

## CPP 18: Polyelectrolytes

Time: Tuesday 9:30–12:30

Location: ZEU 114

CPP 18.1 Tue 9:30 ZEU 114

**Small-angle x-ray scattering of lignosulfonate in aqueous methanol solutions** — ●ULLA VAINIO<sup>1</sup>, ROLF ANDREAS LAUTEN<sup>2</sup>, SYLVIO HAAS<sup>3</sup>, KIRSI LEPPÄNEN<sup>4</sup>, LARISSA VEIGA<sup>1</sup>, RITVA SERIMAA<sup>4</sup>, ARMIN HOELL<sup>3</sup>, and RAINER GEHRKE<sup>1</sup> — <sup>1</sup>HASYLAB at DESY, Hamburg, Germany — <sup>2</sup>Borregaard Lignotech, Sarpsborg, Norway — <sup>3</sup>Helmholtz-Zentrum Berlin für Materialien und Energie, Berlin, Germany — <sup>4</sup>Department of Physics, University of Helsinki, Helsinki, Finland

Lignosulfonate is a binder, dispersant, and emulsion stabilizer. It may be used as a component in plastics and low-cost methanol fuel cell membranes. We studied the structure and aggregation of sodium and rubidium lignosulfonate particles in water-methanol mixtures by small-angle x-ray scattering (SAXS). Volume fraction of lignosulfonate in solution ranged from 0.01 to 0.17, covering the semi-dilute regime. Interestingly, rubidium lignosulfonate particles self-associated more than sodium lignosulfonate particles even though both ions have valence +1. The effect was most pronounced in 1:1 methanol-water mixtures. Measurements were made also for 1:3 methanol-water solution and aqueous solution. We conclude that the heavier rubidium ions associate to the sulfonate groups more readily than sodium ions. Methanol enhanced the self-association tendency for both rubidium and sodium lignosulfonate. A contrast variation method, anomalous small-angle x-ray scattering (ASAXS), was used to study how rubidium is distributed in the lignosulfonate solutions. The measurements were made at the 7T MPW SAXS beamline at BESSY in Berlin.

CPP 18.2 Tue 9:45 ZEU 114

**Reentrant Condensation of Proteins in Solution Induced by Multivalent Ions** — ●LUCA IANESELLI<sup>1</sup>, FAJUN ZHANG<sup>1</sup>, ROBERT M. J. JACOBS<sup>2</sup>, MAXIMILIAN W. A. SKODA<sup>3</sup>, CHRISTOPHER C. MARTIN<sup>4</sup>, SYLVAIN PRÉVOST<sup>5</sup>, and FRANK SCHREIBER<sup>1</sup> — <sup>1</sup>Institut für Angewandte Physik, Universität Tübingen, 72076 Tübingen, Germany — <sup>2</sup>CRL, University of Oxford, UK — <sup>3</sup>ISIS Rutherford Appleton Laboratory, UK — <sup>4</sup>SRS, Daresbury, UK — <sup>5</sup>Helmholtz Center Berlin

Proteins in aqueous solution in the presence of multivalent salt ions can exhibit reentrant condensation [1]. In order to address the dependencies of the phenomenon on protein structure and surface charge density we examined systematically different proteins and multivalent ions systems using UV-Vis spectroscopy and small angle scattering (SAS). Phase diagrams with similar features at the two critical concentrations as expected by the charge inversion theory [2] were determined for wide protein and salt concentration ranges. Positively charged proteins at neutral pH like lysozyme do not show reentrant behavior by using Y3+ as salt ions whereas negative proteins like BSA, OV or HSA do. Al3+ and the organic salt Spermine4+ do not induce reentrant condensation because of their too high and too low charge density respectively. Y3+ however induces reentrant condensation for 5 of the 6 analyzed proteins. Selected samples with fixed protein concentration were studied by SAS. The data analysis provides evidence of the changes in protein-protein interactions, from repulsive to attractive as a function of salt concentration. [1] F. Zhang, et al. Phys. Rev. Lett. 2008,101,148101 [2] A.Y. Grosberg, et al. Rev. Mod. Phys. 2002, 74, 329

CPP 18.3 Tue 10:00 ZEU 114

**Counterion condensation on compact molecules** — UTE BÖHME and ●ULRICH SCHELER — Leibniz-Institut für Polymerforschung Dresden, Hohe Str. 6, 01069 Dresden

