

## CPP 5 Polyelectrolytes

Time: Monday 14:30–17:45

Room: ZEU 160

CPP 5.1 Mon 14:30 ZEU 160

**Fluctuation and correlation effects in charged macromolecular systems studied by molecular dynamics simulations** — ●ARBEN JUSUFI and MATTHIAS BALLAUFF — Physikalisches Chemie I, Universität Bayreuth, 95440 Bayreuth, Germany

We have performed MD simulations of a charged macroion surrounded by counterions. Various scattering contributions result from correlations between counterions, macroion, and between both of them. Experimentally, these scattering contributions can be measured by anomalous small-angle X-ray scattering (ASAXS) experiments. As a result the cross-correlation between the rigid macroion and counterions yields always a meanfield expression for the counterion density distribution even if the counterions exhibit correlated fluctuations. In contrast, in star-like polyelectrolytes, representing a fluctuating macroion, meanfield approximations are valid only if the functionality is sufficiently high. A systematic investigation of the strength of correlated fluctuations and their effect in scattering intensities is demonstrated for these systems.

CPP 5.2 Mon 14:45 ZEU 160

**Engineering Heterogeneously Charged Surfaces by Dendrimer Adsorption: Mechanisms and Interaction Forces** — ●GEORG PAPANASTAVROU, RAMON PERICET-CAMARA, SAMUEL RENTSCH, and MICHAL BORKOVEC — University of Geneva, Laboratory of Colloid and Surface Chemistry, Science II CHIAM, Quai Ernest Ansermet 30, 1211 Geneva, Switzerland

The adsorption of poly(amidoamine) (PAMAM) dendrimers of generations G8 and G10 to a mica surface has been studied by AFM as function of ionic strength and pH. The observed trends of the surface coverage can be described within the effective hard sphere model for Random Sequential Adsorption (RSA). Surfaces with a well-defined density of dendrimers with different surface coverages ranging from 0.05 up to 0.4 can be prepared by selecting an appropriate dendrimer generation, ionic strength of the background electrolyte, and pH-value. These surfaces, although of random nature, exhibit characteristic length scales in the nanometer range for the distances between neighboring adsorbed dendrimer molecules and the approach can be applied as well to colloidal particles. We present measurements on the interaction forces between such heterogeneously charged surfaces by the colloidal probe technique and examine especially the conditions under which the Derjaguin approximation can be applied in the sphere-sphere geometry.

CPP 5.3 Mon 15:00 ZEU 160

**Polyelectrolytes and polyelectrolyte complexes in solution** — ●ULRICH SCHELER and UTE BÖHME — Leibniz Institute of Polymer Research Dresden, Hohe Strasse 6, D-01069 Dresden, Germany

Electrostatic interaction determines the properties of polyelectrolytes in solution. Due to the electrostatic repulsion they adopt a more extended conformation than uncharged polymers in a good solvent. When the ionic strength of the solution is increased, polyelectrolytes adopt a more compact conformation which is reflected in an enhanced diffusion coefficient measured by PFG NMR. This effect becomes more prominent for counterions with higher valence. This effect has been studied on the example of poly(styrenesulfonate) of 77 kg/mol with a monovalent salt (NaCl) and a poly(diallyldimethylammonium chloride) PDADMAC of 5 kg/mol. Upon the addition of PDADMAC acting as a multivalent counterion, the diffusion coefficient is increased more drastically and a primary polyelectrolyte complex is formed. The effective charge of the complexes, measured by electrophoresis NMR, changes according to the composition of the complexes.

CPP 5.4 Mon 15:15 ZEU 160

**Thermosensitive surfaces by self-assembly of PNIPAM microgels on polyelectrolyte layers** — ●THOMAS HELLWEG<sup>1</sup>, STEPHAN SCHMIDT<sup>2</sup>, and REGINE VON KLITZING<sup>3</sup> — <sup>1</sup>TU Berlin, Stranski-Lab. (ER 1), Strasse des 17. Juni 112, 10623 Berlin — <sup>2</sup>MPI-KGF, 14424 Potsdam — <sup>3</sup>Institut für Physikalische Chemie, Christian-Albrechts-Universität Kiel, Ludewig-Meyn-Str. 8, 24118 Kiel

The present contribution describes the behaviour and ordering of thermosensitive PNIPAM and PNIPAM-co-P(AAC) microgels when deposited on layers of the polyelectrolyte PEI. The obtained surface structures change as a function of deposition method (spin-coating or dip-

coating) and also as a function of the interaction between microgel and PEI. The electrostatic part of the interaction can be controlled by pH or ionic strength.

