Dextran-mRNA polyplex



b) SANS of DEAE-Dextran-mRNA polyplex

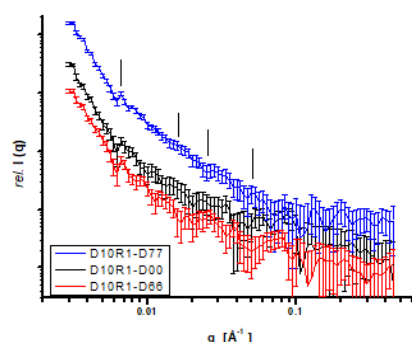


Figure 1. a) SAXS of DEAE-Dextran/mRNA nanoparticles b) SANS of DEAE-Dextran/mRNA nanoparticles at different H₂O/D₂O mixtures

[1] Sahin, U., Karikó, K. & Türeci, Ö. (2014) Nature Reviews Drug Discovery 13, 759–780 mRNA-based therapeutics – dev. a new class of drugs.

[2] Stadler C.R., Bähr-Mahmud H, Celik L, Hebich B, Roth AS, Roth RP, Kariko K, Sahin U (2017) Nature Medicine doi:10.1038/nm.4356

Acknowledgement: The authors thank for support by SFB, MPGC, BioNTech AG, and JCNS/MLZ Garching.

Microgel Arrays for Regulation of Cell Motility and Adhesion

Alexander Töpel^{1,2}, Antonio Sechi³, Patrick Wünnemann² and Andrij Pich^{1,2}

¹ DWI Leibniz Institute for Interactive Materials e.V., Aachen, GERMANY

² RWTH Aachen University, Institut für Technische und Makromolekulare Chemie, Lehr- und Forschungsgebiet Funktionale und interaktive Polymere, Aachen, GERMANY

³ Uniklinik RWTH Aachen, Institute of Biomedical Engineering, Department of Cell Biology, Aachen, GERMANY.

Topology and surface chemistry are powerful tools to affect cell adhesion and migration. In this work we focused on use of microgels as building blocks for the decoration of biointerfaces. Recently we developed a new technique that allows printing microgels on solid substrates. [1]

Using wrinkled PDMS templates we successfully printed stimuli-responsive poly(N-Isopropylacrylamide) (pNIPAm) microgels in form of colloidal arrays on glass supports. The microgels were chemically grafted onto the glass substrates by using low-pressure Argon plasma treatment. This process lead to highly stable microgel arrays in cell culture media. We could show with Liquid cell AFM investigations that surface-grafted microgels retained their swelling behavior and thermo responsiveness in aqueous media. By this technique we could also show, that extracellular matrix protein coating did not alter both their stability and topography. We demonstrated that our surface-grafted microgel arrays could serve as novel substrates for the analysis of cell adhesion and migration.[2] Microgel arrays influenced size, speed and dynamics of focal adhesions as well as cell motility forcing cells to move along highly directional trajectories. Modulation of microgel state or spacing served as an effective tool for regulation of cell motility.

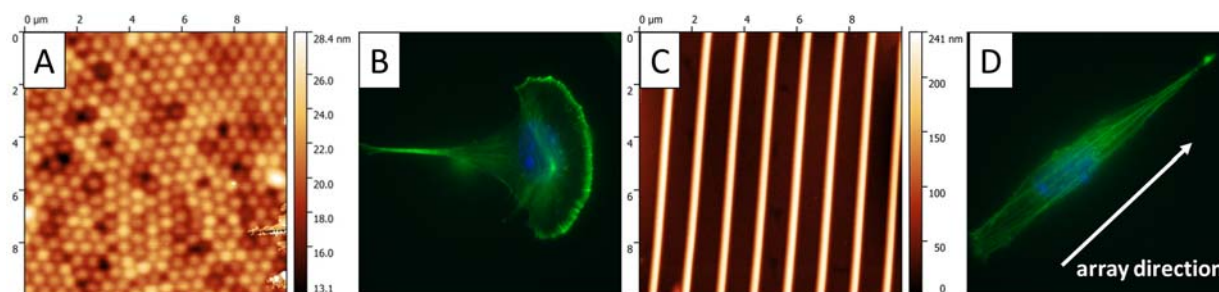


Figure 1. AFM image of pNIPAm microgel monolayer (A) and microgel array (C). Fluorescent microscopy image of a B16F1 (mice skin melanoma cells) on the monolayer (B) and the array (D). Cells were fixed and labelled with fluorescent phalloidin. Nuclei were stained with DAPI (Blue). The cell form on the monolayer (B) typical a large fan-shaped lamellipodium which is characterised by several actin-rich microspikes and filopodia (Green). On the microgel array the cells change shape and stretch along the array direction (D).

[1] S. Hiltl, M. Schürings, A. Balaceanu, V. Mayorga, C. Liedel, A. Pich, A. Böker, *Soft Matter* **7** (2011), 8231.

[2] A. S. Sechi, S. Ullmann, J. M. G. Freitas, R. P. Takehara, P. Wünnemann, R. Schröder, M. Zenke, A. Böker, G. Aydin, S. Rütten, Andrij Pich, *Adv Mater. Interf.* **3** (2016), 20.

Acknowledgement: This work was performed in part at the Center for Chemical Polymer Technology CPT, which was supported by the EU and the federal state of North Rhine-Westphalia (grant EFRE 30 00883 02). This work was supported by the Seed Funds programme of the DFG-RWTH Aachen (project OPSF363 to A.S. and A.P.). The authors acknowledge funding from DFG SFB 985 “Functional Microgels and Microgel Systems.”

Insights into the Immobilization of Enzymes onto Hybrid Hairy Particles for Interfacial Catalysis

Claudia Marschelke^{1,2}, Anke Matura³, Martin Müller¹, Ivan Raguzin¹, and Alla Synytska^{1,2}

¹ Leibniz Institute of Polymer Research Dresden, Institute of Physical Chemistry and Polymer Physics, Dresden, Germany

² Dresden University of Technology, Institute of Physical Chemistry of Polymeric Materials, Dresden, Germany

³ Dresden University of Technology, Institute of Biochemistry, Dresden, Germany

The design of colloidal core-shell particles with advanced architectures and controlled chemical functionalities is highly demanding for discovering responsive and adaptive multifunctional materials. The tunable design of the polymeric shell interface, realized by the polymer brush approach, provides an excellent base for the immobilization of catalytically active species, such as enzymes [1] and metal nanoparticles [2], which may enhance their structural and catalytic stability in different environmental conditions, reducing product inhibition and facilitating their recovery. Although it is of prime importance to control the interface architecture, there is still a lack of systematic investigations concerning the impact of the particles' properties on the designed interface, as well as on the immobilization of biomolecules.

Herein, we propose the immobilization of enzymes onto core-shell particles as an application for interfacial catalysis that would benefit from the unique properties and architecture of these particles. We report on the synthesis of hybrid hairy particles with controllable size (Fig. 1 a,b), grafting density, polymer chain length, chemical functionality, and responsiveness. Thus, we control the interfacial properties of the carrier material, such as swelling, charge, and adhesion, as investigated by (cryo-)TEM, electrokinetics and AFM force distance measurements. Further, we discuss the correlation between the controlled design of polymeric interface and its impact on the immobilization efficiency and enzymatic structure of laccase from *Trametes versicolor*, as well as occurring changes in the surface morphology, charge and adhesion performance of the final polymer-enzyme layer (Fig. 1c).

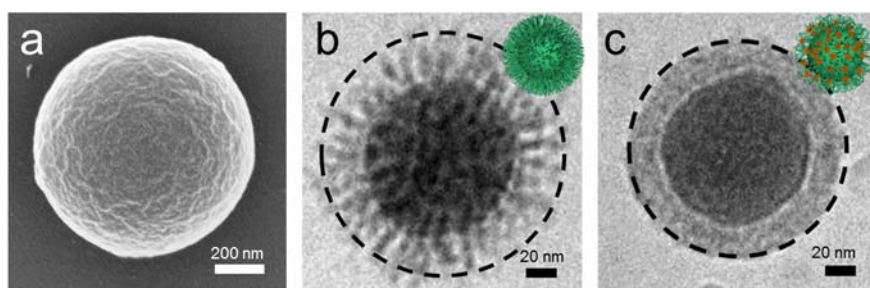


Figure 1. (a) Representative SEM image of a 1 µm hybrid hairy core-shell particle; cryo-TEM images of (b) a 100 nm hybrid hairy particle without any catalytic species, and (c) with immobilized laccase from *Trametes versicolor*. Insets show schematic illustrations.

[1] C. Marschelke, I. Raguzin, A. Matura, A. Fery, and A. Synytska, *Soft Matter* **13** (2017), 1074.

[2] A. Kirillova, C. Schliebe, G. Stoychev, A. Jakob, H. Lang, and A. Synytska, *ACS Appl. Mater. Interfaces* **7** (2015), 21218.

Acknowledgement: The authors acknowledge funding from the AiF (project 18195BR) and DFG community (project SY 125/4-1).

The influence of chain architecture on polyelectrolyte functionalized mesopore accessibility

Robert Brilmayer¹ and Annette Andrieu-Brunsen¹

¹ Technische Universität Darmstadt; Ernst-Berl-Institut für technische und makromolekulare Chemie, 64289 Darmstadt, Germany

Author list: **Robert Brilmayer¹**, Annette Andrieu-Brunsen¹

Controlling nanoscale structure and function is highly important for the fabrication of functional materials which are used, for example, in sensing or drug delivery. In this context the controlled functionalization remains a challenge. In recent years it has been demonstrated that photoiniferter initiated polymerization (PIP) offer the possibility to adjust the polymer amount and with this ionic permselectivity in mesoporous membranes [1]. Based on results on zwitterionic polymers rendering mesopores bipolar and thus inaccessible to ions and calculations on charge transitions of poly(2-(methacryloyloxy)ethyl-phosphat) (PMEP) in spatially confined pores, the question about the polymer chain architecture influence on mesopore performance attracted our interest [2, 3, 4].

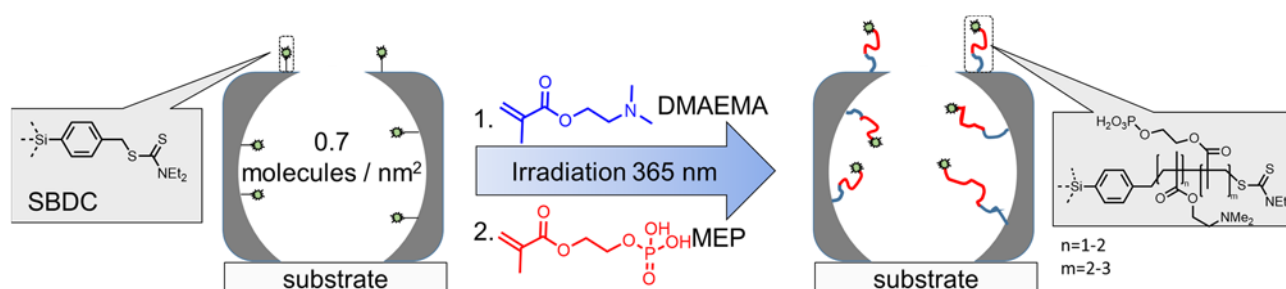


Figure 1. PIP based block copolymer formation in and outside of silica nanopores.

In this frame we present results on the functionalization of silica mesopores with block-co-oligomers using PIP (Fig. 1). Suitable candidates of interest to modulate charge density in mesoporous polymerhybrid films and thus to control their ionic permselectivity is the polyacid PMEP as well as the 2-dimethylaminoethylmethacrylat (DMAEMA)-*co*-MEP block copolymer [5, 6]. In accordance to molecular theory we only observe one *pK*s value for PMEP confined into mesopores [4]. In addition, chains in a block like architecture show a different pH-responsive transport as zwitterionic polymers. Results on ionic permselectivity for mesoporous films of varying pore sizes in dependence of solution pH are presented.

- [1] L Silies et al., *Chem. Mat.* **27** (2015), 1971.
- [2] L Silies et al., *Langmuir* **34** (2017), 807.
- [3] A Calvo et al., *J. Am. Chem. Soc.* **131** (2009), 10866.
- [4] F Gilles et al., *J. Phys. Chem. C* **120** (2016), 4789.
- [5] A Brunsen et al., *Langmuir* **28** (2012), 3583.
- [6] J Tom et al., *Polymers* **9** (2017), 539.

Acknowledgement: The authors kindly acknowledge the financial support by the LOEWE Research Cluster “i-Napo” of the Hessen State Ministry of Higher Education, Research and the Arts.

A near-infrared and temperature-responsive nanoreactor based on core-shell polydopamine@PNIPAm microgel

Xiaohui^{1,2}, Bo Bai², Matthias Ballauff¹, and Yan Lu¹

¹ Soft Matter and Functional Materials, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Berlin, Germany

² College of Environmental Science and Engineering, Chang'an University, Xi'an, P. R. China

Controlled stimuli-responsive release systems are a feasible and effective way to increase the efficiency of pesticides and help improve environmental pollution issues. However, near-infrared (NIR)-responsive systems for controlling release have not been reported because of high cost of conventional NIR absorbers (gold nanorods) and complicated preparation process [1]. A significant strategy has been developed to utilize polydopamine (PDA) microspheres as a new class of photothermal agent owing to their abundant active sites, satisfactory photothermal efficiency, low cost, and easy fabrication.

In this study, we devised an NIR light and temperature remote-triggered pesticide delivery system based on the photothermal PDA dispersed in cross-linked poly(N-isopropylacrylamide) (PNIPAm) matrix, applied as both a thermosensitive gatekeeper and a pesticide reservoir [2]. Such design combines synergistically photothermal properties and thermoresponsive properties in a single nanoplatform; the PDA embedded inside the PNIPAm matrix could serve as an antenna to absorb the light and convert it to heat, which will induce shrinkage of the PNIPAm matrix and facilitate the release imidacloprid (IMI), from the interior of polymer matrix. The application of PDA microspheres embedding immobilized approach is advantageous compared to other photothermal nanoparticles such as gold nanoparticles owing to easy fabrication and scale-up, low cost, and high loading, since the introduced PDA microspheres not only exhibit strong photothermal effect but also provide additional active surface for IMI immobilization. In our future plan, we try to immobilize metal nanocatalysts onto thermosensitive core-shell microgels to solve aggregation problem of nanometer-sized metal nanoparticles. More interestingly, the catalytic activity of metal nanocatalysts can be controlled by the volume transition of thermosensitive shells [3]. The Au interspersed PDA@PNIPAm nanoreactor hold great promise for many smart nanomaterials, such as photothermal therapy, intelligent drug carrier, magnetic separation, and tunable catalysis.

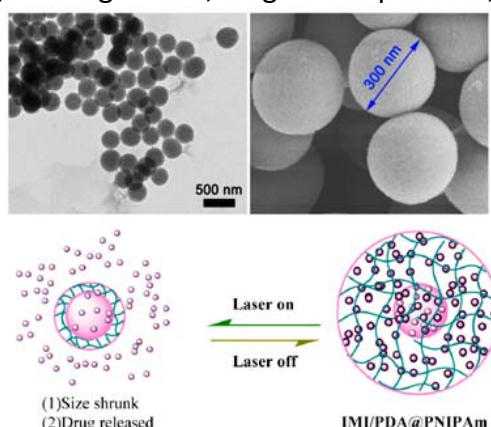


Figure 1. NIR light remote-triggered pesticide delivery of core-shell PDA@PNIPAm microgel.

[1] Y Wang, et al. *ACS Nano*. **7** (2013), 2068.

[2] X Xu, et al. *ACS Appl. Mater. Interfaces*. **9** (2017), 6424.

[3] S Wu, et al. *Angew. Chem. Int. Ed.* **51** (2012), 2229.

Temperature-dependent energy-transfer in colloidal dispersions

Kristina G. Wagner¹, and Matthias Karg¹

¹ *Physical Chemistry I, Heinrich-Heine-University Duesseldorf, Duesseldorf, Germany*

Organic dye molecules are well-known to show fluorescence making them useful for many applications in fields like sensing, spectroscopy and imaging. For many of these applications it would be beneficial if the fluorescence intensity can be controlled in a reversible manner. This can be achieved by reversibly changing the chemical or physical environment of the dye.

We decorated gold nanoparticles with α -trithiocarbonate- ω -dye-terminated poly(N-isopropylacrylamide) (PNIPAM) chains. This was performed by ligand exchange making use of the high affinity of the trithiocarbonate group to the gold surface [1]. PNIPAM shows a thermoresponsive behaviour with a lower critical solution temperature (LCST) of approximately 32°C in water.

This inorganic/organic hybrid system allows to reversibly regulate the distance between the plasmonic nanoparticle and the terminal dye molecules due to the collapse of the polymer linker above the LCST. This distance control has a strong influence on the dye emission because of non-radiative energy-transfer between the excited dyes and the gold nanoparticles [2]. Hence our inorganic/organic hybrid system allows fine adjustment of the fluorescence intensity by temperature.

In this contribution we discuss the optical properties of plasmonic nanoparticles decorated with dye-labelled polymers focussing on steady-state fluorescence as well as lifetime measurements to characterize the emission behavior.

[1] T.Honold *et al.*, *Langmuir*, 2017, **33**, 253.

[2] P.Reineck *et al.*, *ACS Nano*, 2013, **7**, 6636.

Acknowledgement: The authors acknowledge funding from the German Research Foundation (DFG) within the frame of the Emmy Noether programme.

Shear-induced transformation of polymer-rich lamellar phases to micron sized vesicles

Sören Großkopf¹ and Thomas Hellweg¹

¹ Bielefeld University, Department of Chemistry, Physical and Biophysical Chemistry, Bielefeld (Germany)

Shear-induced structures in ternary or quaternary surfactant containing systems have been widely investigated. There are structures which are only stable during shear (L3 to L α) and those who are metastable like multi-lamellar vesicles (MLV). In the presentation the focus lays on the metastable multi-lamellar vesicle structure, which can be transformed to from a lamellar phase[1] containing four components: A) D₂O B) *o*-xylene C) EO₂₁-PO₄₇-EO₂₁ (Pluronic® PE9400) D) C₈TAB. First, we investigated the phase behaviour with different methods. Optical observation was used to find the one-phase regions in the system. The microstructure was then investigated with small-angle X-ray scattering (SAXS), Diffusion ordered spectroscopy (DOSY) NMR and with electric conductometry. The system exhibits a lamellar phase at a specific composition and it has clearly been identified with SAXS due to the very prominent structure factor (*Bragg Peaks*). Hence, the lamellar phase was sheared with a rheometer and the system exhibits a rheopex behaviour which confirms the transformation of the lamellar phase to vesicles. Additionally, the rheometer was equipped with a *rheo*-small-angle light scattering (SALS) module which allows the direct determination of the size of the shear-induced vesicles during the shear process[2]. The vesicle radius nicely follows the predicted linear dependence on $\dot{\gamma}^{-\frac{1}{2}}$. Also, the existence of MLVs has been proven with different optical microscopic methods (Polarized light-, Phase-contrast-, Difference interference contrast microscopy) and with *cryo*-scanning electron microscopy (*cryo*-SEM).

