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Adsorption of colloidal particles on a charged surface: Cluster Monte Carlo simulations

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We investigate the adsorption of colloidal particles on a charged surface by the cluster Monte Carlo simulation. Under the primitive model of asymmetric electrolytes, the density profiles of colloidal particles at a surface are analyzed as a function of the electrostatic coupling parameter. In the strong coupling regime numerical results show the *like-charged adsorption* between colloidal particles and a charged surface, which cannot be explained by the Derjaguin-Landau-Verwey-Overbeek theory.

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I. INTRODUCTION

Electrostatic interaction plays an important role in colloids, polyelectrolytes, and surfactant micelles [1–5]. The linearized screening theory of Debye and Hückel always leads to a repulsive interaction between like-charged colloids in an aqueous solution. In the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory, the electrostatic part of the effective interaction between particles $U_{\mathrm{DLVO}}(r)$ is given by

$$U_{\mathrm{DLVO}}(r)=\frac{Z^2e^2}{4\pi\epsilon}\left(\frac{e^{\kappa r_m}}{1+\kappa r_m}\right)^2\frac{e^{-\kappa r}}{r}, \tag{1}$$

where Z, e, κ, r_m, ϵ, and r denote the surface charge of colloidal particles, the elementary charge of an electron, the inverse of the Debye-Hückel screening length, the radius of colloidal particles, the dielectric constant of the medium, and the center-to-center distance between two colloidal particles, respectively. The inverse screening length κ is given by

$$\kappa^2=4\pi\lambda_B\sum_j n_j q_j^2, \tag{2}$$

where $\lambda_B=e^2/4\pi\epsilon k_BT$ is the Bjerrum length and n_j is the q_j-valent ion density. In general, the effective interaction between colloidal particles is of importance to determine the physical properties of colloidal systems in an aqueous solution [2,6–11].

Recently, lots of works are devoted to clarify the electrostatic effect in soft matters [3,12–29]. Rouzina and Bloomfield [3] and Guldbrand *et al.* [12] have analyzed the attraction between like-charged planer surfaces at a short separation. Linse and Lobaskin have applied their theory into a spherical geometry, and proposed a criterion that the like-charged attraction between colloidal particles can happen when the coupling parameter Γ obeys $\Gamma\approx 2$ or larger, where Γ is the ratio between the characteristic energy of the Coulomb interaction and the thermal energy k_BT [13]. Here the dimensionless coupling parameter Γ is defined to be

$$\Gamma\equiv\frac{q^2\lambda_B}{a_c}=\left(\frac{Z}{4\pi q}\right)^{1/2}\frac{q^2\lambda_B}{r_m+r_c}, \tag{3}$$

where a_c and r_c are the average distances between two neighboring counterions on the charged colloidal particle, and the radius of counterions, respectively. These studies have shown that the effective interaction between colloidal particles becomes repulsive at weak electrostatic couplings, and on the other hand, the attractive force dominates between them at stronger electrostatic couplings [13–15,17,30–34]. At larger concentrations of multivalent ions, it has been clarified that charged colloids or polyelectrolytes in an aqueous solution strongly bind so many oppositely charged microions that the sign of the net macroion charge becomes inverted. The charge inversion is one of the characteristic phenomena in soft matters with strong electrostatic couplings and is of great interest [31,35–41].

In this paper, we study numerically the structural formation of colloidal particles on a charged surface by the cluster Monte Carlo simulation. Using the primitive model of asymmetric electrolytes, the density profile of colloidal particles is clarified, as a function of the strength of the coupling parameter Γ. The effective interaction between colloidal particles and a charged surface has been studied numerically by Svensson and Jönsson [42]. In Ref. [42], they have pointed out that a lot of counterions accumulate on a macroion surface and the mobility of macroions becomes very retarded, which makes it very difficult to reach a thermodynamic equilibrium in the computer simulation. In this paper, we employ the cluster Monte Carlo technique to treat this problem and clarify the physical properties of charged colloidal particles in an aqueous solution [14]. In the strong coupling regime, our numerical results demonstrate the *like-charged adsorption* between macroions and a charged surface.

This paper is organized as follows. In Sec. II, we describe the primitive model of colloidal particles in an aqueous solution. In Sec. III, the numerical results on the density profile of colloidal particles at a charged surface are displayed. Section IV is devoted to discussions and conclusions.

