CPP 45: Charged Soft Matter, Polyelectrolytes and Ionic Liquids II

Time: Friday 11:30–12:45 Location: H38

CPP 45.1 Fri 11:30 H38

Binding of small molecules to polyelectrolytes driven by electrostatics — •Ulrich Scheler — Leibniz-Institut für Polymerforschung Dresden e.V., Hohe Str. 6, 01069 Dresden

The interaction of small molecules or ligands to macromolecules (polyelectrolytes or proteins) in solution is plays an important role in biological and medical applications. Pulsed-field-gradient (PFG) nuclear magnetic resonance (NMR) has been applied to measure translational motion of molecules and complexes in aqueous solution, that may be diffusion orelectrophoretic motion. Two-dimensional NMR experiments correlating chemical shift that is used to assign different species with either the diffusion coefficient or the electrophoretic mobility enable determining the mobility of diffusion coefficient respectively in mixtures for the individual components. From the combination of diffusion and electrophoresis NMR the effective charge of the species under investigation is derived. Weak interaction of the ligand to the macromolecule means that the ligand binds for a fraction of time to the macromolecule and is free in the solution for another fraction. From the thus observed weighted average the bound fraction is calculated for every condition no titration experiment is required. The strong polyelectrolyte PDADMAC has been studied interacting with glutamic acid as a function of pH. The bound fraction of glutamic acid increases with increasing pH and thus increasing negative charge of glutamic acid showing that the interaction is driven by electrostatic interaction rather than other possible interactions. The bound fraction as a function of pH coincides with the charge.

CPP 45.2 Fri 11:45 H38

How charge regulation affects adsorption of proteins into polyelectrolyte brushes: A simulation study — •Keerthi Radhakrishnan and Christian Holm — Institute for Computational Physics, University of Stuttgart, D-70569 Stuttgart, Germany

In recent years, polyelectrolyte (PE) brushes have drawn significant attention for their industrial and biomedical applications, particularly their ability to immobilize proteins via electrostatic interactions, even beyond the isoelectric point where both brush and protein share a similar charge. This counterintuitive phenomenon is normally attributed to "charge patch" effects from protein surface heterogeneity or "charge regulation" involving reionization and charge reversal near charged entities.

Using coarse-grained simulations, we investigate weak PE brushes interacting with pH-responsive ampholytic nanoparticles exhibiting patchy and non-patchy charge distributions. Building on prior single-ion models, we incorporate realistic protein models with asymmetric charge group distributions to explore higher-order and charge patch-induced effects. Our findings reveal the critical role of charge regulation stemming from anisotropic nanoparticle surface charge, brush potential, and brush-induced pH modulation in driving protein adsorption beyond the isoelectric point.

[1] K. Radhakrishnan, D. Beyer, and C. Holm, How Charge Regulation Affects pH-Responsive Ampholyte Uptake in Weak Polyelectrolyte Brushes, https://doi.org/10.26434/chemrxiv-2024-b10lj-v2., Macromolecules, in print.

CPP 45.3 Fri 12:00 H38

Molecular Dynamics Simulations of Structural and Dynamical Properties of Polymerized Ionic Liquids — •Arshid Ahmad and Michael Vogel — Institute for Condensed Matter Physics, Technische Universität Darmstadt, Darmstadt, Germany

Ionic liquids consist of cations and anions and have melting points less than 100°C. Their key features include negligible vapor pressure, high thermal stability, and favorable solvation properties, rendering them valuable materials for applications, e.g., in green chemistry and electrochemistry. In addition to these simple ionic liquids (SILs), polymerized ionic liquids (PILs) receive considerable attention because they add the favorable mechanical properties of polymers to these systems. We present MD simulations of a SIL and a corresponding PIL. The latter comprises BF4 anions and polymerized cations, which feature imidazolium rings connected by 6 methylene groups along the backbone. We use MD simulations to determine both structural and dynamical properties of this PIL. In particular, we relate the temperature-dependent local and diffusive dynamics of the anions and polymerized cations and we analyze dynamical couplings of both components. For the anions, the analysis includes the mechanism and f the motion. For the polymerized cations, we investigate not only the segmental motion but we also tackle the question to which degree the Rouse model is capable of describing the dynamics of highly charged polymer chains, which strongly interact with counter-ions. A detailed comparison of the results for the SIL and PIL reveals the effects of cation polymerization on structural and dynamical properties.

CPP 45.4 Fri 12:15 H38

Condensate size control by charge asymmetry — •Chengjie Luo[1], Nathaniel Hess[2], Dilimulati Aierken[2], Yicheng Qiang[1], Jerelle A. Joseph[2], and David Zwicker[1] — [1]Max Planck Institute for Dynamics and Self-Organization — [2]Princeton University

Biomolecular condensates are complex droplets composed of various types of biomolecules, including nucleic acids and proteins. These condensates form mainly due to liquid-liquid phase separation, which is driven by short-range attraction between biomolecules. Typical biomolecules carry various net charges, so that long-ranged electrostatic interactions could affect phase separation. We study this situation using a simple model of two short-ranged attractive polymers with opposite charges and their counterions. We find that the charged polymers segregate from the solvent, and thus form two macrophases, when their charges are symmetric. In contrast, many droplets of equal size coexist when charge asymmetry is sufficiently strong. Such patterned phases form because the short-range attraction concentrates polymers within droplets, leading to net charges, which prevents droplet growth. Our molecular dynamics simulation and a continuous field theory demonstrate that droplet size decreases with charge asymmetry. Overall, we present a mechanism controlling droplet size via a trade-off between short-ranged attraction driving phase separation and long-ranged electrostatic repulsion if droplets accumulate net charges. Our results are relevant for understanding biomolecular condensates and creating synthetic patterns in chemical engineering.

CPP 45.5 Fri 12:30 H38

Structural transitions of a Semi-Flexible Polyampholyte — •Rakesh Palariya and Sunil P Singh — Indian Institute Of Science Education and Research, Bhopal , India

Polyampholytes (PA) are charged polymers composed of positively and negatively charged monomers. The sequence of the charged monomers and the bending of the chain significantly influence the conformation and dynamical behavior of the PA. Using coarse-grained molecular dynamics simulations, we comprehensively study the structural and dynamical properties of flexible and semi-flexible PA's. The simulation results demonstrate a flexible PA chain, displaying a transition from a coil to a globule in the parameter space of the charge sequence. Additionally, the behavior of the mean-square displacement (MSD), denoted as $< (\Delta r(t))^2 >$, reveals distinct dynamics, specifically for the alternating and charge-segregated sequences. The MSD follows a power-law behavior, where $< (\Delta r(t))^2 >\sim t^{\beta}$, with $\beta \approx 3/5$ and $\beta \approx 1/2$ for the alternating sequence and charge-segregated sequence in the absence of hydrodynamic interactions, respectively. However, when hydrodynamic interactions are incorporated, the exponent β shifts to approximately 3/5 for the charge-segregated sequence and 2/3 for the well-mixed alternating sequence. For a semi-flexible PA chain, varying the bending rigidity and electrostatic interaction strength (Γ_e) leads to distinct, fascinating conformational states, including globule, bundle, and torus-like conformations. The transition between various conformations is identified in terms of the shape factor estimated from the ratios of eigenvalues of the gyration tensor.