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Two Generalizations from a Monte Carlo Study of Colloidal Solutions with Multivalent Electrolytes

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Abstract

A substantial amount of experimental and numerical evidence has shown that the Derjaguin-Landau-Verwey-Overbeek (DVLO) theory is not suitable for describing those colloidal solutions that contain multivalent counterions. Towards improved understanding of such solutions, we report Monte Carlo simulation calculations wherein following Ronzina and Bloomfield, we postulate that, in the absence of van der Waals forces, the overall force between charged colloidal particles in electrolyte solutions is determined by a dimensionless parameter $\Gamma=z^2 l_B/a$ that measures the electrostatic repulsion between counterions adsorbed on the macroion surface; here z = counterion valence; l_B = Bjerrum length; and a = average separation between counterions on the macroion surface calculated as if the macroion were fully neutralized. We find first, that the maximum repulsion between like-charged macroions occurs at $\Gamma\approx0.5$ and second, that onset of attraction occurs at $\Gamma\approx1.8$, essentially independent of the valence and concentration of the surrounding electrolyte. These simple dimensionless results may provide new understanding of interactions between electrostatic double layers and perhaps, offer explanations for some electrostatic phenomena related to interactions between DNA molecules or proteins.

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Applications of colloidal dispersions often require colloidal stability; that stability depends on the interaction potential between colloidal particles[1-7]. The classical inter-colloidal potential is that from Derjaguin-Landau-Verwey-Overbeek (DLVO) theory. This theory predicts that, in the absence of van der Waals attraction, the interaction between like-charged colloidal particles is always repulsive. However, in contrast to this prediction, it is now well known that, under some conditions, the electrostatic forces between like-charged colloidal particles can be attractive[8-15].

Electrostatic attraction between like-charged macroions is most likely to occur when the macroions are surrounded by salt ions that strongly interact with each other, as in a multivalent electrolyte solution or in a solvent of low dielectric constant. This strong ion-ion interaction leads to correlation between small ions and subsequently, to electrostatic attraction between macroions of the same charge. DLVO theory, as well as variations derived from the Poisson-Boltzmann equation, fail to predict the electrostatic attraction because they neglect ion-ion correlation. The contribution of ionic correlation to the inter-colloidal potential can be taken into account, in principle, by solving integral equations[16,17], or applying density-functional approximations[18], or field-theory expansions[19]. With substantial numerical effort, all these theories are able to explain attraction between like-charged macroions. However, because of the arbitrary truncation of perturbation expansions, the credibility of these theories is often questioned and their physical significance is often not clear.

Molecular simulation has been extensively applied to study interactions between charged colloidal particles in a primitive-model electrolyte solution where the solvent is represented by a continuous medium[9-12,20-22]. Simulation results have revealed much of the physics that governs the electrostatic phenomena for macroions dispersed in electrolyte solutions. While much current research concerns the verification of electrostatic attraction

between like charges[23], direct application of available simulation results to practical systems is limited by the numerical nature of molecular simulations.

This letter concerns interactions between like-charged colloidal particles at solution conditions corresponding first, to maximum repulsion and second, to onset of electrostatic attraction. We find that while like-charged colloidal particles can be attractive at low and high Bjerrum length, they are most repulsive at some intermediate conditions. Bjerrum length (l_B) is the separation between two unit charges where the electrostatic energy equals thermal energy k_BT. Weak attraction at low Bjerrum length occurs when the surface-to-surface separation is comparable to the size of surrounding salt ions; this weak attraction follows from entropic depletion of salt ions. Strong attraction between like-charged particles at high Bjerrum length is also related to the depletion of salt ions but, in contrast to the low-Bjerrum-length case, the depletion now arises from strong correlation between small ions due to Coulomb interactions. Our Monte Carlo simulation results suggest that there may be two general, simple relations for describing electrostatic interaction between charged colloidal particles. We found that the electrostatic force between macroions appears to be dictated by a dimensionless parameter that measures the electrostatic repulsion between counterions adsorbed on the macroion surface. Further, it appears that there are simple criteria for maximum repulsion and for onset of attraction between like-charged macroions; these criteria are essentially independent of the valence and concentration of the surrounding electrolyte. Unlike previous simulation results, these simple criteria may be directly applicable to real systems.