Condensation of counterions reduces the effective charge of macromolecules. Electrophoresis NMR provides a versatile tool for the experimental determination of the effective charge [1, 2]. The detection in both diffusion and electrophoresis NMR is performed with chemical shift resolution, enabling the identification of the moving species. Condensation of organic counterions is thus monitored directly [3]. Stiff, rod-like molecules, flexible polymers and globular molecules like proteins [4] have been investigated, proving the concept of counterion condensation. Dendrimers are studied as model systems for nearly spherical polyelectrolytes. Inspection of the proton NMR spectra yields information on the degree of protonation of amino groups and thus the nominal charge of dendrimers. The effective charge of these small globular molecules is a fraction of their nominal charge. The effective charge does not reach the maximal nominal charge even for a small

molecule like citric acid.

[1] U. Böhme, U. Scheler, Colloids and Surfaces A, 222, (2003), 35 [2] K. Grass, U. Böhme, U. Scheler, H. Cottet, C. Holm, Physical Review Letters 100, (2008) 096104 [3] U. Böhme, C. Vogel, J. Meier-Haack, U. Scheler, J. Phys. Chem. B 111, (2007), 8344 [4] Ute Böhme, Ulrich Scheler Chemical Physics Letters 435, (2007), 342

CPP 18.4 Tue 10:15 ZEU 114

**Optimizing end-labeled free-solution electrophoresis by increasing the hydrodynamic friction of the drag-tag** — ●KAI GRASS<sup>1</sup>, CHRISTIAN HOLM<sup>2</sup>, and GARY SLATER<sup>3</sup> — <sup>1</sup>FIAS, Goethe-University Frankfurt, Ruth-Moufang-Strasse 1, 60438 Frankfurt, Germany — <sup>2</sup>ICP, University of Stuttgart, Pfaffenwaldring 27, 70569 Stuttgart, Germany — <sup>3</sup>University of Ottawa, 150 Louis-Pasteur, Ottawa, Ontario K1N 6N5, Canada

We study the electrophoretic separation of polyelectrolytes of varying length in free-solution by means of end-labeled free-solution electrophoresis (ELFSE). A coarse-grained molecular dynamics simulation model, using full electrostatic interactions and a mesoscopic Lattice Boltzmann fluid to account for hydrodynamic interactions, is used to characterize the drag coefficients of different label types: linear and branched polymeric labels, as well as transiently bound micelles.

It is specifically shown that the label's drag coefficient is determined by its hydrodynamic size, and that the drag per label monomer is largest for linear labels. However, the addition of side chains to a linear label offers the possibility to increase the hydrodynamic size, without having to increase the linear length of the label, thereby simplifying synthesis. The third class of labels investigated, transiently bound micelles, seems very promising for the usage in ELFSE, as they provide a significant higher hydrodynamic drag than the other label types.

The results are compared to recent experimental results, as well as to theoretical predictions, and it is analyzed how the efficiency of the ELFSE method can be improved by using smartly designed drag-tags.

CPP 18.5 Tue 10:30 ZEU 114

**Intermediate states in the coil to globule transition of polyacrylate chains: Single chain structures in dilute aqueous solutions and on surfaces** — ●PRASHANT SINHA<sup>1</sup>, SEBASTIAN LAGES<sup>2</sup>, ANTON KIRIY<sup>1</sup>, MANFRED STAMM<sup>1</sup>, and KLAUS HUBER<sup>2</sup> — <sup>1</sup>Leibniz-Institut für Polymerforschung Dresden e.V., Hohe Strasse 6, 01069 Dresden, Germany — <sup>2</sup>Chemistry Department, Universität Paderborn, Warburger Str.100, D-33098 Paderborn, Germany

A cascade of intermediate states appear along the coil to globule transition of polyacrylate chains in dilute aqueous solutions during interactions with specifically binding ions. Conformational changes of these chains induced by Sr2+, Pb2+ and Ca2+ ions have been studied. In the last case, temperature has been introduced as a secondary parameter to substantiate recent findings that the binding of carboxylate groups with calcium ions may be entropic in nature. The samples were characterized using combined static and dynamic light scattering. Intermediate states which exhibited a drastic reduction of coil dimensions upon addition of stoichiometric amounts of specifically binding ions were then investigated for single chain structures using SAXS, ASAXS and SANS, as suitable. The very same samples were also investigated on mica surfaces using Atomic Force Microscopy. Various characteristics of the single chain structures of intermediate states, primarily radius of gyration, have been compared for dilute solution behavior and surface behavior. We believe that the results provide one of the rare direct visual evidences of the coil to globule transition in a regime investigated also through scattering.

