Strong Attractions and Repulsions Mediated by Monovalent Salts

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Controlling interactions between proteins and nanoparticles in electrolyte solutions is crucial for advancing biological sciences and biotechnology. The assembly of charged nanoparticles (NPs) and proteins in aqueous solutions can be directed by modifying the salt concentration. High concentrations of monovalent salt can induce the solubilization or crystallization of NPs and proteins. By using a multiscale coarse-grained molecular dynamics approach, we show that, due to ionic correlations in the electrolyte, NPs pairs at high monovalent salt concentrations interact via remarkably strong long-range attractions or repulsions, which can be split into three regimes depending on the surface charge densities of the NPs.

NPs with zero-to-low surface charge densities interact via a long-range attraction that is stronger and has a similar range to the depletion attraction induced by polymers with radius of gyration comparable to the NP diameter. On the other hand, moderately charged NPs with smooth surfaces as well as DNA-functionalized NPs with no possibility of hybridization between them interact via a strong repulsion of range and strength larger than the repulsion predicted by models that neglect ionic correlations, including the Derjaguin–Landau–Vervey–Overbeek (DLVO) model. Interactions between strongly charged NPs (>2 e/nm²), both types smooth and DNA-functionalized NPs, show an attractive potential well at intermediate-to-high salt concentrations, which demonstrates that electrolytes can induce aggregation of strongly charged NPs. Our work provides an improved understanding of the role of ionic correlations in NP assembly and design rules to utilize the salting-out process to crystallize NPs.

Fig. 1. Three regimes of NP–NP interactions are found in the simulations. In regime I, where the NPs have zero or low charge densities, the interaction is attractive due to depletion interactions mediated by the clustering of ions. In regime II, where the charge is sufficiently large, we find a repulsion that is stronger and longer range than the double-layer force predicted by the DLVO theory. In regime III, where the NPs have very high charge densities resulting in strong counterion condensation on the NP surfaces, the potential shows a strong short-range repulsion and a deep long-range attractive well. van der Waals interactions between NPs are not included in our model.

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