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Understanding Depletion Induced Like-Charge Attraction from Self-Consistent Field Model

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Abstract. The interaction force between likely charged particles/surfaces is usually repulsive due to the Coulomb interaction. However, the counterintuitive like-charge attraction in electrolytes has been frequently observed in experiments, which has been theoretically debated for a long time. It is widely known that the mean field Poisson-Boltzmann theory cannot explain and predict this anomalous feature since it ignores many-body properties. In this paper, we develop efficient algorithm and perform the force calculation between two interfaces using a set of self-consistent equations which properly takes into account the electrostatic correlation and the dielectric-boundary effects. By solving the equations and calculating the pressure with the Debye-charging process, we show that the self-consistent equations could be used to study the attraction between like-charge surfaces from weak-coupling to mediate-coupling regimes, and that the attraction is due to the electrostatics-driven entropic force which is significantly enhanced by the dielectric depletion of mobile ions. A systematic investigation shows that the interaction forces can be tuned by material permittivity, ionic size and valence, and salt concentration, and that the like-charge attraction exists only for specific regime of these parameters.

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Key words: Like-charge attraction, self-consistent field model, dielectric-boundary effect, correlation energy, Green's function.

1 Introduction

The anomalous attraction between likely charged particles has been widely discussed during the past decades [21] since the experimental observation in colloidal [19] and

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biological systems [1, 25]. The like-charge attraction (LCA) at strong-coupling regime (high surface charge, multivalent counterions or low temperature) has been reported by particle-based simulations and theoretical studies such as density functional theory and strong-coupling theory [18, 32, 38, 39, 43–46]. Colloidal suspensions in monovalent electrolytes are usually considered as systems in weak-coupling regime at which the mean-field Poisson-Boltzmann (PB) theory is generally useful. The forces between charged surfaces are usually modelled through the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory, which combines the linearized PB equation with the Van der Waals interaction. However, the PB theory always predicts repulsive interaction between like charges [48, 56], and the DLVO theory overestimates the repulsion or underestimates the attraction [28], in contrast to the results of LCA experiments for colloids [34, 35], which demonstrates many-body effects are still significantly important at weak-coupling conditions and can not be ignored in order to understand the LCA phenomenon systematically.

For two colloidal particles with a small separation, the depletion force induced by the entropic repulsion of smaller mobile ions in the solvent could result in an effective inter-colloid attraction. The excluded volumes of small particles lead to a depletion layer. When the separation between surfaces is at the range of the particle diameter, they are attractive due to this depletion interaction [2, 55]. In electrolytes, the attractive distance can be much larger, comparable with the Debye screening length due to the long-range nature of electrostatic interaction [15]. In this sense, the attractive Van der Waals and the Casimir force [14, 31, 54] can be ignored in the LCA analysis. In the presence of inhomogeneous dielectric permittivity (whose properties have attracted wide recent interest [5,16,17,20,30,59,63]), ions are repelled from the low dielectric surfaces by their image charges, which has been shown in particle-based simulations [11, 24]. When the separation of surfaces becomes narrower, the repulsion becomes stronger, resulting in lower ionic concentration between the surfaces, and thus leading to an entropic driven attraction. The electrical field can also influence the solvent alignment and dielectric property, which is considered to be important for high ionic concentration or at the strong coupling region. This solvent polarization effect could be modelled through the Langevin theory to yield a field-dependent dielectric coefficient [4,7,8]. Recently, a continuum theory with a set of self-consistent equations including fluctuation effects of ions is introduced as a variational approach with general Gaussian ansatz [47,58], which have been generalized to take into account the image charge effects on attractive forces between neutral plates and in weak coupling region [57]. In the theory, the self energy of mobile ions is used as a correction to the mean potential in the PB theory, leading to a more accurate approximation of the potential of mean force (PMF) in the Boltzmann distribution, which consists of contributions from both the local ionic correlation and the ion-interface interaction energy. Although the LCA phenomenon has been predicted, it is less understood what is the effects of salt property as well as the charged surface.

In this paper, we study the interaction between plates in electrolytes by the self-consistent field model developed in [41, 60] which includes a modified treatment of the self energy. Through the modification, we include the ionic size effect to avoid the ion