

CPP 40: Charged Soft Matter II

Time: Wednesday 9:30–11:30

Location: PC 203

CPP 40.1 Wed 9:30 PC 203

Molecular Dynamics Simulations of Ultracentrifuged Polyelectrolyte Complexes — ●DIDDO DIDDENS, ALBERT JOHNER, and JÖRG BASCHNAGEL — Institut Charles Sadron, Université de Strasbourg, 23 Rue du Loess, BP 84047, 67034 Strasbourg Cedex 2

Polyelectrolyte complexes (PECs) are formed by the aggregation of positively and negatively charged polymer species, which precipitate rapidly from solution in case of equimolar mixing. As the fast complexation kinetics prevents the formation of an optimized pairing between positive and negative charges, the microstructure of these aggregates is ill-defined, resulting in a material that is difficult to process further.

Recently, Schlenoff *et al.* [1] have demonstrated that the precipitates can be reshaped via ultracentrifugation in concentrated sodium chloride solutions, yielding a compacted, gel-like material, whose rheological properties make them interesting candidates for bioimplants [2]. However, despite the success of this novel route to post-process PECs, the underlying molecular mechanisms are not yet fully resolved.

We study the complex structure before, during and after centrifugation in a non-equilibrium Molecular Dynamics simulation of a fully atomistic simulation model. In a second step, we investigate the effect of these structural changes on the dynamics inside the PECs, and discuss these findings in context with the experimental observations.

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

[2] Hariri and Schlenoff, *Macromolecules*, **2010**, 43, 8656

CPP 40.2 Wed 9:45 PC 203

Coarse-grained models for simulations of polyelectrolyte multilayers and complexes — ●MARTIN VÖGELE^{1,2}, JENS SMIAŁEK¹, and CHRISTIAN HOLM¹ — ¹Institut für Computerphysik, Universität Stuttgart — ²Max-Planck-Institut für Biophysik, Frankfurt am Main

We present coarse-grained models for the polyelectrolytes Poly(styrene sulfonate) (PSS) and Poly(diallyldimethylammonium) (PDADMA) in terms of a MARTINI based approach. Our models allow us to study the properties of polyelectrolyte complexes and polyelectrolyte multilayers on large length and long time scales while still taking into account chemical details. In our simulations, we use the new polarizable coarse-grained MARTINI water model. We further studied the behavior of this water model in presence of varying sodium chloride concentrations. The numerical findings are compared to experimental results and atomistic models.

Our results validate that the MARTINI water model can be used to reproduce the properties of aqueous salt solutions in good agreement to atomistic models. The polyelectrolyte models further reproduce the correct charge compensation mechanism as well as the recently observed lower water dielectric constants which can both be interpreted as the underlying reasons for the stability of polyelectrolyte multilayers and complexes.

CPP 40.3 Wed 10:00 PC 203

Absorption of a polyelectrolyte star by an oppositely charged polyelectrolyte brush: A molecular dynamics simulation study — ●MAJID FARZIN^{1,2}, TORSTEN KREER¹, and JENS-UWE SOMMER^{1,2} — ¹Leibniz Institute for Polymer Research Dresden — ²Technische Universität Dresden

By means of molecular dynamics simulations, we study interactions between a polyelectrolyte brush and an oppositely charged polyelectrolyte star. We explicitly include counter-ions of two different sizes and vary the strength of Coulomb interactions in two ways; by varying the Bjerrum length of fully charged polyelectrolytes and by choosing different charge fractions of polyelectrolyte brush monomers for a Bjerrum length corresponding to the value in water. Simulations show that there is a Bjerrum length at 10^{-3} (Lennard-Jones units) above which the polyelectrolyte star undergoes a discontinuous absorption transition by the polyelectrolyte brush. For a Bjerrum length of 10^{-2} the polyelectrolyte star has the minimum extension in the direction perpendicular to the brush. Finally, for a Bjerrum length of 0.5 the polyelectrolyte brush undergoes a collapse transition.

CPP 40.4 Wed 10:15 PC 203

Stimuli-responsive polyampholyte hydrogels - influence of charge asymmetry and ionic strength — ●MARGARITA DYAKONOVA¹, MARIA T. POPESCU², KONSTANTINOS KYRIAKOS¹, SE-

BASTIAN JAKSCH³, CONSTANTINOS TSITSILIANIS², and CHRISTINE M. PAPADAKIS¹ — ¹TU München, Physik-Department, Physik weicher Materie, Garching — ²University of Patras, Greece — ³JCMS at FRM II, Garching

We investigate the rheological and structural properties of physical hydrogels, formed via charge driven self-association of triblock polyampholytes PAA-P2VP-PAA and PAA-QP2VP-PAA (PAA, P2VP and QP2VP are poly(acrylic acid), poly(2-vinylpyridine) and quaternized poly(2-vinylpyridine)), which have attracted a considerable interest for use as injectable hydrogels and drug carriers. Both, the PAA and P2VP blocks are ionizable. PAA is deprotonated at high pH, whereas P2VP is positively charged at low pH. QP2VP is highly charged, independently of pH. In water, the gelation threshold is at 1.0 wt% [1]. Small-angle neutron scattering (SANS) experiments revealed the morphological changes depending on the charge asymmetry. The structure develops from uncorrelated globular aggregates to a network. These findings corroborate the ones from rheological studies, implying the formation of stiff hydrogels at low pH. Ionic strength is an alternative way of controlling the strength of electrostatic interactions. Combined SANS and rheological studies have revealed a different structure evolution inside the polyampholyte networks depending on ionic strength. [1] N. Stavrouli *et al.*, *Polymer* 49, 1249 (2008).

