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Abstract

A new technique for Monte-Carlo sampling of the hard-sphere collision force has been applied to study the interaction between a pair of spherical macroions in primitive-model electrolyte solutions with valences 1:2, 2:1, and 2:2. Macroions of the same charge can attract each other in the presence of divalent counterions, in analogy with earlier observations for planar and cylindrical geometries. The attraction is most significant at intermediate counterion concentrations. In contrast to the entropic depletion force between neutral particles, attraction between macroions is of energetic origin. The entropic contribution to the potential of mean force is generally repulsive at conditions corresponding to aqueous colloids with or without salt. For systems with divalent counterions, the potentials of mean force predicted by mean-field approximations like the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory or the Sogami-Ise (SI) theory are qualitatively different from that observed in the simulations. However, for systems with monovalent counterions, predictions of DLVO theory are in fair agreement with simulation results.

I. Introduction

Physico-chemical properties of colloidal suspensions (e.g. solutions of latex particles, proteins or micelles[1-2]) are essentially controlled by electrostatic macroion/ macroion interactions. Due to the large practical importance of colloidal solutions, interactions between macroions in electrolyte solutions have been extensively studied for many years. In numerous application-oriented situations electrostatic repulsion among colloids of like charge was essential for the apparent stability of the dispersion. The destabilizing effect of multivalent ions has traditionally been ascribed to the strong screening of the macroion/macroion repulsion in multivalent electrolytes. There is, however, considerable experimental[3-5] and numerical evidence[6-9] of electrostatic attraction between like-charged plates or cylindrical particles surrounded by divalent counterions. This attractive interaction is inconsistent with widely-used mean-field calculations using the Poisson-Boltzmann theory[1]. Although several theoretical investigations[10-12] suggested that similar attractions may exist between spherical macroions, direct experimental evidence for such attractions has not yet been established.

Attraction between colloidal spheres has been observed in confined ionic colloids but not in a homogeneous medium[13-14]. At finite macroion concentrations, theoretical calculations[15-19] and measurements[16-17] of pair-correlation functions for like-charged macroions often reveal oscillating distributions with attractive and repulsive domains. This apparent attraction is, however, partly due to correlations among many repelling macroions, and that is very different from the interaction between two isolated macroions in a saline solution. To eliminate the many-body effect from many macroions, we consider here a sole pair of interacting macroions in a salt-containing medium.

A recent Monte-Carlo simulation of a pair of macroions and neutralizing monovalent counterions revealed attractions at extremely low dielectric constant[20]; however, the origin of the attraction observed in this system was different from that reported in other simulated geometries (plates and cylinders) and in established theoretical models[10-12]. Moreover, because of the low permittivity of the medium, conclusions regarding attractions observed in the above study are not directly applicable to aqueous systems. Related simulations for macroions surrounded by multivalent salt ions[21] or by divalent counterions[22] revealed attractive Coulombic forces between isolated colloids in a water-like medium. Strictly speaking, the counterion-only case[22] necessarily implies a non-zero macroion concentration; electrostatic screening due to the counterions alone is not sufficient to exclude many-body interactions among the colloids. These calculations appear more suitable for studies of the osmotic behavior than for a rigorous calculation of the potential of mean force between a lone pair of macroions. Addition of a screening electrolyte removes this limitation. Furthermore, the presence of salt is important because of its prevalence in biophysical and technological systems and because of its practical utility for regulating colloidal interactions by varying salt concentration and composition.

In a recent preliminary report[21], we have shown that spherical macroions of the same charge can attract each other when immersed in a solution of a symmetric divalent electrolyte. We found that the attractive force derives from the internal-energy contribution of counterion mediation. In this work, we provide a detailed description of our simulation method and extend the calculations to different concentrations and salt valences. New calculations reinforce the evidence of attractive interactions between

macroions in multivalent electrolytes and elucidate the role of counterion and coion charge and concentration. We present results for potentials of mean force between like-charged macroions in electrolyte solutions of valences 1:2, 2:1, and 2:2 at several concentrations. The univalent (1:1) electrolyte case has been considered earlier[22]. Further simulations for the univalent system have not been carried out since its behavior appears to be successfully explained by classical methods[1,2]. In the presence of divalent ions, the attraction between macroions is most prominent at moderate salt concentrations. While the attractive force between macroions is mainly of electrostatic origin, hard-sphere collisions can also induce weak attractions at certain intermediate macroion-macroion separations. In general, we find that the mechanism responsible for the attraction between like-charged colloids in ambient aqueous solutions is different from that considered by Allahyarov and coworkers.[20]

II. Model and Methods

II.1 Model

For the sake of simplicity, as well as for easier comparison with analytic results, we represent macroions and electrolytes using the primitive model for ionic solutions[23]. In the primitive model, the solution is considered to be an ensemble of hard spheres of different charge and size dispersed in a dielectric continuum whose permittivity corresponds to that of the solvent. The pair potential, $\varphi_{ij}(r)$, between ionic particles i and j separated by the 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 for the diameter and charge of ith species; $\varepsilon_0 = 8.854 \cdot 10^{-12} C^2 / (Jm)$ is the permittivity of vacuum, and ε the dielectric constant of the medium. In the present work, the primitive model, along with canonical Monte Carlo simulations, is used to study colloidal interaction in electrolyte solutions. The mean force between two macroions surrounded by small ions comprises three distinct 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 brackets denote the ensemble average, r is the separation between two macroions and r_{iM} is the distance between a small ion and a macroion; subscript M denotes a macroion. 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 Coulombic force exerted on either of the macroions by all small ions. The last term represents the mean force resulting from the collisions between hard-sphere macroions and simple ions. In view of the impulse form of the collision force, this term cannot be directly sampled in a Monte Carlo simulation. At non-zero macroion concentrations, it is usually easier to determine the total potential of mean force from the macroion-macroion distribution. If separate contributions are of interest, the collision force can then be calculated as the difference between the gradient of the potential of mean force and the Coulombic interaction. In systems containing a single pair of macroions in a sea of small ions, however, calculation of the radial distribution function between two macroions can become prohibitively slow, first, because of poor statistics obtained by sampling a sole pair of particles and second, because of extremely

low acceptance of macroion moves due to collisions with highly concentrated counterions in the ionic atmosphere of the macroion. Below, we describe a novel method for the calculation of the collision force at fixed separation between the two macroparticles.

