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An efficient method for computation of long-ranged Coulomb forces in computer simulation of ionic fluids

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Angular averaging of Ewald sums eliminating the nonphysical cubic symmetry of electrostatic field in the uniform ionic system under conditions of computer simulation with periodic boundaries is proposed. The resulting effective potential is central, has simple analytical form and its range is correspondent to the main box size. The approach provides a fast method for computation of electrostatic contribution to the energy of ionic fluids and other dense, uniform Coulomb systems in Monte Carlo or molecular dynamics computer simulation. © 2003 American Institute of Physics. [DOI: 10.1063/1.1624364]

I. INTRODUCTION

Long-ranged Coulomb forces determine to the largest extent the macroscopic behavior of plasmas, ionic crystals, and polar fluids, as well as other kinds of condensed matter. Along with intense short ranged forces, they are responsible for the stability of crystalline structures, and strongly affect most thermodynamic and transport properties of ionic and polar fluids. The problem of realistically formulating the long ranged Coulomb forces has a long history, and though great progress has been achieved in the microscopic description of condensed matter since the pioneering works of Madelung¹ and Ewald,² their correct description still remains a topical issue. The modern microscopic theory of the equilibrium structure and properties of ionic fluids is advancing along two main directions: Applications of integral equations theory³ and use of computer simulation methods like Monte Carlo or molecular dynamics.^{4,5} Due to the progress in computing technology, the last method is now going beyond the limits of simple model systems, providing tools for the investigation of complex multicomponent Coulomb systems like nonideal plasmas, solutions in molten salts, etc. Accurate simulations of dilute electrolyte solutions, polymeric and other fluids with complex composition require sometimes up to a million particles⁵ in the main Monte Carlo or molecular-dynamics computation cell (hereinafter simply called *main cell*). Obviously, the larger the number of charged particles in the main cell, the more acute is the problem of the evaluation of the effective electrostatic potential.

The most conventional way to solve this problem is the well-known Ewald summation procedure.^{2,6} This approach was initially proposed for the description of the electrostatic contribution to the energy of a crystalline lattice, and was later necessarily invoked in Monte Carlo and molecular-dynamics simulation of both crystalline and fluid ionic systems, because of the unavoidable periodic boundary conditions^{6,7} inherent in such simulations. Yet, this standard approach, if applied to uniform Coulomb systems—like, for

instance, plasma or ionic fluids—is facing two principal difficulties:

(1) The computer processor load essentially increases due to the summation over the reciprocal lattice. In the standard version of Ewald method it is proportional to the second power of the number N of particles in the main cell. Several alternative procedures^{5,8,9} have been so far proposed to reduce the processor load.

(2) The combination of long ranged Coulomb forces with periodic boundaries must invoke a nonisotropic electric field having the cubic symmetry of the crystalline lattice composed of main cells as elementary units. In this view, any procedure for the evaluation of the Coulomb forces in uniform systems can be considered as satisfactory only if this non-physical effect of artificial cubic symmetry is practically negligible.

The latter remark does not only pertain to the significance of the theoretical formulation, but is also very important from the practical point of view. In fact, in simulations of ionic fluids or plasmas based on Ewald's summation procedure the lion's share of the computer time is normally spent just to reproduce this nonphysical cubic symmetry of the electrostatic potential.

In this paper, a modification of the Ewald method suitable for simulation of ionic fluids and other spatially uniform Coulomb systems is proposed. An effective electrostatic interaction potential of two ions is introduced, pre-averaged over all orientations of the main cell. This potential in the bulk of fluid is pair-wise and central. Explicit expressions for this pre-averaged potential are presented and discussed together with examples in specific applications on strongly nonideal Coulomb systems.

