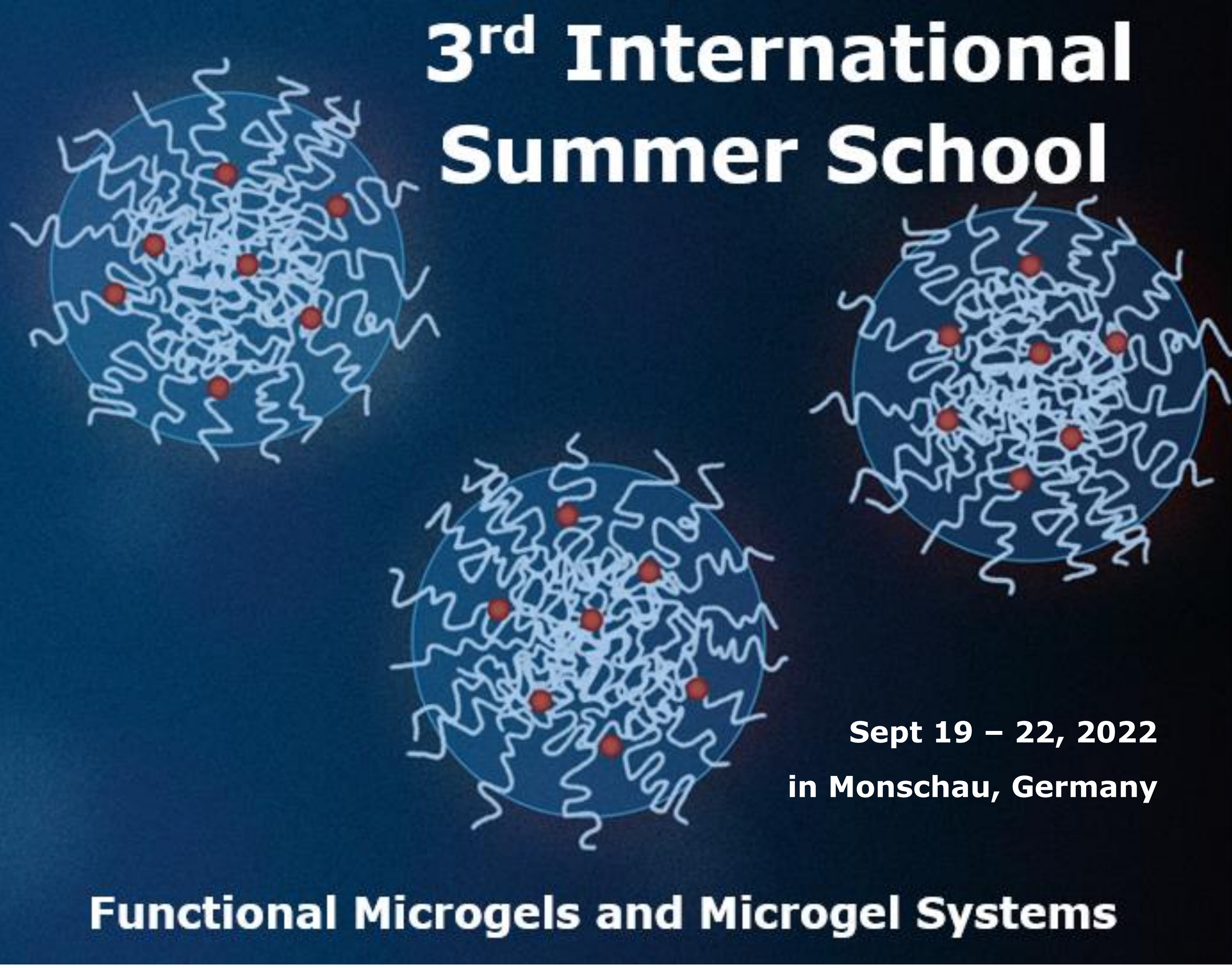


3rd International Summer School

Sept 19 – 22, 2022
in Monschau, Germany

Functional Microgels and Microgel Systems

Book of Abstracts

SFB 985

RWTH AACHEN UNIVERSITY

3rd International Summer School

Functional microgels and microgel systems are becoming of increasing importance in the chemistry community as well as for many other research areas from the point of view of possible applications. The school aims at presenting some of the current approaches in microgel synthesis, catalysis, characterization, modeling, and more.

This school will cover a wide class of models and applications including synthesis strategies for functionalized microgels, characterization techniques for microgels, computer simulations on different length scales, physical properties and behavior of microgels and microgel suspensions, as well as applications and uses of microgels across disciplines.

We hope you enjoy the school.

Speakers

Andrij Pich
RWTH Aachen University
Germany

Matthias Karg
Heinrich Heine University
Düsseldorf
Germany

Michel Cloitre
ESPCI Paris
France

Adel Mhamdi
RWTH Aachen University
Germany

Kai Leonhard
RWTH Aachen University
Germany

Emanuela Zaccarelli
Sapienza University of Rome
Italy

Igor Potemkin
RWTH Aachen University
Germany

Sonja Herres-Pawlis
RWTH Aachen University
Germany

Laura De Laporte
RWTH Aachen University
Germany

Judith Houston
European Spallation Source ESS
Sweden

Yuri Gerelli
Polytechnic University of Marche
Italy

Andrea Scotti
RWTH Aachen University
Germany

Alberto Fernandez-Nieves
University of Barcelona
Spain

Thomas Hellweg
Bielefeld University
Germany

Brian Saunders
The University of Manchester
United Kingdom

Jérôme Crassous
RWTH Aachen University
Germany

Organizers

Walter Richtering
RWTH Aachen University
Germany

Stefanie Schneider
RWTH Aachen University
Germany

Jenna Lynn Head
RWTH Aachen University
Germany

Table of Contents

Speakers

Posters – Monday

Posters – Tuesday

THIRD INTERNATIONAL SUMMER SCHOOL on Functional Microgels and Microgel Systems

September 19 – 22, 2022 in Monschau, Germany

Monday, September 19

09:00 Departure from Aachen

10:00 Registration/Coffee

10:45 Opening Remarks

11:00 **Engineering Crosslinks in Microgels: Towards Soft Adaptive Colloidal Systems**
Andrij Pich
(RWTH Aachen University)

12:00 **Core-Shell Microgels with Rigid Cores**
Matthias Karg
(Heinrich Heine University Düsseldorf)

13:00 Lunch

14:00 **Rheological Signatures of Softness in Microgel Suspensions**
Michel Cloitre
(ESPCI Paris)

15:00 Coffee and Check-In

15:45 **Model-Based Experimental Analysis of Microgel Synthesis: Valid Models at Minimal Effort**
Adel Mhamdi
(RWTH Aachen University)

16:45 **Physical Modelling of Thermodynamic and Kinetic Properties of Microgels and their Synthesis**
Kai Leonhard
(RWTH Aachen University)

18:00 Dinner

19:00 Posters I

Tuesday, September 20

08:30 **Computer Simulation of Realistic Microgels: from Individual to Collective Behavior**
Emanuela Zaccarelli
(Sapienza University)

09:30 **On the Nature of the High Elasticity and Swelling of Gels an Microgels**
Igor Potemkin
(RWTH Aachen University)

10:30 Coffee

11:00 **Tailored Metal Complexes for Oxidation, Polymerisation and Depolymerisation and their Anchoring in Microgels**
Sonja Herres-Pawlis
(RWTH Aachen University)

12:00 **Microgels to Solve Tissue Engineering Challenges**
Laura De Laporte
(RWTH Aachen University)

13:00 Lunch

14:30 - ~17:00 Hiking Tour

18:00 Dinner

19:00 Posters II

Wednesday, September 21

08:30 **Exploring the Structure of Microgels In Bulk Using Small-Angle Scattering**
Judith Houston
(European Spallation Source ESS)

09:30 **Microgels at Liquid Interfaces: What can Neutron Reflectometry Tell?**
Yuri Gerelli
(Polytechnic University of Marche, Ancona)

10:30 Coffee

11:00 **How Can We Define and Measure the Nanogel's Softness?**
Andrea Scotti
(RWTH Aachen University)

12:00 **The Ionic Cloud around "Neutral" Microgels: Its Importance and an Estimate Using SANS**
Alberto Fernandez-Nieves
(University of Barcelona)

13:00 Lunch

14:00 **Soft non-NIIPAM Based "Core-Shell" Microgels – Core-Shell vs. Interpenetrating Network Structure**
Thomas Hellweg
(Bielefeld University)

15:00 Coffee

16:00 Monschau Guided Tou

18:00 Dinner / Game Night

Thursday, September 22

08:30 Check-Out

09:00 **How Microgels can Provide New Types of Hydrogels and Improve the Performance of Solar Cells**
Brian Saunders
(The University of Manchester)

10:00 **Does Size Matter for Microgels?**
Jérôme J. Crassous
(RWTH Aachen University)

11:00 Coffee

11:30 **Phase Transitions in Dense Microgel Systems: Crystallization and Melting**
Janne-Mieke Meijer
(Eindhoven University)

12:30 Closing Remarks

13:00 Lunch

14:00 Bus leaving to Aachen

16:30 Guided Tour Aachen Cathedral

19:00 Farewell Dinner (IPC)

Train Station: Aachen West
Busses: 1, 1E, 3A, 3B, 30, 33, 41, 43, 43E, 73, 73E, 74

Staircase

Meeting point at IPC

This bridge is currently under construction and the way is completely blocked!

Busses: 12, 13A, 13B, 22, 23, E, V

For travel within the city, we can recommend the app **naveo** for the bus system.

A taxi from the main station should cost under 15€.

Monschau

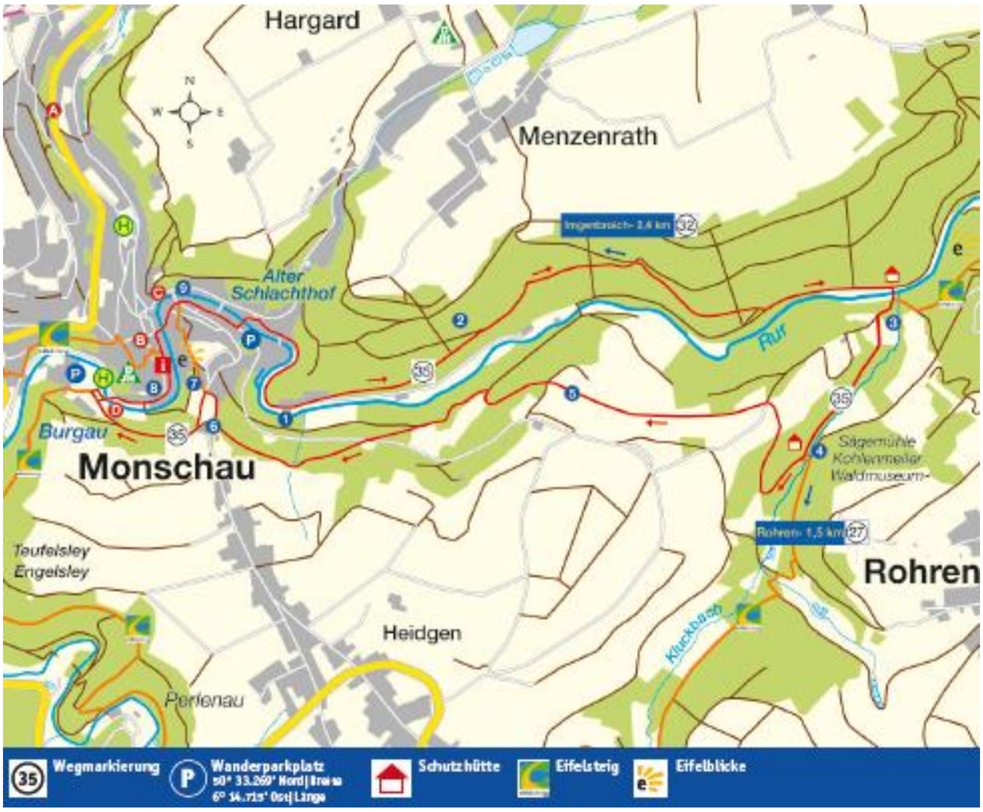
Monschau attracts many visitors with its picturesque views especially in the warm months. Set in the medieval town facility that is traversed by the river Rur, it is dominated by slate paneled and Tudor style houses with cafes, restaurants, craft and souvenir shops.

The town is located in the hills of the North Eifel, within the Hohes Venn – Eifel Nature Park in the narrow valley of the Rur river. The historic town center has many preserved half-timbered houses and narrow streets have remained nearly unchanged for 300 years, making the town a popular tourist attraction nowadays

– "Monshau," Wikimedia Foundation, 20.08.2022, en.wikipedia.org/wiki/Monschau

Hiking in Monschau

As a group activity, there will be a led hike through some of the beautiful trails in and surrounding Monschau. The route is marked below.



Speaker Abstracts

Engineering Crosslinks in Microgels: Towards Soft Adaptive Colloidal Systems

Andrij Pich[1]

[1]*DWI, Leibniz Institute for Interactive Materials e.V., Aachen, Germany*
Functional and Interactive Polymers, Institute of Technical and Macromolecular Chemistry, RWTH Aachen University, Aachen, Germany

pich@dwi.rwth-aachen.de

Biological tissues are frequently composed of macromolecular and low-molecular components, containing covalent and non-covalent crosslinks, and are assembled in a modular way exhibiting different hierarchy levels.[1] Such hydrogel-like materials often exhibit hysteresis effects and non-linearity of their properties, which is essential to functions like adaptability and time-programming. At present, the performance of synthetic hydrogel materials is not on par with these advanced biological hydrogels.

This contribution will focus on chemical design of stimuli-responsive microgels exhibiting no-covalent dynamic crosslinks based on host-guest complexes, ionic bonds or hydrogen bonds.[2-9] The development of new synthesis methods that allow controlled integration of supramolecular functionalities into microgels opens new ways to generate functional polymer materials and systems with unique functions like stimuli-responsiveness, re-shaping, and triggered disassembly.

Stimuli-responsive aqueous microgels containing degradable crosslinks based on the supramolecular host-guest complexes between β-cyclodextrin and cholesterol or ferrocene were synthesized.[2,3]

Microgels functionalized with zwitterionic units contain two types of crosslinks: -covalent and ionic.4,5,6 Monodisperse colloidally stable microgels with a high amount (> 30 mol-%) of zwitterionic groups were synthesized using W/O miniemulsion approach. High contents of zwitterionic groups in microgels led to the formation of dynamic reversible ionic crosslinks along with permanent covalent crosslinks generated by bisacrylamide. Obtained microgels exhibit temperature-triggered swelling/deswelling behavior and co-existence of UCST- and LCST-type transitions in aqueous solutions.

A new synthesis method to obtain aqueous supramolecular temperature-responsive microgels using tannic acid as multifunctional physical cross-linker was developed recently.[7,8] The precipitation polymerization of N-vinylcaprolactam in the presence of tannic acid leads to the formation of well-defined stimuli-responsive microgels cross-linked by hydrogen bonds. We demonstrate that obtained microgels exhibit reversible temperature-triggered swelling/deswelling and undergo pH-triggered degradation and re-shaping in aqueous solutions.

Microgels equipped with non-covalent crosslinks exhibit unique properties like on-demand degradation, controlled release of ions and small molecules and mechanical re-enforcement.[9]

Keywords: Microgels, Supramolecular Bonds, Soft Materials

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L2

Core-Shell Microgels with Rigid Cores

Matthias Karg[1]

[1] *Heinrich-Heine-University Düsseldorf, Institut für Physikalische Chemie 1: Kolloide und Nanooptik,*
Düsseldorf, Germany

karg@hhu.de

The surfactant-free precipitation polymerization is one of the most common synthesis routes used for the wet-chemical preparation of responsive microgels. When performed in presence of slightly hydrophobic nanoparticles (seeds), this approach can be used to prepare structurally well-defined core-shell (CS) microgels [1]. This seeded precipitation polymerization gives access to microgels with cores of different material, size and even shape and excellent control over the microgel shell thickness, even up to micron-sized total dimensions [2]. Such CS microgels (Fig. 1) are interesting for fundamental studies, for example with respect to crystallization, melting and jamming in dense packings (3D) [3] or confined at liquid interfaces (2D) [4], and also for applications, for example in sensing, optics and mechano-optical actuators. For such applications it is often required that the microgels are deposited on solid substrates, ideally with control over their arrangement and interparticle distance. A very powerful way to achieve this is the interface-mediated self-assembly using liquid interfaces [5].

In this contribution, CS microgels with rigid cores will be introduced focusing first on their general properties and methods of preparation. Then, the assembly and phase behavior at liquid interfaces will be discussed. I will show and discuss results form ex-situ and in-situ analysis of CS microgels at air/water interfaces under the influence of uniaxial compression. The combination of a classical Langmuir trough (LT) with small-angle light scattering (SALS) will be introduced as a powerful tool to monitor the behavior of colloidal monolayers in real time [6].

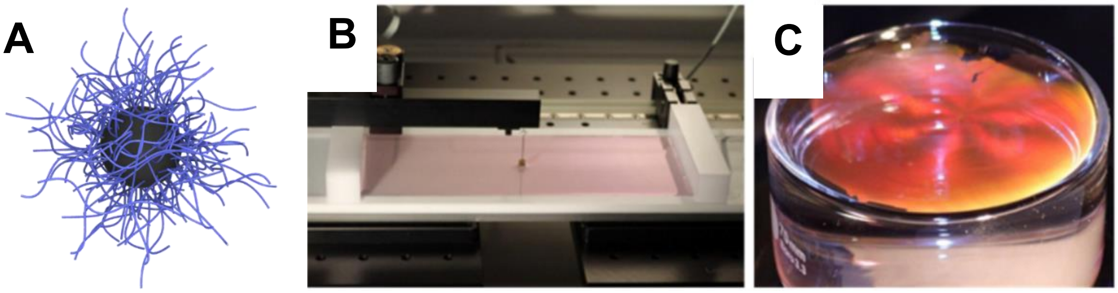

Figure 1. A: Schematic depiction of a core-shell microgel with a rigid, non-deformable core (black) and a soft, deformable and cross-linked microgel shell (blue lines). B: Monolayer of core-shell microgels at an air/water interface in a Langmuir trough. C: Freely-floating monolayer at the air/water interface in a crystallization dish.

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Acknowledgement: The author acknowledges funding from the German Research Foundation (DFG) under grant no.KA3880/6-1.

Rheological signature of softness in microgel suspensions

Michel Cloitre[1]

[1]*Molecular, Macromolecular Chemistry, and Materials*
ESPCI Paris, 10 rue Vauquelin, France

michel.cloitre@espci.psl.eu

Microgel particles constitute an important class of soft colloids, both for fundamental science and applications. They consist of a crosslinked polymeric network swollen by a solvent. Because of this architecture, microgels are partially impenetrable, just like hard colloids, but at the same time soft and deformable like polymers. They are central components of advanced functional colloidal materials, with promising applications for bioencapsulation and controlled targeted drug release, metal ion adsorption, photonic materials, and rheology control.

Nowadays, chemistry offers a panel of strategies to tune the internal architecture of microgels and their interactions. The number of crosslinks and their spatial distribution determines the local microstructure which can be homogeneous, core-shell, or even hairy, resulting in different manifestations of softness (*Curr. Opin. Colloid Interface Sci.* 19, 561, 2014). Microgels repel elastically and change their shape when they are in contact at high concentration. They swell and deswell under the action of external stimuli, or at high concentrations. Weakly crosslinked microgels with dangling hairs can interpenetrate at high concentrations. Finally, since microgel are inherently porous, they can host a variety of guest molecules such as surfactants and form soft composites, which are controlled by an interplay between entropic and enthalpic effects.