CPP 18.6 Tue 10:45 ZEU 114

**Self-stretching of DNA-amphiphile complexes on pre-coated graphite surfaces** — ●HUA LIANG, WEI ZHUANG, NIKOLAI SEVERIN, and JÜRGEN P. RABE — Department of Physics, Humboldt University Berlin, Newtonstr.15, D-12489 Berlin, Germany

Stretching single DNA molecules on a surface is important, for instance for the purpose of direct DNA sequencing with scanning probe techniques and for studies of enzyme activities [1]. Micrometer-long single DNA molecules have been deposited and aligned on a poly-L-lysine modified mica surface [2]. However this method does not allow

to stretch the molecules perfectly, which makes sequencing a difficult task. Here we report a method which allows us to stretch both single- and double-stranded DNA (ss-, ds-DNA) and even overstretch ds-DNA on an amphiphile pre-coated graphite surface. DNA-amphiphile complexes form during adsorption of DNA molecules on the amphiphile pre-coated surface. The complex self-stretches on the HOPG surface. Annealing at 60 °C stretches ds-DNA furthermore up to 1.42 times its original B-form length. ss-DNA can be stretched up to 0.45 nm/base, compared to 0.39 nm/base on poly-L-lysine pre-coated mica [2]. A mechanism for self-stretching is also suggested.

[1] X. Michalet, *Nano Letters* 1 (2001) 341-343 [2] A. T. Woolley, R. T. Kelly, *Nano Letters* 1 (2001) 345-348

CPP 18.7 Tue 11:00 ZEU 114

**DNA cholesteric phases: the role of DNA molecular chirality and DNA-DNA electrostatic interactions** — ●ANDREY CHERSTVY — IFF, Theorie-II, FZ Jülich, 52425 Jülich, Germany

DNA molecules form dense liquid crystalline twisted phases in vivo and in vitro. How the microscopic DNA chirality is transferred into intermolecular twist in these mesophases and what is the role of chiral DNA-DNA electrostatic interactions is still not completely clear. First, we give an extended overview of experimental observations on DNA cholesteric phases and discuss the factors affecting their stability. Then, we consider the effects of steric and electrostatic interactions of grooved charged helical molecules on the sign of cholesteric twist. We present some theoretical results on the strength of DNA-DNA chiral interactions, on DNA azimuthal correlations in cholesteric phases, on the micron-range pitch of DNA cholesteric phases, and on the regions of existence of DNA chiral phases stabilized by DNA-DNA electrostatic interactions [AC, JPCB, 112 12585 (2008)]. We suggest that 146 bp long DNA fragments with stronger affinities for nucleosome formation can form less chiral phases, with a larger left-handed cholesteric pitch. Also, the value of left-handed pitch formed in assemblies of homologous DNA fragments is predicted to be smaller than that of randomly sequenced DNAs. We expect also the cholesteric assemblies of several-kbp-long DNAs to require higher external osmotic pressures for their stability than the twisted phases of short nucleosomal DNA fragments at the same DNA lattice density.

15 min. break

CPP 18.8 Tue 11:30 ZEU 114

**Bundle Formation in Polyelectrolyte Brushes** — JENS-UWE GÜNTHER, ●HEIKO AHRENS, and CHRISTIANE A. HELM — Institut für Physik, Uni Greifswald, Felix-Hausdorff-Str. 6, 17487 Greifswald

Bundle formation in the vertically oriented polyelectrolytes within polyelectrolyte brushes is studied with x-ray reflectivity and grazing-incidence diffraction as a function of grafting density and ion concentration. At 0.5 Molar monomer concentration and without added salt, a bundle consists of two chains and is 5 nm long. On the addition of up to 1M CsCl, the aggregation number increases up to 15 whereas the bundle length approaches a limiting value, 2 nm. We suggest that the bundle formation is determined by a balance between long-ranged electrostatic repulsion, whose range and amplitude is decreased on salt addition, and short-ranged attraction.