II.2 Hard-Sphere Collision Force

According to traditional methods, the collision force can be calculated from the pressure exerted on the surface of the macroparticles by surrounding small molecules[20,24]. In the present context, the small molecules are salt ions surrounding the macroions (water is represented by a continuous medium). The procedure requires calculation of contact densities for all salt ions with subsequent extrapolation of the distribution functions to the macroion surfaces. In anisotropic geometry, the situation is exacerbated because the contact densities have to be determined as functions of the position on the contact surface. The mean hard-sphere collision force ($\bar{F}$) between two macro-spheres (macroions) in a sea of small spheres (small ions) shown in Fig. 1 is evaluated using the contact theorem[25]

$$\bar{F}^{hs} = -kT\int \rho(S)\bar{n}dS\,, \tag{3}$$

where k stands for the Boltzmann constant and T for temperature; $\bar{n}$ is the outward normal unit vector at the surface; $\rho(S)$ is the contact density of small spheres on the surface of the macro-sphere, and dS is an infinitesimal area element on the surface. The integral in Eq.(3) runs over the macro-sphere surface. Due to the symmetry of the system, the direction of the force coincides with the vector connecting the two macrospheres (Hereafter, we omit the vector notation of the force). The unit vector $\bar{n}$ in the integrand

of Eq.(3) determines the direction of collision force at a given point on the macrosphere/small-sphere contact plane.

Although Eq.(3) is exact, a numerical application of this equation in a nonplanar geometry is time-consuming because of the inhomogeneous distribution of small hard spheres. For adjacent macrospheres or ionic colloids, $\rho(S)$ depends on the orientation angle θ and on the separation between the two macro-spheres. Figure 2 illustrates a typical distribution of counterions and coions around adjacent colloids obtained in our simulations. When the contact theorem is used in a simulation, extrapolation is needed to determine contact densities for a multitude of orientation angles on the macrosphere surface resulting in time-consuming computations.

We now describe a new technique for the calculation of the hard-sphere collision force that bypasses the sampling of the anisotropic distribution of small-solute molecules. We consider a general situation where two large hard-sphere solutes are surrounded by small hard-sphere solutes. In addition to the hard-sphere interactions, we allow other forces to exist among the large solute and small-solute molecules. For macroions in electrolyte solutions, other forces arise from electrostatic interactions among macroions and small ions. The total intermolecular potential Φ can be divided into two additive terms,

$$\Phi = \Phi^{hs} + \Phi' . \tag{4}$$

where Φ^{hs} is the total hard-sphere potential that is zero if there is no overlap among hard spheres and infinite otherwise. Φ' comprises all the remaining interactions. For macroions in a primitive-model electrolyte solution that we discuss later, Φ' represents a

pairwise sum of Coulombic interactions among all charged particles. The mean force between two solute molecules at separation r is

$$F(r) \equiv -\frac{\partial A}{\partial r} = kT\frac{\partial \ln Z}{\partial r} \tag{5}$$

where $A = -kT \ln Z$ is the Helmholtz energy. The configuration integral, Z, is given by

$$Z = \int d\vec{r}^{\,N} e^{-\beta\Phi}, \tag{6}$$

where $\beta = 1/(kT)$, $d\vec{r}^{\,N} \equiv d\vec{r}_1 d\vec{r}_2 \cdots d\vec{r}_N$, and N is the number of small-solute molecules. Substituting Eqs (4) and (6) into Eq. (5) gives

$$\begin{aligned} F(r) &= kT\frac{1}{Z}\int d\vec{r}^{\,N}\frac{\partial e^{-\beta\Phi}}{\partial r} \\ &= kT\frac{1}{Z}\int d\vec{r}^{\,N}\left[e^{-\beta\Phi'}\frac{\partial e^{-\beta\Phi^{hs}}}{\partial r} + e^{-\beta\Phi^{hs}}\frac{\partial e^{-\beta\Phi'}}{\partial r}\right] \\ &= kT\frac{1}{Z}\int d\vec{r}^{\,N} e^{-\beta\Phi'}\frac{\partial e^{-\beta\Phi^{hs}}}{\partial r} + \left\langle -\frac{\partial \Phi'}{\partial r}\right\rangle \\ &= kT\lim_{\Delta r\to 0}\frac{1}{Z}\int d\vec{r}^{\,N}\frac{e^{-\beta\Phi}(e^{-\beta\Delta\Phi^{hs}}-1)}{\Delta r} + \left\langle -\frac{\partial \Phi'}{\partial r}\right\rangle \\ &= kT\lim_{\Delta r\to 0}\frac{\langle e^{-\beta\Delta\Phi^{hs}}-1\rangle}{\Delta r} + \left\langle -\frac{\partial \Phi'}{\partial r}\right\rangle \end{aligned} \tag{7}$$

The limit in Eq. (7) depends on the sign of Δr; when $\Delta r > 0$, Eq. (7) gives the collision force from the opposite side of the other solute molecule leading to an effective attraction; and for $\Delta r < 0$, the collision force points outwards leading to an effective repulsion. The net collision force stems from the imbalance of the two contributions:

$$F(r) = -kT\lim_{\Delta r\to 0^+}\frac{\langle 1-e^{-\beta\Delta\Phi^{hs}}\rangle}{\Delta r} - kT\lim_{\Delta r\to 0^-}\frac{\langle 1-e^{-\beta\Delta\Phi^{hs}}\rangle}{\Delta r} + \left\langle -\frac{\partial \Phi'}{\partial r}\right\rangle. \tag{8}$$

Equation (8) implies that the average collision force can be effectively separated from all other forces.

Equation (8) indicates that the magnitude of the force depends on the probability of collisions between the large solute and the small solute. Consider first the case when all small-solute molecules are identical. When one of the solute particles is shifted by Δr, $(1-e^{-\beta\Delta\Phi^{hs}})$ equals unity if the move results in one or more collisions with small-solute molecules, and vanishes otherwise. The average $<1-e^{-\beta\Delta\Phi^{hs}}>$ is therefore the probability of at least one collision for given Δr. Let ΔN_C be the number of small-solute molecules that collide with the large solute molecule during a trial displacement, Δr. The probability of at least one collision is given by one minus the probability of no collision, i.e.,

$$<1-e^{-\beta\Delta\Phi^{hs}}>=1-<\left(1-\frac{\Delta N_C}{N}\right)^N>\approx 1-<1-\Delta N_C>=<\Delta N_C>. \tag{9}$$

Eq.(9) can be extended to the conditions where the small solute comprises several components. In that case, ΔN_C is the total number of collisions between a large solute molecule and all small-solute molecules due to a trial displacement. The hard-sphere force is therefore directly related to the average number of collisions due to a small displacement of a large solute molecule. Substitution of Eq.(9) into Eq.(8) yields

$$F(r)=-kT\lim_{\Delta r\to 0^+}\frac{<N_C>}{\Delta r}-kT\lim_{\Delta r\to 0^-}\frac{<N_C>}{\Delta r}+<-\frac{\partial\Phi'}{\partial r}>. \tag{10}$$

The number of collisions due to a small displacement of a solute molecule can be conveniently calculated in a Monte-Carlo simulation. For each macroion-macroion separation, a series of small Δr should, in principle, be used to obtain the limit in Eq. (8). However, we find that the ratio $<\Delta N_C>/\Delta r$ is insensitive to Δr as long as Δr is small enough. At the conditions of the present work, the optimal magnitude of Δr corresponds

to the average collision probability of about 10-15%. If Δr is much bigger, the average collision force deviates from the limiting value of vanishing Δr ; on the other hand, if Δr is too small, the statistics of sampling becomes less accurate and the simulation time must be increased. A trial displacement about two orders of magnitude smaller than the macroion diameter provides a good initial estimate of Δr in most of the situations considered below.

