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Ewald Summation for Uniformly Charged Surface

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Abstract: We have developed an algorithm to calculate the long-range Coulomb interactions for the slab system with a uniformly charged surface that is periodic in two dimensions and finite extent in the third dimension. This method, which is a modification of the three-dimensional Ewald summation with a correction term, is tested via molecular dynamics simulations of the adsorption of co-ions on the charged surface. The simulation results of counterion distribution show a good agreement with theoretical prediction especially at low surface charge density. Furthermore, we compute the force exerted on the particles for different systems. The consistency of results demonstrates that the proposed algorithm is applicable to the system with a smoothly charged surface in only two dimensions and is benefited from the widely used Ewald summation method in all three dimensions.

1. Introduction

With recent advances in computer simulations of aqueous biological systems and nanotechnology, the accurate computation of long-range Coulombic interactions for charged systems is becoming more and more important. The well developed approach to this problem for the three-dimension (3D) periodic system is the Ewald summation technique.[1] Several optimization methods such as the smooth particle mesh Ewald (SPME) method[2] have been proposed in order to perform effectively for large systems.

However, for many situations especially in the simulations of surface and interfacial systems, the conventional Ewald summation method cannot be used directly and needed modification because the system is finite in one direction and infinite in the other two dimensions. To treat the electrostatic interactions of such slab geometry the two-dimensional Ewald summation (EW2D) technique was first reported by Parry[3] and was subsequently extended by various authors.[4,5] Unfortunately, the applications of these techniques are still limited for complex systems such as membranes and surfactants since the direct use of the EW2D method is not as simple and efficient as the EW3D method.[6,7] Recently, to solve this problem, an approximation method added a correction term to the three-dimensional Ewald summation (EW3D) technique for the simulation cell which is sufficiently elongated in the direction of nonperiodicity to create large empty spaces outside the system so as to minimize an artificial influence from the periodic images in that direction.[8] Particularly, Yeh et al.[9] introduced the shape-dependent correction term given by Smith[10] into the EW3D technique to calculate the electrostatic forces for systems with slab geometry. It has been shown that this method termed as the three-dimensional Ewald summation with the correction term (EW3DC) is a good approximation to the exact EW2D method with a significant reduction in computing time.

An alternative analytical method which needed to evaluate trigonometric functions and Bessel functions of imaginary arguments to deal with the long-range electrostatic interactions in the three-dimensional system was proposed by Lekner.[11] Taking advantage of the symmetry given by the periodicity of the lattice summation, the charge−charge interaction was calculated and the interaction energy was obtained by integrating the force expression. Based on Lekner's summation technique, several authors[12−16] derived expressions for the electrostatic force in systems periodic in

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one or two dimensions. Recently, the comparison between the Ewald quasi-2D and Lekner summation methods has been carried out by Mazars,[17] which shows that they are in close agreement when correctly implemented for the computation.

Although the charged surface with molecular details is modeled by the EW3DC method mentioned above, many charged surfaces could be simulated by a coarse-grained model of a uniformly charged surface to make the calculations more efficient. The coarse-grained model of the uniformly charged surface may be described by just one parameter, i.e. the charge density at the surface. For this kind of model, we would like to substitute the atomistic detail of the surface by a uniformly charged surface to speed up the simulation. The purpose of our work is to extend the method based on the EW3DC technique to the electrostatic interaction calculation of smooth surface systems with uniform charges in computer simulations. Section 2 describes the expression of Ewald summation we developed for a two-dimensional (2D) system with a uniformly charged surface. To test this method we performed simulations on the counterion distribution next to the uniformly charged surface. Results for counterion density profiles compared with the Poisson−Boltzmann (PB) theory are presented in section 3. For a more direct test, force calculations of particles for different systems have been carried out, and the results are also shown in section 3. Finally, we draw a conclusion of our work in section 4.