Ordered monolayers of microgel particles were obtained and characterized by in-situ ellipsometry measurements. The films are still responsive and change thickness with increasing temperature making them possible candidates for sensoric surfaces.

— 15 min. break —

CPP 5.5 Mon 15:45 ZEU 160

**Structuring of polyelectrolytes in thin aqueous nanofilms** — ●DAN QU<sup>1</sup>, KATARZYNA CIUNEL<sup>2</sup>, JAN SKOV PEDERSEN<sup>3</sup>, TOMMY NYLANDER<sup>4</sup>, and REGINE V. KLITZING<sup>5</sup> — <sup>1</sup>MPI für Kolloid- und Grenzflächenforschung, D-14224 Potsdam — <sup>2</sup>Stranski-Laboratorium, TU Berlin, Str. d, 17. Juni 112, D-10623 Berlin — <sup>3</sup>Department of Chemistry, University of Aarhus, Langelandsgade 140, DK-8000 Aarhus C — <sup>4</sup>Department of Chemistry I, Lund University, Box 124 SE-221 00 Lund — <sup>5</sup>Institut für Physikalische Chemie, CAU Kiel, Ludewig-Meyn-Strasse 8, D-24118 Kiel

Confinement effects on the structuring of polyelectrolyte chain in aqueous media are studied within nanofilms. The effect of interfaces is studied by choosing films with different surfaces, which are foam films (air/liquid/air), wetting films and films between two solid interfaces. The measurements are carried out in a Thin Film Pressure Balance (TFPB), a Colloidal Probe Atomic Force Microscope (CP-AFM) and a Surface Force Apparatus (SFA). In the semi-dilute regime the confined polyelectrolyte solutions show a force oscillation in a TFPB and in a CP-AFM. While in CP-AFM the whole oscillation is detectable, the TFPB measures only the repulsive parts which leads to steps in the isotherm. The step width corresponds to the period of the oscillation which leads to the conclusion that the properties of the interfaces do not affect the structuring of the polyelectrolytes. In addition the comparison between CP-AFM and SAXS studies shows that there is no confinement effect on the characteristic lengths of the polyelectrolyte system and the counterion distribution.

CPP 5.6 Mon 16:00 ZEU 160

**Ion Profile in Polyelectrolyte Multilayers Studied by Standing Wave X-ray Fluorescence** — ●HAUKE SCHOLLMAYER<sup>1,2</sup>, REGINE VON KLITZING<sup>3</sup>, PATRICK GUENOUN<sup>1</sup>, and JEAN DAILLANT<sup>1</sup> — <sup>1</sup>LIONS bât. 125, CEA Saclay, F-91191 Gif Cedex, France — <sup>2</sup>Institute for X-Ray Physics, Georg-August-University, Friedrich-Hund-Platz 1, 37077 Göttingen, Germany — <sup>3</sup>Institut für Physikalische Chemie, CAU Kiel, Ludewig-Meyn-Str. 8, D-24118 Kiel, Germany

The alternating electrostatic adsorption of cationic and anionic polyelectrolytes has attracted some attention over the last years. These multilayer complex films are a good model system to study permeability of ions. They are prepared using layer-by-layer adsorption of oppositely charged polyelectrolytes. Only little work was done on the study of permeabilities of protons and ions through these layers. In most cases fluorescence dyes were used to measure the ion distribution in the films. The influence of these dyes on the ion diffusion through the polymeric film is not known. In particular for thin films these dyes disturb the system. Furthermore this technique is limited to specific molecules respective to the dye. A comprehensive study of the ion distribution and ion diffusion in these layers, in particular without grafting a disturbing molecule, is missing. For this we used standing waves x-ray fluorescence to measure the ion distribution of polyelectrolyte multilayers. With that technique it is possible to measure the permeabilities of polyelectrolyte multilayers with respect to small ions of different size and charge.

CPP 5.7 Mon 16:15 ZEU 160

**Micelle formation of amphiphilic poly(2-alkyl-2-oxazoline) block copolymers** — ●C.M. PAPADAKIS<sup>1</sup>, T. BONNÉ<sup>1</sup>, R. IVANOVA<sup>1</sup>, P. ŠTĚPÁNEK<sup>2</sup>, K. LÜDTKE<sup>3</sup>, and R. JORDAN<sup>3</sup> — <sup>1</sup>Physikdepartment E13, Technische Universität München, James-Frank-Str. 1, D-85747 Garching — <sup>2</sup>Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Prague — <sup>3</sup>Lehrstuhl für Makromolekulare Stoffe, Chemiedepartment, Technische Universität München, 85 747 Garching

Amphiphilic copolymers find numerous applications, e.g. for drug del-

livery or as nanoreactors. Poly(2-oxazoline) block copolymers constitute a very versatile system: The amphiphilicity can be controlled by the choice of side groups, and in aqueous solution, unimers, micelles or micellar hydrogels are formed, depending on the block copolymer architecture.

