Effective interaction between highly charged colloidal particles under geometrical confinement

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Takamichi Terao and Tsuneyoshi Nakayama

Department of Applied Physics, Hokkaido University, Sapporo 060-8628, Japan

Abstract.   We investigate numerically the effective force between charged colloidal particles in an aqueous solution. By Monte Carlo simulation using the primitive model of strongly asymmetric electrolytes, we show that a pair of colloidal particles under geometrical confinements develop an attraction for strong electrostatic coupling. We also confirm that such attraction vanishes for high salt content. These features explain well the recent experiments on polystyrene latex particles.

1. Introduction

Colloidal suspensions (e.g., polystyrene latex and silica particles) have attracted much attention in the field of statistical physics [1]. It is of fundamental interest to understand the effective interaction between charged colloidal particles in an aqueous solution [2–10], because a vast number of industrial and natural processes depend on controlling the interaction between micron- or submicron-sized colloidal particles. While the bare Coulomb interaction between charged colloidal particles is purely repulsive, the problem is made non-trivial by the presence of the microscopic counterions, which are dispersed in an aqueous solution and screen the direct Coulomb repulsion. In the framework of continuum theory, effective potentials between charged colloidal particles (macroions) have been derived from the Poisson–Boltzmann equation [2]. For weak Coulomb interaction or high dilution of the macroions, the linearized screening theory of Debye and Hückel always leads to an effective pure-repulsive interaction between macroions.   This phenomenon is described by the Derjaguin–Landau–Verwey–Overbeek (DLVO) theory, which predicts the screened Coulomb repulsion between charged colloidal particles in an aqueous solution.

Recently, the effective interactions between charged colloidal particles have been measured in experiments [11–15]. Kepler and Fraden have performed measurements on colloidal suspensions confined between two glass plates, and determined the effective pair potential between colloidal particles from the pair correlation function $g(r)$ [12]. Crocker and Grier have investigated the effective interactions between charged polystyrene latex particles using the optical tweezer technique [13,15]. These studies have clarified that the pair interaction between unconfined pairs of charged colloidal spheres is purely repulsive, but when the same pairs of spheres are confined by parallel glass plates an attraction develops in the pair potential. They have observed that the attractive interactions are strong and long ranged, which cannot be explained by van der Waals interaction. These results imply that the fundamental theory of colloids is now unreliable: negatively charged colloidal particles in a solution can attract each other, and these phenomena are inconsistent with the conventional DLVO theory.

Bowen and Sharif [16] have performed a numerical calculation with the continuum mean-field approximation, and claimed that the attractive interaction appears in confined geometries. However, Neu [17] and Sader and Chan [18] have proved analytically that the non-linear Poisson–Boltzmann equation can only yield repulsion in confined geometry and the numerical result given by Bowen and Sharif [16] is not correct. To date, the microscopic origin of these attractive interactions between charged colloidal particles could not be explained by the traditional theories, and this remains an open question. In this paper, we perform Monte Carlo simulation of charged colloidal particles, which are confined (i) by a cylindrical pore and (ii) between two parallel plates. The effective forces $F(r)$ between a pair of colloidal particles are clarified with different surface charges and valences of microions in an aqueous solution. We observe an attractive interaction between like-charged colloidal particles when the electrostatic couplings are strong, which gives a consistent explanation for the recent experiments in low-salt-content conditions [15].

This paper is organized as follows. In section 2, we describe the primitive model of colloidal particles under geometrical confinement. In section 3, the numerical results on the effective force between highly charged colloidal particles are displayed. Section 4 is devoted to discussion and conclusions.

