

CPP 25: Polyelectrolytes

Time: Wednesday 14:30–16:00

Location: C 230

CPP 25.1 Wed 14:30 C 230

Effect of preparation parameters on the D₂O/H₂O uptake of polyelectrolyte multilayers — ●SAMUEL DODOO¹, ROLAND STEITZ², and REGINE VON KLITZING¹ — ¹Stranski-Laboratorium für Physikalische & Theoretische Chemie, Institut für Chemie, TU Berlin, Strasse des 17. Juni 124, D-10623 Berlin — ²Hahn-Meitner Institut, Glienicker Strasse 100, D-14109 Berlin

Polyelectrolyte multilayers (PEM) present a novel material of increasing interest. Their preparation via the layer-by-layer adsorption method offers a wide range of applications. We have investigated PEM of poly(styrene sulfonate) (PSS) and poly(diallyldimethyl ammoniumchloride) (PDADMAC) prepared at different NaCl concentrations, against water of different isotopes by neutron reflectometry^{2,3}. The study addresses the effect of ionic strength and polymer charge on the water uptake by the multilayers. Increasing ionic strength increases thickness and swelling of the multilayers. The PEM swelled more in D₂O than in H₂O but this could not be attributed to replacement of H by D at the polymer. Two types of water were observed, "void water" about 10 vol-% which goes to fill the voids in the multilayers and "free water" about 40 vol-% which directly contributes to swelling of the multilayers. Measurements of effect of type of ions (Hoffmeister effect) are underway.

[1] Decher, G Science 1997, 277, 1232. [2] Steitz, R.; Leiner, V.; Siebrecht, R.; v. Klitzing, R. Colloids and Surfaces A 2000, 163, 63-70. [3] Steitz, R.; Leiner, V.; Tauer, K.; Khrenov, V.; v. Klitzing, R. Applied Physics A 2002, 74, S519-S521.

CPP 25.2 Wed 14:45 C 230

Conformational changes in polyelectrolyte polymer brushes - A strategy for locally controlled surface properties — ●ROSA POETES¹, ULLRICH STEINER¹, TIM KELBY², RON OREN², FENG ZHOU², and WILHELM HUCK² — ¹Cavendish Laboratory, University of Cambridge, Cambridge, UK — ²Melville Laboratory, University of Cambridge, Cambridge, UK

Stimuli-responsive polymer brushes are promising systems for local triggering of surface properties. Conformational states of polymer brushes in the liquid environment can be monitored using spectroscopic ellipsometry. We hope to achieve local switching of surface properties using stimuli-responsive polyelectrolyte polymer brushes. Binary polymer brushes with responsive and non-responsive components are particularly adapted for such applications.

Temperature induced conformational changes of Poly[N-isopropylacrylamide] (PNIPAM) in water were observed and characterised to show the applicability of the technique. Studies of patterned binary brush systems containing PNIPAM and Poly[oligo(ethylene glycol) methacrylate] (POEGMA) demonstrated the possibility of following localised conformational changes using imaging ellipsometry.

Conformational changes in polyelectrolyte polymer brushes are being studied in response to electric fields. Current work is focusing on the characterisation of polyelectrolyte polymer brushes in the liquid environment. The effects of electric fields on poly[2-(methacryloyloxy)ethyl trimethylammonium chloride] (PMETAC) in water are currently being investigated.

CPP 25.3 Wed 15:00 C 230

Small-angle x-ray scattering studies on lignosulfonate, a complex polyelectrolyte — ●ULLA VAINIO^{1,3}, ROLF ANDREAS LAUTEN², and RITVA SERIMAA³ — ¹HASYLAB at DESY, Notkestr. 85, D-22603 Hamburg, Germany — ²Borregaard Lignotech, P.O. Box 162, NO-1701 Sarpsborg, Norway — ³Department of Physical Sciences, P.O.Box 64, FI-00014 University of Helsinki, Finland

Lignosulfonate is a colloidal polyelectrolyte produced during sulfite pulping process of plants. Plant cell walls consist mostly of cellulose, hemicelluloses and lignin. During pulping lignin is made soluble and removed from the cell walls as lignosulfonate. Various uses have been invented for this byproduct of the pulping process, but even more could be possible once the behaviour of lignosulfonate in solution can be correlated to its structure.

Lignosulfonate particles of mass weighted molar mass 18 000 g/mol were studied in water and salt solutions using small-angle x-ray scattering and rheology. The concentration of the polyelectrolyte was varied from semidilute to concentrated.