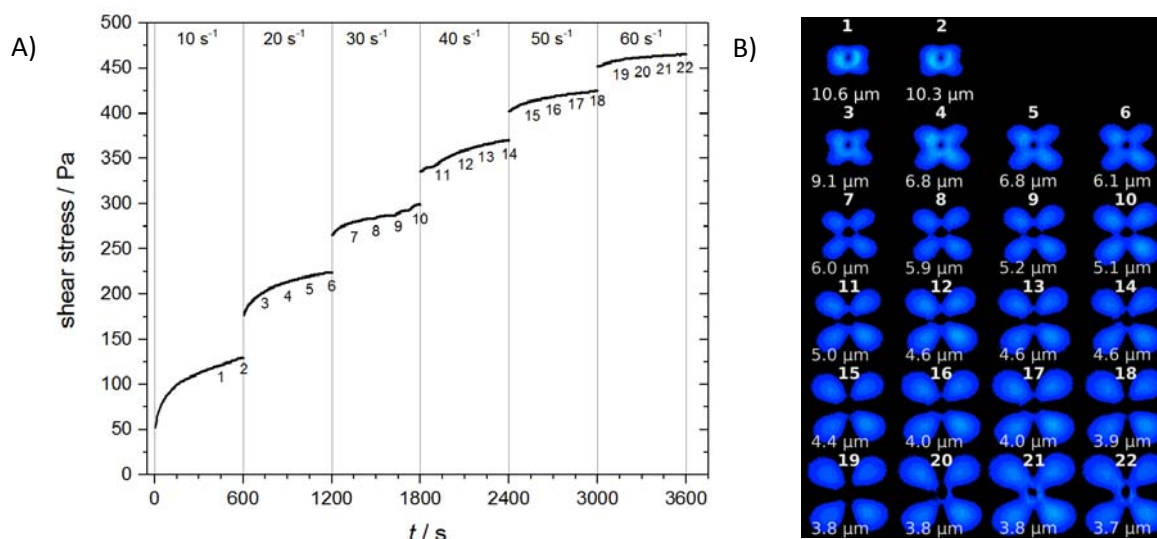


Figure 1. A) Shear-stress increases with time and shear-rate and shows rheopex behaviour. B) *rheo*-SALS depolarized scattering intensities at different times and shear-rates including the corresponding sizes (numbers refer to 1A).

[1] Diat O., Roux D., Nallet F., *J. Phys. II France*. **3** (1993), 1427-1452.

[2] Samuels R., *Journal of Polymer Science Part A-2: Polymer Physics* **9** (1971), 2165-2246

Acknowledgement: The authors acknowledge Prof. B. Koetz and Dr. B. Tiersch for the *cryo*-SEM measurements and Dr. A. Mix for the DOSY NMR measurements.

Gelled lyotropic liquid crystals: visual, rheological and thermal phase studies

Katja Steck¹, Natalie Preisig¹, and Cosima Stubenrauch¹

¹ *Institute of Physical Chemistry, University of Stuttgart, Stuttgart, Germany*

Gelled lyotropic liquid crystals (Gelled LLCs) can be prepared by (a) adding a gelator to an existing LLC phase or (b) replacing the solvent in a gel network by an LLC (Figure 1). Generally speaking, gelled LLCs combine the mechanical stability of a gel with the microstructure of an LLC phase [1] which makes them an interesting candidate in transdermal drug delivery systems [2]: drugs can be solubilized in the LLC phase whereas the gel provides convenient application. From a fundamental point of view, there are two questions that have to be answered: (1) Are gelled LLCs orthogonal self-assembled systems [3], i.e. do the two coexisting structures form simultaneously but independently? (2) Does the chronology of gel and LLC formation influence the domain size of the LLC and the alignment of the gelator fibers, respectively [4,5]? To answer these questions, a water – surfactant system that forms LLC phases with moderate melting temperatures and a gel whose sol-gel transition temperature depends on the concentration, are required. We choose the system H₂O – heptaethylene glycol monododecyl ether (C₁₂E₇) [6] as it forms three LLC phases, namely the lamellar phase L_α, the bicontinuous cubic phase V₁ and the hexagonal phase H₁ in specific temperature and concentration ranges. Moreover, we choose the organogelator dibenzylidene-D-sorbitol (DBS) [7] as its presence, irrespective of its concentration, only slightly influences the LLC phase boundaries of the system H₂O – C₁₂E₇ as opposed to the organogelator 12-hydroxyoctadecanoic acid (12-HOA). The latter was found to act as co-surfactant and to stabilize the lamellar phase [8]. In this contribution we present rheological and differential scanning calorimetry (DSC) measurements of the binary system H₂O – C₁₂E₇, the gelled system H₂O – C₁₂E₇ – DBS as well as of the respective binary gel ethylene glycole – DBS and we discuss the results in term of orthogonal self-assembly. Rheology and DSC measurements revealed that the sol-gel transition temperatures of the gelled LLCs are about 50 K below the sol-gel transition temperatures of the binary gel. However, phase diagram measurements and transmission electron microscopy (TEM) pictures show that the general LLC and gel phase behaviour is maintained in the gelled LLCs. In addition, the gelled LLCs and the binary gel show similar rheological properties.

- [1] C. Stubenrauch, F. Gießelmann *Angew. Chem. Int. Ed.* **2016**, *55*, 3268.
- [2] D.-H. Kim, A. Jahn, S.-J. Cho, J.S. Kim, M.-H. Ki, D.-D. Kim *J. Pharm. Invest.* **2015**, *45*, 1.
- [3] Y. Xu, M. Laupheimer, N. Preisig, T. Sottmann, C. Schmidt, C. Stubenrauch *Langmuir* **2015**, *31*, 8589.
- [4] T. Kato, Y. Hirai, S. Nakaso, M. Moriyama *Chem. Soc. Rev.* **2007**, *36*, 1857.
- [5] S. Koitani, S. Dieterich, N. Preisig, K. Aramaki, C. Stubenrauch *Langmuir* **2017**, *33*, 12171.
- [6] T. Inoue, M. Matsuda, Y. Nibu, Y. Misono, M. Suzuki *Langmuir* **2001**, *17*, 1883.
- [7] B.O. Okesola, V.M.P. Vieira, D.J. Cornwell, N.K. Whitelaw, D.K. Smith *Soft Matter* **2015**, *11*, 4768.
- [8] publication in preparation.

Acknowledgement: The authors acknowledge funding from the German Research Foundation.

Study on Interactions between Surfactant, Polymer and Dye in Solution and at Interfaces

Yifei Zhan^{1,2}, Claus A. M. Seidel¹, Birgit Glösen², and Wolfgang von Rybinski¹

¹ Institute of Molecular Physical Chemistry, Heinrich-Heine-University Düsseldorf, Düsseldorf, Germany

² Faculty of Applied Natural Sciences, University of Applied Sciences Cologne, Leverkusen, Germany

The interactions between surfactant, polymer and dye in solution and at interfaces were studied by tensiometry, UV/Visible spectroscopy and atomic force microscopy (AFM). The water soluble copolymer of 1-vinyl-2-pyrrolidone and 1-vinylimidazole (PVPVI) shows interactions with the anionic surfactant sodium dodecyl sulfate (SDS) not only at the air-water interface but also in the bulk phase. However, no interaction in solution was observed between the nonionic surfactant alkyl heptaglycoether ($C_{12}E_7$) and PVPVI. In the aqueous solution of acid blue 113, the addition of appropriate SDS, $C_{12}E_7$ and PVPVI led to a red shift in absorption spectra of the dye respectively. The ratios of surfactant or polymer to dye were determined.

At graphite-solution interfaces, the aggregates of SDS and $C_{12}E_7$ alone appear as periodic parallel stripes in AFM images, which are interpreted as hemicylindrical structures in previous researches of other authors [1-3]. PVPVI adsorbed on graphite shows globular structures at a concentration of 0.1 mM. By adding nonionic surfactant $C_{12}E_7$ into the PVPVI solution, the adsorption of polymer onto graphite is markedly inhibited. Thus, in presence of PVPVI the aggregate structure of $C_{12}E_7$ on graphite was not visibly changed. At the high SDS concentration of 100 mM, the added PVPVI did not alter the aggregate structure of SDS on graphite, whereas the globular structure of polymer was not observed. This indicates a stronger interaction between the surfactant and substrate.

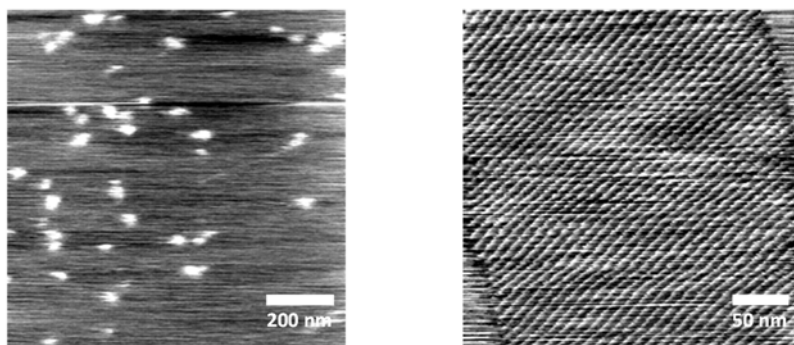


Figure 1. AFM images of 0.1 mM PVPVI (left) and 0.1 mM $C_{12}E_7$ + 0.1 mM PVPVI (right) at the graphite-solution interface. Measurements were performed at room temperature by contact mode.

[1] Patrick, H. N., Warr, G. G., Manne, S. & Aksay, I. A. Self-Assembly Structures of Nonionic Surfactants at Graphite/Solution Interfaces. *Langmuir* **13**, 4349–4356 (1997).

[2] Wanless, E. J. & Ducker, W. A. Organization of Sodium Dodecyl Sulfate at the Graphite–Solution Interface. *J. Phys. Chem.* **100**, 3207–3214 (1996).

[3] Rybinski, W. von, Jabnoun, M., van Megen, J., Oesterhelt, F. & Seidel, C. Structures of adsorption layers of surfactant mixtures on nonpolar solid surfaces. *Colloid Polym Sci* **293**, 3107–3117 (2015).

Acknowledgement: The authors acknowledge funding from the Ministry of Culture and Science of the German State of North Rhine-Westphalia within the FH STRUKTUR project “FunktioPol – The Polymer Solution”.

Poster abstracts

Droplet impact dynamics on solid surfaces: bubble entrapment and high speed jet

Longquan Chen

Institute of Fundamental and Frontier Sciences, University of Electronic Science and Technology of China, Chengdu 610054, China

When a droplet impacts onto a solid surface, the entrapment of a submillimeter-sized bubble and the emission of a high speed jet can be observed at low impact velocities. In this work, we show that bubble entrapment occurs only on sufficiently hydrophobic surfaces within a narrow range of impact velocities. The bubble is entrapped on hydrophobic surfaces, whereas it is trapped into the top of the droplet on superhydrophobic surfaces. The collapse of the air cavity formed during droplet impact, which is dominated by inertia and influenced by surface wettability, is the cause of the bubble entrapment. The velocity of liquid jets emitted after cavity collapse for drop impact with and without bubble entrapment scales with their sizes according to different power laws, which is explained by simple scaling analyses. Moreover, bubble entrapment does not only occur in perpendicular droplet impacts but also in oblique droplet impacts, indicating the universality of the phenomenon. For oblique droplet impacts on superhydrophobic surfaces, the entrapped bubble can be moved to liquid-air interface after rebound and subsequently burst, emitting a secondary jet with a velocity inversely proportional to the bubble size.

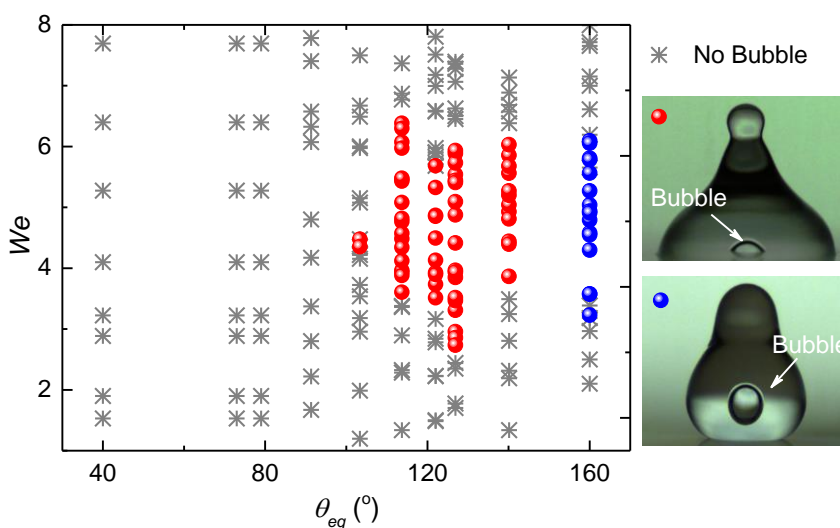


Figure 1. Impact phase diagram for bubble entrapment.

Acknowledgement: The authors acknowledge funding from the National Young 1000 Talents Plan and the Young 1000 Talents Plan of Sichuan province.

Investigation of reaction parameters in one-step surfactant-free emulsion polymerization reactions

Salvatore Chiera,¹ Karina Bley¹ and Nicolas Vogel¹

¹ *Institute of Particle Technology, Friedrich-Alexander University Erlangen-Nürnberg (FAU), Haberstrasse 9A, 91058 Erlangen, Germany*

Monodisperse polymer colloids are applied both in fundamental research and applied technology. For fundamental investigations on self-organization, such particles are used as defined building blocks[1]. The fabrication of surface patterns with nanoscale precision can arise from such self-assembled templates by colloidal templating and lithography[2]. In more practical applications, these colloids find application in size exclusion and high-performance liquid chromatography, calibration standards and in molecular biology by isolating proteins and nucleic acids for analysis and purification [3].

In the present study, the influence of both chemical engineering aspects and physicochemical parameters on the one-pot surfactant-free emulsion polymerization of styrene and acrylic acid were investigated with the goal to provide a scalable and robust approach towards monodispersed polymer colloidal particles. Four stirrer types were tested for various specific power inputs and stirring speeds. Both radial and radial/axial stirrers fulfilled the mixing task for specific power inputs from 1.4 to 200 W/m³. The influence of a range of process parameters was investigated as well. The variation in temperature, initiator concentration, monomer concentration and electrolyte addition showed the most significant effect on particle size, particle size distribution, and yield.

We found that a careful combination of stirrer type and speed as well as an optimization of the involved reaction parameters is necessary to produce polymer colloidal particles with narrow size distribution and controlled sizes.

[1] KR Phillips et al., *Chem. Soc. Rev.*, **45**, (2016) 281.

[2] A Nemiroskis et al., *ACS Nano*, **8**, (2014) 11061.

[3] J Ugelstad et al., *Prog Polym Sci* **17** (1992) 87.

Thermo-responsive polymer brush-coated titanium to control bacterial biofilm colonization for enhanced biocompatibility

Hongsuh Choi¹, Suenghwan Jo², Byung Wook Jo³ and Holger Schönherr¹

¹ Universität Siegen, Department of Chemistry & Biology, Physical Chemistry I and Research Center of Micro and Nanochemistry and Engineering (Cμ), Siegen, Germany

² Chosun University, School of Medicine, Department of Orthopaedic Surgery, Gwang Ju, Republic of Korea

³ Chosun University, Department of Biochemical & Polymer Engineering, Gwangju, Korea

Infection is a leading cause of failure in many biomedical devices, since the infection rate of the implant or surrounding area during or after surgery may be as high as 20%. Considering colonization of bacterial biofilms on the metallic surfaces, such as titanium, upon implantation, which cannot be cured with the host immune response, surface modification that allows protection against bacteria in the early stages is very important [1].

Thermo-responsive polymeric biomaterials, such as poly(di(ethylene glycol) methyl ether methacrylate) (PDEGMA) and poly(oligo(ethylene glycol) methylether methacrylate) (POEGMA) show unique behaviour with reversible shrinkage and restoration of their structures below and above the lower critical solution temperature (LCST). Their biocompatibility was already proven as they have been used to study cell adhesion and cell release [2,3].

Here, we report on the use of surface-initiated polymerization to obtain thermo-responsive polymer brushes on Titanium substrates to control bacterial colonization. A temperature increase mimicking inflammation sites may be utilized as trigger for controlled release of active compounds [4]. Utilizing a post-polymerization method, in which drugs targeted against infectious bacteria are loaded inside the polymer brush, we target the prevention of bacterial attachment and also complete elimination of any nearby bacteria. Dopamine, which is known as bio-mimic of mussel adhesion proteins and compatible with a variety of surfaces, was used as an initiator on titanium substrates [5]. On initiator covered Ti the oxygen-tolerant variant of atom transfer radical polymerization (ATRP) called activator regeneration by electron transfer (ARGET) was applied for surface polymerization, using ascorbic acid as a reducing agent to obtain thick polymer brushes. The composition and properties of PDEGMA brushes were confirmed by Fourier transform infrared (FTIR) spectroscopy, X-ray photoelectron spectroscopy (XPS), ellipsometry, and water contact angle measurements. Polymerization was observed to be rapid and PDEGMA brushes of nearly 180 nm thickness were grown in 1 hr. Preliminary data of drug loading in thick polymer brushes and release profile below and above the LCST of PDEGMA brushes will be discussed.

[1] D. Davies, *Nat Rev Drug Discov* **2003**, 2, 114-122.

[2] I. Lilge, H. Schönherr, *Langmuir* **2016**, 32, 838-847.

[3] E. Wassel, S. Y. Jiang, Q. M. Song, S. Vogt, G. Nöll, S. I. Druzhinin, H. Schönherr, *Langmuir* **2016**, 32, 9360-9370.

[4] S. Müller, A. Cavallaro, K. Vasilev, N. H. Voelcker, H. Schönherr, *Macromol. Chem. Phys.* **2016**, 217, 2243-2251.

[5] X. W. Fan, L. J. Lin, P. B. Messersmith, *Compos Sci Technol* **2006**, 66, 1198-1204.

Acknowledgement: The authors acknowledge stimulating discussions with Siyu Jiang, Sabine Wenderhold-Reeb, and Dr. Mareike Müller as well as financial support from the University of Siegen.

