

This article was downloaded by:

On: 14 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Molecular Simulation

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713644482>

The Dot and Line Method: A Long Range Correction to Coulomb Interaction in a Cylindrical Pore

Yuk Wai Tang^a; Kwong Yu Chan^a

^a Department of Chemistry, The University of Hong Kong, Hong Kong SAR, People's Republic of China

To cite this Article Tang, Yuk Wai and Chan, Kwong Yu(2004) 'The Dot and Line Method: A Long Range Correction to Coulomb Interaction in a Cylindrical Pore', *Molecular Simulation*, 30: 1, 63 — 70

To link to this Article: DOI: 10.1080/0892-7020310001598069

URL: <http://dx.doi.org/10.1080/0892-7020310001598069>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

The Dot and Line Method: A Long Range Correction to Coulomb Interaction in a Cylindrical Pore

YUK WAI TANG and KWONG YU CHAN*

Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong SAR, People's Republic of China

(Received June 2003; In final form June 2003)

The charge line (CL) method had been used in the past to represent the periodic charges in Monte Carlo simulations of ions in a cylindrical pore. In this method, there exists a possible singularity when the edge of the image line overlaps with an ion in the central cylinder. This singularity is more problematic for molecular dynamics when the force is evaluated. Molecular dynamics simulations with the CL method have not been reported in the literature. By replacing the first section of the image charge line with an image point, we show that the CL method can be improved and be applicable in the molecular dynamics simulation of electrolytes in a cylindrical geometry. The modified method is demonstrated to be effective by simulations of a high packing primitive model electrolyte, representing the state of a molten salt.

Keywords: Charge line method; Molecular dynamics simulation; Coulomb interaction; Dot and line method; Nanopore

INTRODUCTION

Recently, molecular simulations of ions in a cylindrical geometry have received much attention [1–6]. The relevant scientific and technological systems of interest include ion channels in biological membranes [7] and porous materials [8]. Whether for a pore of finite length [7] or infinite length [4], periodical charge images are assumed in at least one dimension. One of the technical difficulties involved in the simulation of electrolytes is the accuracy in treating the long range Coulomb interaction of charges. The classic Ewald summation can be applied to a system periodic in three dimensions [9], two dimensions [10,11], and one dimension [12].

Adaptation to a pseudo two-dimensional system has been reported [13]. An Ewald summation, specifically for a cylindrical geometry has not been reported, though the pseudo two-dimensional method can be applied when the system is modeled as a bundle of parallel cylinders far from each other. In any case, the Ewald summation requires much more additional computational time for the calculation of terms in the reciprocal space. Other methods of reaction field [14] and particle–particle and particle–mesh method [15] have also been proposed and are more easily applicable in a three-dimensionally isotropic system.

By smearing out the long range periodic charges and representing them with charged sheets at regular intervals, Torrie and Valleau [16] successfully simulated the electrochemical double layer in a two dimensional slab of finite thickness. Boda *et al.* [17] modified the method by representing each ion with a single charge sheet at the same location of the ion and making the simulation more conformed to a Markov chain process. With a similar principle, a charged line method has been applied to the Monte Carlo simulation of ions in a cylindrical geometry [3,18]. The concept is shown here in Fig. 1(a). The periodic images of ion j in the axial direction are represented by two half lines extending from the edges of the simulation cell. The charged lines have the same linear charge density, q_j/H , as the ion j in the central section, where q_j is the charge of ion j and H is the length of the simulation cell. Without considering the images of ion i , the Coulomb

*Corresponding author: Fax: +86-2857-1586. E-mail: hrsccy@hku.hk

interaction energy between ions i and j including j 's images is given by

$$U_{ij} = \frac{q_i q_j}{4\pi\epsilon_0\epsilon_r r_{ij}} - \frac{q_i q_j}{4\pi\epsilon_0\epsilon_r H} \times \left[\ln\left(\frac{H/2 - z_{ij} + \sqrt{x_{ij}^2 + y_{ij}^2 + (H/2 - z_{ij})^2}}{H/2 + z_{ij} + \sqrt{x_{ij}^2 + y_{ij}^2 + (H/2 + z_{ij})^2}}\right) \right] \quad (1)$$

In Eq. (1), ϵ_0 is the permeability in free space, ϵ_r is the relative permeability of the medium, and x_{ij} , y_{ij} and z_{ij} are the Cartesian components of the inter-particle distance r_{ij} . The first term of Eq. (1) is the interaction of ions i and j in the central simulation cell, whereas the second and third term represent the interaction of ion i with the upper image line and lower image line of ion j , respectively, according to Fig. 1(a).

