A substantial amount of experimental and numerical evidence has shown that the Derjaguin–Landau–Verwey–Overbeek theory is not suitable for describing those colloidal solutions that contain multivalent counterions. Toward improved understanding of such solutions, the authors report Monte Carlo calculations wherein, following Rouzina and Bloomfield, they postulate that, in the absence of van der Waals forces, the overall force between two isolated charged colloidal particles in electrolyte solutions is determined by a dimensionless parameter $\Gamma = \frac{z^2}{l_B^2}a$, which measures the electrostatic repulsion between counterions adsorbed on the macroion surface, where $z$ = counterion valence, $l_B$ = Bjerrum length, and $a$ = average separation between counterions on the macroion surface calculated as if the macroion were fully neutralized. The authors find, first, that the maximum repulsion between like-charged macroions occurs at $\Gamma \approx 0.5$ and, second, that onset of attraction occurs at $\Gamma \approx 1.8$, essentially independent of the valence and concentration of the surrounding electrolyte. These observations might 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. © 2002 Elsevier Science (USA)

Key Words: colloidal forces; electrostatic double layers; simulation.

INTRODUCTION

Applications of colloidal dispersions are often concerned with colloidal stability; that stability depends on the interaction potential between colloidal particles (1–9). The classical intercolloidal 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 also be attractive (10–21).

Electrostatic attraction between two isolated like-charged macroions is most likely to occur when the macroions are surrounded by counterions 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. The DLVO theory and 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 intercolloidal potential can be taken into account, in principle, by solving integral equations (22, 23), by applying density functional approximations (24), or by using field theory expansions (25). With substantial numerical effort, these theories are often able to capture the electrostatic attraction between like-charged macroions. However, because of the arbitrary truncation of perturbation expansions, the credibility of these theories (with the exception of the anisotropic HNC approximation [22]) is often questioned, and the theories’ physical significance is not always clear.

Molecular simulation has been applied extensively to study interactions between charged colloidal particles in a primitive model electrolyte solution, where the solvent is represented by a continuous medium (14–17, 26–28). Simulation results have revealed much of the physics that governs the electrostatic phenomena for macroions dispersed in electrolyte solutions. Although much current research concerns the verification of electrostatic attraction between like charges (29), direct application of available simulation results to practical systems is limited by the numerical nature of molecular simulations.

This work concerns interactions between two isolated, like-charged colloidal particles at solution conditions corresponding, first, to maximum repulsion and, second, to onset of electrostatic attraction. We find that in the absence of van der Waals attractions, although like-charged colloidal particles can be attractive at low and high Bjerrum length, they are most repulsive at some intermediate conditions. Bjerrum length, defined as $l_B = \frac{e^2}{4\pi \varepsilon \varepsilon_0 k_B T}$, is the separation between two unit charges ($e$) in a solvent of dielectric constant $\varepsilon$, where the electrostatic energy equals thermal energy $k_B T$. Weak attraction in the limit of zero 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 (30).
Strong attraction between like-charged particles at high Bjerrum length is also related to the depletion of salt ions, but in contrast to the case of low Bjerrum length, the depletion now arises from strong correlation between small ions due to Coulomb interactions. Our Monte Carlo simulation results suggest two general simple relations for describing electrostatic interaction between a pair of charged colloidal particles. According to these relations, 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. Furthermore, it appears that there are simple criteria for maximum repulsion and for the onset of attraction between like-charged macroions; these criteria are essentially independent of the valence and concentration of the surrounding electrolyte. These simple criteria may be directly applicable to real systems.

**MONTE CARLO CALCULATIONS**

In this work, because we assume that the van der Waals forces are relatively well understood, attention is given only to electrostatic and hard sphere collision forces between colloidal particles. 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 represented as a dielectric continuum. The pair potential, \( \phi_{ij}(r) \), between ionic particles \( i \) and \( j \) separated by a center-to-center distance \( r_{ij} \) is given by

\[
\phi_{ij}(r) = \begin{cases} 
q_i q_j/(4 \pi \epsilon_0 \epsilon r_{ij}) & r_{ij} \geq (\sigma_i + \sigma_j)/2, \\
\infty & \text{otherwise}
\end{cases}
\]

where \( \sigma_i \) and \( q_i \) stand for the diameter and charge, respectively, of particle \( i \); \( \epsilon_0 = 8.854 \times 10^{-12} \text{C}^2/(\text{J} \text{m}) \) is the dielectric permittivity of free space (2, 4); and \( \epsilon \) is the dielectric constant of the solvent. The average force \( F(r) \) between two macroions surrounded by small ions is given by three contributions:

\[
F(r) = -\frac{\partial \phi_{MM}(r)}{\partial r} = -\sum_{i=1}^{N} \frac{\partial \phi_i M(r_i M)}{\partial r} + F_{hs}(r), \tag{2}
\]

where the angular bracket denotes an ensemble average with respect to the configuration of small ions, \( r \) is the separation between two macroions, and \( r_{i M} \) is the distance between a small ion \( i \) and a macroion \( M \). The first term on the right hand 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 can be calculated from the following expression (31):