We consider the potential of mean force between two isolated like-charged colloidal particles (macroions) in an electrolyte solution. Within the primitive model, charged hard spheres are used to represent both colloidal particles and salt ions; the solvent is a dielectric

continuum. The pair potential, $\varphi_{ij}(r)$, between ionic particles i and j separated by a center-to-center distance r_{ij} is given by

$$\varphi(r_{ij}) = \begin{cases} q_i q_j / (4\pi\varepsilon_0 \varepsilon r_{ij}) & r_{ij} \geq (\sigma_i + \sigma_j)/2 \\ \infty & \text{otherwise} \end{cases} \tag{1}$$

where σ_i and q_i, stand, respectively, for the diameter and charge of particle i; $\varepsilon_0 = 8.854 \cdot 10^{-12} C^2 / (Jm)$ is the dielectric permittivity of free space, and ε is the dielectric constant of the solvent. The average force $F(r)$ between two macroions surrounded by small ions is given by three contributions:

$$F(r) = -\frac{\partial \varphi_{MM}(r)}{\partial r} - < \sum_{i=1}^{N} \frac{\partial \varphi_{iM}(r_{iM})}{\partial r} > + F^{hs}(r), \tag{2}$$

where the angular bracket denotes an ensemble average with respect to the configuration of small ions; r is the separation between two macroions; and r_{iM} is the distance between a small ion i and a macroion M. The first term on the right side of Eq. (2) is the direct Coulomb interaction between macroions; this term is always repulsive for like-charged macroions. The second term accounts for the electrostatic force exerted on each macroion by surrounding dissolved small ions. The last term represents the average force resulting from collisions between macroions and simple ions. The force due to hard-sphere collisions is[24]

$$F^{hs}(r) = -kT \lim_{\Delta r \to 0^+} \frac{< N_C >}{\Delta r} - kT \lim_{\Delta r \to 0^-} \frac{< N_C >}{\Delta r}, \tag{3}$$

where N_C is the number of salt ions that collide with the macroion resulting from a small variation of distance Δr. Eq.(3) implies that the hard-sphere collision force is repulsive when small ions are accumulated between the macroions and is attractive when they are depleted. The ensemble averages in Eqs.(2) and (3) can be conveniently calculated using a canonical ensemble Monte-Carlo simulation[24].

As observed by others[20,21,25], we find that at ambient conditions, the overall force

between like-charged ions is attractive in a solution containing multivalent counterions but is repulsive in a solution containing monovalent counterions. Figure 1 shows the force profiles in three divalent and one monovalent electrolyte solutions. Whereas the repulsive force in the monovalent case decays monotonically with macroion-macroion separation, the total force exhibits maximum attraction at approximately $r=1.3\sigma_M$, essentially independent of electrolyte concentration. Further, the magnitude of the attraction appears to be insensitive to the concentration of electrolyte. Maximum attraction at $r=1.3\sigma_M$ is consistent with the prediction of a recent theoretical investigation by Rouzina and Bloomfield[14]. Based on a pseudo-two-dimensional model for electrostatic double layers, they found that the attraction is largest when the macroion-macroion separation is close to the average distance between neighboring counterions adsorbed at the charged surface. In addition, Rouzina and Bloomfield indicated that the attraction between two like-charged surfaces occurs when a coupling parameter $\Gamma=z^2 l_B/a>2$, where z is the counterion valence and a is the average distance between neighboring counterions at the charged surface calculated as if the macroion were fully neutralized. Our proposed simple criterion for the onset of macroion attraction agrees well with simulation results in the literature[21].

The attraction between similarly charged colloidal particles has been explained by density functional theory and field theory calculations[16,18 19,26], by one-component plasma theory[27], by van-der-Waals-like fluctuation of counterion distributions[28], by a 2-dimensional lattice model[14], and by Coulomb depletion[20]. While each of these explanations illuminates one or more aspects of the complicated physics responsible for electrostatic double-layer interactions, they are not completely consistent with each other. To shed new light on the electrostatic interaction between like charges, using Monte Carlo simulation, we investigated

the total force as a function of Bjerrum length at a fixed inter-macroion separation $r=1.3\sigma_M$ where attraction is most likely to occur. For two identical macroions immersed in a solution of monovalent electrolyte, Figure 2 shows the total force, that due to hard-sphere collisions, and that from electrostatic contributions, as functions of Bjerrum length. Assuming that ionization is not affected, a large Bjerrum-length condition can be achieved by using a concentrated aqueous solution of a polar organic solvent. At low Bjerrum length (high temperature or high solvent dielectric constant), the system resembles that for two hard macrospheres immersed in a solvent of small spheres; at large separation of two macrospheres, both hard-sphere collision forces and electrostatic forces are essentially zero. As the Bjerrum length increases, the force profiles rise and exhibit a maximum at slightly different values of l_B for hard-sphere collision and electrostatic repulsion. At intermediate l_B, the distribution of small ions is dictated by electrostatic attractions between macroions and counterions. Attraction between macroion and small ions leads to accumulation of small ions between macroions ($F^{hs}>0$) and to screened electrostatic repulsion. At small l_B, where correlation between salt ions plays a minor role on the total double-layer force, a mean-field theory (e.g. DLVO) is suitable. However, as l_B increases, ion-ion correlation becomes more significant and eventually leads to electrostatic attraction. Onset of like-charge attraction occurs when repulsion due to accumulation of counterions counteracts the electrostatic attraction due to correlation of ion distributions. When l_B is large, counterions strongly repel each other, leading to Coulomb depletion of small ions between macroions ($F^{hs}<0$). At large l_B, the overall electrostatic force is insensitive to variations in l_B and becomes less important compared to the hard-sphere collision force. Qualitatively, the force profiles for like-charged macroions in multivalent and in asymmetric electrolyte solutions are similar to those shown in

Figure 2. Our simulation results suggest that attraction between like charges is possible in both monovalent and divalent electrolyte solutions provided that the correlation between small ions is strong. Coulomb depletion between like-charged macroions has been reported by Allahyarov et al[20].

