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Chemical Sciences Division

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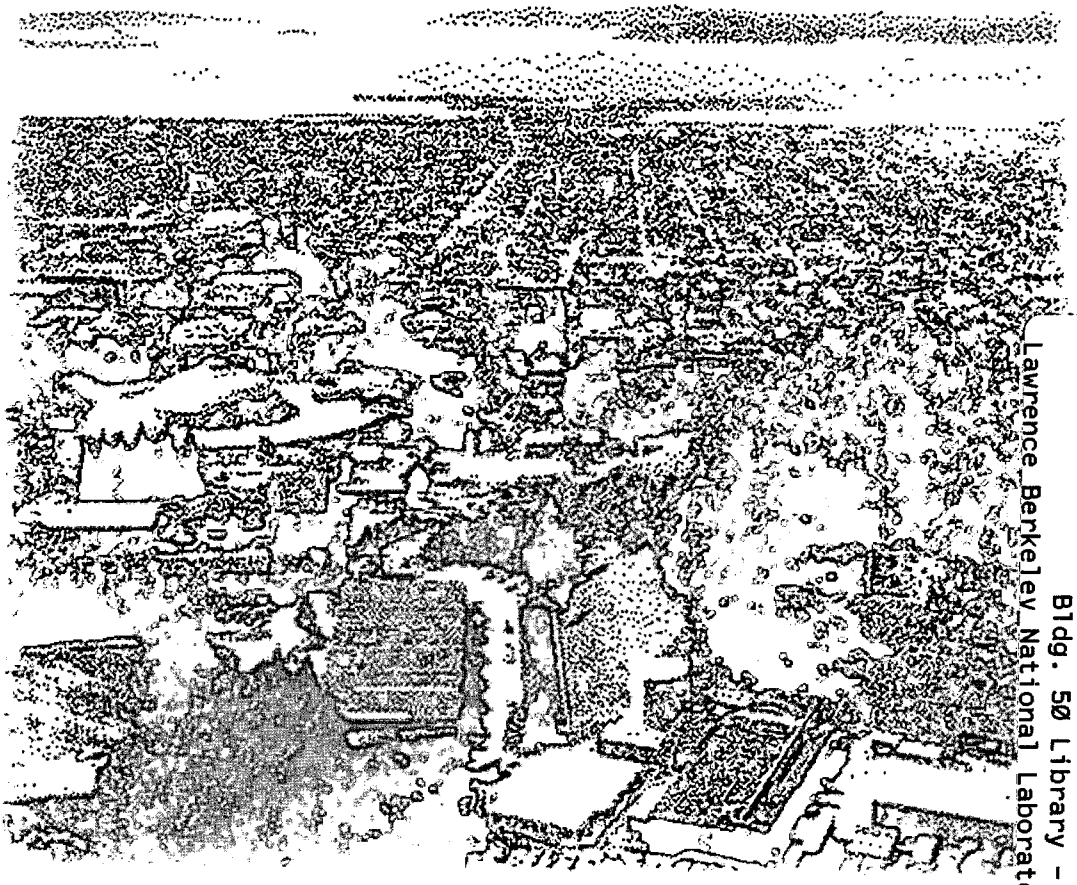

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Abstract

Statistical-thermodynamic theory for predicting the phase behavior of a colloidal solution requires the pair interaction potential between colloidal particles in solutions. In practice, it is necessary to assume pairwise additivity for the potential of mean force between colloidal particles, but little is known concerning the validity of this assumption. Monte Carlo simulations for isolated colloidal triplets in equilateral configurations show that, while the three-body force is repulsive when the three particles are near contact, it becomes short-ranged attractive at further separations, contrary to a previous study where the triplet force is attractive at all separations. The three-body force arises mainly from hard-sphere collisions between colloids and small ions; it is most significant in solutions of monovalent salt at low concentration where charged colloids experience strong electrostatic interactions. To illustrate the effect of three-body forces on the phase behavior of charged colloids, we calculated the densities of coexisting phases using van-der-Waals-type theories for colloidal solutions and for crystals. For the conditions investigated in this work, even though the magnitude of the three-body force may be as large as 10% of the total force at small separations, three-body forces do not have a major effect on the densities of binary coexisting phases. However, coexisting densities calculated using DLVO theory are much different from those calculated using our simulated potential of mean force.