\[
F_{hs}(r) = -kT \lim_{\Delta r \to 0^+} \frac{C}{\Delta r} - k_BT \lim_{\Delta r \to 0^+} \frac{C}{\Delta r}, \tag{3}
\]

where \( C \) is the number of salt ions that collide with the macroion on a small variation of distance \( \Delta r \). Equation [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 detailed simulation procedure has been reported in our previous publications (17, 31–33). In brief, the cubic simulation box contains two identical macroions and about 140 small ions that satisfy the overall charge neutrality. The exact number of small ions varies slightly with salt valence and concentration. The box length is about an order of magnitude larger than the Debye screening length so that electrostatic interactions between macroions due to the introduction of periodic boundary conditions can be neglected. The standard NVT ensemble Monte Carlo simulation is applied to calculate the average forces and internal energies. During each run, the two macroions are fixed at a given separation along the box diagonal while the small ions are free to move throughout the simulation box. The classical Ewald sum method was applied to account for long-range electrostatic interactions. Trial moves of the macroions were used to determine collision probabilities. The limit in Eq. [3] is calculated by selecting \( \Delta r \) that yields an average collision probability for each trial close to 10%. We found that at this collision probability, sampling of the hard sphere collision force is most efficient and the results are essentially independent of \( \Delta r \). For each macroion separation, the system reaches equilibrium after about \( 10^5 \) configurations per particle, while up to a million configurations per particle are used to calculate the average forces. At small macroion separations, the relative statistical uncertainty in calculated forces is small (about 1–2%). However, because the absolute fluctuation in the calculated force depends only weakly on macroion separation, the relative statistics are better at short distances where interactions are relatively strong. The statistical uncertainty in the total internal energy is generally small (<0.01%).

The primitive model might be problematic at small length scales where a constant dielectric constant becomes insufficient to take into account the effect of water molecules in between and those surrounding macroions. But given the ubiquity of this model for electrolyte solutions, our simulation (and essentially all other similar calculations in the literature) at small colloidal separations may provide benchmark data toward development of an improved analytical theory.

**RESULTS AND DISCUSSION**

As observed by others (26, 27, 34), we find that, at ambient conditions, the overall force between like-charged ions can be attractive in a solution containing multivalent counterions but is generally 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 forces in divalent solutions exhibit maximum attraction at approximately $r = 1.3 \cdot \sigma_M$, corresponding to about a single layer of small ions. As observed by Lobaskin et al. (35), the separation at maximum attraction is essentially independent of electrolyte concentration. Furthermore, for the ion concentrations shown in this figure, the magnitude of the attraction appears virtually independent of the concentration of electrolyte.

The attraction between similarly charged colloidal particles has been discussed in the contexts of density functional theory and field theory calculations (22, 24, 25, 36), one-component plasma theory (37), van der Waals-like fluctuation of counterion distributions (38), a two-dimensional lattice model (19), and Coulomb depletion (26). Although each of these theories illuminates one or more aspects of the complicated physics responsible for electrostatic double-layer interactions, the theories are not completely consistent with each other.

To shed new light on the electrostatic interaction between like charges, we investigated the total force as a function of Bjerrum length at a fixed intermacroion separation to $r = 1.3 \cdot \sigma_M$, corresponding to about a layer of small ions. At this separation, the attraction between macroions is most likely to occur. The Bjerrum length (equivalent to the inverse of reduced temperature) used in this simulation is from 0.05 to 5 nm for 2:2 electrolyte solutions. At ambient conditions, the Bjerrum length for pure water is about 0.7 nm. For 3:1 electrolyte solutions, the range of Bjerrum lengths is from 0.05 to 1 nm. The large and small Bjerrum lengths used in this work might not directly correspond to any real system, but the main purpose here is to reveal the hard sphere collision and electrostatic forces according to the primitive model. However, all systems have an effective temperature higher than the critical temperature for phase transition.

For two identical macroions immersed in a solution of monovalent electrolyte, Fig. 2 shows the total force, that due to hard sphere collisions and that from electrostatic contributions, as functions of Bjerrum length. At low Bjerrum length (high temperature or high solvent dielectric constant), the system resembles two hard macrospheres immersed in a solvent of small spheres; in this case, the electrostatic interactions are slightly repulsive (as predicted by the DLVO theory), and the force due to hard sphere collision shows a small attraction due to the excluded volume effect. As the Bjerrum length rises (by lowering the solvent dielectric constant or lowering temperature), the total force increases and exhibits 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 $l_B$, a mean field theory (e.g., DLVO) is suitable because in this case the correlation between salt ions plays a minor role in the total double-layer force. 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 is balanced by 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 electrostatic term is insensitive to variations in $l_B$ and

![FIG. 1. Overall force $F$ between two identical macroions ($\sigma_M = -20, \sigma_M = 2$ nm) in monovalent and 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 the Boltzmann constant, and $T$ is temperature. Diameter of small ions is 0.4 nm. Counterions are identical to the cations.](image1)

![FIG. 2. Interaction force $F$ between two identical macroions at a fixed separation $r = 1.3 \cdot \sigma_M$ 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 Fig. 1.](image2)
becomes less important as compared with the hard sphere collision contribution. The disappearance of the Coulomb force between macroions at large \( l_B \) is understandable because in this case macroions are essentially neutralized by the counterions near the surface. The hard sphere contribution to the total force is temperature dependent because the hard sphere force is determined by the temperature-dependent distribution of small ions. Qualitatively, the forces as functions of \( l_B \) for like-charged macroions in multivalent and asymmetric electrolyte solutions are similar to those shown in Fig. 2. Our simulation results prove 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. (26).

