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A LONG-RANGED ELECTROSTATIC INTERACTION IN COMPUTER SIMULATIONS

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Abstract—Molecular dynamics simulations for the primitive model systems of 1-1 and 2-2 electrolyte solutions were carried out to investigate the influence of system size and long-ranged potentials. Both the nearest image convention and the Ewald summation method were employed to handle the effective electrostatic interactions. For the thermodynamic and structural properties of such systems, the resulting calculations obtained from both two methods do not show any measurable inaccuracy except for the system of 2-2 electrolytes at $M_t=6.0$. However, the nearest image results indicate lower self-diffusion coefficients compared with those given by the Ewald method. In this case, the time-dependent dynamic properties are shown to be sensitive to the treatment of long-ranged Coulombic interactions.

INTRODUCTION

Over last thirty years computer simulations of many particle systems have provided the most satisfactory basis for our understanding and interpretation in the study of condensed phases, especially for liquid state [1, 2]. As an intermediate between theory and experiment, simulations via Monte Carlo (MC) and molecular dynamics (MD) techniques can, in principle, yield essentially 'exact' experimental data for precisely defined model systems. Only the input information required in performing machine experiments (computer simulations), apart from some fixed initial parameters, is the description of the model potentials interacting among atoms or molecules.

Typically, for the purpose of computation expenses, such simulation studies deal with the fundamental cubic box containing only a few hundreds or a thousand particles. The periodic boundary conditions are usually imposed at the boundary walls not only to minimize surface effects but also to approximate an infinite system. It is then unavoidable that the intermolecular potentials employed in computer simulations must be truncated at some finite separation related to the finite size and periodicity of a unit cell. The use of small numbers of particles confined within the simulation cell may introduce non-ergodic or quasi-ergodic behavior over phase space, which would not occur in the true thermodynamic limit.

This is not severe problems in the MC and the MD computations for the systems of the short-ranged model potentials such as hard-core and Lennard-Jones fluids. In this case, a continuum tail-correction may be required in estimating the properties of an infinite system from the configurations of a small number of particles [3]. However, the long-ranged effective interactions cause methodological difficulties [4], for instance, in the systems of charged particles including molten salts, plasmas, and ionic solutions. The range of the intermolecular potential between a pair of charges is much larger than the periodic cell size itself. In fact, the electrostatic Coulombic potential changes very slowly as 1/r so that more distant periodic images can make a substantial contribution to the net energy of charges or the forces acting on it.

Several methods have been employed to investigate the effect of the long-ranged potentials under the various conditions of the periodic cell in shape (For more detailed discussion of this subject, we refer the reader to Ref. [5] and the references are therein quoted). There are, in general, three different ways of handling the long-ranged potentials: (i) the spherical truncation method (the potential is simply set equal to zero for separation larger than a cut-off distance); (ii) the nearest image or minimum image convention (each ion interacts only with the nearest images in

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a periodic unit cell); (iii) the Ewald summation method (the effective potential is evaluated by the summation over the infinite lattice of periodically repeated cells).

For the systems of electrostatic Coulombic interactions, it is well-known that the spherical truncation method must be rejected outright since the simple truncation method violates the charge neutrality condition. More unlike ion-pairs tend to remain within the truncation sphere while less like ions in this region. The nearest image (NI) convention, which has great computational advantages, automatically satisfies the local neutrality condition in a unit image cell. The main deficiency, however, rests in the structural inconsistency and the noticeably strong number, or conversely, size dependency for the systems of highly charged and high concentrations [6, 7]. In the Ewald summation method [8, 9], the periodicity can be exploited in order to calculate energies and forces for the infinite lattice system. This method is generally preferred since it gives the thermodynamic and structural properties that are slowly varying functions of system size [10].

In the present paper, we will address this question by performing molecular dynamics simulations for the systems of charged hard-sphere ions, so-called the primitive model electrolyte solutions [11]. As far as the time-dependent transport properties are concerned, there are quite a few MD calculations of such model fluids [12, 13]. For the asymmetrically charged 1-3 electrolyte systems, one of the authors reported the MD results using the full Ewald approximations in the previous paper [13]. In this MD study of symmetrically charged 1-1 and 2-2 electrolytes, we will investigate the influence of system size and long-ranged Coulombic interactions using both the NI convention and the Ewald method. The MD results will provide useful insight into the interplay between the short-ranged repulsion and the long-ranged electrostatic interaction in determining the equilibrium and dynamic properties of such model systems.