II. MODELS

We adopt the primitive model of strongly asymmetric electrolytes to describe colloidal suspensions in an aqueous solution, involving the excluded volume and the Coulomb interaction of negatively charged colloidal particles and counterions [13,16,30]. Employing the primitive model, fluctuation-induced attraction between like-charged colloids has been found in computer simulations [14,18,40]. In this model, all particles are represented by hard spheres with different charges and sizes. The model contains two types of spherical charged particles: (i) colloidal particles (macroions) of radius r_m and charge $-Ze$, and (ii) counterions of radius r_c and charge qe, whereas the discrete structure of the solvent is neglected and the solvent enters into the model via its dielectric constant ϵ, which reduces the Coulomb interaction. We consider N_m spherical macroions with the surface charge $-Ze$ $(Z>0)$. In addition, counterions carrying an opposite charge $qe(q>0)$ are fully taken into account. These macroions and counterions are dispersed in the cubic box, where the positions of these particles are randomly moved in the simulation. The linear system size of the cubic box in the x, y, and z directions is taken to be L $(-L/2\leqslant x,y,z\leqslant L/2)$. The pair potential $V_{ij}(r)$ between particles i and j is given by

$$V_{ij}(r)=\begin{cases}\infty & \text{for } r\leqslant r_i+r_j\\ \dfrac{q_iq_je^2}{4\pi\epsilon r} & \text{for } r>r_i+r_j\ ,\end{cases} \tag{4}$$

where q_i and r_i are the valence and the radius of a particle i, respectively. In the absence of salt, only the macroions and the counterions are treated in Eq. (4), and this level of description is also referred to as the two-component model [27]. The model system is described by physical parameters, such as Z, q, r_m, r_c, ρ_m, ρ_c, and σ, where ρ_i is the number density of particles $i(=m,c)$, and σ is the surface charge density of a surface. The macroion charge Z is varied from 20 to 60, the counterion valence q from 1 to 3, and the electrostatic coupling parameter Γ from 0.4 (weak coupling regime) to 3.7 (strong coupling regime).

In this study, the effect of a charged surface is treated as follows: we impose periodic boundary conditions in the x and y directions, and the hard-wall condition in the z direction. We place uniformly discrete negative charges on a surface perpendicular to the z axis, and the other parallel surface is set to be electrically neutral. We assume that the image charge effect across the surfaces in the z direction, due to a lower dielectric constant than the medium, is expected to be small and can be neglected in the following simulation. This corresponds to the matching ϵ boundary condition at the surface. The counterions discharged from the negatively charged surface are included explicitly. We also consider the condition of global charge neutrality such as

$$-\rho_mZ+\rho_cq+\frac{\sigma}{L}=0. \tag{5}$$

TABLE I. System parameters for the runs A, B, C, and D.

Run	q	Z	N_m	L (nm)	Γ
A	1	20	20	40.0	0.4
B	1	20	44	52.0	0.4
C	2	40	20	40.0	1.6
D	3	60	20	40.0	3.7

III. NUMERICAL RESULTS

The long-range nature of the Coulomb interaction is usually handled by the Ewald summation technique. However, the simulation becomes more difficult to treat in a *quasi-two-dimensional system*, because we have to take into account the effect of surfaces and interfaces (e.g., membranes) [43]. To treat the periodic boundary condition in a quasi-two-dimensional system, we adopt the Lekner summation technique in the following simulation [44]. In the Lekner summation technique, the pair potential $V_{2d}(x,y;z)$ between two particles in a quasi-two-dimensional system is given by

$$\begin{aligned}V_{2d}(x,y;z)&=\frac{q_iq_je^2}{4\pi\epsilon}\sum_{n_x=-\infty}^{\infty}\sum_{n_y=-\infty}^{\infty}\frac{1}{|\mathbf{r}+n_xL\mathbf{e}_x+n_yL\mathbf{e}_y|}\\&=\frac{q_iq_je^2}{4\pi\epsilon}\biggl[4\sum_n\sum_k K_0(2\pi n\sqrt{\{y+k\}^2+z^2})\\&\quad\times\cos(2\pi nx)-\ln\{\cosh(2\pi z)\\&\quad-\cos(2\pi y)\}+c_2\biggr],\end{aligned} \tag{6}$$

where the indices n_x and n_y run over the periodic images of the simulation box, and $\mathbf{e}_x$, $\mathbf{e}_y$, $K_0(x)$, and c_2 are unit vectors in the x and y directions, the modified Bessel function, and the constant to be added, respectively [44]. Equation (6) is rapidly convergent due to the asymptotic behavior of the modified Bessel function, such as

$$K_0(x)\sim\sqrt{\frac{\pi}{2x}}\exp(-x). \tag{7}$$

For the more technical details of treating periodic image charges, see Ref. [44].

