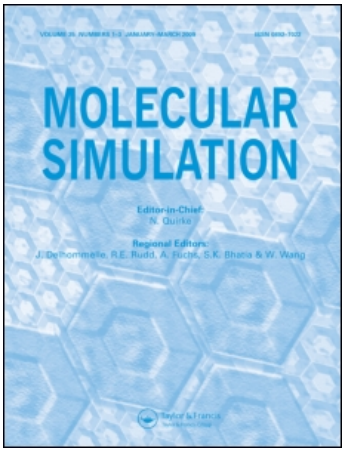

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Simulation of Confined Primitive Electrolytes: Application of a New Method of Summing the Coulomb Field

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SIMULATION OF CONFINED PRIMITIVE ELECTROLYTES: APPLICATION OF A NEW METHOD OF SUMMING THE COULOMB FIELD

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Recently, Lekner has presented a new method to sum the Coulomb forces between charged particles of a central system and its images extended periodically in 2- and 3- dimensions. In this paper we apply the new method in canonical ensemble Monte Carlo (CMC) simulations of the primitive electrolyte confined between two planar surfaces: one is charged and the other is neutral. The anions and cations have identical size with diameter $d = 4.25$ Å and interact with a hard sphere repulsion and Coulomb interaction. In Lekner's method the long range Coulomb potential is computed from a series of Bessel functions. We have demonstrated that the series converges after about 10 terms and so is computationally quite simpler than the Ewald sum methods. The method is also faster for confined electrolytes than are those Ewald-like sum methods with which we compared it. In our simulations, we obtained the density distributions and mean electrostatic potentials of the confined system for the 1 : 1 electrolyte having concentrations equal to those of 1 M and 2 M bulk electrolyte and having different surface charge densities. For large separation of confining walls, the canonical ensemble Monte Carlo results agree with previously reported grand canonical Monte Carlo results.

KEY WORDS: Primitive electrolytes, Lekner method, slit pores, Monte Carlo.

1 INTRODUCTION

The investigation of electrolytes in confined geometry has attracted a lot of attention in recent years. The work has been driven by the potential for applications in electrochemistry, microelectronics, biological systems, colloidal dispersions, and clay and soil systems. However, these kinds of systems are difficult to study at the molecular level, either experimentally or theoretically. Therefore computer simulation, usually either molecular dynamics or the Monte Carlo method, is a valuable tool for trying to understand ion distributions and the double layer potential of confined electrolytes. Compared with the minimum image method, the accuracy of a simulation is increased by periodic extension of the system in its unconfined dimensions.

The common examples of electrical double layers are electrolytes near metal surfaces or surrounding the particles of an electrically stabilized colloidal suspension, or the charge distribution around the biological membranes. For point charges near a planar surface, Gouy and Chapman developed a formal theory 70 years ago [1] to describe the charge distributions near the surface by using the Poisson–Boltzmann equation (PDE). With the realization of the importance of double layers in stabilizing the colloidal systems, the DLVO theory [2] aroused a renaissance of double layer

theory. Because of the advent of large fast computers and the advancement of density functional theories, much research has been done on double layers in recent years [3, 4].

For meaningful computer simulations, one must have good models of the interparticle interaction. In the case of nonpolar fluids, interactions are short-ranged and so the introduction of cutoffs can be used to reduce the cost of computations. However, the coulomb interactions of electrolytes are long-ranged and so it is not desirable to use a cut-off. Although for bulk electrolyte systems the minimum image short cut has provided an approximate method to account for the long-range forces, it may cause unphysical results for confined systems. An alternative is to use the conventional Ewald sum method [5], but rather lengthy summations must be evaluated by this method.