The long-range term in Eq. (1) is derived by integrating the interaction of ion i with a differential element of the charge line, from the edge of the simulation cell to infinity. In the process of integration to infinity, two additional divergent

terms appear, but they can be cancelled out if electroneutrality of the system is assumed [3]. Equation (1) is finite in all situations except when x_{ij} , y_{ij} are both equal to 0 and z_{ij} equals to $H/2$. This is the situation when ion i overlaps with an image charge line at the edge of the half line. This singularity is more problematic in molecular dynamics since when z_{ij} approaches $H/2$ with $x_{ij} = y_{ij} = 0$, the force in z direction approaches faster to infinity, compared to the interaction energy. Such a condition leads to a very large force experienced by the particle when it is near the singular point and causes instabilities in the MD simulation.

In this paper, we propose a modification of the charge line (CL) method to eliminate this singularity problem. We call this the dot and line (DL) method. Two explicit point charge images, one above and one below the simulation cell, are used to replace the first sections of the two half lines. By molecular simulations of a primitive model electrolyte confined in a nanopore, we show that this image point/charge line hybrid method is effective and with only marginal increase in computational effort.

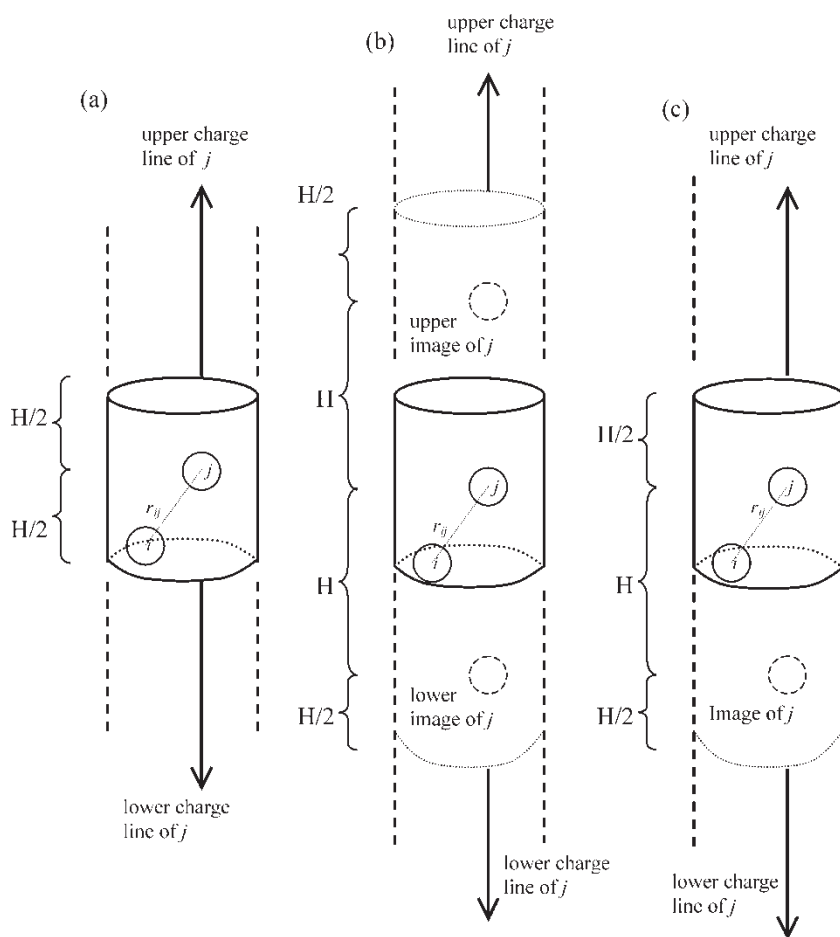


FIGURE 1 Setup of the charge images for long-range treatment of Coulomb interaction. (a) The charge line (CL) method: image of j represented by an upper half line and a lower half line. (b) The dot and line (DL) method: image of j represented by an explicit point charge followed by a half line in both the upward and downward directions. (c) The asymmetric dot and line (ADL) method: image of j represented by an explicit point charge only in the direction of ion i .

THE DOT AND LINE METHOD

The set up of the DL method is shown in Fig. 1(b) for the interaction of ion i with ion j including the images of ion j . In the positive z direction (upward), ion j is represented by an explicit point charge (the dot) a distance H directly above ion j and a half line (the line) starting a distance $3H/2$ directly above. The axial periodic images of ion j in the negative z direction (downward) are represented similarly by a point charge and then by a charge line. Without a better and simpler name, we call this the DL method. With the introduction of two explicit image point charges, the interaction energy between ion i and ion j including the images of ion j , becomes

$$U_{ij} = \frac{q_i q_j}{4\pi\epsilon_0\epsilon_r} \left(\frac{1}{r_{ij}} + \frac{1}{\sqrt{x_{ij}^2 + y_{ij}^2 + (H+z_{ij})^2}} + \frac{1}{\sqrt{x_{ij}^2 + y_{ij}^2 + (H-z_{ij})^2}} \right) - \frac{q_i q_j}{4\pi\epsilon_0\epsilon_r H} \left[\ln(3H/2 - z_{ij} + \sqrt{x_{ij}^2 + y_{ij}^2 + (3H/2 - z_{ij})^2}) + \ln(3H/2 + z_{ij} + \sqrt{x_{ij}^2 + y_{ij}^2 + (3H/2 + z_{ij})^2}) \right] \quad (2)$$