Eq.(8) can also be derived by considering the change in the volume accessible to small-solute molecules in calculating the configuration integral Z. As a small displacement is applied to one of the large-solute molecules, the large-solute molecule occupies some free volume of the small-solute molecules; at the same time, the displacement creates some new free volume. The difference in the number of particles in these two small volumes leads to the overall hard-sphere force on the large-solute molecule.

To test the above procedure, we repeated some of the calculations of the solvation force between neutral hard spheres immersed in a dense fluid of smaller spheres described by Dickman et al.[25]. Figure 3 shows the comparison between our calculations and reported results[25]. At identical simulation conditions, our new sampling method reproduces the results of Dickman et al. using about ten times shorter production runs than those reported in the earlier study[25]. This improvement is significant because very long runs, up to a million per particle, are often required for sampling the hard-sphere collision force.

The main purpose of this work is to investigate interactions between a pair of macroions in electrolyte solutions. The collision force is an important part of this

interaction. Before terminating this section, we review briefly a simple phenomenological theory of Asakura and Oosawa[26] for interactions between a pair of neutral macrospheres in a solution of smaller spheres. That theory is based on a simple geometrical argument. As the excluded volumes of two macrospheres overlap, the overall free volume available to small spheres increases which yields an increase in the translational entropy of small spheres. The resulting attraction is given by

$$F^{AO}(r) = \begin{cases} \frac{\pi\rho kT}{4}(r+\sigma_M+\sigma_S)(r-\sigma_M-\sigma_S) & r < \sigma_M+\sigma_S \\ 0 & r \geq \sigma_M+\sigma_S \end{cases}, \tag{11}$$

where ρ is the bulk density of small spheres, r is the center-to-center distance between two macrospheres, σ_M and σ_S are, respectively, diameters of macro and small spheres. The range of the attractive force is limited to separations below $\sigma_M + \sigma_S$. While integral-equation theory[27] and simulations[25] reveal the propagation of the potential of mean force to greater distances, this simple theory[26] yields a qualitatively correct prediction for the short-range interaction between hard macrospheres. The underlying assumption of uniform small-sphere density is, however, not applicable to the ionic-colloid case where the distribution of the small ions is strongly nonuniform. As will be shown shortly, for present solution conditions, the collision force due to small ions is generally repulsive in contrast to the predictions of the Asakura-Oosawa theory[26] and simulation results[28] for the solvation force, i.e. the force mediated by water molecules in aqueous colloids.

II.3 Details for Calculation of Mean Force Between Macroions

To calculate the mean force between a pair of macroions in a primitive-model electrolyte solution, we use the standard NVT ensemble Monte-Carlo simulations[29] for selected electroneutral combinations of small ions and two identical macroions at a fixed

separation r. For each set of solution conditions, separate simulation runs are required for all considered macroion-macroion distances r. In principle, interaction between a pair of macroions in an electrolyte medium should be solved using simulations at constant chemical potentials of small ions rather than at constant number of particles in the system[24,30]. Using the canonical ensemble, we assume that the variation in the numbers of small ions in the simulation box at various macroion separations has a negligible effect on sampled colloidal forces. The validity of this assumption has been verified by a comparison of simulation results for different sizes of simulated systems. Significantly increasing the simulation box produced no visible differences in any of the relevant calculated quantities. The system size we used was therefore sufficient to reduce any related effect below the statistical uncertainty of the simulation.

During each run, the two macroions separated by distance r were fixed along the box diagonal while the small cations and anions were free to move throughout the simulation box. Trial moves of the macroions were used to determine collision probabilities. The classical Ewald-sum method was applied to account for long-range electrostatic interactions[29,31]. To test the reliability of the code and the sampling technique for interparticle forces, we first considered the mean force between two identical small ions in a colloid-free 1:1 electrolyte solution. Here, the mean force between two ions can be calculated from the pair correlation function, $g(r)$

$$F(r) = kT\frac{\partial \ln g(r)}{\partial r}. \tag{12}$$

that is easily obtained by a conventional Monte-Carlo simulation for simple electrolyte solutions. Because a simple electrolyte solution contains many identical small ions,

Eq.(12) is more efficient than the direct sampling based on Eq. (10). Comparison of mean forces from Eq.(10) with that from Eq. (12) therefore provides a critical test of our simulation algorithm. Figure 4 shows a comparison between the forces calculated using Eq.(12) and those from Eq. (10). The two different methods are in excellent agreement.

Table I lists some common simulation parameters used in this work. In general, the length of the simulation box is more than an order of magnitude larger than the Debye-screening length to make sure that interactions between macroions in different simulation boxes can be ignored. The Debye-screening length, $1/\kappa$, is defined by

$$\kappa^{-1} = \left(\sum_i \frac{\rho_i q_i^2}{\varepsilon_0 \varepsilon kT} \right)^{-1/2} \tag{13}$$

where ρ_i is the number density of small ions (counterions and added electrolyte). 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 mean 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 electrostatic term generally converges much faster than the collision contribution.

The total internal energy is also sampled in our simulations. The statistical uncertainty in the internal energy is generally small (<0.01%).

IV. Results and Discussion

We have investigated interactions between a pair of macroions of valence z_M=-20 and diameter σ_M=2 nm in aqueous solution of 1:2, 2:1 and 2:2 electrolytes at different

concentrations. Here, the first number represents the valence of the cation and the second corresponds to the valence of the anion of the salt. The diameter of small ions is 0.4 nm. Short-range attractions are found between two like-charged macroions in electrolyte solutions containing divalent counterions (2:1, and 2:2 electrolytes for negatively charged macroions). However, at ambient conditions, the interaction is always repulsive in an aqueous solution containing monovalent counterions.

IV.1 Mean force between macroions in asymmetric electrolyte solutions

Figure 5(a) shows the reduced total force between two negatively charged macroions in a 1:2 electrolyte solution, along with the hard-sphere and electrostatic contributions (r is the center-to-center distance between the macroions, and σ_M is the macroion diameter). The Bjerrum length, $l_B = e^2 / (4\pi\varepsilon_0 \varepsilon kT)$, represents the distance between two unit charges (e) where the pair potential equals thermal energy kT. The total force, as well as its electrostatic and hard-sphere contributions shown in Figure 5(a), are repulsive at all distances. For ionic strength 0.28 M, both the hard-sphere and electrostatic interactions become insignificantly weak at center-to-center distances beyond about 2 macroion diameters. The electrostatic force decays monotonically with the separation, as expected from DLVO theory. The hard-sphere term, however, displays a weak maximum at small inter-macroion separation, and then decreases monotonically at larger distances. The maximum is associated with the existence of a region where the small ions are sterically excluded when the distance between the two macroion surfaces falls below the diameter of the ions (0.4nm). This exclusion results in the reduction in the collision force between adjacent macroions, a mechanism already discussed in context of Asakura-Oosawa theory[26]. Nevertheless, the overall hard-sphere collision force between

ionic colloids is quite different from that observed in uncharged systems. At short distances, the solvation force between neutral hard-sphere particles is generally attractive. However, for like-charged macroions dispersed in a simple electrolyte solution, because of electrostatic attraction, the concentration of the counterions in the accessible region between adjacent macroions is much higher than that in the bulk solution and also exceeds the ion concentration at the macroion surface opposite the neighboring macroion (see Figure 2). As a result, the net hard-sphere collision interaction is by-and-large repulsive, albeit reduced by the short-range exclusion-volume effect.