Recently, Lekner has presented a summaton method that evaluates the long-range Coulomb interactions in bulk or confined electrolytes. The interaction potential is given as a series expansion of modified Bessel functions K_ν [6, 7]. The series is expected to require evaluation of far fewer terms than does the Ewald method. To examine the applicability of Lekner's method we have carried out canonical ensemble Monte Carlo (CMC) simulations on confined 1 : 1 electrolytes having an average charge density equal to bulk ion concentrations of 1 M and 2 M, respectively. Different surface charge densities and different separations of the confining walls are studied. The results are compared to those of a grand canonical Monte Carlo (GCMC) simulation in which the long-ranged interactions are handled by the minimum image and the contributions from the charge distributions everywhere outside the ion's minimum image [3]. To further test the scheme on confined systems, we also carried out MD and GCMC simulations on the Cray 2 using this method, all the results are consistent.

2 SUMMATION OF LONG RANGE POTENTIALS

We give here a brief sketch of the summation method [6, 7]. Consider a simulation box with side length L along the x and y directions and H along the z direction with N particles inside. To imitate the real system that is confined between two planar surfaces, we assume the box is repeating to infinity in both x and y axis. The coulomb interaction potential energy between ions i and j in the medium with the dielectric constant ε is then

$$U(r_{ij}) = \sum_{\mathbf{R}} \frac{q_i q_j}{\varepsilon |\mathbf{R} + \mathbf{r}_i - \mathbf{r}_j|}. \tag{1}$$

Here the indices i and j are from 1 to N and the summation over $\mathbf{R}$ is for the 2-dimensional Bravais lattice in xy plane. If we define the relative distances in dimensionless quantities ξ, η, ζ,

$$\xi = (x_i - x_j)/L, \qquad \eta = (y_i - y_j)/L, \qquad \zeta = (z_i - z_j)/L, \tag{2}$$

with $\xi \leqslant 1$, $\eta \leqslant 1$, and $\zeta \leqslant H/L$. The the potential can be expressed as

$$U(r_{ij}) = \sum_{l,m=-\infty}^{\infty} \frac{q_i q_j}{\varepsilon L} \frac{1}{[(\xi + l)^2 + (\eta + m)^2 + \zeta^2]^{1/2}}. \tag{3}$$

To sum up the potential one uses the definition of the Γ function [6]

$$\frac{1}{x^\nu} = \frac{1}{\Gamma(\nu)} \int_{-\infty}^{\infty} dt\, t^{\nu-1} e^{-xt}, \qquad \nu > 0, \tag{4}$$

the identity

$$\sum_{-\infty}^{\infty} \exp\{-(\xi + l)^2 t\} = \sqrt{\frac{\pi}{t}} \sum_{-\infty}^{\infty} \exp(-\pi^2 l^2/t) \cos(2\pi l \xi), \tag{5}$$

and the integral representations of the modified Bessel function K_ν

$$\int_{-\infty}^{\infty} dt\, t^{\nu-1} \exp(-\pi^2 l^2/t - m^2 t) = 2\left(\pi\left|\frac{l}{m}\right|\right)^\nu K_\nu(2\pi|lm|). \tag{6}$$

After lengthy mathematical manipulations, the Coulomb interaction energy between ions i and j in the central box is given in units of $q_i q_j/\varepsilon L$, by the expression [7]

$$U(\xi, \eta, \zeta) = 4 \sum_{l=1}^{\infty} \cos(2\pi l \xi) \sum_{-\infty}^{\infty} K_0(2\pi l \sqrt{(\eta + m)^2 + \zeta^2}) - \log[\cosh(2\pi\eta) - \cos(2\pi\zeta)]. \tag{7}$$

The modified Bessel function $K_0(x)$ decays very fast with distance [6]. For an accuracy of order 10^{-4} we only need terms up to $x = 8$. If we keep terms up to $x = 10$ the contributions from the long range tail will be of order $\sim 10^{-5}$. This is acceptable in the light of the simulation requirement which has been discussed by others [8, 9].