Biodegradable Monodisperse Polymer Foams

Miriam Dabrowski, Cosima Stubenrauch

University of Stuttgart, Institute of Physical Chemistry, 70569 Stuttgart, Germany

Polymer foams as scaffolds in the field of tissue engineering have to be biodegradable, biocompatible, cytocompatible as well as three-dimensional and with a interconnected, porous structure. The particular application (like neural, cartilage or bone) depends on the scaffold's mechanical properties, which should be comparable to the body's own tissue [1,2]. One example of such a scaffold is propylene fumarate dimethacrylate (PFDMA) which was used for the synthesis of polydisperse scaffolds for bone tissue engineering [2]. Concerning the pore structure, Costantini et al. [3] tested seeding efficiencies of cells in polydisperse and monodisperse alginate based scaffolds and indeed found that the monodisperse material has better properties than the polydisperse counterpart. Against this background, we aim at synthesising **monodisperse PFMDA-based scaffolds**. Since PFDMA can not be purchased and since its synthesis is time-consuming, we use 1,4-butandiol dimethacrylate (1,4-BDDMA) as "scouting system" to synthesise **monodisperse 1,4-BDDMA-based scaffolds**. This presentation is about the synthesis of monodisperse open- and closed-cell polymer foams as well as of their polydisperse counterparts. The synthesis of the monodisperse polymer foams is based on the polymerisation of liquid monodisperse templates, namely foamed monomer-in-water emulsions and water-in-monomer emulsions, respectively, both of which are generated via microfluidics (see Figure 1). Their structures are analyzed with scanning electron microscopy (SEM) and with micro-computed-tomography (μ CT), whereas their mechanical properties are measured with a dynamic mechanical analyser (DMA).

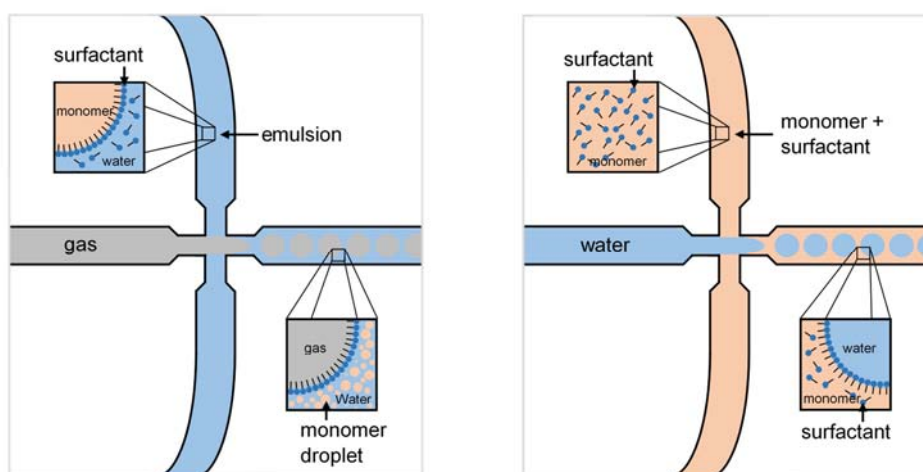


Figure 1: Schematic drawing of the generation of foamed emulsions (left) and emulsions (right) via microfluidics (redrawn and modified from [4]).

- [1] P A De Bank et al. in *"Macroporous Polymers Production Properties and Biotechnological / Biomedical Applications"*, B Mattiasson et al. (CRC Press, Boca Raton, 2010), 467.
- [2] J L Robinson et al., *Tissue Engineering: Part A* **20** (2014), 1103.
- [3] M Costantini et al. *Materials Science and Engineering C* **62** (2016), 668.
- [4] A Quell et al. *Adv. Eng. Mat.* **17** (2015), 604.

Smart membranes by electron beam cross-linking of copolymer microgels

Maxim Dirksen¹, Johannes Bookhold¹, Lars Wiehemeier¹ and Thomas Hellweg¹

¹ University Bielefeld, Department of Chemistry, Physical and Biophysical Chemistry, Bielefeld, Germany

Due to their responsive properties microgels based on Poly(*N*-Isopropylacrylamide) (pNIPAM) are suitable for a large number of applications e.g. for drug targeting, as chemical sensors or as carriers for catalysts [1]. In recent years surface coatings and their modifications have become more and more important, so that microgels are also used as membrane material. In general, microgel coatings have to be prepared on the substrate they are intended to be used on. Therefore, a porous organic or inorganic membrane is modified with microgel particles such as pNIPAM [2].

The focus of this work is the synthesis of free-standing, temperature responsive polymer films. In order to achieve this, NIPAM is copolymerized with aromatic acrylamides and the achieved particles are cross-linked by electron irradiation to keep their thermoresponsive behavior [3]. These unique systems can be used as transferable coatings and as thermoresponsive membranes. As a proof of principle we studied the ion transport by resistance measurements at different temperatures for different microgel films. We observed drastic changes in resistance when the volume phase transition temperature of the copolymer systems is reached.

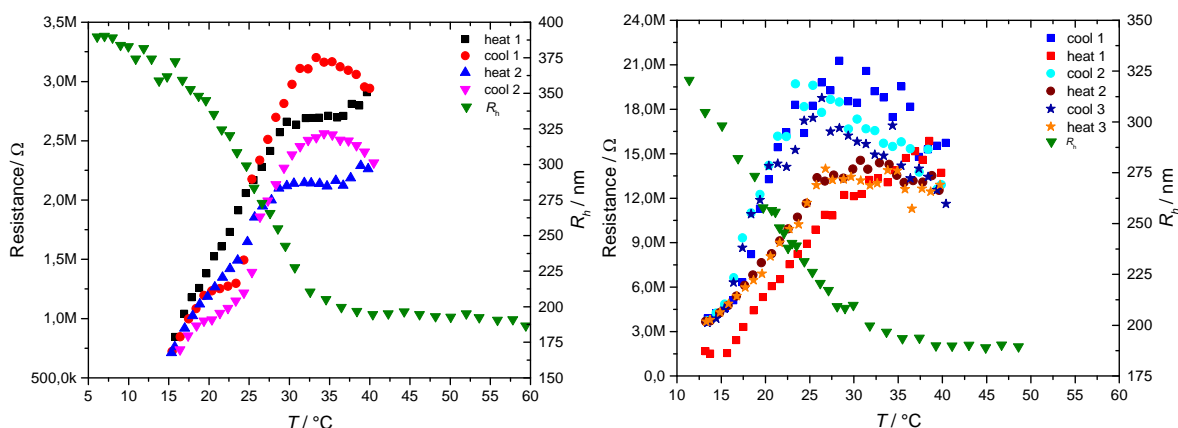


Figure 1. Resistance for membranes from the NIPAM microgel with 5 mol% *N*-benzylhydriylacrylamide (BHAm) (left) and 10 mol% BHAm (right) in a phosphate-buffer 20 mM KCl, 20 mM monosodium phosphate (NaH_2PO_4) solution at pH 7.0 and the swelling curves of the corresponding microgel (green triangle) obtained from PCS measurements.

[1] Y. Lu et al., *Angew. Chem. Int. Ed.* **45** (2003), 813-816.

[2] S. Frost and M. Ulbricht, *Journal of Membrane Science* **448** (2013), 1-11.

[3] R. Pelton, *Adv. Colloid Interf. Sci.* **85** (2000), 1-33.

Ionic liquid-Infused nanostructures as repellent surfaces

Yaraset Galvan^{1,2}, Ramon Zarraga², and Nicolas Vogel¹

¹ Institute of Particle Technology, Friedrich-Alexander University Erlangen-Nürnberg, Erlangen, Germany

² Departamento de Química, División de Ciencias Naturales y Exactas, Universidad de Guanajuato, Guanajuato, Mexico

The design of slippery liquid-infused porous surfaces (SLIPS) has brought a new strategy to create liquid repellent coatings [1]. In some aspects, such coatings can outperform traditional superhydrophobic coatings based on the Lotus effect, especially with respect to pressure tolerance and to self-heal after damage [1,2]. Such improved characteristics arise from the liquid nature of the lubricant. However, by the same token, using a liquid to create a repellent coating poses challenging questions with respect to the long-term stability of the coating. One important degradation mechanism is the loss of lubricant by evaporation. To overcome this issue, the use of ionic liquids has been proposed due to their negligible vapor pressure [3,4].

In this study we prepared lubricant-infused repellent surfaces using ionic liquids as lubricants. We studied the wetting behavior of imidazole-based ionic liquids with different alkyl chain length (fig. 1c) as a function on the applied surface chemistry (fig. 1d). We took advantage of the structural color of the inverse opals (fig. 1a) to observe the infiltration of the different ionic liquids into this highly ordered porous surfaces, as shown in figure 1b [4]. Upon infiltration, the structural color of the inverse opals vanishes as a result of the lowered refractive index contrast. This methodology provides a simple read-out characteristic to assess the wetting situation at the nanoscale.

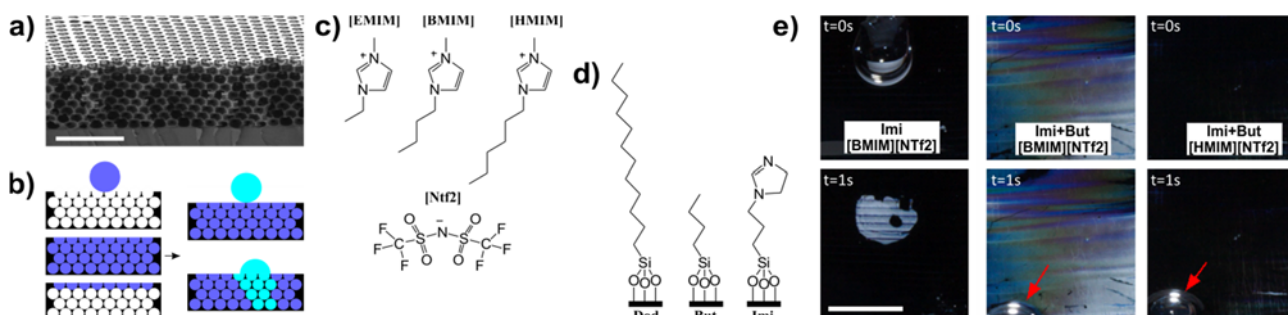


Figure 1. a) SEM image of inverse opal, scale bar= 2µm. b) Schematic representation of the possible wetting states of an inverse opal in a lubricant infused coating and its stability. c,d) Chemical composition of the ionic liquids and silanes used in this study. e) Time-lapse images of a water droplet on an inv. opal with different surface functionalities infiltrated with different ILs, scale bar=5mm. Failure of the coating can be seen on the left side with imidazole surface chemistry, while successful water repellency arises from a mixed surface chemistry of imidazole and alkyl silanes.

We found that the more hydrophobic ionic liquids with long hydrocarbon chains can infiltrate the porous surfaces and form stable systems when the inverse opals are functionalized with a mixed monolayer of imidazole group and hydrocarbon chains silanes (figure 1e). These results highlight the influence of matching chemical affinity between the lubricating liquid and the surface to form stable repellent surfaces.

[1] T.S. Wong et al., *Nature* **477** (2011), 443.

[2] F. Schellenberger et al. *Soft Matter*. **11** (2015), 7617.

[3] Y. Ding et al. *Adv. Mater. Interfaces* **2** (2015), 150.

[4] Y. Galvan et al. *Langmuir* Just accepted (2018).

Evaluation of interfacial free energy of charged colloidal crystals

S. Heidt^{1,2}, M. Hofmann¹, M. J. Scherf¹, G. Jung¹ and Thomas Palberg¹

¹ Institute of physics, Johannes Gutenberg University, Staudingerweg 7, D-55128 Mainz, Germany

² Graduate School Materials Science in Mainz, Staudingerweg 9, D-55128 Mainz, Germany

Charged colloidal systems are well known model systems to study the phase behavior and crystallization kinetics of solids on a mesoscopic scale [1]. Their interaction closely resembles that of hard core Yukawa spheres used in computer simulations [2]. We are here interested in the interfacial free energy between the emerging crystal nuclei and the surrounding meta-stable shear-melt. According to classical nucleation theory, these should strongly influence the nucleation rate densities and – in combination with the meta-stability dependent crystal growth velocity determine the resulting crystallite size distribution [3]. Recently, we found that the interfacial free energy in such systems decreases with increasing polydispersity of the particles [4].

In the present paper, we therefore determine the interfacial free energies from measurements of the crystallite size distribution by static light scattering. The latter is typically evaluated from the width of Bragg reflections following Scherrer [5, 6]. We here test an alternative evaluation based on a procedure originally proposed by Laue [7]. The average crystallite sizes obtained from these methods differ systematically, but only by about 10 %. This does not significantly influence the inferred interfacial free energies. We then compare our data on the reduced interfacial free energies extrapolated to zero meta-stability with the data sets available from literature. Furthermore, we discuss our findings with respect to the recent proposal of a decreasing interfacial free energy for increasing polydispersity. After a first evaluation the new data point taken on our low polydispersity sample contradicts the previous data. Possible origins of this deviation are discussed.

[1] T. Palberg, *J. Phys.: Condens. Matter* **26**(2014), 333101.

[2] A. Ivlev, *World Scientific Complex plasmas and colloidal dispersions*, **308**(2012).

[3] P. Wette, H. J. Schöpe, T. Palberg, *J. Chem. Phys.* **123**(2005), 174902 .

[4] T. Palberg, P. Wette, D. M. Herlach, *Phys. Rev. E* **93**, 022601 (2016).

[5] P. Scherrer, *Nachr. Ges. Wiss Göttingen*, (1918) 82-100.

[6] J I. Langford, A. J. C. Wilson, *J. Appl. Cryst.* **11**(1978), 102-113.

[7] M. V. Laue, *Ann. Phys.* **481**(1936), 55-68.

Acknowledgement: The authors acknowledge financial support the Graduate School Materials Science in Mainz (GSC 266) and the DFG (PA 459/19). Thanks to the BASF Ludwigshafen for provided samples.

Directing supraparticles architecture by controlled evaporation and dewetting of magnetic nanoparticle suspensions on superamphiphobic surfaces

Minghan Hu¹, Hans-Jürgen Butt², Sanghyuk Wooh³, Markus Bannwarth¹, H  lo  se Th  rien-Aubin¹, and Katharina Landfester¹

¹ Physical Chemistry of Polymers, Max Planck Institute for Polymer Research, Mainz, Germany

² Physics at Interfaces, Max Planck Institute for Polymer Research, Mainz, Germany

³ School of Chemical Engineering & Materials Science, Chung-Ang University, Seoul, Korea

The formation of macroscopic particles with mesoscopic substructures, called supraparticles, has attracted many research interests in recent years. Supraparticles can be fabricated by evaporating colloidal droplets on superhydrophobic[1] and superamphiphobic surfaces[2,3]. The sizes and compositions of supraparticles can be easily changed through varying the composition and the concentration of nanoparticles in the drop. To direct the shape of the supraparticles into new architectures, we introduced magnetic force to assist in the preparation of the supraparticles and investigated the fundamentals of colloids assembly.

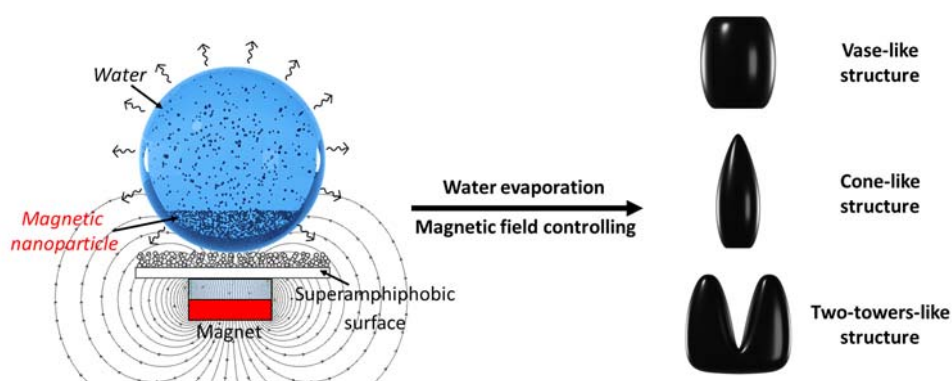


Figure 1. Scheme of fabricating supraparticles by evaporating magnetic nanoparticles dispersion drop on a superamphiphobic surface. By controlling the drying process and magnetic field, supraparticles form different interested shapes in micron size.

[1] Mar  n   lvaro G. et al., *P. Natl. Acad. Sci. USA* **41** (2012), 109.

[2] Wooh S. et al., *Adv. Mater.* **45** (2015), 27.

[3] Sekido, T. et al., *Langmuir* **33** (2017), 8.

Acknowledgement: The authors are grateful for the support of the Max Planck Society. M. H. acknowledge the China Scholarship Council for the graduate scholarship. H. T. A. is grateful to the Alexander von Humboldt Stiftung for financial support.

Gradually controlled wetting properties and its influence on ionic transport in mesoporous silica thin films

Adnan Khalil¹ and Annette Andrieu-Brunden¹

¹ Technische Universität Darmstadt; Ernst-Berl-Institut für technische und makromolekulare Chemie, 64289 Darmstadt, Germany

Author list: Adnan Khalil¹, Annette Andrieu-Brunden¹

Mesoporous silica materials have a wide range of application in science due to very peculiar properties like high surface area, controlled porosity and high flexibility in surface design and composition. Exemplary applications would be sensor technology, drug release or energy storage, where the diffusion of molecules in the porous system is of importance. However, the influence of wetting of complex, porous structures on water imbibition and ionic pore accessibility is rudimentarily investigated [1]. On the other hand a direct dependence of surface wettability on the character and physicochemistry of the surface exists. Via functionalization by silane chemistry, e.g. hydrophobic perfluorinated alkyl silanes, the wetting properties of the intrinsically hydrophilic silica matrix can be rationally designed [2, 3].