Figure 5(b) presents the force between two negatively-charged macroions in a 2:1 electrolyte solution at about the same ionic strength as that considered in Figure 5(a). In this case, the counterions are divalent. An attractive force is observed within a range of small separations between the macroions. For macroions near contact, the net force is strongly repulsive due to both electrostatic and hard-sphere interactions. The electrostatic force declines quickly with the distance and reaches a negative minimum at about $1.2\sigma_M$, a separation sufficient to accommodate a monolayer of counterions between the two macroions. As the separation increases further, the force begins to decay and becomes insignificant. The attractive electrostatic force can be attributed to two combined effects: an attraction from the intervening counterion layer, and an attraction due to the correlated density fluctuations in the double layers surrounding the two particles. While the same mechanisms operate in solutions with monovalent counterions, the net force remains repulsive in this case due to a higher entropic penalty associated with localization of the screening monovalent counterions. Further, Figure 5(b) shows that the fluctuations in the local charge density are more pronounced in double layers with divalent counterions

because the charge-density fluctuation is proportional to the square of charge numbers. In either case, the mean force becomes undetectable when the distance between the two macroion surfaces exceeds about twice the Debye screening length. The hard-sphere collision force in the 2:1 salt is, again, predominantly repulsive at short separations, but displays weak oscillations with attractive minima at intermediate distances. This behavior resembles the excluded-volume effects observed for neutral hard spheres. The attractive hard-sphere force first appears when the separation between macroion surfaces exceeds the small-ion diameter, σ_s whereas in the neutral case the attraction is strongest when that separation is less than σ_s. This difference results from the strong electrostatic attraction between the macroions and the counterions. When the counterions are excluded from the region close to the macroion-macroion axis, they accumulate within the remaining free volume between the macrospheres and therefore continue to exert a repulsive collision force. The position of the observed minimum in the collision force at $r \sim 1.3\sigma_M$ approximately coincides with the second minimum in the solvation force between neutral macroparticles. The difference between the numbers of mono- and divalent counterions needed to neutralize the macroion charge, and the associated difference in steric exclusion effect, explains the differences between collision terms observed in the two cases. In the monovalent case, about twice the number of small ions compete for the limited free space between the macroions, thus increasing the apparent repulsion. As a result, an attractive collision force is not observed in an electrolyte solution with monovalent counterions, Figure 5(a).

The overall force profile shown in Figure 5(b) is similar to that reported by Valleau et al[8] for the interaction between two parallel charged walls, but the individual

contributions are qualitatively different. The electrostatic force for the planar geometry at conditions presumed by Valleau et al[8] is attractive for all distances, and its magnitude decreases monotonically with increasing wall-wall separation. For spherical macroions considered in the present work, the electrostatic force is strongly repulsive at short distances, but turns to attraction at certain intermediate separations. We consider the whole range of intercolloidal separations including those when the counterions are sterically excluded from the energetically most favorable region between the macroions. In studies of the planar case[6-8], on the other hand, the wall charge was typically considered to be neutralized by counterions confined between the two walls. This precluded calculations for systems with wall-wall separations below σ_s where the neutralizing counterions are excluded between the walls[32] and the overall Coulombic force is always repulsive.

IV.2 Potentials of mean force from simulation and from classical theories

The potential of mean force can be obtained by integration of the mean force obtained from Monte-Carlo simulations,

$$W(r) = \int_r^{\infty} F(r)dr . \qquad [14]$$

The integral in Eq.(14) is evaluated numerically. In calculating this integral, we assume that the mean force between macroions vanishes beyond about 3 macroion-diameter separations. Figures 6(a) and 6(b) show the potential of mean force between adjacent macroions obtained by integrating the mean force as a function of inter-macroion separation . Simulation results are compared with predictions of DLVO theory[33], and SI

theory[10]. In DLVO theory, where the linearized Poison-Boltzmann equation is applied, the electrostatic interaction between two macroions in an electrolyte solution is given by

$$\frac{W^{DLVO}(r)}{kT} = \frac{z_M^2 l_B}{r} \frac{\exp[-\kappa(r-\sigma_M)]}{(1+\kappa\sigma_M/2)^2} \tag{15}$$

where z_M is the macroion valence, σ_M is the macroion diameter, κ is the Debye screening parameter and l_B is the Bjerrum length. SI theory is also based on the linearized Poison-Boltzmann equation but uses the Gibbs energy (instead of Helmholtz energy). It includes a repulsive Helmholtz energy term and an attractive term due to volume change associated with the varying distance between the macroions. The SI potential for interaction between two identical macroions in electrolyte solutions is given by

$$\frac{W^{SI}(r)}{kT} = z_M^2 l_B \left[\frac{\sinh(\kappa a)}{\kappa a}\right]^2 \left[\frac{1+\kappa a \coth(\kappa a)}{r} - \frac{\kappa}{2}\right] \exp(-\kappa r) \tag{16}$$

where $a=\sigma_M/2$. The attractive interaction appears at large inter-macroion separations where the first term in the parenthesis is smaller than $\kappa/2$. Eq (16) implies that an attractive electrostatic force exists for all situations as long as the center-to-center distance r is sufficiently large. Because all effects of small ions are absorbed in the Debye screening parameter, neither DLVO nor SI theory can distinguish between divalent and monovalent salts at the same ionic strength.

Figure 6(a) shows the potential of mean force between two negatively-charged macroions in a 1:2 electrolyte solution. Results from DLVO theory agree fairly well with simulation results. This good agreement is somewhat misleading because it conceals the cancellation of errors made in DLVO theory. Specifically, the Poisson-Boltzmann

approximation ignores two opposing effects: the finite ion size, and the correlated fluctuations in ion distribution. On the other hand, SI theory underestimates repulsive interaction between macroions over all distances. The weak, long-range attraction predicted by SI theory is not confirmed by our results for an electrolyte solution with monovalent counterions.