2. Models

We adopt the 'primitive model' of strongly asymmetric electrolytes involving the excluded volume and the Coulomb interaction of charged particles (colloidal particles and microscopic counterions), to describe colloidal suspensions under geometrical confinement [2, 8, 9]. The solvent enters into this model via its dielectric constant ϵ, which reduces the Coulomb interaction. We consider two spherical macroions with the surface charge $-Ze$ ($Z > 0$), where e is the elementary charge of an electron. In addition, N_c counterions are dispersed, carrying an opposite charge qe ($q > 0$). The number of counterions N_c is determined by other parameters ($q, Z, \ldots$) by a condition of global charge neutrality:

$$-2Z + N_c q + 2\sigma_p L^2 = 0 \tag{1}$$

where σ_p is the surface charge density of each parallel plate. In the following calculation, the value of σ_p is set to be $\sigma_p = 0$. The interactions between particles are given by

$$V_{mm}(r) = \begin{cases} \infty & \text{for } r \leqslant d \\ Z^2 e^2/4\pi\epsilon r & \text{for } r > d \end{cases} \tag{2}$$

$$V_{mc}(r) = \begin{cases} \infty & \text{for } r \leqslant d/2 + r_c \\ -Zqe^2/4\pi\epsilon r & \text{for } r > d/2 + r_c \end{cases} \tag{3}$$

$$V_{cc}(r) = \begin{cases} \infty & \text{for } r \leqslant 2r_c \\ q^2 e^2/4\pi\epsilon r & \text{for } r > 2r_c \end{cases} \tag{4}$$

where $V_{mm}(r)$, $V_{mc}(r)$, and $V_{cc}(r)$ represent the pair potentials of macroions (m) and counterions (c), and d and r_c are the diameter of the colloidal particles and the core radius of the counterions, respectively.

In the following, we consider two different types of geometry. One is that of two charged colloidal particles confined by a cylindrical pore (figure 1). In this case, the linear system size in the z-direction is taken to be L, and the radius of the cylindrical pore is defined as L_d ($-L/2 \leqslant z \leqslant L/2$ and $\sqrt{x^2 + y^2} \leqslant L_d$). In this case, the two macroions are placed at the positions $\boldsymbol{R}_1 = (0, 0, -r/2)$ and $\boldsymbol{R}_2 = (0, 0, r/2)$, where r ($\ll L$) denotes the centre-to-centre interparticle distance. The other case is that of colloidal particles confined between
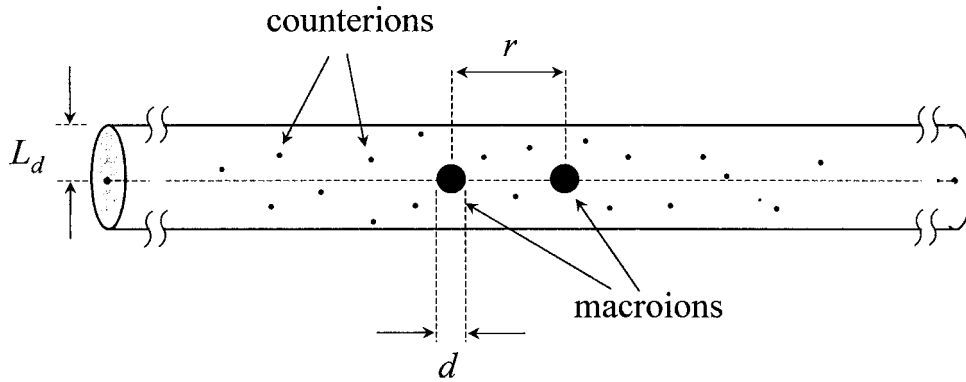
Figure 1. Geometry of colloidal particles in an aqueous solution confined by a cylinder.

parallel plates. The linear system sizes in the x- and y- directions are taken to be L, and the distance between two parallel plates is defined as L_z ($-L/2 \leqslant x, y \leqslant L/2$ and $-L_z/2 \leqslant z \leqslant L_z/2$). The two macroions are placed at the positions $\boldsymbol{R}_1 = (-r/2\sqrt{2}, -r/2\sqrt{2}, 0)$ and $\boldsymbol{R}_2 = (r/2\sqrt{2}, r/2\sqrt{2}, 0)$.