The first three terms in Eq. (2) represent the interaction with ion j and the point images in the adjacent upper and lower image cells. The last two terms represent the interaction with the two charge lines. Compared to Eq. (1), two terms representing the interaction with image points are added. With $H/2$ replaced by $3H/2$ in the last two terms, the singularity in Eq. (1) for $x_{ij} = 0$, $y_{ij} = 0$, $z_{ij} = H/2$ no longer exists. The DL method should therefore be more stable, compared to the CL method.

The corresponding interaction force in the axial direction between ions i and j , including the images of ion j can be derived as

$$f_{ij}^z = -\frac{q_i q_j}{4\pi\epsilon_0\epsilon_r H} \left[\frac{z_{ij}}{r_{ij}^3} + \frac{H - z_{ij}}{[x_{ij}^2 + y_{ij}^2 + (H - z_{ij})^2]^{3/2}} - \frac{H + z_{ij}}{[x_{ij}^2 + y_{ij}^2 + (H + z_{ij})^2]^{3/2}} \right] \frac{z_{ij}}{z_{ij}} + \frac{q_i q_j}{4\pi\epsilon_0\epsilon_r H} \left(\frac{1}{\sqrt{x_{ij}^2 + y_{ij}^2 + (3H/2 + z_{ij})^2}} - \frac{1}{\sqrt{x_{ij}^2 + y_{ij}^2 + (3H/2 - z_{ij})^2}} \right) \frac{z_{ij}}{z_{ij}}. \quad (3)$$

Note that \mathbf{z}_{ij} is a vector and $\mathbf{z}_{ij} = \mathbf{z}_i - \mathbf{z}_j$, where \mathbf{z}_i , \mathbf{z}_j are z -position of ions i and j , respectively. The long-range forces in radial directions can be calculated but they are ignored in the simulation process because they are of negligible magnitudes. Since Eq. (2) has two divergent terms due to electroneutrality, Eq. (3) should be derived from the interaction with a differential element on the charge line. Differentiation was carried out first on the differential element, dz , on the charge line with charge $q_j dz/H$ to yield a force expression, before integrating along the whole line to infinity. It turns out that the divergent terms do not contribute to the axial force and therefore the final expression is the same as a direct differentiation of Eq. (2). In principle, Eq. (3) does not require electroneutrality and therefore molecular dynamics simulation can be performed for a non-neutral system. The expression for energy, Eq. (2), however, requires electroneutrality and further analyses are needed to calculate the energy in a non-neutral system.

With only a few additional terms in the energy and force expressions, the DL method eliminates the singularity problem of the simple CL method. This requires only a marginal increase in computational effort for the Monte Carlo and molecular dynamics simulations of charges in a cylindrical geometry.

SIMULATIONS OF A PRIMITIVE MODEL ELECTROLYTE WITH THE DOT AND LINE METHOD

To test the effectiveness of the DL method, equilibrium molecular dynamics simulations of a symmetric univalent molten salt were carried out in a cylindrical pore. The ion-ion interaction in the simulation is a soft core potential plus the Coulomb interaction,

$$u(r_{ij}) = \begin{cases} 4\epsilon \left\{ \left(\frac{d}{r_{ij}} \right)^{12} - \left(\frac{d}{r_{ij}} \right)^6 \right\} + \epsilon + \frac{q_i q_j}{4\pi\epsilon_0\epsilon_r r_{ij}} & \text{if } r_{ij} \leq d \\ \frac{q_i q_j}{4\pi\epsilon_0\epsilon_r r_{ij}} & \text{if } r_{ij} > d \end{cases} \quad (4)$$

where d and ϵ are the Lennard-Jones parameters. The ion-wall interaction is also a shifted LJ-type described in a previous paper [4].