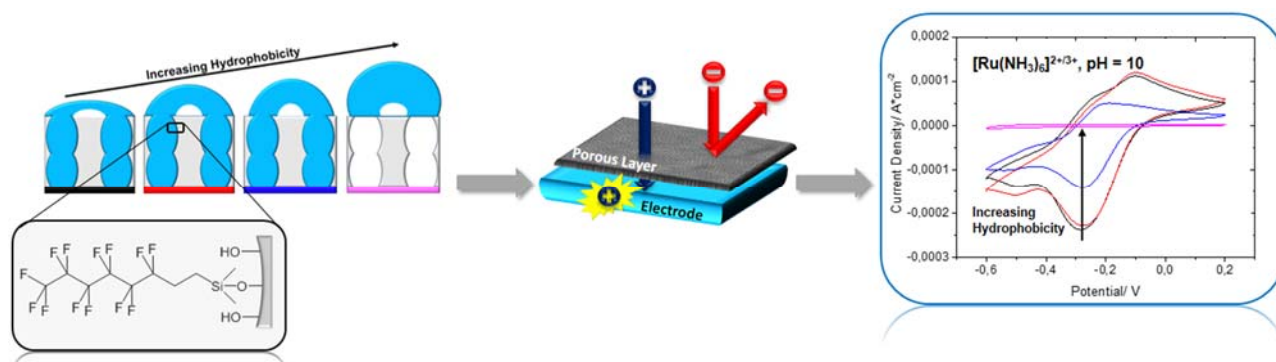


Figure 1. Chemical functionalization of a mesoporous thin silica film with PFODMCS and its effect on ionic pore accessibility.

In this work, chemical vapor phase deposition of 1H,1H,2H,2H-Perfluorooctyl dimethylchlorosilane (PFODMCS) is used to gradually adjust the wetting properties of mesoporous silica thin films. We systematically investigated the mutual dependence of wetting and ionic transport in these functionalized mesopores. One key result is the observation of three wetting regimes determining ion transport and a threshold hydrophobicity. A second one is that at the threshold hydrophobicity the pores can be opened by electrostatic attraction (Fig 1). Consequently, we are giving insights into the complex interplay of wetting and charge in nanopores on molecular transport.

[1].D. R. Ceratti et al., *Nanoscale*, 2015, **7**, 5371.

[2] J. Kujawa et al., *ACS Appl. Mater. Interfaces*, 2016, **8**, 7564.

[3] L. Nicole et al., *J. Mater. Chem.*, 2005, **15**, 3598.

Acknowledgement: We kindly acknowledge the financial support by the German Research Foundation (DFG) within the Collaborative Research Centre 1994 "Interaction between Transport and Wetting Processes", C04

Finetuning the properties of styrene-based porous polymers via emulsion templating

Lukas Koch, Cosima Stubenrauch

Institute of Physical Chemistry, University of Stuttgart, Pfaffenwaldring 55, 70569 Stuttgart, Germany

In previous studies [1-4], monodisperse porous polystyrene was synthesised from monodisperse water-in-oil HIPEs (high internal phase emulsion) which were generated via microfluidics. The continuous monomer/crosslinker phase was polymerised and the solid foam was subsequently dried. Depending on the chosen initiator, different structures were obtained: with the oil-soluble initiator azobisisobutyronitrile (AIBN) a solid foam with a spherical, open-cell pore structure and non-layered, porous pore walls was produced (see Figure 1, bottom). However, using the water-soluble initiator potassium peroxydisulfate (KPS) one obtains a hexagonal, closed-cell pore structure with layered, thick pore walls (see Figure 1, top). A possible explanation for this observation is the fact that in case of KPS a crosslinker-rich polymer forms at the oil-water interface because the polymerisation of the crosslinker is faster than the one of the monomer [5]. Therefore, a concentration gradient of the crosslinker between the films separating the water droplets and the plateau borders arises. This results in an osmotic transport of crosslinker monomers to the films and thereby causes the structures and microstructures shown below (see Figure 1, top). Despite having carried out experiments which support this theory [3], a quantitative explanation is still lacking since it is not possible to calculate the pressure caused by the osmotic pressure which must oppose the capillary pressure. Another reason for the transport could be a negative interfacial tension which arises during polymerisation – in this case an enlargement of the interface would be the driving force for the material transport (we recall that the surface of a solid foam consisting of regular hexagons is 10% larger than the surface of the liquid template consisting of spherical water droplets [3]). This contribution deals with a more detailed description of previous findings as well as with a strategy on how to prove / disprove the idea of an osmotic transport.

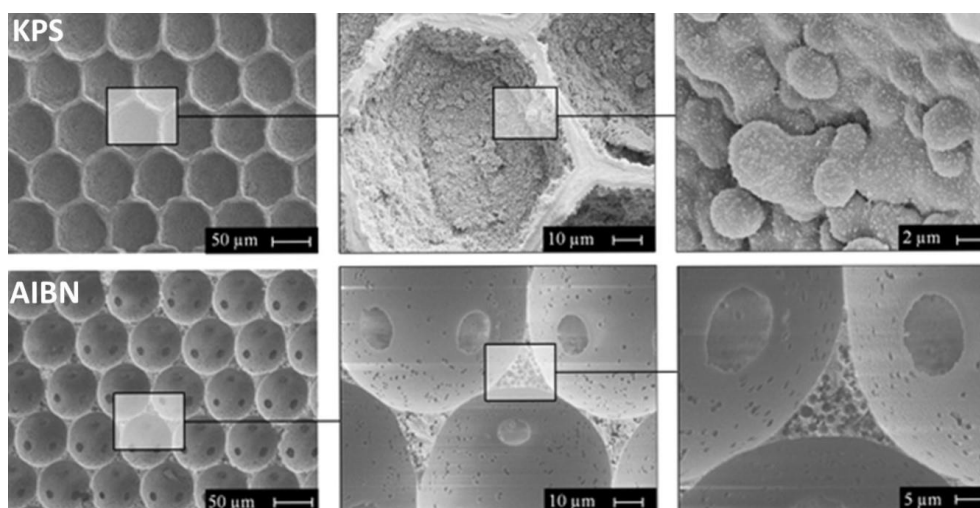


Figure 1. SEM (scanning electron microscope) pictures of porous polystyrene synthesized from monodisperse emulsion templates with the initiator (top) KPS and (bottom) AIBN. [4]

- [1] A Quell et al., *Adv. Eng. Mater.* **17** (2015), 604; [2] A Quell et al., *Macromolecules* **49** (2016), 5059
[3] A Quell et al., *Chemphyschem* **18** (2017), 451; [4] A Quell et al., *Langmuir* **33** (2017), 537 [5] G Schwachula, *J. Polym. Sci., C Polym. Symp.* **53** (1975), 107

Ice Adhesion Test Data for Ice-Phobic and Durability Testing of Lubricant Impregnated Slippery Surfaces

Alexandre Laroche¹, Vittorio Vercillo¹, Maria-Jose Grasso¹, and Elmar Bonaccorso¹

¹ Airbus Central Research & Technology, Materials X, Ottobrunn, Germany.

Ice formation on large commercial aircraft is rarely an issue thanks to robust anti-icing systems. One system, the bleed-air system, draws hot air from the engines of an aircraft and passes it through the leading edge of the wings, for example, or to other components which need protection [1]. The designers of future aircraft however are continuously searching for ways to make their designs more energy-efficient. One promising avenue for the reduction of energy consumption is in the aforementioned ice protection system. If a passive ice protection system, one that requires no energy input, is used in conjunction with an active one, like the bleed-air system, then the energy required by the active system should be significantly reduced [2 – 4].

Ice adhesion strength is a metric used to compare the performance of surfaces with respect to their passive ice protection qualities. The interfacial shear adhesion strength of ice may be calculated using measurements from a vibrating cantilever onto which ice has been accreted. Figure 1 is an image of the ice adhesion test viewed from above. A strain gauge located on the back of the cantilever provides raw data for the calculation of interfacial shear strength at the time of ice delamination.

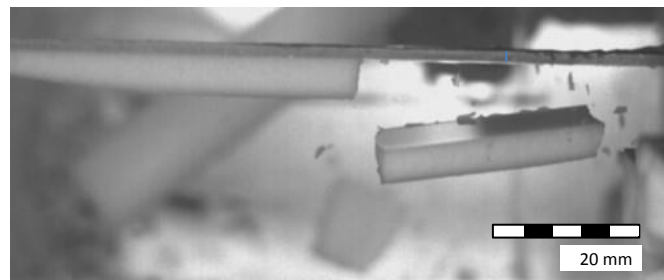


Figure 1. Partial ice delamination during cantilever shear ice adhesion strength test.

In this work, three reference surfaces are presented. One which is “hydrophilic,” another which is “hydrophobic,” and finally one which is “superhydrophobic.” The ice adhesion values on these reference surfaces are then compared to a number of polyurethane coatings, whose formulations are based on modified in-service aerospace coatings. Ice adhesion values are shown over a range of four icing conditions: rime, mixed/rime, mixed/glaze, and glaze. Results show critical dependences of ice adhesion strength from surface properties like wettability and roughness and from atmospheric conditions like airspeed and temperature.

[1] A Heinrich et al. in “*Aircraft Icing Handbook Vol. 2 of 3*”, (National Technical Information Service, Springfield, 1991).

[2] T Strobl et al., *29th Congress of the International Council of the Aeronautical Sciences* (2014) 891.

[3] T Strobl et al., *Journal of Aircraft* **52** (2015), 2064.

[4] K Al-Khalil et al., *35th Aerospace Sciences Meeting & Exhibit* (1997) 302.

Acknowledgement: This research was supported by the European Union’s Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 722497 – LubISS.

Targeting Drug-Nanoparticles: Liposomes and Polymer - Study by SANS and DLS

Thomas Nawroth^{1,2}, Lidija Krebs¹, Christian Siewert¹, Michael Klak¹, Lukas Uebbing¹,
Peter Langguth¹, Raphael Johnson³, and Ralf Schweins⁴

¹ Pharmacy and Biochemistry Inst., Pharma-Technology, Gutenberg-University, D-55099 Mainz, Germany

² Nanovel Ltd. & Co. KG, Biomedical Development, D-55450 Langenlonsheim, Germany

³ Pharmaceutics Dept., Kwame Nkrumah University of Science, Kumasi, Ghana

⁴ ILL, Large Scale Structure group LSS, F-38042 Grenoble, France

Nanoparticles for medi-pharm application [1], e.g. in cancer treatment, were prepared from phospholipids, cholesterol and bio-degradable polymers, cold isotope radiotherapy drug [2] and novel hydrophobic targeting excipients for specific cell targeting after ligand loading by particle surface modification. The nanoparticles were unilamellar liposomes and porous polymer-particles (PLGA), both depicting a size of 100 nm. The nanoparticle matrix contained typically 2% of a lipophilic excipient material, depicting a terminal SH-group, e.g. the cholesterol derivative shown in fig.1a for liposomes [3], or a corresponding commercial SH-oligo-lactide oligomer (Nanovel). Both materials can bind, after activation with di-Thiopyridine, SH-functional receptor ligands, e.g. bovine serum albumin (BSA-SH), or artificially SH-functionalized proteins or enzyme substrates.

The nanoparticles were prepared including the pre-activated targeting excipient and a concentrated solution of the cancer drug (1M Erbium-, or Gadolinium-Aceteate [2], Boron-phenylalanine BPA) at sterile conditions (GMP). The surface modification by SH-proteins, which shall in the final product lead to a person-specific medicine, was done as final step by fast mixing of activated pre-target nanoparticles and SH-protein solution at pH 7.2. Structure and target-ligand loading (click-linking) was studied at the ILL Grenoble, instrument D11, by time resolved neutron scattering SANS plus DLS using a projecting DLS device [4] with external sample unit (Nanovel ProSpecD). The internal nano-domain structure was studied by SANS with contrast variation using the D-solvent method, as introduced earlier for reconstituted membrane-proteins in liposomes [5]. The surface modification by formation of a covalently bound protein corona [6] (fig.1b) was detected as time resolved appearance of the corona structure on lipid-D₂O-matched liposomes in SANS (fig.1c).

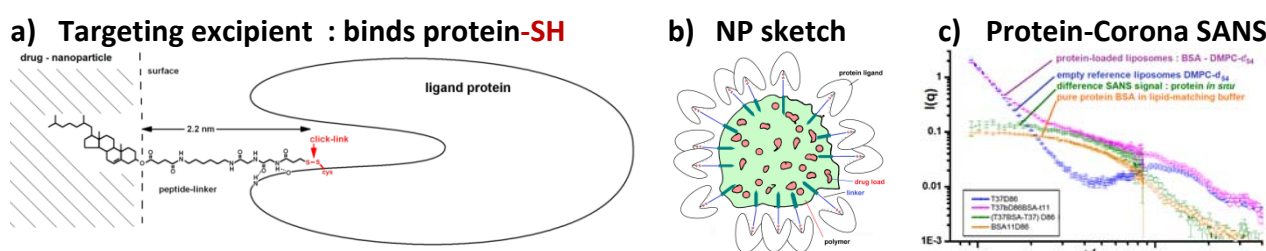


Figure 1. a) Targeting excipient Cholesterol-succinyl-hexamethyldiamido-GlycylGlycyl-Thio-Propionic-acid [3]; sketch of protein-loaded drug-nanoparticles; c) SANS of Protein-Corona-(BSA) on Deuterium-matched liposomes from DMPC-d₅₄ after covalent S-S-binding of H-BSA for 1h protein coupling time.

[1] Nawroth T, Krebs L, Langguth, et al „Target Nanoparticles SANS-DLS“ (2016) J Phys Conf S. 746, 012069.

[2] Buch K, Nawroth T, Langguth P, Schmidberger H : **EU-patent 11 007 401.0**; University Mainz (2012)

[3] Krebs, Lidija, “Targeted drug carriers with cholesterol-based lipids”, Diploma thesis, Uni Mainz [2014].

[4] Nawroth T, Buch P, Buch K, Langguth P, Schweins R; (2011) Mol. Pharm. 8, 2162

[5] Nawroth T, Conrad H, Vienken J, Dose K. (1983) Hoppe Seylers Z. Physiol. Chem. 364, 923.

[6] Tenzer S, Docter D, Rosfa S, Nawroth T, Maskos M, Schild H, Stauber RH et al. (2011) ACS Nano 5, 7155.

Acknowledgement: The authors thank for support by BMBF, Nanovel Langenlonsheim , and ILL Grenoble.

Synthesis of anisotropic hollow microgels

Anne C. Nickel¹ and Walter Richtering¹

¹ *Institute of Physical Chemistry, RWTH Aachen University, Aachen, Germany*

Spherical and hollow microgels, where a temperature sensitive monomer like *N*-isopropylacrylamide (NIPAm) is used for the shell synthesis, are interesting candidates for nano-carriers. Given that, with a change in temperature the permeability of the shell is influenced, obtaining the possibility to store drugs inside the void. Those hollow microgels are generated via a core shell synthesis, using silica as sacrificial cores [1].

In this work, we address the challenge to create rodlike-shaped nano-carriers. Due to the more complex shape, those particles receive different diffusion properties and ordering phenomena, compared to spherical ones. Rodlike silica particles are synthesized according to the procedure of Kuijk et al. as sacrificial cores [2]. Subsequently, their surface is functionalized with 3-(trimethoxysilyl)-propylmethacrylate (MPS) to gain a reactive surface for the shell synthesis. The shell is synthesized via a seed and feed precipitation polymerization of NIPAm and *N,N'*-methylenebisacrylamide (BIS) as cross-linker. To generate hollow microgels, the core is etched in a sodium hydroxide solution (Fig. 1). When changing the cross-linker content and the thickness of the shell, the dissolution of the anisotropic core leads to hollow microgels with different shapes compared to the silica template used. Furthermore, we see an anisotropic collapse of the microgels when heated above the volume phase transition temperature.

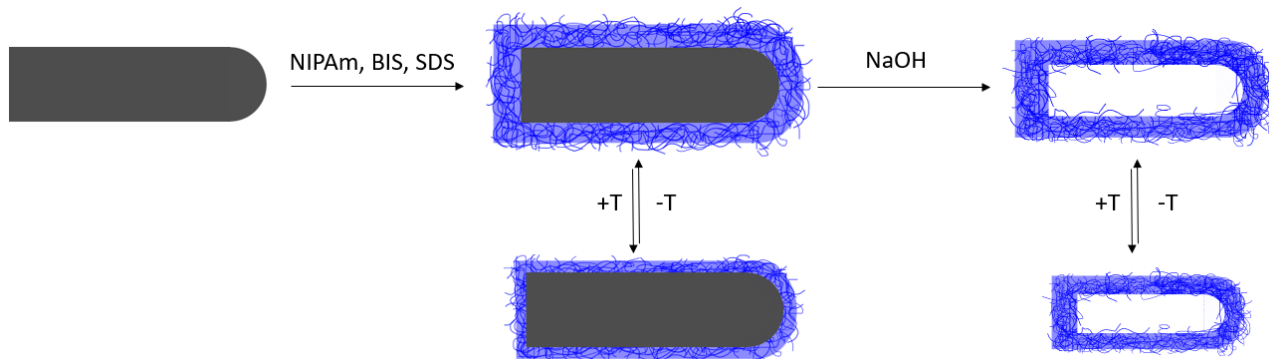


Figure 1. Sketch of the synthesis generating core-shell and hollow microgels using rodlike silica templates and their respective temperature dependent change in size.

[1] J. Dubbert et al., *Macromolecules* **47** (2014), 8700.

[2] A. Kuijk et al., *Journal of American chemical society* **133** (2011), 2346.

Acknowledgement: The authors acknowledge funding from Research Foundation (DFG) within the SFB 985 (Functional Microgels and Microgel Systems).

Formation of a transient amorphous solid in low density aqueous charged sphere suspensions

Ran Niu,¹ Sabrina Heidt,^{1,2} Ramsia Sreij,³ Riande I. Dekker,⁴ Maximilian Hofmann,¹ and Thomas Palberg¹

¹ *Institute of Physics, Johannes Gutenberg University, D-55099 Mainz, Germany*

² *Graduate School Materials Science in Mainz, Staudinger Weg 9, D-55128 Mainz, Germany*

³ *Department of Chemistry Physical and Biophysical Chemistry (PC III), Bielefeld University, D-33615 Bielefeld, Germany*

⁴ *Debye Institute for Nanomaterials Science, Utrecht University, NL-3584 CC Utrecht, The Netherlands*

Colloidal glasses formed from hard spheres, nearly hard spheres, ellipsoids and platelets or their attractive variants, have been studied in great detail. Complementing and constraining theoretical approaches and simulations, the many different types of model systems have significantly advanced our understanding of the glass transition in general. Despite their early prediction, however, no experimental charged sphere glasses have been found at low density, where the competing process of crystallization prevails. We here report the formation of a transient amorphous solid formed from charged polymer spheres suspended in thoroughly deionized water at volume fractions of 0.0002 – 0.01 [1]. From optical experiments, we observe the presence of short-range order and an enhanced shear rigidity as compared to the stable polycrystalline solid of body centred cubic structure. On a density dependent time scale of hours to days, the amorphous solid transforms into this stable structure. We further present preliminary dynamic light scattering data showing the evolution of a second slow relaxation process possibly pointing to a dynamic heterogeneity known from other colloidal glasses and gels. We compare our findings to the predicted phase behaviour of charged sphere suspensions and discuss possible mechanisms for the formation of this peculiar type of colloidal glass [2].