Introduction

The potential of mean force between charged colloidal particles in electrolyte solutions plays a central role in determining the stability of colloidal suspensions as encountered in inks, paints, cosmetic products, food colloids and pharmaceutical dispersions[1,2]. The recent revival of intensive research interest on colloidal suspensions is motivated first, by a desire to use colloids as model systems to study structural phase transition[3], and second, by a need to provide guidance for growing colloidal crystals, for example, to determine the three-dimensional structures of globular proteins using X-ray diffraction[4,5], and for fabricating advanced ceramic materials[6] and photonic crystals[7]. It is customary to represent the interaction between charged colloidal particles in electrolyte solutions by the Derjaguin-Landau-Verwey-Overkeek (DLVO) theory[8,9]. That theory predicts that an isolated pair of like-charged colloidal spheres experiences a repulsive screened Coulomb potential in addition to a hard-core repulsion and a van-der-Waals attraction. Whereas hard-core repulsion and van-der-Waals attraction are well understood, there remains controversy concerning the electrostatic potential; since the early days of colloid science, mounting evidence suggests electrostatic-induced attraction between like-charged colloidal spheres[10]. Recent results from molecular simulations have shown that, in the absence of van-der-Waals interactions, two isolated like-charged plates[11], cylinders[12], or spheres[13], can be attractive at small separations in an electrolyte solution containing multivalent counterions. DLVO theory fails to account for such attraction because it neglects charge fluctuations in the electrostatic double layers. Little is known concerning how the phase behavior of charged colloids predicted using DLVO

theory differs from that using a more accurate pair-interaction potential. Further, because interactions between charged colloidal particles in an electrolyte solution are influenced by many-body contributions of small ions and solvent molecules, pairwise additivity is not assured.

Recently, Löwen and Allahyarov reported triplet forces for colloidal particles in a small volume of electrolyte solution[14]. Using molecular-dynamics simulation and an extended Debye-Hückel-type theory, Löwen and Allahyarov found that, near touching of a colloidal triplet, the three-body interaction yields a significant attractive correction to the repulsive pairwise interaction that decays monotonically at larger separations. However, an independent study by Tehver et al. using *ab initio* density-functional theory indicated the absence of three-body effects for interactions among charged colloidal particles[15].

This work investigates three-body interactions among charged colloidal particles and their effect on phase behavior. Using a novel, recently proposed simulation method, we studied interactions among isolated colloidal triplets dispersed in an electrolyte solution in equilateral-triangle configurations. We considered only equilateral triplets where non-pairwise additivity is expected to be most pronounced. In contrast to previous results in the literature[14,15], we find that the triplet force is repulsive at short distances and becomes attractive at larger separations. Non-pairwise additivity for interaction among colloidal spheres is largely due to hard-sphere collisions; it is magnified in solutions of low ionic strength where charged colloids experience strong electrostatic

interactions. We calculated the effect of three-body forces on the phase behavior of charged colloids using van-der-Waals-type theories for the colloidal solutions and for crystals. The densities of coexisting phases are not significantly affected by three-body interactions at conditions investigated in this work. However, the coexisting densities are very different from those predicted using the DLVO potential.

Molecular Model and Simulation Methods

Three-body interactions among colloidal triplets were studied using a simulation method reported earlier[16]. Three colloidal spheres are arranged in perfect triangles dispersed in a primitive-model electrolyte solution. According to the primitive model, the macroions and simple ions are represented by charged hard spheres immersed in a dielectric continuum, an approximation that often yields excellent agreement between solution structures obtained from scattering experiments and from theoretical calculations[17-19]. We investigated interactions among isolated colloidal triplets in monovalent as well as in divalent electrolyte solutions at different concentrations. To find the effect of non-pairwise additivity, we calculated interactions between isolated colloidal pairs at solution conditions identical to those for triplet forces, i.e., at the same concentrations of counterions and coions. Figure 1 shows the arrangements of colloidal triplets and pairs for sampling three-body and pair forces. The simulation-box length is always much larger than the Debye-screening length such that periodic boundary conditions (using Ewald summation) can be applied in calculating the interaction energy. We assumed that interactions among colloidal particles beyond one simulation-box

length are negligible. Therefore, the simulation results can be approximated by those for isolated colloidal particles surrounded by an electrolyte solution. Table 1 presents simulation parameters for triplet interactions. The diameters of colloidal spheres and small ions are, respectively, 2 nm and 0.4 nm in all calculations. Each colloidal particle contains 20 negative charges. The forces on each particle in lateral directions are sampled using a novel, recently proposed simulation method for hard-sphere collisions and electrostatic interactions[16]. Due to system symmetry, the total force on each particle is obtained by averaging over all lateral directions. Details of the simulation procedure are given in a previous report[16].

As shown in Figure 1, F_2 represents the average force between two isolated colloidal particles in the solution; F_3 represents the average total force between any two particles in the triplet in a lateral direction. For triplet interactions, F_3 contains contributions from two particles. The effective two-body force, given by $2F_3/3$, represents the force between two particles in the triplet as if pairwise additivity were applicable. The three-body force in a triplet, ΔF_3, is defined as the non-pairwise-additive part of the force between particle pairs:

$$\Delta F_3 = 2F_3/3 - F_2 \ . \tag{1}$$

When $\Delta F_3 = 0$, we have pairwise additivity. F_3 and F_2 were calculated using Monte Carlo simulation for colloidal triplets and pairs in monovalent and divalent electrolyte solutions.