In order to compare the results with previous literature data of bulk electrolyte models [19], the set of parameters chosen are: temperature, $T = 1529$ K; $\epsilon = 4.3674 \times 10^{-21}$ J; $d = 3$ Å; mass of ions, $m = 23$ a.u.; and reduced density, $\rho^* = 0.8$, corresponding to a real unit of 1132 kg m^{-3} . Each MD time step is 1 fs. A cylindrical nanopore with radius five times the diameter of the ion ($R = 5d$) is chosen. Simulations of different lengths of the cylindrical

cells are set up. The setup parameters of different runs and their results are listed in Table I. For each size of simulation cell, runs using different long-range correction or image treatment were made. The DL method is compared with the simple CL method of Eq. (1). The corresponding force for the CL method with a potential singularity is

$$\begin{aligned} \mathbf{f}_{ij}^z = & -\frac{q_i q_j}{4\pi\epsilon_0\epsilon_r H} \left[\frac{z_{ij}}{r_{ij}^3} \right] \frac{\mathbf{z}_{ij}}{z_{ij}} \\ & + \frac{q_i q_j}{4\pi\epsilon_0\epsilon_r H} \left(\frac{1}{\sqrt{x_{ij}^2 + y_{ij}^2 + (H/2 + z_{ij})^2}} \right. \\ & \left. - \frac{1}{\sqrt{x_{ij}^2 + y_{ij}^2 + (H/2 - z_{ij})^2}} \right) \frac{\mathbf{z}_{ij}}{z_{ij}}. \end{aligned} \quad (5)$$

Variations can be made to the DL method by using different numbers of extended point images. A higher accuracy may be achieved by using more explicit point charges to replace a longer section of the charge line. We found that using multiple point charges gives little or no improvement but demands more computational effort. On the other hand, a single image point may be used, replacing either only the upper or lower charge line that has the singularity problem. This is shown by the setup in Fig. 1(c). Since the possible singularity exists only in the last term of Eq. (5), just this term can be replaced by the dot and line interaction term as shown by the equation

$$\begin{aligned} \mathbf{f}_{ij}^z = & -\frac{q_i q_j}{4\pi\epsilon_0\epsilon_r H} \left[\frac{z_{ij}}{r_{ij}^3} + \frac{H - z_{ij}}{[x_{ij}^2 + y_{ij}^2 + (H - z_{ij})^2]^{3/2}} \right] \frac{\mathbf{z}_{ij}}{z_{ij}} \\ & + \frac{q_i q_j}{4\pi\epsilon_0\epsilon_r H} \left(\frac{1}{\sqrt{x_{ij}^2 + y_{ij}^2 + (H/2 + z_{ij})^2}} \right. \\ & \left. - \frac{1}{\sqrt{x_{ij}^2 + y_{ij}^2 + (3H/2 - z_{ij})^2}} \right) \frac{\mathbf{z}_{ij}}{z_{ij}}. \end{aligned} \quad (6)$$

Equation (6) removes the singularity and allows a reasonably accurate force calculation in molecular dynamics. Compared to the double image DL method proposed in Eq. (3), the computational effort is slightly less because of one less term in Eq. (6). However, the unsymmetrical and inconsistent image treatment in the upward and downward directions will cost a little accuracy in calculation of the total energy. We have included this method in the simulation runs for comparison and will denote this

method as the asymmetric Dot and Line (ADL). We will show this ADL method to be undesirable. In Table I, the suffix of a run number refers to the method of long-range correction, e.g. run 5DL refers to the run with a simulation cell length five times the diameter of the ion and using the DL method. In addition to the CL, DL and ADL methods, we made simulation runs without any long-range correction. These runs will be denoted by the suffix *N*.

The effect of long-range treatment on the total pressure is also compared. The axial pressure is calculated by the virial equation,

$$P_z = \frac{\left[(N-1)kT + \sum_{i \neq j} \mathbf{f}_{ij}^z \cdot \mathbf{z}_{ij} \right]}{V}, \quad (7)$$

where the summation of the scalar product of force in the axial direction and the relative axial displacement is over all ion pairs, *N* is the number of particles in the pore, *k* is the Boltzmann constant, *T* is the instantaneous temperature of the system and *V* is the volume of the pore. While the long-range correction is applied in the evolution of the MD simulation, it is ignored in the calculation of pressure for which only particles within the minimum image cell are considered.

Transport properties of ions are related to the pair correlation function. For example, diffusion coefficient in axial direction *D_z* is related to the autocorrelation function of velocity in the same direction [20],

$$D_z = \int_0^\infty \langle v_z(t) \cdot v_z(0) \rangle dt. \quad (8)$$

In the above equation, (*v_z*(*t*) *v_z*(0)) is the average of product of velocity in the axial direction at time *t* and time 0. The effect of long-range force on the position and the velocity of particles in the system can also be observed in the autocorrelation function of velocity.