Figure 6(b) shows the potential of mean force between two macroions in a 2:1 electrolyte solution. In this case, neither DLVO nor SI theory reproduces the attractive potential seen at intermediate macroion separations. Although SI theory predicts an attractive electrostatic force between macroions of like charge, the depth of the attractive potential is much smaller while its range extends to separations much larger than those found in the simulation. Very recently, Tokuyama[34] derived an expression for the intercolloidal potential comprising a repulsive Yukawa term and an attractive part decaying as $exp(-\kappa r)/r^3$ .While this potential captures qualitative features observed in our work, it has been derived assuming a finite macroion concentration in the absence of salt which precludes quantitative comparisons with present calculations.

To obtain additional insights for electrostatic interaction between like-charged macroions, we calculated the internal energies of the system at different macroion separations. Figure 7 presents the relative internal energy as a function of the distance between two macroions in 1:2 and 2:1 electrolyte solutions. The relative internal energy, $\Delta E(r)=E(r)-E(\infty)$, is defined as the difference between the internal energy of the system when two macroions are separated by a distance r and that when they are separated infinitely apart. In accord with DLVO theory, the internal energy displays an attractive minimum regardless of the valences of the small ions. In solutions with monovalent

counterions, the minimum is observed around $r \sim 1.2\sigma_M$ corresponding to the separation where a single-layer of counterions can be simultaneously in contact with both macroions. In the monovalent case, the contact energy of two macroions exceeds the value characteristic of large separations. However, for macroions in the 2:1 electrolyte solution, the contact value of relative internal energy is negative and the position of the energy minimum is shifted to a separation about one-half σ_M that for the monovalent case. This difference is consistent with our earlier discussion of steric exclusion of simple ions from the region between adjacent macroions. As screening divalent ions require less space (because of smaller number of ions) than the equivalent number of monovalent ions, monovalent counterions neutralize the macroions most efficiently at separations somewhat bigger than those for divalent counterions.

In the remaining example, we consider the effect of salt concentration on the interaction between macroions in 2:2 electrolyte solutions. We consider three concentrations, c_s=0.01, 0.1, and 1 M. As shown in Figure 8, the attraction between like-charged macroions is most prominent at the intermediate concentration of divalent counterions. The nonmonotonic effect of the electrolyte concentration can only be explained by considering all the different contributions to the colloid-colloid interaction. We therefore survey these contributions before we proceed with a discussion of the results presented in Figure 8.

IV.3 Origin of electrostatic attraction between like-charged macroions

The origin of electrostatic attractive forces between macroions of like charge has been a subject of many discussions[33-37]. Some observations originally believed to reveal such attractions have been explained[35] in terms of the collective effect of screened

repulsion between the macroions. In other scenarios, the attraction was attributed to a combination of effects including accumulation of counterions and depletion of coions in the region between the two macroions and significant correlations between ionic-density fluctuations[6,40,41] in adjacent double layers.

Some classical theories like Sogami-Ise (SI) theory[10] predict attractions based on purely mean-field arguments. Our simulation results show that attractive interaction typically occurs when one or two layers of counterions fill the gap between the macroions, suggesting that the attraction between the macroions of like charge is related to counterion mediation. However, this contribution alone is not sufficient to overturn the strong repulsive force due to direct interaction between equally charged macroions, and between counterions themselves. An additional effect ultimately responsible for the attraction between the macroions is the correlation between ion density fluctuations in the adjacent double layers surrounding the two macroions. Interpretations of the correlation effect exploit the analogy with induced polarization giving rise to the van der Waals attractive force between adjacent atoms[6-8]. Similar reasoning has been used to describe counterion-mediated attractions between two like-charged rods in electrolyte solutions[38].

The analogy between double-layer correlations and quantum-mechanical dispersion forces has also been pointed out in perturbation theory for interacting polyions[39,42] and for reverse micelles[41]. While the method provides valuable insights into attraction between macroions, quantitative comparisons with computer simulation or experiments also require an account of hard-sphere interactions.

A counterion-condensation theory developed by Ha and Liu[38] for interaction between charged rods is in qualitative agreement with computer simulations[9]. Other

sources of electrostatic attraction between equally charged colloids include fluctuations in total macroion charge (resulting in a potential that decays as the square of the direct[41] or screened[42,43] Coulombic interaction), and in a charge-reversal model by Sjostrom et al[44]. All these theories emphasize the attractive contribution of the correlations among small ions in the vicinity of the macroions. Within linear approximations, the ion-ion correlation effect should depend primarily on the ionic strength of the solution. This prediction seems to be borne out by our observation of a similar attractive energy minimum displayed by macroions in mono- and divalent salts at the same ionic strength. The potential of mean force, however, is repulsive in the monovalent-salt solution while it can be attractive in the presence of divalent ions. This difference is explained in terms of the repulsive entropic term related to the localization of the counterions surrounding the two macroions. This term is weaker in the divalent-salt solution where the number of localized ions is about one-half that in the monovalent case.

The qualitative difference between the behaviors of solutions with mono- and divalent counterions is not related to any qualitative differences in underlying mechanisms for ions with different valences. The various opposing contributions can, however, differ in magnitude and hence produce different overall results. The net force often amounts to a small fraction of either of the leading terms. Relatively small changes in individual contributions can, therefore, shift the force balance from overall repulsion to overall attraction.

Divalent counterions generally result in stronger screening of the macroion charge (a mean-field effect), as well as stronger correlations between charge-density fluctuations in the double layers surrounding the polyions. These fluctuations are more pronounced at

higher concentrations of small ions. It is therefore not surprising that there is a change in the macroion-macroion potential of mean force observed in Figure 8 upon transition from weak screening at c_s=0.01 M to moderate concentration c_s=0.1 M.

The explanation of the maximum of the salt effect is, however, less obvious. The free energy reduction due to ion-ion correlations intensifies with increasing ion densities in overlapping double layers. The effect is most pronounced at larger differences in these densities and the corresponding densities in the bulk solution. At low salt concentrations, these differences grow with increasing c_s but the trend is reversed at moderate concentrations. At very high ionic strength, differences between ionic densities in the double layer and the bulk solution gradually diminish, thus reducing the energetic incentive of bringing the two macroions together.

The resulting behavior (illustrated in Figure 8) is of practical importance. First, we note that the concentration range around the observed maximum in salt effect includes the concentration of physiological solutions suggesting that physiological solutions with divalent ions correspond to a concentration range where variations in salt concentration have a minimum effect on the intercolloidal or interprotein potential of mean force. Second, our results can be of help in choosing the optimal concentration range to be considered when salting-out is used in procedures such as colloid precipitation, purification of water, or separation of proteins[45-48]. The nonmonotonic effect of salt concentration on protein-protein interaction has been revealed in recent measurements in our laboratory. We have monitored the cloud point temperature, T_c, of lysozyme solutions as a function of the concentration of various salts with divalent cations (magnesium) or anions (sulfate ion). A maximum in T_c was repeatedly observed[49] within

the concentration interval 0.2-0.5 M. Similarly, Taratuta *et al*[46] observe a weak maximum in T_c of lysozyme solutions as a function of the ionic strength of the sodium phosphate buffer (containing a mixture of mono- and dibasic phosphate salts) around 0.4-0.5 M. Further examples of nonmonotonic salt effects on the behavior of protein solutions include the minima in the diffusion coefficients of lysozyme and concanavalin as functions of ammonium sulfate concentration[50], and the extrema in the insulin dimerization constant[51], and in the activity of β-lactoglobulin[52] measured as functions of the concentration of NaCl or $MgCl_2$, respectively. The ion-correlation effect on optimal salting-out concentration discussed along with Figure 8 is expected to play a significant role in systems dominated by electrostatic considerations.