Results and Discussion

Figure 2 shows three-body forces ΔF_3 vs. inter-particle separation. As expected, the simulation results indicate that the three-body force is most significant when colloidal triplets are close to each other. The three-body-force profile qualitatively resembles a Lennard-Jones potential that is repulsive near contacts and becomes attractive at larger separations. Our results differ from those reported by Löwen and Allahyarov primarily at distance near contacts[14]. Löwen and Allahyarov reported a three-body force that is always attractive. The qualitative difference between our results and those reported previously may follow from the size ratio of colloidal particles to small ions. Löwen and Allahyarov used a very high ratio of diameters equal to 1000. When salt ions are much smaller than colloidal spheres, the excluded-volume effect of small ions on the potential of mean force becomes less pronounced, while the multi-body electrostatic correlation leads to an additional attraction. Indeed, Löwen and Allahyarov showed that their simulation results can be quantitatively reproduced using an analytical theory that neglects excluded-volume interactions. In our case, because the diameter ratio of colloidal spheres to small ions is only 5, the size of small ions plays a major role. For the solution conditions considered here, the three-body force is most significant when colloidal particles are dispersed in a monovalent-salt solution at low salt concentration, whereas it is almost negligible in a divalent-salt solution at a moderate salt concentration. Figure 3 shows the three-body force and the corresponding pair-interaction force for colloidal particles in a 1:1 electrolyte solution. At small separations, the three-body force

may be as much as 10% of the total force between colloidal pairs. By sampling the average force due to hard-sphere collisions and that due to electrostatic interactions, we found that the three-body repulsive force is mainly due to hard-sphere collisions at small separations, whereas the electrostatic contribution to the three-body force is almost everywhere attractive. This electrostatic attraction is responsible for the results given by Löwen and Allahyarov. In that work, hard-sphere interactions among small ions make only a very small contribution.

To investigate the effect of three-body forces on the phase behavior of a charged colloid, we applied van-der-Waals-type theories for the colloidal solution and for the crystal. A similar procedure has been used by Baus et al. to study the phase diagram of colloidal dispersions using model inter-colloidal potentials[20,21]; they found that the results from van-der-Waals-type theories for the phase behavior of colloidal solutions can be in quantitative agreement with results from more rigorous calculations.

For a monodisperse colloidal solution consisting of N colloidal particles of diameter σ at temperature T and colloidal number density ρ, the Helmholtz energy $A_{solution}$ is given by three contributions. The first contribution arises from the ideal gas; the second from hard-sphere repulsion, as represented by the Carnahan-Starling equation of state[22]; and the third from a perturbation due to an attractive or repulsive tail in the potential of mean force:

$$\frac{A_{solution}}{NkT} = \ln(\rho\Lambda^3) - 1 + \frac{4\eta - 3\eta^2}{(1-\eta)^2} + \frac{\rho}{2kT}\int d\vec{r}\, W(r), \qquad (2)$$

where k denotes the Boltzmann constant, Λ is the thermal wave length, $\eta = \pi\rho\sigma^3/6$ is the packing fraction, and $W(r)$ represents the potential of mean force between colloidal particles beyond the hard-sphere repulsion. According to the DLVO theory, $W(r)$ is given by

$$\frac{W^{DLVO}(r)}{kT} = \frac{n_z^2 l_B}{r} \frac{\exp[-\kappa(r-\sigma)]}{(1+\kappa\sigma/2)^2}, \tag{3}$$

where n_z is the number of charges on each colloidal sphere, κ is the Debye screening parameter and l_B is the Bjerrum length. The Debye-screening length, κ^{-1}, is defined by

$$\kappa^{-1} = \left(\sum_i \frac{\rho_i q_i^2}{\varepsilon_0 \varepsilon kT} \right)^{-1/2}, \tag{4}$$

where ρ_i and q_i stand, respectively, for the number density and charge of a small ion; $\varepsilon_0 = 8.854 \cdot 10^{-12} \mathrm{C}^2/(\mathrm{Jm})$ is the permittivity of vacuum; and ε is the dielectric constant of the medium. 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 in a medium of dielectric constant ε equals thermal energy kT. The potential of mean force between colloidal spheres can also be obtained by integration of the mean force $F(r)$ from simulation over separations,

$$W(r) = \int_r^\infty F(r')dr'. \tag{5}$$

Within the pairwise-additivity assumption, $F(r)$ is the pair interaction force as calculated using Monte Carlo simulation for two isolated colloidal particles. To estimate the upper bound of the three-body effect, we use in Eq.(5) the effective two-body force $2F_3/3$ as obtained by Monte Carlo simulation for the colloidal triplets.

