

CPP 17: Polyelectrolytes

Time: Tuesday 9:30–12:30

Location: H40

Invited Talk

CPP 17.1 Tue 9:30 H40

Molecular Dynamics Simulations of Compacted Polyelectrolyte Complexes — ●DIDDO DIDDENS, JÖRG BASCHNAGEL, and ALBERT JOHNER — Institut Charles Sadron, Université de Strasbourg, CNRS UPR22, 23 Rue du Loess, 67034 Strasbourg Cedex 2, France

Compacted polyelectrolyte complexes (CoPECs) are gel-like materials created by ultracentrifugation [1] or extrusion [2] from solution-precipitated polyelectrolyte complexes. Usually, polyelectrolyte complexes have an ill-defined microscopic structure due to the fast aggregation kinetics of polyanions and polycations, which prevents the formation of an optimized ion pairing between positive and negative charges. Here, the two experimental strategies mentioned above offer a novel route to densify/reshape the complexes, which is difficult to achieve otherwise. However, although it is known from micrograph imaging that the CoPECs are highly porous, the precise effect of the centrifugation/extrusion on the polymer matrix is less clear.

We address this issue by mimicking the experimental centrifugation protocol in a fully atomistic Molecular Dynamics simulation. In particular, we identify the structural and dynamical changes during the individual stages of the compaction, which includes sedimentation, subsequent compression at the boundary and the behavior after centrifugation. These findings are discussed in context with the experimental observations.

[1] Porcel, Schlenoff, *Biomacromolecules*, **2009**, 10, 2968

[2] Shamoun, Reisch, Schlenoff, *Adv. Funct. Mater.*, **2012**, 22, 1923

CPP 17.2 Tue 10:00 H40

Long-ranged steric forces between physisorbed polyethylenimine-iron complexes — ●HEBA S. MOHAMAD, HEIKO AHRENS, and CHRISTIANE A. HELM — Inst. for Physics, Uni Greifswald, 17487 Greifswald, Germany

The conformation of branched polyethylenimine (PEI) layers physisorbed from 1 mM Fe₂SO₄ solution is determined by force measurements. The colloidal probe technique (CPT) is used. PEI adsorbs flatly as purely electrostatic forces indicate. Addition of EDTA to the adsorption solution leads in pure water to steric forces as predicted for neutral grafted brushes. On addition of NaCl to the solution, the grafting density remains constant, yet the brush thickness shrinks and swells reversibly with the NaCl concentration.

X-ray reflectivity demonstrates that iron(II) is incorporated in the adsorbed polyethylenimine-iron complexes. Iron(II) can be washed from the adsorbed complex without removing the PEI. Adsorption of gold nanoparticles (AuNP) onto a PEI layer with chains protruding into solution leads to an increased AuNP coverage compared to flat positively charged surfaces.

CPP 17.3 Tue 10:15 H40

Polyelectrolyte complex nanoparticles: Adhesive material for local delivery of drugs and proteins — ●MARTIN MÜLLER^{1,2}, DAVID VEHLow^{1,2}, RICHARD PETZOLD^{1,2}, BEATRICE WOLTMANN³, DIANA WEHRUM³, and UTE HEMPEL³ — ¹Leibniz-Institut für Polymerforschung Dresden e.V. — ²Technische Universität Dresden, Chemie und Lebensmittelchemie — ³Technische Universität Dresden, Physiologische Chemie

Mixing aqueous solutions of oppositely charged biorelated polyelectrolytes (PEL) in the presence of ionic compounds results in colloid dispersions of PEL complex (PEC) nanoparticles (NP) [1], which have potential for drug and protein delivery [2,3,4]. Casting these loaded PEC NP dispersions onto material surfaces results in coatings, from which drugs and proteins can be released into relevant aqueous media under local and kinetic control. Charged drugs like antibiotics and bisphosphonates and proteinogenic growth factors relevant for bone healing were loaded. Herein results on the adhesiveness and release kinetics of drug loaded PEC NP coatings under variation of drug/polycation/polyanion composition using in-situ-ATR-FTIR-, UV/VIS- and circular dichroism spectroscopy and SFM are presented [2,3,4]. Furthermore, results on the cytocompatibility of PEC NP coatings with respect to bone cells under variation of composition and net charge sign are given [4,5]. This work is sponsored by DFG (Transregio 79, Project M7). [1] *Adv. Polym. Sci.* **2014**, 256, 197. [2] *J. Pharm. Biomed. Anal.* **2012**, 66, 183. [3] *Biointerphases* **2013**, 8, 25. [4] *Biointerphases* **2015**, 10(1), 011001. [5] *Int. J. Nanomedicine* **2014**,

9, 2205.