Rheology has emerged as an exquisite diagnostic tool for solid-liquid-solid transitions and for distinguishing metastable states such as gels and glasses. Actually, softness imparts a plethora of rheological phenomena and transitions in microgel suspensions and offers unprecedented opportunities for tailoring the flow properties with important implications in applications. We will discuss the impact of the microstructure on the yielding and flow properties of concentrated suspensions both at steady state and in transient situations. A wealth of nonlinear rheological features will be analyzed and rationalized: shear thinning, yielding and flow of glassy and jammed suspensions, wall slip and shear banding instabilities.

L 4

Model-based experimental analysis of microgel synthesis: valid models at minimal effort

Adel Mhamdi[1]

[1] *Process Systems Engineering, RWTH Aachen University, Lehrstuhl für Prozesstechnik, Turmstraße 46, D-52064 Aachen, Germany*

adel.mhamdi@avt.rwth-aachen.de

Microgels are novel functional polymers with diverse applications, such as liquid-liquid phase separation, switchable membranes, or drug delivery. The diverse applications require microgels with specific product properties that are determined during the microgel production process. Model-based methods are a potential engineering approach to design and operate efficient plants for the synthesis of functional microgels. Such model-based techniques require quantitative and predictive models that describe how the microgel synthesis conditions affect the properties of the microgel product.

In this lecture, we discuss the modeling process allowing to derive mechanistic models of the microgel synthesis to describe key microgel properties, such as microgel growth, the hydrodynamic microgel radius, the cross-linker density. We also introduce the model-based experimental analysis, which is an iterative methodology that allows to identify the models based on experimental data. The main ingredients are identifiability analysis, parameter estimation and experiment design.

In the lecture, we demonstrate briefly how such process model could be used to get optimal operation conditions, e.g. to determine fed-batch recipes based on dynamic optimization that allow for desired microgel properties, while maintaining the monomer conversion.

Physical Modelling of Thermodynamic and Kinetic Properties of Microgels and their Synthesis

Kai Leonhard[1]

[1]*Institute of Technical Thermodynamics, RWTH Aachen University, Schinkelstraße 8, 52062 Aachen, Germany*

kai.leonhard@ltt.rwth-aachen.de

The properties of stimuli-sensitive microgels are determined by their particular structure. Experimental investigations of many of these properties and the mechanisms causing them are possible, but sometimes cumbersome. Nevertheless, certain desirable experimental investigations at the microscopic scale are not possible at all. Therefore, simulation methods ranging from quantum mechanical (QM) simulations of molecular properties and of reactions in the condensed phase via molecular to mesoscopic simulations are a powerful tool to improve the understanding of microscopic effects. Methods for all three levels as well as their combination to bridge scales will be presented.

L 6

Computer Simulation of Realistic Microgels: from Individual to Collective Behavior

Emanuela Zaccarellli[1]

[1] *Dipartimento di Fisica, CNR-INFM-SOFT, Universita` di Roma La Sapienza, Piazzale A. Moro 2, 00185 Roma, Italy.*

emanuela.zaccarelli@cnr.it

In this talk I will briefly illustrate the protocol that we recently developed to synthesize microgels *in-silico*, that is able to provide a realistic description of the particles in bulk and at liquid-liquid interfaces. I will also describe how we can make hollow microgels and ultrasoft ones. Then, I will discuss the role of charges and, in particular, focus on the effect of the initiator molecules, which should accumulate on the periphery of the microgels, having an effect on the swelling behavior. Finally, I will move to first results of simulations of a few realistic microgels in suspension as a function of packing fraction, again highlighting the role of charges.

On the nature of the high elasticity and swelling of gels and microgels

Igor I. Potemkin[1,2], Rustam A. Gumerov[1,2], Mikhail V. Anakhov[1,2], Andrey A. Rudov[1,2], Vitaly S. Kravchenko[1], Stepan I. Zholudev[1], Ivan V. Portnov[1]

[1] *Physics Department, Lomonosov Moscow State University, Moscow, Russian Federation*
[2] *DWI-Leibniz Institute for Interactive Materials, Aachen, Germany*

potemkin@dwi.rwth-aachen.de

This lecture is addressed to diploma- and PhD-students working in the field of gels and microgels. We start with discussion of the basic physical principles behind the high elasticity of polymer networks (rubbers) and the ability of gels and microgels to swell and collapse. The lecture will be started from a quantitative description of high elasticity of a single polymer chain (very simple math. formalism!). Then the results will be generalized for a polymer network as an ensemble of cross-linked chains. Then we plan to discuss physical reasons for swelling and collapse of gels. Both neutral and polyelectrolyte gels will be considered. The difference in the swelling degree of polyelectrolyte and neutral gels will be discussed. Effects of counterions, their excluded volume and interaction with the network on the character of swelling-collapse transition will be discussed. Then we will consider swelling of gels and microgels in mixtures of two immiscible liquids (like oil and water) [1-3] and talk about peculiarities in swelling and collapse of cylindrical microgels (Fig. 1). Both, neutral and charged microgels will be considered [4].

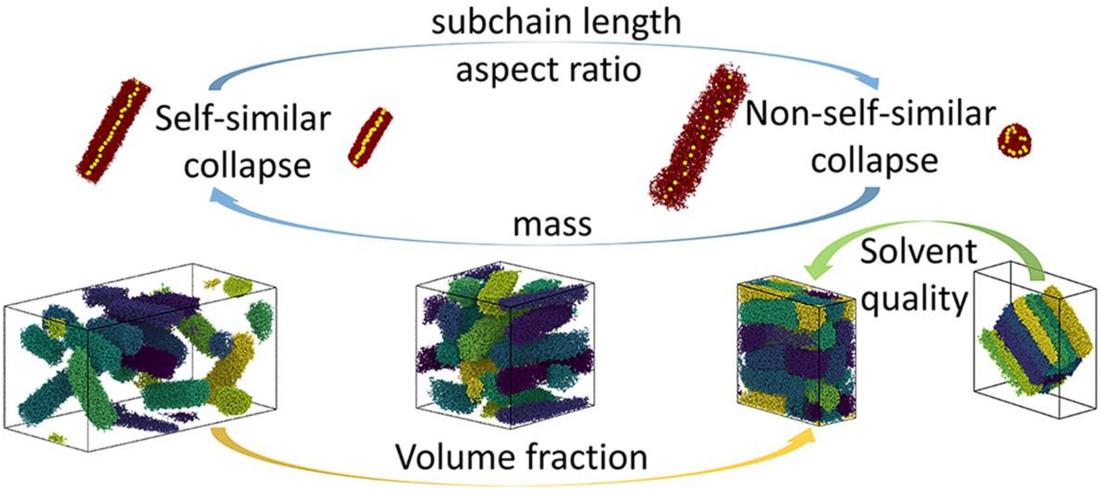

Figure 1. Self-similar and non-self-similar (rod-to-sphere) collapse of the cylindrical microgels caused by solvent worsening as revealed in computer simulations. The cylindrical microgels are capable of the nematic ordering upon concentrating.

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Acknowledgement: Financial support from SFB 985 "Functional Microgels and Microgel Systems" of the Deutsche Forschungsgemeinschaft and the Russian Science Foundation (project no. 21-73-30013) is gratefully acknowledged.

L 8

Tailored Metal Complexes for Oxidation, Polymerisation and Depolymerisation and Their Anchoring in Microgels

Sonja Herres-Pawlis[1]

[1] *Institut für Anorganische Chemie, RWTH Aachen University, Landoltweg 1a, 52074 Aachen, Germany*

sonja.herres-pawlis@ac.rwth-aachen.de

Metal complexes can be designed to act as catalysts for multiple reactions types - depending on their ligands, their donor strength, their spacers and many more influences. Our research group is active in the field of tyrosinase models, entatic state models, ATRP catalysts, ROP catalysts and depolymerisation catalysts using polyfunctional guanidines and bis(pyrazolyl)methanes. In this talk, the underlying principles of their reactivity and relation to each other are highlighted. Moreover, the challenges to anchor these systems in microgels AND transfer their reactivity are presented.

Microgels to Solve Tissue Engineering Challenges

Laura De Laporte[1]

[1]*DWI – Leibniz-Institute for Interactive Materials, 52074 Aachen, Germany*

delaporte@dwi.rwth-aachen.de

Tissue regeneration of sensitive tissues calls for injectable scaffolds, which are minimally invasive and offer minimal damage to the native tissues. However, most of these systems are inherently isotropic and do not mimic the complex hierarchically ordered nature of the native extracellular matrices. Moving forward from the conventional hydrogel systems, incorporation of engineered microgels could bring in the necessary complexity in tissue regenerative scaffolds. These microgels can be produced either by batch processes, such as Particle Replication in Non-wetting Templates (PRINT) or via semi-continuous production methods like microfluidics. One of the most important requirements for successful regeneration of tissues *in vivo* is to facilitate cell infiltration inside biomaterial scaffolds via the presence of sufficiently large pores. Porosity is also essential to allow diffusion of nutrients, oxygen, and growth factors and for the development of vasculature for tissue maturation and survival. Over the past few years, granular hydrogels or microporous annealed particle scaffolds have shown promise in creating macroporosity in injected scaffolds by tuning the microgel geometry, size, and reactivity. In addition, injectable and magnetoresponsive microgel rods can be used to form aligned structures to direct cellular growth. This approach is beneficial for cellular organization in aligned/hierarchical tissues. To mechanically stimulate cells, photothermally responsive microgels can potentially be added to dynamically actuate the cells inside 3D scaffold. Introducing movement into regenerative materials may result in more functional tissue by mimicking a more natural and realistic environment. Lastly, microgels can operate as local responsive drug depots in regenerative materials by incorporating drugs into the polymer matrix of the microgel, or encapsulating the drug in a separated hollow core. While the release can be varied through customizing the network porosity, internal and external triggers are useful to control the timing and location of release. As injectable materials are also pipettable and printable, microgels have also found their way into the fields of high-throughput hydrogel production to create *ex vivo* 3D cell and tissue models for potential drug testing and 3D bioprinting. By combining these complementary approaches, microgel-based injectable scaffolds could not only act as a supportive environment for an enhanced cell infiltration due to their macroporosity, but also actively promote and direct tissue repair during regeneration in a spatially and temporally controlled manner.

L 10

Exploring the structure of microgels in bulk using small-angle scattering

Judith Houston[1]

[1] *European Spallation Source ERIC, P.O. Box 176, 22100 Lund, Sweden*

judith.houston@ess.eu

The interactions and assembly behaviour of a microgel’s constituents in the nano-range, determine not only its structure at the nanoscale, but also directly influence its structure, rheology and functional properties at the macroscopic scale. Therefore, it is important to understand the relationship between the structural and functional properties of that material’s constituent components.

Small-angle X-ray and neutron scattering (SAXS/SANS) are ideal techniques to help us unravel complex soft matter structures on the 1-400 nm scale. While X-rays and light interact with the electron clouds of the atoms in a molecule, the specific properties of neutrons, such as their capability to distinguish light elements and their isotopes (e.g. ^{1}H (hydrogen) and ^{2}H (deuterium)), or their negligible absorption, make them particularly useful in the field of soft matter. Firstly, by selectively deuterating components of a complex material, we can create contrast in an otherwise homogenous system with only small changes in its physico-chemical properties. Such components can then be rendered effectively invisible in the measured coherent scattering data when combined with judicious selection of the solvent. Therefore, this method of contrast-variation enables full structural characterisation of not only the global structure, but also its constituent components and their interaction, which cannot be obtained by light or x-ray scattering. In addition, the comparatively weak interaction between neutrons and matter, enables them to penetrate most materials. As a result, we can design relatively complex sample environments for *in situ* studies with neutrons. This has powerful implications for studying the evolution of nanoscale structures in industrial processes, without the need for overly simplified model set-ups. Finally, their non-invasive nature makes neutron perfect to study bio-relevant material without radiation damage.

Furthermore, an object's bulk modulus quantifies its resistance to an isotropic compression. For soft deformable colloids, such as microgels, the bulk modulus must be known to predict their response to crowding. Here, after an introduction to the principles and potential applications of small-angle scattering, I will also present a new approach to exert osmotic stress on soft objects using partially-deuterated, high molecular weight polyethylene glycol (dPEG). In this study, microgels were used as a model system for soft compressible spheres and their bulk modulus is determined by means of SANS with contrast matching. By partial deuteration the scattering length density of the dPEG was matched in pure heavy water. Consequently, no contribution of the osmotic stress polymer is measured during the scattering experiments, and the form factor of the microgels was directly measured. Furthermore, in addition to the total radius, the variation of the different parts of the microgels can be also measured as a function of the external osmotic stress. Therefore, using this method the different elasticity along a single particle, such as proteins or viruses, can be determined directly.

L 11

Microgels at Liquid Interfaces: What can Neutron Reflectometry tell?

Yuri Gerelli[1]

[1] *Department of Life and Environmental Sciences, Marche Polytechnic University, 60131, Ancona, Italy*

y.gerelli@staff.univpm.it

Neutron and X-ray reflectometry (NR and XRR) are two techniques able to probe the structure of films deposited or adsorbed at various interfaces such as solid-air, liquid-air, solid-liquid, and liquid-liquid. In the case of disordered or unstructured films, the main information that can be derived from these experiments is a volume fraction profile of the sample along the direction perpendicular to the interface plane. Volume fraction profiles can be interpreted to determine the total thickness of the film, its morphology, roughness, and compactness as well as any internal structure or organisation with sub-nanometre resolution.

In the first part, the lecture will provide a description of NR and XRR fundamentals with special focus on the case of disordered colloidal systems. In the second part, the lecture will provide an in-depth description of a generalised algorithm for the analysis of experimental data as well as a discussion on the planning/optimisation of experiments for microgels at liquid-air interfaces.

L 12

How can we define and measure the nanogel's softness?

Andrea Scotti[1]

[1] *Institute of Physical Chemistry, RWTH Aachen University, Landoltweg 2, 52056 Aachen, Germany*

scotti@pc.rwth-aachen.de

In this lecture, I discuss what the term softness means. The focus is to quantify all the different definitions of softness and discuss how these affect the properties of individual nanogels and the macroscopic phase behavior of the suspensions. I will also discuss which experimental techniques can be used to measure the relevant quantities needed to quantify the different expressions of softness for nanogel suspensions, both in two and three dimensions.

The Ionic Cloud around “Neutral” Microgels: Its Importance and an Estimate Using SANS

Alberto Fernandez-Nieves[1]

[1]*Department of Condensed Matter Physics, University of Barcelona, 08028 Barcelona, Spain.*

a.fernandeznieves@ub.edu

We will discuss recent experiments where we attempt to access the properties of the ion cloud surrounding pNIPAM microgels. When in close proximity, clouds of different microgels overlap, effectively freeing the associated ions, which are then able to exert an osmotic pressure that can potentially cause microgel shrinking. The same effect is at play in charged hard colloids, where the ion cloud is known as electric double layer; however, in this case, the effectively infinite rigidity of the particles prevents any change in size and thus in suspension polydispersity. This this is not necessarily the case with compressible colloids. As a result, suspensions of compressible colloids do not have a quenched size distribution, a fact that can enrichen suspension behavior. We will discuss recent small angle neutron scattering experiments using ions with significantly different scattering contrast to access the signal of the ion cloud surrounding pNIPAM microgels and determine its properties.

L 14

Soft non-NIP AM based "core-shell" microgels - Core-shell vs. interpenetrating network structure

T. Hellweg[1]

[1]*Physikalische und Biophysikalische Chemie, Universität Bielefeld, Universitätsstr. 25, 33615 Bielefeld, Germany*

thomas.hellweg@uni-bielefeld.de

Since nearly 40 years so-called smart microgels are studied and the yearly number of published works on such systems exceeds 500. The most studied type of these colloidal gels is based on poly(*N*-isopropylacrylamide) (PNIPAM). However, recently also other acrylamides came into focus. All these microgels exhibit a so-called volume phase transition (VPT) at the lower critical solution temperature (LCST) of the respective polymer [1] leading to drastic changes in particle size. This behaviour grants them the adjective “smart” and makes them interesting as actuators or sensors in mesoscale devices or for drug delivery applications. The characteristics of microgels were reviewed recently [2].

The properties of such microgels can be varied in two ways. One is the use of comonomers e.g. to shift the LCST or to change the response with respect to pH and ionic strength. The second possibility is to change the architecture. The most prominent and most versatile example for this is the use of core shell systems [3,4].

The talk will focus on our recent contributions to the study of non-NIPAM based core-shell microgels. In this context, scattering experiments are of paramount importance and especially neutron scattering provides very interesting information about the internal structure of colloidal core-shell gels. This is related to the unique possibility to use contrast variation by employing deuterated monomers.

The focus of the talk will be on recent studies of the structure of core-shell microgels using neutron scattering (collaboration with Julian Oberdisse) [5].

Moreover, also some recent dSTORM results for non-NIPAM based core-shell microgels will be presented which are in line with the SANS results [6].

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How microgels can provide new types of hydrogels and improve the performance of solar cells

Brian R. Saunders[1]

[1]*Department of Materials, The University of Manchester, Manchester, UK*

brian.saunders@manchester.ac.uk

Microgels have excellent colloidal stability and are well suited to structural manipulation to introduce functional groups and/or alter their hydrophilicity/hydrophobicity balance. These abilities enable potential applications in healthcare and optoelectronics. Their colloidal stability enables them to be mixed with a wide range of solution additives to form new hydrogels or to be used as additives in solar cells. In this lecture fundamental principles and research examples will be presented encompassing the use of microgels to prepare new types of electrically conducting hydrogels and perovskite solar cells. In both cases it will be shown that the intrinsic properties of the microgels uniquely enable creation of these new advanced composite materials and strongly influence their properties.

L 16

Does size matter for microgels?

Jérôme J. Crassous[1]

[1] *Institute of Physical Chemistry, RWTH Aachen University, DE-52074 Aachen, Germany*

crassous@pc.rwth-aachen.de

Responsive microgels are swollen polymer networks which are highly sensitive to external stimuli following their degree of crosslinking and chemical composition [1-5]. Besides, they can be easily synthesized with various functional moieties and narrow size polydispersity. Their responsivity and intrinsic softness constitute the main ingredients for their applications in various fields such as drug delivery vehicles, smart emulsion stabilizers, actuators and sensors. Often considered as model systems for the soft colloids [1-5], understanding their properties in bulk and interface has been the focus of numerous studies often reporting dissimilar and even sometimes contradicting observations. However, when most of the current reviews have focused on the effect of the microgel composition, crosslinking and architecture [1-5], it appears to us that the influence of the microgel dimensions have not been clearly addressed yet. We will therefore ask ourselves whether size matters for microgels and discuss this question in diverse areas of the Soft Matter from the individual microgel properties in bulk and at interfaces to their collective behavior.