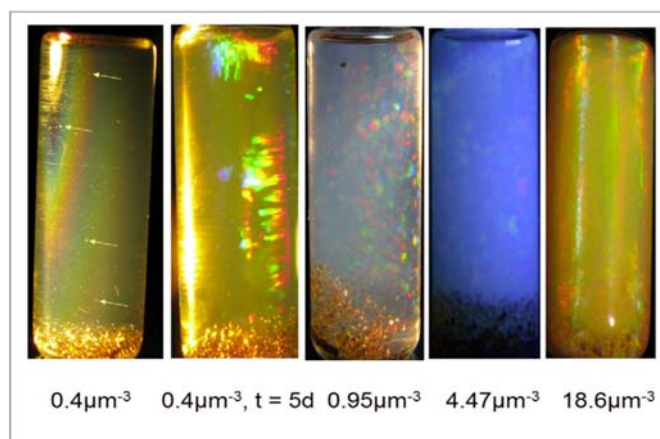


Figure 1. The amorphous solid was first discovered recognizing unsettled ion exchange debris in a non crystalline sample [1]. Later finite shear moduli were determined by TRS and short range order demonstrated from SLS measurements.

[1] T. Palberg et al., J. Stat Phys. **2016** (2016), 074007.

[2] R. Niu et al., Sci. Rep. **7** (2017), 17044.

Acknowledgement: We are pleased to thank P Wette and E. Bartsch for fruitful discussions on amorphous solids and crystallization kinetics, Thomas Hellweg for the discussion of SAXS data, B. Barton and F. Depoix for technical assistance in TEM measurements and BASF, Ludwigshafen for the kind gift of particles. We

gratefully acknowledge financial support by the Deutsche Forschungsgemeinschaft (DFG) (Pa459/16, Pa459/17, INST 215/432-1 FUGG) and the JGU (interne FoFö 1. Stufe). S. H. is a recipient of a fellowship through the Excellence Initiative (DFG/GSC 266). R. I. D. is an Erasmus+ Trainee and recipient of a fellowship through the Duitsland Intstituut Amsterdam (DIA).

Microgel Surfaces for Temperature-Enhanced Adhesion of Proteins and Bacteria

Tanja Paul¹, Pauline Watermann¹, Sophie Rübel¹ and Stephan Schmidt¹

¹ *Institute of Organic and Macromolecular Chemistry, Heinrich-Heine-Universität Düsseldorf, Universitätstraße 1, 40225 Düsseldorf, Germany*

Multivalent carbohydrate interactions at the cells glycocalyx are of great importance for many biological processes. A broad aim is to get insight into the involved molecular mechanisms and utilize them for switchable interactions on surfaces [1-2]. Our specific aim is to establish surfaces that specifically bind proteins or bacteria in a stimuli responsive fashion to enable capture and release of carbohydrate binding species.

Such surfaces can be prepared by ligand presenting responsive microgel coatings. Thermosensitive poly(*N*-isopropyl acrylamide) microgels are functionalized with carbohydrates via different synthetic approaches and additionally the influence of charged groups, ligand concentration and architecture of microgels are investigated. The temperature controlled phase transition of microgels leads to an increase of hydrophobicity at the surface and a decrease of steric repulsion. This effect leads to a rise of ligand density on the surface and increases specific binding of proteins. We tested the properties of our synthesized bioactive coatings via fluorescence microscopy, STED and Bradford-Assay. Results show that carbohydrate-receptor interactions can be controlled by temperature stimulus (see Figure 1). Further work will focus on the exact mechanism of ligand presentation and investigation of multivalency effects as well as studying the temperature dependent presentation of hydrophobic and charged ligands.

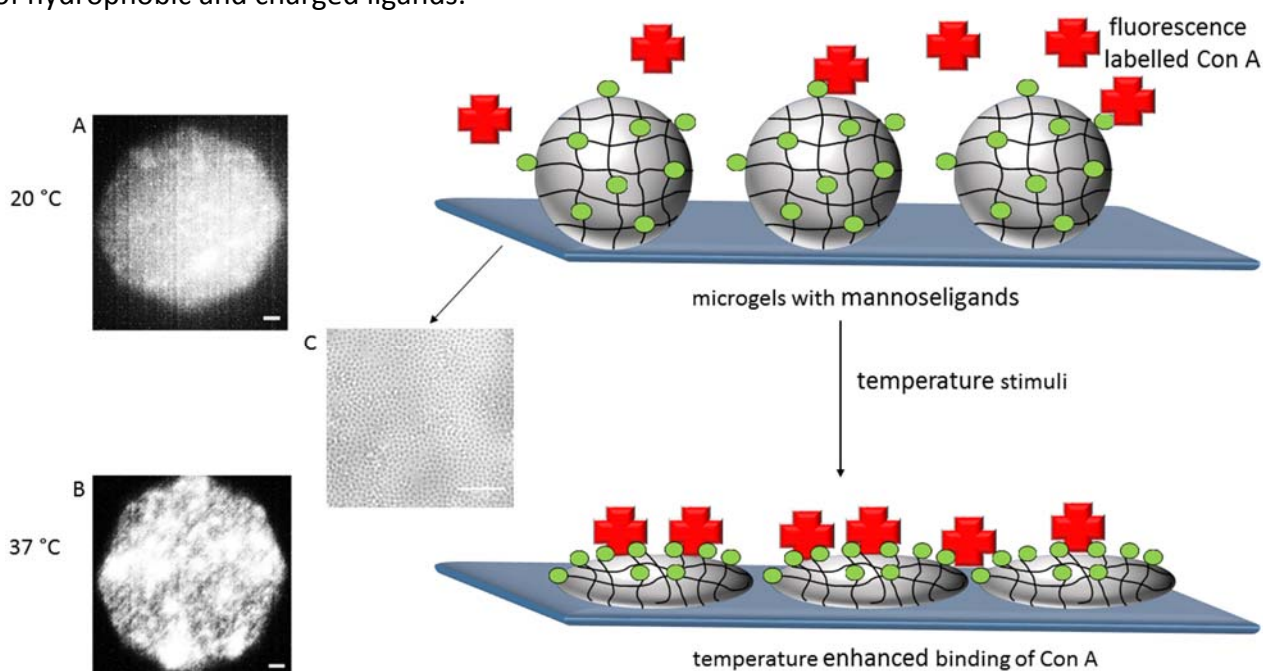


Figure 1. Fluorescence image of labelled Con A on a glyco microgel functionalized surface at 20 °C (A) and at 37 °C (B). Transmitted light image of dense packed microgel surface (C). Schematic presentation of temperature switchable specific interactions between Con A and a bioligand bearing microgel surface.

[1] S. Schmidt et al., *BJOC* **2015**, 11, 720-729.

[2] D. Pussak et al, *Angew. Chem., Int. Ed.* **2013**, 52 (23), 6084-6087.

Gelled non-toxic bicontinuous microemulsions: a phase behavior study

Ke Peng¹, Thomas Sottmann¹, and Cosima Stubenrauch¹

¹ Institute of Physical Chemistry, University of Stuttgart, 70569 Stuttgart, Germany

Gelled bicontinuous microemulsions (GBMEs) can be prepared either (a) by adding a gelator to an existing microemulsion or (b) by replacing the solvent of a gel by a bicontinuous microemulsion (Fig. 1). The GBME system water–*n*-dodecane–tetraethylene glycol monodecyl ether (C₁₀E₄)–12-hydroxyoctadecanoic acid (12-HOA) has been proven to be orthogonally self-assembled [1]. In other words, the non-gelled bicontinuous microemulsion and the binary gel form independently, thus sustaining the microstructure of the microemulsion and the mechanical stability of the gel. These properties are interesting for transdermal drug delivery systems [2]: lipophilic/amphiphilic drugs can be solubilized in the microemulsion whereas the gel provides convenient applications.

Up to now there is no study about GBMEs formulated with sugar surfactants. In order to fill this gap, we studied the phase behavior of systems containing octyl β -D-glucopyranoside (β -C₈G₁) with the view to formulate non-toxic GBMEs at room temperature. Sugar surfactants are less temperature-sensitive than ethylene glycol surfactants, but they are so hydrophilic that the mean curvature H of the amphiphilic film is always positive, i.e. only o/w-microemulsions are formed. In order to tune the curvature and thus to obtain a bicontinuous microemulsion, one needs to add a hydrophobic co-surfactant (alcohol) [3]. Our phase studies started with visual observations of changes caused by the titration of 1-octanol to the ternary system H₂O–*n*-octane– β -C₈G₁. Adding the gelator 12-HOA one indeed obtains a GBME. However, the surface-activity of 12-HOA influences the phase behavior. To avoid this and to achieve a truly orthogonal self-assembled system, we used the surface-inactive LMOG 1,3:2,4-Dibenzylidene-D-sorbitol (DBS) instead. Finally, we replaced *n*-octane and 1-octanol by isopropyl myristate (IPM) and 1,2-octanediol, respectively, to formulate non-irritating, bio-compatible GBMEs.

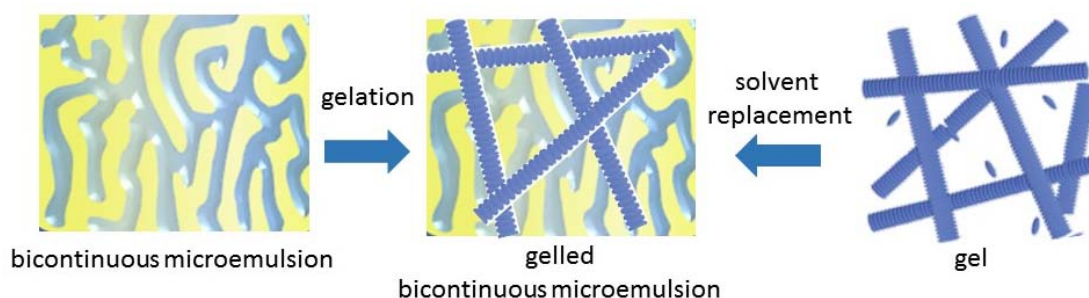


Figure 1. A schematic presentation of the formation of GBME.

- [1] M. Laupheimer, T. Sottmann, R. Schweins, C. Stubenrauch, *Soft Matter*. **10**, 8744–8757 (2014).
- [2] M. Kreilgaard, *Adv. Drug Deliv. Rev.* **54**, 77–98 (2002).
- [3] K. Kluge, C. Stubenrauch, T. Sottmann, R. Strey, *Tenside, surfactants, Deterg.* **38**, 30–40 (2001).

Spectroscopic investigation of periodic plasmonic superstructures

Ekaterina Ponomareva¹ and Matthias Karg¹

¹Heinrich-Heine-University Düsseldorf, Physical Chemistry I, Düsseldorf, Germany

Nanoparticles with a plasmonic metal core and a soft cross-linked hydrogel shell spontaneously self-assemble at an air/liquid interface forming periodic monolayers [1]. These layers can be transferred on glass substrates yielding substrate-supported superstructures with hexagonally arranged plasmonic nanoparticles at inter-particle distances of a few hundred nm. The distance between the cores varies in dependence of the thickness of the soft hydrogel shell. Due to the spatial proximity and the periodicity of the array, localized surface plasmons of metal cores can couple to diffractive modes and thus support surface lattice plasmon resonances [2]. By embedding the monolayer into a gain-medium these resonances can be enhanced.

Here we will demonstrate the angular-dependent optical behavior of periodic plasmonic monolayers. UV-vis measurements show different optical properties for dilute particles in aqueous dispersion, the assembled monolayers and the monolayers upon embedding in a gain matrix. Self-assembled particles show shifted and narrower resonance peaks than single particles. A home-made lasing-spectrometer was used to investigate the collective optical response of the plasmonic lattices in dependence on the detection and incident angle (Fig. 1). With the set-up it is possible to observe the near-field and radiative plasmonic coupling effects in colloidal monolayers. Additionally, we used theoretical simulations to support the experimental data.

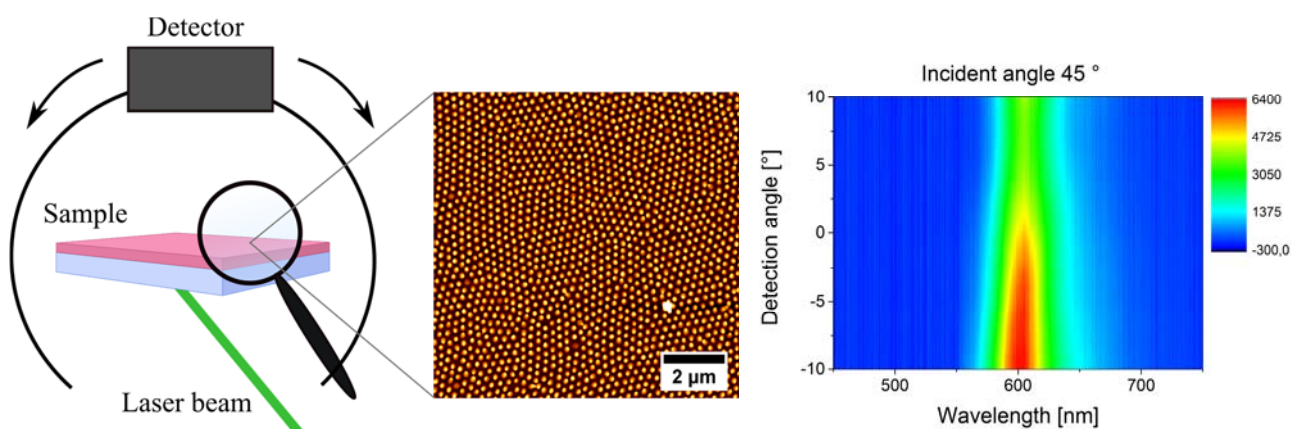


Figure 1. Left: schematic set-up for angular-dependent measurements. The sample and the detector are mounted on a rotation stage. Middle: AFM height profile of a representative monolayer. Right: detection angle dependent emission spectrum of a representative monolayer embedded in a gain-medium when stimulated by a 532 nm laser.

[1] K. Volk et al., *Adv. Mater.* **24** (2015), 7332

[2] K. Volk et al., *Adv. Optical Mater.* **5** (2017), 1600971

Acknowledgement: The authors acknowledge funding from the Deutsche Forschungsgemeinschaft (DFG) through the Emmy Noether Programme (KA3880/1-1).

Synthesis of colloidal BaTiO₃ nanoparticles with paramagnetic properties

Ivan Raguzin¹, Lisa Fruhner², Liming Wang², Xiao Sun², Oleg Petrarcic², Margarita Kruteva², Alla Synytska^{1,3}

¹ Department of Polymer Interfaces, Leibniz-Institut für Polymerforschung Dresden e.V., Dresden, Germany

² Forschungszentrum Jülich GmbH, Jülich, Germany

³ Technische Universität Dresden, Dresden, Germany.

For the last couple of decades synthesis of ferroelectric perovskites has gained considerable attention due to the wide spectrum of possible applications ranging from electronics and sensing to catalysis and non-linear optics. Barium titanate (BaTiO₃), as one of the most promising and important among them, is known from development of multilayer ceramic capacitors (MLCCs) for smaller size dielectric ceramic powders [1] and positive-temperature-coefficient (PTC) thermistors [2]. Regarding miniaturization in microelectronics, the investigation, development and synthesis of nanosized, monodispersed free-standing BaTiO₃ particles with controlled size, well-defined shape, good yields and high degree of compositional homogeneity has become increasingly essential. It can ease investigation of their ferroelectric and magnetic properties at the nanoscale, and can provide the possibility to assemble the nanoparticles into complex 3D nanocrystal structures.

In present work we show a robust route for the synthesis of BaTiO₃ nanoparticles by the hydrothermal method with the use of oleic acid as a surfactant. It allows preparation of a stable, homogeneous dispersion of the cube-shaped nanoparticles in nonpolar solvents (Figure 1). The synthesised BaTiO₃ nanoparticles are studied with respect to their structural, morphological and magnetic properties. They were characterised by DLS, TEM and SAXS providing information about the microstructure and size. In particular, it was found that intrinsically ferromagnetic and macroscopically superparamagnetic properties of the nanoparticles were demonstrated by magnetometry measurements.

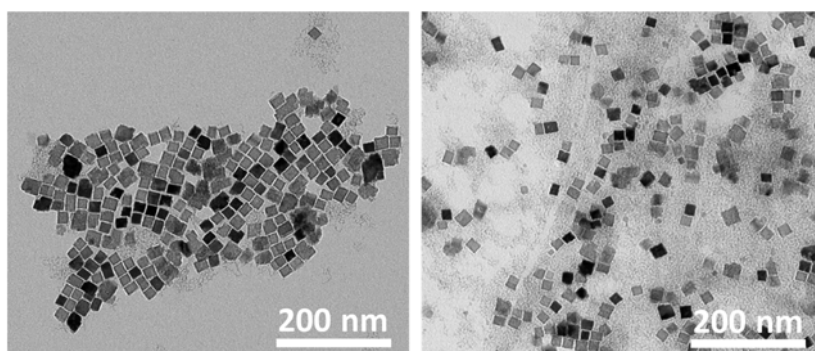


Figure 1. Representative TEM images of the BaTiO₃ cubic particles dispersed in toluene with oleic acid as surfactant.

Pickering Janus Emulsions stabilized by magnetic nanoparticles

Rajarshi Roy Raju¹, Ferenc Liebig¹, and Joachim Koetz¹

¹ *Institute for Chemistry, University of Potsdam, 14476 Potsdam, Germany*

Complex emulsions, synthesized through simple emulsification routes, have recently attracted significant research interests. Particularly, Janus emulsions have shown potential applications in various research fields including detection of bacteria, fabrication of porous scaffolds, and templates for anisotropic particle synthesis. These emulsions contain so-called ‘Janus droplets’ which are composed by two sub regions of immiscible oils components [1].

Our present research is focused on preparation of Janus emulsions through vibrational emulsification as well as ultrasonication, with controllable droplet size, engulfment and long-term stability. Our study has revealed that polyelectrolytes, polyelectrolyte complexes (PEC) and metal nanoparticles can play a crucial role to stabilize Janus emulsions, based on olive oil (OO) and silicone oil (SiO). It is possible to adjust Janus droplet size between 50 and 200 μm by changing the gelatin/Na-polyacrylate complex particle size between 200 and 400 nm [2]. Adsorption of PECs on oil interfaces drastically reduces the interfacial tension between the liquids. In presence of gelatin/Na-carboxymethylcellulose complexes long-term stable Janus gels with thixotropic properties can be observed. Chitosan, as emulsifier, applied at different pH ranges can tune the droplet size and shape from completely engulfed double emulsions to dumbbell shaped Janus droplets. Magnetic Pickering Janus emulsions can be formed by incorporating magnetic nanoparticles with a particle size of 13 ± 2 nm into the olive oil phase (Fig. 1). Superior emulsion stability, droplet size reduction to submicron ranges and desired movement of Janus droplets according to an externally applied magnetic field are some of prominent features achieved in this case.

