Structure and cluster formation in size asymmetric soft electrolyte systems

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We examine the structure and thermodynamic properties of systems composed ions with rigid Gaussian charge distributions of differing widths that only interact electrostatically. These ultrasoft electrolytes [1,2] provide insight into the role of electrostatics in colloidal systems and have been observed to exhibit a liquid-vapor phase transition, as well as aggregation.

We perform molecular dynamics and Monte Carlo simulations over a broad range of ion densities and electrostatic coupling strengths for systems containing ions with different width charge distributions. Under certain conditions, these systems are observed to form large, finite sized clusters in an isotropic phase. The structure of these clusters, their charge and electrostatic potential distribution, and energetics of formation are analyzed in detail.

We compare and interpret the simulation results with a splitting field theory [3] framework that focuses on fluctuations in the electrostatic potential. Within this approach, the short wavelength and long wavelength fluctuations are treated within different approximation schemes. This theory can accurately describe the counterion mediated attractive interactions between like-charged plates [3,4] and the one-component plasma (OCP) [5] from the weak, intermediate, and strong coupling regimes. As the charge distribution of one of the ion species in the ultrasoft electrolyte broadens, the system more closely resembles the OCP, where the splitting theory is known to work well. We carefully examine the evolution of ultrasoft electrolyte as the width of one of the ions changes from being infinitely broad to smaller sizes. In particular, we present spatial correlations in the fluctuations of the electrostatic potential, decomposing them into short and long wavelength contributions. This information is used to extend the splitting theory to capture the region of cluster formation.

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