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L 17

Phase Transitions in Dense Microgels Systems: Crystallization and Melting

Janne-Mieke Meijer[1]

[1]*Soft Matter and Biological Physics, Department of Applied Physics, Eindhoven University of Technology, Eindhoven, The Netherlands*
Institute for Complex Molecular Systems (ICMS), Eindhoven University of Technology, Eindhoven, The Netherlands

j.m.meijer@tue.nl

In this lecture, I will address the phase behavior of dense colloidal suspensions. In general, colloidal suspensions can form many different phases, including fluids, crystals, glasses and gels. The phase behaviour is determined by the particle volume fraction and the interparticle interactions that can be tuned from hard to soft and from repulsive to attractive for both polymeric and microgel particles. I will address how these tuneable colloidal particles have been employed to investigate into microscopic structures and dynamics of the different phases. I will further address how the the availability of microgels made from thermoresponsive polymers allow one to change the volume fraction of the system with temperature in-situ. The availability of these thermoresponsive microgels have led to detailed microscopic studies into to the influence of volume fraction changes on the overall phase behaviour of the dense microgel suspensions including crystallization, melting and defect structures. In the last part of this lecture, I will discuss our recent investigations of the freezing and melting transitions in dense phases of composite core-shell microgels using Ultra Small Angle X-ray Scattering (USAXS) and confocal laser scanning microscopy, where we try to unravel the microscopic details of the phase transitions. I will also briefly address how we try to employ thermoresponsive microgels to study of defect diffusion and dynamics in colloidal crystals.

Poster Abstracts

Monday

Transient Yielding of Microgel Particle Glasses

Bruno Di Dio[1], Michel Cloitre[1]

[1] *Molecular, Macromolecular Chemistry, and Materials, ESPCI Paris, CNRS, PSL University, 10 Rue Vauquelin, 75005 Paris, France*

Soft particle glasses (SPGs) are densely-packed assemblies of soft and deformable particles dispersed in a solvent. These materials are characterized by a yield stress σ_Y below which the sample responds as a solid, and above which it flows like a liquid. Yielding properties of soft glasses are employed in many industrial formulations (coatings, cosmetics, pharmaceuticals…). Therefore, understanding and predicting how these systems deform and flow has important implications in their industrial processing and design.

Our investigations address the case of soft glasses made from microgel particles. We study their yielding properties by performing startup flow experiments, where a constant shear rate is applied to a sample initially maintained at rest and the transient stress response is monitored over time. On a fundamental level, the transient response of SPGs during a startup flow provide important insights into the microscopic mechanisms that drive the solid-to-liquid transition. However, the experimental characterization of SPGs poses specific challenges because of mechanical memory and physical aging effects [1]. In fact, the long-lived internal stresses and strains impart a directional bias inside the material, which remembers the last direction it has been sheared. Not secondarily, physical aging is responsible for the evolution of the material properties at quiescent state.

We present and discuss the results of startup flow experiments measured for different mechanical histories. A special attention has been given to the implementation of specific protocol to minimize mechanical memory effects. Our results provide a systematic and reliable way to determine of the transient response of SPGs without artefacts associated with uncontrolled mechanical preparation.

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M2

NMR Investigations on the Salt Dependent Volume Phase Transition of DNA-Modified pNipmam Microgels

Rebecca Hengsbach[1], Gerhard Fink[1], and Ulrich Simon[1]

[1] *Institut für Anorganische Chemie, RWTH Aachen University, Landoltweg 1a, 52074 Aachen, Germany*

The incorporation of short oligonucleotides (DNA) in thermoresponsive microgels (µG) enables multi-responsiveness on external stimuli. Such systems can be synthesized by a precipitation polymerization of the µG followed by a reduction step and the coupling of DNA via a thiol-ene reaction. DNA functionalized µG (DNA-µG) are considered promising for programmable loading and release of e.g. dyes, nanoparticles or biomolecules via DNA hybridization [1].

For these applications it is necessary to analyze the properties of the DNA-µG as well as of the µG under physiological conditions. The quantitative analysis of the volume phase transition temperature (VPTT) independent of unavoidable aggregation effects is enabled by temperature dependent ^{1}H-NMR spectroscopy. The VPTT is accompanied by a loss of mobility of the chains inside the µG which leads to a decreasing NMR signal, as documented for different µG before [1-3]. It was observed that the VPTT is shifted by the addition of salts [1,4]. In our work we investigated the differences between the VPTT of the µG and DNA-µG and analyzed both systems under physiological conditions which was done by measuring in phosphate buffered saline (PBS). Additionally, the systems were analyzed in 0.1 M and 0.14 M NaCl. We observed a shift of the VPTT from 40-42 °C in pure D_2O to 37-38 °C under physiological conditions which is in the range of the body temperature for both, µG and DNA-µG (Figure 1). We furthermore derived the corresponding thermodynamic values, which are associated with the phase transition. These results are very promising for triggered drug release, where a VPTT close to body temperature is desirable.

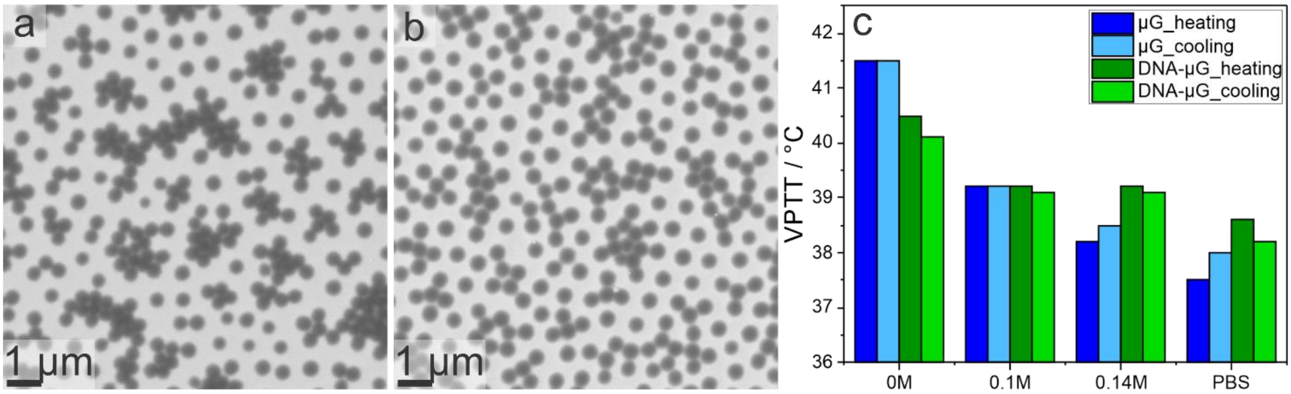

Figure 1. SEM images of the µG (a) and the DNA-µG (b) and dependency of the VPTT of the µG and DNA-µG on salt concentrations, determined by NMR measurements (c).

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Acknowledgement: The authors acknowledge funding from the German Research Foundation DFG for funding this work as a part of the project A6 in the SFB 985. Additionally, we thank Niklas Lothmann for the microgel synthesis and Pia Lenßen for optical microscopy images.

M3

pH-Responsive Supramacromolecular Gels with Tunable Size and Morphology via Droplet-based Microfluidics

Se-Hyeong Jung[1], Selin Bulut[1], Fabian Meyer[1], Sven Hönig[1], Michelle Bund[1], Bernhard Häßel[1], Luis Guerzoni[1], Laura De Laporte[1] and Andrij Pich[1]

[1] *DWI-Leibniz Institute for Interactive Materials e.V., Aachen, Germany*

Among the plethora of polymer networks, colloidal supramolecular hydrogels have raised strong interest in many scientific areas due to their wide applications depending on size, shape and internal structures as well as their responsibilities which can be controlled by introducing supramolecular functionalities.[1,2] The present work is dedicated to the design of supramacromolecular microgels and suprastructures with various morphologies (spherical, rod-shaped, cone-shaped, anisotropic hollow) and size via droplet-based microfluidics (**Fig. 1**).[3] The natural polyphenol tannic acid (TA) is used as a physical cross-linker which enables hydrogen bonding with the carbonyl group of the poly(*N*-vinylcaprolactam) (PVCL) chain. We synthesized a series of spherical microgels (different sizes and swelling degrees) at a fixed pre-polymer PVCL concentration with a variable content of tannic acid. Having identical chemical components with on-chip gelation, we could control the gelation on microfluidic devices and achieve rod-shaped microgels with tunable aspect ratios. Furthermore, supramolecular colloidosomes and suprastructures were fabricated by combining the advantages of self-assembly of small colloidal gels and microfluidics. Depending on the flow rates and microgel concentrations, different types of morphologies and internal architectures of the suprastructures were obtained. Since the cross-linking of the polymers are based on reversible supramolecular interactions (hydrogen bonds), the resulted colloidal gels show pH-responsiveness. Considering the non-covalent nature of the microgel networks, hollowness, controllable morphologies and pH-responsiveness, this microfluidic technology can become a powerful tool for the fabrication of colloidal gels for various applications.

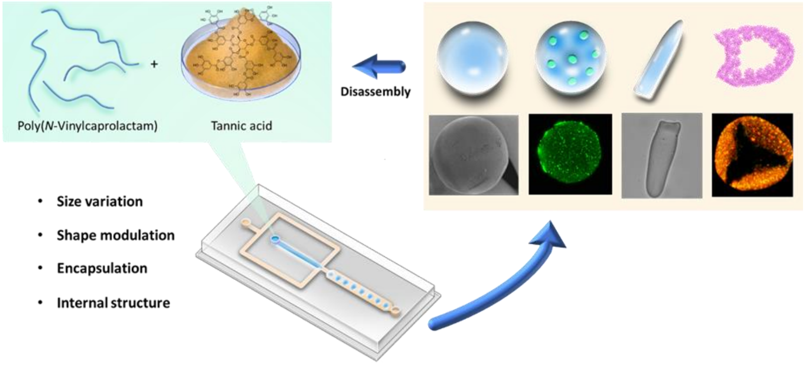

Figure 1. Fabrication of supramacromolecular microgels with tunable shape via microfluidics [3,4]

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Acknowledgement: Financial support of the Deutsche Forschungsgemeinschaft (DFG) within Collaborative Research Center SFB 985 "Functional Microgels and Microgel Systems" is gratefully acknowledged.

M4

Rheo-DLS Investigation of the Nonaffine Dynamics of Microgel Suspension

Chiara Marraffa[1], Michel Cloitre[1], and Stefano Aime[1]

[1] *Molecular, Macromolecular Chemistry, and Materials, ESPCI Paris, CNRS, PSL University, 10 Rue Vauquelin, 75005 Paris, France*

Yield Stress Fluids (YSFs) form an extensive and interesting area of soft matter. They are defined as materials that exhibit solid-like behavior at rest and flow when a large enough stress is applied. Soft Particle Glasses (SPGs) belong to this class of material. They are concentrated suspensions composed of deformable colloidal particles packed at large volume fractions even exceeding close-packing examples include concentrated emulsions, microgel pastes or star polymer solutions. Here we focus on SPGs made from stimuli responsive microgels above the jamming transition.

Experiments show that the flow curves are well described by the empirical Herschel-Bulkley equation. Recent particle-scale simulations suggest that the flow properties are intimately connected to the dynamics at the microscopic scale [1]. An outstanding challenge is to connect the macroscopic rheology and the microscopic dynamics.

In this work, we address the challenges related to understanding this connection coupling macroscopic rheology to the measurement of microscopic rearrangements at very small-scale, ideally resolving them in space and time [2]. In order to achieve this, we build a novel platform for the simultaneous measurement of the rheological properties and the microscopic nonaffine motion in microgel suspensions. This platform consists of a custom-made parallel-plate rheometer coupled to a dynamic light scattering setup. Moreover, we implement a data analysis protocol that allows us to measure particle motion along different directions with respect to the applied flow field.

We exploit this rheo-optical platform to investigate the nonaffine dynamics in microgel suspensions under steady shear flow and show that these dynamics change qualitatively upon yielding.

These preliminary results open new pathways for the investigation of the microscopic origin of yielding in YSFs.

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M5

Architectural Design of Polyampholyte Nanogel-in-Microgel Constructs

Hannah F. Blasius[1,2], Maria I. Pieper[1,2], Se-Hyeong Jung[1,2] and Andrij Pich[1,2,3]

[1] *Functional and Interactive Polymers, Institute of Technical and Macromolecular Chemistry, RWTH Aachen University, 52074 Aachen, Germany*

[2] *DWI-Leibniz Institute for Interactive Materials e.V., 52074 Aachen, Germany*

[3] *Maastricht Institute for Biobased Materials (AMIBM), Maastricht University, 6167 RD Geleen, The Netherlands*

Microgels containing transiently charged functions are promising candidates for the targeted uptake and release of medically active substances by electrostatic interaction [1]. For drug molecules such as Doxorubicin or small peptides like Cytochrome C, microgel-based delivery systems have already been investigated [2, 3]. Larger biomolecules, for example DNA or proteins, however, assemble into 3D structures that might not fit into the pore size constraints of conventional microgels [4].

In our work, we fabricate polyelectrolyte and polyampholyte nanogel-in-microgel (nG-in-µG) constructs that allow for targeted uptake and release of more complex proteins. First, pH-responsive polyelectrolyte nG based on *N*-isopropylacrylamide (NIPAAm) were synthesized by batch precipitation polymerization. Negative transient charges were implemented by copolymerization with methacrylic acid (MAAc) whereas positive transient charges were integrated using *N*-(3-aminopropyl)methacrylamide hydrochloride (AMPH). The obtained polyelectrolyte nG were labeled with two different fluorescent dyes and integrated into micron-sized P(NIPAAm) µG by subsequent inverse microemulsion polymerization via droplet-based microfluidics (Fig. 1). After purification, we analysed the nG-in-µG constructs by means of confocal laser scanning microscopy (CLSM) to verify incorporation of each nG species and investigate the internal structure of the microgels (Fig. 1, A-D). The nG-in-µG constructs were also examined regarding their swelling behavior in response to changes in pH, ionic strength and temperature.

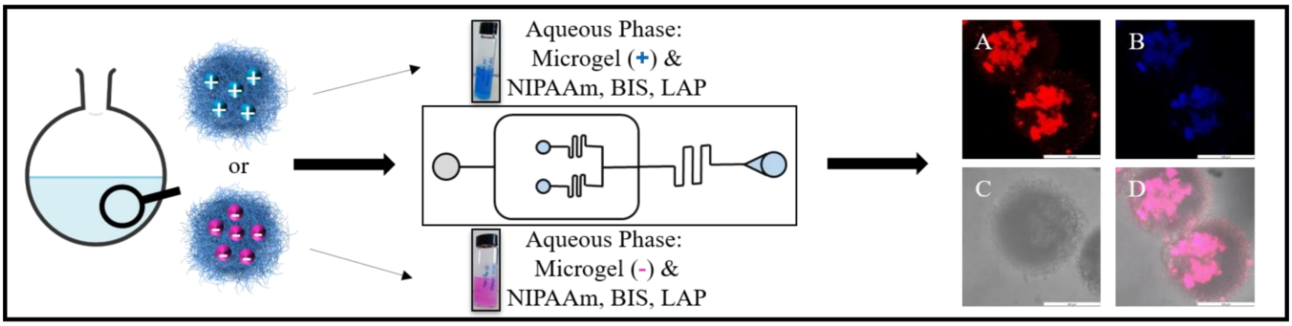

Figure 1. Schematic reaction procedure with precipitation polymerization (left), microfluidic channel (middle) and CLSM imagery (right). Nanogel dispersions were used at c = 10 mg mL^{-1}: P(NIPAAm-AMPH) nG labeled by postmodification with Cyanin5 derivative (top), P(NIPAAm-MAAc) nG labeled by copolymerization with Rhodamine B derivative (bottom). CLSM images show nG-in-µG constructs at λ = 575 – 620 nm (A), λ = 650 – 750 nm (B), in brightfield (C) and as an overlay (D); scale bar of 100 µm.

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Acknowledgement: The authors acknowledge funding from the Deutsche Forschungsgemeinschaft (DFG) within Collaborative Research Center SFB 985 “Functional Microgels and Microgel Systems”.

M6

Diarylethene-crosslinked photoswitchable Poly(N-vinylcaprolactam)-based microgels

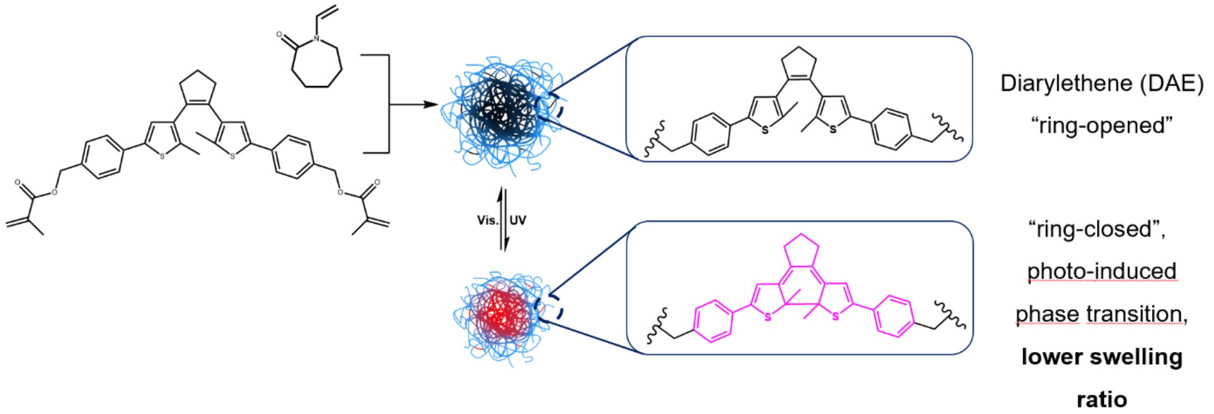
Siyang He[1, 2], Robert Göstl[1]

[1] *DWI – Leibniz Institute for Interactive Materials, Aachen, Germany*
[2] *Institute of Technical and Macromolecular Chemistry, RWTH Aachen University, Aachen, Germany*

Responsive microgels (μgels) are three-dimensional polymer networks which can react to external stimuli such as temperature, pH, and electrical field. These unique properties render μgels eligible for various applications: soft robotics, drug delivery, cancer therapy, and tissue engineering. Within the field of drug delivery, poly(N-vinylcaprolactam) (PVCL) has garnered particular attention since it exhibits a lower critical solution temperature (LCST) at about 32 °C in water, close to human body temperature. Above the LCST, PVCL is hydrophobic and insoluble, whereas it becomes soluble below this value. This property qualifies it as a targeted drug delivery agent capable of reacting to the different temperatures of normal and pathological tissues [1].

However, the reversible modulation of the mechanical properties of such μgels was rarely reported, although it can be assumed that properties, such as stiffness, elasticity, and toughness, contribute to the interaction of μgels with cells or tissues as well as distribution behavior within the blood stream [2]. Through the integration of a photoswitchable diarylethene (DAE), which can reversibly isomerize from the ring-open form to the ring-closed form by irradiation of light, as crosslinker into PVCL μgels, resulting in a photo-induced phase transition and therefore changes of mechanical properties, we aim to prepare μgels with photo-modulable mechanical properties such as for applications in mechanical cloaking systems. (Fig. 1).

Figure 1. Reversible photoisomerization of DAE-crosslinked PVCL μgels.



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Acknowledgement: The authors acknowledge funding from the Deutsche Forschungsgemeinschaft within SFB 985 Functional Microgels and Microgel Systems.