MODEL AND COMPUTATIONS

We consider a system of N hard-sphere ions interacting through the primitive model potential,

$$u_{ij}(r_{ij}) = \left[\begin{array}{ll} \infty & \text{if } r_{ij}<d \\ \dfrac{q_i\ q_j}{\varepsilon_r\ r_{ij}} & \text{if } r_{ij}>d \end{array} \right. \qquad (1)$$

where r_{ij} is the relative distance between ions i and j and ε_r is the uniform dielectric constant of the medium relative to the permittivity of free space, ε_o. For the simplicity of notation, all factors of $4\pi\varepsilon_o$ are omitted in this pair potential, and the charges, q_i and q_j, are both divided by $(4\pi\varepsilon_o)^{1/2}$. As used in most other simulation studies, the relative dielectric constant, ε_r, is chosen to be 78.356 corresponding to those for water at the room temperature, T=298.16 K. The diameter of charged hard-sphere ions, d, are identically equal to be 0.425 nm with the atomic mass, m, of 100 a.m.u.

In a unit cubic cell of the side length, L, and the volume, $V(=L^3)$, the charge density of an array of N ions is expressed by the standard delta function notation,

$$\rho(\underline{r}) = \sum_{i=1}^{N} q_i\ \delta(\underline{r}-\underline{r}_i) \qquad (2)$$

By the definition of the Fourier transformation, the periodic charge density over a cubic lattice can be expanded using the Fourier series

$$\rho(\underline{r}) = \frac{1}{V} \sum_{\underline{k}} \rho(\underline{k})\ \exp(i\underline{k}\cdot\underline{r}) \qquad (3)$$

and the corresponding Fourier component is

$$\rho(\underline{k}) = \int_V \rho(\underline{r})\ \exp(-i\underline{k}\cdot\underline{r})\ d\underline{r} \qquad (4)$$

The reciprocal lattice vectors $\underline{k}$, where $\underline{k}=2\pi/L(k_x, k_y, k_z)$ and k_x, k_y, $k_z=0$, ±1, ±2,$\cdots$,±∞, should satisfy the Bragg condition of the cubic lattice constant L, and, for any other k, $\rho(\underline{k})=0$.

Substituting $\rho(\underline{r})$ into Eq. (4) and then the resulting $\rho(\underline{k})$ into Eq. (3), one finds

$$\rho(\underline{r}) = \frac{1}{V} \sum_{k} \sum_{i=1}^{N} q_i\ \exp\{i\underline{k}\cdot(r-\underline{r}_i)\} \qquad (5)$$

The charge density can be related to the electric potential according to Poisson's equation, i.e., $\nabla^2\ \phi\ (\underline{r}) = -4\pi\rho(\underline{r})$. Again, by an aid of the Fourier analysis, $\phi(\underline{r})$ can be similarly obtained from Poisson's equation,

$$\phi(\underline{r}) = \frac{1}{V} \sum_{\underline{k}\neq 0} \frac{4\pi}{k^2} \sum_{i=1}^{N} q_i\ \exp\{i\underline{k}\cdot(\underline{r}-\underline{r}_i)\} \qquad (6)$$

and, the potential energy per a unit cubic cell is

$$U = \frac{1}{2}\int_V \rho(\underline{r})\phi(\underline{r})\ d\underline{r} - \frac{1}{2}\sum_{i=1}^{N} q_i^2 \int_V \frac{\delta(\underline{r}-\underline{r}_i)}{|\underline{r}-\underline{r}_i|} d\underline{r} \qquad (7)$$

The second term on the RHS of Eq. (7) comes from the fact that each ion contributes a self-energy arising from the interaction with its own periodic images.

Inserting Eqs. (1) and (6) into Eq. (7), we get

$$U=\frac{4\pi}{2V}\sum_{i=1}^{N}\sum_{j\neq i}^{N} q_iq_j \sum_{\underline{k}\neq 0}\frac{\exp(i\underline{k}\cdot\underline{r}_{ij})}{k^2} + \frac{4\pi}{2V}\sum_{i=1}^{N} q_i^2\left(\sum_{\underline{k}\neq 0}\frac{1}{k^2}-\int_V \frac{\delta(\underline{r})}{|\underline{r}|}\,d\underline{r}\right) \qquad (8)$$

If we define

$$\varphi(\underline{r})=\frac{4\pi}{V}\sum_{k\neq 0}\frac{\exp(i\underline{k}\cdot\underline{r}_{ij})}{k^2} \qquad (9)$$

then, Eq. (8) can be simply represented as

$$U=\frac{1}{2}\sum_{i=1}^{N}\sum_{j\neq i}^{N} q_iq_j[\varphi(\underline{r})-\lim_{r\to 0}(\varphi(r)-1/r)] \qquad (10)$$

The expression in the bracket of Eq. (10) can be regarded as the effective Coulombic pair potential, which is anisotropic and has the symmetry in the periodic boundary condition.