To investigate conditions at onset of macroion attraction or maximum repulsion, we further studied the total force between two macroions in monovalent and in multivalent solutions at different concentrations. Figure 3 shows the total force as a function of coupling parameter Γ at a fixed inter-macroion separation $r=1.3\sigma_M$. Whereas the absolute values of the total forces depend strongly on the counterion valence and on salt concentration, all the force profiles exhibit a maximum repulsion when Γ~0.5 and onset of attraction when Γ~1.8. Onset of attraction between macroions of like charges when Γ~2 has been reported for like-charged plates[14], cylinders[9] and spheres[21]. The results presented in Figure 3 provide a systematic confirmation of the simple criterion proposed by Rouzina and Bloomfield for attraction between like charges. To our best knowledge, generalized occurrence of maximum repulsion has not been previously reported. Identification of maximum repulsion and onset of attraction between colloidal particles is often important for applications of colloids where colloid stability is essential. The trends observed here, coupled with those observed by others, appear to be general, essentially independent of surrounding electrolyte and insensitive to macroion shape.

Our general criteria for maximum repulsion and onset of attraction between like-charged particles may provide a useful explanation for some complicated electrostatic phenomena. For example, despite much effort for understanding the counterion-mediated condensation of negatively charged DNA molecules, a good quantitative theory for the

pertinent electrostatics remains challenging because of the complicated solution conditions in a bioenvironment [29]. An unfolded double-strand DNA chain has one negative charge every 0.17 nm and it is fully extended at the length scale of ions. Parameter Γ for DNA molecules in an aqueous solution of a simple electrolyte can be estimated from the cross-section diameter of the chain (~2 nm), and from the valences and diameters of small ions (~0.4 nm). According to our simple criterion for electrostatic double layer interactions, when the DNA solution contains only monovalent counterions, the scaling parameter Γ~0.5; it follows that a monovalent solution provides the optimum condition for the stability of DNA molecules (most repulsive between DNA chains). However, upon introducing a small amount of divalent counterions, when Γ~1.8, interaction between DNA chains becomes attractive. Because Γ is proportional to $z^{1.5}$, where z is the counterion valence, DNA condensation may readily follow in the presence of multivalent counterions (e.g. histone proteins[29]). As observed, DNA condensation is not strongly sensitive to ion concentration[29].

Another example for applying our criteria is provided by recent work of Petsev and coworkers on interactions between apoferritin molecules in solution [30]. Petsev et al. found that the overall interactions between monomer apoferritin molecules in sodium acetate aqueous solution are repulsive at intermediate concentration of monovalent Na^+ ions (0.1-0.2 M). However, in the presence of a much lower concentration of divalent Cd^{2+} ions (0.01M), the dominant repulsions shift to attraction, regardless of monovalent Na^+ concentration. Petsev et al. pointed out that Na^+ and Cd^{2+} ions have similar hydration ability. Therefore, this remarkable result cannot be explained by conventional colloidal theories for electrostatic interactions. However, the general criteria reported here can readily explain the effect of Cd^{2+} because addition of even a small amount of divalent Cd^{2+} ions changes significantly the

characterizing scaling parameter Γ.

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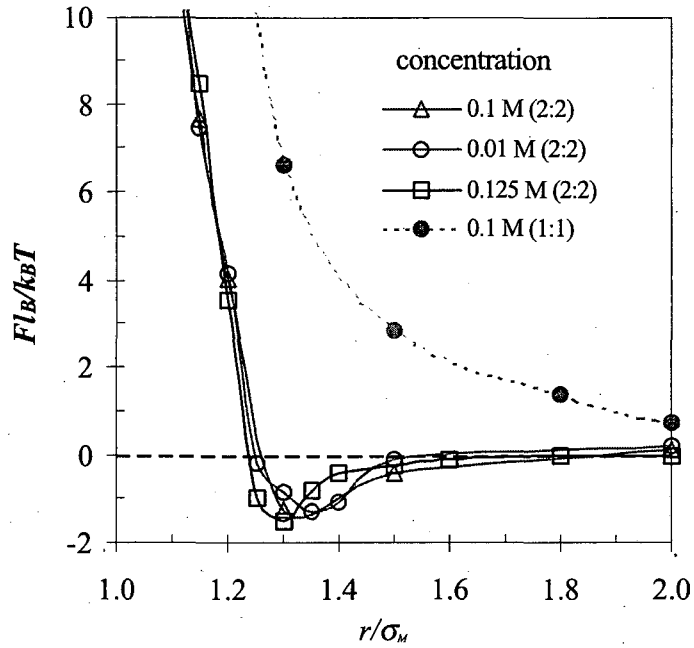