2. Algorithm

We first give a brief review of the EW2D technique[9] and then present our method for treating Coulomb interactions in 3D systems with a smoothly charged surface. It is known that the electrostatic energy for a system of N point charges q_i at position $\mathbf{r}_i$ can be written as

$$E = \frac{1}{2} \sum_n{}' \sum_{i,j=1}^{N} \frac{q_i q_j}{|\mathbf{r}_{ij} + nL|} \tag{1}$$

The sum over n takes into account all of the periodic images of the charges, and the prime indicates that in the case of $i = j$ the term $n = 0$ must be omitted. We are omitting all factors of $1/(4\pi\epsilon_0)$ for clarification (ϵ_0 is the vacuum permittivity). For long-range potentials, this sum is conditionally convergent, which means the result depends on the order in which it adds up the terms. If we add up our infinite system by sphere layers,[1] the electrostatic energy could be obtained by the Ewald sum, and the final result is

$$E = E^r + E^k + E^s + E^d \tag{2}$$

where the contribution from real space E^r, the contribution from reciprocal space E^k, the self-energy E^s, and the shape-dependent dipole correction for the spherical geometry E^d are respectively given by[1,10]

$$E^r = \frac{1}{2} \sum_{i,j} \sum_m{}' q_i q_j \frac{erfc(\kappa|\mathbf{r}_{ij} + mL|)}{|\mathbf{r}_{ij} + mL|} \tag{3}$$

$$E^k = \frac{1}{2\pi V} \sum_{i,j} \sum_{k\neq 0} q_i q_j \left(\frac{4\pi^2}{k^2}\right) \exp\left(-\frac{k^2}{4\kappa^2}\right) \cos(\mathbf{k}\cdot\mathbf{r}_{ij}) \tag{4}$$

$$E^s = -\frac{\kappa}{\sqrt{\pi}} \sum_i q_i^2 \tag{5}$$

$$E^d = \frac{2\pi}{(1 + 2\epsilon_s)V} \left(\sum_i q_i \mathbf{r}_i\right)^2 \tag{6}$$

By modifying the shape-dependent dipole correction E^d to the geometry of a rectangle plate, i.e.

$$E^d = \frac{2\pi}{V} \left(\sum_i q_i \mathbf{r}_{i,z}\right)^2 \tag{7}$$

Yeh et al.[9] show that the 3D Ewald summation with the correction term can be used with sufficient accuracy in the calculation of electrostatic energy of a system with slab geometry, even better than the 2D Ewald sum. More importantly, the computing time by using modification of the 3D Ewald sum is about 10 times faster than the time for the 2D Ewald sum.

In MD simulation, the evaluation of force is much more important. The force F_i exerted on particle i is obtained by differentiating the electrostatic energy E, and the results are given by

$$F_i = F_i^r + F_i^k + F_i^d \tag{8}$$

where

$$F_i^r = q_i \sum_j q_j \sum_m{}' \left(\frac{2\kappa}{\sqrt{\pi}} \exp(-\kappa^2|\mathbf{r}_{ij} + mL|^2) + \frac{erfc(\kappa|\mathbf{r}_{ij} + mL|)}{|\mathbf{r}_{ij} + mL|}\right) \frac{\mathbf{r}_{ij} + mL}{|\mathbf{r}_{ij} + mL|^2} \tag{9}$$

$$F_i^k = \frac{q_i}{V} \sum_j q_j \sum_{k\neq 0} \frac{4\pi\mathbf{k}}{k^2} \exp\left(-\frac{k^2}{4\kappa^2}\right) \sin(\mathbf{k}\cdot\mathbf{r}_{ij}) \tag{10}$$

$$F_x^d = F_y^d = 0, \quad F_{i,z}^d = -\frac{4\pi q_i}{V} \sum_j q_j \mathbf{r}_{j,z} \tag{11}$$

Consider a uniformly charged surface with charge density $\rho = q_i^s/L_x L_y$, the electric field acting on the particles i around the surface is given by[18,19]

$$E_i = \frac{\rho}{2\epsilon_0} \tag{12}$$

The x, y, and z components of the force are given by

$$F_i^S = \left(F_{i,x}^S = 0, F_{i,y}^S = 0, F_{i,z}^S = \frac{\rho q_i}{2\epsilon_0}\right) \tag{13}$$

and the co-ions of the surface charges will distribute around the surface. When we put the co-ions in the simulation box, the simulation system is not electroneutral if the surface charge q_i^S is not included in the Ewald summation of eqs
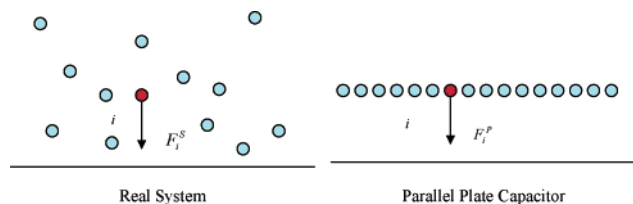
Figure 1. The force contributed from surface charges i in real system and the one in the parallel plate capacitor.