The sum over reciprocal lattice space for evaluating $\varphi(\underline{r})$ in Eq. (9) is, however, conditionally convergent and the results depend on the order in which we add up the terms. By the Ewald summation method [8-10], this conditionally convergent series can be transformed into two rapidly convergent sums: one in real space, $U_{\underline{n}}$, and the other in reciprocal space, $U_{\underline{k}}$. The essential point of the Ewald treatment is that both of which may be truncated with the minimal error. In this sense, for a short-ranged nature of $U_{\underline{n}}$ potential, the cut-off or truncated calculation is fully valid, while the smoothly varying function of U_k is approximated by the superposition of the continuous functions.

For real space of a short-ranged potential,

$$U_{\underline{n}}=\frac{1}{2}\sum_{i=1}^{N}\sum_{j=i}^{N}\sum_{\underline{n}=0}{}' q_iq_j\frac{\operatorname{erfc}(\alpha r_{ij,n})}{r_{ij,\underline{n}}} \qquad (11)$$

where $\underline{n}$ is the lattice vector and the prime on the summation implies the absence of n=(0, 0, 0) for i=j in the series. The function, erfc(x), is the complementary error function which falls to zero rapidly with increasing the argument value of x. For the large value of an arbitrary parameter α, typically set to 5/L, the only term contributes to the sum in the real space is that $\underline{n}$=(0, 0, 0). This simply reduces to the normal minimum image convention.

For reciprocal lattice space of periodic Fourier domain,

$$U_{\underline{k}}=\frac{2\pi}{L^3}\sum_{i=1}^{N}\sum_{j=i}^{N}\sum_{\underline{k}\neq 0} q_iq_j\frac{\exp(-k^2/4\alpha^2)}{k^2}\cos(\underline{k}\cdot\underline{r}_{ij}) \qquad (12)$$

Note that k=2π/L (k_x, k_y, k_z) is a reciprocal wave vector in units such that its components, k_x, k_y, and k_z, are all integers.

The order of computations in Eq. (12) can be reconstructed using the charge neutrality condition. The double sum over ions i and j is now simplified into the single sum over ion i [14]

$$\sum_{i=1}^{N}\sum_{j=i}^{N} q_iq_j\cos(\underline{k}\cdot\underline{r}_{ij}) = \left[\sum_{i=1}^{N} q_i\cos(\underline{k}\cdot\underline{r}_i)\right]^2+\left[\sum_{i=1}^{N} q_i\sin(\underline{k}\cdot\underline{r}_i)\right]^2 \qquad (13)$$

For the reciprocal part of the Ewald summation in the MD computations, a total of 618 wave vectors were evaluated using a recurrence relationship of complex arithmetic to avoid repeated computations.

In the system of primitive model electrolytes, we combined two distinct algorithms of a 'discontinuous' hard-sphere repulsion with 'continuous' interactions into the same MD program by returning to the hybrid step-by-step approach described elsewhere [3, 12, 13]. In our MD computations the time step interval was selected to be of order of femtoseconds, which is small compared to the average time between hard-sphere collisions. During this time step, the equations of hard-sphere collisions were first solved for all possible colliding pairs, and the system trajectories were then advanced using the leapfrog version of the Verlet algorithm. The MD calculations here were carried out for the systems of various sizes containing the total number of 64, 216, and 512 ions, respectively. In addition, the initial configurations were generated by randomly inserting particles to assist in the equilibration of the system. Configurations were aged, or equilibrated, for 4,000 steps before accumulating the final ensemble averages and we generated 2-40,000 configurations after equilibrium to yield the final simulation results.

