

CPP 68: Hydrogels and Microgels II

Time: Friday 10:15–13:15

Location: ZEU 260

CPP 68.1 Fri 10:15 ZEU 260

Modelling photothermal control of gold nanoparticle loaded microgel systems — ●DMITRY CHIGRIN^{1,2}, GERO VON PLESSEN¹, AHMED MOURRAN², and MARTIN MÖLLER^{2,3} — ¹Institute of Physics (1A), RWTH Aachen University, Aachen, Germany — ²DWI - Leibniz Institute for Interactive Materials, and Functional Interactive Polymers, Aachen, Germany — ³Institute of Technical and Macromolecular Chemistry, RWTH Aachen University, Aachen, Germany

Temperature-responsive microgels can exhibit extremely large deformations due to the volume transition in response to changes in temperature. Combining photothermal materials, e.g. plasmonic nanoparticles, with microgels opens a unique opportunity to design microdynamical systems (microswimmers, microactuators, micromachines) which can be controlled all-optically. In this presentation we discuss physical modelling of gold nanoparticle loaded microgels. A description of photothermally activated microgels involves self-consistent coupling of diffusion, elasticity, heat transfer and electrodynamic models. Using simple examples we discuss how swelling/de-swelling dynamics of microgels can be controlled and guided using light.

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Magneto-optical and magneto-rheological properties of a physical hydrogel based on 12-hydroxystearic acid — HAJNALKA NÁDASI¹, RALF STANNARIUS¹, PETER SALAMON², TAMAS BÖRZSÖNYI², and ●ALEXEY EREMIN¹ — ¹Institute of Experimental Physics, Otto von Guericke University Magdeburg, Universitätsplatz 2, 39016 Magdeburg, Germany — ²Wiegner Research Centre for Physics, Institute for Solid State Physics and Optics, Budapest, H-1525, Hungary

We investigate magneto-responsive physical ferrogels based on 12-hydroxystearic acid in dodecane, doped with commercial magnetic nanoparticles APG 935. The gelator molecules form a hydrogen-based gel network at room temperature. The pure gels exhibit extraordinary helical filament nanostructures similar to those of the HNF(B4) liquid crystal phase formed by bent-core mesogens. The rheological behaviour of the ferrogel is found to be strongly dependent on the preparation protocol. The ferrogels prepared in a magnetic field exhibit lower storage modulus, which can be attributed to rearrangements of the magnetic particles embedded in the gel matrix. At higher shear rates, a gel-sol transition occurs. In a magnetic field, the interaction between the magnetic particles and the matrix lead to an increase of both storage and loss moduli.

The authors acknowledge the support by DFG (SPP 1681, STA 425/36-2)

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Structure and rheology of microgel monolayers at the water/oil interface — ●SHILIN HUANG¹, KORNELIA GAWLITZA², REGINE VON KLITZING², WERNER STEFFEN¹, and GÜNTER K. AUERNHAMMER¹ — ¹Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany — ²Stranski-Laboratorium für Physikalische und Theoretische Chemie, Technische Universität, Berlin, Strasse des 17. Juni 124, 10623 Berlin, Germany

We investigate the rheological property of microgel monolayers at the water/oil interface using passive and active microrheological methods. At low surface coverage, the microgels at the water/oil interface have a tendency to form aggregated structures (networks) with dominating elasticity. At high surface coverage the microgels form densely packed monolayers. Using micro-sized magnetic particles as the local rheological probes in the dense microgel monolayers, we perform in situ study of their rheological properties and structures. We observe four regimes where the elasticity of the microgel monolayer has different dependence on the microgel concentration at the interface. The rheological properties of the microgel monolayers are not only dependent on the concentration, but also strongly correlated with the inter-microgel distance and spacial arrangement of the microgels at the interface. Our results also show that the microgel monolayers act similar to soft glassy materials.