9−11, although the real physical system is still electroneutral. Thus we could not directly obtain the electrostatic energy and Coulombic force by eqs 2 and 8. In the following parts, with the modification of the EW3DC technique, we put forward an approach to solve the Ewald summation for the system with a smoothly charged surface.

The Coulombic force on particle i, if we include the charges of surface in the Ewald sum, is given by

$$F_i = F_i^{\mathrm{r}} + F_i^{\mathrm{k}} + F_i^{\mathrm{d}} = F_i^{\mathrm{r,S}} + F_i^{\mathrm{r,NS}} + F_i^{\mathrm{k,S}} + F_i^{\mathrm{k,NS}} + F_i^{\mathrm{d}} \tag{14}$$

where $F_i^{\mathrm{r,S}}$ and $F_i^{\mathrm{k,S}}$ are contributions from surface charges q_i^{S}, and $F_i^{\mathrm{r,NS}}$ and $F_i^{\mathrm{k,NS}}$ are contributions from other charged particles q_i. Since there is no possible surface structure to obtain the positions of the surface charges, the EW3DC technique cannot be used directly to calculate the electrostatic interactions between surface charges and non-surface charges.

As shown in Figure 1, given that the surface charge density is the same, the force F_i^{S} (eq 13) contributed from surface charges in a real system is equal to the force F_i^{P} in the parallel plate capacitor. From Yeh et al.'s modification,[9] the force F_i^{P} in the parallel plate capacitor could be calculated with sufficient accuracy by

$$F_i^{\mathrm{S}} = F_i^{\mathrm{P}} = F_i^{\mathrm{r,P}} + F_i^{\mathrm{k,P}} + F_i^{\mathrm{d,P}} \tag{15}$$

In the parallel plate capacitor system, the system is electroneutral if we include the surface charge in the calculations of the Ewald summation; we have $F_i^{\mathrm{P}} = F_i^{\mathrm{r,S}} + F_i^{\mathrm{k,S}} + F_i^{\mathrm{d,P}}$ because the force contributed from nonsurface charges is zero in the parallel plate capacitor system. Thus the force F_i in the system with a smoothly charged surface at position $r_{S,z}$ is given by

$$F_i = F_i^{\mathrm{S}} - F_i^{\mathrm{d,S}} + F_i^{\mathrm{r,NS}} + F_i^{\mathrm{k,NS}} + F_i^{\mathrm{d}} \tag{16}$$

where

$$F_i^{\mathrm{S}} = (0,0,F_{i,z}^{\mathrm{S}}) = \left(0,0,\frac{\rho q_i}{2\epsilon_0}\right) \tag{17}$$

$$F_i^{\mathrm{d,S}} = \left(0,0,-\frac{4\pi q_i \rho L_x L_y (\mathbf{r}_{S,z} - \mathbf{r}_{i,z})}{V}\right) \tag{18}$$

$$F_i^{\mathrm{d}} = \left(0,0,-\frac{4\pi q_i}{V}\left[\sum_j q_j \mathbf{r}_{j,z} + \rho L_x L_y \mathbf{r}_{S,z}\right]\right) \tag{19}$$

$$F_i^{\mathrm{r,NS}} = q_i \sum_{j \notin S} q_j \sum_m{}' \left(\frac{2\kappa}{\sqrt{\pi}} \exp(-\kappa^2 |\mathbf{r}_{ij} + mL|^2) + \right.$$
$$\left. \frac{erfc(\kappa|\mathbf{r}_{ij} + mL|)}{|\mathbf{r}_{ij} + mL|}\right) \frac{\mathbf{r}_{ij} + mL}{|\mathbf{r}_{ij} + mL|^2} \tag{20}$$

$$F_i^{\mathrm{k,NS}} = \frac{q_i}{V} \sum_{j \notin S} q_j \sum_{\mathbf{k} \neq 0} \frac{4\pi\mathbf{k}}{k^2} \exp\left(-\frac{k^2}{4\kappa^2}\right) \sin(\mathbf{k}\cdot\mathbf{r}_{ij}) \tag{21}$$

Note that eqs 20 and 21 have the same forms of the Ewald summation but perform the force evaluation for the nonsurface particles. The Coulombic interaction between the surface charges and co-ions is merged into eqs 17−19 and has nothing to do with the position of the surface. In conclusion, the eqs 16−21 give the formula for the force in the system with a uniformly charged surface of charge density ρ.