M 7

Microgels as Building Blocks to Bioengineer Tissue Constructs

Maritza M. Rovers$^{1\text{-}3}$, Annika F. Vrehen$^{1\text{-}3}$, and Patricia Y.W. Dankers$^{1\text{-}3}$

[1]Institute for Complex Molecular Systems, [2]Laboratory for Cell and Tissue Engineering and [3]Chemical Biology, Department of Biomedical Engineering, Eindhoven University of Technology, The Netherlands

Tissue engineering entails the combination of mechanical, chemical and biological components to process materials that can be engineered towards artificial tissue structures in order to mimic the extracellular matrix (ECM). The ECM provides cells with structural support as well as biochemical, biophysical, and mechanical cues. Biomaterials such as hydrogels have been studied as ECM-mimicking substrates by cell culture to assess the influence of material cues (e.g. stiffness, porosity, and adhesion-ligands) on cellular mechanisms. To study the cell-material interactions, cells could be encapsulated in a micro-hydrogel (microgel). Microgels can assemble into macroscopic aggregates, which are formed due to cell migration and proliferation from cells within the microgel to the surface where they interact with other microgels. This principle is attractive in the field of regenerative medicine because microgels are well-defined, biocompatible, resemble the natural ECM, can entrap cells, and have good regulation over biodegradability, porosity and mechanical properties. For this purpose, synthetic microgels were generated based on supramolecular ureido-pyrimidinone (UPy) molecules [1] using droplet microfluidics [2]. Two UPy-molecules can self-assemble by the formation of non-covalent complementary quadruple hydrogen bonds. Bioactivity can easily be introduced to the hydrogel system by a modular approach via the incorporation of UPy-functionalized additives, such as UPy-cRGD. The modularity of the UPy-hydrogel system provides the opportunity to create a variety of different microgel compositions, e.g. bioactivity, mechanics and dynamics.

Here we report the encapsulation of primary keratocytes in 2.5 w/v% microgels via droplet microfluidics. At the start, the cell encapsulation rate was 7.8% (1a). Then, the microgels assembled into macroscopic aggregates via cell interactions by cell migration and proliferation (1b). At day 10, the cells were fixated and stained for immunofluorescence microscopy (1 c&d). Cells were positive for α-sma (1d). Also, collagen 6 and tubulin β3 were expressed, the proliferation marker ki67 was expressed throughout the whole sample and YAP was localized in the nuclei (results not included).

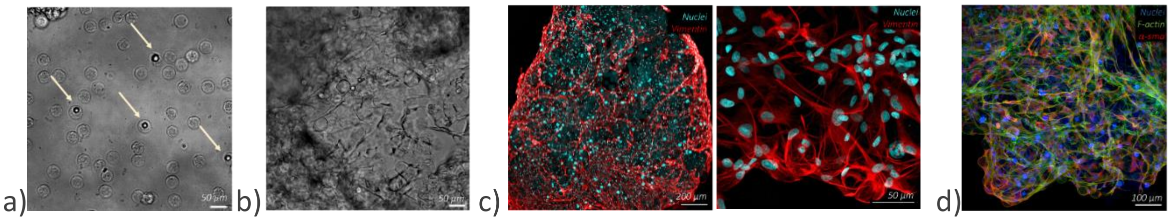

Figure 1. Brightfield images show a ~8% cell encapsulation rate (a) and a cell sheet was formed after 7 days of culture (b). Cells were fixated after 10 days and stained for fluorescence microscopy analysis.

To summarize, cell encapsulated UPy-based supramolecular microgels were successfully generated by droplet microfluidics and formed aggregates. In general, these microgels are easily tunable due to the modularity of the UPy-building blocks and allow it to be used as building blocks towards bioengineered tissue constructs.

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Acknowledgement: The authors acknowledge funding from the Dutch Research Council (NWO) and The Chemelot Institute for Science & Technology (InSciTe).

M 8

A study of injectable doubly crosslinked PEA-MAA/PNVF microgel gel composites

Xuelian Wang[1] and Brian Saunders[1]

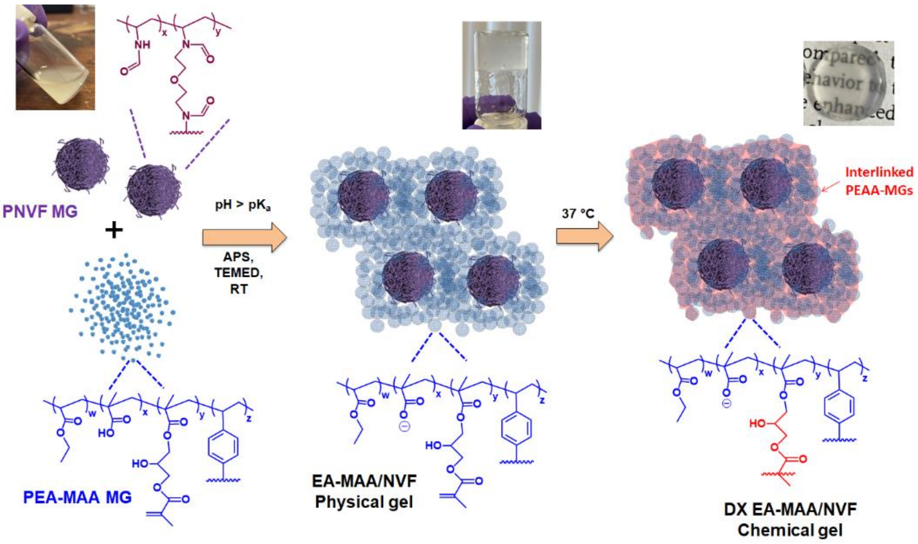
[1] *University of Manchester, School of Materials, Manchester, the United Kingdom.*

INTRODUCTION: Injectable hydrogels have great potential to repair damaged or degraded soft tissue because of the highly porous structure and large water content[1,2]. They are also potential new systems for intervertebral disc degeneration (IVD) treatment. Most practical applications, however, are constrained by cell not permeating through their small pore structure[1]. This is a major obstacle to the preparation of injectable doubly crosslinked microgels (DXMGs) that can promote and guide tissue growth. This study will introduce an injectable macroporous DXMGs that can remedy this limitation. DXMGs composed of poly(*N*-vinylformamide) (PNVF) and poly(ethylacrylate-*co*-methacrylic acid) (PEA-MAA) MGs and constructed with interconnected pores that are sufficiently large to enable cells to infiltrate the gels.

EXPERIMENTAL METHODS: DXMGs were formulated by mixing two microgels and adjusting pH to 7.4 and add initiator to form chemical crosslinking. They were characterised using a range of techniques including Dynamic light scattering (DLS), ^{1}H NMR spectra, scanning electron microscope (SEM) and Confocal scope. Dynamic rheology measurements and compression are used to characterise the mechanical property.

RESULTS & DISCUSSION: The morphology and mechanical properties of these novel injectable double cross-linked microgel composites were investigated. The results show that the mechanical properties can be adjusted by using PNVF MGs content. The fracture strain increases with the increase of NVF content, and the fracture stress decreases with the increase of NVF content. These new PH-responsive gels were shown to be injectable and to have very low cytotoxicity.

CONCLUSIONS: The data indicate that this new system may have good potential to be a platform for tissue growth. For the future work, more methods will be used to study these porous hydrogels.



Scheme 1. Synthesis of injectable macroporous doubly crosslinked microgels.

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M 9

Ionization Equilibria and Swelling Behaviour of Weak Polyampholyte Core-shell Microgels - A Monte Carlo Study

Christian Strauch[1], Stefanie Schneider[1]

[1] *Institute of Physical Chemistry, RWTH Aachen University, Landoltweg 2, DE-52056 Aachen, Germany*

The charge of polyampholyte microgels can be tuned by varying the pH, and a charge reversal from a positively charged microgel at low pH to a negatively charged microgel at high pH can be achieved. A swelling transition from a collapsed to a swollen state occurs when the pH is increased or decreased, starting from an intermediate value. While the ionization and swelling behaviour of microgels depend on many parameters coupled in experiments, simulations can systematically provide information about the influence of one particular parameter. Building on our earlier work on alternating polyampholyte microgels, we now investigated the pH-dependent ionization and the swelling behaviour of polyampholyte core-shell microgels using Monte Carlo simulations with the constant-pH method for a bead-spring polymer model[1,2]. While in many studies, the degree of ionization is a predefined input parameter, in our work, it is a direct result of the simulation.

In principle, the width of the U-shaped transition of the microgel swelling depends on the relative dissociation constants of acid and base[1]. Due to the spatial separation of acidic and basic monomers, the ionization is enhanced less compared to a microgel with an alternating distribution of the two species. Furthermore, we saw a shift of the isoelectric point caused by an increased charge density in the core. Added salt screens the charges within the network, and the U-shape transition becomes more narrow. Radial distribution functions show a clear core-shell structure both at low and high pH and a microgel collapse accompanied by a complete interpenetration of the shell and the core at intermediate pH values.

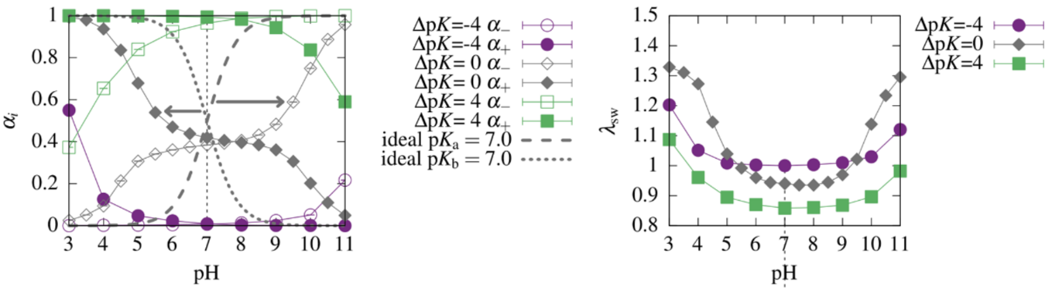

Figure 1. Degree of ionization as a function of pH and different Δp*K* (Δp*K*=-4: pK_a =9.0, pK_b=5.0; Δp*K*=0: pK_a =7.0, pK_b=7.0; Δp*K*=+4: pK_a =5.0, pK_b=9.0). Dotted lines represent the ionization of a system without interactions for pK_a=7.0 and pK_b=7.0 (left). Degree of swelling as a function of pH (right).

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Acknowledgements: Financial support from the Deutsche Forschungsgemeinschaft within the SFB 985 - Functional Microgels and Microgel Systems is acknowledged.

M 10

Effect of Machine-Learning Many-Body Interactions on the Phase Behavior of Soft-Repulsive Potentials

Susana Marín Aguilar[1], and Marjolein Dijkstra[2]

[1,2] Soft Condensed Matter, Debye Institute for Nanomaterials Science, Utrecht University, Princetonplein 5, 3584 CC Utrecht, The Netherlands

One of the main challenges in recent years in the soft matter community has been to establish the way microgel particles interact. One possible route is to approximate their interactions through pairwise additive soft repulsive potentials, such as the Hertzian pair potential. However, this approximation is only valid for small deformations [1]. Therefore, in the high-density regime, the Hertzian potential stops capturing the behavior of microgel particles. Moreover, the pairwise additivity assumption breaks down in the same regime, where the softness of the particles allows them to overlap or facet, and thus, many-body interactions play an important role.

Here, with the use of molecular simulations and machine-learning, I will show the effect of many-body interactions on the phase diagram of colloidal particles interacting with a soft repulsive potential, which present a rich reentrant crystalline phase diagram at low temperatures. To do so, I make use of a simple model of a core-shell particle (shown in Fig. 1), where its surface is discretized to capture the deformations due to multiple overlaps [2]. I will demonstrate that the addition of many-body interactions modifies the equation of state of the pair-potential at high densities and that extends the stability regimes of the crystalline phases towards higher temperatures.

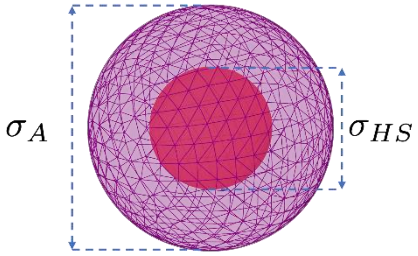

Figure 1: Schematic representation of a core-shell particle with diameter σ_A, where its core is model through a hard sphere of varying diameter σ_{HS}. The shell is discretized through a Voronoi construction to account for many-body deformations.

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M 11

Simulation of ionic microgels in concentrated suspension – How counter-ions influence the swelling behaviour

Tom Höfken[1], Stefanie Schneider[2], and Andrea Scotti[3]

[1] *Institute of Physical Chemistry RWTH Aachen, Germany*

Microgels, cross-linked polymer networks in the nano- to micrometre size range, are an important class of soft-matter materials. They have possible applications in drug delivery, catalysis or as a building block for smart materials and, therefore, have been investigated thoroughly in the last decades. Due to their soft nature, they deform under external stress, e.g., in a highly concentrated suspension of microgels. Microgels may respond by (i) isotropically deswelling, (ii) their dangling chain ends interpenetrating or (iii) faceting, changing their shape. It has been postulated that the origin of deswelling is an increase in osmotic pressure induced by the counter-ions of the microgel. To accurately calculate osmotic pressure and its effect, it is important to estimate the fraction of counter-ions that are "bound" in or near the microgel and how many counter-ions are "free" in solution and, therefore, contribute to osmotic pressure. We model these charged microgels using permeable spheres and perform Monte-Carlo simulations to gain insight into concentration dependent counter-ion distributions, electric potentials, and osmotic pressures.

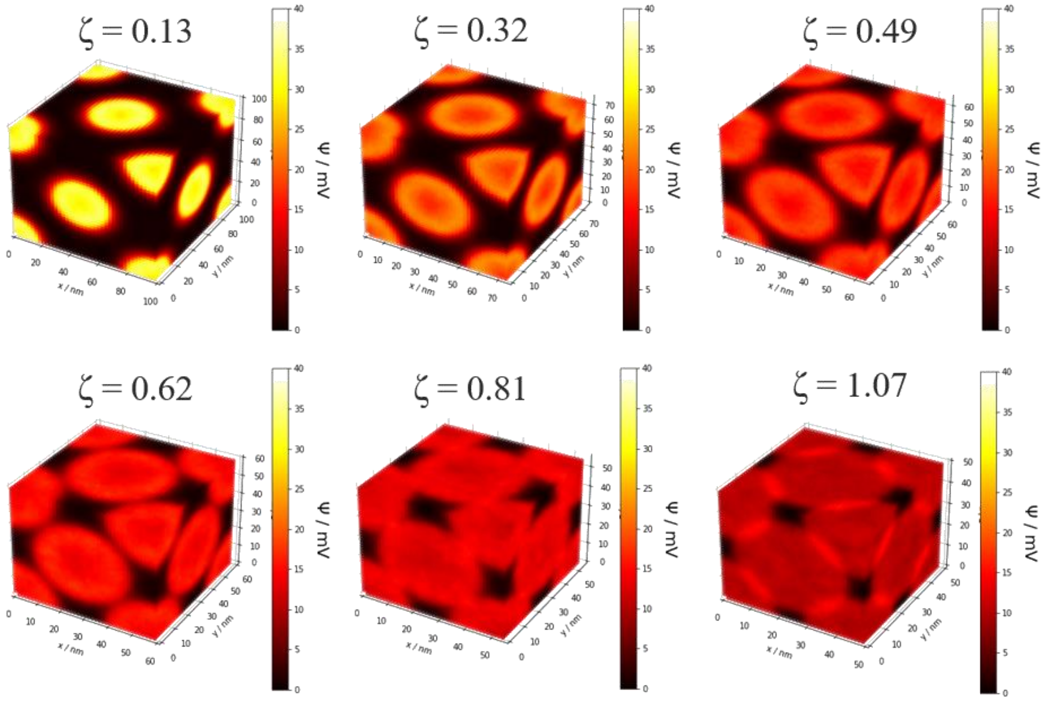

Figure 1: Electric potentials of microgel suspensions for varying generalized volume fractions.

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M 12

Effect of Temperature and Softness on *N*-Isopropylacrylamide-Based Microgels at Liquid Interfaces

Steffen Bochenek[1], Andrea Scotti[2], and Walter Richtering[3]

[1] *Institute of Physical Chemistry, RWTH Aachen University, Landoltweg 2, 52056 Aachen, Germany, European Union*

Microgels, spherical, three-dimensional crosslinked polymer networks,[1] are prospect materials for responsive or 'smart' emulsions, foams, and coatings. Tailoring them for these tasks requires a deep understanding of their phase behavior and structure at interfaces as a function of the environmental conditions, such as temperature, and the microgels' softness, i.e., their crosslinker content.

In this poster presentation, we summarize our work exploring the effects of their softness and of temperature on the interfacial properties of microgels. [2, 3, 4, 5, 6] This work has been carried out over the last 6 years in collaboration with many colleagues and partners around the world. By changing the crosslinker content, the shape of the microgels at the interfaces can be changed from the familiar core-corona structure [7] to a disk shape (Figure 1A). It also impacts on their phase behavior: Microgels synthesized with additional crosslinker, i.e., standard microgels, pack into ordered hexagonal lattices. In contrast, ultra-low crosslinked (ULC) microgels form disordered monolayers.[2] The thermo-responsiveness of standard microgels is perturbed at interfaces. The total lateral size of the standard microgels is determined by the surface tension and decreases in the same proportion with temperature as the latter. The core, however, can de-swell in both vertical and lateral dimension very similar to microgels in bulk.[3.4,6] The collapse of the core with temperature not only impacts their phase behavior, but also leads to a decrease in the repulsive interaction of microgel covered interfaces, as revealed by force measurements (Figure 1B).[3,5]

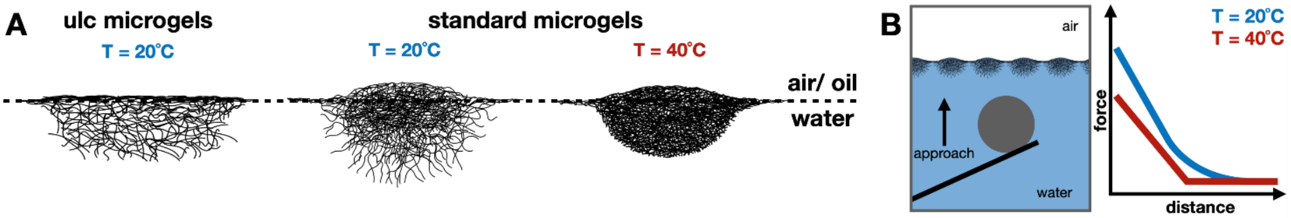

Figure 1. (A) Sketches of microgels with different crosslinker concentration at 20 and 40˚C at the liquid interface. (B) Sketch of force measurements at the air-water interfaces between a microgels monolayer and a functionalized colloidal probe and resulting force-distance curves at 20 and 40˚C.

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Acknowledgement: The authors acknowledge funding from the Deutsche Forschungsgemeinschaft within SFB 985 "Functional Microgels and Microgel Systems", projects A3 and B8.

Inducing defects in colloidal crystals

Max Schelling[1,2], and Janne-Mieke Meijer[1,2]

[1] *Soft Matter and Biological Physics, Department of Physics, Eindhoven University of Technology, Eindhoven, The Netherlands*
[2] *Institute for Complex Molecular Systems, Eindhoven University of Technology, Eindhoven, The Netherlands*

Crystal defects are imperfections that can occur in any crystalline material and can crucially influence the mechanical, structural, and optical properties of the material. Colloidal crystals are useful model systems to study defect phenomena due to their similarities with atomic/molecular crystal systems. Although defect structures in colloidal crystals have been addressed, little is known about how (point) defects interact and the mechanisms of their diffusion in 3D, due to the lack of experimental control over the defect formation.