CPP 40.5 Wed 10:30 PC 203

Specific salt effects on thermophoresis of charged colloids — ●ARGHYA MAJEE¹, KYRIAKOS A. ESLAHIAN², MICHAEL MASKOS², and ALOIS WÜRGER³ — ¹Max Planck Institute IS & University of Stuttgart, Germany — ²Fraunhofer ICT-IMM, Mainz, Germany — ³LOMA, Université de Bordeaux & CNRS, France

The electrolyte Seebeck effect determines to a large extent the properties of charged colloids that are heated or subject to a thermal gradient. The electric double layer responds to a non uniform temperature through several mechanisms, resulting in a significant thermocharge and transport to the hot or to the cold side [1]. In this contribution we discuss the Soret effect of charged polystyrene particles as a function of temperature and electrolyte composition [2]. As a main result we find that the Soret coefficient is determined by charge effects, and that non-ionic contributions are small. In view of the well-known electric-double layer interactions, our thermal field-flow fractionation data lead us to the conclusion that the Soret effect originates to a large extent from diffusiothermophoresis in the salt gradient and from the electrolyte Seebeck effect, both of which show strong specific-ion effects. Moreover, we find that thermophoresis of polystyrene beads is fundamentally different from proteins and aqueous polymer solutions, which show a strong non-ionic contribution.

References:

[1] A. Majee, A. Würger, *Phys. Rev. Lett.* **108**, 118301 (2012).

[2] Kyriakos A. Eslahian, A. Majee, M. Maskos, and A. Würger, *Soft Matter* **10**, 1931 (2014).

CPP 40.6 Wed 10:45 PC 203

Molecular dynamics simulation of sulfone linked sulfonated dimers — ●ANAND NARAYANAN KRISHNAMOORTHY¹, JENS SMIAŁEK², and CHRISTIAN HOLM³ — ¹Institute for Computational Physics, University of Stuttgart — ²Institute for Computational Physics, University of Stuttgart — ³Institute for Computational Physics, University of Stuttgart

This project focuses on the investigation of structural properties of sulfone linked sulfonated dimers in lithium form via all atom molecular dynamics simulations. Previous research has been primarily focused on sulfonated polyelectrolytes in apolar and aprotic solvents in sodium form. But it is quite interesting to study the conformations and binding mechanisms of these typical dimers in lithium form in a broad range of solvents. The results show that the typical conformations of these dimers plays a vital role in determining the suitable ion binding mechanism to the dimer. Triple binding mechanism is favored for sulfonic acid ortho form of the dimer where a single and double binding mechanism is favored for the meso form. Also the condensation behavior of these dimers were studied under various aprotic, protic, polar and apolar solvents.

CPP 40.7 Wed 11:00 PC 203

Mechanisms underlying reentrant phase behavior of proteins: a model system — •MICHAL BRAUN¹, MARCELL WOLF¹, OLGA MATSARSKAIA¹, GUDRUN LOTZE², FAJUN ZHANG¹, and FRANK SCHREIBER¹ — ¹Institut für Angewandte Physik, Universität Tübingen, 72076 Tübingen — ²ESRF, Grenoble, France

Controlling and tuning the phase behavior of proteins is important in many areas such as structural biology including protein crystallization, pharmacology and biotechnology. One important effect in protein phase behavior is reentrant condensation (RC) which can be induced and controlled by multivalent ions ([1], [2], [3]). For example, YCl₃ leads to RC in bovine serum albumin (BSA). This system features a macroscopic phase separation, which makes it difficult to study the mechanisms behind RC using scattering. LaCl₃, on the other hand, induces cluster formation and RC in BSA without phase separation and the BSA-LaCl₃ system is therefore highly suitable for the study of the physical mechanisms behind RC. Here, we discuss our findings from systematic SAXS and light scattering (LS) experiments as a function of both protein and salt concentrations. SAXS curves can be fitted using a sticky hard sphere model and the reentrant behavior is reflected in the stickiness parameter. LS helps to reveal the dependency of the cluster sizes on the interactions. These measurements thus provide detailed insights into the interactions in a system featuring RC. [1] Zhang et al., *PRL*, **101**, 148101, 2008, [2] Zhang et al., *Soft Matter*, **8**, 1313, 2012, [3] Roosen-Runge et al., *PNAS*, **108**, 11815, 2011

CPP 40.8 Wed 11:15 PC 203

The effect of variable charge patterns: interactions and phase behaviour of a non-monoclonal antibody mixture — •STEFANO DA VELA¹, FAJUN ZHANG¹, MICHAEL SZTUCKI², RALF SCHWEINS³, and FRANK SCHREIBER¹ — ¹Institut für Angewandte Physik, Universität Tübingen, 72076 Tübingen — ²ESRF, Grenoble, France — ³ILL, Grenoble, France

Bovine γ -globulin is an easily available mixture of antibodies (immunoglobulins) with different specificities: this implies that the constituents feature a manifold of surface charge distribution patterns. The main component is Immunoglobulin G (IgG), an anisotropic, Y-shaped protein. We aim to understand the relationship between the profusion of anisotropic charge driven interactions present in the system and the macroscopic phase behaviour. Solutions of γ -globulin in a wide range of protein volume fractions (0.001 up to 0.27) are investigated with and without added salts using predominantly turbidimetry, dynamic light scattering, small angle x-ray and neutron scattering. We show how the heterogeneity of the charge distribution in different proteins accounts for sample bidispersity and explains self-association and turbidity in γ -globulin dispersions at low ionic strengths. At high volume fractions, the repulsive component of the effective interaction is modelled considering protein anisotropy. Our work has potential applications in the stability enhancement of analogous therapeutic blood products.