Comparisons of the relative computational efficiencies were made between this new summation method and the Ewald type summation methods which divide the summation into a sum on lattice vectors and a sum on reciprocal lattice vectors. The calculation was carried out by taking a system of 40 particles, 20 cations and 20 anions, confined between two neutral surfaces. In each step k we put them in positions that are accepted from the Monte Carlo criteria, and calculated the potential

$$U^{(k)} = \sum_{i<j}^{N} U(r_{ij}) \tag{8}$$

to the accuracy that each method can achieve in the same computational time. The falling off parameter α of the spherical charge distribution $\rho(r, \alpha)$ [10, 11] is chosen to be $\alpha = 1.1/L$ for scheme b, and $\alpha = 8/L$ for c. In cases b and c, the maximum number of reciprocal space vectors is roughly $K_{\max} = 5$ in both x and y directions. With these choices, the relative error for this case is calculated as

$$\Delta = \frac{1}{n_{\text{step}}} \sum_k \frac{|U^{(k)}_{\text{exact}} - U^{(k)}|}{|U^{(k)}_{\text{exact}}|}, \tag{9}$$

where $|U^{(k)}_{\text{exact}}|$ is calculated to an accuracy of 10^{-5} by summing more terms in the series. The test results are listed in table 1. Lekner's method is the best among those compared.

3 CANONICAL ENSEMBLE MONTE CARLO SIMULATION

In this paper we used the canonical ensemble Monte Carlo to carry out the simulations. The long range coulomb potential was calculated by the method given in

Table 1 Relative efficiencies that different schemes can achieve in the same computational time (about 0.002 on the Cray 2). Here $\rho(r, \alpha)$ is the spherical charge distribution given in References [10, 11] and α is the parameter which determines how fast the charge falls off radially.

Method	$\rho(r, \alpha)$	Δ
a	$\delta(r)$	0.1
b	$\alpha^3 \frac{e^{-r^2\alpha^2}}{\pi^{3/2}}$	0.05
c	$\alpha^3 e^{\frac{-\alpha r}{8\pi}}$	0.05
Lekner	$\delta(r)$	0.002

Section 2 and the calculations were accurate to higher order term must be $\leqslant 10^{-4}$. The simulation was done at different surface charge densities σ and concentrations for 1 : 1 electrolyte. Both ion species are hard spheres with diameter $d = 4.25$ Å. The surface at $z = 0$ is charged and the one at $z = H$ is neutral. The temperature for the simulation was fixed at 300 K. The dielectric constant was taken to be 78.5. The parameters used in this paper are given in Table 2 for reference. In the table ΔN is the difference of number of ions inside the box. N_+ and N_- are the number of positive and negative ions with $\Delta N = N_- - N_+ = \sigma A$ and $A = L^2$. n_0 is the bulk density of the electrolyte which is the asymptotic value of the electrolyte and fixed to be 1 M or 2 M and V is the volume of the box. In this paper, $n_0 = 0.46/d^3$ or $0.092/d^3$.

During this simulation, the system was equilibrated for 20 000 steps to reach equilibrium and another 2×10^5 steps to accumulate configurations to calculate average quantities. The density profiles and mean electrostatic potential ψ were calculated. At each step, the particle is moved to a random position inside a cube of side R. The move is accepted if the energy change is negative, i.e., $\delta V_{nm} \leqslant 0$, and accepted with the probability

$$\rho(n \to m) = \frac{\exp(-\beta V_n)}{\exp(-\beta V_m)} = \exp(-\beta \delta V_{nm}), \tag{10}$$

when $\delta V_{nm} > 0$, where n and m are initial and final states in an attempt and $\beta = 1/kT$ with k the Boltzmann constant and T the temperature. To accept a move with this probability, a random number θ is generated in the range of 0 to 1. If $\theta < \rho(n \to m)$ the move is accepted. To sample the phase space as much as possible we vary R so that the probability of acceptance is about 50 percent.