The aim of this project is to develop a colloidal system in which defect formation in 3D crystals can be controlled in-situ. For this the aim is to embed thermoresponsive colloids in a crystal of non-responsive particles. By heating or cooling, the thermoresponsive particles can collapse or swell, and will subsequently induce vacancy-like defects or interstitials, respectively (Fig. 1a). To realize this system, we synthesized thermoresponsive colloids with a poly(*N*-isopropyl acrylamide) microgel shell and non-responsive poly(2,2,2-trifluoroethyl methacrylate) (pFEMA) core [1], and non-responsive core-shell pFEMA particles of the same size that can be refractive index matched. Using a confocal microscope equipped with a temperature-controlled stage, the mixed system is visualized on a single particle level (Fig. 1b). By changing the particle mixing ratios, volume fractions and temperature ramps, we have studied if point defects can be created upon switching. Using existing particle tracking and image analysis procedures, we will study if local stress- and strain-fields around these crystal defects can be visualized [2]. Ultimately, this project aims to provide fundamental insight into the formation and dynamics of defects.

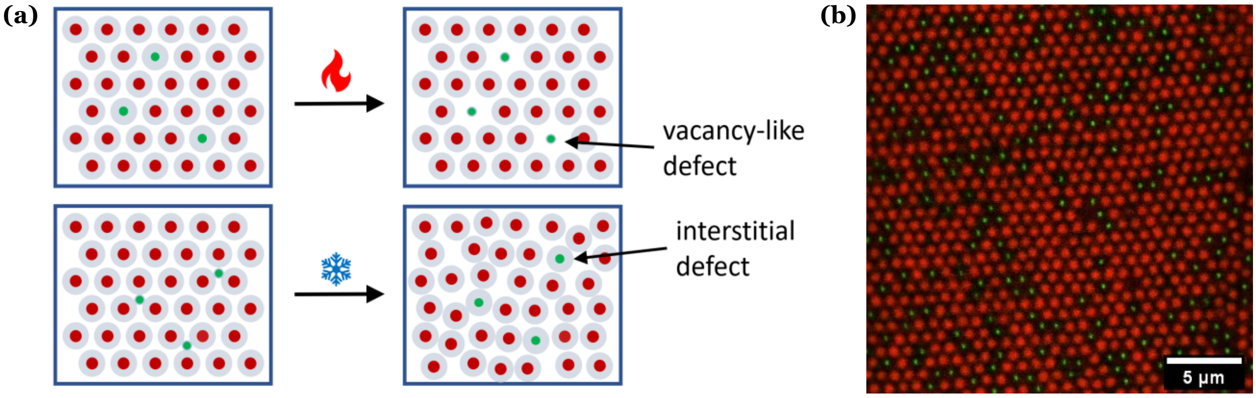

Figure 2. (a) Conceptual visualization of inducing vacancy-like and interstitial defects using thermoresponsive particles. **(b)** Confocal image of successful embedding of swollen thermoresponsive microgels (green) in a crystal of non-responsive particles (red) at 20 °C.

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M 14

Interaction of Microgels with the Biomimetic Surface

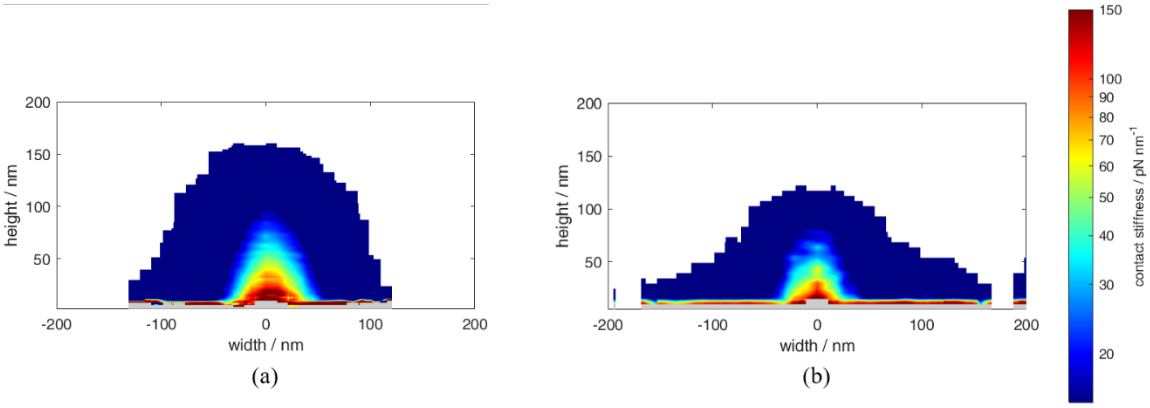
Andrey Babenyshev[1], Nabanita Hazra[1], Jérôme J. Crassous and Walter Richtering[1]

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

PNIPAM and PNIPMAM microgels are promising agents for various biomedical applications. Adding extra-monomers during synthesis or post-modification could customize pH- photo- or temperature-sensitive features. Though some articles studied how some physicochemical properties of microgels influence their interaction with cells [1], the main mechanism of internationalization is still unknown. Recently it was shown that stiffness and size of the microgels strongly influence their cellular uptake and impact the uptake pathway [2]. In this work we investigated how mechanical properties of microgels affect interaction with lipid bilayer with atomic force microscopy and confocal fluorescence microscopy.

Atomic force microscopy is a powerful method that allows investigation of mechanical properties, that are related to the internal structure of the material. With this technique we can determine how microgels deforms on the interface. Moreover, Force Volume measurements allow determining the stiffness as a function of the three-dimensional position and could be used even for ultra-soft materials [3].

Previously in our group was shown interaction of microgels with solid-air and solid-liquid interfaces. To continue those findings, we made a first step to the cell membrane surface. We used the simplistic model of the cell surface – supported lipid bilayer (SLB). We prepared SLB based on 1,2-dioleoyl-sn-glycero-3-phosphatidylcholine (DOPC) as model systems for biomimetic surfaces. Then we quantified microgels deformation upon the adsorption to the bilayers (Fig. 1).



(a) (b)

Figure 1. Average contact stiffness profile of microgels on glass slide (a) and SLB in water at 27 °C

Those results show that microgels probably spread more on the SLB than on the glass slide which mean additional affinity of polymeric shell of the microgel to lipid bilayer. However, it does not correlate with the fact that adhesive energy of conventional microgels on the glass slide is usually higher than adhesive energy of SLB. These all mean that additional experiments are needed.

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Computer Simulations of Responsive Microgels at Lipid Membranes

Rustam A. Gumerov[1], Anastasia S. Sorokina[2], and Igor I. Potemkin[1]

[1] DWI Leibniz Institute for Interactive Materials, Aachen 52056, Germany
[2] Technische Universität Dresden, 01062 Dresden, Germany

Soft permeable particles such as nano- and microgels have been considered as promising candidates for targeted drug delivery [1]. Here a successful intracellular incorporation of a drug nanocontainer lies both in the evading of organism's immune cells and by the eventual engulfment by the tumor cell membrane. While the increase in particles' softness solves the first problem, it also may provide an obstacle in solving the latter one by providing a longer cell uptake time [2]. Meanwhile, a universal solution can be found by using the responsive microgels whose softness and swelling ratio can be tuned via the external stimuli. Simultaneously, a key point lies in the understanding of the interactions between the soft particles and the cell membrane. Using mesoscopic computer simulations, we studied the behavior of single responsive microgels on the model lipid membranes. The effects of particle's molecular weight, cross-linking density and the affinity to the lipid heads were considered. The results showed that the swollen microgels tend to spread on the membrane while their collapse may lead to the complete wrapping by the lipid bilayer. Particularly, it was found that the lower the cross-linking density the stronger hydrophobicity is required for the engulfing. At the same time, the molecular weight appeared to have a significantly lower influence on the behavior at the membrane. Our findings may be useful in the design of responsive microgel-based containers for an efficient drug delivery.

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Acknowledgement: Financial support from SFB 985 "Functional Microgels and Microgel Systems" of the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

M 16

In Situ and Ex Situ Characterization of Self-Assembled Colloidal Monolayers at Air-Water Interfaces

Vahan Abgarjan[1] and Matthias Karg[1]

[1] *Institut für Physikalische Chemie I – Kolloide und Nanooptik, Heinrich-Heine-Universität Düsseldorf, Universitätsstraße 1, 40225 Düsseldorf, Germany*

Self-assembly at interfaces is an effective and versatile strategy for the fabrication of highly ordered two dimensional colloidal films. Studies on the self-assembly of hard colloidal spheres are typically done with silica and polystyrene particles as building blocks, where the film formation is assisted by various techniques such as a Langmuir-Blodgett trough, spin-coating or self-assembly during solvent evaporation [1, 2]. In general, rigid spheres tend to self-assemble into close-packed particle films due to capillary forces at the interface and therefore have only one length scale in interparticle distance [3]. In contrast to that, soft colloidal spheres such as microgels can have a range of interparticle distances due to their deformable nature [4]. In the past few years, core-shell hybrid microgels have received a lot of attentions as they possess properties from both hard and soft spheres [5, 6]. However, not much is known about binary systems containing hard and soft spheres. Mixing both types of colloids could introduce controllable defects in assembled colloidal films.

In this study, we investigate binary mixtures of hard and soft colloids at the air-water interface. Previously, we observed strong attractive interactions between both types of colloids in bulk, which led to clustering and gelation of the dispersion. This attraction, already reported in the literature, is a challenge that must be overcome [7]. We tackled this by introducing a thin polymer layer covering the surface of the hard sphere colloids. By means of microscopy, small-angle light scattering and Langmuir-Blodgett deposition the system was investigated in terms of number ratio under various surface pressures both in and ex situ.

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M 17

Stiffness tomography – how to resolve the internal structure of super-soft objects at solid/liquid interfaces

M. Friederike Schulte[1], Steffen Bochenek[1], Andrea Scotti[1], and Walter Richtering[1]

[1] *Institute of Physical Chemistry – RWTH Aachen University, Aachen, Germany, European Union*

Interfaces are the boundary between two phases. They are omnipresent and the origin for many natural phenomena. While interfaces are relevant on all length scales, many fascinating macroscopic features result from the properties of the interface on the nanoscale. Today's knowledge is the result of the humongous development of surface investigation tools during the last decades. One of these tools is the atomic force microscope (AFM) invented in 1986. It allows to visualize the surface topography as well as to quantify its mechanical properties down to atomic resolution [1]. But what kind of information is gained for a sample not exhibiting a surface in a classical sense - namely microgels?

Microgels are three-dimensional intramolecularly cross-linked polymeric networks swollen by a good solvent.[2] The most prominent example are poly(*N*-isopropylamide) (PNIPAM)-based microgels - owning a unique architecture: They possess a decaying density profile from the center towards their periphery, caused by a heterogeneous distribution of cross-links. These microgels do not exhibit a clear boundary but an open structure with dangling polymeric chains at their periphery. Microgels adsorbed at solid interfaces gained a lot of attention since they are promising candidates for smart coatings with tunable properties. Still, their interfacial behavior is not entirely understood.

In our work, we shed light on PNIPAM microgels adsorbed to solid/liquid interfaces. An AFM equipped with a sharp tip was employed to investigate the internal structure of these unique objects. Force volume measurements are used to create three-dimensional maps of the network density, i.e., their topography and their internal network density combined. A particular focus was on the variation in softness: Microgels of various architecture were examined at different temperature-induced swelling states. This gives us new insights into microgels adsorbed at solid/liquid interfaces - beyond their surface - which are relevant for all porous materials [3,4].

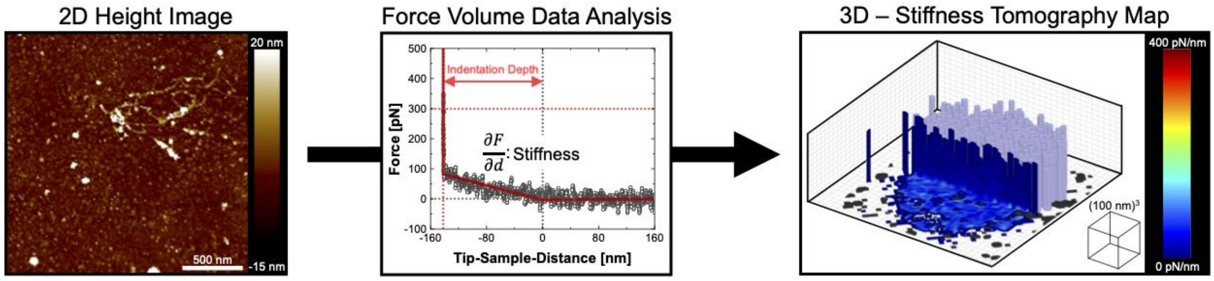

Figure 1. Force volume measurement of super-soft microgels at the solid/liquid interface. Ultra-soft microgels are „invisible" in classical 2D height images but a detailed analysis of force-spectroscopic measurements resolves their overall shape and at the same time their internal structure with nanometric and piconewton resolution in all three dimensions.

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M 18

In-situ Monitoring of Core-Shell Microgel Assembly at Interfaces

Keumkyung Kuk[1], Vahan Abgarjan[1], and Matthias Karg[1]

[1] Institut für Physikalische Chemie I - Kolloide und Nanooptik, Heinrich-Heine-Universität, Düsseldorf, Germany

Nano and micro-scaled surface patterning have been fuelling advancements in the field of nanoscience and technology. Understanding the principles of structural formation at interfaces and properties thus is of paramount importance. Several methods have been developed to fabricate such materials. One of the routes is colloidal assembly, which has advantages over other routes especially in terms of cost and time efficiency due to the parallel nature of its process [1-2]. Hard core-soft shell (HCSS) type hybrid microgels are promising candidates of building blocks for such materials, as they can have a variety of properties, fine-tunable interparticle distance [3] as well as possibilities to be assembled into surprisingly complex structures despite their isotropic shape [4].

Previously, our group has investigated assembly behaviour of silica core-poly(N-isopropylacrylamide) (PNIPAM) shell microgel monolayers at different interfaces [5]. Recently we have observed noticeable differences in assembly behaviour of the same type but larger micron-sized microgels during the monolayer transfer from air-water interface to the substrate surface, see Figure 1. This result further supports the importance of in-situ observation. With the aim of revealing microstructure formation at interfaces, structural changes during the transfer/drying and their correlations to the microgel sizes/structures, we have built an in-situ microscope and small angle light scattering set up combined with a Langmuir trough. Here we demonstrate in-situ observation of 2D colloidal monolayer assembly via compression of HCSS type microgels at air-water interface.

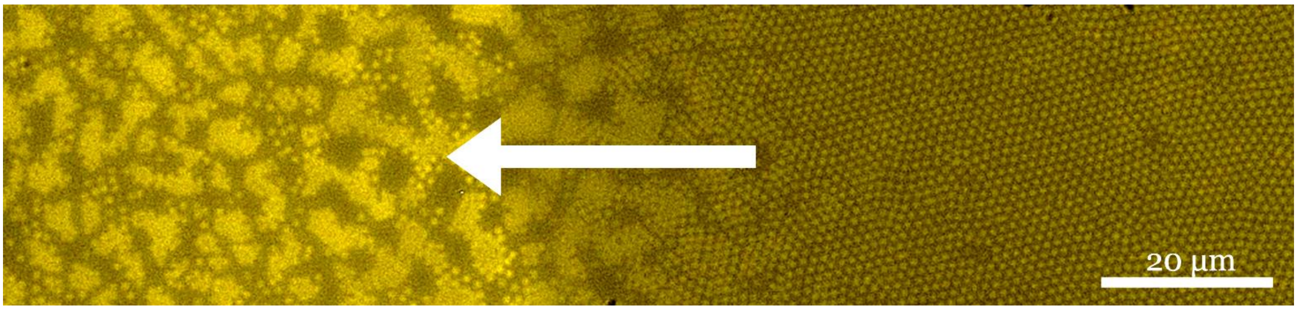

Figure 1. Monolayer of core-shell microgel on a glass substrate after drying (left) and during the transition from air-water interface to water-glass interface (right).

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Acknowledgement: Deutsche Forschungsgemeinschaft (DFG) and Dr. Virginia Carrasco Fadanelli, Dr. Ivo Buttinoni, Experimental Colloidal Physics, Heinrich-Heine-Universität Düsseldorf

Synthesis of Hydrophilic Arborescent Polymers as Building Blocks for ULC-Microgel Production

Jonas Quandt[1,2], Robin Höhner[1,2], Rustam A. Gumerov[1,3], Igor I. Potemkin[1,3] and César Rodriguez-Emmenegger[4]

[1] *DWI – Leibniz Institute for Interactive Materials, Aachen, Germany*
[2] *Institute of Technical and Macromolecular Chemistry, RWTH Aachen University, Aachen, Germany*
[3] *Physics Department, Lomonosov Moscow State University, Moscow, Russian Federation*
[4] *Institute for Bioengineering of Catalonia (IBEC), Barcelona, Spain*

Topology, chemical composition, and softness of macromolecules program their behavior at interfaces. In particular, the introduction of controlled branching and amphiphilicity are essential concepts for introducing shape-controlled functionality. In arborescent polymers, the dendritic, multilevel branched architecture leads to a duality in the properties of particles and molecules. They are soft objects when swollen in a solvent, but exhibit spherical behavior similar to colloidal particles and do not aggregate. Nevertheless, they respond to external stimuli and their flexibility dominates the behavior at interfaces.

We recently reported the advancement of the concept of arborescent or graft-on-graft macromolecules from hydrophobic to hydrophilic polymers [1]. Hydrophilic arborescent polymers up to generation three (G3) were synthesized in an iterative grafting-from scheme by single electron transfer living radical polymerization (SET-LRP) of ethylene glycol methyl ether acrylate (EGMEA) and hydroxyethyl acrylate (HEA). The total molecular weights of the obtained polymers ranged from 35×10^3 g·mol^{-1} for G0 to 3×10^6 g·mol^{-1} for G3 with a polydispersity of $Đ \leq 1.1$ and $Đ \leq 1.2$ respectively. In solution, the molecules adopt a spherical conformation, as demonstrated by dynamic light scattering (DLS) in tetrahydrofuran, while simultaneously spreading into a flat, disk-like shape at liquid-liquid and solid-air interfaces, as shown by spinning-drop tensiometer (SDT) measurements and atomic force microscopy (SFM). Thus, arborescent poly(EGMEA-co-HEA) are globular polymers with high interfacial activity and conformational flexibility, a property usually found only in proteins. However, unlike proteins, the obtained arborescent polymers were only water-soluble at 0 °C. To endow a broader water-solubility we grafted very hydrophilic monomers (cationic, anionic, zwitterionic, and neutral) by SET-LRP as an outermost generation of G2-arborescent poly(EGMEA-CO-HEA). Thereby obtaining a library of arborescent polymers with different functionalities. By intramolecular crosslinking of the end-groups of the last generation with macromolecular crosslinkers in microemulsion to produce arborescent ultralow crosslinked (A-ULC) microgels. We envision that the visco-elastic properties of the A-ULC will be different as compared to other ULC systems due to the superposition of the elasticity of each elementary arborescent molecule.

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Acknowledgement: The authors acknowledge financial support from the Deutsche Forschungsgemeinschaft (DFG) within the SFB 985 “Functional Microgels and Microgel Systems”.