As explained in the preceding section, there is a difficulty in performing the traditional Monte Carlo (MC) simulation of asymmetric electrolytes with strong electrostatic couplings, where the accumulation of counterions close to the macroion surface depresses the macroion mobility [13,14,42]. We apply a cluster-move technique in the MC simulation to enhance the mobility of macroions, where we define a cluster by selecting a macroion, and surrounding counterions within a distance r_{cl} from the center of the macroion [45]. Then we perform a trial move of the whole cluster with an acceptance probability P_{accept} such as

$$P_{\text{accept}}=\min\{1,\exp(-\Delta E/k_BT)\}\delta_{n_{\text{new}},n_{\text{old}}}, \tag{8}$$

where ΔE, n_{new}, and n_{old} denote the total energy difference between, after, and before its trial move, the number of counterions inside the cluster $(r<r_{\text{cl}})$ after the move, and that before the move, respectively. The factor $\delta_{n_{\text{new}},n_{\text{old}}}$ in Eq. (8) is required to satisfy the detailed balance condition. The advantage of the cluster MC method will be greater as the electrostatic coupling is increased. In the MC procedure, translational displacements in the x, y, and z directions are made with step lengths uniformly sampled from $[-\Delta/2, \Delta/2]$, where Δ is the translational displacement parameter. In

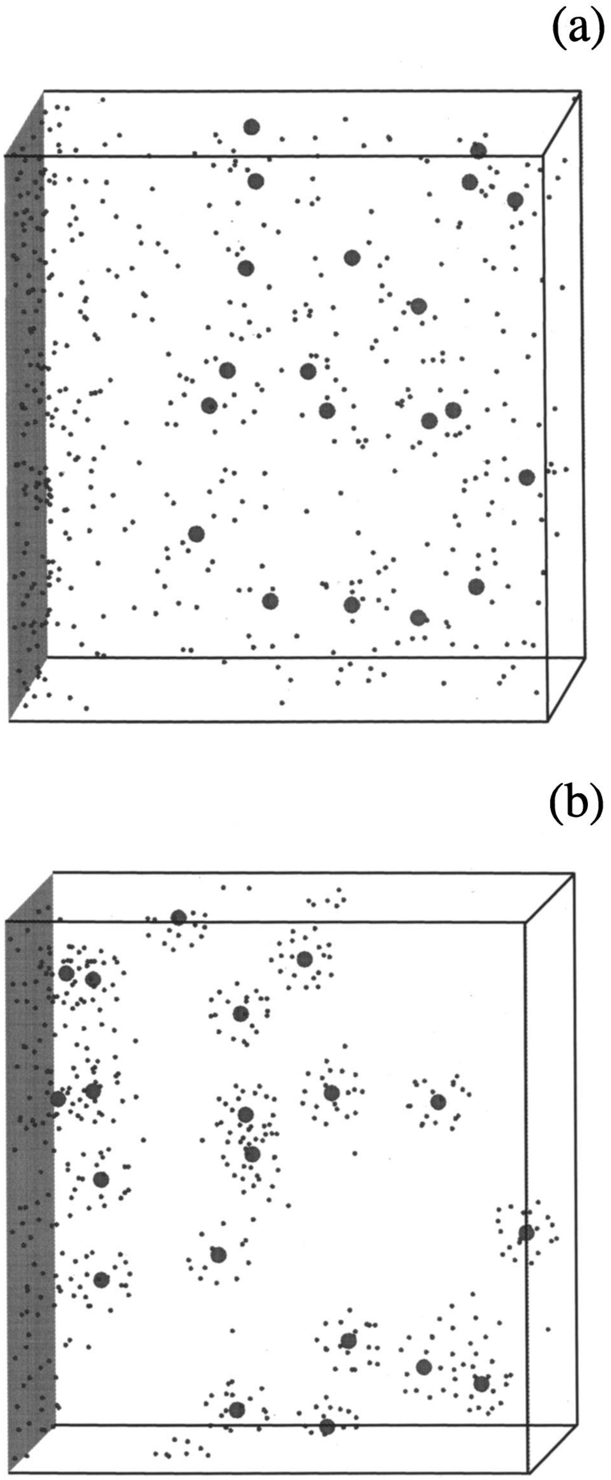

FIG. 1. Snapshot of colloidal particles with a planer charged surface. (a) The electrostatic coupling parameter Γ is taken to be $\Gamma = 0.4$. (b) The electrostatic coupling parameter Γ is taken to be $\Gamma = 3.7$.

the following simulations, we take the same magnitude of the translational displacement parameter Δ for all colloidal particles and counterions.