RESULTS AND DISCUSSION

We can compare the values of the interaction energy and force calculated by various methods using some selected configurations. It is, however, more relevant to compare statistically averaged equilibrium thermodynamic properties in actual simulation runs. The results of runs of different pore lengths using different long-range correction methods are obtained over a sufficient number of equilibrium time steps and are tabulated in Table I. For a longer pore, more ions are required and the run time required increases quadratically. The calculated averages include the Coulomb energy per particle reduced to the LJ energy parameter *U_{cc}*/*Nε*, the reduced long-range correction energy *U_{LR}*/*Nε* to the Coulomb

TABLE I Thermodynamic and transport properties simulated for a pore with radius $R = 5d$

MD run	Length of pore H/d (No. of ions)	Number of steps	$U_{LR}/N\epsilon$	$U_{cc}/N\epsilon$	$U/N\epsilon$	P_z	D_+^*	D_-^*
5CL	5	50,000	-0.088 ± 0.2	-140.0 ± 3.3	-131.5 ± 5.1	2.16 ± 12	0.10	0.091
5ADL	(254)	50,000	4.71 ± 0.6	-140.2 ± 1.3	-131.5 ± 1.7	3.94 ± 2.3	0.083	0.081
5DL		50,000	1.54 ± 1.0	-143.8 ± 1.8	-135.0 ± 2.2	3.98 ± 2.3	0.079	0.080
10CL	10	50,000	1.23 ± 0.1	-135.9 ± 0.4	-129.2 ± 0.7	-14.7 ± 1.5	0.00032	0.00062
10ADL	(508)	50,000	1.89 ± 0.2	-142.7 ± 0.6	-134.0 ± 0.9	3.89 ± 1.6	-0.0021	0.0026
10DL		50,000	0.051 ± 0.2	-144.5 ± 0.6	-135.8 ± 0.9	3.86 ± 1.7	0.077	0.073
10N		50,000	—	-164.6 ± 0.1	-156.2 ± 0.3	-5.34 ± 2.1	0.080	0.080
15CL	15	50,000	4.76 ± 0.2	-129.7 ± 0.6	-122.5 ± 0.8	-8.55 ± 1.1	0.00046	0.0015
15ADL	(764)	50,000	1.22 ± 0.1	-143.4 ± 0.4	-134.6 ± 0.6	3.99 ± 1.3	0.0055	0.0049
15DL		50,000	-0.004 ± 0.1	-144.6 ± 0.4	-135.9 ± 0.7	3.99 ± 1.3	0.080	0.076
15N		50,000	—	-155.3 ± 0.1	-146.7 ± 0.1	0.16 ± 1.2	0.074	0.076
25CL	25 (1272)	20,000	1.86 ± 0.02	-139.0 ± 0.2	-131.3 ± 0.4	-2.93 ± 0.9	0.00023	0.00034
50CL	50	10,000	0.442 ± 0.01	-143.9 ± 0.2	-135.7 ± 0.3	0.82 ± 0.6	0.082	0.081
50ADL	(2544)	10,000	0.351 ± 0.01	-144.2 ± 0.2	-135.5 ± 0.3	4.02 ± 0.7	0.0028	0.0024
50DL		10,000	$(7 \pm 0.7) \times 10^{-4}$	-144.6 ± 0.2	-135.9 ± 0.3	3.99 ± 0.7	0.080	0.075
50N		10,000	—	-144.6 ± 0.02	-135.9 ± 0.03	3.92 ± 0.7	0.083	0.076
—	Bulk	—	—	-141.6 ± 0.01	-128.2 ± 0.01	—	—	—

The data of long range potential ($U_{LR}/N\epsilon$), Coulomb interaction ($U_{cc}/N\epsilon$), total interaction energy ($U/N\epsilon$), pressure in axial direction (P_z) and diffusion coefficients of cations and anions are shown in reduced units.

energy, the reduced total energy $U/N\epsilon$ of the system, and the pressure P_z in the axial direction. The error bars are statistical fluctuations in the final block of equilibrated steps. Also shown are diffusion coefficients of the cations and the anions obtained using velocity autocorrelation functions.

Comparing the Coulomb energy per particle calculated with the four different methods in Fig. 2, they come to agreement only when the pore length is ten times the radius of the pore (runs 50CL, 50ADL, 50DL, 50N). In this situation, there are 2544 ions in the system and the axial distance between particles in the central simulation cell and the images are sufficiently large so that the long-range correction is negligible. This critical length of $H/R = 10$, for which the long-range correction could be neglected was also adopted in earlier simulations [1,4]. It is reliable to assume that the value of $U_{cc}/N\epsilon$ for the molten salt in an infinite long pore of radius $5d$ should be -144.6 ± 0.2 . This value is slightly more negative than the bulk value of -141.6 ± 0.01 reported earlier [19]. The small difference is likely due to the difference between the bulk state and the confined pore geometry. Taking this $U_{cc}/N\epsilon$ value as the reference, we observe that the different methods give various degrees of accuracy for simulation runs of shorter pores. Without any long-range correction, the simulations (runs 10N, 15N) are expected to fail for short pores. But even with the CL method (runs 5CL, 10CL, 15CL, 25CL), the results are erroneous. In fact, the run of a longer pore (15CL) gives worse results than the runs of shorter pores (5CL, 10CL), having a relative error of 10%. On the other hand, the DL method gives the best results. Even with the shortest pore with 254 ions,