II. PRE-AVERAGED INTER-IONIC POTENTIALS

Consider a standard cubic main cell of edge L and volume $V=L^3$, and containing $N=\sum_{\alpha=1}^M N_{\alpha}$ ions of M sorts. The inter-ionic force acting between the i th and the j th ion obeys the Coulomb law:

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$$F_{ij} = \frac{Q_i Q_j}{4\pi\epsilon_0 r_{ij}^2}.$$

Here $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ is the distance between ions and Q_i is the electric charge of the i th ion of type α : $Q^{(\alpha)} = \{Q^{(1)}, \dots, Q^{(M)}\}$. We shall here assume that the electro-neutrality condition

$$\sum_{i=1}^N Q_i = \sum_{\alpha=1}^M N_{\alpha} Q^{(\alpha)} = 0, \quad (1)$$

is satisfied, and that periodic boundary conditions as described in Refs. 7 and 9 are imposed. The total Coulomb energy of N ions in the main cell is

$$U_N^{(C)} = \sum_{1 \leq i \leq N} Q_i \varphi(\mathbf{r}_i),$$

where $\varphi(\mathbf{r}_i)$ is the electrostatic potential at the position \mathbf{r}_i of i th ion. According to Ewald,² this contribution is in turn the sum of one- and two-particle terms

$$\varphi(\mathbf{r}_i) = \varphi_1(\mathbf{r}_i) + \frac{1}{2} \sum_{j \neq i}^N \varphi_2(\mathbf{r}_i, \mathbf{r}_j).$$

In the absence of external field, the unary potential is a constant

$$\varphi_1 = \frac{Q_i}{4\pi\epsilon_0 L} \left(\frac{1}{2\pi} \sum_{n>0} \frac{1}{n^2} e^{-\pi^2 n^2 / \delta^2} - \frac{\delta}{\sqrt{\pi}} \right), \quad (2)$$

and the binary contribution can be written as follows:^{2,6}

$$\begin{aligned} \varphi_2(\mathbf{r}_{ij}) = & \frac{Q_j}{4\pi\epsilon_0} \left(\frac{\operatorname{erfc}\left(\delta \frac{r_{ij}}{L}\right)}{r_{ij}} \right. \\ & \left. + \frac{1}{2\pi L} \sum_{n>0} \frac{1}{n^2} e^{-\pi^2 n^2 / \delta^2} \cos\left(\frac{2\pi}{L} \mathbf{n} \cdot \mathbf{r}_{ij}\right) \right). \quad (3) \end{aligned}$$

Here δ/L is the conventional Ewald parameter,^{2,6} \mathbf{n}/L is the three-dimensional reciprocal lattice site vector ($n = |\mathbf{n}|$), and $\operatorname{erfc}(x)$ is the complementary error function.¹⁰

Keeping in mind that all orientations of the main cell in an isotropic fluid should be equivalent, we can average both sides of Eq. (3) over all directions of the vector \mathbf{n} at a fixed distance r_{ij} . If brackets $\langle \dots \rangle$ indicate averaging, we can write

$$\langle \dots \rangle = \frac{1}{4\pi} \int_{-1}^{+1} d(\cos \vartheta) \int_{-\pi}^{\pi} d\psi \dots,$$

where ψ , ϑ are the polar and azimuthal angles defining the direction of the vector $\mathbf{n}(\mathbf{n} \cdot \mathbf{r} = nr \cos \vartheta)$. We can determine the pre-averaged inter-ionic potential as $\varphi_2(r_{ij}) \equiv \langle \varphi_2(\mathbf{r}_{ij}) \rangle$. Integration of Eq. (3) over all orientations of the vector \mathbf{n} gives immediately:

$$\begin{aligned} \varphi_2(r_{ij}) = & \frac{Q_j}{4\pi\epsilon_0 r_{ij}} \left(\operatorname{erfc}\left(\delta \frac{r_{ij}}{L}\right) \right. \\ & \left. + \frac{1}{2\pi^2} \sum_{n>0} \frac{1}{n^3} e^{-\pi^2 n^2 / \delta^2} \sin\left(\frac{2\pi}{L} n r_{ij}\right) \right). \quad (4) \end{aligned}$$

The pre-averaged ion-ion potential Eq. (4) is a continuous function of the inter-ionic distance r_{ij} and can be expanded in converging power series in terms of this distance. Since both $\operatorname{erfc}(x) - 1$ and $\sin(x)$ are odd functions, the following series form holds:

$$\varphi_2(r_{ij}) = \frac{Q_j}{4\pi\epsilon_0 r_{ij}} \left(1 + \sum_{k \geq 0} C_k r_{ij}^{2k+1} \right). \quad (5)$$