CPP 68.4 Fri 11:00 ZEU 260

Linear thermoresponsive acrylamid based microgels adsorbed on a surface — ●MARIAN CORS¹, JULIAN OBERDISSE², and

THOMAS HELLWEG¹ — ¹Bielefeld University, Bielefeld, Germany — ²Laboratoire Charles Coulomb, Université de Montpellier, Montpellier, France

A gel is a dispersed system which consists of at least two different components: a solid or flexible mesh and a fluid. If the fluid is water the gel is called a hydrogel. Microgels are gels smaller than 10 μm and can be used in a wide range of applications like drug delivery and smart surface coatings. If the microgel consists of acrylamides like N-isopropylmethacrylamide (NIPMAM) or N-n-propylacrylamid (NNPAM) as network component, they show a volume phase transition (VPT) at a certain temperature, the volume phase transition temperature (VPPT). An increase in temperature above the VPPT leads to an abrupt decrease in size and a decrease in temperature leads to an abrupt increase in size. The VPPT is specific for each monomer. To use microgels in sensors or for nanoactuators the thermoresponse has to be precise and well known. That is why we investigated microgels with a complex architecture containing NIPMAM and NNPAM. These particles show a tunable linear change in size between the two VPPTs of NNPAM (22 °C) and NIPMAM (43 °C). Furthermore, we deposited these microgels on surfaces and investigated the properties of the microgel coating. The properties of these particles (like phase transition behavior or particle size) can be adjusted by selecting specific synthesis conditions.

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Analysis of PDMAEMA Polymer Brushes: A TOF-SIMS Study — ●MARC THOMAS^{1,2}, ULRICH HAGEMANN^{2,3}, STEFFEN FRANZKA^{2,3}, MATHIAS ULBRICHT^{1,2}, and NILS HARTMANN^{1,2,3} — ¹Chemistry Department, University of Duisburg-Essen, Germany — ²Center for Nanointegration Duisburg-Essen (CENIDE), University of Duisburg-Essen, Germany — ³Interdisciplinary Center for Analytics on the Nanoscale (ICAN), University of Duisburg-Essen, Germany

Stimuli-responsive polymer brushes are widely applicable, i.e. for self-cleaning coatings, switchable adsorbers and sensors. Using controlled reaction schemes, e.g. ATRP (atom transfer radical polymerization), tailor-made ultrathin brushes can be synthesized. These brushes respond reversibly to stimuli, e.g. temperature, pH, or biomolecules within micro-/milliseconds. Hence, these brushes pose a pathway to innovative miniaturized devices. Tailoring the brushes towards bioapplications requires an insight on their inner structure without and with biomolecules. Here, TOF-SIMS has been applied to obtain three-dimensional molecular information from PDMAEMA (Poly(N,N-dimethylaminoethyl methacrylate) brushes with nm depth resolution. For varying initiator densities, the relative density of initiator prior and after the polymerization as well as the polymer chain density has been obtained. Further, the distribution of BSA (bovine serum albumin) has been examined. The TOF-SIMS experiments were complemented by XPS, AFM and fluorescence spectroscopy measurements. The results reveal the inner structure of polymer brushes of varying grafting densities without and with protein.

CPP 68.6 Fri 11:30 ZEU 260

Uptake and stability of pH-Sensitive Gold Nanoparticles (AuNPs) in Thermoresponsive Polymer Brushes — ●DIKRAN KESAL¹, PATRICK KRAUSE¹, MARCUS TRAPP², and REGINE VON KLITZING¹ — ¹TU Berlin, 10623 Berlin, Germany — ²Helmholtz Zentrum Berlin, 14109 Berlin, Germany

Polymer brushes are polymers tethered to a surface or interface by one end, which at sufficiently high grafting densities show a stretched conformation away from the surface. Many of its applications, for e.g. sensoric and catalysis, involve interaction with particles of some kind, so understanding the interactions between nanoparticles and polymer brushes is of great importance. Embedding nanoparticles, e.g. AuNPs, in polymer brushes result in nanocomposite materials with novel optical properties.