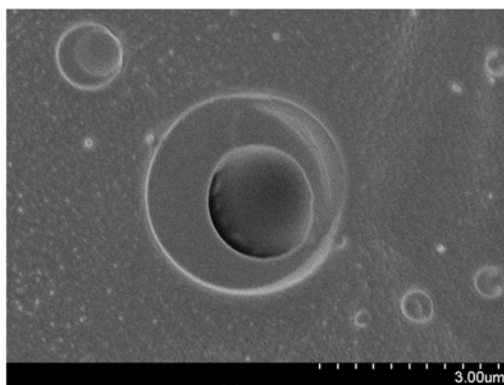


Figure 1. Cryo-SEM micrograph of OO/SiO Janus emulsion stabilized by magnetic nanoparticles and chitosan.

[1] S. E. Friberg, I. Kovach, and J. Koetz, *ChemPhysChem* **14** (2013) 16, 3772-3776.

[2] R. R. Raju, S. Kosmella, S. E. Friberg, and J. Koetz, *Colloids Surfaces A* **533** (2017), 241-248.

Dissipative disassembly of colloidal microgel crystals driven by a coupled cyclic reaction network

Dirk Rommel¹, Dennis Go¹, Yi Liao², Tamás Haraszti¹, Joris Sprakel³, and Alexander J. C. Kuehne¹

¹ DWI – Leibniz Institute for Interactive Materials, Forckenbeckstraße 50, 52076, Aachen, DE.

² Department of Chemistry, University of Central Florida, Orlando, Florida, 32816, USA.

³ Physical Chemistry and Soft Matter, Wageningen University & Research, 6708 WE Wageningen, NL.

Dissipative assembly can be used to drive temporally controlled arrangement of colloidal building blocks into useful structures [1]. However, the opposite scenario where reversible structural breakdown is controlled using a dissipative cycle remains almost unexplored. Herein we propose a dissipative disassembly process using two coupled cyclic reactions, in which protons mediate the interaction between the cycles [2]. Amphoteric core-shell microgels arrange into a soft colloidal crystal morphology induced by Coulomb interactions. Irradiation with light leads to a switch of an added merocyanine photoacid into the spiropyran geometry, releasing protons (H^+). These H^+ protonate the assembled microgels, leading to a net zero charged shell. This leads to deswelling of the shell and suppressed electrostatic repulsion between the microgels, resulting in colloidal melting. When the light is switched off, the spiropyran form relaxes back into its thermodynamically stable merocyanine form, which is protonated in this process. This leads to deprotonation and charging of the microgel shell, effectively closing the two reaction cycles. We showcase the mechanism on a soft photonic crystal which can reversibly transform into a disordered state by addition of light energy. This system is an experimental realization of a cyclic reaction-assembly network, and its principle can be extended to other types of structure formation.

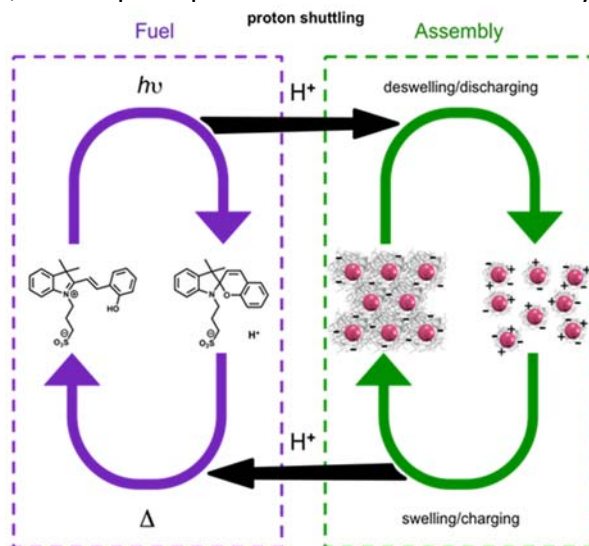


Figure 1. Dissipative disassembly realized by coupling two reaction cycles in which protons mediate the interaction between the reaction cycles.

[1] J. H. van Esch et al., *Chem. Soc. Rev.*, (2017), **46**, 5474.

[2] D. Go et al., *Soft Matter*, (2018), **14**, 910.

Acknowledgement: The authors D. G., D. R., T. H., J. S. and A. J. C. K. gratefully acknowledge funding by the Deutsche Forschungsgemeinschaft DFG through the collaborative research center SFB 985.

The Drop Adhesion Force Instrument

A. Saal, N. Gao, F. Geyer, D.W. Pilat, P. Papadopoulos, D. Schäffel, F. Schellenberger, D. Vollmer, R. Berger and H.-J. Butt

Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany

Sessile liquid drops on solid surfaces experience a lateral adhesion force owing to surface tension and contact angle hysteresis. Investigating lateral adhesion forces, F_{LA} , on drops is of interest not only for fundamental wetting science but also for industrial applications like self-cleaning surfaces, spraying of paint [1] or water drop removal. Lateral adhesion forces can be further distinguished as static and dynamic, depending on whether the drop is stationary or moves relative to the surface. The Transition between these forces has already been observed and seems to be similar to the classical case of solid-solid friction [2].

With present methods it is either impossible or very cumbersome to gain information about the dynamic lateral adhesion force. And it is not sufficient to only consider the static lateral adhesion force, since it gives no information about the dynamic lateral adhesion force [3]. We present the DAFI, an instrument for directly measuring the dynamic lateral adhesion force on liquid drops on solid surfaces during movement [4].

[1] ElSherbini, A. I.; Jacobi, A. M., Journal of Colloid and Interface Science 2006

[2] Gao, N., Geyer, F., Pilat, D. W., Wooh, S., Vollmer, D., Butt, H.-J., & Berger, R., Nature Physics 2017

[3] Suzuki, S.; Nakajima, A.; Kameshima, Y.; Okada, K., Surface Science 2004

[4] Pilat, D. W.; Papadopoulos, P.; Schäffel, D.; Vollmer, D.; Berger, R.; Butt, H. J., 2012

Acknowledgement: The authors acknowledge funding from the European Research Council for funding previous work and the Collaborative Research Center 1194 for funding future work.

Interaction of well-ordered paramagnetic chains through a PDMS polymer matrix

Henrik Schmidt¹ and Günter K. Auernhammer^{1,2}

¹ Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany

² Leibnitz Institute for Polymer Research, Hohe Str. 6, 01069 Dresden, Germany

In recent years, we focused on the interaction between magnetic particles in 3D and 2D magnetic hybrid materials systems. We investigated the interaction of the magnetic particles with the surrounding matrix in applied magnetic fields [1-3]. The elastic modulus of the material was adjusted to be below 10 Pa. The magnetic particles rearranged to chains while crosslinking the polymer in the presence of an external magnetic field. Microscopy images revealed buckling of the magnetic chains depending on their length, orientation to the magnetic field and the gels modulus.

In previous studies, the behaviour of single, well separate chains were in the focus. Now, the coupling of the buckling instability between neighbouring chains will be studied. We observed antisymmetric buckling of nearest neighbour chains (Fig. 1). Still, the physical origin is not yet fully clarified. Thus, while the distribution of the chains is momentarily random in space, main focus of current research is on the variety of strategies to get adjustable, spaced chains. Adapting the magnetic field, as decreasing the magnetic field strength, creates already promising chain configuration. The reproducibility has to be improved, e.g by carefully adjusting the magnetic field. An alternative route is templating the substrate through soft lithography.

With these adjustably spaced chains, we intend to extract matrix-mediated interactions between magnetic particle chains and the deformation of the gel to get insight in the interaction processes. These data may allow us to compare our experiments with existing continuum models of internal deformations in soft magnetic hybrid materials.



Figure 1. In white the super paramagnetic particle chains, in red the orientation of the external magnetic field. Buckling of two neighbour chains. Distance is $\approx 55 \mu\text{m}$. Antisymmetric deformation of chains.

- [1] Collin, D., et al., *Frozen-in magnetic order in uniaxial magnetic gels: preparation and physical properties*. Macromol. Rapid Commun., 2003. **24**: p. 737 - 741.
- [2] Huang, S., et al., *Buckling of paramagnetic chains in soft gels*. Soft Matter, 2016. **12**(1): p. 228-237.
- [3] Puljiz, M., et al., *Forces on Rigid Inclusions in Elastic Media and Resulting Matrix-Mediated Interactions*. Physical Review Letters, 2016. **117**(23): p. 238003.

Acknowledgement: The authors thank for support by the Deutsche Forschungsgemeinschaft (DFG) through the SPP 1681

Polyethylene glycol-based microgels for selective inhibition of pathogens

F. Schröer¹, Tanja Paul¹ and Stephan Schmidt¹

¹ Heinrich-Heine-Universität Düsseldorf, Institut für Organische und Makromolekulare Chemie, Universitätsstraße 1, 40225 Düsseldorf, Germany

Antibiotic resistance is a well-known problem of conventional antibiotics, which involves huge costs in clinical therapies and the development of new antibiotics. Many Pathogens bind to the sugar ligands of cell surfaces for tissue invasion [1]. Instead of promoting resistant species by outright killing most of the pathogens, the pathogen surface could be inhibited by presenting macromolecular ligand scaffolds [2]. This presentation prevents the pathogen to interact with the shell surface.

Clinical studies already showed that the taking of monosaccharides reduced the chronical affection with pseudomonas aeruginosa [3]. To maximise this effect, our approach is to use biocompatible polyethylene glycol-based microgels with sugar ligands for inhibition of bacterial adhesion. This leads to maximized multivalent binding sites to deactivate the pathogens with a shielding effect (Fig. 1). With this approach, the pathogens will not be killed but hindered from infecting a healthy cell and a resistance towards the antibiotic is therefore less likely.

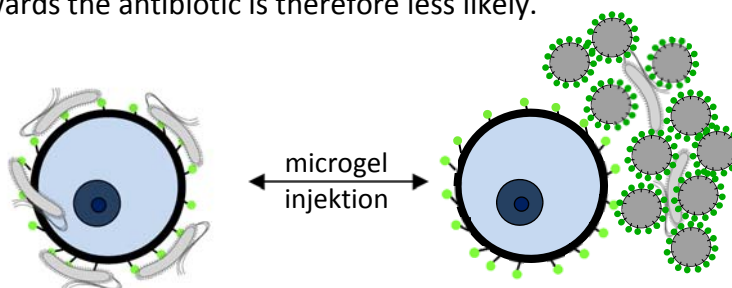


Figure 1. Schematics of the pathogens inhibition by biocompatible microgels presenting sugar ligands. Left: Active, non-bonded pathogens bind to the sugar on the cell surface to invade the cell; Right: Deactivated and bonded pathogens by the sugars on the microgel surface

The current focus is to establish the synthesis of mannose-presenting polyethylene glycol microgels with a high content of sugar in the microgel shell. The binding of proteins, which are a model for pathogens, to microgel-coated surfaces will be tested. The results so far show that a copolymerization of 2-(2-methoxyethoxy)ethyl methacrylate, poly(ethylene glycol) methyl ether methacrylate, ethylene glycol dimethacrylate [4] and N-ethylacrylamide- α -D-mannopyranose lead to mannose containing microgels. This LCST-microgel with a particle size about 400 nm is monodisperse, which is important to produce well-ordered microgel films on surfaces [5]. Overall, a synthesis for a biocompatible sugar ligand-containing microgel as a basis for pathogen inhibition is established.

[1] L. L. Kiessling, J. C. Grim, *Chem. Soc. Rev.* **42** (2013), 4476-4491.

[2] C. Fasting et al., *Angewandte Chemie International Edition* **51** (2012), 10472-10498.

[3] H.-P. Hauber et al., *International Journal of Medical Sciences* **5** (2008), 371-376.

[4] T. Cai et al., *Langmuir* **23** (2007), 8663-8666.

[5] S. Schmidt et al., *Advanced Functional Materials* **20** (2010), 3235-3243.

Acknowledgement: The authors acknowledge funding from the Hans-Böckler-Stiftung.

Design of Functional Heterogeneous Particle-Based Surfaces with Controlled Ice Nucleation and Adhesion

Madeleine Schwarzer^{1,2}, Thomas Otto^{1,2}, and Alla Synytska^{1,2}

¹ Leibniz Institute of Polymer Research Dresden, Polymer Interfaces, Dresden, Germany

² Dresden University of Technology, Institute of Physical Chemistry of Polymeric Materials, Dresden, Germany

Ice accumulation causes several problems on wind turbines, ships, aircrafts and power lines [1-2]. Therefore, the development of new multifunctional polymeric materials with anti-icing and de-icing capabilities is of crucial importance to prevent ice formation for the reduction of unnecessary expenses, to decrease the number of accidents and to achieve better energy efficiency. It still remains a very challenging task and requires the control of several parameters such as ice nucleation and adhesion [3].

Herein, we report on an approach for the design of heterogeneous surfaces based on different polymer-modified hybrid core-shell particles. Therefore, we mixed hydrophilic and hydrophobic particles of various sizes to obtain surfaces with a controlled and tuneable chemical composition. These heterogeneous surfaces were fundamentally investigated regarding their wettability, ice nucleation and growth as well as ice adhesion [3]. We will discuss the impact of chemical and topographical heterogeneities on the above mentioned phenomena.

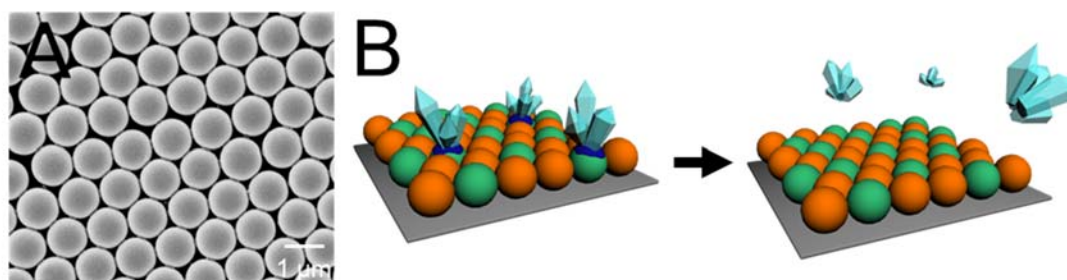


Figure 1. A) SEM image of a particle-based surface, B) schematic picture of the removal of ice from heterogeneous surfaces with a mixture of two different functionalized particles.

[1] J. Chanda, L. Ionov, A. Kirillova, and A. Synytska, *Soft Matter* **11** (2015) 9126.

[2] A. Kirillova, L. Ionov, I. V. Roisman, and A. Synytska, *Chem. Mater.* **28**, **19** (2016), 6995.

[3] M. Schwarzer, D. Fischer, and A. Synytska, submitted.

Acknowledgement: The authors acknowledge funding from the supporters of IPF, the DFG community, project SY 125/4-1.

Active nematics in confinement

Kristian Thijssen¹, Amin Doostmohammadi¹, Tyler Shendruk² and Julia Yeomans¹

¹ Rudolf Peierls Centre for Theoretical Physics, University of Oxford, Oxford OX1 3NP, UK

² The Rockefeller University, 1230 York Avenue, New York, New York, 10021, US

The spontaneous emergence of collective flows is a generic property of active fluids [1]. It is caused by the self-propelled, microscopic particles that drive the fluid out-of-equilibrium [2]. In these active fluids, various collective flows can emerge including lamellar flow [3], vortex lattices [4] and active turbulence [5-8] with flow structures scaling by an intrinsic length scale many times larger than that of the individual particles [9]. Here we consider active nematics in a channel where the channel height and the intrinsic active length scale compete, and show that their ratio governs a sequence of dynamical flow transitions. Understanding the mechanism of the flow transitions is of considerable importance in the design and control of active materials.

[1] S. Ramaswamy, *Annu. Rev. Cond. Mat. Phys.* **1**, 323 (2010).

[2] M. C. Marchetti, J. F. Joanny, S. Ramaswamy, T. B. Liverpool, J. Prost, M. Rao, and R. A. Simha, *Rev. Mod. Phys.* **85**, 1143 (2013).

[3] R. Voituriez, J. F. Joanny, and J. Prost, *Europhys. Lett.* **70**, 404 (2005).

[4] T. N. Shendruk, A. Doostmohammadi, K. Thijssen, and J. M. Yeomans, *Soft Matter*, **13**, 3833 (2017)

[5] H. H. Wensink, J. Dunkel, S. Heidenreich, K. Drescher, R. E. Goldstein, H. Löwen, and J. M. Yeomans, *PNAS* **109**, 14308 (2012).

[6] C. Dombrowski, L. Cisneros, S. Chatkaew, R. E. Goldstein, and J. O. Kessler, *Phys. Rev. Lett* **93**, 098103 (2004)

[7] A. Creppy, O. Praud, X. Druart, P. L. Kohnke, and F. Plouraboué, *Phys. Rev. E* **92**, 032722 (2015).

[8] A. Doostmohammadi, T. N. Shendruk, K. Thijssen, and J. M. Yeomans, *Nat. Commun.* **8**, 15326 (2017)

[9] S. Heidenreich, J. Dunkel, S. H. L. Klapp, and M. Bär, *Phys. Rev. E* **94**, 020601 (2016)

Acknowledgement: KT was funded by the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 722497. AD was supported by a Royal Commission for the Exhibition of 1851 Research Fellowship. This work was furthermore supported through funding from the ERC Advanced Grant 291234 MiCE and we acknowledge EMBO funding to TNS (ALTF181-2013). We thank Hugo Wioland for helpful discussions

Surface properties of deposits composed of casein micelles

Sebastian Thill¹, Dimitrij Rogalski¹, Ronald Gebhardt¹, Alex Oppermann², Dominik Wöll²

¹Aachener Verfahrenstechnik (AVT), Soft Matter Process Engineering (SMP), RWTH Aachen University, Aachen Germany

²Institut für Physikalische Chemie, RWTH Aachen University, Aachen Germany

Knowledge of the structure and dynamics of deposition layers is very important for the understanding of mass transport through membranes during microfiltration. During the microfiltration of milk, so called casein micelles deposit on the membrane while smaller components such as whey proteins, peptides or minerals pass through. Casein micelles are spherical protein aggregates with a diameter between 50 and 500 nm [1]. They have many structural similarities to microgels such as architectural versatility, permeability, functionality and deformability [2, 3]

We have developed a fractionation process to isolate stable size fractions of casein micelles from fresh milk. In order to understand deposition layers on membranes, we first prepared and investigated films from these fractions. We dried suspensions with different mass content of casein micelles at 20°C and 30-39 % relative humidity. The residual water content of the dried films increased significantly above ($w = 0.05$) and remained constant from ($w = 0.08$) for films with higher casein content. In films prepared from solutions with casein content $w > 0.08$, casein micelles are deformed and densely packed as shown by AFM. The hexagonal distortion leads to a higher packing density, which may result in a higher evaporation barrier and residual water content.