Poster Abstracts

Tuesday

T1

Capillary Driven Self-Assembly of Ellipsoidal Composite Microgels at the Air/Water Interface

Nabanita Hazra[1], Jiarul Midya[2], Andrey Babenyshev[1], Steffen Bochenek[1], Walter Richtering[1], Thorsten Auth[2], Gerhard Gompper[2] and Jérôme J. Crassous[1]

[1]RWTH Aachen University, Institute of Physical Chemistry, Aachen, Germany
[2] Theoretical Physics of Living Matter, Institute of Biological Information Processing and Institute for Advanced Simulation, Forschungszentrum Jülich, Jülich, Germany

In this study, we explored the spontaneous capillary driven self-assembly of composite prolate shaped microgels at air-water interface. The core-shell microgels contain a polystyrene (PS) core surrounded with a cross-linked fluorescently labelled poly(*N*-isopropylmethylacrylamide) (PNIPMAM) shell. The aspect ratios of the composite microgels can be finely adjusted upon uniaxial stretching the particles embedded into polyvinyl alcohol films [1]. The ellipsoidal particles obtain an aspect ratio range ρ varying from 1 to 8.8, measured from confocal laser microscopy (CLSM) in their swollen conformation at 20°C. Using inverted fluorescence microscopy, we investigated their spontaneous interfacial self-assembly at the air-water interface. Comparing with spherical particle ($\rho=1$) with small assembly having weak capillary forces to an apparently random trigonal assembly for $\rho=2.1$ to highly elongated particle ($\rho=8.8$) with a side-to-side assembly into long chains transition is observed. The transition occurs between $\rho=2.6$ and 3.3 for which a trigonal and trigonal/side to side coexistence assembly are respectively identified. The influence of the microgel anisotropy and softness on their interfacial deformation and is further discussed supported by computer simulations.

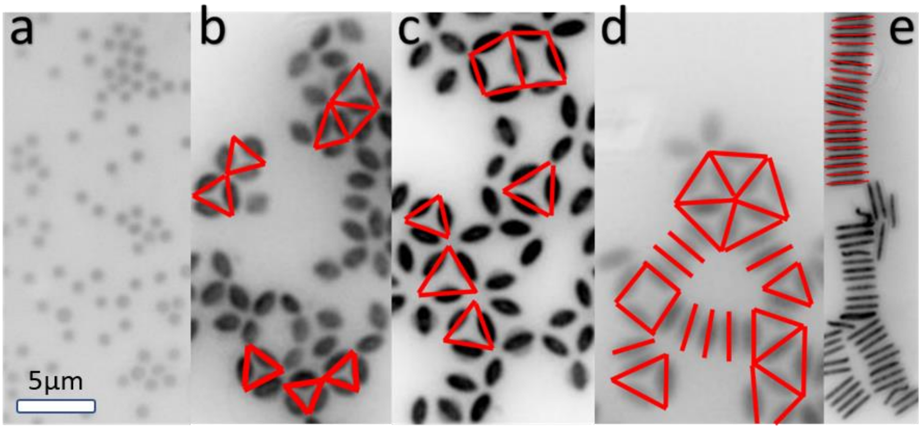

Figure 3. Colour inverted fluorescence micrographs of spherical composite microgels (a) and ellipsoidal composite microgels with an aspect ratio ρ equal to 2.1 (b), 2.6 (c), 3.3 (d) and 8.8 (e) assembled at the air-water interface at 20°C. Some of the typical assemblies are highlighted with red lines.

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T2

Predicting the Volume Phase Transition Temperature (VPTT) of Multi-Responsive Poly(N-isopropylacrylamide)-Based Microgels Using a Cluster-Based Partial Least Squares Modelling Approach

Seyed Saeid Tayebi[1], Todd Hoare[2], and Prashant Mhaskar[3]

[1]*Department of Chemical Engineering, McMaster University, Hamilton, Ontario, Canada, L8S 4L7*

Temperature-responsive microgels that exhibit a volume phase transition temperature (VPTT) have attracted considerable practical interest in multiple applications, with dual temperature/pH-responsive microgels attracting particular interest due to their potential to respond to a range of different environmental stimuli. While the application of such microgels is highly dependent on achieving a targeted VPTT swelling response, the multiple (and often interacting) physical and chemical factors that influence the VPTT in such multi-functional microgels make it challenging to design a microgel recipe that will yield a fully predictable swelling response. Herein, we address this challenge by designing and implementing a data-driven model that is able to directly predict the swelling profile and subsequently the VPTT based only on the recipe of a dual pH/temperature-responsive microgel. A clustering-based adaptation of partial least squares (PLS) modelling was developed in which the data are clustered either in the recipe space or the swelling profile space and then implemented on a data library of 32 pH/temperature-responsive poly(N-isopropylacrylamide)-based microgels copolymerized with various carboxylic acid-functionalized comonomers, including 8 recipe variables (i.e., different comonomers, cross-linker, and surfactant amounts) as the model input and 12 swelling profile variables (particle sizes measured at 6 different temperatures in the fully protonated regime at pH 4 and the fully ionized regime at pH 10) as the model output. Various data arrangements and clustering policies are screened involving five different re-arrangements of the dataset under 3 clustering policies: no clustering, clustering based on recipes, and clustering based on swelling profiles. We demonstrate that the best-performing strategy can predict the VPTT of microgels with an accuracy of 1.0°C at pH=4 and 2.4°C at pH=10 based only on the recipe of the microgel; the accuracy of these predictions is similar to the magnitudes of the error bars of the measured transition temperatures (0.6°C and 2.2°C at pH=4 and pH=10, respectively). Such an approach thus paves the way for a priori customization of microgel swelling profiles as is most suitable for a particular target application.

Acknowledgement: The Natural Sciences and Engineering Research Council of Canada (NSERC, Discovery Grant RGPIN-2017-06455), The McMaster Advanced Control Consortium (MACC), and the Canada Research Chairs program (to both TH and PM) are gratefully acknowledged for funding this work.

Microfluidic Fabrication of Degradable Cell-supportive Zwitterionic Microgels

Afshin Arishamkar[1], Cynthia Pham[1], and Todd Hoare[1]

[1] *Department of Chemical Engineering, McMaster University, Hamilton, ON L8S 4L8, Canada.*

Micrometer-sized hydrogel particles (microgels), offer many favorable properties for developing functional cell therapeutics including their facile injectability, biomimetic mechanics, and ability to regulate diffusion in and out of the gel. However, alginate-calcium chemistry, which is often used as at least one of the crosslinking mechanisms to form existing cell-laden microgels offer limited long-term stability and can induce long-term fibrotic responses at the microgel-tissue interface. This is particularly problematic when the implanted cells are intended to continually release therapeutic products (i.e., cell therapy), which significantly limits their application. To overcome this challenge, we have leveraged hydrazone click chemistry to fabricate zwitterionic hydrogel-based microgels using a microfluidic platform, resulting in continuous production of cell-laden microgels that can maintain high cell viability [1,2]. A droplet-based microfluidic device (Figure 1) fabricated using a silicone replica molding technique was employed for microgel fabrication. The microfluidic chip design, flow conditions, and polymer concentrations were optimized to allow continuous and reproducible fabrication of monodisperse cell-loaded microgels of 30-40 µm in diameter with high cell viability of ~94% after eight days. This work demonstrated the potential of microfluidic technologies and developed click chemistry zwitterionic hydrogels to effectively encapsulate living cells into microgels in a reproducible and controlled manner with high cell viability. While preliminary results suggest the hydrogels can support both the viability and proliferation of cells, the combination of the covalent hydrazone crosslink and physical zwitterion fusion is expected to result in long degradation times (>6 months). This work can be extended to encapsulate various cell lines, produce microgels with different dimensions, and adapt the collection/storage approach, which can open avenues for applications including cell therapeutics, tissue engineering, and 3D bioprinting.

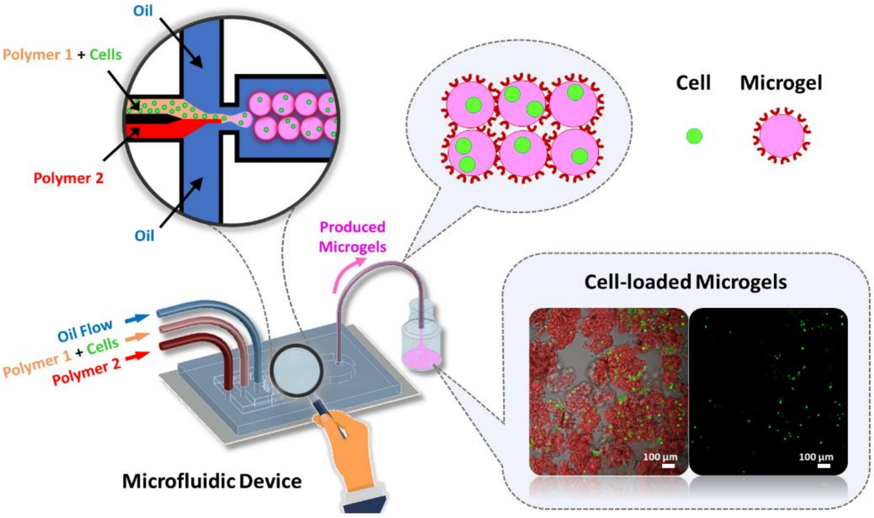

Figure 1. Droplet-based microfluidic platform used for production and collection of cell-laden microgels.

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Acknowledgement: This work was partially supported by the Mitacs Accelerate Grant (project no. IT27833).

T4

Pre-Programmed Rod-Shaped Microgels to Create Multi-Directional Anisogels for 3D Tissue Engineering

Dominik L. Braunmiller,[1] Susan Babu,[2,3] David B. Gehlen,[2] Maximilian Seuß,[2] Tamás Haraszti,[2,3] Andreas Falkenstein,[1] Julian Eigen,[1] Laura De Laporte [2,3] and Jérôme J. Crassous[1]

[1] RWTH Aachen University, Institut für Physikalische Chemie, Aachen, Germany
[2] DWI Leibniz-Institut für Interaktive Materialien, Aachen, Germany
[3] RWTH Aachen University, Institut für Technische und Makromolekulare Chemie, Aachen, Germany

Microscale anisotropic building blocks have been receiving increasing attention in respect to their use as model systems to study complex phase diagrams, dynamics and self-assembly processes and for their biomedical applications. Tissue engineering is one of them, where rod-like magnetic microgels loaded with superparamagnetic iron oxide nanoparticles (SPIONs) were found to direct cell growth when aligned under a homogeneous magnetic field [1]. We are currently aiming at controlling the magnetic orientation and actuation of such microgels using maghemite spindles as anisotropic magnetic fillers instead of SPIONS [2].

Polyethyleneglycol based rod-shaped microgels were produced using particle replication in non-wetting templates (PRINT). The maghemite spindles were pre-aligned and self-assembled into dipolar chains during the microgel synthesis as evidenced by the examination of the resulting composite microgels through scanning electron microscopy (SEM) (Figure 1A). This procedure allows us to pre-program the orientation of the composite microgels parallel or perpendicular to the applied magnetic field as shown in Fig. 1B,C. The actuation of these systems by an external rotating magnetic field further offers the possibility to dynamically align the microgel rods with an orthogonal magnetic moment in the third dimension (Figure 1D).

When embedded in Anisogels for cell culture, cell growth can be directed in the orientation of the pre-programmed microgel rods. Depending on the pre-alignment of the nanoparticles inside, different orientations are possible, e.g. parallel and perpendicular (Figure 1E).

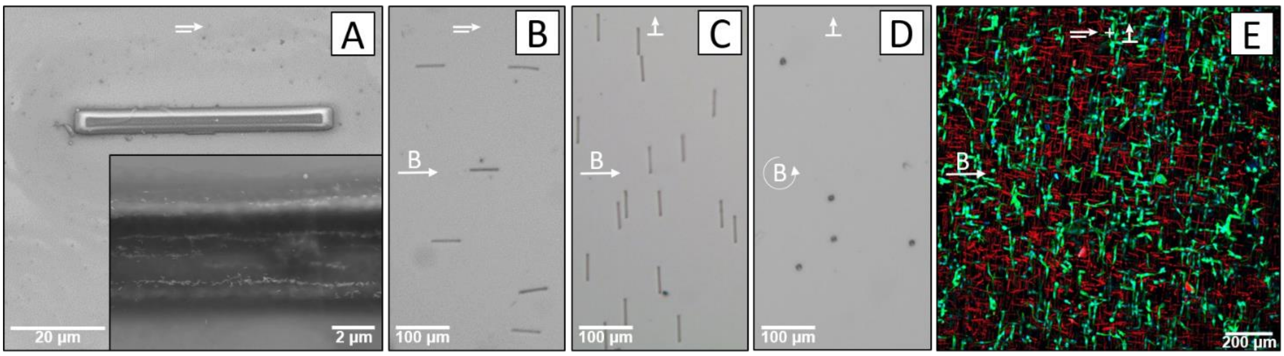

Figure 1. (A) SEM image of incorporated maghemite nanoparticles inside a rod-like microgel. (B,C) Bright field micrographs of the composite microgel alignment parallel and perpendicular to the applied magnetic field. (D) Vertical alignment of the composite microgels with an orthogonal magnetic moment under rotating field (70 mT, 10 rpm). (E) Mouse fibroblast cells (green) growing along parallelly and perpendicularly aligned rod-shaped microgels (red).

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Design of asymmetric microgels with liquid crystalline domains via precipitation polymerization

Nadja Wolter [1,2] and Andrij Pich [1,2,3]

[1]*Functional and Interactive Polymers, DWI – Leibniz Institute for Interactive Materials e.V., Aachen, Germany*
[2]*Institute of Technical and Macromolecular Chemistry, RWTH Aachen University, Aachen, Germany*
[3]*Aachen Maastricht Institute for Biobased Materials (AMIBM), Maastricht University, Geleen, The Netherlands*

Microgels exhibit unique properties and therefore gain rising attention due to their versatile fields of applications [1]. Microgels demonstrate huge potential in drug delivery and catalysis processes, or as surface coatings. However, the fabrication of asymmetric microgels that are anisotropic in shape and surface chemistry using conventional polymerization techniques is challenging [2].

In our work, we present an alternative approach towards the design of asymmetric microgels by making use of liquid crystalline monomers. Liquid crystals have the ability to self-organize depending on external stimuli such as temperature. They have been used to design polymer films and particles that exhibit shape-shifting behavior [3].

Our approach is to implement liquid crystalline domains into microgels to introduce permanent or reversible shapes. Therefore, we used a semi-batch precipitation polymerization approach to synthesize N-vinylcaprolactam (VCL) based microgels with 4-Methoxybenzoic acid 4-(6-acryloyloxy-hexyloxy)phenyl ester as liquid crystalline co-monomer (LCM), crosslinked with N,N-Methylenebis(acrylamide) (BIS). Depending on the reaction temperature, the time at which the LCM is added or the VCL:LCM ratio, the morphology of the microgels was tuned to versatile shapes such as multilobe-, dumbbell- or raspberry-like shapes (Fig. 1). The microgel morphologies were characterized by transmission and scanning electron microscopy while the incorporation of the LCM into the microgel structure was determined via 1H-NMR and Raman spectroscopy. We believe that this method can increase the accessibility of asymmetric microgels and has the potential of introducing shape-shifting behavior within microgels.

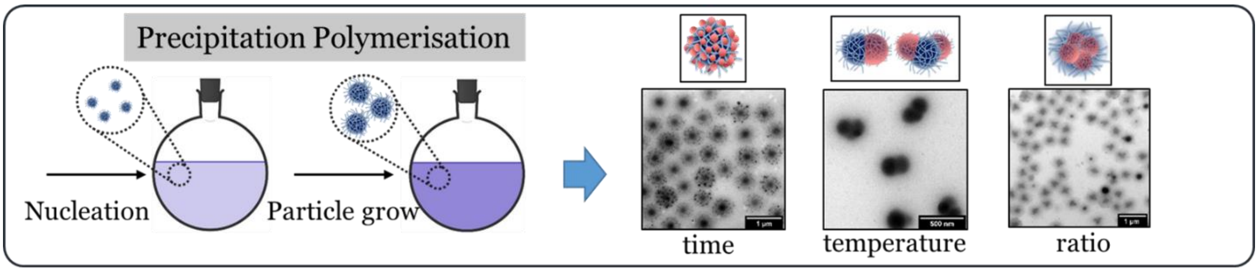

Figure 1. Schematic reaction procedure of the precipitation polymerization of p(VCL-co-LC) microgels (left) and TEM images of the different morphologies resulting from varied reaction conditions (right); scale bars from left to right: 1 µm – 500 nm – 1 µm.

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Acknowledgement: This work was performed as a part of the Collaborative Research Center SFB 985 "Functional Microgels and Microgel Systems" funded by Deutsche Forschungsgemeinschaft (DFG).

T6

Hybrid soft micro-actuators with thermo-programmable response to external magnetic fields

Meriem Saadli[1], Ahmed Mourran[2], and Jérôme Crassous[3]

[1] Institute of Physical Chemistry, RWTH Aachen, Aachen, Germany
[2] DWI-Leibniz-Institute for Interactive Materials, Aachen, Germany

Hybrid materials that can respond to multiple stimuli are promising materials with the potential to be employed as carrier materials in biological systems [1]. Poly(N-isopropylacrylamide) PNIPAm hydrogels are an excellent option to achieve such systems. Their thermo-responsive nature allows a reversible switch from a swollen to a shrunken state. By adding maghemite nanoparticles and pre-programming their alignment in the matrix of those hydrogels, thermo- and magneto-responsive systems can be designed.

Different microgel shapes with embedded maghemites were synthesized using Particle Replication in non-wetting template (PRINT). Their thermo-and magneto- responsivity was determined through swelling experiments and through the investigation of their response under rotating magnetic fields of different strengths. These systems were characterized by a maximum rotation speed ω_c marking their transition from a synchronous to an asynchronous rotation. ω_c showed to be strongly varying with the temperature (Figure 1a).

When the hydrogels were additionally coated with a metal layer, the restricted swelling of the soft layer enabled the creation of more complex shapes [2-3]. The conformations and polarizability to the applied magnetic field of such shapes can be controlled by the temperature (Figure 1 b). These properties were further utilized to create diverse actuations combining the response to temperature, magnetic field, and light. Additionally, active micro-swimmers made from such a system can be designed and their swimming can be directed when an external magnetic field is applied [4].