RESULTS AND DISCUSSION

System characteristics and the MD calculations for the thermodynamic and transport properties obtained from both the NI convention and the full Ewald method are presented in Tables 1 and 2, respectively. In an attempt to correct for the use of finite systems, the results were linearly extrapolated as a function of 1/N, and the extrapolated values to approximate an infinite system (N→∞) were evaluated by the uniformly weighted least-square method. We also report the contact values of pair distribution functions for like, $g_l(d)$, and unlike ion-pairs, $g_u(d)$, in the columns 7 and 8 of these tables. In the present study, we consider the two sets of concentration conditions, M_t=0.2 and 6.0, where M_t is the total ion concentration in units of moles of ions per liter, but not the stoichiometric concentration, M_s (Note that $M_t=2M_s=21.6318\ nd^3$

Table 1. System characteristics and the MD results using the nearest image convention

	M_t (mol/l)	N	$-U/NkT^{a)}$	$PV/NkT^{b)}$	$PV/NkT^{c)}$	$g_l(d)$	$g_u(d)$	D (10^{-4} cm^2/s)
1-1	0.2	64	0.2726(0.0425)	0.9435	0.9429	0.33	3.16	54.28
		216	0.2735(0.0218)	0.9438	0.9460	0.33	3.50	60.89
		512	0.2689(0.0137)	0.9445	0.9411	0.31	2.87	62.26
		∞	0.2704	0.9444	0.9432	0.32	3.13	63.50
	6.0	64	0.7437(0.0378)	1.6759	1.6968	0.84	2.41	3.329
		216	0.7332(0.0248)	1.6916	1.6910	0.82	2.40	3.419
		512	0.7250(0.0175)	1.7029	1.6969	0.81	2.42	3.379
		∞	0.7247	1.7036	1.6938	0.81	2.41	3.412
2-2	0.2	64	2.0583(0.1504)	0.6266	0.6065	0.08	30.15	30.96
		216	2.0088(0.0763)	0.6223	0.5797	0.07	25.68	29.29
		512	2.0246(0.0405)	0.6248	0.5929	0.07	27.59	29.84
		∞	2.0079	0.6230	0.5825	0.06	25.95	29.27
	6.0	64	3.7567(0.1007)	1.1867	1.1773	0.31	4.61	2.100
		216	3.7557(0.0559)	1.1386	1.0880	0.30	4.32	2.210
		512	3.7652(0.0426)	1.1332	1.1087	0.30	4.40	2.170
		∞	3.7623	1.1229	1.0809	0.29	4.30	2.208

$^{a)}$The values in parentheses indicate statistical uncertainties in the MD simulations.

$^{b,c)}$The reduced osmotic pressure coefficients calculated by Eqs. (14) and (16), respectively.

Table 2. System characteristics and the MD results using the Ewald summation method

	M_t (mol/l)	N	$-U/NkT^{a)}$	$PV/NkT^{b)}$	$PV/NkT^{c)}$	$g_l(d)$	$g_u(d)$	D (10^{-4} cm^2/s)
1-1	0.2	64	0.2760(0.0430)	0.9431	0.9449	0.25	3.56	61.32
		216	0.2743(0.0232)	0.9448	0.9440	0.30	3.36	61.87
		512	0.2691(0.0132)	0.9454	0.9433	0.32	3.09	61.06
		∞	0.2702	0.9457	0.9432	0.32	3.11	61.42
	6.0	64	0.7202(0.0448)	1.6961	1.6497	0.76	2.30	3.215
		216	0.7250(0.0255)	1.6919	1.6980	0.81	2.42	3.165
		512	0.7243(0.0191)	1.6986	1.7019	0.82	2.43	3.504
		∞	0.7257	1.6957	1.7127	0.83	2.46	3.396
2-2	0.2	64	1.9962(0.1186)	0.6191	0.5914	0.05	26.48	28.11
		216	1.9948(0.0771)	0.6249	0.5942	0.06	26.70	29.08
		512	2.0075(0.0498)	0.6243	0.5791	0.06	25.58	29.68
		∞	2.0036	0.6259	0.5840	0.07	25.95	29.75
	6.0	64	3.6761(0.0916)	1.2048	1.1551	0.30	4.45	2.354
		216	3.6899(0.0485)	1.1926	1.1789	0.28	4.57	2.494
		512	3.6886(0.0318)	1.2016	1.1510	0.27	4.48	2.480
		∞	3.6924	1.1961	1.1647	0.27	4.54	2.518

$^{a,b,c)}$As in Table 1.

and nd^3 is the total number density).