Currently, we develop a sample environment to study the structure and dynamics of casein deposits on solid-liquid interfaces. For this purpose, we design microfluidic devices with imprinted membranes to allow in-situ observations with confocal fluorescence microscopy during the microfiltration process. Therefore, we covalently label the casein micelles with fluorescent dyes and investigate the colloidal stability of the labeled micelles. Furthermore, we want to investigate the influence of temperature on the fouling behavior of the filtration process.

[1] Kruif, C. G. de (1998): *Journal of Dairy Science* **81** (11), S. 3019–3028

[2] Olivares, M. L. et al. (2013): *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **436**, S. 337–342.

[3] Plamper, F.; Richtering, W. (2017): *Accounts of chemical research* **50** (2), S. 131–140.

mRNA-lipoplexes for controlled delivery in personalized cancer vaccines

Ziller Antje¹, Uebbing Lukas¹, Hühn Eva¹, Funari Sergio², Hartmann Hermann³,
Haas Heinrich⁴, Sahin Ugur⁴, Langguth Peter¹

¹ Institute of Pharmacy and Biochemistry, Johannes Gutenberg University, 55099 Mainz

² HASYLAB, 22607 Hamburg

³ Institute for Molecular Biophysics, Johannes Gutenberg University, 55099 Mainz

⁴ BioNTech RNA Pharmaceuticals, 55131 Mainz

mRNA-based drug products for cancer treatment have shown to be of particular interest. The ability to utilize the patients' own immune defence mechanisms for the fight against cancer has been a goal aimed for by many researchers, as it seems to be a promising alternative - or add-on - to classical chemo- and radiotherapy, but with a lower risk of side effects. [1] This work aims to fully characterize mRNA-delivering lipoplexes in order to understand targeting and release mechanisms and therefore gaining the ability to modify these parameters.

We characterized mRNA-containing lipoplexes using a combination of zeta potential measurements, differential scanning calorimetry (DSC), and small-angle X-ray scattering (SAXS). [2] We also determined free mRNA as an indication of encapsulated mRNA using the RiboGreen® RNA Assay (Life Technologies). SAXS measurements were performed at the A2 beamline at HASYLAB/DESY (German Electron Synchrotron, Hamburg, Germany).

We were able to derive a concise model for mRNA insertion into lipid matrices by combining the results from different methods of lipoplex characterization (see Figure 1). By measuring both pure EPC-liposomes, as well as adding increasing fractions of DOTAP and mRNA, a trend could be observed, that the measured lipoplex characteristics correspond to the overall charge of the lipoplex, which is dependent on the DOTAP/mRNA ratio (N/P ratio).

Increasing the amount of mRNA results in its full incorporation into lipoplexes, until a ratio of 1:1 is reached, leading to the conclusion that a binding of mRNA to cationic lipid occurred at this stoichiometric ratio. Accordingly, the overall charge of the lipoplexes is driven by the DOTAP/mRNA ratio, as shown by the observed zeta potentials. D-spacing, as measured by SAXS, was shown to be independent from the DOTAP molar fraction in the DOPC matrix, but dependent on the charge ratio. As long as DOTAP was present in excess, d-spacing resembles that of pure DOPC liposomes, but adding mRNA in excess lead to a monotonous increase in d-spacing. From the SAXS data we were also able to show that adding DOTAP to pure DOPC or EPC liposomes results in the loss of lamellar organization indicated by the absence of Bragg peaks. Adding negatively charged mRNA restores the lamellar organization and the Bragg peaks. The balance of repulsive and attractive forces between the positively charged lipid layers and the negatively charged RNA is considered the driving force for these structural coherencies.

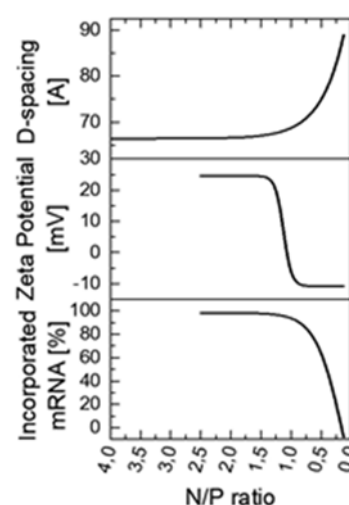


Figure 1. Basis for the derivative model

[1] Sahin et al., *Nature*. **547**(7662)222-226.

[2] Ziller et al., *Mol Pharm*. **15**(2)642-651.

Sulfur-based polymer nanocolloids

Fabian Uebel¹, Héloïse Thérien-Aubin¹ and Katharina Landfester¹¹ Max Planck Institute for Polymer Research, 10, Ackermannweg, 55116 Mainz, Germany

Sulfur is a versatile element which finds application in various modern fields but still remains an underused feedstock. However, a new generation of functional sulfur-based materials is being developed. The next generation of lithium batteries uses sulfur as cathode material providing energy densities surpassing the densities obtained in the common lithium-ion (Li-ion) batteries [1]. The high molar refraction of functional groups containing sulfur allows the synthesis of materials with high refractive indices [2], while the high transparency of sulfur-rich materials in the IR region enables the use of sulfur in IR optical materials [3]. However, these applications do either only need minute amounts of sulfur or are in an early stage of development. Therefore, new strategies to convert the unused sulfur feedstock into valuable functional materials are needed.

We have synthesized and characterized novel sulfur-based polymer nanocolloids prepared from elemental sulfur (Figure 1 b), by introducing the techniques of miniemulsion (Figure 1 a). The utilization of a suitable system (surfactant, solvent and co-monomer) lead to sulfur-rich particles of nanometer scale (Figure 1 c). The effect of different co-monomers and different co-monomer concentrations on the resulting sulfur particles was studied by characterizing particle diameter, morphology and glass transition temperature. Optimization of reaction parameters such as reaction time, sonication time and purifications steps was performed. Characterization of the optical and electrochemical properties of the sulfur nanoparticles was carried out. The nanoparticles obtained could be easily processed in preparation of thin sulfur films allowing the analysis of electrical conductivity with a four-point-probe.

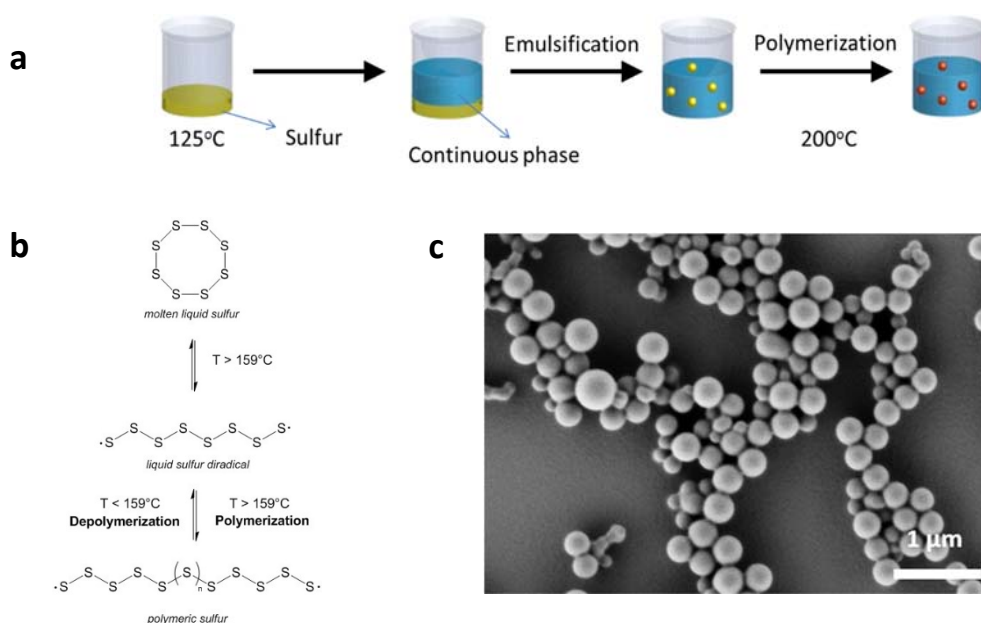


Figure 1: A) Miniemulsion technique to obtain polymeric sulfur particles, B) equilibrium reactions of sulfur at high temperature resulting in linear sulfur polymer, C) SEM image of obtained sulfur particles of nanometer scale

- [1] Yin, Y.-X., et al., *Angewandte Chemie*, 2013. **125**(50): p. 13426-13441.
 [2] Liu, J.-g. and M. Ueda, *Journal of Materials Chemistry*, 2009. **19**(47): p. 8907.
 [3] Griebel, J.J., et al. *Adv Mater*, 2014. **26**(19): p. 3014-8.

The influence of a temperature-responsive polymer brush on the Brownian motion of a microbead

David van Duinen¹, Dominik Pilat¹, Hans-Jürgen Butt¹, and Rüdiger Berger¹

¹ *Physics at Interfaces, Max Planck Institute for Polymer Research, Mainz, Germany*

On this poster, we present on a simple method that allows characterising a polymer brush layer. The brush is between a micrometer sized bead and a planar surface, in which the bead sticks to the wall due to the brush. By analysing the Brownian motion of the bead, mechanical properties of the brush have been determined. Our polymer layer is a linear brush of poly(N-isopropylacrylamide) (PNIPAM), with a reversible coil-to-globule transition at its lower critical solution temperature (LCST). Applications of such brushes have been envisioned in medical and biological fields.

We have used a reflection interference technique to investigate the Brownian motion of individual microbeads at temperatures above and below the LCST. The incident laser light reflects off both interfaces: bead and surface. The reflected light's intensity depends on the distance between the bead and surface. The beads stick to the surface; the bead's motion can be described with an overdamped spring model. The spring constant of the bead-surface system is obtained by analysing the power spectrum of the reflected light. We found that the spring constant increases by at least one order of magnitude upon PNIPAM collapse.

Acknowledgement: David van Duinen acknowledges funding from the ERC SuPro grant number 340391.

Analysis and modelling of icing of engines' air intake protection grid structures

Vittorio Vercillo¹, Alexandre Laroche¹, Javier Alejandro Mayèn Guillèn¹, Norbert Karpen¹, Raphael De Andrade Jorge², and Dr. Elmar Bonaccorso¹

¹ Airbus Central Research & Technology, Materials X, Ottobrunn, Germany.

² University of Sao Paulo, Engineering School of Sao Carlos, Sao Paulo, Brazil.

Icing represents a major problem in the aviation industry. While icing of common components such as airfoils due to the impingement of (supercooled) liquid water droplets is widely studied, even if not yet fully understood, supporting structures like grids on engine air intakes have been investigated to a lesser extent (Figure 1) [1]. An optimization of these protection grids will lead to reduce icing severity and, subsequently, to avoid loss of efficiency and safety issues that can lead to hazardous situations [2].



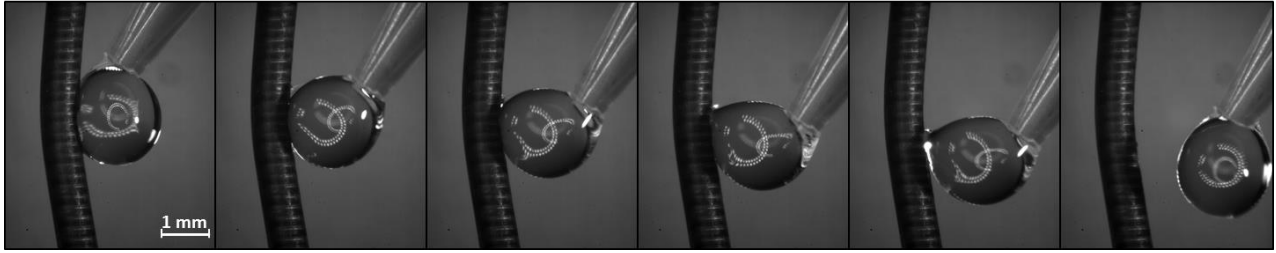
[3]

Figure 1. Helicopter air intake protection grids of the AIRBUS H 225 of the SuperPuma family and their icing. (Airbus Helicopters).

The presented study investigates the icing behaviour of steel grids in use on helicopters and turboprop engines through the development of new analytical tools that enables a quantitative study of the icing phenomena of such structures. Additionally, an ice accretion model is hereby proposed and different surface treatments, e.g. short/ultra-short laser treatments as showed in Figure 2, are investigated to improve the passive icing protection properties of these components. The experimental work is carried out in the Airbus' lab-sized icing wind tunnel iCORE (icing and CONtamination REsearch facility). A variation of the most relevant parameters, i.e. air stream velocity, air temperature, angle of attack, liquid water content of the cloud and mesh size of the grid, will allow identifying their influence on the icing behaviour of the grid components. After comparing the icing behaviours of the different surface treatments, the best solution could be selected.



(a)



(b)

Figure 2. Water droplet interacting with: (a) untreated stainless steel; (b) Direct Laser Interference Patterning (DLIP) treated stainless steel.

References:

- [1] J. Helbach, Empirical Investigation on the Icing Behaviour of Grid Structures in a Lab-scale Icing Wind Tunnel, Bachelor Thesis submitted to the Institute of Product Development and Design at Hochschule Koblenz, Germany (2015).
- [2] N. Karpen, Empirical Investigation on the Icing and De-icing Behaviour of Grid Structures in a Lab-scale Icing Wind Tunnel, Bachelor Thesis submitted to the Institute of Aerodynamics and Chair of Fluid Mechanics at RWTH Aachen, Germany (2016).
- [3] Transport Canada: <https://www.tc.gc.ca/eng/civilaviation/publications/tp185-4-07-winter-operations-4043.htm>

Acknowledgement: The authors acknowledge J. Helbach and R. Entz for their contribution, and A. Aguilar, A. Garcia Giron and J. M. Romano for the Manufacturing of the samples. Part of this work was carried out in the framework of the LASER4FUN project (laser4fun.eu), which has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 675063.

Creation of submicron patterns by using microcontact printing for plasmonic templates

Xuepu Wang^{1,2}, Dr. Nikolay Puretskiy¹, and Prof. Alexander Böker^{1,2}

¹ Fraunhofer Institute for Applied Polymer Research IAP, Geiselbergstr. 69, 14476 Potsdam-Golm, Germany

² Chair of Polymer Materials and Polymer Technology, University of Potsdam, 14476 Potsdam-Golm, Germany.

The elastomeric poly(dimethylsiloxane) (PDMS) bilayer wrinkled films were used for the surface pattern with the formation of complex structures. This process is also known as soft lithography [1, 2]. The alignment of metallic nanoparticles and nanorods on polymer patterns has been investigated, since these nano-objects could be used in photonics, integrated circuits and sensors [3, 4]. First soft lithography with hydrophobic ink was developed to produce alternating stripe patterns, and the precise placement of gold nanoparticles (AuNPs) and gold nanorods (AuNRs) on these patterns was investigated systematically.

Then a series of polystyrene-poly(2-vinylpyridine) (PS-P2VP) patterns were created by microcontact printing, and the period of PS-P2VP could vary from several micrometers to submicron scale by tuning the wavelength of PDMS wrinkle. To form positively charged PS-P2VP patterns (PS-P2VP⁺), the P2VP domains were quarternized with 1, 4-diiodobutane. Different kinds of gold nanoparticles (AuNPs) and gold nanorods (AuNRs) were synthesized by seed-growth method and modified with negatively charged ligands (AuNPs⁻ and AuNRs⁻). AuNPs⁻ and AuNRs⁻ were selectively deposited on PS-P2VP⁺ patterns through electrostatic interaction. Widths of P2VP domains, quantity of AuNPs and AuNRs adsorbed on the surface and surface charge density of patterns were investigated.

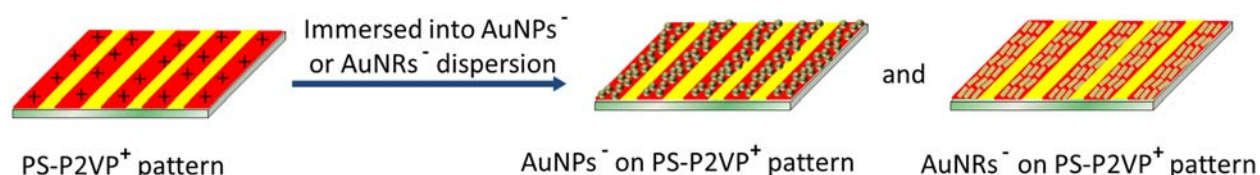


Figure 1. Illustration of nanoparticles / nanorods arrays after depositon on modified polystyrene-poly(2-vinylpyridine) (PS-P2VP⁺) pattern.

[1] M. Pretzl, A. Böker, A. Fery, et al. *Langmuir* **24** (2008), 12748.

[2] A. Horn, A. Fery, A. Böker, et al. *Small* **6** (2010), 2122.

[3] T. Wagner, R. Shenhar, A. Böker, et al. *Polym. Adv. Technol.* **28** (2017), 623.

[4] E. Michman, R. Shenhar, *Polym. Adv. Technol.* **28** (2017), 613.

Acknowledgement: The research leading to these results has received funding by the European Research Council (Replicoll; Project 64d8365) and the Volkswagen foundation (FR: 91 791). Also many thanks are given to China Scholarship Council (CSC) for the PhD scholarship.

Durable Transparent Superhydrophobic Surfaces via Sprayable Interpenetrated Polymer Networks

William S. Y. Wong^{1,2}, Zbigniew Stachurski¹, Antonio Tricoli¹, Vincent Craig¹

¹ Research School of Engineering, The Australian National University, Australia

² Max Planck Institute for Polymer Research, Germany

Since the advent of biomimetics, superhydrophobic plants [1,2] have received much industrial and research interest [3]. Their natural durability stems partly from the strongly cohesive properties of multi-scale organic tissue. Today, although a myriad of synthetic variants has been achieved, real-world impact continues to be diminished by the poor chemical-structural stability of nano-microstructures required for retaining superhydrophobic states [6]. Here, we present a bi-layer composite design that biomimics the soft but tough nature of organic tissues in plants, enabling enhanced abrasion resistance. This was achieved by a self-stabilized, sprayable polyurethane-acrylic colloid (Fig. 1) [7].