Every 10th of the configuration was saved during the run to accumulate the averages for the calculation of density profiles $n(z)$ and mean electrostatic potential $\psi(z)$ where z is the distance from the charged wall. The density $n(z)$ was obtained by

Table 2 Parameters used in this paper, $\sigma^* = \sigma d^2/e$, side length L, surface separation H, number of positive and negative ions N_+ and N_-, $\Delta N = N_- - N_+ = \sigma A$, $A = L \times L$, n_0 is the bulk concentration in units of $1/d^3$.

$H(d)$	$L(d)$	σ^*	N_+	N_-	ΔN	$n_0(1/d^3)$
29.0	3.09	0.42	12	16	4	0.046
30.0	2.93	0.7	11	17	6	0.046
13.0	4.50	0.396	21	29	8	0.092

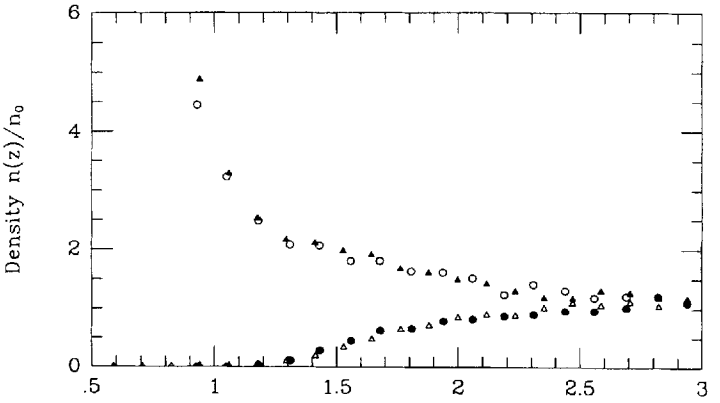

Figure 1 Density profiles $n(z)/n_0$ for the 1 : 1 electrolyte at surface charge density of $\sigma^* = \sigma d^2/e = 0.42$ and separation $H \sim 29d$ and concentration 1 M. Circles denote GCMC results (Reference [3a]), and triangles CMC results.

counting the number of particles in slices parallel to the charged wall and dividing by the volume. Then $\psi(z)$ is calculated via the relation

$$\psi(z) = \frac{4\pi}{\varepsilon} \int_z^H dz_1 (z - z_1) \sum_i q_i n_i(z_1). \tag{11}$$

4 RESULTS AND DISCUSSION

The computed density profiles and mean electrostatic potential ψ are reported in what follows. Surface charge density and mean electrostatic potential are reported in

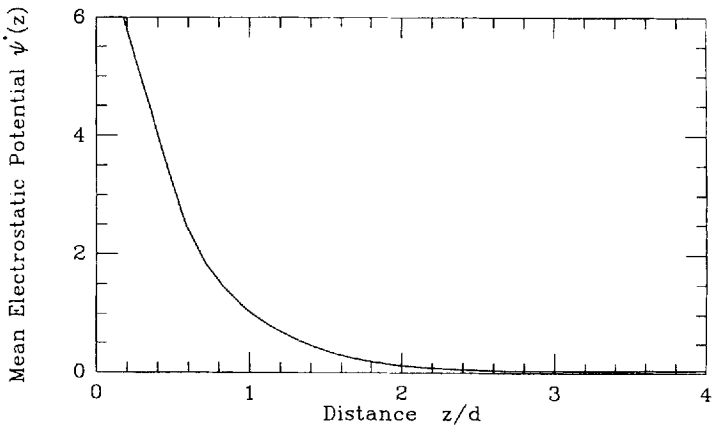

Figure 2 Mean electrostatic potential $\psi^*(z)$ for the 1 : 1 electrolyte at the same conditions as in Figure 1. Dotted line correspond to CMC results.