The coefficients C_k in Eq. (5) are found by direct expansion of Eq. (4) in a MacLaurin's series. The procedure is straightforward: By applying the Euler-MacLaurin formula¹⁰ generalized for summation over three-dimensional integers \mathbf{n} ¹¹ one can find the following:

$$C_0 = \frac{1}{\pi} \sum_{n>0} \frac{1}{n^2} e^{-\pi^2 n^2 / \delta^2} - \frac{2\delta}{\sqrt{\pi}},$$

$$C_1 = \frac{2\pi}{3L^3},$$

$$C_k = 0, \quad k > 1.$$

By taking into account the electroneutrality condition Eq. (1), it can be seen that the term in Eq. (5) which is independent of the inter-ionic distance (proportional to C_0) and the one-particle contribution Eq. (2) cancel one another. This implies that the total Coulomb energy of N ions in the main cell can be described by the sum $U_N^{(C)} = \sum_{1 \leq i \leq N} \phi^{(C)}(r_{ij})$ of the following pair potentials:

$$\phi^{(C)}(r_{ij}) = \frac{Q_i Q_j}{4\pi\epsilon_0 r_{ij}} \left(1 + \frac{1}{2} \left(\frac{r_{ij}}{r_m} \right)^3 \right), \quad (6)$$

where $r_m = (3/4\pi)^{1/3} L$ is the radius of the volume-equivalent sphere of the main cell:

$$\frac{4}{3}\pi r_m^3 = L^3.$$

The pre-averaged pair interionic potential Eq. (6) has the following properties:

- (i) It tends to the pure Coulomb pair potential at small inter-ionic distances;
- (ii) its first derivative is zero at $r = r_m$;
- (iii) Its value at the minimum $r = r_m$ is nonzero ($\phi^{(C)}(r_m) = 3Q_i Q_j / 8\pi\epsilon_0 r_m$), and though it tends to zero with the increasing of the main cell size, in practical cases this decrease is very slow.

The comparison of the pre-averaged potential with the Ewald potential evaluated along the three primary crystal directions: [100] (main cell axis), [110] (face diagonal), and [111] (cube diagonal) is schematically shown in Fig. 1. As one can see, observable deviations of the pre-averaged potential from the "exact" Ewald formula appear only in the vicinity of the edge of the main cell. The effective pre-averaged potential is lower along the [100] direction, and

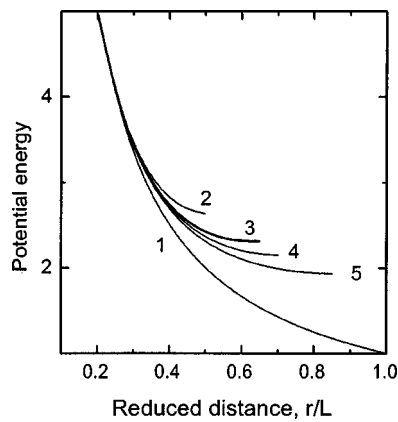


FIG. 1. Comparison of the pre-averaged ion-ion potential with Ewald potentials (in $Q_i Q_j / 4\pi\epsilon_0 L$ units): (1) pure Coulomb potential; (3) pre-averaged ion-ion potential Eq. (6); Ewald potentials for different directions in the main cell (2) [100]; (4) [110]; (5) [111].

higher along the [110] and [111] directions. Another visible difference is the range of interaction. The maximum distance between the center and the border of the main cell varies from $L/2$ on the [100] axis up to $L\sqrt{3}/2$ on the [111] diagonal. On the other hand, the intrinsic limit for the pre-averaged potential is represented by the value of the radius of the equivalent sphere, r_m . Beyond this limit the pre-averaged pair potential is not well defined.

If the value of the potential minimum at $r = r_m$ is zero, the extrapolation to larger distances (outside the equivalent sphere, for $r > r_m$) is trivial. However, one can easily see that such a continuation can be generally obtained by adding a constant equal to $-\phi^{(C)}(r_m)$ to bring the boundary value to zero.