the result is within 0.6% of the reference value. The method of using only one dot image (runs 5ADL, 10ADL, 15ADL) gives results of intermediate accuracy, and the accuracy improves gradually with a larger system size. As discussed earlier, we would, however, not recommend this ADL method since

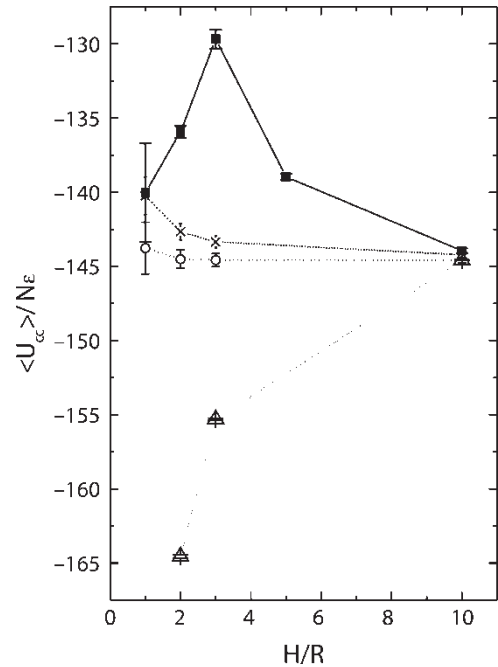


FIGURE 2 Comparison of the average reduced Coulomb interaction per ion computed in simulation runs using different long-range correction methods. (The circles, crosses, solid squares, triangles are run with the DL, ADL, CL methods, and no long range correction, respectively. The error bars are the statistical deviations of each run in Table I).

TABLE II CPU time required to complete a 50,000-step simulation for runs with different methods of long range correction and $R = 5d$

Run no.	No. of ions	CPU time (s)	Ratio to run 5N
5N	254	823	1
5CL	254	1388	1.69
5ADL	254	1822	2.21
5DL	254	1906	2.32
50N	2544	88525	107.6

there is an inherent consistency problem in choosing the lower or upper image. As will be discussed in Table II, there are few CPU time savings in this ADL method compared to the two images in DL method.

Similar conclusions can be drawn when comparing the values of pressure obtained in different runs, as shown in Fig. 3. Large deviations and inconsistencies are shown in the CL method and the method without any long-range correction, when shorter pores are used. The error bar for the CL method (± 12) is very large for the shortest run (run 5CL). Even for the run with the longest pore (50CL), the pressure is still not quite accurate and is worse than the run without any long-range correction (50N). On the other hand, the DL method yields very steady and accurate values of pressure for runs of different pore lengths.

While the CL method gives rather erroneous results, the difference in the averaged long-range correction term $U_{LR}/N\epsilon$ is smaller compared to the difference in the $U_{cc}/N\epsilon$ term. This means that the CL method actually gives a different equilibrium configuration and different spatial distributions of

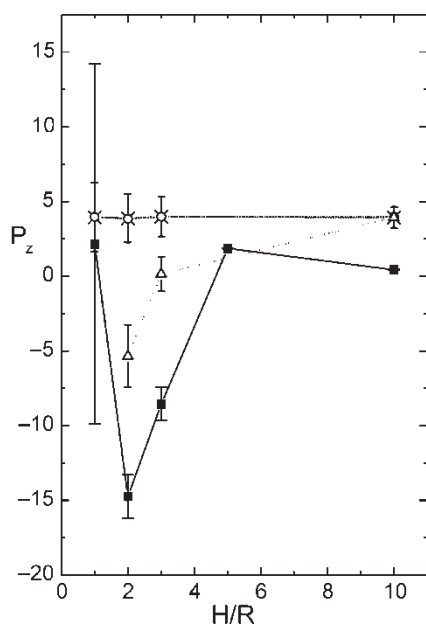


FIGURE 3 Comparison of the average reduced pressure computed in simulation runs using different long-range correction methods. (The legend is the same as Fig. 2).