3. Molecular Dynamics Simulations of Co-Ions on a Uniformly Charged Surface

3.1. Model. To test the validity of the algorithm referred to above, we performed the simulations of co-ions adsorbed on the full-atom surface (simulation I) and smooth surface (simulation II), respectively, with the same charge density ρ of the surface. Figure 2 shows the snapshots of the adsorption of co-ions in simulation I and simulation II at different surface charge densities.

For simulation I, we chose a simulation box with the orthorhombic boundary condition having dimension $L_z = 480.0\ \sigma$ (σ is the length unit in the simulation) normal to the surfaces eight times larger than the lateral dimension $L = 60.0\ \sigma$. Two impermeable rectangle slabs of thickness σ constructed by a number of 420 atoms are respectively located at $z = 1/8\ L_z$ and $z = -1/8\ L_z$ of the central simulation box perpendicular to the z-axis. Different numbers of atoms carrying charge are uniformly distributed on the slab at $z = -1/8\ L_z$ in order to obtain various surface charge density ρ. To maintain the electroneutrality of the system, monovalent co-ions are confined in the z direction between two slabs. Therefore, the closest approaches of the co-ions to the impenetrable surfaces are $z = \pm(1/8)L_z \mp \sigma$. We employed a shifted Lennard-Jones (LJ) potential to describe the pure repulsive excluded volume interactions between any pair of particles in the simulations.

$$U_{\mathrm{LJ}}^{\mathrm{S}}(r) = \begin{cases} 4\epsilon_{\mathrm{LJ}}\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6\right] + \epsilon_{\mathrm{LJ}} & r \leq 2^{1/6}\sigma \\ 0 & r > 2^{1/6}\sigma \end{cases} \tag{22}$$

σ and ϵ_{LJ} are respectively the LJ units of length and energy. The strength of the short-range interactions is controlled by the parameter ϵ_{LJ}. As far as simulation II is concerned, the charged smooth surface is substituted by the effect of the external field. We developed our modification code based on the DL_POLY version 2.12 software package.[20] To avoid the co-ions moving out of the simulation box when the distance between ions and surface is less than σ, a potential provided by the software package named containing wall with the expression $U = A(R_0 - r)^{-n}$ is employed to confine