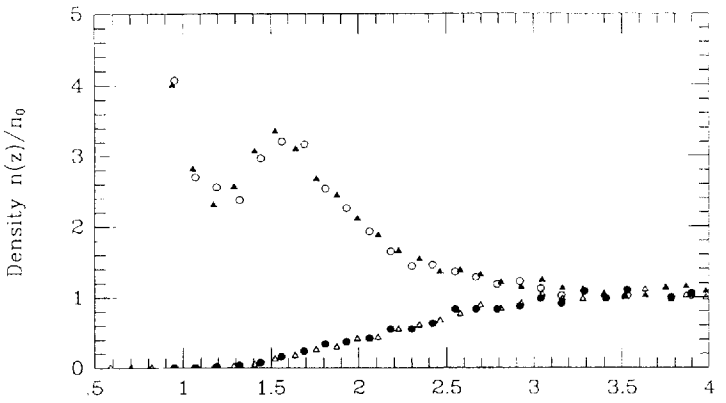

Figure 3 Density profiles $n(z)/n_0$ for the same conditions as in Figure 1 except charge density of $\sigma^* = 0.7$ and separation $H \sim 30d$. Circles denote GCMC results (Reference [3a]), and triangles denote CMC results.

dimensionless forms

$$\sigma^* = \frac{\sigma d^2}{e} \quad \text{and} \quad \psi^* = \beta e \psi. \tag{12}$$

Figure 1 shows the density profiles from the CMC simulation compared with the results from the GCMC simulations for the surface charge density $\sigma^* = 0.42$. The GCMC calculations are for an open system in equilibrium with a bulk phase at 1 M concentration. The figure shows the density in reduced unit $n_i(z)/n_{i0}$, with i specifying the ion species and n_{i0} is the bulk density corresponding to a concentration of 1 M. From the figure we see that the results of CMC and GCMC are in agreement within the variance of the simulated results. The mean electrostatic potential from our

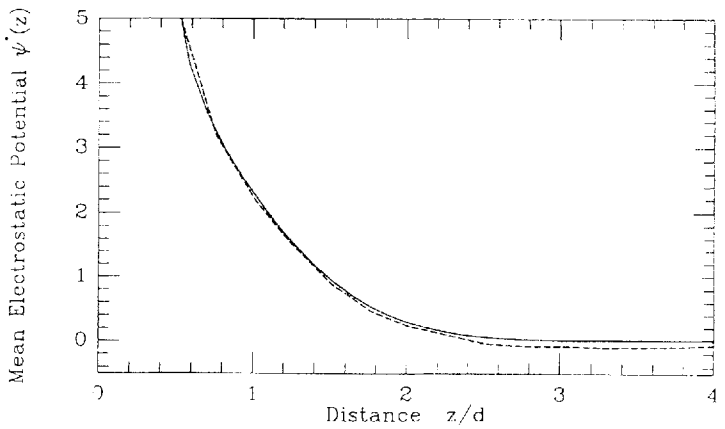

Figure 4 Mean electrostatic potential $\psi^*(z)$ for the 1 : 1 electrolyte at the same conditions as in Figure 3. The dotted line corresponds to CMC results, and the dashed line to GCMC results (Reference [3a]).

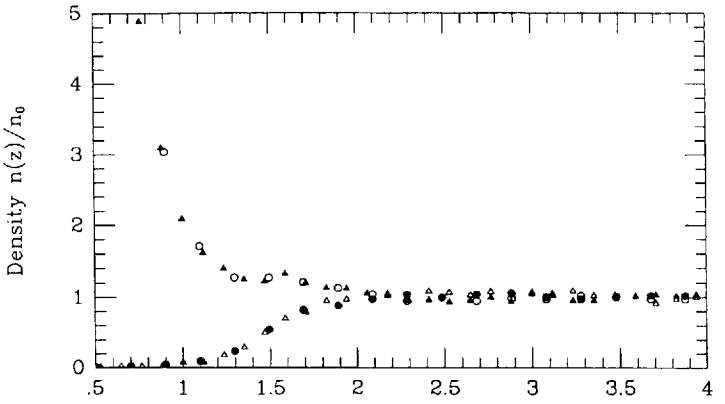

Figure 5 Density profiles $n(z)/n_0$ for the 1 : 1 electrolyte at surface charge density of $\sigma^* = 0.396$ and separation $H \sim 13d$ and concentration 2 M. Circles denote GCMC results (Reference [3a]), and triangles denote CMC results.

simulations is shown in Figure 2. We have no GCMC results to compare with the electrostatic potential.