The statistical errors quoted in the column of the configurational energy were estimated from the standard deviation of the subaverage mean of each 10 step during the MD simulations. The energy fluctuations observed in both the NI and the Ewald results exhibit the similar behavior, where the statistical errors are seen to be strong number dependent. For the large systems, such systematic errors may be unimportant, whereas, for the small system of N=64, serious problems may occur due to large statistical uncertainties. This trend is comparable to those reported in the previous simulation studies of primitive model electrolytes [15-18], in which almost all computations have been carried out using the MC calculations. Valleau and his collaborators have extensively reported the canonical [16] and the grand canonical MC results [15]. In their canonical MC results, the NI method was adopted to evaluate the Coulombic part of potentials and the resulting energy was linearly extrapolated by the same procedure employed here. Their calculations should be accepted with some care because the data with as few as 200 ions could yield results strongly depending on system size. Admittedly, in their MC work, more accurate extrapolations were obtained from the systems of $N=64$ and 200, but not including the results for $N=32$.

The NI results of $-U/NkT$ given in Table 1 are also shown to be some increase in the configurational energy compared with those for the Ewald results in Table 2, particularly for the system of highly charged 2-2 electrolytes and high concentration of $M_r=6.0$. A similar drift of the internal energy towards unreasonably low values was observed for the LiCl systems [19] using the Evjen method [20]. The NI convention is equivalent to the Evjen approximation in calculating the lattice energy. Woodcock and Singer [21] later found that this drift did not occur when they evaluated the energy by the Ewald method instead of the Evjen approximation. The Ewald energy is correct for a perfect lattice so it may also be successful for dense systems where ions depart little from a close-packed configuration. As far as the static equilibrium properties are concerned, both the NI and the Ewald methods give reasonable results under the conditions investigated here. In this sense, at least for 1-1 electrolytes, these two methods to treat long-ranged Coulombic interactions seem to be satisfactory.

For the primitive model fluids containing a hard-sphere element with continuous Coulombic interactions, the osmotic pressure can be determined by evaluating the contact value of pair distribution functions,

$$\frac{PV}{NkT}=1+\frac{U}{3NkT}+\frac{\pi n d^3}{3}[g_s(d)+g_u(d)] \qquad (14)$$

where kT is Boltzmann's constant times the absolute temperature. In this equation, we have used the symmetric properties of pair distribution functions for 1-1 and 2-2 electrolytes,

$$g_s(r)=g_{++}(r)=g_{--}(r) \qquad (15a)$$

$$g_u(r)=g_{+-}(r)=g_{-+}(r) \qquad (15b)$$

Alternatively, the MD calculations can provide a simple and accurate means in computing the pressure of hard-core systems. The third term on the RHS of Eq. (14), which is directly related to the hard-sphere contributions to the pressure, is then replaced by the time average, i.e., a sum over all collisions occurring in the total simulation time, τ. As a result, the virial expression for the osmotic pressure in the MD method can be rewritten as

$$\frac{PV}{NkT}=1+\frac{U}{3NkT}+\frac{m}{3NkT\tau}\sum_{\{all\ coll.\}}(\underline{r}_{ij}\cdot\Delta\underline{v}_{ij})_{contact} \qquad (16)$$

The contact values of the pair distribution functions, however, cannot be calculated directly during the simulation. In the MC calculations, these contact values can be only determined by extrapolating backwards to $r=d$ from values close to contact. The extrapolation procedure may introduce large uncertainties when the corresponding pair functions can rise or fall rapidly near contact. This gives rise to poor statistical accuracy for the MC pressure in such systems. For this reason, the MC pressure results are known to be less accurate than those obtained from the MD method [3]. Moreover, in a convergence problem, the Metropolis sampling of the standard MC simulations is also inefficient for the system of low concentrations due to the energy traps over phase space [22]. When one configuration favored energetically is accepted between unlike ions, many trial configurations may be required to escape the energy pocket in the Markov chain of such MC calculations.

The reduced osmotic pressure coefficients obtained from Eqs. (14) and (16) are presented in Tables 1 and 2. As shown in these tables, the NI and the Ewald results for the pressure calculated by Eq. (14) indicate reasonable agreement with the MD pressure in Eq. (16) except for the system of 2-2 electrolytes. As mentioned earlier, the failure in this case is undoubtedly due to a lack of success in extrapolating to the contact point. For the 1-1 and 2-2 electrolyte systems employed in this work, the Ewald results of the configurational energy and the osmotic pressure in Table 2 are shown to be in excellent agreement with one of the best theoretical approaches, namely, the hypernetted chain theory [2, 23]. This again confirmed the good quality of the Ewald method.