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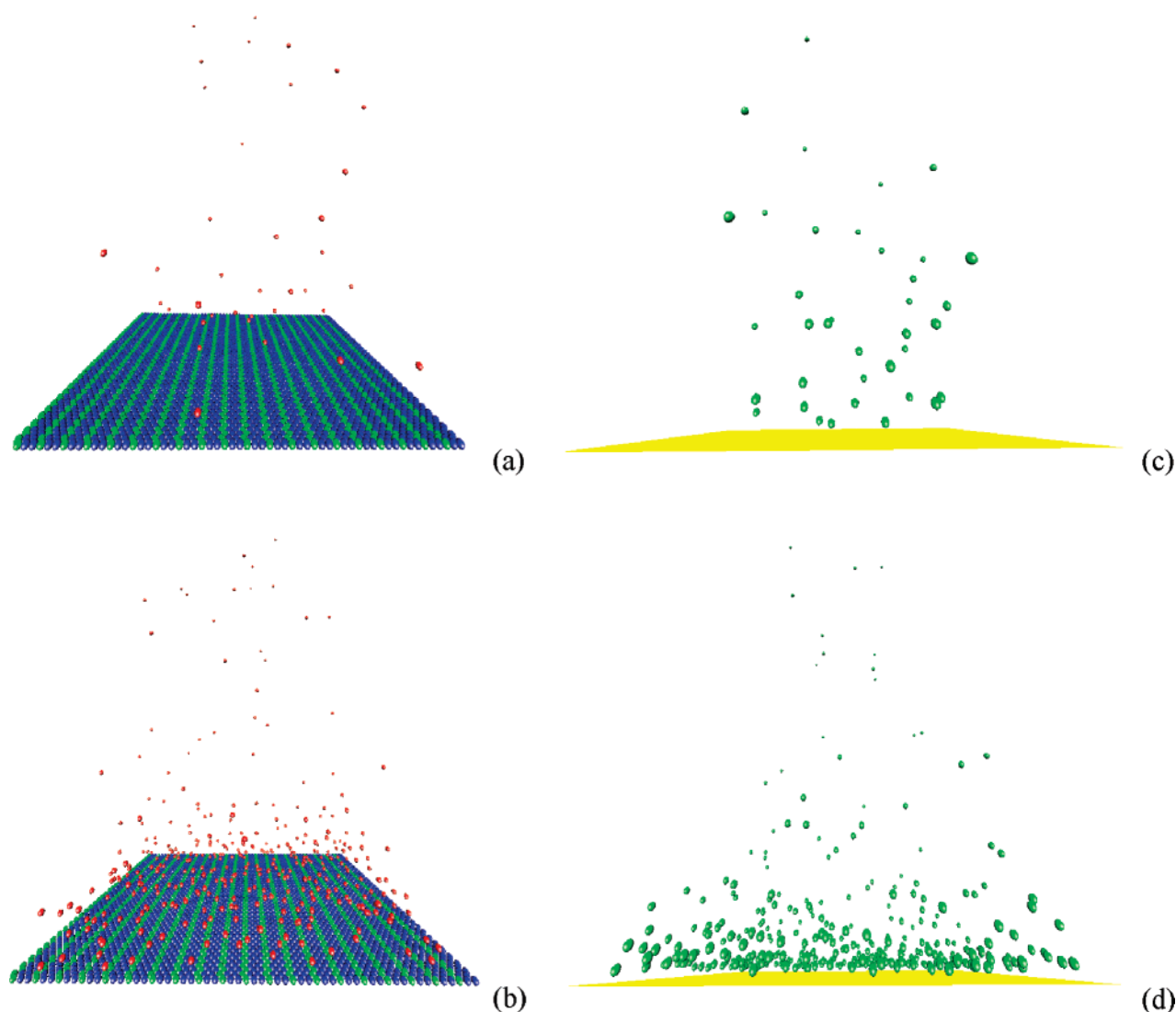*J. Chem. Theory Comput., Vol. 2, No. 6, 2006* **1621**

Figure 2. Snapshots of the adsorption of co-ions on the full-atoms surface with the charge densities of 0.01(a) and 0.1(b) and the smooth surface with the charge densities of 0.01(c) and 0.1(d). For (a) and (b), co-ions are red spheres, charged atom on the surface − green spheres, and neutral ones − blue spheres. For (c) and (d), co-ions are green spheres, and the charged surface is yellow.

Table 1. Dependence of Co-Ions Number N on Surface Charge Density ρ for Both Simulation I and Simulation II

ρ	0.01	0.02	0.05	0.1	0.2	0.3	0.4	0.8
N	37	73	182	364	728	1092	1455	2910

the co-ions between $z = (1/8)L_z - \sigma$ and $z = -(1/8)L_z + \sigma$. The interactions between any couple of co-ions are the same as the ones performed in simulation I. Solvent molecules, which are not included explicitly in simulation I and simulation II, are modeled by a continuum with the dielectric constant ϵ. In such a medium, the electrostatic interactions between nonsurface charges in the simulation box and their periodic images are computed by the smoothed particle mesh Ewald (SPME) algorithm[2] implemented in the DL_POLY version 2.12 software package.[20]

After the initial conformation was constructed as above (see Table 1 for details), we performed the molecular dynamics simulations (MD) for both simulation I and simulation II with different surface charge densities at constant temperature $T = 1.0\epsilon_{LJ}/k_B$ using the Langevin thermostat,

where k_B is the Boltzmann factor. The propagation of the trajectories was done using the Verlet algorithm with a time step equal to $\Delta t = 0.005\tau_{LJ}$, where $\tau_{LJ} = \sqrt{m\sigma^2/k_B T}$ is the standard time unit for Lennard-Jones fluid. In all simulations, a period of 450 000 MD steps was recorded in every 2500 MD step runs for further data analysis after the equilibration period of 50 000 MD steps, which is long enough to relax the whole system.

