

Density Functional Theory for Polyelectrolytes Near Oppositely-Charged Surfaces

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We report a non-local density functional theory (NLDFT) for polyelectrolyte solutions within the primitive model, i.e., the sizes and charges of polymer chains and small ions are explicitly considered but the solvent is represented by a dielectric continuum. The excess Helmholtz energy functional incorporates a modified fundamental measure theory for the excluded-volume effects, a hypernetted-chain theory for the electrostatic interactions, and a generalized thermodynamic perturbation theory for the intra-chain correlations. With the analytical expressions for the cavity correlation functions (CCF) and direct correlation functions (DCF) of the corresponding monomeric fluids as input, the NLDFT yields the segment-level polymer density profiles and local distributions of small ions in excellent agreement with available simulation results. Unlike a typical coarse-grained mean-field method, the NLDFT faithfully captures both short- and long-range correlations in a polyelectrolyte system, and predicts that the adsorption of polyelectrolyte chains at an oppositely-charged surface is dominated by direct Coulomb interactions and a short-range excluded-volume effect. The NLDFT also enables us to describe the influence of the polyion chain length and small ion valence on the layering effect and charge inversion.