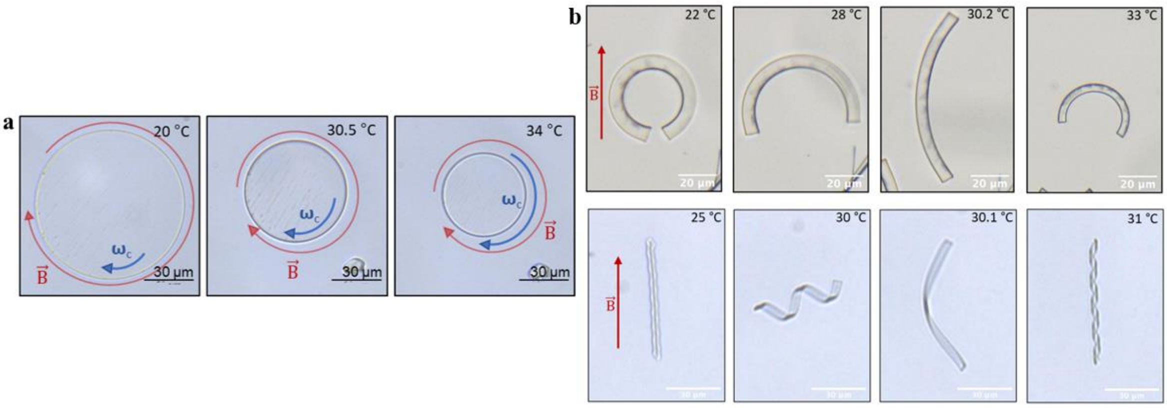

Figure 4. *Thermo-responsive and magnetic microgels a) Hybrid disks with tunable response under an applied rotating field b) Arc and helix bilayer structures that change their alignment to the field when the temperature is varied.*

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Importance of pH in Synthesis of pH-responsive Cationic Core and Core-Shell Microgels

Marco Annegarn[1], Maxim Dirksen[1] and Thomas Hellweg[1]

[1] *Physical and Biophysical Chemistry, Department of Chemistry, Bielefeld University, Bielefeld, Germany*

While cationic nano- and microgels are potentially useful for transfection of cells or the immobilization of biomacromolecules, their synthesis often has certain drawbacks regarding size, polydispersity, yield and incorporation of the cationic comonomer. Since many cationic comonomers like primary or secondary amines are pH-responsive, their charge relies on the surrounding pH. Therefore, a range of poly(*N*-isopropylacrylamide) (PNIPAM) microgels with the primary amine *N*-(3-aminopropyl)methacrylamide hydrochloride (APMH) as the cationic comonomer were synthesized at different reaction pH values. The microgels were analyzed with respect to their size, thermoresponsive swelling behavior, synthesis yield, polydispersity and APMH-incorporation.

The results show that the reaction pH has a strong influence on all the mentioned parameters and can be utilized to tailor the microgels properties. While the influence of the pH on such microgels has been examined repeatedly after synthesis, the influence of the reaction pH during synthesis is mostly ignored. Hence, a precise pH-control during the synthesis of microgels with pH-responsive moieties is crucial to gain reproducible and comparable results.

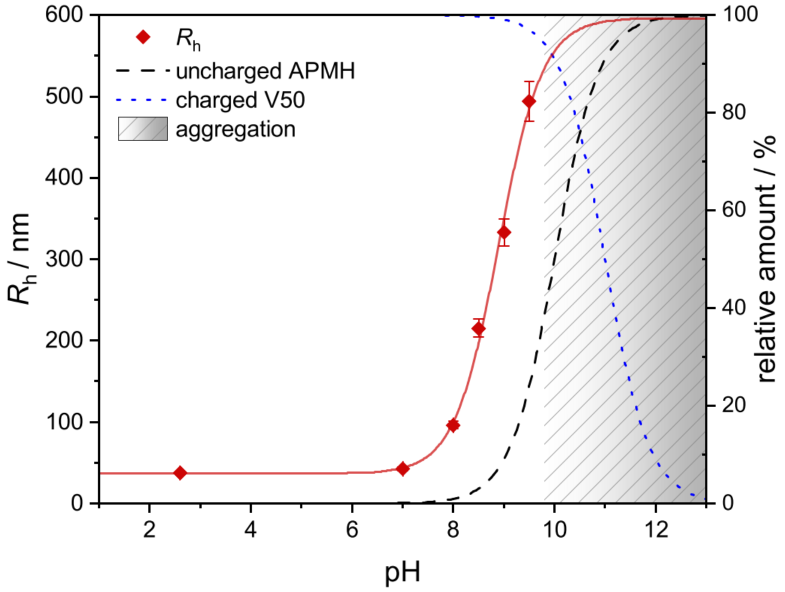

Figure 1. Influence of the reaction pH on the hydrodynamic radius (R_h) of poly(NIPAM-*co*-APMH) microgels (10 °C). Additionally, the relative amounts of uncharged APMH and charged initiator (V50) are shown. Due to the deprotonation of both, aggregation occurs during synthesis at high pH-values.

Furthermore, these results can be transferred to the synthesis of pH-responsive core-shell microgels. The reaction pH during synthesis of cationic core-shell microgels by seeded precipitation polymerization can be utilized to modify the morphology of the resulting shell. Besides microgels with a very fuzzy shell, particles with a raspberry-like shell can be produced.

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T8

Anisotropic Microgels by Supramolecular Assembly and Precipitation Polymerization of Pyrazole-Modified Monomers

Frédéric Grabowski[1,2], Vladislav S. Petrovskii[2], Fabian Fink[3], Dan Eugen Demco[2], Sonja Herres-Pawlis[3], Igor I. Potemkin[2], and Andrij Pich[1,2]

[1]Chair of Functional and Interactive Polymers, Institute of Technical and Macromolecular Chemistry, RWTH Aachen University, Worringerweg 2, 52074 Aachen, Germany
[2]DWI – Leibniz-Institute for Interactive Materials, Forckenbeckstraße 50, 52074 Aachen, Germany
[3]Chair of Bioinorganic Chemistry, Institute for Inorganic Chemistry, RWTH Aachen 13 University, Landoltweg 1a, 52074 Aachen, Germany

Soft colloidal macromolecular structures with programmable chemical functionalities, size and shape are extremely important building blocks for various applications. However, the development of easy up-scalable and template-free synthesis methods to obtain such colloids lacks an understanding of molecular interactions that occur in the formation mechanisms of polymer colloids.

Herein, we developed a computer simulation-driven experimental synthesis approach based on the supramolecular self-assembly followed by polymerization of tailored pyrazole-modified monomers. Therefore, we first performed simulations for a series of pyrazole-modified monomers with different numbers of pyrazole groups, different length and polarity of spacers between pyrazole groups and the polymerizable group. Using simulations, we elaborated the relationship between the chemical structure and ability to undergo π-π-stacking behavior in aqueous solutions. Based on these results, we synthesized monomers able to undergo π-π-stacking and guide the formation of supramolecular bonds between polymer segments and used them in precipitation polymerization.

We demonstrate that microgel morphologies can be tuned from spherical, raspberry-like to dumbbell-like by the increase of the pyrazole-modified monomer loading (from 5 to 15 mol%) in periphery of growing microgels (Fig. 1). In addition, the simulations provide insight into the formation mechanism of various microgel morphologies. Combining experimental and simulation results, our work provides a predictive and quantitative approach for guiding microgel design by specific monomer structures combined with their addition mode and can be further extended to a diversity of colloidal soft materials with outstanding properties.

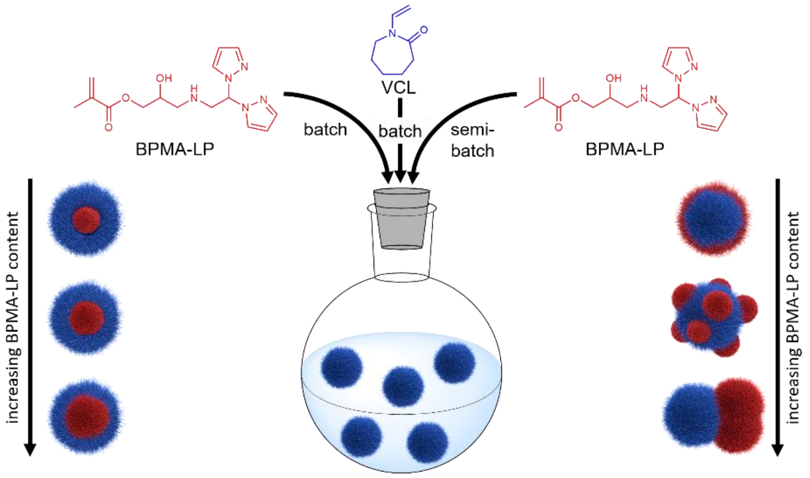

Figure 1. Schematic synthesis of microgels containing the comonomer BPMA-LP with different morphologies *via* batch (B-MG-BPMA-LP, left) and semi-batch (SB-MG-BPMA-LP, right) precipitation polymerization.

Acknowledgement: The authors thank the German Research Foundation (DFG) of the Collaborative Research Center SFB 985 “Functional Microgels and Microgel Systems” for financial support.

T9

Deuteration Effect on the Volume Phase Transition Temperature of NIPAM Microgels

Thomas Nevolianis[1], Andrea Scotti[2], Alexander Petrunin[2], Walter Richtering[2], Kai Leonhard[1]

[1] *Institute of Technical Thermodynamics, RWTH Aachen University, Aachen, Germany, European Union*
[2] *Institute of Physical Chemistry, RWTH Aachen University, Aachen, Germany, European Union*

The use of deuterated microgels to study phase transitions is essential to understanding and developing soft materials for industrial applications. However, to date, the effect of deuteration on the phase transition is not well known. Understanding this is fundamental since it affects the swelling degree and, therefore, the softness of the microgels. In the current work, we study the effect of deuteration on the volume phase transition temperature (VPTT) of NIPAM-based microgels. Using quantum mechanical methods, we study different NIPAM-$(H_2O)_n$ complexes with n being the number of water molecules and calculate the change of the Flory interaction parameter as a consequence of deuteration. The study of complexes shows that 25 water molecules are necessary to hydrate the isopropyl group of NIPAM fully. The resulting parameter is used in a Flory-Huggins model to predict the hydrodynamic radius Rh of microgels over the temperature T (Fig. 1). The model predictions -solid lines - indicate a VPTT shift of 6 °C, which agrees with the experimental values as determined from multi-angle dynamic light scattering – circles - conducted in this study. The VPTT shift is mainly due to the zero-point energy difference between complexes containing water and NIPAM or D_7NIPAM.

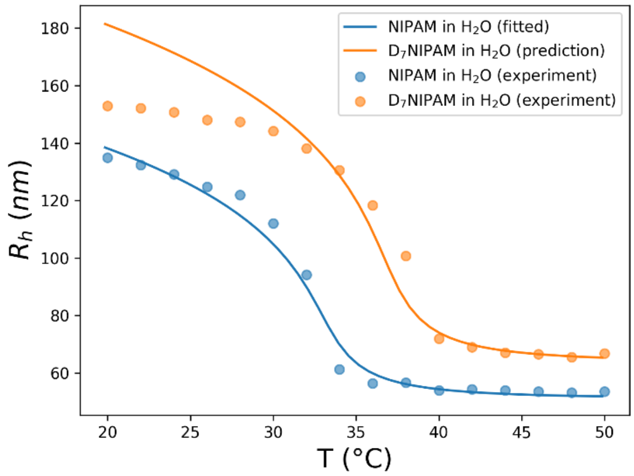

Figure 5: Hydrodynamic radius R_h against temperature T of NIPAM and D7NIPAM in H_2O for both experiments and simulations, respectively.

Acknowledgment: The authors gratefully acknowledge financial support from the SFB 985 "Functional Microgels and Microgel Systems of Deutsche Forschungsgemeinschaft". Simulations were performed with computing resources granted by RWTH Aachen University under project rwth0687.

T10

Microgel Supported L-Prolin and Platinum Nanoparticles Catalyst

Jonas Runge[1], and Thomas Hellweg[2]

[1] *Bielefeld University, Physical and Biophysical Chemistry, Bielefeld Germany*
[2] *Bielefeld University, Physical and Biophysical Chemistry, Bielefeld Germany*

Microgels are crosslinked polymers that are often soft, spherical particles in the range of several nanometersup to some micrometres. The so-called smart microgels do undergo a change of confirmation due to external stimuli such as pH and temperature. Due to their smart behavior microgels are promising candidates as drug delivery agents or carrier systems for catalysts. Especially the colloidal stability of metal nanoparticles can be enhanced by a supportive microgel matrix which can even be more enhanced if so-called anchor points such as acids or amines are included in the microgel matrix.

The stereoselective aldol condensation of 4-nitrobenzaldehyde with cyclohexanone can be catalyzed with L-Prolin (Fig. 1). Kleinschmidt et al. showed that by the incorporation of a polymerizable form of L-Prolin in a microgel matrix the reaction can be performed in water with a high conversion rate and high enantiomeric excess (*ee*).[1] They found the catalytic activity is enhanced if the L-Prolin is located in the microgel core due to the hydrophobic nature of the reactants.

This work aims to develop a catalyst for a stereoselective two-step reaction combining the organocatalysts L-Prolin with platinum nanoparticles. The L-prolin is covalently bound to the N-N-propylacrylamide (NNPAM) microgel matrix whereas the platinum nanoparticles will be attached to amine anchor points. The microgels are synthesized by radical precipitation polymerization and are characterized by photon correlation spectroscopy (PCS). The conversion rate of the aldol reaction is determined by nuclear magnetic resonance (NMR) spectroscopy.

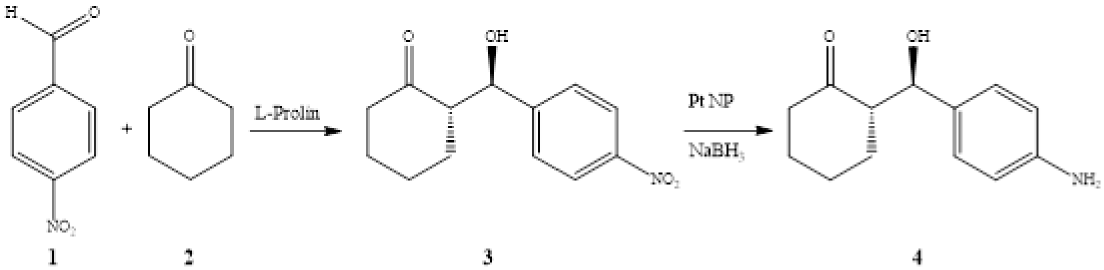

Figure 1. Reaction scheme of the aldol reaction of 4-nitrobenzaldehyde (1) with cyclohexanone (2) followed by the reduction of the nitro group to the amine.

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Overcharging in Microgel & Surfactant Mixtures

Arnaud Chaub[1], Sarah Goujard[1], Michel Cloitre[1]

[1] *ESPCI Paris – PSL, Chimie Moléculaire, Macromoléculaire et Matériaux ; CNRS, Paris, France*

Stimuli-responsive microgels are colloidal particles made of cross-linked polymeric networks that undergo a volume transition in response to changes in pH, temperature, or solvent quality. As particle swelling provokes a dramatic increase of the volume fraction, randomly close-packed suspensions with remarkable rheological properties and optical transparency, can be obtained at very low polymer content. These features are exploited to design rheological modifiers used in cosmetics, pharmaceuticals, and food products.

A wide-spread trigger of microgels in industrial applications is pH. Crosslinked acrylic acid or alkyl acrylate/methacrylic acid microgels swell by a large amount when the carboxylic functions borne by the polymer network are ionized. In general pH-sensitive microgels suffer from a great sensitivity to ionic strength variations and to the fact that the optimum rheology is reached at high pH, which is detrimental to their use in personal care products.

Here we explore another strategy that consists in triggering the swelling of microgels by the addition of guest molecules such as surfactants or oligomers, which adsorb onto the polymeric network and induce swelling. The great challenge is to control and model the volume transition and the rheological properties in terms of the enthalpic, entropic, and electrostatic interactions that develop between the polymeric network and the guest molecules. We address this question in the case of alkyl acrylate/methacrylic acid copolymers carrying negative charges which are activated by cationic surfactants. Using rheology, electrophoresis, microscopy, and light scattering, we elucidate the microscopic mechanisms that connect the composition of the microgel/surfactant mixtures to the phase behavior and rheological properties. When the cationic surfactant concentration increases, initially swollen microgels successively deswell until they fully collapse and precipitate due to attractive interactions. An excess of surfactant reswells the microgels and restabilizes the suspensions due overcharging. This host-gest paradigm opens the route to new applications, for instance to adsorb toxic residues or undesirable moieties from complex formulations.

T12

Nano-Ions in Interaction with Microgels

Jasmin Simons[1], Max Hohenschutz[1], and Walter Richtering[1]

[1] *Institute of Physical Chemistry, RWTH Aachen University, Landoltweg 2, DE-52056 Aachen, Germany*

Microgels are soft, deformable, and penetrable three-dimensional macromolecular networks, which are swollen in a suitable solvent. Due to their ability to respond to external stimuli like temperature, ionic strength, pH and pressure, the possibility arises to reversibly tune their physicochemical properties. Microgels can further encapsulate solutes, which can strongly affect the properties of the microgels in solution. Their properties make microgels important in, for example, biomedical applications or catalysis [1].

As model solutes, nanometer-sized ions, such as polyoxometalates and boron clusters, have recently gained much attention due to their special behavior in water. Owing to a water-mediated driving force, called the chaotropic effect, these nano-ions exhibit a pronounced affinity to non-charged soft matter interfaces, such as polymers or surfactant assemblies. Chaotropic nano-ions have thus emerged as potentially useful soft matter additives owing to dramatic effects on the non-ionic solutes solution structure and a conveying of their inorganic traits (for example catalytic) to the soft matter material [2,3].

This leads us to explore the influence of different nano-ions on the swelling behavior of microgels by means of dynamic light scattering (Figure 1). The outcomes of the study on the swelling behavior of microgels in the presence of three different nano-ions – the boron cluster $B_{12}I_{12}^{2-}$ and the polyoxometalates $SiW_{12}O_{40}^{4-}$ and $PW_{12}O_{40}^{3-}$ – revealed that the nano-ions at low millimolar concentrations may induce swelling below the VPTT (HSiW and HPW) or above the VPTT (NaBI). Furthermore, at high concentrations of SiW and PW the microgels were found to collapse even below the VPTT. By choice of the nano-ion it is thus possible to tune the swelling behavior of microgels in solution.

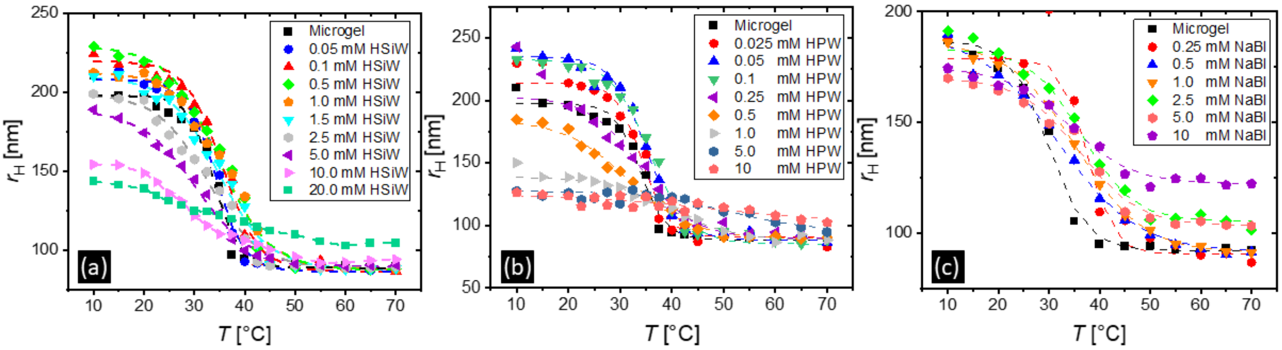

Figure 1. Hydrodynamic radius r_H of a microgel with 5 % cross-linker (c = 0.01 mg mL^{-1}) with different concentrations of (a) HSiW, (b) HPW and (c) NaBI versus temperature T.

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T13

Deswelling of Thermoresponsive Microgels Interacting with Nanoparticles

Francesco Brasili[1], Giovanni Del Monte[2], and Emanuela Zaccarelli[3]

[1] Institute for Complex Systems (ISC-CNR), National Research Council, Rome, Italy.