In a van-der-Waals-type theory for a colloidal crystal[20], the Helmholtz energy includes a reference term that is represented by a cell model for the corresponding hard-sphere crystal, and an additional term due to the perturbation potential $W(r)$,

$$\frac{A_{crystal}}{NkT} = -\ln\left[\frac{4\pi(a-\sigma)^3}{3\Lambda^3}\right] + \frac{1}{2kT}\sum_{j}^{shells} z_j W(R_j), \tag{6}$$

where a is the lattice constant, z_j is the number of neighbors in shell j that are separated by R_j from a center particle. Here we consider only nearest-neighbor interactions in the crystal phase. The lattice constant is related to the average number density of the crystal, $\overline{\rho}$, and the maximum density at close packing, $\overline{\rho}_c$

$$\sigma / a = (\overline{\rho} / \overline{\rho}_c)^{1/3}. \tag{7}$$

Colloidal spheres may form both body-centered cubic (BCC) and face-centered cubic (FCC) crystals. In a BCC crystal, each colloidal particle has 8 nearest neighbors and the maximum density is $\overline{\rho}_c^{BCC} = 3\sqrt{3}\sigma^{-3}/4$; in a FCC crystal, each particle has 12 nearest neighbors and $\overline{\rho}_c^{FCC} = \sqrt{2}\sigma^{-3}$.

The densities of coexisting phases can be found by solving standard thermodynamic equilibrium equations

$$\mu^{\alpha} = \mu^{\beta}, \tag{8}$$

$$\Pi^{\alpha} = \Pi^{\beta}, \tag{9}$$

where superscripts α and β designate coexisting phases; the chemical potential of colloidal spheres, $\mu = (\partial A / \partial N)_{T,V}$, and the osmotic pressure, $\Pi = -(\partial A / \partial V)_{T,N}$, are obtained from the corresponding Helmholtz energy, as given in Eq.(2) for the liquid

solution and in Eq.(6) for colloidal crystals. For a given potential of mean force between colloidal spheres, there may exist solution-FCC, solution-BCC and FCC-BCC equilibria.

We calculated solution-crystal (BCC or FCC) and crystal-crystal equilibria using a potential of mean force from 1) simulated two-body potential, 2) simulated effective two-body potential, 3) and DLVO theory. The effective two-body potential from three-body simulations has been used to account for the three-body effect. Table 2 gives reduced densities ($\rho\sigma^3$) of binary coexisting phases obtained from van-der-Waals-type theories with inter-colloidal potentials from Monte Carlo simulations, or from DLVO theory. For the conditions considered here, we find that, within the van-der-Waals framework, the three-body force does not significantly affect the coexisting densities, even when there is a considerable deviation from pairwise additivity, as in a solution containing monovalent salt at low concentration. However, the phase behavior predicted using the DLVO potential can be significantly different from those using our potential of mean force as obtained by Monte Carlo simulations, especially in divalent-salt solutions where short-range attraction is observed between colloidal pairs, and in monovalent-salt solutions at very low concentration. As reported by others[23], we found that at low salt concentrations (<0.1M), DLVO theory is unable to reproduce the Monte Carlo simulation results even for colloidal spheres in monovalent-salt solutions, in contrast to our previous results for interactions between colloidal spheres in monovalent salt solutions at higher concentrations (~0.3M). Because of cancellation of errors, the DLVO theory agrees almost quantitatively with simulation data at higher monovalent-salt concentrations[16].

Figure 4 illustrates typical chemical potentials of macroions in solution or in a crystal, as functions of colloidal concentration for a charged colloid in a 1:1 electrolyte solution at 0.05M. Also shown in Figure 4 are coexisting densities for several binary-phase equilibria. Figure 4(a) is predicted using the effective potential of mean force from Monte Carlo simulation. At high colloid concentrations, a colloidal solution can be in equilibrium with a FCC crystal, while a BCC crystal can be in equilibrium with a FCC crystal phase at relatively low concentrations.

Figure 4(b) gives the coexisting phases predicted using DLVO theory. The phase behavior according to the DLVO potential resembles that in Figure 4(a) at high colloidal concentrations. However, here a colloidal solution can be in equilibrium with a BCC crystal at very low concentration, as shown in the inserted plot. The fluid-BCC equilibrium at low concentrations is most probable when we have long-range repulsion between colloidal spheres. For the solution conditions investigated here, we do not observe phase equilibrium between two liquid solutions because such phase coexistence usually appears at conditions where there is significant attraction between colloidal particles.

Finally we note that, although thermodynamic properties may be insensitive to three-body forces, selected measurable nonequilibrium properties like precipitation kinetics may be controlled by nearest-contact configurations. In view of our present results, three-body forces appear to stabilize triplets at intermediate macroion-macroion distances while reducing the probability of macroion collisions. Therefore, three-body

force may significantly affect the potential barrier which is often responsible for the apparent stability of a dispersion.

Conclusions

Prediction of the phase-behavior of colloidal solutions remains theoretically challenging even for simple colloidal systems. We apply van-der-Waals-type theories here because the main focus of this work is to study the three-body force and its consequences on phase behavior.. Upon using Monte Carlo simulations to obtain qualitative results for interactions among colloidal triplets and pairs, we found that the three-body force can be repulsive or attractive, depending on macroion-macroion separation. The three-body effect is largely due to the finite size of salt ions, and magnifies at small colloid-colloid separations or at solutions of low electrolyte concentration where colloidal particles interact intensively with each other. Within the van-der-Waals theory, the three-body force appears to have only a minor effect on phase behavior, suggesting that pairwise additivity is satisfactory for predicting the phase diagrams of colloidal systems. However, densities of coexisting phases predicted with the DLVO potential can be very different from those predicted with a more accurate potential of mean force.