3. Numerical results

First, we briefly mention the numerical technique used in this study. In general, the amount of computation required to evaluate all pairwise interactions for the N-body system with *long-range* interaction increases as $\sim O(N^2)$. Such simulation becomes costly for large N. The tree algorithm [19, 20] can circumvent this difficulty; it is based on the hierarchical grouping of interactions between particles and a tree-type data structure to represent an N-body system. The whole system is recursively divided into subcells each including more than one particle, which construct a hierarchical tree structure for the system [20, 21]. Once such a hierarchical tree has been constructed, the interaction of any particles can be estimated by a recursive calculation. To obtain the interaction between particles at larger distance, the grouping of particles is taken to be larger under the condition $l/D < \theta$. Here l, D, and θ (<1) represent the size of the subcell, the distance between the subcell and the particle, and a fixed accuracy parameter, respectively. This becomes equivalent to the traditional Monte Carlo algorithm in the limit of $\theta \to 0$. In the actual calculation, we have confirmed that our conclusions do not change with the choice of θ. For the more technical details of the hierarchical tree structure, see reference [20]. These procedures reduce greatly the amount of computation required to evaluate the interaction between particles—to $\sim O(N \log N)$—without loss of the required numerical precision [20]. We apply this hierarchical tree algorithm to a Monte Carlo simulation: the *tree–MC algorithm.*

The effective forces between like-charged colloidal particles confined between parallel plates are studied in the (N, V, T) ensemble. We start with an arbitrary counterion configuration which does not penetrate into the two colloidal particles. It takes 2×10^4 Monte Carlo steps (MCS) to get the system into equilibrium, and 1×10^5 MCS to take the canonical average after the equilibrium has been reached. We also take the sample average over 60 samples for each run. In the following, the temperature T and the relative dielectric constant of water ϵ_r are taken to be $T = 300$ K and $\epsilon_r = 78$, respectively. The diameter of the macroions d and the radius of the microion core r_c are taken as $d = 20$ nm and $r_c = 2.8$ Å, respectively.

These are realistic values for actual colloidal particles which are experimentally studied. We impose the hard-wall condition in the confined directions (the x- and y-directions in the case of confinement by a cylindrical pore, and the z-direction for confinement by parallel plates), and the periodic boundary condition in the others. Comparing the results calculated by the minimum-image convention with those calculated by the Lekner summation technique [22] including periodic image charges, we have checked that boundary effects are not relevant, at least for the parameters in the following calculations. Figure 2 is a typical snapshot of colloidal particles and counterions. The distance between two parallel plates L_z and the interparticle distance r between two colloidal spheres are taken to be $L_z = 2.5d$ and $r = 4d$, respectively. The magnitude of the charges on the colloidal particles, Z, and surrounding counterions, q, are taken to be $Z = 600$ and $q = 1$, respectively. We can see that counterions surround a pair of colloidal particles and screen the Coulomb repulsion.
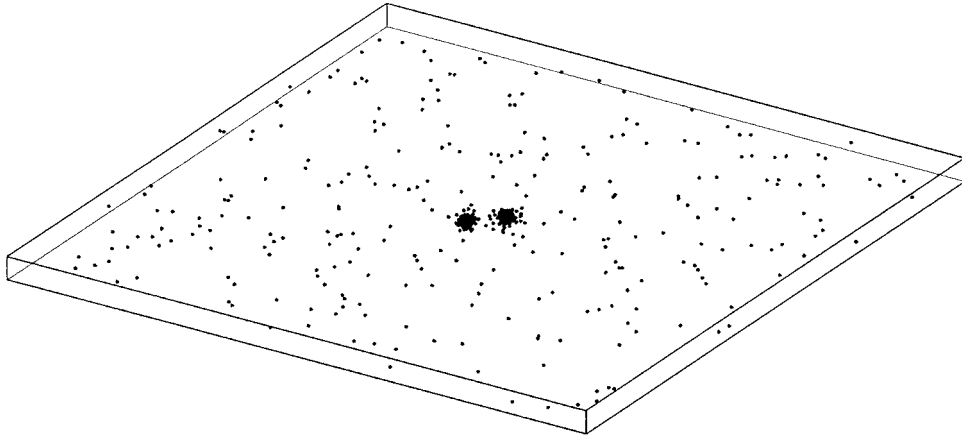

Figure 2. A snapshot of the equilibrium state of counterions surrounding two colloidal particles, which are confined between parallel plates.