CPP 17.4 Tue 10:30 H40

Effect of Binary Polymer Mixtures on the Growth of Polyelectrolyte Multilayers (PEMs) — ●MALTE PASSVOGEL¹, PETER NESTLER¹, RALF KÖHLER², OLAF SOLTWEDEL³, and CHRISTIANE A. HELM¹ — ¹Inst. for Physics, Uni Greifswald, 17487 Greifswald, Germany — ²Helmholtz-Zentrum Berlin, 14109 Berlin, Germany — ³MPI for Solid State Research, Outstation at FRM-II, 85747 Garching, Germany

Non-linear growth regimes of electrostatically assembled PEMs are investigated with in-situ ellipsometry. Poly(styrene sulfonate) (PSS) and poly(diallylmethylammonium) (PDADMA) are used ($c_{NaCl} = 0.1$ mol/L). Always, linear growth is preceded by a parabolic growth regime. For films of binary PDADMA mixtures, the composition in the film appears to be the same as in the adsorption solution. If PSS molecular weight (M_w) is below a threshold, 25 kDa, film build-up starts with an exponential growth regime, and pronounced PSS interdiffusion is found with neutron reflectivity using deuterated PSSd. 0.5 mol % PSS with high M_w in the adsorption solution prevents exponential growth. Neutron reflectivity shows no vertical center of mass movement of PSS with M_w above the threshold, both in the parabolic and the linear growth regimes. We suggest that polyelectrolytes (PEs) with high M_w adsorb with trains, tails and loops, while PEs with M_w below the threshold adsorb with one train and one tail only.

CPP 17.5 Tue 10:45 H40

Polyelectrolyte Multilayers – A Coarse-Grained Simulation Approach — DIDDO DIDDENS¹, MARTIN VÖGELE², ANDREAS HEUER¹, CHRISTIAN HOLM³, and ●JENS SMIAATEK³ — ¹Institut für Physikalische Chemie, Westfälische Wilhelms-Universität Münster, Corrensstraße 28/30, 48149 Münster — ²Max-Planck-Institut für Biophysik, Max-von-Laue-Straße 3, 60438 Frankfurt am Main — ³Institute for Computational Physics, University of Stuttgart, Allmandring 3, 70569 Stuttgart

Polyelectrolyte multilayers are thin films created by the alternate adsorption of polyanions and polycations on a charged substrate. Due to the controlled layer-by-layer assembly, these materials offer a wealth to create tailored materials such as surface coatings or membranes. However, the detailed molecular structure in these films is difficult to probe by experimental techniques, whereas atomistic simulations, which are in principle able to capture the full microscopic details, are currently too demanding to study the layer-by-layer assembly beyond the first few adsorption steps [1].

To bridge this gap, we employ simulations of the coarse-grained MARTINI model, which has recently been adapted to poly(styrene sulfonate) (PSS) and poly(diallyl dimethyl ammonium) (PDADMA). A clear advantage of this model is that it – in contrast to very generic polyelectrolyte models – still retains the relevant chemical details. We mimic the layer-by-layer assembly in our simulations, and discuss the results in context with experimental data.

[1] Micciulla *et al.*, *Soft Materials*, **2014**, 12, S14

15 min. break

CPP 17.6 Tue 11:15 H40

Mutual effects in the temperature responsive behaviour of brush/multilayer composites — ●SAMANTHA MICCIULLA¹, OLAF SOLTWEDEL², OLIVER LÖHMANN¹, and REGINE VON KLITZING¹ — ¹TU Berlin, Germany — ²FRM-II, MLZ Garching, Germany

The extensive use of polymers to prepare smart coatings is reasoned by their versatility to be assembled or synthesized in different geometries and to the large variety of responsiveness obtained by the choice of specific functionality. The present study focuses on the investigation of the temperature-responsive behavior of a composite made by polyelectrolyte multilayers (PEMs) physisorbed onto temperature-sensitive brushes. Ellipsometry was used to monitor the brush collapse from the thickness decrease as a function of temperature, while neutron reflectometry was applied to deduce the change of monomer distribution perpendicular to the substrate at temperatures below, across and above the phase transition, respectively. The results showed that the adsorption of PEMs enhanced the hydrophobicity of the charged region of

the polymer brush, which directly interacts with the adsorbing chains, and this caused a shift of its phase transition to lower temperature. Moreover, the internal contrast obtained by combining hydrogenated brushes with deuterated PEMs allowed to highlight the penetration of polyelectrolyte chains inside the charged brush by comparing the neutron scattering length density profile of pure and corresponding PEM-capped brushes. This study demonstrates the possibility of creating complex brush/multilayer composites preserving the responsive behavior behind the significant interpolyelectrolyte interactions.

CPP 17.7 Tue 11:30 H40

Uptake and Spatial Distribution of Thiol-Capped Gold Nanoparticles in Strong Polyelectrolyte Brushes — •DIKRAN KESAL, STEPHANIE CHRISTAU, PATRICK KRAUSE, TIM MÖLLER, and REGINE VON KLITZING — TU-Berlin, Straße des 17. Juni 124, 10623 Berlin, Germany

Polymer brushes are suitable candidates for the design of responsive smart surfaces which can be prepared by end-grafting polymers with the desired chain functionality on solid substrates. These surfaces have the ability to respond to external stimuli by changing their chemical or physical properties and can be used as a matrix for the immobilization of gold nanoparticles (AuNPs), which induce optical properties due to their surface plasmon resonance. In order to use the Brush/AuNP hybrids as smart surfaces, we must be able to control the arrangement of the NPs inside the brush and to correlate it with the optical properties of the composite system.