CPP 18.9 Tue 11:45 ZEU 114

**Conformation of poly(styrene sulfonate) layers physisorbed from high salt solution studied by force measurements on two different length scales** — ●STEPHAN BLOCK and CHRISTIANE A. HELM — Institut für Physik, Uni Greifswald, Felix-Hausdorff-Str. 6, 17487 Greifswald

The colloidal probe technique (CPT) is used to measure distance-dependent interaction forces between polyelectrolyte layers physisorbed from 1 M NaCl solution in salt solutions between 0.1 mM

and 1 M. Both linear polycations (poly(allylamine)hydrochloride, poly-L-lysine) and linear polyanions (poly(styrenesulfonate)) are used. The repulsive interaction energies in the range between 10(-7) and 10(-4) J/m(2) are described by the theory of Alexander and de Gennes for surfaces covered with neutral anchored polymers. However, the brush thickness scales with molecular area and salt concentration with a power of -1/3 as known from a salted brush and reaches approximately 50% of the contour length in diluted solutions. For PSS at low salt conditions, the brush length amounts to 30% of the contour length, a behavior known for polyelectrolyte brushes and attributed to the entropy of the counterions trapped in the brush. A negatively charged AFM tip penetrates the brush—a repulsive electrostatic force between the tip and surface is found, and single chains can be imaged. Thus, with the nanometer-sized AFM tip, the flatly adsorbed fraction of the PSS chains is seen, whereas the micrometer-sized colloidal probe interacts with the fraction of the chains penetrating into solution.

CPP 18.10 Tue 12:00 ZEU 114

**Change in Molecular Ordering in Mechanically Stressed Polyelectrolyte Films** — JOHANNES FRÜH<sup>1</sup>, RUMEN KRASDEV<sup>2</sup>, and ●RALF KÖHLER<sup>3,1</sup> — <sup>1</sup>MPI of Colloids and Interfaces, Dept. Interfaces, Potsdam, Germany — <sup>2</sup>NMI, WB Bioanalytik, Tübingen, Germany — <sup>3</sup>Helmholtz Centre Berlin for Materials and Energy, Dept. SF1, Berlin, Germany

Polyelectrolyte Multilayers (PEM) are organic films which consist in complexed layers of two polyions of opposite charge commonly build-up on solid substrate. The widely used layer-by-layer preparation method allows for a high tunability of the properties of the PEM. Although several studies exist about mechanical behaviour of these films, relatively little is known about the underlying internal structure and the structural changes on molecular level caused by external load/stimulus.

We are interested in the local distribution of micro- and mesoscopic substructures in the PEM-network (e.g., voids or cross-linker points) and their implications on general macroscopic properties, as stability and reversibility (ageing, fatigue) of the films. Especially the effects of external and internal mechanical load shall be examined.

Two strategies are pursued: firstly, the manipulation of internal mechanical stress by incorporation of solvent molecules into the polymer network (swelling experiments); and secondly, the application of external mechanical stress on soft matter-supported PEM samples. Here neutron reflectometry proves to be a powerful tool due to its ability to test for the thickness of the sample and for its specific material content at the same time.

CPP 18.11 Tue 12:15 ZEU 114

**Immobile Light Water and Proton-Deuterium Exchange in Polyelectrolyte Multilayers** — ●OXANA IVANOVA<sup>1</sup>, OLAF SOLTWEDEL<sup>1</sup>, ROLAND STEITZ<sup>2</sup>, RALF KÖHLER<sup>2</sup>, and CHRISTIANE A. HELM<sup>1</sup> — <sup>1</sup>Institut für Physik, Uni Greifswald, Felix-Hausdorff-Str. 6, 17487 Greifswald — <sup>2</sup>Leibnitz-Zentrum für Material- und Energieforschung Berlin

To describe the swelling of polyelectrolyte multilayers (PEMs) on a molecular scale, the PEM architecture is varied. The polyanion is poly(styrenesulfonate) (PSS) and the polycation poly(allylamine hydrochloride) (PAH). PEM either consists of 10 protonated polyelectrolyte bilayers (p<sub>10</sub>), 10 deuterated bilayers (d<sub>10</sub>), or two different blocks, p<sub>5</sub>d<sub>5</sub> or d<sub>5</sub>p<sub>5</sub>. Prior to the exposure to 100 % relative humidity (RH) D<sub>2</sub>O or H<sub>2</sub>O, the PEM is immersed in liquid D<sub>2</sub>O or H<sub>2</sub>O, respectively. The obtained scattering length density profiles provide insight into the exchange rates of the constituent molecules: The data indicate that three mobile protons of each PAH monomer are replaced by deuterium ions, yet most of the H<sub>2</sub>O molecules found in PEM at 0% RH remain bound at 100% RH D<sub>2</sub>O. This is in consistency with the fact that the core of PEM is in a glassy state. At 0% RH, the amount of bound water in the deuterated layers does not depend on the film architecture, whereas in the protonated layers it does.