The effective force $\boldsymbol{F}_1(r)$ acting on the first colloidal particle can be obtained from

$$\boldsymbol{F}_1(r) = \boldsymbol{F}_1^{dir}(r) + \boldsymbol{F}_1^{ind}(r). \tag{5}$$

In equation (5), $\boldsymbol{F}_1^{dir}(r)$ is a direct Coulomb repulsion:

$$\boldsymbol{F}_1^{dir}(r) = -\nabla\left(\frac{Z^2 e^2}{4\pi\epsilon}\frac{1}{r}\right) \tag{6}$$

and $\boldsymbol{F}_1^{ind}(r)$ is the indirect part induced by counterions, written as

$$\boldsymbol{F}_1^{ind}(r) = \nabla\left(\sum_j \frac{Zqe^2}{4\pi\epsilon}\frac{1}{r_j}\right) \tag{7}$$

where r_j is the distance between the first macroion and the jth microion. In the following calculations, we neglect the influence of the force caused by the depletion effect. This is because the main interest of this study is in explaining the long-range attractive component observed in recent experiments [15], but the range of the depletion force becomes very short for highly charged colloidal particles ($Z/q \gg 1$); it is proportional to $\sqrt{q/Z}$ [23].

Figure 3 shows the dimensionless effective force $F(r)/F_0$ between a pair of colloidal particles confined by a cylinder, where F_0 is defined to be $F_0 \equiv k_B T/\lambda_B$ ($\lambda_B \equiv e^2/4\pi\epsilon k_B T$ is the Bjerrum length). In figure 3, $F(r)$ is defined as $F(r) \equiv \boldsymbol{F}_1(r)\cdot(\boldsymbol{R}_1 - \boldsymbol{R}_2)/|\boldsymbol{R}_1 - \boldsymbol{R}_2|$, where
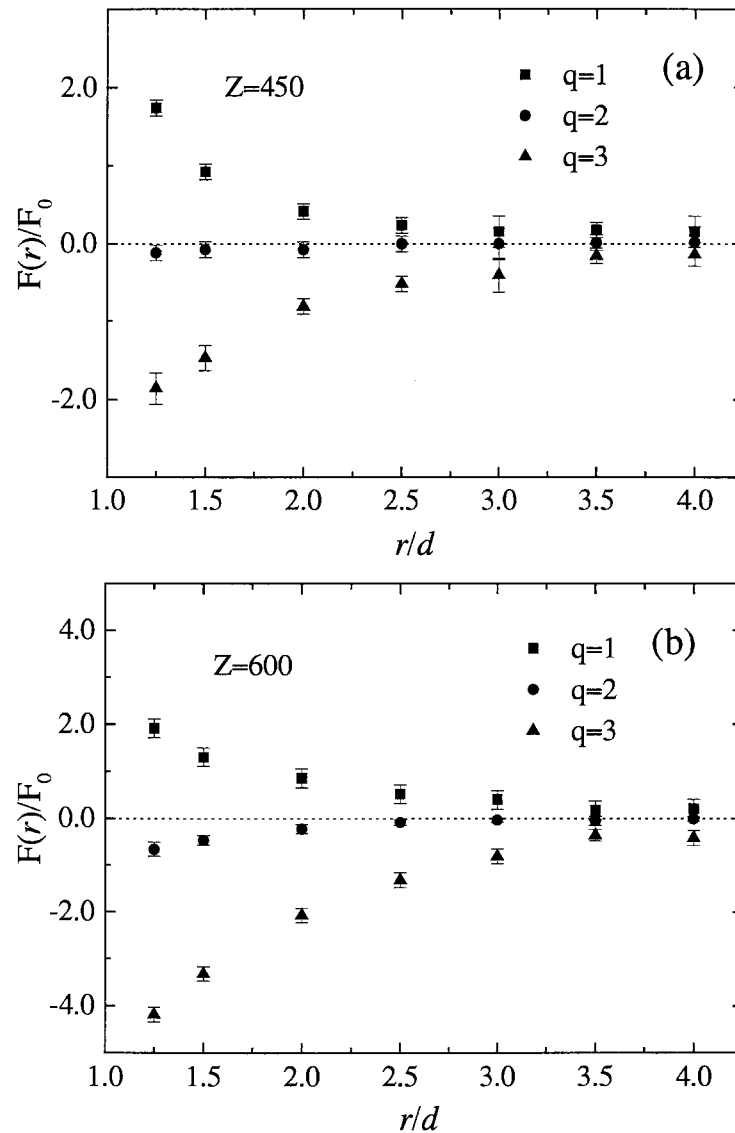
Figure 3. (a) The dimensionless effective force $F(r)/F_0$ between two colloidal particles versus the interparticle distance r for confinement by a cylinder. The surface charge Z is taken to be $Z = 450$. Solid squares, solid circles, and solid triangles denote the results for $q = 1$ (monovalent), 2 (divalent), and 3 (trivalent), respectively. (b) The dimensionless effective force $F(r)/F_0$ between two colloidal particles versus the interparticle distance r. The surface charge Z is taken to be $Z = 600$. Solid squares, solid circles, and solid triangles denote the results for $q = 1$, 2, and 3, respectively.