The present study addresses the distribution and uptake of charge switchable AuNPs inside poly-[2-(Methacryloyloxy) ethyl] trimethylammonium chloride (PMETAC) which yields a strong positively charged polyelectrolyte brush. The 5 nm AuNPs are capped with mercaptopropionic acid and are either negatively or uncharged depending on the pH. While some recent efforts have been made in terms of particle uptake and distribution in neutral (PNIPAM) and weakly charged (PDMAEMA) polymers by changing the thickness of the brushes and particle size, here the focus is on understanding how charges affect particle loading and penetration into the brush.

CPP 17.8 Tue 11:45 H40

Steady-state shear motion of polyelectrolyte-brush bilayers with oppositely charged polyelectrolyte stars — •MAJID FARZIN^{1,2}, TORSTEN KREER¹, and JENS-UWE SOMMER^{1,2} — ¹Leibniz Institute of Polymer Research Dresden Germany — ²Institute of Theoretical Physics, Department of Mathematics and Natural Sciences, Technical University of Dresden Germany

Molecular dynamics simulations are employed to study polyelectrolyte-brush bilayers (PEB) with embedded polyelectrolyte stars (PES) under steady-state shear motion of two grafting surfaces. We use the Ewald-summation method to incorporate electrostatic interactions and the dissipative-particle-dynamics thermostat to account for hydrodynamic correlations. To study the influence of electrostatic interactions, we vary both the Bjerrum length and the fraction of charged brush monomers. Increasing the strength of electrostatic interactions leads to a slightly smaller osmotic pressure concomitant with a larger shear stress. Consequently, the resulting kinetic friction coefficient increases

upon increasing of Bjerrum length or charge density. We relate this result to conformational properties, such as the distribution of stars within the bilayer, which depend strongly on the electrostatic interactions. Our study provides a significant advance towards a more realistic modeling of biological transport processes as they have previously preformed for electrically inert brushes of PEB without inclusions.

CPP 17.9 Tue 12:00 H40

Modified Dendrimers for drug delivery - a charge and size investigation — BRIGITTE WIESNER, DIETMAR APPELHANS, and •ULRICH SCHELER — Leibniz-Institut für Polymerforschung Dresden e.V.

Dendrimers are frequently used as drug carriers. The high charge density makes them an ideal candidate for electrostatic binding. A combination of diffusion and electrophoresis NMR has been applied to study the effective size and charge of dendrimers and aggregates. The additional chemical information from chemical-shift resolution is used to differentiate dendrimers from small ligands bound. Thus the electrostatic interaction between PAMAM dendrimers and poly(styrene sulfonate) has been investigated as a function of pH. Functionalization of dendrimers with sugars like maltose control the interaction with lipids and model membranes. The effective charge of the modified dendrimers over pH is monitored in E-NMR. At low pH, the highly charged state, the hydrodynamic is larger because of the enhanced interaction with water. Diffusion NMR shows, that strong binding to lipid vesicles is hindered by the modification with maltose.

CPP 17.10 Tue 12:15 H40

The influence of transition metal cation size on protein phase behaviour — •OLGA MATSARSKAIA¹, MICHAL BRAUN¹, FELIX ROOSEN-RUNGE², FAJUN ZHANG¹, and FRANK SCHREIBER¹ — ¹Institut für Angewandte Physik, Universität Tübingen, 72076 Tübingen — ²Institut Laue-Langevin, Grenoble, France

Transition metal cations induce many different types of interesting phase behaviour in aqueous solutions of negatively charged proteins, including reentrant condensation and liquid-liquid phase separation (LLPS) [1] which are involved in protein condensation diseases and may be used to optimise protein crystallisation [2]. We present a systematic study of the dependence of cation size on phase transitions in bovine serum albumin (BSA) using small-angle X-ray scattering (SAXS) and isothermal titration calorimetry (ITC). SAXS reveals an increase of the reduced second virial coefficient B_2/B_2^{HS} , i.e. a weaker interprotein attraction, with increasing cation size from Gd^{3+} to La^{3+} . This is consistent with a weaker LLPS with increasing cation size at room temperature and its eventual disappearance in the presence of La^{3+} . ITC shows cation-protein binding to be an entropy-driven process, presumably induced by the release of hydration water around the cations and surface residues of the protein. With decreasing cation size, the entropy-enthalpy balance of this reaction changes, as shown by both ITC and calculations [3], which has important implications for the understanding of the entropy balance of ions in solution.

[1] Zhang et al. (2014). PAC, 86, 191; [2] Sauter et al. (2015). JACS, 137, 1485; [3] Ciupka et al. (2010). PCCP, 12, 13215.