Acknowledgments

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Reference:

[1] D. H. Everett, *Basic Principles of Colloid Science* (Royal Society of Chemistry, London, 1988).

[2] D. F. Evans and H. Wennerström, *The Colloidal Domain : Where Physics, Chemistry, Biology, and Technology Meet*, 2nd ed. (Wiley-VCH, New York, 1999).

[3] W. C. K. Poon and P. N. Pusey, in *Observation, Prediction and Simulation of Phase Transitions in Complex Fluids*, edited by M. Baus, L. F. Rull, and J.-P. Ryckaert (Kluwer Academic Publishers, Dordrecht ; Boston, 1995), pp. xvii, 664.

[4] M. L. Grant and D. A. Saville, *Journal of Physical Chemistry* **98,** 10358-10367 (1994).

[5] N. Asherie, A. Lomakin, and G. B. Benedek, *Physical Review Letters* **77,** 4832-4835 (1996).

[6] E. J. A. Pope, S. Sakka, and L. C. Klein, *Sol-Gel Science and Technology* (American Ceramic Society, Westerville, Ohio, 1995).

[7] J. D. Joannopoulos, P. R. Villeneuve, and S. H. Fan, *Nature* **386,** 143-149 (1997).

[8] B. V. Derjaguin and L. Landau, *Acta Physicochim. (USSR)* **14,** 633-662 (1941).

[9] E. J. Verwey and J. T. G. Overbeek, *Theory of the Stability of Lyophobic Colloids* (Elsevier, Amsterdam, 1948).

[10] K. S. Schmitz, *Langmuir* **13,** 5849-5863 (1997).

[11] L. Guldbrand, B. Jonsson, H. Wennerstrom, and P. Linse, *Journal of Chemical Physics* **80,** 2221-8 (1984).

[12] N. Gronbech-Jensen, R. J. Mashl, R. F. Bruinsma, and W. M. Gelbart, *Physical Review Letters* **78,** 2477-2480 (1997).

[13] J. Z. Wu, D. Bratko, and J. M. Prausnitz, *PNAS* **95,** 15169-15172 (1998).

[14] H. Lowen and E. Allahyarov, *Journal of Physics-Condensed Matter* **10,** 4147-4160 (1998).

[15] R. Tehver, F. Ancilotto, F. Toigo, J. Koplik, and J. R. Banavar, *Physical Review E* **59,** R1335-R1338 (1999).

[16] J. Z. Wu, D. Bratko, H. W. Blanch, and J. M. Prausnitz, *Journal of Chemical Physics* **111,** 7084-7094 (1999).

[17] D. Bratko, H. L. Friedman, S. H. Chen, and L. Blum, *Physical Review A (General Physics)* **34,** 2215-19 (1986).

[18] D. Bratko, H. L. Friedman, and E. C. Zhong, *Journal of Chemical Physics* **85,** 377-84 (1986).

[19] D. Bratko, D. Wang, and S. H. Chen, *Chemical Physics Letters* **167,** 239-245 (1990).

[20] A. Daanoun, C. F. Tejero, and M. Baus, *Physical Review E* **50,** 2913-2924 (1994).

[21] T. Coussaert and M. Baus, *Physical Review E* **52,** 862-869 (1995).

[22] N. F. Carnahan and K. E. Starling, *Journal of Chemical Physics* **51,** 635-6 (1969).

[23] A. E. Larsen and D. G. Grier, *Nature* **385,** 230-233 (1997).

Figure Captions

Figure 1 Arrangements of colloidal particles in simulation boxes for sampling interaction forces in colloidal pairs and triplets. In both pair and triplet interactions, the coordinate origin is at the center of the simulation box, and positions of the colloidal particles are given in units of half of inter-particle separation. The particle numbers (N) and box volumes (V) in pair and triplet simulations are in proportion such that the colloidal particles experience the same solution conditions.

Figure 2 Three-body force (ΔF_3) for colloidal triplets in symmetric electrolyte solutions vs. inter-particle separation (r). The three-body force is most significant at short distances where it is repulsive when colloidal spheres are nearly in contact; it decays monotonically at larger separations (l_B: Bjerrum length, k: Boltzman constant, σ: particle diameter, C_s: salt concentration).

Figure 3 Pair interaction force F_2 and three-body force ΔF_3 for interaction between colloidal spheres in a monovalent salt solution at $C_s = 0.05$ M. Non-pairwise additivity is largely due to the excluded-volume effects of small ions.

Figure 4 Chemical potentials and coexisting densities for colloidal spheres dispersed in a monovalent electrolyte solution at $C_s = 0.05$ M predicted from the van-der-Waals-type theories (a) using the potential of mean force from effective two-body force; (b) using the DLVO potential.