R_1 and R_2 are the positional vectors of the first and the second colloidal particles, respectively. Hence a positive value of $F(r)$ implies repulsion, and a negative value indicates attraction. For the charge of the counterions q, we consider three different cases: monovalent ions ($q = 1$) and multivalent ones ($q = 2, 3$), to clarify the effect of the strength on the electrostatic coupling. Figures 3(a) and 3(b) show the results calculated with the surface charges $Z = 450$ and

$Z = 600$, respectively. Solid squares, solid circles, and solid triangles denote the results with $q = 1$ (monovalent), 2 (divalent), and 3 (trivalent), respectively. In these calculations, the radius of the cylinder L_d is set to be $L_d = 1.25d$. In figure 3(a), the interparticle force $F(r)$ is approximately equal to zero in the case of $q = 2$. In figure 3(b), however, $F(r)$ apparently takes a negative value in the case of $q = 2$, where attractive interactions are enhanced for more highly charged colloids ($Z = 600$). From these results, the effective forces between colloidal particles are *repulsive* with smaller electrostatic coupling. With larger Z and q, in contrast, a pair of colloidal particles show an attraction.

Figure 4 shows the effective force $F(r)/F_0$ between two colloidal particles confined between parallel plates. The distance between parallel plates L_z is given by $L_z = 2.5d$. Solid squares, solid circles, and solid triangles denote the results obtained with $q = 1$, 2, and 3, respectively. In this study, we consider colloidal particles confined by uncharged parallel plates, and the effect of image charges is neglected. As in figure 3, we can observe attractive interaction between highly charged colloidal particles for strong electrostatic couplings. These results give a consistent explanation with regard to the recent experiments, which show that the interaction between charged colloidal particles cannot be described by the conventional DLVO theory for low salt content: the interaction between colloidal particles becomes attractive when the electrostatic coupling is strong.
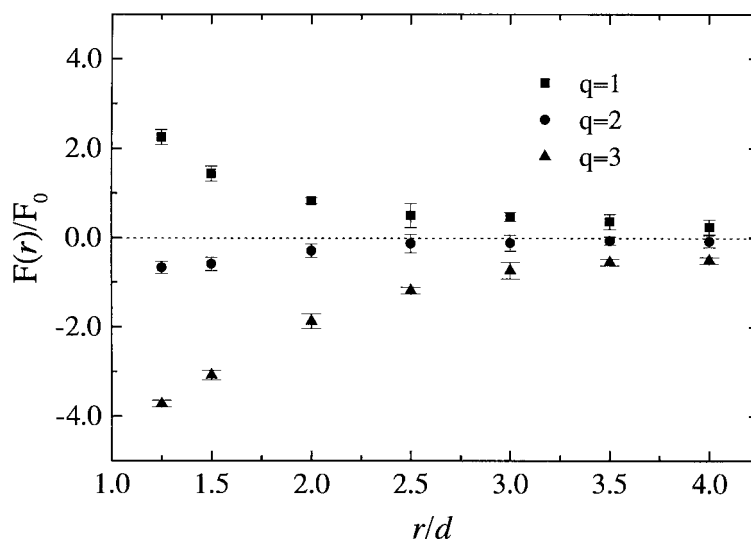

Figure 4. The dimensionless effective force $F(r)/F_0$ between two colloidal particles versus the interparticle distance r for confinement between parallel plates. The surface charge Z is taken to be $Z = 600$. Solid squares, solid circles, and solid triangles denote the results for $q = 1$ (monovalent), 2 (divalent), and 3 (trivalent), respectively.