3.2. Results and Discussion. A. Adsorption of Co-Ions on the Surface. The results of the co-ions density profile with different surface charge densities for simulation I (full-atoms surface) and simulation II (smooth surface) are presented in Figure 3 (parts a and b, respectively). From these two figure parts, we easily observe that the density of co-ions decays with distance z from the plane and at a large distance becomes independent of the surface charge density because of the screening of the surface charge by the cloud of co-ions. Meanwhile, the data from simulation II are almost identical to those obtained by simulation I when the parameters used in all the simulations are the same.
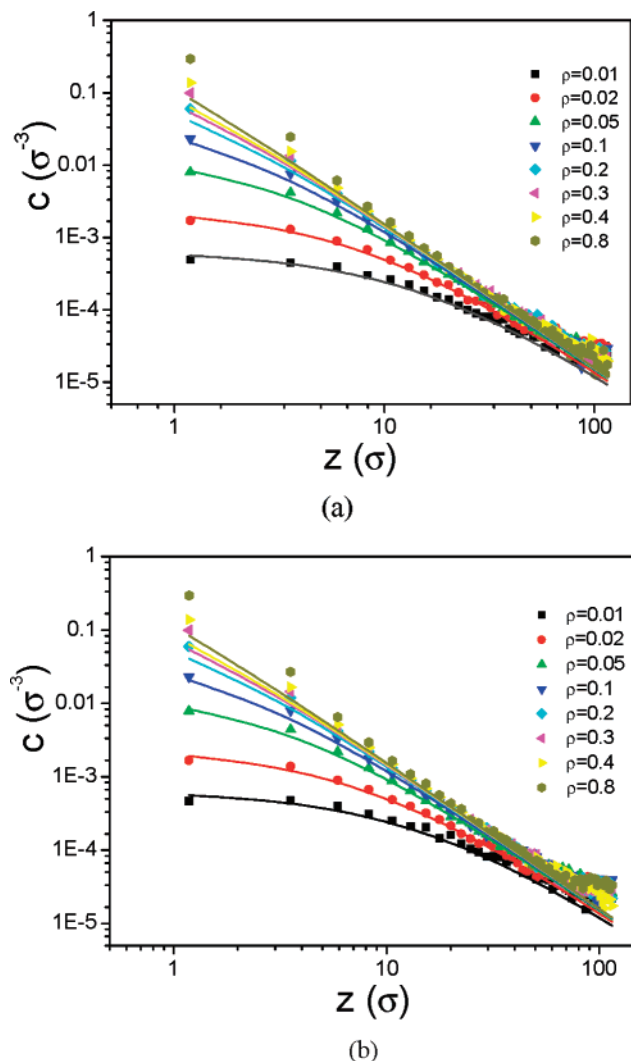
(a)

(b)

Figure 3. The co-ions density profiles at different surface charge densities in double-logarithmic coordinates for (a) full-atoms surface and (b) uniformly charged surface. The theoretical prediction $c_i(z) = [2\pi l_B(z + \Lambda)^2]^{-1}$ is shown by the solid line.

To compare with the theoretical results, we first reviewed the Poisson–Boltzmann theory for a charged flat surface in the presence of co-ions.[21,22] Considering a uniformly charged infinite flat surface with charge density ρ, the distribution of the dimensionless electrostatic potential in the direction z perpendicular to the surface can be represented as $\Psi(z) \equiv e\psi(z)/k_B T$ from the electrochemical potential of any ion. Since the electrochemical potential must be constant throughout the solution, we can get the Boltzmann distribution of the neutralizing monovalent co-ions at any position in the solvent. The density profile of the co-ions, $c_i(z)$, in the case of no added electrolyte solution, can be obtained on the basis of the Poisson–Boltzmann equation

$$\frac{d^2\Psi}{dz^2} = -4\pi l_B c_i(z) \tag{23}$$

$$c_i(z) = c_i(0) \exp(-\Psi(z)) \tag{24}$$

where l_B is the Bjerrum length $l_B = e^2/k_B T\epsilon$ and ϵ is the dielectric permittivity of the solvent. With the boundary
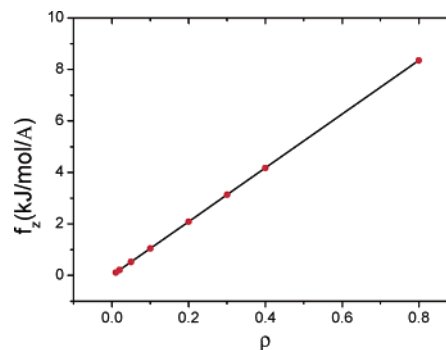