In this work, the assembly of charge switchable AuNPs inside neutral charged Poly(N-isopropylacrylamide) (PNIPAM) brushes will be discussed. The 5 nm AuNPs are capped with mercaptopropionic acid (MPA, pKa 5.5) which bears a carboxylate group and is either protonated (uncharged) or deprotonated (negatively charged) depending on the pH. While some recent efforts have been made in terms of particle uptake and distribution in weakly (PDMAEMA) and strongly

(PMETAC) charged polymers due to electrostatic interaction between particle and brush. While PNIPAM brushes are neutral charged and can only interact via H-bonding with the AuNPs, here the focus is on understanding how protonating and deprotonating of the AuNPs affect particle loading, distribution and stability in PNIPAM brushes.

15 min break

CPP 68.7 Fri 12:00 ZEU 260

Surface forces of polyelectrolyte multilayers in different growth regimes — ●HEBA S. MOHAMAD, MALTE PASSVOGEL, ANNKATRIN SILL, and CHRISTIANE A. HELM — Inst. of Physics, Greifswald University, D-17487 Greifswald

Interaction with the surface of polyelectrolyte multilayer films is important for many application. The films built from Poly (styrenesulfonate) (PSS) and poly (diallylmethylammonium) (PDADMA) in 0.1 Mol/L NaCl start with a parabolic growth regime. Then a transition to linear growth occurs. In the linear growth regime, there are more positive PDADMA than negative PSS monomers in the film; therefore Na^+ ions are incorporated. PDADMA and PSS terminated films in the parabolic growth regime show flat surfaces which interact purely electrostatically, as surface forces measurements with the colloid probe technique show. In the linear growth regime, PSS terminated films are also flat, but PDADMA terminated films interact by steric forces which are analysed with the Alexander-de-Gennes theory. The PDADMA chains protruding into solution are attributed to the excess PDADMA monomers within the film. We conclude that choosing the growth regime allows to control the surface interactions.

CPP 68.8 Fri 12:15 ZEU 260

Composition of polyanion mixtures influence exponential growth of polyelectrolyte multilayers — ●ANNKATRIN SILL¹, MALTE PASSVOGEL¹, ANTONIA WELTMAYER¹, OLAF SOLTWEDEL², AMIR AZINFAR¹, PETER NESTLER¹, and CHRISTIANE A. HELM¹ — ¹Inst. of Physics, Greifswald University, Germany — ²Physics Department, TU Munich, Germany

The exponential growth regime of polyelectrolyte multilayer films made from binary polyanion mixtures is investigated. Films were assembled by the layer-by-layer (LbL) technique using poly(styrene sulfonate) PSS as polyanion and poly (diallyldimethylammonium) (PDADMA) as polycation and investigated with in-situ ellipsometry and neutron reflectivity. The films grow exponentially if molecular weight $M_w(\text{PSS})$ is below 25 kDa; no exponential film growth occurs if $M_w(\text{PSS})$ is above this threshold. Exponential growth is characterized by diffusion of PSS within the film; in non-exponential growth regimes PSS is immobile. The influence of PSS molecular weight distribution on exponential film growth is investigated using a PSS mixture with molecular weight below and above the threshold value. Multilayer films grow exponentially if the mole fraction of non-diffusing PSS is less than 1 %. Neutron reflectivity shows that the mole fraction of non-diffusing PSS in the film is much larger than in the preparation solution. The effect gets more pronounced with increase of the adsorption time. This finding is attributed to the irreversible adsorption of immobile PSS which replaces mobile PSS which adsorbed first.