We also calculate the effective interaction between charged colloidal particles in *high*-salt-content conditions, as well as in *low*-salt-content conditions. Figure 5 shows the results on the interparticle force $F(r)$ for colloidal particles ($Z = 600$) confined by a cylinder, with additional salt ions. Solid squares and open squares denote the results with the additional salt densities $\rho_s = 0.0$ and 10^{-4} M, respectively. Figures 5(a) and 5(b) display the results for monovalent microions ($q = 1$) and divalent ones ($q = 2$), respectively. In figure 5(a), the effective force $F(r)$ becomes small for $\rho_s = 10^{-4}$ M, since the screening effect due to microions becomes dominant and the screening length is small. In figure 5(b), the attraction
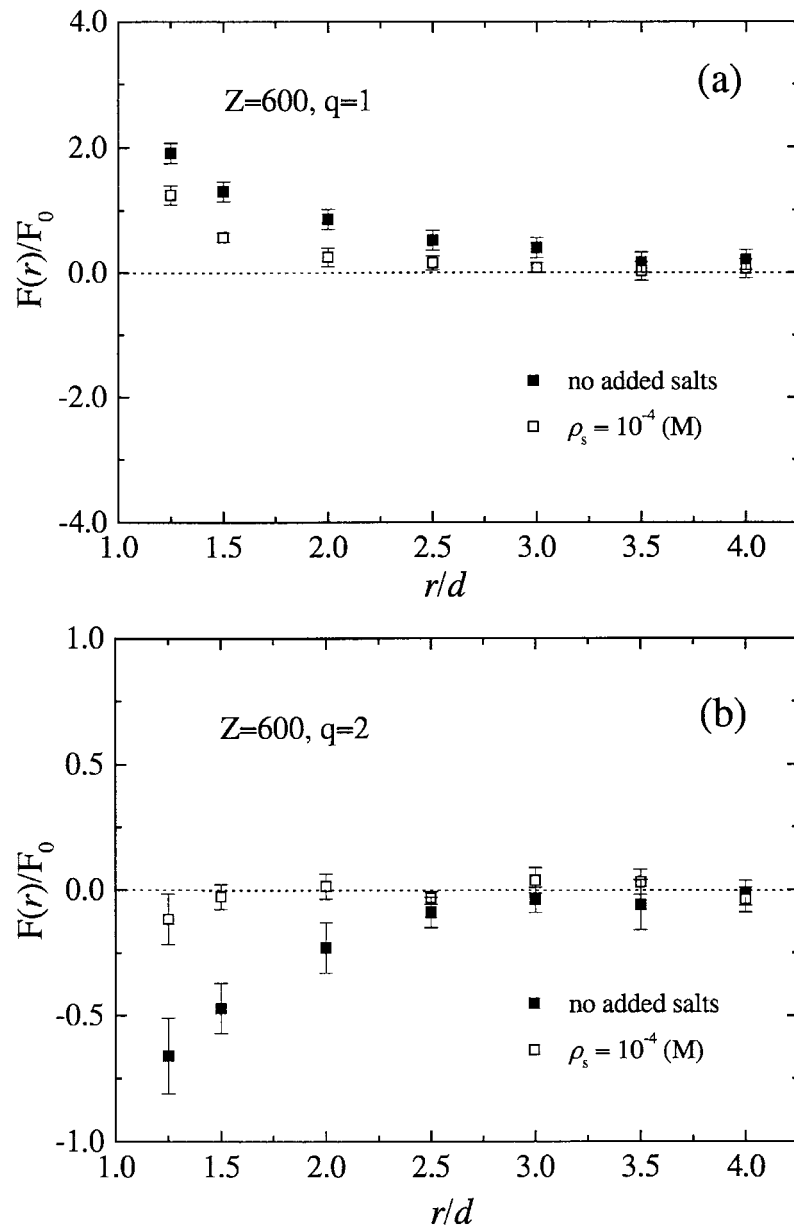
Figure 5. (a) The effective force $F(r)$ for monovalent microions ($q = 1$). The value of Z is taken to be $Z = 600$. Solid squares and open squares denote the results calculated with the densities of additional salt ions $\rho_s = 0.0$ M and $\rho_s = 10^{-4}$ M, respectively. (b) The effective force $F(r)$ for divalent microions ($q = 2$). The value of Z is taken to be $Z = 600$. Solid squares and open squares denote the results calculated with the densities of additional salt ions $\rho_s = 0.0$ M and $\rho_s = 10^{-4}$ M, respectively.