The design of hybrid smart materials based on the conjugation of stimuli-responsive microgel with plasmonic nanoparticles (NPs) has attracted increasing interest in recent years, due to the peculiar properties of the two components and to the intriguing features arising from their interplay [1]. Responsive microgels are soft colloidal particles made of cross-linked polymeric networks able to undergo a Volume Phase Transition (VPT) upon variation of external stimuli such as temperature or pH [2]. The peculiarity of plasmonic NPs resides in their resonant absorption of light in the visible spectral range, called Localized Surface Plasmon Resonance (LSPR), that is strongly sensitive to the dielectric properties at their interface and to NPs aggregation [3].

We adopted a combined numerical and experimental approach to perform a detailed study of the structural and optical properties of a hybrid system, based on the complexation of thermo-responsive ionic microgels – obtained by the crosslinking of poly(N-isopropylacrylamide) (PNIPAM) chains, initiated by charged groups – with gold NPs. By varying the NP-microgel number ratio, we analyzed in detail the microgels-NPs interaction unveiling the effects of NPs adsorption at different scales, from the single polymer chains composing the network up to the overall stability of the colloidal suspension and eventual aggregation of NPs-decorated microgels.

Our results represent a key step for the comprehension of microgels-NPs interactions and provide an effective route for the rational design of novel smart materials with tunable structural and optical properties.

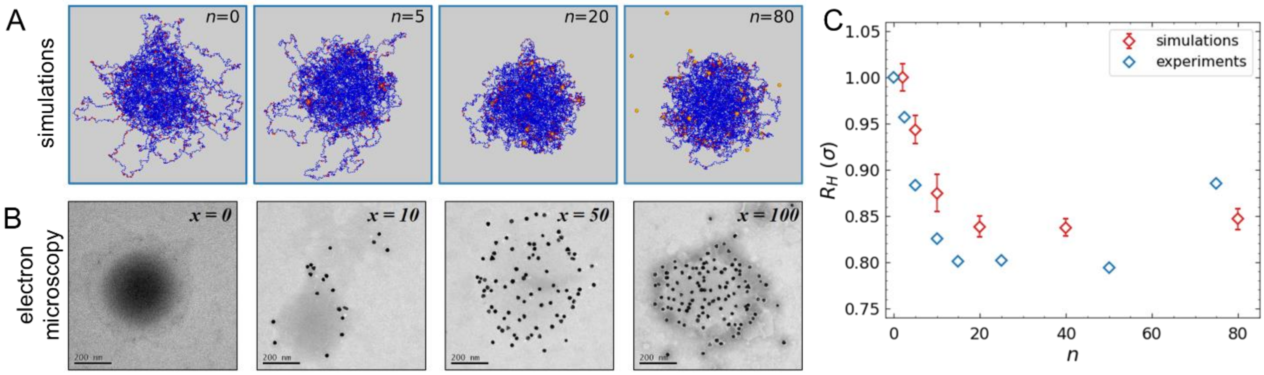

Figure 1. Snapshots of the NPs-microgel simulations (A) in comparison with electron microscopy images (B) for different values of the number *n* of NPs. Hydrodynamic radius of the NPs-microgels complexes as a function of *n* (C).

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T14

Opportunities for the Use of Force Spectroscopy in the Investigations of Responsive Microgel Monolayers

Timon Kratzenberg[1], Friederike Schulte[2], and Walter Richtering[3]

[1] *Institute of Physical Chemistry, RWTH Aachen Germany*

Microgels are soluble and cross-linked polymer networks in the range of micro- to nanometers which share features with colloids, macromolecules and surfactants. Their high interfacial activity combined with the possibility to react to external stimuli like temperature or pH allows the creation of active surface coatings and smart emulsions which can be created and broken on demand [1,2].

While several studies have assessed the mechanism of emulsion stabilization, it is not fully understood yet [3]. Atomic force microscopy in combination with the colloidal probe technique yields a versatile toolbox to study the behaviour of microgel monolayers under controlled conditions to get further insights into the microgel emulsion stabilization mechanisms by probing the micromechanical response and the interactions at the interface.

Our work is about the force spectroscopic investigation of pNIPAM microgel monolayers at the solid-liquid interface to study the effect of temperature and the interfacial concentration on the proprieties of the interface. The goal is to further understand the emulsification mechanism and develop basic principles for the nanomechanical analysis for microgel based systems. This might further contribute to the design of advanced smart emulsion systems and microgel coatings for medical applications.

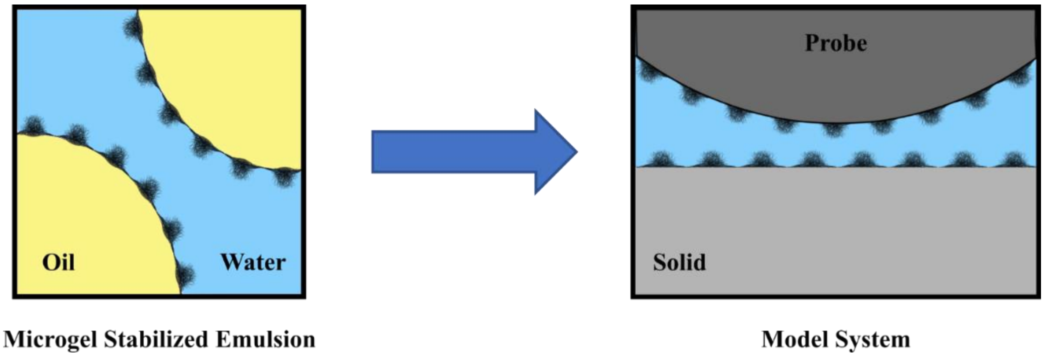

Figure 1. Transition from a microgel stabilized emulsion to the use of a model system with a microgel coated colloidal probe and a microgel monolayer at the solid-liquid interface for which the interaction can be measured with an atomic force microscope.

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Acknowledgement: Dr. S. Bochenek and S. Schog is thanked for many useful discussions and their contributions to this work.

Photolithographic Approach Towards Targeted Microgel Deposition

Pia Lenssen[1], Rebecca Hengsbach[2], Michael Noyong[2], Ulrich Simon[2] and Dominik Wöll[1]

[1] Institute of Physical Chemistry, RWTH Aachen University, Aachen, Germany
[2] Institute of Inorganic Chemistry, RWTH Aachen University, Aachen, Germany

In the past decades, research on microgels (µG) at solid interfaces has contributed to their impact in the scientific community. [1,2] However, depositing µG on solid interfaces results either in random distributions that are not applicable to functional interfaces or hexagonal close-packed films that may not serve the desired interface properties. [3] More specialized interfaces can be gained with a targeted deposition with predefined order.

We deposited µG to predefined locations using a combination of photolithography and chemical electron beam lithography (c-EBL). [4] More specifically, to address specific positions of a pattern predefined by c-EBL, we use a photolabile protecting group, which allows deprotecting specific parts of the pattern. [5] With this approach, patterns can be created from various µG using DNA hybridization. The deprotected spots are grafted by short oligonucleotide acid (DNA) strands that act as anchor points for our DNA functionalized µG. The use of complementary DNA strands results in strong microgel-interface connections due to DNA hybridization. [6]

At solid interfaces, µG typically deform into flat shapes, thus loosing their native spherical shape. Keeping their native spherical shape is, however, essential for some application and studies. To achieve strong selective binding of microgels without significant deformation, we combine the strong attractive forces of DNA hybridization with low attractive forces to an additional surface coating. [7,8] The result is a c-EBL pattern that is modified to hold µG in place, surrounded by a surface coating that keeps the native spherical shape of µG (Fig. 1).

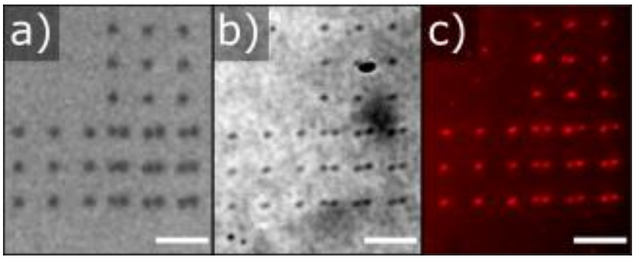

Figure 1. a) c-EBL pattern in scanning electron microscopy (SEM). b) µG bound to pattern via DNA hybridization, in optical transmission microscopy. c) µG labelled with fluorescent DNA via hybridization, in fluorescence microscopy. a), b) and c) show the same pattern at different stages. Scale bar equals 5 µm.

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T16

Simulating Microgels in Solid-Liquid interfaces

Rodrigo Rivas-Barbosa[1], Xhorxhina Shaulli[2], Maxime Jolisse Bergman[2], Nicoletta Gnan[1,3], Frank Scheffold[2], and Emanuela Zaccarelli[3,1]

[1] *Department of Physics, Sapienza University of Rome, Rome, Italy*
[2] *Department of Physics, University of Fribourg, Fribourg, Switzerland*
[3] *CNR Institute of Complex Systems, Uos Sapienza, 00185, Rome, Italy*

Microgels are cross-linked polymer networks that present a reversible size transition at a critical temperature: the microgel changes from a swollen to compact state as temperature is raised from below to above the so-called volume phase transition temperature. The on-demand response to external cues makes microgels a system of interest both for applications such as drug delivery purposes, and for addressing fundamental questions like jamming [1,2]. A realistic numerical description of microgels has been developed [3,4], tested and used to explain new observations such as microgels placed in liquid-liquid interfaces and the swelling of charged microgels [5,6].

Here, we investigate the volume phase transition of similarly assembled microgels in solid-liquid interfaces, in particular, we study microgels on hydrophilic and hydrophobic surfaces and compare them to super-resolution measurements. The volume phase transition of microgels on hydrophilic surfaces is insignificantly perturbed with respect to the bulk case. On the other hand, on hydrophobic surfaces, microgels spread over the interface in order to decrease the liquid-solid contact area; as temperature is increased, a competition between the self-collapse of the microgel and the expansion over the interface is seen.

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Acknowledgement: The authors acknowledge funding from H2020 Marie Curie Actions of the European Commission (ITN SUPERCOL, Grant Agreement 860914).

T17

From Single Microgels to Dense Microgel Layers – Investigation by Atomic Force Microscopy

Simon Schog[1], M. Friederike Schulte[1], Steffen Bochenek[1], and Walter Richtering[1,2]

[1] RWTH Aachen University, Institute of Physical Chemistry, Aachen, Germany
[2] DWI-Leibniz Institute for Interactive Materials, Aachen, Germany

Microgels are three-dimensionally crosslinked polymer networks that swell in a good solvent. They can change their size and internal structure in response to external stimuli such as temperature, pH or ionic strength. In addition, they are highly interfacial active and possess a rich phase behavior due to their soft and inhomogeneous structure. Based on their interfacial properties, they can be used in various applications, e.g., as emulsion stabilizers or surface coatings. However, there is very little data on the internal structure of microgels in dense layers.

In this study, we used Langmuir-Blodgett type depositions to transfer microgel monolayers at different surface pressures onto solid substrates [1]. These monolayers were then investigated ex-situ by atomic force microscopy to investigate (a) their two-dimensional structure and (b) the topography and internal structure of the microgels within the monolayers via force volume measurements. The results of our measurements show that the confinement of microgels within dense monolayers has a profound impact on their internal structure. Single microgels exhibit an inhomogeneous internal structure at the solid-liquid interface with a stiff core in the center and a decreasing stiffness towards the periphery of the microgels [2]. With increasing compression of the monolayer, the microgels become noticeably stiffer in their core (see fig. 1) [3].

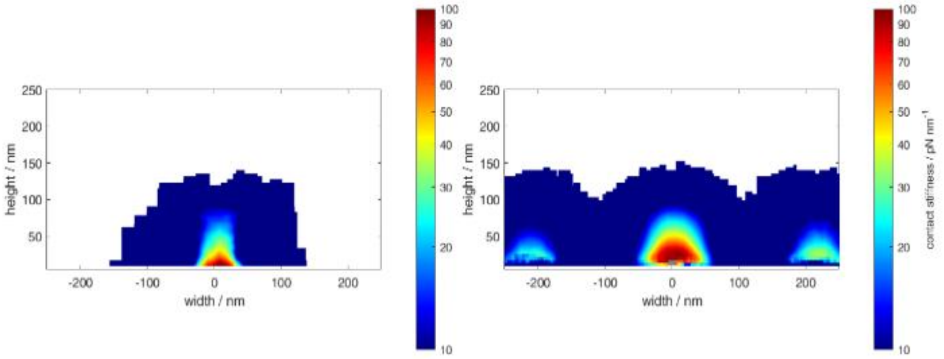

Figure 1. Average contact stiffness profiles of single microgels (left) and microgels in a dense microgel layer (right) at 27°C at the solid-water interface.

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Acknowledgement: The authors acknowledge funding from the Deutsche Forschungsgemeinschaft (DFG) for financial support within the Sonderforschungsbereich SFB 985 "Functional Microgels and Microgel Systems" (Project B8).

T18

Swelling of pH-responsive “defects” in overcrowded nanogel suspensions

Alexander V. Petrunin[1], Maximilian M. Schmidt[1], Ralf Schweins[2], Tomàs S. Plivelic[3], and Andrea Scotti[1]

[1] Institute of Physical Chemistry, RWTH Aachen University, 52056 Aachen, Germany, EU.
[2] Institut Laue-Langevin ILL DS/LSS, 71 Avenue des Martyrs, F-38000 Grenoble, France, EU.
[3] MAX IV Laboratory, Lund University, P.O. Box 118, 22100 Lund Sweden, EU.

Nanogels are often considered a classical model system to study crystallization and glass transition of soft particles. Their responsiveness to various external stimuli, such as temperature, pH, and ionic strength, also makes them attractive building blocks to create responsive materials *via* controlled self-assembly [1]. Of particular interest for this purpose are mixtures of nanogels with different functionality, for example a system composed of a majority of regular nanogels modified by a few nanogels with different softness or responsiveness, like hollow nanogels or ionic nanogels.

It is known that the size and shape of nanogels can change in crowded environments due to deswelling or elastic deformation [2]. Since it is often the concentrated (crowded) suspensions that are most relevant for fundamental studies and applications, it is crucial to understand the behaviour of single particles in them.

In this contribution, we focused on pH-responsiveness of a few ionic poly(*N*-isopropyl acrylamide-*co*-methacrylic acid) nanogels, which we refer to as “defects”, embedded in the majority of neutral poly(*N*-isopropyl acrylamide) ones. We used small-angle neutron scattering (SANS) with contrast variation to directly measure the form factors of these few “defects”, while the neutral nanogels were contrast-matched. In addition, small-angle X-ray scattering (SAXS) measurements were performed on the same suspensions to obtain their structure factors and average nearest-neighbour distances.

We show that the ionic “defects” retain their charge-induced swelling (pH 9), and deswell only marginally as concentration increases. Instead, they prefer to deform and develop facets at contacts with the neighbours. For comparison, we also studied the suspensions composed of only ionic nanogels. In this case, we observed preferential deswelling, triggered by the osmotic pressure of free counter-ions. We explain the different results by considering the difference in counter-ion osmotic pressure inside and outside of the nanogels and the difference in elastic moduli that we expect for charged and neutral nanogels. The interplay between these properties determines the dominant response of nanogels to crowding (deformation or deswelling) in their binary mixtures and should be considered when designing new materials from ionic nanogels.

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Acknowledgement: The authors acknowledge funding from the Deutsche Forschungsgemeinschaft within the SFB 985 “Functional Microgels and Microgel Systems”.

T19

Complex Interactions in Concentrated Microgel Suspensions: a Microscopic Perspective from Numerical Simulations

Giovanni Del Monte[1], Emanuela Zaccarelli[1]

[1] *Istituto dei Sistemi Complessi – CNR, Department of Physics, Sapienza University of Rome, Rome, Italy*

Microgels are one of the most versatile example of soft particles. The possibility to finely tailor their structure and their ability to change size in response to a large variety of environmental parameters (such as temperature and pH) make them highly suitable in the design of smart materials and in the study of open issues in fundamental research (such as the glass transition).

Despite the large amount of devoted studies and developed applications, it remains still unknown how the structural features of single microgel particles determine their mutual interactions in concentrated suspensions [1], in turn defining their phase and dynamical behaviour.

Recently, advanced microscopy [2] and scattering [3,4] techniques have been employed to observe the structure of single microgels in concentrated suspensions. In this contribution I will show the results of molecular dynamics simulations of many microgels systems [6] exploiting a recently proposed numerical model [5], building on a coarse-grained description of the polymer network at a monomer resolved level. The aim of the work is to explain the microscopic origin of the complex deswelling mechanisms taking place when the concentration of the suspension is progressively raised, assessing the role of compression, shape deformation and electrostatics on single-particle and collective properties. Our numerical simulations [6] would complement the experimental observations [2-4], making a step further towards the definition of an effective potential capable of reproducing the complex phase behaviour and dynamics of microgels at any concentration.

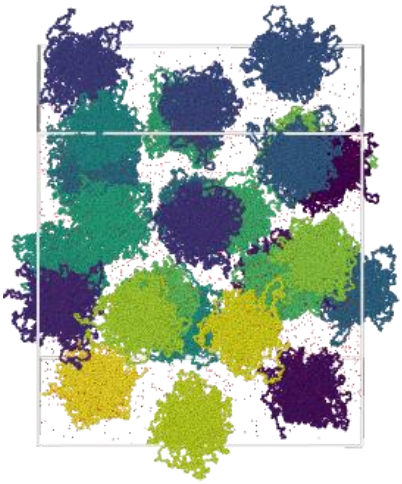

Figure 1. Representative snapshot of a system of 27 microgels at a volume fraction ζ~0.35.

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Acknowledgement: The authors acknowledge funding from the ERC, Consolidator Grant Number 681597, MIMIC.

T20

Active centres embedded in microgels

Lukas Schubert[1] and Dominik Wöll[1]

[1] *Institute of Physical Chemistry, RWTH Aachen University, 52074 Aachen, Germany*

Microgels are soft polymeric particles that bear the possibility to carry and protect different catalysts [1]. A great advantage is the almost free diffusion of small molecules within the microgels to reach active centres [2]. The number of active catalysts can thus be significantly increased compared to solid particles. Furthermore, a switching of microgels can be fostered to introduce swelling or deswelling which can be used to separate microgels from a reaction solution [3].

Enzymes are catalysts that bring extraordinary selectivity for reactions. Unfortunately, most processes apply enzymes as a single use catalyst due to complicated recycling procedures and huge loss of reactivity. To overcome the downsides of enzymes we immobilize them within microgels to easily separate the precious catalyst from the reaction under mild conditions and offer the possibility of repeated use [4].

For the first time different binding methods, such as covalent binding, electrostatic interactions or entrapment of enzymes in microgels with respect to different external parameter are compared via fluorescence microscopy. The number of enzymes embedded in microgels is determined in order to evaluate the influence of property changes. Consequently, an optimized microgel-enzyme system can be obtained.

Furthermore, the number of enzymes is correlated to the activity of the microgel-enzyme system. These activity measurements give information on the possible accessibility of the catalytic centre within the microgels and we can determine the optimal microgels-to-enzymes ratio for a reaction.

This knowledge can be used to describe different microgel-enzyme systems. Thus, under the right conditions, a large-scale enzyme catalytic reactor can be designed without continuously adding catalyst. Different reaction can be realized by simply changing the enzymes in the system and thereby different products can be obtained.

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Acknowledgement: The authors acknowledge funding from the Deutsche Forschungsgemeinschaft within SFB 985 “Functional Microgels and Microgel Systems”, Project C5.