Fluorescence correlation spectroscopy (FCS) experiments on aqueous solutions of poly[(2-nonyl-2-oxazoline)<sub>n</sub>-b-(2-methyl-2-oxazoline)<sub>m</sub>], P[(MOx)<sub>m</sub>(NOx)<sub>n</sub>], diblock copolymers with a small fraction of identical, fluorescence-labeled polymers as tracers allowed us to study the micelle formation at very low concentrations [1]. In contrast, low molar mass fluorescence tracers lead to an overestimation of the micellar diffusion coefficients, because of the exchange dynamics of the tracer. Micelles formed by P[(MOx)<sub>m</sub>(NOx)<sub>n</sub>(MOx)<sub>m</sub>] triblock copolymers are smaller than the ones from the corresponding diblock copolymers, as expected from the additional constraints for the hydrophobic blocks.

[1] T.B. Bonn , K. L dtke, R. Jordan, P. St p nek, C.M. Papadakis, *Coll. Polym. Sci.* **282**, 833 (2004)

CPP 5.8 Mon 16:30 ZEU 160

**Imaging of rodlike polyelectrolyte micells** — •INGO LIEBERWIRTH, ANJA KR GER, J RG BELACK, and GERHARD WEGNER — Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz

Mimicking the intricate structures and complex function of biological macromolecules with synthetic polymers is an attractive challenge. Research in this area will provide fundamental insights into the behavior and function of biopolymers and produce new materials as well for advanced applications in areas ranging from materials science to medicine. Biogenic polymers can frequently be considered as wormlike polyelectrolytes that have the tendency to self-aggregate into well-defined superstructures.

Serving as a model system, the self-assembly of rod-like polyelectrolytes consisting of a poly (p-phenylene) backbone with sulfonic acid and dodecyl side groups was investigated by transmission electron microscopy (TEM). In consistency with the DLS and SAXS measurements, the observed morphologies yield cylindrical micells with morphologies ranging from individual strands and loops to gel-like networks.

A feature which is clearly established is the formation of closed loops and lasso-like structures starting from the individual micelles. Based on the reasonable assumption that the packing of the constituent PPPSH chains within the individual micelles is of nematic and thus fluid character, a mechanism for the formation of closed loops has been suggested.

CPP 5.9 Mon 16:45 ZEU 160

**Polypyrrole Nanowires Grown From Single Adsorbed Polyelectrolyte Molecules** — •ANTON KIRIY<sup>1</sup>, VERA BOCHAROVA<sup>1</sup>, MANFRED STAMM<sup>1</sup>, HARTMUT VINZELBERG<sup>2</sup>, and INGOLF M NCH<sup>2</sup> — <sup>1</sup>Leibniz Institute of Polymer Research Dresden, D-01069 Dresden — <sup>2</sup>Leibniz Institute for Solid State and Materials Research, D-01069 Dresden

One-dimensional nanostructures of conductive polymers have attracted a great interest as building blocks for future miniaturized nanoelectronic devices and highly sensitive chemical or biological sensors. We have developed a simple chemical route to conductive polypyrrole nanowires by the grafting of polypyrrole from isolated synthetic polyelectrolyte molecules. The location and length of the synthesized Ppy nanowires are defined by the location and length of adsorbed single-molecule templates. Diameter of the nanowires varies from few nanometers to hundreds of nanometers and can be adjusted by polycondensation time and concentration of reagents. The dc conductivity of individual polypyrrole nanowires approaches the conductivity of polypyrrole in the bulk. A possibility to use the nanowires as active elements of sensors on acids and bases was evaluated. These results open broad opportunities for fabrication of electronic devices and sensors at molecular level (Bocharova, V.; Kiriya, A.; Vinzelberg, H.; M nch, I.; Stamm, M. *Angew. Chem. Int. Ed.* **2005**, *44*, 6391).

CPP 5.10 Mon 17:00 ZEU 160

**Structure and Dynamics of Bottle-brush Polymers** — •S. RATHGEBER<sup>1</sup>, T. PAKULA<sup>1</sup>, A. WILK<sup>1</sup>, K. MATYJASZEWSKI<sup>2</sup>, K.L. BEERS<sup>2</sup>, and P. PANINE<sup>3</sup> — <sup>1</sup>Max Planck Institute for Polymer Research, Mainz, Germany. — <sup>2</sup>Carnegie Mellon University, Pittsburgh, USA. — <sup>3</sup>ESRF, Grenoble, France.