Combined with molecular mass distribution obtained from gel permeation chromatography the model shape of an average lignosulfonate particles was discovered to be a flat ellipsoid by fitting different models to SAXS data. At water solutions below 0.1 mass fraction positions of the correlation peak observed in SAXS patterns scaled with concentration of lignosulfonate through a scaling law with exponent 0.28. Selfassociation of lignosulfonate particles was observed at higher concentrations from the SAXS data.

CPP 25.4 Wed 15:15 C 230

Challenging scaling laws of flexible polyelectrolyte solutions with effective renormalization concepts — ●STEPHAN A. BAEURLE¹ and EVGENIJ A. NOGOVITSIN² — ¹Institute of Physical & Theoretical Chemistry, University of Regensburg, D-93053 Regensburg, Germany — ²Institute of Solution Chemistry, Russian Academy of Sciences, 153045 Ivanovo, Russia

Recasting a many-particle problem in a field-theoretic formalism is nowadays a well-established theoretical tool used by scientists across a wide spectrum of research areas, ranging from polymer physics to molecular electronic structure theory. It has shown to provide useful results in many complex situations, where the physics of the system involves many degrees of freedom and a multitude of different length-scales, generally rendering its numerical treatment on a detailed level computationally intractable. To reduce the computational burden, field-theoretic methodologies usually take advantage of the mean field approximation, which is known to give reliable information about the system in the high concentration regime, where the interactions are highly screened. However, it is well-established that the ranges of interest in most technological applications, lie in the intermediate to low concentration regimes, where fluctuations beyond the mean field level of approximation become important and dominate the overall physical behavior. In this talk we introduce a new renormalized self-consistent field theory for flexible polyelectrolyte chains, in which the monomers interact via a pair potential of screened Coulomb type, and derive suitable thermodynamic expressions for all concentration regimes.

CPP 25.5 Wed 15:30 C 230

Swelling of PEM with different charge densities at solid support in humid nitrogen atmosphere: A neutron reflectometry study — ●RALF KÖHLER^{1,2}, INGO DÖNCH², ANDRÉ LASCHEWSKY³, ANDREAS FERY⁴, and RUMEN KRASSTEV² — ¹HMI Berlin, Abt. SF1, Berlin — ²MPI KGF, Abt. GF, Potsdam — ³Fraunhofer IAP, Abt. Wasserbasierte Systeme, Potsdam — ⁴Universität Bayreuth, Phys. Chemie II, Bayreuth, Germany

Polyelectrolyte Multilayers (PEM) are composites of self-assembled (layered) polyions of alternating charges. They are interesting materials for technical application and fundamental research with a high potential for appliance in medical, biotechnological and pharmaceutical purposes. NR may be expected to be the perfect tool for measuring of swelling behaviour of PEM (here PSS/PDADMAC) because both, thickness change and water content can be obtained simultaneously. The samples were prepared in Layer-by-Layer technique (spraying) applying PDADMAC with different charge densities (100%, 89% and 75%). It was found that the water uptake is almost linear with the relative humidity of surrounding vapour. The swelling of the PEM depends nonlinearly from the water content of the multilayers. Significant dependence of the swelling and/or water uptake on the charge density was not observed on ultra-thin PEM. Further experiments were addressed to the swelling behaviour by variation of the initial PEM thickness. No intense thickness dependence was observed but a well pronounced non equal distribution of the polymer chains (respectively water uptake) normal to the surface was documented.

CPP 25.6 Wed 15:45 C 230

Wrinkling for measuring charge density effects in polyelectrolyte multilayers and as a novel approach towards templating — ●INGO DOENCH¹, CONGHUA LU¹, PATRICK OTT², ANDRÉ LASCHEWSKY³, and ANDREAS FERY^{1,4} — ¹Max Planck Institute of Colloids and Interfaces, Potsdam, Germany — ²Universität Potsdam, Germany — ³Fraunhofer Institute for Applied Polymer Research, Potsdam, Germany — ⁴University of Bayreuth, Germany

Polyelectrolyte Multilayers find various applications as coatings or

semi-permeable membranes. Their mechanical properties are relevant for stability as well as in general for their deformation properties (pressure sensing). Still, classical indentation tests for determining mechanical properties of solid-supported films face serious problems due to substrate effects when the film thickness is below a micron. Therefore, we use an alternate approach in which we investigate wrinkling of these films and derive elastic constants from the measurement of the wrinkle period. We are able to change the charge density of the polycation for film preparation and find that this allows tuning the

mechanical properties of the multilayers. Furthermore, humidity has strong effects on the multilayers and we find that the degree of softening / swelling of the multilayers by increasing humidity can be determined by the charge density as well. Apart from the possibility to determine elastic constants of thin films, wrinkling provides a simple pathway to lithography-free topographical patterning on the micron- and sub-micron-scale. We present first results for templating of colloidal particle-deposition and discuss perspectives.