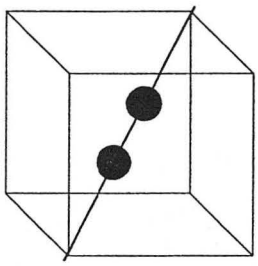
Table 1 Cubic simulation-box length L, the numbers of cations and anions, N^+ and N^-, for sampling average forces among colloidal triplets in equilateral configurations

salt	L, nm	N^+	N^-
1:1	125.8	120	60
2:2	125.8	120	90
1:1	584.0	120	60

Table 2 Reduced densities ($\rho\sigma^3$) of binary coexisting phases calculated using van-der-Waals-type theories for colloidal solutions and for crystal.

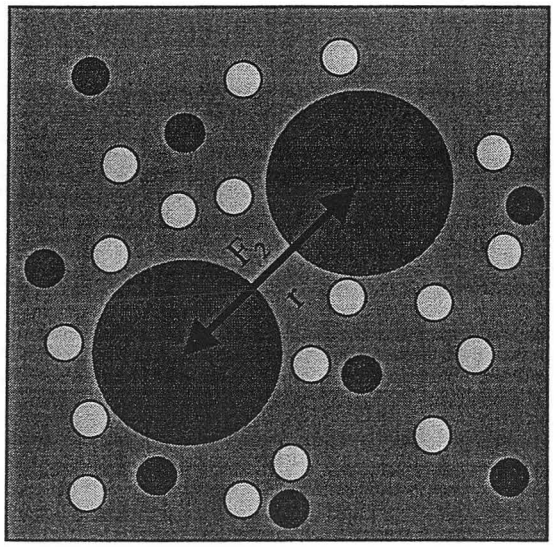
	Fluid-FCC		Fluid-BCC		BCC-FCC	
C_s=0.05 M, 1:1						
two-body potential	0.797	0.995	0.015	0.044	0.781	0.873
effective two-body potential	0.907	1.271	-	-	0.843	0.961
DLVO theory	1.035	1.284	3.85×10^{-3}	3.94×10^{-3}	0.79	1.073
C_s=0.075 M, 2:2						
two-body potential	1.04	0.88	0.955	0.792	0.171	0.154
effective two-body potential	1.038	0.863	0.928	0.754	0.173	0.184
DLVO theory	0.039	0.044	0.04	0.045	1.34×10^{-4}	1.34×10^{-4}
C_s=0.0005 M, 1:1						
two-body potential	1.40×10^{-5}	2.51×10^{-3}	8.40×10^{-5}	2.30×10^{-3}	0.363	0.183
effective two-body potential	7.57×10^{-4}	3.22×10^{-3}	8.56×10^{-4}	2.96×10^{-3}	0.38	0.155
DLVO theory	3.95×10^{-6}	1.73×10^{-6}	3.91×10^{-6}	1.70×10^{-6}	2.60×10^{-6}	2.61×10^{-6}

Figure 1

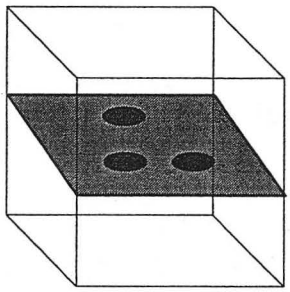


$(1/\sqrt{3}, 1/\sqrt{3}, 1/\sqrt{3})$

$(-1/\sqrt{3}, -1/\sqrt{3}, -1/\sqrt{3})$



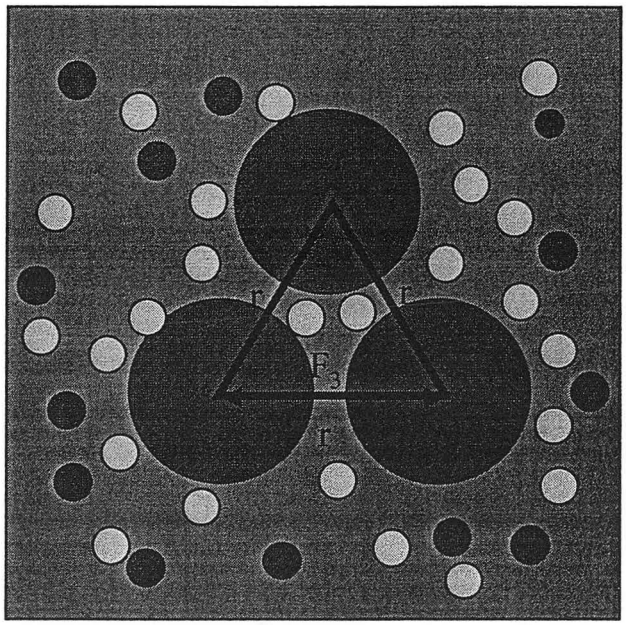
$$\frac{N_2^+}{N_3^+} = \frac{N_2^-}{N_3^-} = \frac{V_2}{V_3} = \frac{2}{3}$$