Figures 3 and 4 are the density and mean electrostatic potential profiles for the case of $\sigma^* = 0.7$ and $H = 30d$. Except for the small shift of the second peak in the density profile, CMC and GCMC results are quite close and both show the layer of negative ions at $z \sim 3d/2$. The mean electrostatic potentials of the CMC and GCMC calculations are also in good agreement.

To see how the density profiles and the mean electrostatic potentials would vary when the concentration is changed and to demonstrate the applicability of the canonical Monte Carlo method in this kind of simulations, the following simulation is done for a 2 molar concentration 1 : 1 electrolyte with $\sigma^* = 0.396$ and $H = 13d$. These results

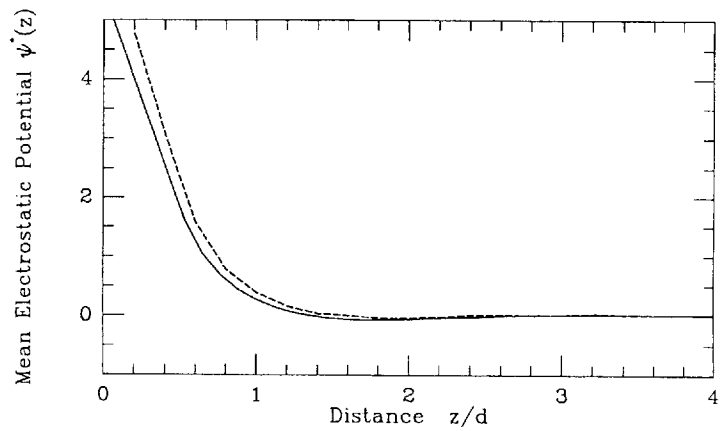

Figure 6 Mean electrostatic potential $\psi^*(z)$ for the 1 : 1 electrolyte at the same conditions as in Figure 5. The dotted line correspond to CMC results, and the dashed line correspond to GCMC results (Reference [3a]).

Table 3 The diffuse layer potential $\psi^*(\frac{1}{2}d)$ and the total potential drop $\psi^*(0)$ for different surface charge densities σ^* and bulk concentration n_0 from CMC and GCMC [3].

$\psi^*(\frac{1}{2}d)$	σ^*	n_0	CMC	GCMC
$\psi^*(\frac{1}{2}d)$	0.42	0.046	3.13(0.13)	3.08(0.10)
	0.7	0.046	5.28(0.04)	5.71(0.14)
	0.396	0.092	1.83(0.06)	2.29(0.09)
$\psi^*(0)$	0.42	0.046	7.58(0.13)	7.52
	0.7	0.046	12.70(0.04)	13.10
	0.396	0.092	6.15(0.06)	6.47

are shown in Figures 5 and 6. We can see that the ion densities approach the bulk values faster than in the 1 M concentration electrolyte: The ion densities predicted by the CMC and GCMC simulations agree well, but the ion density profiles differ sufficiently to yield observable differences in the mean electrostatic potential.

The diffuse layer potential $\psi^*(\frac{1}{2}d)$ and the total potential drop $\psi^*(0)$ from CMC and GCMC are given in Table 3 for comparison. The errors given in Table 3 are obtained from the difference between the mean value of half simulation averages with the final average results. We do not know if the small differences arise from real differences between ensembles or from differences between Lekner's sum and the minimum image potential used in the GCMC simulations carried out by Torrie *et al.*

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