In Fig. 1, we have plotted the pair distribution functions, $g_s(r)$ and $g_u(r)$, respectively, of the systems of $N=64$, 216, and 500 for 2-2 electrolytes at $M_r=6.0$ (Fig. 1a corresponds to the results obtained from the NI convention and Fig. 1b from the Ewald method). As has been observed from the earlier MC studies of 2-2 primitive electrolytes [16-18], the salient features displayed in these figures are a strong tendency to the formation of linear ion triplets and probably even larger clusters. The presence of (+ − +) or (− + −) ion triplets is illustrated in a local maximum

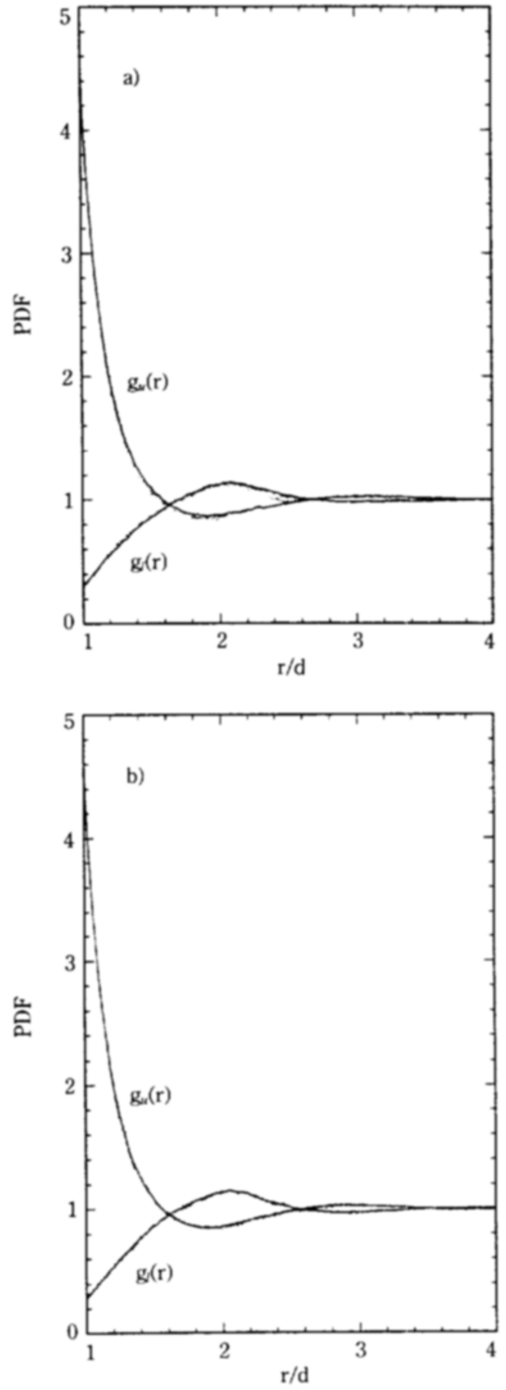

Fig. 1. The like and unlike pair distribution functions for 2-2 primitive model electrolytes at $M_l=6.0$.
(a) the NI method, (b) the Ewald method
The dotted, the medium dash, and the solid lines are corresponding to the systems of N=64, 216, and 512, respectively.

in $g_l(r)$ near $r \cong 2d$. The MD pair distribution functions of N=64 (the dotted lines) exhibit a high degree of statistical noise which decays significantly with increasing sample size. In this figure, both the NI and the Ewald pair functions for the large system of N=512 (the solid lines) are seen to behave smoothly. The Ewald pair functions (Fig. 1b) also indicate only a weak number dependency compared with the pair functions given by the NI method (Fig. 1a).