Figure 4. The comparison of force in the z direction with a charged smooth surface between simulation and theory for different surface charge densities. The solid line is the theoretical value calculated via eq 13.

conditions $\Psi(0) = 0$ and $(d\Psi(z)/dz)_{z=0} = 2/\Lambda$, because of the zero surface potential at electric field and the requirement of overall electro neutrality, the solution is given by

$$\Psi(z) = 2 \ln(1 + z/\Lambda) \tag{25}$$

$$c_i(z) = [2\pi l_B(z + \Lambda)^2]^{-1} \tag{26}$$

where $\Lambda = (2\pi l_B \rho)^{-1}$ is the Gouy–Chapmann length, which characterizes the thickness of the co-ions cloud above a homogeneously charged planar surface.

From the analysis above, we also plotted the theoretical curves of the co-ions density distribution for different surface charge densities in the same figures. The graph exhibits that they agree with the simulation results especially at a small surface charge density. As far as the co-ions density distribution at high surface charge density is concerned, since the Poisson–Boltzmann equation is no longer available, the computing results deviate from the theoretical value.

B. Forces between Charged Surface and Co-Ions. The most accurate and direct means to affirm the validity of the methodology is the calculation of the interaction force. The same geometry of the simulation cell with uniformly charged surface and parameters mentioned in simulation II have been used here. The co-ions are arranged symmetrically on a plate that is parallel with the charged surface because we want to model the system of the parallel plate capacitor. Theoretically, eq 13 shows that the z component of the force exerted on any particle is independent of distance away from the surface in the parallel plate capacitor system if the charge density of the surface is constant. We calculated the force of the particles located at $z = -58.0 \ \sigma$ contributed from the surface with different charged density after one MD step, which are presented in Figure 4. The simulation results are in excellent agreement with theoretical values obtained from eq 13. This implies that applying the parallel plate capacitor model to deal with the long-range interaction for a uniformly charged surface is feasible.

We also computed the force on particles for simulation I and for the same model except for replacing the full-atoms surface with a uniformly charged surface. At the same time the force exerted on particles for the simulation with full-atoms charged surface was calculated by EW3DC and EW3D, respectively. Figure 5 shows the comparison of the
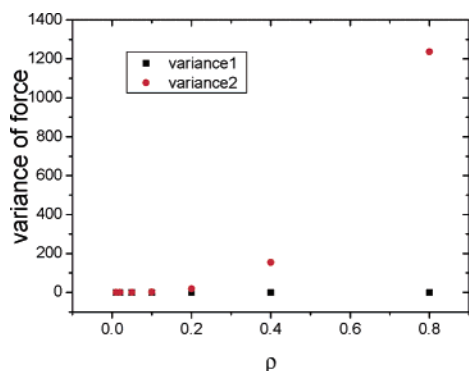
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Figure 5. The comparison for the variance of force in the *z* direction for the full-atoms surface with the smooth surface (variance 1) and with the full-atoms surface using no correction term (variance 2).

variance of forces for each case at different charge densities. The variance of forces is calculated as follows: $\Delta f = \sum_{i=1}^{\text{ions}} (f_i^1 - f_i^2)^2$, where the superscript represents two systems which are to be compared. The plot clearly implies that the correction term is necessary to be considered for computing long-range Coulombic interactions in the interfacial system, and it is also reported in Yeh's work.[9] After comparing with the data obtained from the calculation for full-atoms surface, we also conclude that the algorithm of the electrostatic force for a uniformly charged surface gives good numerical results.

4. Conclusion

In this study, we introduced a modification of the previously developed Ewald summation technique to apply to systems with uniformly charged surfaces. The Yeh's algorithm, which just adds a correction term to 3D Ewald summation, could be benefited from the development of the Ewald summation method. Molecular dynamics simulations of co-ions adsorbed on the charged surface and detailed comparison of forces were performed to test the validity of the algorithm. Comparing the simulation results with the theoretical prediction, we clearly demonstrated that the method we adopted to treat the electrostatic interaction is suitable to study systems with a smoothly charged surface.

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