However, optimum conditions can be modified by the presence of specific ion-ion, ion-colloid, and ion-solvent interactions. Further, more systematic data for a variety of conditions would be needed to formulate general guidelines regarding the salting-out effect of multivalent electrolytes. At finite colloid concentration, the question of the pairwise additivity of intercolloidal potential[53] must also be addressed. An accurate account of different and often opposing contributions is essential in such calculations. The interaction between macroions in electrolyte solutions involves complicated many-body effects including the correlations among ion-density fluctuations and steric exclusion of small ions. These effects can be considered by molecular simulations that require substantial numerical effort. Integral equation theories represent an inviting alternative for systematic calculations. The double-layer interaction between two parallel charged walls has been successfully described by the anisotropic hypernetted-chain equation (AHNC)[54-57] and by the non-local density functional theory proposed by Tang et

al[58]. Despite the lower symmetry of the present system with accompanying numerical complexity, variations of these theories are likely to be promising for deriving a successful theory for colloidal interactions.

V. Conclusions

We have studied interactions between like-charged macroions in primitive-model electrolyte solutions at various conditions. Attractive interaction between equally charged macroions is observed at certain conditions when the solution contains divalent counterions. This attraction appears to be most significant at intermediate salt concentrations, an observation of practical importance. In the absence of multi-valent counterions, macroions of the same charge repel each other at all separations. At these restricted conditions, the classical DLVO theory agrees surprisingly well with the simulations. The long-range attractions between macroions as predicted by the SI theory are not confirmed by our study.

The mechanism of inter-macroion interaction is elucidated by a separate evaluation of the different contributions to the mean force between particles. The attractive-energy term is opposed by the entropic penalty associated with the localization of the screening counterions. In a solution containing only monovalent counterions, the entropy term outweighs the electrostatic interaction at all separations. In a solution with divalent counterions, fewer counterions are needed to screen the polyion charge. As a result, the repulsive entropic effect is not always sufficient to reverse the short-range electrostatic attraction that originates from Coulombic macroion-counterion forces and ion-ion correlations. The hard-sphere term related to collisions between the macroions

and surrounding simple ions is strongly repulsive at small distances but rapidly decays with inter-macroion separation.

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Figure Captions

Figure 1 Interaction between two neutral macrospheres surrounded by small hard spheres. As two macro-spheres approach each other, the two big-sphere/small-sphere excluded volumes overlap creating additional free volume for small hard spheres. The increase in free volume leads to an attractive entropic force between a pair of neutral macrospheres .

Figure 2 Distributions of monovalent counterions and divalent coions at a small macroion separation.

Figure 3 Reduced entropic force between two large hard spheres in a medium of small spheres. Squares are simulation results of Dickman, Attard and Simonian (1997)[25]. Solid circles are calculated by the direct-sampling technique introduced in the present work, and the dashed line is predicted by the Asakura-Oosawa theory. The reduced force is defined as $F^*(D) = 2F(D)/(\pi\sigma_M\sigma_S\rho kT)$, where $F(D)$ is the force at contact distance D,; σ_M is the diameter of big hard spheres and σ_S is the diameter of small hard spheres; ρ is the number density of small hard spheres; k is the Boltzmann constant; and T is temperature. The diameter ratio of large and small hard spheres $\sigma_L / \sigma_S = 5$; the packing fraction of small hard spheres is $\eta \equiv \pi\rho\sigma_S^3 / 6 = 0.341$.

Figure 4 Mean force (F) between identical small ions of a 1:1 primitive-model electrolyte solution vs. inter-ion separation (r). The curve is calculated from the pair correlation function between ions of the same charge; and circles represent the results of the direct-sampling technique discussed in the text. The concentration of the salt is 2 M (M=mol dm^{-3}), Bjerrum length l_B=0.714 nm, temperature T=298.15 K, and diameter of ions σ=0.425 nm.

Figure 5(a) Mean force (F) between identical macroions in a 1:2 primitive-model electrolyte solution of ionic strength I=0.28M. Solid circles represent the total force; open circles correspond to the collision force and squares to Coulomb interaction. The lines are to guide the eye. Symbol size corresponds to error bars of the simulation.

Figure 5(b) Same as Figure 6(a) but for macroions in a 2:1 electrolyte solution of ionic strength I=0.31M.

Figure 6(a) Potential of mean force (W) between identical macroions in a 1:2 electrolyte solution of ionic strength I=0.28 M. Circles: simulation results; solid curve: DLVO theory; dashed line: Sogami-Ise theory.

Figure 6(b) Same as Figure 7(a) but for macroions in a 2:1 electrolyte solution of ionic strength I =0.31M.

Figure 7 Reduced internal energy, $\Delta E(r)/kT$ as a function of the macroion separation r in 1:2 and 2:1-electrolyte solutions considered in Figure 4.

Figure 8 Comparison of macroion-macroion potentials of mean force at three different concentrations, c_s, of 2:2 electrolyte, c_s=0.01, 0.1, and 1 M.

Table I Simulation Parameters Used in This Work

Number of particles	180
Temperature, T (K)	298
Dielectric constant, ε_r	78.5
Macroion diameter, σ_M (nm)	2
Macroion charge, z_M	-20
Small ion diameter (cations & anions), σ_s (nm)	0.4
Bjerrum length, l_B (nm)	0.714