vanishes in high-salt-content conditions, which agrees very well with the recent experiments, where the attraction between like-charged colloids is observed only in well-deionized, low-salt-content conditions.

Our study has shed light on the microscopic origin of the attractive force between negatively charged colloidal particles. For strong electrostatic coupling, the attraction becomes dominant due to the 'overscreening' (non-linear screening) effect produced by surrounding counterions [14, 15]. This overscreening effect induces a strong cationic atmosphere around a pair of negatively charged colloidal particles, which produces an attractive interaction. It is noteworthy that we can explain the attraction between charged colloidal particles solely on the basis of the Coulomb interaction with non-linearity and under geometrical confinement [15]. Comparison between our work and previous studies [17, 18] suggests that the observed attractive interaction between like-charged colloids in an aqueous solution is essentially a fluctuation-based phenomenon, while the effect of fluctuations is neglected in the traditional Poisson–Boltzmann equations [2, 17, 18]. In the theoretical treatment, the continuum mean-field approximation [16–18] is not appropriate for describing this problem, but the primitive-model approach including the spatial and temporal density fluctuation of counterions is required, which is a characteristic feature of *fluctuation-induced attractions* [24]. These results will become important for understanding the physical nature of colloidal crystal [1, 25, 26].

4. Conclusions

In conclusion, we have investigated the effective interaction between charge-stabilized colloidal particles numerically, using the primitive model of strongly asymmetric electrolytes. By Monte Carlo simulation combined with the tree algorithm, we have clarified the effective force between colloidal particles under geometrical confinements. With smaller electrostatic coupling, the effective forces between colloidal particles are pure *repulsive* over the range of distances explored. With larger coupling, in contrast, the attractive interaction dominates. We have shown that the effective interaction between highly charged colloidal particles under low-salt-content conditions contradicts the theoretical prediction of the conventional DLVO theory. We have also demonstrated that such attractive interaction vanishes in high-salt-content conditions. These results explain well recent experiments using polystyrene latex particles [13, 15], where attraction between highly charged colloids is observed only under low-salt-content conditions, and the strength of the electrostatic coupling in an aqueous solution is an essential parameter for determining the effective potential between like-charged colloidal particles. From this point of view, it is remarkable that reference [25] has indicated a relationship between the magnitude of the surface charge Z and the re-entrant solid–fluid transition of three-dimensional colloidal crystal.

In this paper, a cylinder (figure 1) or parallel plates (figure 2) are treated as being uncharged, while parallel glass plates or walls are highly charged in references [13] and [15]. We consider that highly charged glass plates in these system work as the third charged body in an electrolyte, in addition to like-charged colloidal particles, in confined geometry. In general, many-body effects cannot be negligible in low-salt-content conditions when the screening length becomes large. Charged bodies in an aqueous solution—such as highly charged glass plates or walls—will enhance the attractive interaction by means of a 'non-additive many-body effect' [27], which has been pointed out in the field of polyelectrolytes.

Most of the previous simulations using the primitive model have treated relatively small charge asymmetries Z/q, since you have to perform calculations for a large number of particles in a highly asymmetric system—for example, highly charged colloidal suspensions. The tree–MC algorithm enables us to treat a large number of particles in a solution with a fairly small amount of computation. This tree–MC algorithm is also applicable to other systems such as polyelectrolytes, micellar solutions, and biomolecules, but these are future problems.

Acknowledgments

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