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Segmental Dynamics of Spin-Labeled Poly(acrylic acid) in Polyelectrolyte Complex Coacervates Studied by CW EPR Spectroscopy — ●UWE LAPPAN, BRIGITTE WIESNER, and ULRICH SCHELER — Leibniz-Institut für Polymerforschung Dresden e.V., Hohe Straße 6, 01069 Dresden, Germany

The complex coacervation of oppositely charged polyelectrolytes has been studied by continuous wave (CW) EPR spectroscopy. The spin-label technique employs stable radicals which are covalently attached

to macromolecules. Rotational dynamics of such spin labels on time scales between 10 ps and 1 μs can be characterized by basic and fast CW EPR spectroscopy. The dynamics of the spin labels is influenced by the restricted motion of the side group bearing the label and local polymer backbone motions at the point of the covalent attachment of the label. The dynamics of polyelectrolyte complexes (PECs) composed of poly(diallyldimethylammonium chloride) (PDADMAC) and poly(acrylic acid) (PAA) was studied in dependence on pH and temperature using a spin-labeled PAA as reporter molecule. All of the experimental spectra were well reproduced by simulations based on the microscopic order/macrosopic disorder (MOMD) model. It was found that the segmental mobility of the PAA in the PECs is nearly constant in the range of pH from 10 to 5 but decreases dramatically for pH values lower than 5. It has been confirmed that the dynamics in the PECs is strongly influenced by the degree of dissociation of the weak polyacid.

CPP 68.10 Fri 12:45 ZEU 260

Drug delivery by thermoresponsive polyelectrolyte complex coatings for bone healing — ●MARTIN MÜLLER^{1,2}, DAVID VEHLW^{1,2}, and BIRGIT URBAN¹ — ¹Leibniz-Institut für Polymerforschung Dresden e.V., Abteilung Polyelektrolyte und Dispersionen, 01069 Dresden, Germany — ²Technische Universität Dresden, Fachrichtung Chemie und Lebensmittelchemie, 01062 Dresden, Germany

Recently, polyelectrolyte complex (PEC) particle coatings were shown to release ionic bone therapeutic drugs in sustained manner immediately after contact to buffer solutions. To trigger thermally on demand the drug release thermoresponsive PEC particle coatings based on poly(N-isopropylacrylamide-co-acrylic acid) (PNIPAM-AA) and cationic cellulose (EDAC) were fabricated. EDAC/PNIPAM-AA dispersions featured hydrodynamic radii $R_H=260\text{-}860$ nm for $T=25^\circ\text{C}$ and $RH=60\text{-}140$ nm for $T=50^\circ\text{C}$ due to coil/globule transition (CGT) of PNIPAM moieties above lower critical solution temperature (LCST). Coatings of EDAC/PNIPAM-AA particles at germanium model substrates kept adhesive after buffer rinsing. FTIR spectroscopy at EDAC/PNIPAM-AA revealed significant hydrogen bonding state changes and broad phase transitions as a function of temperature as well as higher LCST values for dispersions (45°C) and coatings (50°C) compared to PNIPAM solutions (33°C). EDAC/PNIPAM-AA coatings were loaded with zoledronate (ZOL) and at $T>\text{LCST}$ ZOL was released faster compared to $T<\text{LCST}$. Presumably, CGT partly compacts and defects the PEC phase enabling faster ZOL elution.

CPP 68.11 Fri 13:00 ZEU 260

Spontaneous jumping and long-lasting bouncing of solid Leidenfrost drops — ●DORIS VOLLMER, MAXIME PAVEN, TADASHI KAJIYA, HANS-JÜRGEN BUTT, and JONATHAN PHAM — MPI for Polymer Research, Mainz

The impact and rebound of liquid drops on hot, solid surfaces is of practical importance in industrial processes, such as thermal coating and spray cooling. The impact of solid spheres is also a commonly encountered event in ball milling, powder processing, and everyday activities, such as ball sports. Liquid drop and solid ball impacts are distinct from each other in terms of their mechanics. Here, we show that hydrogels display unique characteristics of both solids and liquids when heated above the Leidenfrost temperature. Using high speed video microscopy, we demonstrate that millimetric hydrogel drops jump from a hydrophilic surface upon heating and continue to bounce several times with increasing height. While elasticity dominates the mechanics of contact, evaporation supports long-lasting bouncing. This interplay between elastic and liquid properties results in intriguing dynamics, which is reflected in spontaneous jumping, long-lasting bouncing, trampolining, and the shortest contact times ever observed for water-like systems.