Figure 1

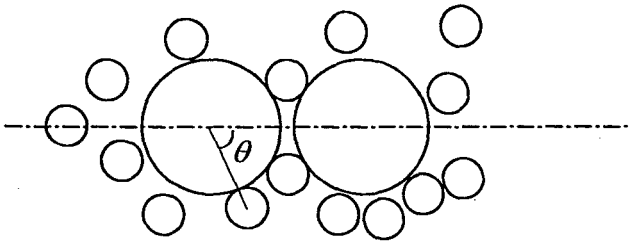

Figure 2

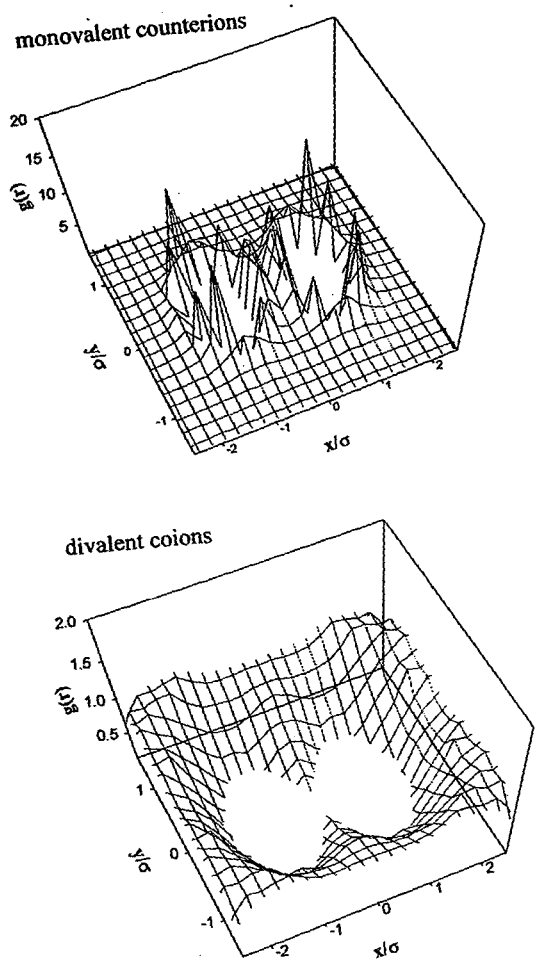
monovalent counterions
20
15
10
5
(x)g
1
0
-1
y/σ
-2
-1
0
1
2
x/σ
divalent coions
2.0
1.5
1.0
0.5
(x)g
1
0
-1
y/σ
-2
-1
0
1
2
x/σ

Figure 3

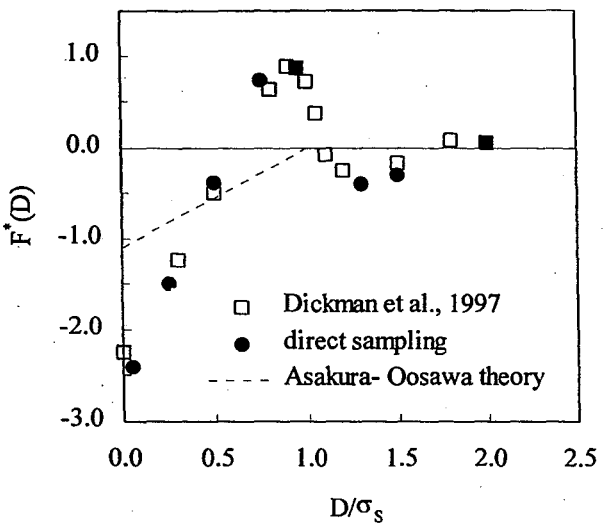
1.0
0.0
-1.0
-2.0
-3.0
F*(D)
0.0
0.5
1.0
1.5
2.0
2.5
D/σs
Dickman et al., 1997
direct sampling
Asakura- Oosawa theory

Figure 4

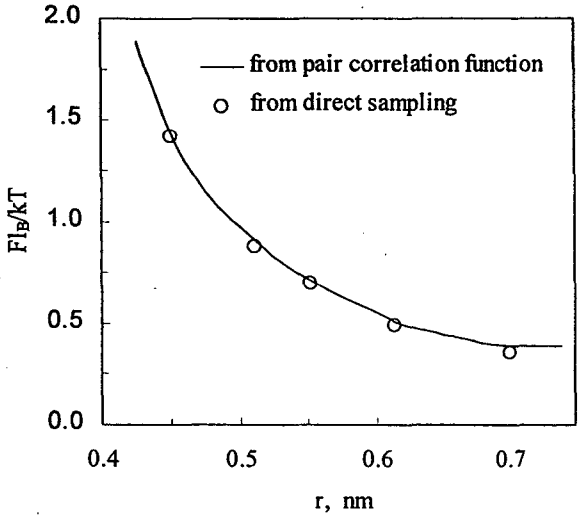
2.0
1.5
1.0
0.5
0.0
$F1_B/kT$
from pair correlation function
from direct sampling
0.4
0.5
0.6
0.7
r, nm

Figure 5(a)

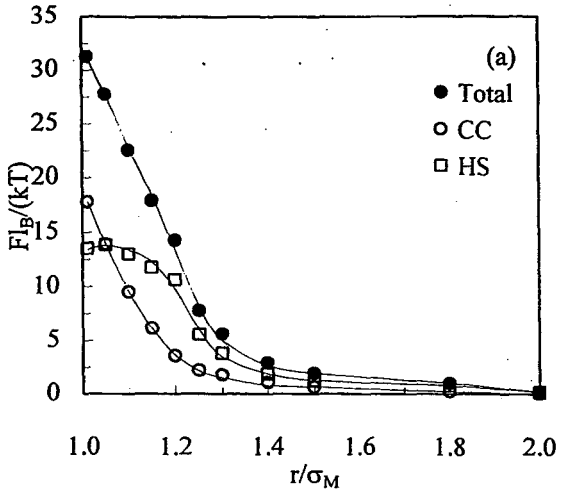

Figure 5(b)

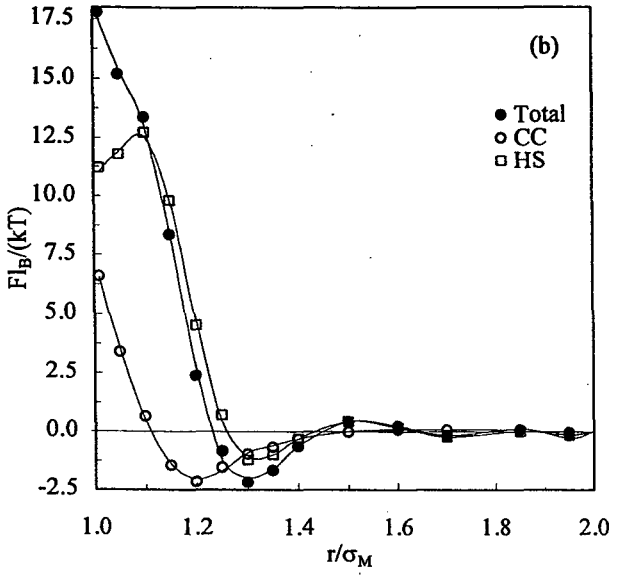
(b)
Total
CC
HS
17.5
15.0
12.5
10.0
7.5
5.0
2.5
0.0
-2.5
$FI_B/(kT)$
1.0
1.2
1.4
1.6
1.8
2.0
r/σ_M

Figure 6(a)