The most interesting feature in this figure is the peculiar local peak displayed in the NI pair functions of N=64. As we increase system size, such humps are gradually disappeared for the systems of N=216 and 512. This structural effect in pair distribution functions can be explained in terms of the shape of the periodic cell. The lowest interaction energy between unlike ion-pairs is found when each ion is located in a diagonal corner of the nearest image cube. For the small system, as shown in Fig. 1a, this leads to the certain special positions in favor of the cube corners rather than the perfect radial symmetry. In the MC computations of molten salts [24], Adams employed the two different shapes of periodic boundary conditions: the usual cubic cell with N=512 ions and the truncated octahedral cell with N=864 ions. The thermodynamic and structural properties obtained from the Ewald summation were found to be the same within statistical errors for both the two sets of boundary conditions. In contrast, the NI calculations were totally different from those by the Ewald summation. The empirical conclusion drawn in his MC work, together with previously published evidence [6, 7, 25], is that the Ewald method is an excellent method for the highly charged systems.

The self-diffusion coefficients can be calculated from the slope of the mean-square displacement (MSD) versus time using the Einstein equations

$$D=\lim_{t\to 0}\frac{1}{6t}\frac{1}{N}\sum_{i=1}^{N}<|\underline{r}_i(t)-\underline{r}_i(0)|^2> \tag{17}$$

and from the integration of the velocity autocorrelation function (VACF) using the Green-Kubo relations

$$D=\frac{1}{3}\int_0^\infty\frac{1}{N}\sum_{i=1}^{N}<\underline{v}_i(t)\cdot\underline{v}_i(0)>dt \tag{18}$$

in which the symbol ⟨ ⟩ represents the ensemble average over equilibrium configurations.

Typically, for the systems of short-ranged potentials, the MD computations of the time-dependent transport properties are only marginally influenced by finite system size when the simulations are executed for a fundamental cell containing approximately a few hun-

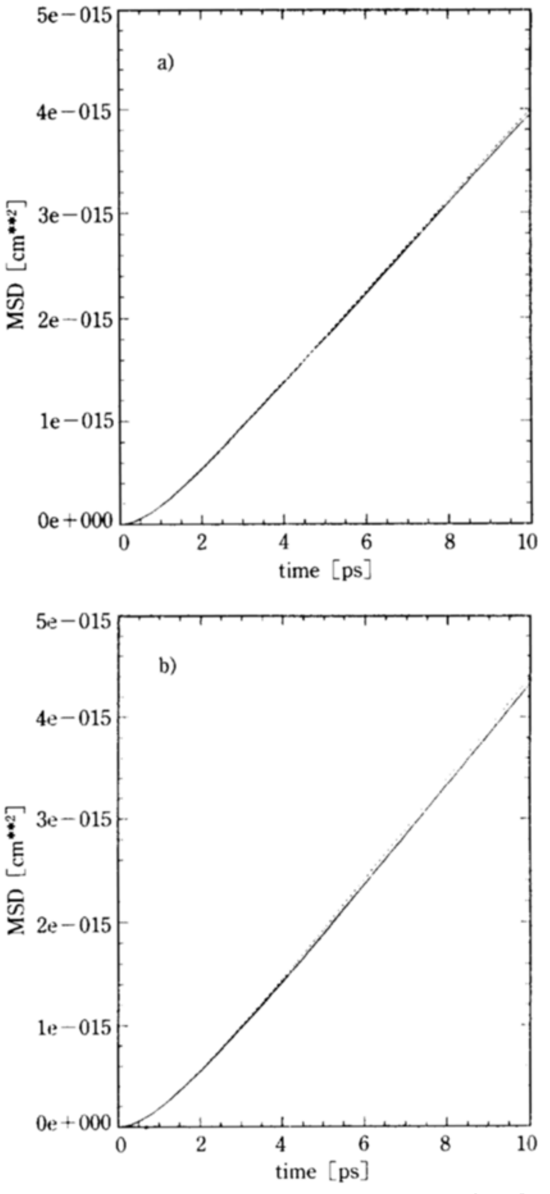

Fig. 2. Mean-square displacement curves versus time for 2-2 primitive model electrolytes at $M_r=6.0$.
(a) the NI method, (b) the Ewald method
The lines are as in Fig. 1

dreds particles. The accuracy will of course be much greater with increasing system size. In the case of bulk hard-sphere fluids, it was found that increasing the number of particles in the system to 432 particles had little or no effect [26]. However, for the systems of primitive model electrolytes, only a limited information is available [12, 13].