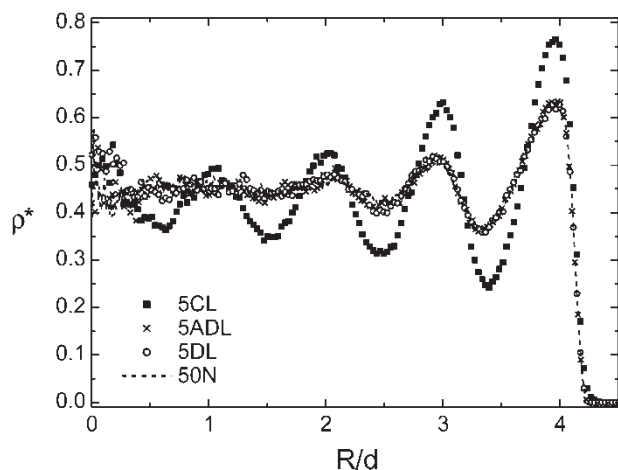


FIGURE 4 Radial density profiles of cations computed in simulation runs using different methods. (The legend is the same as Fig. 2 except that the dash line represents data of run 50N).

ions. The image charge line in the immediate periodic cell starts from the boundary. This is much closer to the central cell than what an image ion should be. This stronger interaction between the charge line and the ions in the central cell eventually affects the equilibrium distribution of ions. We can confirm this by comparing in Fig. 4 the equilibrium radial density profiles of ions obtained by the different methods. The density profile of the longest pore run 50N can be used as a reference. The run of the CL method (run 5CL) gives much larger oscillations in density profiles compared to the DL method (run 5DL). Comparing the two runs 5CL and 5DL, the difference between the peaks of density profiles in Fig. 4 is larger than 20%, while the difference in the average Coulomb energy is only 2.6%.

The effect of the long-range correction method on transport properties can be revealed in the time correlation function of velocity, as shown in Fig. 5.

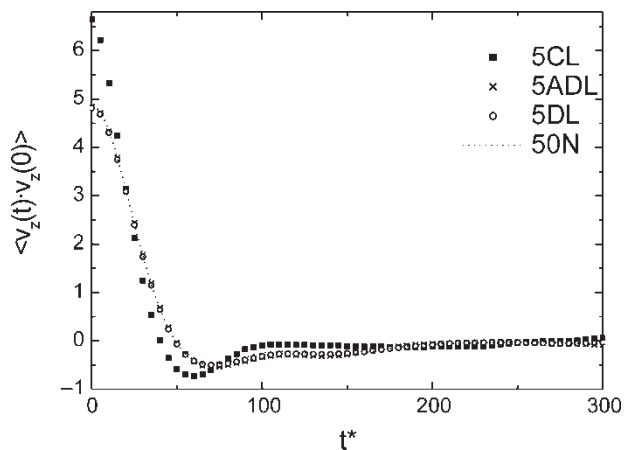


FIGURE 5 Autocorrelation functions of velocity of cations as a function of reduced time computed using different long-range correction methods. (The legend is the same as Fig. 4).

The autocorrelation functions of velocities of cations obtained by methods ADL and DL are in agreement with that of the longest pore (run 50N), while the autocorrelation function obtained by CL method is quite different. Diffusion coefficients of ions are found by integrating the autocorrelation functions, and results are listed in Table I. Looking at the results for the longest pore, the correct reduced diffusion coefficient of the ions should be around 0.080. Only the DL method gives consistent values close to the correct answer for different pore lengths. The CL, ADL and the N methods all give unsatisfactory results, particularly for short pore lengths.

While the DL method has been demonstrated to give the best results, it will be important to investigate the additional computational effort required. Table II compared the CPU time required for 50,000 time steps of different MD simulation runs of 254 ions in a pore of length $H = 5d$, running on a Digital 600 AU Alpha personal workstation. The DL method (run 5DL) requires 2.3 times the CPU time for a simple cutoff (run 5N with no long range correction). The accuracy of run 5DL, however, is the same as run 50N, which has 10 times more ions and requires 100 times more CPU time. This represents a CPU time saving by a factor of 1/50. Comparing with the CL method (run 5CL), the CPU time required for the DL method (run 5DL) is only 37% more. The accuracy of the DL method, as shown in above sections, far exceeds that of the CL method. Lastly, the ADL method requires a CPU time similar to the DL method, but inherently inferior to the DL method in accuracy.

The present study demonstrates the effectiveness of the DL method for simulation of ions in a cylindrical pore. The CL method is found to be unreliable. The conclusions are drawn from MD runs of a rather narrow pore and based on the computed thermodynamic, structural and transport properties of a molten salt. The charge density for a molten salt state is rather high and the requirement for a good long-range correction is more stringent than the case of a primitive model for an aqueous electrolyte. The dielectric constant in an aqueous electrolyte also damps the Coulomb interaction significantly. The diameter of the pore, which determines the number of ions per length, will also affect the accuracy of the different long-range corrections. With the limited runs made here, we can make the preliminary judgment that replacing the immediate sections of the upper and lower charge lines by two point images (the DL method) can significantly improve the accuracy of the simulations. In the case of the CL method or the case where no long-range correction is made, a minimum pore length of ten times the radius of the pore should be used to ensure acceptable results.