$(1, -1/\sqrt{3}, 0)$

$(-1, -1/\sqrt{3}, 0)$

$(0, 2/\sqrt{3}, 0)$



$$\Delta F_3 = 2F_3/3 - F_2$$

Figure 2

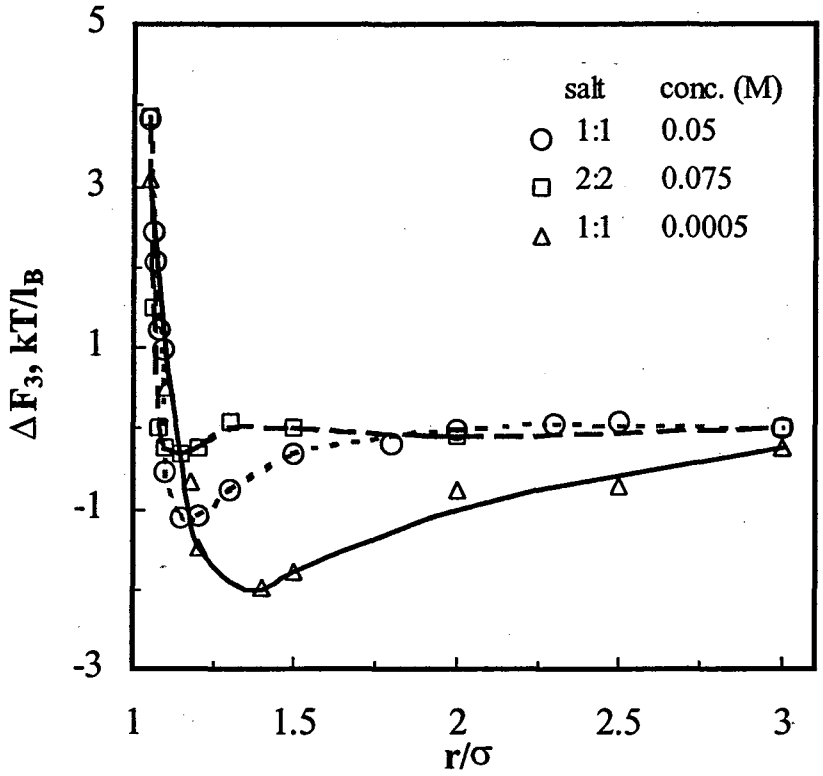


Figure 3

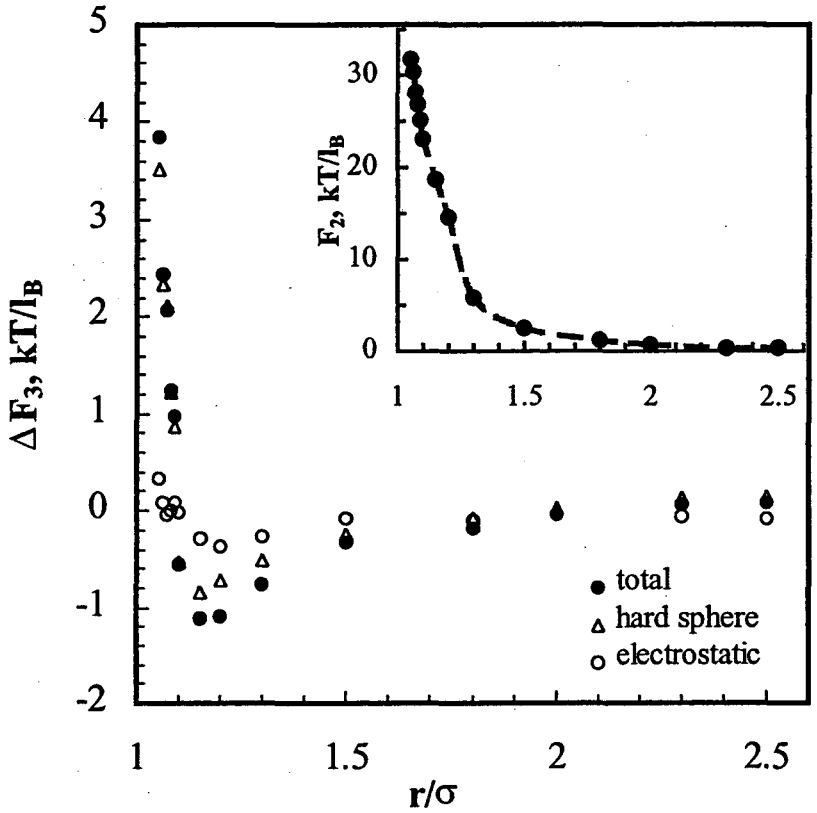
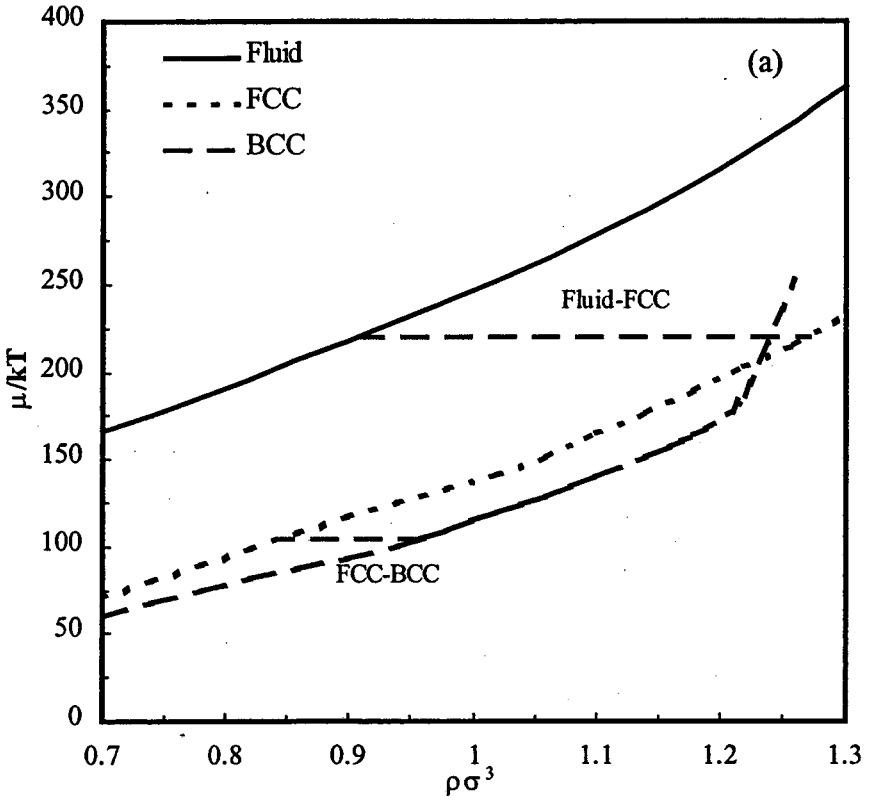
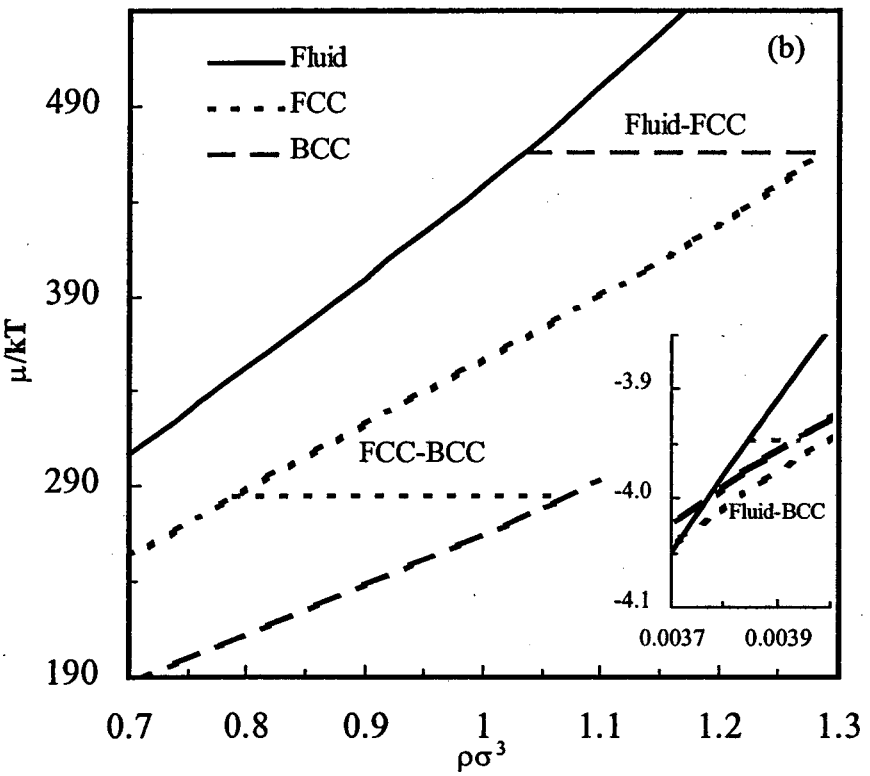

5
4
3
2
1
0
-1
-2
ΔF3, kT/lB
1
1.5
2
2.5
r/σ
30
20
10
0
F2, kT/lB
1
1.5
2
2.5
total
hard sphere
electrostatic

Figure 4


(a)
Fluid
FCC
BCC
Fluid-FCC
FCC-BCC
μ/kT
ρσ³
400
350
300
250
200
150
100
50
0
0.7
0.8
0.9
1
1.1
1.2
1.3


(b)
Fluid
FCC
BCC
Fluid-FCC
FCC-BCC
Fluid-BCC
μ/kT
ρσ³
490
390
290
190
-3.9
-4.0
-4.1
0.0037
0.0039
0.7
0.8
0.9
1
1.1
1.2
1.3

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