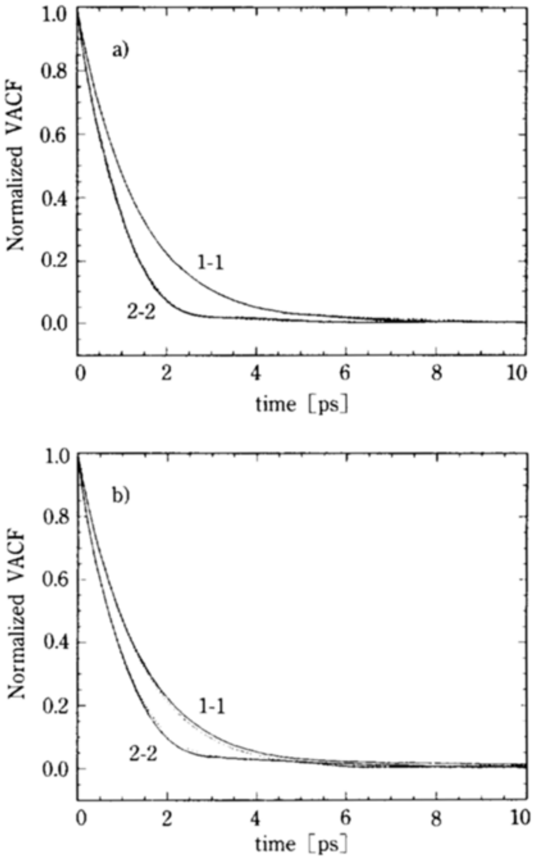

Fig. 3. Normalized velocity autocorrelation functions versus time for 1-1 and 2-2 primitive model electrolytes at $M_r=6.0$.
(a) the NI method, (b) the Ewald method
The lines are as in Fig. 1

Returning to Table 1 and 2, we report here the self-diffusion coefficients of 1-1 and 2-2 electrolyte solutions in the last column of these tables. The results obtained from the MSD in Eq. (17) and the VACF in Eq. (18) should agree with each other within the statistical errors. In these tables, the self-diffusion coefficients obtained from the MSD curves were only reported since the two methods gave the results in good agreement, typically less than 5% difference. Even though our MD calculations for the static equilibrium properties do not show any measurable inaccuracy, the results for the time-dependent transport coefficients were seen to be unexpectedly sensitive to the treatment of the long-ranged electrostatic interactions rather than system size.

In an effort to assess the effect of long-ranged interactions on the time-dependent properties, the MSD curves versus time for 2-2 electrolytes at $M_t=6.0$ are displayed in Figs. 2a (the NI convention) and 2b (the Ewald method), respectively. In this case, there are substantial differences in the resulting self-diffusion coefficient between the NI and the Ewald methods. In Figs. 3a and 3b, we have also plotted the normalized VACFs for a few selected runs to illustrate the manner in which the VACF changes with increasing system charge and system size. It is worth noting that the VACFs for 2-2 electrolytes exhibit non-exponential behavior. Although not apparent in this figure, the VACFs for 2-2 electrolytes given by the Ewald method display stronger correlations in velocity than those by the NI method. Consequently, the Ewald approximation results in larger diffusion coefficients. The long-ranged Coulombic potential increasingly influences the collective motion of ionic fluids. In addition, the electrostatic interaction enhances correlations between unlike ion-pairs while decorrelation between like pairs.

CONCLUSION

In the present study, we investigated the influence of system size and long-ranged electrostatic interactions for the primitive model systems of 1-1 and 2-2 electrolyte solutions. In order to determine the number of ions required to ensure negligible size effects on the final results, the MD computations using the NI convention and the full Ewald method were carried our for the systems of various sizes containing the total number of 64, 216, and 512 ions, respectively.

Under the concentration conditions employed in this work, the configurational energy coefficients from both the NI and the Ewald methods are shown to be in good agreement with each other when the runs were excuted for a fundamental cubic cell containing approximately 200 particles or more. For the NI pressure results, however, number dependencies, or conversely size dependencies, turned out to be large and erratic, particularly for the system of 2-2 electrolytes at $M_t=6.0$. In this case the transport diffusion results of the NI convention are much lower than those given by the Ewald method. The time-dependent dynamic properties also indicate the significant influence of long-ranged Coulombic potentials as displayed in the mean-square displacement curves and the velocity autocorrelation functions. In addition, better accuracies for the pressure were achieved from the MD-type time average in Eq. (16) rather than from the MC-type configurational average in Eq. (14) using the extrapolated contact values of pair distribution functions. The MD results reported here have a direct bearing on transport phenomena in variety of ionic systems. It would be of great interest to extend to more realistic fluids in order to verify a number of the conclusions observed in our MD simulations.

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