The talk will address the structure and dynamics of bottle-brush polymers (BB) in solution. Due to high branching densities the hybrid character of BB between a flexible polymer and compact colloid is reflected their structure and dynamics. We investigated the dilute solution properties

with static scattering methods, Monte Carlo simulations and measured the internal dynamics with neutron-spin echo spectroscopy. Collective breathing modes of the side chains in the brush lead to a slowing down of the dynamics on length scales of the brush diameter  $D$ . Attachment of longer, more space demanding side chains does not induce higher persistence to the overall brush. The persistence length  $\lambda$  is independent of the side chain length  $N_s$ . Thus, the ratio  $\lambda/D$  is decreasing with increasing  $N_s$  and lyotropic behavior becomes unlikely. We also looked at the lyotropic behavior and the rheological response of highly concentrated BB solutions. Structural changes occurring in a disordered and in a, perpendicular to the shear field pre-aligned sample, in response to the external shear field were measured by time-resolved x-ray scattering. Above a threshold torque the BB start to align in flow direction inducing a shear thinning process lasting two hours accompanied by a reduction in viscosity by two orders of magnitude. Above a higher threshold torque the alignment of the BB spontaneously flips into the flow direction.

CPP 5.11 Mon 17:15 ZEU 160

**Melting of Polyelectrolyte Multilayer Capsules Investigated with AFM Force Spectroscopy** — •RENATE MUELLER and ANDREAS FERY — Max Planck Institute of Colloids and Interfaces, 14424 Potsdam

Microcapsules formed from polymer networks play an important role in both applications like encapsulation (drugs, cosmetics) and in microbiology where these structures are abundant (cell walls, virus capsids). We use Polyelectrolyte multilayer capsules as model systems to study the physico-chemical background of polymeric microcapsule mechanics.

The combination of the colloidal probe AFM technique and an optical microscope allows us to investigate the compliance of individual shells and derive elastic constants of the shell's wall material [1]. Here we explore how temperature affects the mechanical properties of our system. We find a strong softening for capsules formed from Poly(styrene sulfonate)/Poly(diallyldimethylammonium chloride), which we explain as transition from a glassy/rubbery to a viscoelastic state [2]. Shape changes occur in the viscoelastic state like shrinking for spherical shells [3] or more complex phenomena for non-spherical objects; we discuss them as surface tension effects. The shape can be *frozen* upon returning to  $T = 25^\circ\text{C}$ , thus the shape can be controlled on the nanoscale. Additional calorimetric experiments on the system will clarify the nature of the softening transition.

[1] F. Dubeuil et al., *Eur. Phys. J. E*, **2003**, *12*, 215-221.

[2] R. Mueller et al., *Macromolecules*, **2005**, *38*, 9766-9771.

[3] K. K hler et al., *Macromolecules*, **2005**, *109*, 18250-18259.

CPP 5.12 Mon 17:30 ZEU 160

**Strong and weak adsorption of polyelectrolyte chains onto the oppositely charged sphere** — •ANDREY CHERSTVY<sup>1,2</sup> and ROLAND WINKLER<sup>1</sup> — <sup>1</sup>Institut f r Festk rperforschung, Theorie-II, Forschungszentrum J lich, D-52425 J lich, Germany — <sup>2</sup>Max-Planck-Institut f r Physik komplexer Systeme, N thnitzerstrasse 38, 01187 Dresden, Germany

We investigate the complexation of long thin polyelectrolyte (PE) chain with an oppositely charged sphere. In the limit of strong adsorption, when PE chain adapts a definite wrapped conformation on the sphere, we analytically solve the linear Poisson-Boltzmann equation and calculate the electrostatic potential and the energy of the PE complex. We discuss possible attractive interactions between two such non-homogeneously charged complexes and its application to nucleosome core particles. In the limit of weak adsorption, when chain fluctuations are important and PE is crowded around the sphere, we solve the Edwards equation for PE conformations in the Hulthen potential, used as an approximation for the Debye-H ckel potential of the sphere. We predict the shape of the monomer profile away from the sphere and the critical conditions for PE adsorption. We find that the critical sphere charge density depends in a different manner on the Debye screening length than for PE adsorption onto flat surfaces. Our critical adsorption condition is consistent with experiments on complexation of PE with oppositely charged surfactant micelles. We also present results of numerical solutions of the self-consistent field equations for PE adsorption in assemblies of PEs with the oppositely charged spheres.