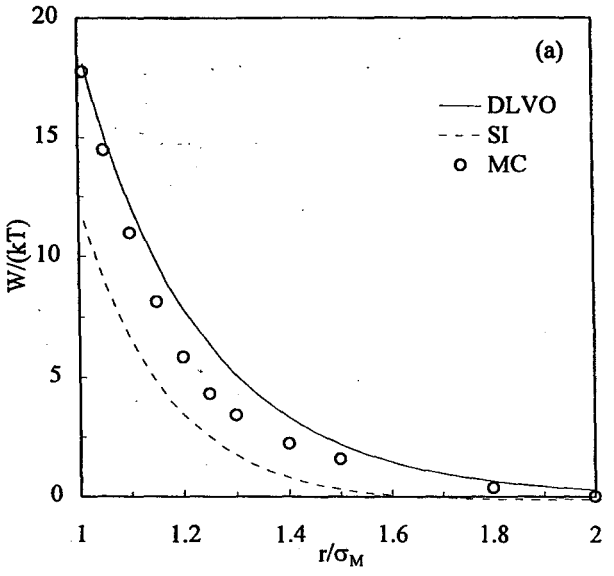

Figure 6(b)

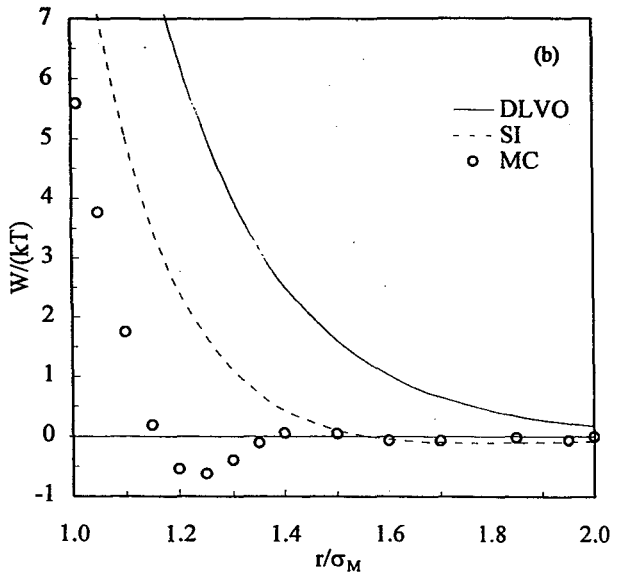

Figure 7

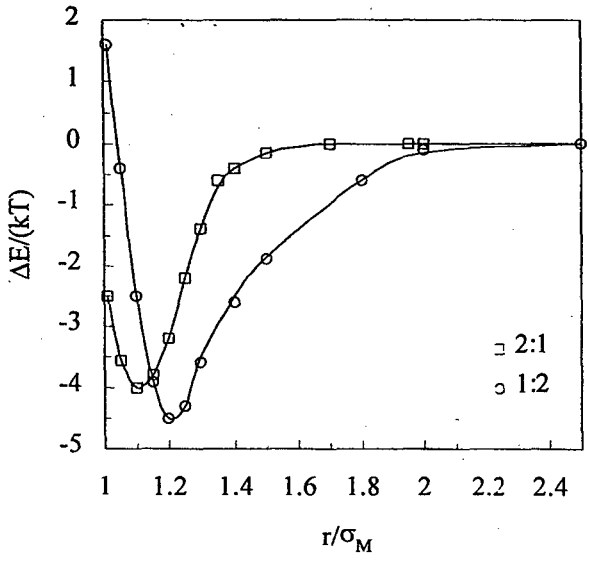

Figure 8

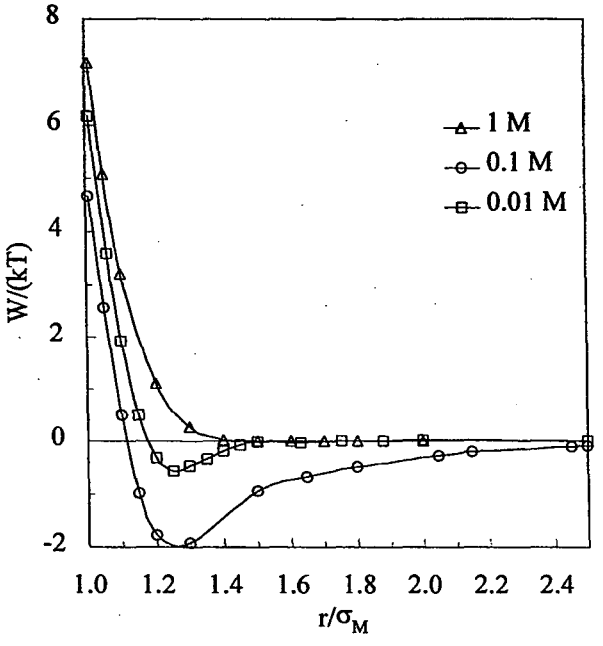

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Figure 7

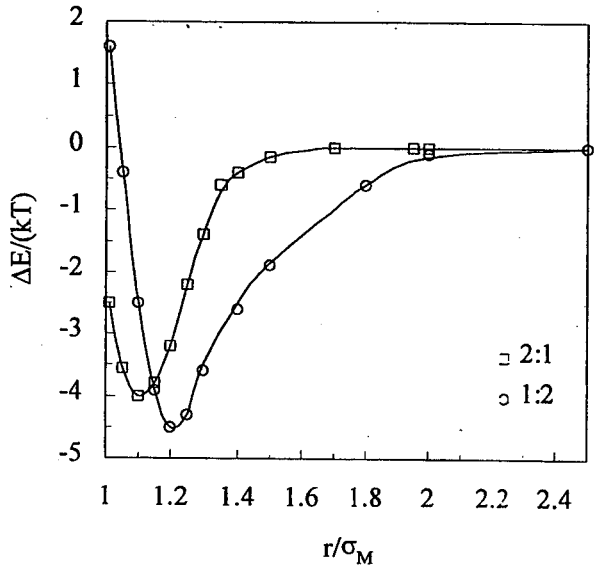
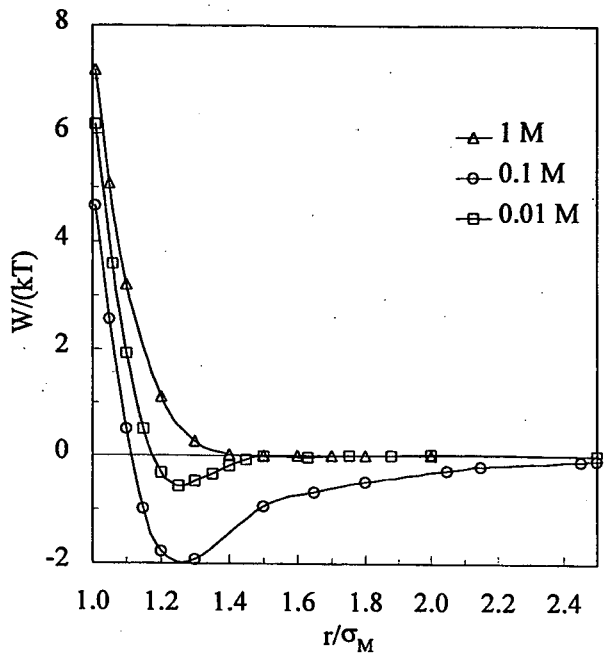


Figure 8



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