CONCLUSIONS

From molecular dynamics simulations of a molten salt in a cylindrical nanopore, the CL method for treating the long-range interaction with axial images of ions is found to be unsatisfactory. This arises from a singularity problem when two ions are aligned axially and are half-cell length distance away from each other. This deficiency leads to errors in thermodynamic properties, as well as structural properties and transport properties. By replacing the immediate upper and lower sections of the charge line by explicit point charges (we call it the DL method), the problem is eliminated and the results are significantly more accurate. With this modification to the CL method, accuracy results can be obtained for a much smaller system size, leading to large savings in CPU time.

Acknowledgements

The financial support from the Research Grants Council of Hong Kong under a project HKU 7213/99P is acknowledged.

References

- [1] Lo, W.Y. and Chan, K.Y. (1995) "Nonneutrality in a charged capillary", *Mol. Phys.* **86**, 745–758.
- [2] Lynden-Bell, R.M. and Rasaiah, J.C. (1996) "Mobility and solvation of ions in channels", *J. Chem. Phys.* **105**, 9266–9280.
- [3] Boda, D., Busath, D.D., Henderson, D. and Sokolowski, S. (2000) "Monte Carlo simulations of the mechanism for channel selectivity: the competition between volume exclusion and charge neutrality", *J. Phys. Chem. B* **104**, 8903–8910.
- [4] Tang, Y.W., Szalai, I. and Chan, K.Y. (2001) "Diffusivity and conductivity of a primitive model electrolyte in a nanopore", *Mol. Phys.* **99**, 309–314.
- [5] Nicholson, D. and Quirke, N. (2003) "Ion pairing in confined electrolytes", *Mol. Simul.* **29**, 287–290.
- [6] Chan, K.Y., Tang, Y.W. and Szalai, I. (2003) "Ion transport in simple nanopores", *Mol. Simul.*, (in press).
- [7] Boda, D., Henderson, D. and Busath, D.D. (2002) "Monte Carlo study of the selectivity of calcium channels: improved geometrical model", *Mol. Phys.* **100**, 2361–2368.
- [8] Berezhkovskii, A. and Hummer, G. (2002) "Single-file transport of water molecules through a carbon nanotube", *Phys. Rev. Lett.* **89**, art no.: 064503.
- [9] De Leeuw, S.W., Perram, J.W. and Smith, E.R. (1980) "Simulation of electrostatic systems in periodic boundary conditions", *Proc. R. Soc. Lond. A* **373**, 27–56.
- [10] Parry, D.C. (1975) "Electrostatic potential in surface region of an ionic-crystal", *Surf. Sci.* **49**, 433–440.
- [11] Parry, D.C. (1976) "Correction", *Surf. Sci.* **54**, 195.
- [12] Porto, M. (2000) "Ewald summation of electrostatic interactions of systems with finite extent in two of three dimensions", *J. Phys. A* **33**, 6211–6218.
- [13] Yeh, I.C. and Berkowitz, M.L. (1999) "Ewald summation for systems with slab geometry", *J. Chem. Phys.* **111**, 3155–3162.
- [14] Barker, J.A. and Watts, R.O. (1969) "Monte Carlo studies of the dielectric properties of water-like models", *Mol. Phys.* **26**, 789–792.
- [15] Eastwood, J.W., Hockney, R.W. and Lawrence, D.N. (1980) "P3M3DP—the 3-dimensional periodic

- particle-particle-particle-mesh program", *Comput. Phys. Commun.* **19**, 215–261.
- [16] Torrie, G.M. and Valleau, J.P. (1980) "Electrical double-layers—1. Monte Carlo study of a uniformly charged surface", *J. Chem. Phys.* **73**, 5807–5816.
- [17] Boda, D., Chan, K.Y. and Henderson, D. (1998) "Monte Carlo simulation of an ion-dipole mixture as a model of an electrical double layer", *J. Chem. Phys.* **109**, 7362–7371.
- [18] Murthy, C.S., Bacquet, R.J. and Rossky, P.J. (1985) "Ionic distributions near poly-electrolytes—a comparison of theoretical approaches", *J. Phys Chem.* **89**, 701–710.
- [19] Svishchev, I.M. and Kusalik, P.G. (1994) "Nonequilibrium molecular dynamics of a dense ionic fluid", *Phys. Chem. Liquid* **26**, 237–246.
- [20] Allen, M.P. and Tildesley, D.J. (1987) *Computer Simulation of Liquids* (Oxford Press, New York).