Figure 1 Overall force F between two identical macroions (z_M=-20, σ_M= 2 nm) in monovalent and in divalent primitive-model electrolyte solutions from Monte Carlo simulations. Here r is the center-to-center distance between macroions, l_B =0.714 nm is Bjerrum length, k_B is Boltzmann constant and T is temperature; diameter of small ions is 0.4 nm. Counterions are identical to the salt's cations.

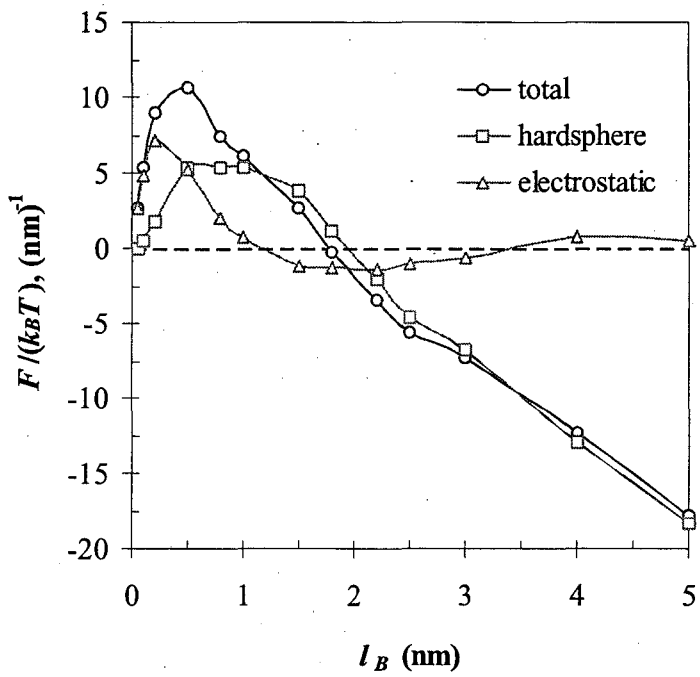

Figure 2 Interaction force F between two identical macroions at a fixed separation $r=1.3\sigma_M$ immersed in a 1:1 electrolyte solution of ionic strength I=0.06 M. Parameters for macroions and salt ions are identical to those in Figure 1.

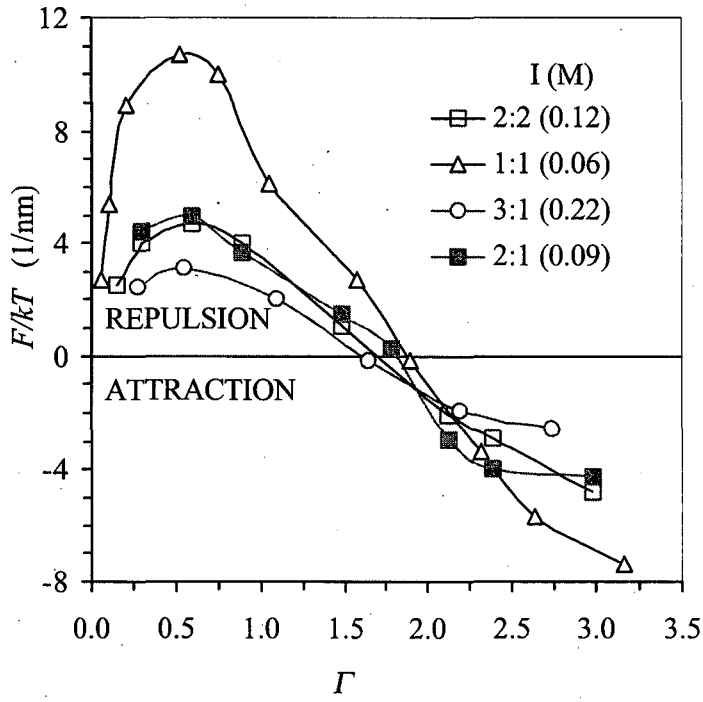

Figure 3 Total force F between two isolated macroions at a fixed separation $r=1.3\sigma_M$ in electrolyte solutions of different ionic strength and valence as a function of dimensionless parameter $\Gamma=z^2 l_B/a$. Here z is the valence of counterions; a is the average separation between adsorbed counterions assuming the macroion is fully neutralized. Parameters for macroions and salt ions are identical to those in Figure 1.

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