Figure 3 shows the total force as a function of coupling parameter \( \Gamma \) at the same intermacroion separation as in Fig. 2. The dimensionless parameter \( \Gamma \) is defined as

\[
\Gamma = \frac{z^2 l_B}{a},
\]

where \( a = \sqrt{ze/\sigma} \) is the average distance between neighboring counterions at the charged surface calculated as if the macroion were fully neutralized, \( z \) is the counterion valence, \( e \) is unit charge, and \( \sigma \) is macroion surface charge density. The parameter \( \Gamma \) reflects electrostatic interactions between counterions on the macroion surface. Alternatively, \( \Gamma \) can be expressed as

\[
\Gamma = l_B \sqrt{z^3 \sigma/e}.
\]

Whereas the absolute values of the total forces depend strongly on the counterion valence and on salt concentration, all of the force profiles exhibit a maximum repulsion when \( \Gamma \sim 0.5 \) and onset of attraction is around \( \Gamma \sim 1.8 \). Onset of attraction between macroions of like charges when \( \Gamma \sim 2 \) has been reported for like-charged plates (19), cylinders (14), and spheres (27). To our best knowledge, generalized occurrence of maximum repulsion has not been reported previously. 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.

General criteria for maximum repulsion and onset of attraction between like-charged particles may provide insight into a partial explanation for some complex biological 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 (39). An unfolded double-strand DNA chain has one negative charge every 0.17 nm and is fully extended at the length scale of ions. Parameter \( \Gamma \) for DNA molecules in an aqueous solution of a simple electrolyte can be estimated from the cross-section diameter of the chain (\( \sim 2 \) nm) and from the valences and diameters of small ions (\( \sim 0.4 \) nm). According to our simple criterion for electrostatic double-layer interactions, when the DNA solution contains only monovalent counterions, the scaling parameter \( \Gamma \sim 0.5 \); it follows that a monovalent solution is likely to provide the optimum condition for the stability of DNA molecules (most repulsive between DNA chains). However, on introducing a small amount of divalent counterions, the parameter \( \Gamma \) should be calculated using divalent ions as the counterion, \( \Gamma \sim 1.8 \), and interaction between DNA chains becomes attractive. (Such attraction may or may not lead to condensation.) Because \( \Gamma \) is proportional to \( z^{1.5} \), where \( z \) is the counterion valence, it is possible that DNA condensation can be triggered by the addition of multivalent counterions. As observed, DNA condensation is not strongly sensitive to ion concentration (39).

The generalizations reported here might also provide some useful clues on some interesting results by Petsev and coworkers on interactions between apoferritin molecules in solution (40). Petsev et al. found that the overall interactions between monomer apoferritin molecules in sodium acetate aqueous solution are repulsive at an 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 (0.01 M), 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 could help to explain the effect of Cd\(^{2+}\) because addition of even a small amount of divalent Cd\(^{2+}\) ions changes significantly the characterizing scaling parameter \( \Gamma \).
CONCLUSIONS

The potential of mean force between two colloidal particles in an electrolyte solution in general depends on many independent parameters, including effective temperature, surface charge density of colloidal particles, salt concentration, and ion valences. However, we find that the maximum repulsion and onset of attraction between like-charged macroions may be described by a single dimensionless parameter that reflects interactions between counterions near the macroion surfaces. Although we do not have a theoretical explanation for the generalizations reported here, we found that intercolloidal forces are most sensitive to the surrounding counterions. At small intercolloidal separation, the macroions experience essentially an environment consisting of only counterions, and the interactions between macroions depend primarily on counterion correlations. The dimensionless parameter $\Gamma$, which reflects electrostatic interactions between counterions on the macroion surface, provides a natural measure of the interaction (correlation) strength.

ACKNOWLEDGMENTS

We have benefited from discussions with D. Bratko, A. Chakraborty, W. Russel, and H. Lowen; we thank all of them. This work was supported by the director of the Office of Energy Research, Office of Basic Sciences, Chemical Sciences Division, U.S. Department of Energy. We are grateful to the supercomputing centers National Partnership for Advanced Computational Infrastructure (NPACI) at the University of California, San Diego and National Energy Research Scientific Computing Center (NERSC) at Lawrence Berkeley National Laboratory for generous allocations of computing time.

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