At first, the profile of negatively charged colloidal particles is studied by cluster Monte Carlo simulation in the (N,V,T) ensemble. We start with an arbitrary particle configuration that does not penetrate into other particles. The diameter of colloidal particles is set to be $2r_m = 4.0$ nm, and the magnitude of the surface charge on colloidal particles Z is taken to be $Z = 20$, 40, and 60. It takes 10^4 Monte Carlo steps (MCS) to get the system into equilibrium, and 10^5 MCS to take the canonical average after the equilibrium has been reached. We also take the sample average over 20 samples for each run. In the following, the temperature T and the relative dielectric constant of water $\epsilon_r (\equiv \epsilon/\epsilon_0)$ are taken to be $T = 300$ K and $\epsilon_r = 78$, respectively, where ϵ_0 is the vacuum dielectric constant. The surface charge density σ of a charged surface is set to be $\sigma = -0.03\,(\mathrm{C/m^2})$, and the radius of counterions r_c is taken as $r_c = 2.0$ Å. Other parameters of the system are displayed in Table I.

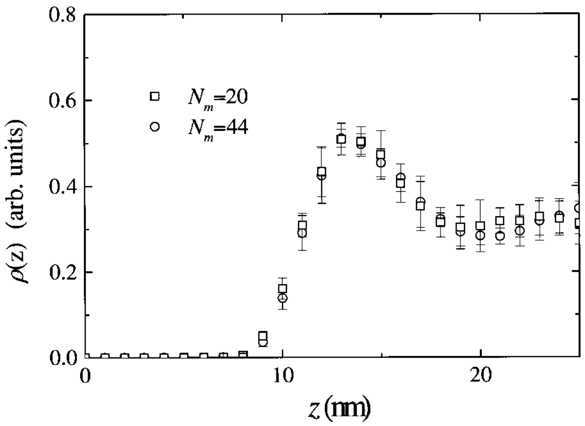

FIG. 2. Density distribution function $\rho(z)$ of colloidal particles at a charged surface with different number of colloidal particles N_m. The electrostatic coupling parameter Γ is taken to be $\Gamma = 0.4$.

Figure 1 shows the snapshot of colloidal particles and counterions, where the left side of the box corresponds to the negatively charged surface. Figures 1(a) and 1(b) denote the results with the electrostatic couplings $\Gamma = 0.4$ (run *A*) and 3.7 (run *D*), respectively, and we can see that these two results are apparently different. As the electrostatic coupling parameter Γ increases, diffusing counterions are bound to macroion surfaces. In Fig. 1(a), there is no colloidal particle near the charged surface, reflecting the double-layer repulsion between colloidal particles and the surface. In Fig. 1(b), on the contrary, we can see that negatively charged colloidal particles are adsorbed on the surface. The latter result cannot be explained by the mean-field DLVO theory.

To check the finite-size effect, we study the density distribution function $\rho(z)$ of colloidal particles at a charged surface. Figure 2 shows the normalized densities of colloidal particles $\rho(z)$ with the different number of colloidal particles N_m and the system size L. Here z is the distance between the surface and the center of colloidal particles. The density distribution function $\rho(z)$ is sampled by use of a uniform grid of $2.5r_c$. Here the macroion volume density ϕ_m is fixed to be $\phi_m = 0.01$. In Fig. 2, open squares and open circles represent the calculated results with $N_m = 20$ and 44, respectively. The abscissa and the ordinate denote the distance between the surface and the center of colloidal particles, and the normalized density of colloidal particles, respectively,