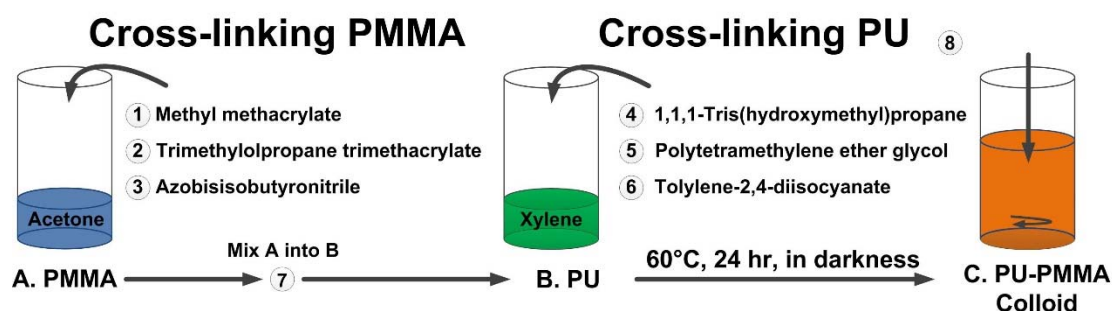


Figure 1. Synthesis of a sprayable stable PU-PMMA pre-IPN colloid.

Upon spray-forming, the colloidal solution self-assembles into a micro-roughened surface that is reminiscent of the epidermal layers of superhydrophobic plants. During the same process, the pre-polymer undergoes complete interpenetration, forming stable; tough and elastic interpenetrated polymer networks (IPNs) [7]. The sequential deposition and integration of a superhydrophobic nanomaterial facilely imparts superhydrophobic functionalities. These hierarchically textured superhydrophobic IPN films demonstrate enhanced thermal-mechanical, abrasion, chemical and photo-stability.

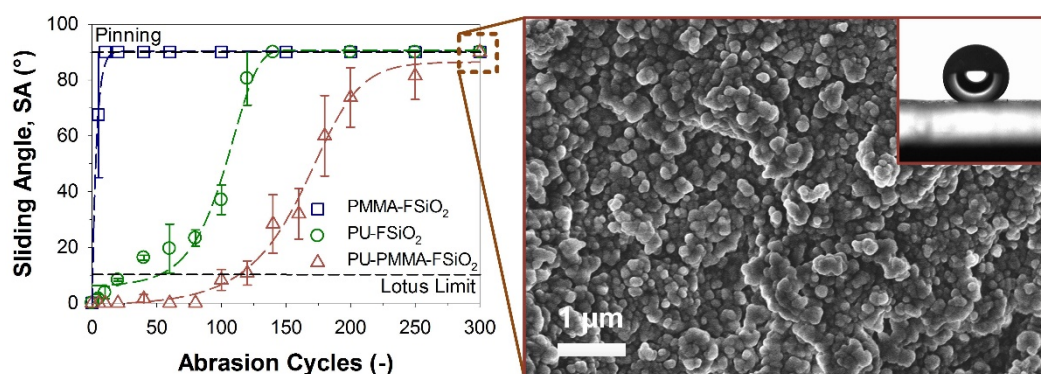


Figure 2. Abrasion resistant superhydrophobic PU-PMMA-based interface vs. controls

References

- [1] Barthlott, W.; Neinhuis, C., *Planta* **202** (1997), 1-8.
- [2] Wong, W. S. Y., et al., *Adv. Mater. Interfaces* **2** (2015), doi: 10.1002/admi.201500071.
- [3] Jiang, L., et al., *Angew. Chem. Int. Ed.* **43** (2004), 4338-4341.
- [4] Xue, F., et al., *J. Mater. Chem. A* **3** (2015), 13856-13863.
- [5] Lu, Y., et al., *Science* **347** (2015), 1132-1135.
- [6] Liu, G., et al., *Nanoscale* **8** (2016), 6085-6093.
- [7] Wong, W. S. Y., et al., *ACS Appl. Mater. Interfaces* (2016), 10.1021/acsami.6b03414.

Unlimited Reconfiguring Surface Functions Using Visible-Light-Controlled Metal-Ligand Coordination

Chaoming Xie^{1,2}, Wen Sun¹, Annika Kretzschmann¹, Sarah Backfisch¹, Xu Deng^{1,2*}, Hans-Jürgen Butt¹, and Si Wu^{1*}

¹ Max Planck Institute for Polymer Research, Mainz, Germany

² Institute of Fundamental and Frontier Sciences, University of Electronic Science and Technology of China, Chengdu, China

Spatially and temporally manipulating surface properties by light is highly important for a variety of advanced applications. However, most of the reported photoreactions are irreversible or triggered by UV light, resulting in static and limited surface functions. Herein, we demonstrate the construction of a dynamic surface, which can be interconverted among an unlimited number of functions, using visible-light-controlled metal-ligand coordination. In our design, the Ru complex (Ru-H₂O) acts as the molecular “multi-bit screwdriver”; the thioethers with different functional groups (S-R₁, S-R₂, S-R₃...S-R_n) act as the molecular “bits” (Fig. 1a). The removal of the “bit” on the “screwdriver” is driven by visible light via photosubstitution, while the attachment of another “bit” to the “screwdriver” is achieved automatically in the dark via thermal substitution. To construct a dynamic surface with interconvertible functions, Ru-H₂O is grafted onto a substrate (Fig. 1b). Substitution of the coordinated H₂O molecule in Ru-H₂O with the thioether (S-R₁) endows the surface with the function of R₁ (Step 1 in Fig. 1b). To change the surface function to R₂, S-R₁ is substituted by H₂O under light irradiation (Step 2) and the coordinated H₂O is substituted by S-R₂ in the dark (Step 3). The surface can be interconverted among an unlimited number of functions using different thioethers based on the approach in Fig. 1b. This new approach enables fabrication of reconfigurable and customized surface functions readily. We demonstrate rewriting surface patterns, manipulating protein adsorption, and controlling wettability based on visible-light-controlled metal-ligand coordination [1].

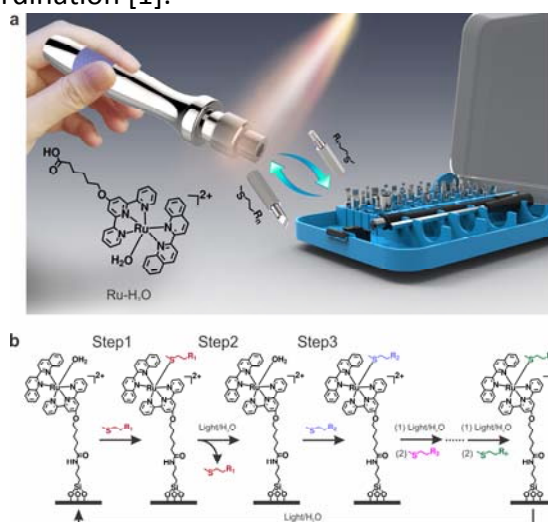


Figure 1 (a) Schematic diagram of the visible-light-controlled reconfigurable multi-functionalized platform. The Ru-H₂O can be used as a “screwdriver”, which can change its function through replacing the “bits” (thioethers with different functional groups) by visible light irradiation. (b) The mechanism of the dynamic surface with interconvertible functions.

[1]C. Xie, S. Wen, et al. submitted

Mechanical property of water-air interface in superhydrophobic nanopores

Binyu Zhao¹, Youquan Jia², Xin Jiang², and Longquan Chen¹

¹ Institute of Fundamental and Frontier Sciences, University of Electronic Science and Technology of China, Chengdu 610054, China

² School of Mechanics and Engineering, Southwest Jiaotong University, Chengdu 610031, China

In the past decade, superhydrophobic surface, which refers to surfaces with ultralow surface energy, has attracted considerable attention for interfacial scientists and engineers, due to its potential applications in many technological processes. The mechanical stability of the water-air interface is the key to facilitate the static and dynamic superhydrophobicity [1-3]. In this work, we investigated the topography and mechanical property of water-air interface on nanoporous superhydrophobic surfaces using atomic force microscopy (AFM). The in-situ imaging revealed that the water-air interface in nanopores is soft and can be significantly deformed under high imaging forces (Fig. 1a). The stiffness of the interface increases with the decrease of the pore size (Fig. 1b). Moreover, a stick-slip behavior has been observed in the force-distance curve (Fig. 1c), which suggests that a threshold force should be exceeded to puncture the water-air interface using the AFM tip.

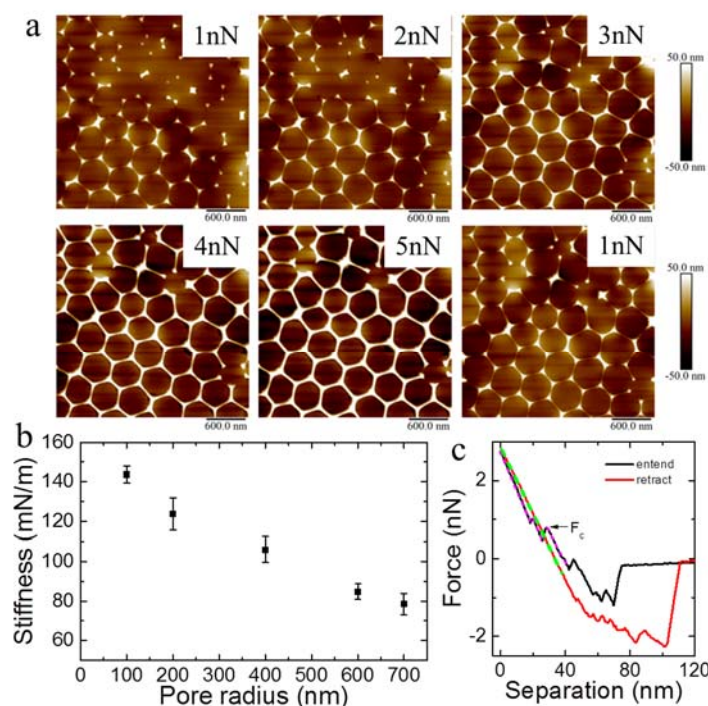


Figure 1. Mechanical stability of water-air interface. (a) In situ AFM height images of a nanoporous superhydrophobic surface in water under different forces; (b) size-dependence of the stiffness of the water-air interface; (c) a typical stick-slip force curve on the water-air interface.

[1] N. Vrancken et al., *Langmuir*, **33** (2017), 3601.

[2] C. Ran et al., *Langmuir*, **24** (2008), 9952.

[3] P. Chen et al., *Small*, **5** (2009), 908.

Acknowledgement: The authors acknowledge funding from the National Young 1000 Talents Plan and the National Natural Science Foundation of China (Grant Number 11772271).

Patchy Silica Particles via Micro Contact Printing

Marc Zimmermann¹², Dmitry Grigoriev¹, Nikolay Puretskiy¹ and Alexander Böker¹²

¹ Functional Protein Systems, Fraunhofer Institute for Applied Polymer Research IAP, Geiselbergstraße 69, 14476 Potsdam-Golm, Germany

² Polymer Materials and Polymer Technologies, University of Potsdam, 14476, Potsdam-Golm, Germany

The precise and selective modification of silica microparticles is a challenging task, which led to very different approaches over the years reaching from dip coating, etching processes and interface reactions in two phase systems [1 – 3].

Our group works with PDMS as a substrate for microcontact printing (μ CP). In comparison to other researches concerning μ CP of particles we work with polymeric inks instead of molecular inks, in particular with polyelectrolytes [4]. This gives us enhanced control over patch size, patch geometry (2D or 3D), pH dependent patch release and a new accessible volume for the incorporation of nano additives.

After printing, these patches can be modified with reversible (supramolecular) or irreversible crosslink chemistry (click reactions) to achieve the possibility of switchable colloidal assemblies. We were able to precisely functionalize the surface of silica particles in a size range between 5 μ m down to 1 μ m particles with a single or two opposite polyelectrolyte patches (see Fig. 1). Additionally we aim to create multivalent patchy particles which are not constrained to a high symmetry of the patches (e.g. 90° angle) by using our μ CP approach with a combination of structured and unstructured PDMS substrates.

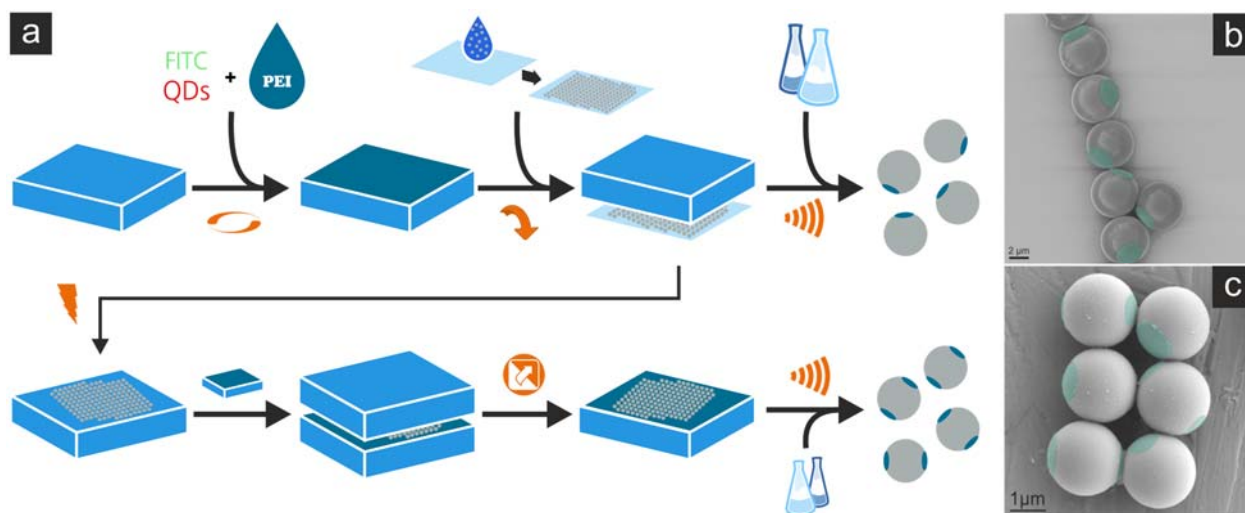


Figure 1 a) Visualization of our microcontact printing approach for single and double patched particles. b) SEM image of 5 μ m single patched particles. c) SEM image of 2 μ m double patched particle (Patches on image subsequently colored for better visualization).

[1] M. Sabapathy, et al., *Langmuir* **31** (2015), 1255.

[2] Z. Zhao, et al., *Langmuir* **28** (2012), 1382.

[3] S. Jiang, et al., *Adv. Mat.* **22** (2010), 1060.

[4] M. Zimmermann, et al., submitted.

Acknowledgement: The authors acknowledge funding from the European Research Council (RepliColl; Project 648365).

Social program

Social Program

Tuesday, April 10 at 18:00

Option 1 (max 30-35 persons)

Carnival Museum
Proviant-Magazin (Westeingang)
Neue Universitätsstr. 2
55116 Mainz

<http://www.mainzer-fastnachtsmuseum.de/>

The Mainz Carnival (*Mainzer Fastnacht*, „*Määnzer Fassenacht*“ or „*Meenzer Fassenacht*“) is a months-long citywide carnival celebration. It traditionally begins on 11 November and culminates in the days before Ash Wednesday in the spring. It is one of the largest carnival events in Germany.

The Carnival Museum in Mainz displays a hundred and sixty years of Mainz Carnival. From fools' caps, medals, guards' uniforms to excerpts from the German TV show "Mainz bleibt Mainz – wie es singt und lacht" (Mainz is Mainz as it sings and laughs), this exhibition presents a lively part of Mainz history and culture.



Social Program

Tuesday, April 10 at 18:00

Option 2 (German) and Option 3 (English) (max 60 persons)

Sightseeing tour of Mainz

Mainz for beginners: the golden Mainz and its sights

Meeting point: Domininformation

(Cathedral info point - <https://mainzerdom.bistummainz.de/dominformation-neu/>)

Marktportal, Markt 10, 55116 Mainz

Discover Mainz from an entirely new perspective, dive into the art, culture and history of the city, and enjoy the spellbinding charm of bygone times. A tour around town will take you to places with famous monuments in the footsteps of celebrities, and surprise you with unusual views of the city.



© Pedro Szekely, (CC BY-NC-SA 2.0)

Conference dinner

Conference dinner

Tuesday, April 10 at 19:30

In Proviantamt
Schillerstraße 11a
D-55116 Mainz

Encompassing more than 50,000 square feet, the Proviantamt is one of the few military structures from the era of the German Confederation, which are still preserved. The German Confederation (German: *Deutscher Bund*) was an association of 39 German states in Central Europe, created by the Congress of Vienna in 1815 to coordinate the economies of separate German-speaking countries and to replace the former Holy Roman Empire, which the French Emperor Napoleon I had brought to an end in 1805. The German Confederation fell apart after the Prussian victory in the Seven Weeks' War over Austria (also known as the Austro-Prussian War) of 1866.

In 1860's, a large number of soldiers were based in Mainz. It was thus necessary to draw plans for a new granary and an adjoining field bakery. A year later the original plans of the building were revised and simplified - the height of the stories was unceremoniously reduced to eight feet - in order to save on the horrendous building costs. Nonetheless, this measure did not make the building any cheaper. Four years later, the construction of the Proviantamt was finally completed. It was however never put to military use.

Inside this historic building in the center of Mainz, you will experience the tavern culture of Mainz and its hospitality – the Rheinhessen Tradition.



Organizers

The colloquium is organized by Dr. Günter Auernhammer (Leibniz-Institut für Polymerforschung Dresden e. V.) und Prof. Dr. Doris Vollmer (Max Planck Institute for Polymer Research) with the support of Natacha Bouvier (Max Planck Institute for Polymer Research).

The colloquium is supported by the Max Planck Institute for Polymer Research and the German Colloid Society.

Imprint

Max Planck Institute for Polymer Research
Postal Address: P.O. Box 3148
D-55021 Mainz
Ackermannweg 10
D-55128 Mainz
Email: info@mpip-mainz.mpg.de
Homepage: <http://www.mpip-mainz.mpg.de/>

All rights reserved (including those of translation into other languages). No part of the memory stick may be reproduced in any form - by photoprinting, microfilm, or any other means - nor transmitted or translated into a machine language without written permission from the publisher. Registered names, trademarks, etc. used in this memory stick, even when not specifically marked as such, are not to be considered unprotected by law.

The Zsigmondy team will not be responsible for any errors within the documents on this memory stick.

Thank you for visiting
homepage: www.zsigmondy2018.de
Your Zsigmondy Team