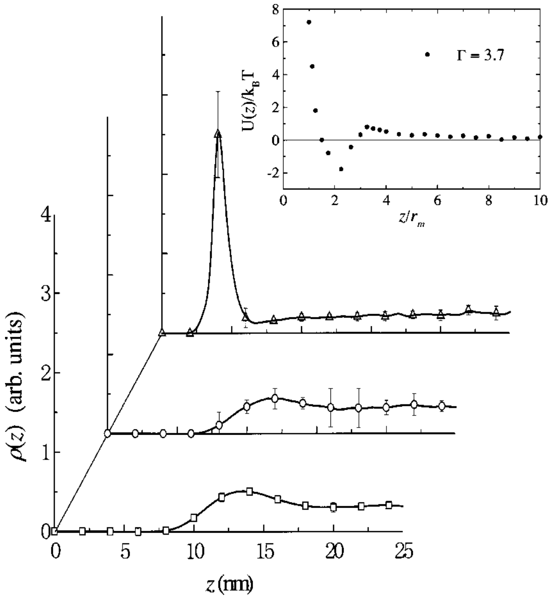

FIG. 3. Density distribution function $\rho(z)$ of colloidal particles at a charged surface with different strength of electrostatic couplings Γ. The inset shows the effective potential $U(z)\equiv -k_BT\ln\rho(z)$ between colloidal particles and a charged surface.

and the statistical error is also shown by the vertical bar. The magnitude of the surface charge Z and the valence of counterions q are taken to be $(Z,q)=(20,1)$. In Fig. 2, we have an agreement between calculated results with $N_m=20$ (run *A*) and 44 macroions (run *B*) within the statistical error.

Figure 3 shows the density distribution function $\rho(z)$ of colloidal particles at a negatively charged surface with monovalent, divalent, and trivalent counterions. Open squares, open circles, and open triangles show the results with the electrostatic couplings $\Gamma=0.4$ (run *A*), 1.6 (run *C*), and 3.7 (run *D*), respectively. The solid lines are only guides to the eye. The translational displacement parameter Δ, the acceptance ratio of the cluster movements p_{cl}, and that of the counterion movements p_{co} are shown in Table II. These results indicate that the profile of the density distribution function $\rho(z)$ drastically changes at $\Gamma\geqslant 2$. The inset shows the effective potential $U(z)$ between colloidal particles and a charged surface obtained by $U(z)\equiv -k_BT\ln\rho(z)$. Solid circles correspond to the result with the electrostatic coupling $\Gamma=3.7$, and we can see that the magnitude of attractive well at $z\approx 2r_m$ is larger than k_BT. This indicates that the attractive interaction between colloidal particles and a charged surface is strong enough, compared with the thermal fluctuation energy $(\sim k_BT)$.

IV. CONCLUSIONS

In conclusion, we have investigated the adsorption phenomena of colloidal particles on a charged surface by the cluster Monte Carlo simulation. From the technical point of view, it is very important to study the adsorption of fine colloidal particles to a surface. We have studied the structure and thermodynamics of colloidal suspensions on a charged surface, where the electrostatic coupling parameter Γ is varied systematically. Using the primitive model of asymmetric electrolytes, the density profile of colloidal particles has been numerically clarified as a function of the electrostatic coupling parameter Γ, from $\Gamma=0.4$ (weak coupling regime) to $\Gamma=3.7$ (strong coupling regime). It has been found that the structural formation of colloidal particles on a charged surface is sensitive to Γ in an aqueous solution. In the strong coupling regime, numerical results have indicated the *like-charged adsorption* between colloidal particles and a charged surface, which the DLVO theory cannot reproduce. These features have shown a good agreement with the previous study by Svensson and Jonsson [42], and the importance of the Coulomb correlation and the fluctuation effect in the system. In an aqueous solution with the strong electrostatic coupling, such like-charged adsorption will occur not only in colloidal suspensions, but also in polyelectrolyte solutions. We have applied the cluster Monte Carlo technique to treat the difficulty, due to the accumulation of counterions close to the macroion surface [14]. It has been confirmed that the cluster MC technique is efficient to study the adsorption phenomena in an asymmetric electrolyte, especially in the case of the stronger electrostatic coupling.

TABLE II. Simulation parameters for each run (see the text for notation).

Run	Δ (nm)	$p_{\rm cl}$	$p_{\rm ca}$
A	1.0	0.11	0.76
B	1.0	0.11	0.78
C	1.0	0.24	0.39
D	0.5	0.35	0.25

It has been suggested that multivalent counterions are condensed and form a two-dimensional strongly correlated liquid at the surface of a macroion [32]. In previous studies, the counterion condensation has been studied by molecular simulations in a solution of highly charged rigid polyelectrolytes [46] and in spherical colloidal suspensions [40]. They have indicated that while the agreement between the Poisson-Boltzmann theory and simulation is excellent in the monovalent, weakly charged case, it deteriorates with increasing the strength of the electrostatic interaction and, in particular, with increasing the valence of microions. Our results will shed light on a characteristic feature in soft matters beyond the mean-field theory. The application of these properties to produce various molecular assemblies is highly desirable, and these are future problems.

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