By using once more the electroneutrality condition Eq. (1) we can rewrite the expression for the total Coulomb energy of the main cell in the following form:

$$U_N^{(C)} = - \sum_{i=1}^N \frac{3Q_i^2}{16\pi\epsilon_0 r_m} + \frac{1}{2} \sum_{i=1}^N \sum_{j=1, j \neq i}^N \tilde{\phi}(r_{ij}), \quad (7)$$

where

$$\tilde{\phi}(r) = \begin{cases} \frac{Q_i Q_j}{4\pi\epsilon_0 r} \left[1 + \frac{1}{2} \left(\frac{r}{r_m} \right) \left[\left(\frac{r}{r_m} \right)^2 - 3 \right] \right] & r < r_m \\ 0 & r \geq r_m, \end{cases} \quad (8)$$

is an effective inter-ionic potential which is zero together with its first derivative at $r = r_m$ and remains zero at $r > r_m$.

III. DISCUSSION

The continuity and isotropy of the effective potential obtained by pre-averaging of Eq. (3) entail some inconsistency with the initial main cell configuration and periodic boundary conditions assumed in computer simulations. This difficulty can be, however, readily solved in practical applications. For instance, the effective potential applied in simulation procedures with a cubic main cell has an implicit range $r_m = 0.62035 L$, i.e., larger than half of the cell size. If interaction range does not exceed $L/2$ (which is the most

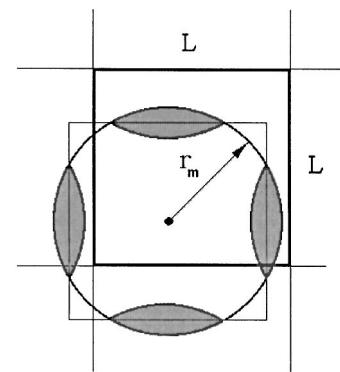


FIG. 2. Main cell and equivalent sphere for an ion. The shadowed domains contain ions, which contribute twice to the effective potential (the first time as ions themselves and the second time as their images).

conventional choice for short ranged potentials⁶) each particle in the cell contributes (or not) to the sum of interactions with the selected one just one time: Either as original object (inside the main cell) or as one of its images. This is not the case for potential Eq. (8) because $r_m > L/2$. Figure 2 illustrates schematically the existence of two different zones inside the effective sphere surrounding an arbitrary ion inside the main cell. The first zone (the blank area inside the circle) is similar to that discussed above: It contains ions (inside the main cell) or their images (outside it) that contribute to the sum of pair interactions of the chosen ion just one time. The second zone (shadowed in Fig. 2) contains those ions, which contribute twice to the interaction energy with the given ion—both as original ions and as their images. This peculiarity of the evaluation of the electrostatic energy must be taken into account in the simulation algorithm.

Finally, one positive feature of the proposed method is closely related to the above mentioned property and to the explicit condition of local electro-neutrality that was applied by deriving Eq. (7). Actually, use of the effective inter-ionic potentials in the form of Eq. (8) instead of Eq. (6) makes practical applications of the method simpler and numerically more robust. The fact that the effective potentials are naturally truncated at $r = r_m$; where both their values and slopes are zero, radically diminishes the sensitivity of the interaction energy to the number and to the charge of the ions inside the equivalent sphere in computer simulations. Actually, the number of particles and the net charge inside this sphere is continuously fluctuating during numerical calculations, contrary to the case of a main cell where artificial periodic boundary conditions are imposed and these quantities are kept constant (or zero). In fact, the net charge inside the equivalent sphere of each ion during a computer simulation vanishes only in average. The first example shown demonstrates that correct results can be obtained even if the number of ions inside the equivalent sphere differs from the number of ions in the main cell, and the net charge is nonzero. For testing the ability of the proposed method to predict reasonable values of the electrostatic energy in a condensed ionic system, we have chosen the perfect NaCl structure. The values of Madelung constant computed from Eqs. (7) and (8) are presented in Table I for different numbers of ions in the

TABLE I. Predicted values of the Madelung constant for the NaCl lattice.

L/a	Number of ions		Net charge		Madelung constant	
	Cell	Sphere	$\Delta = \sum Q_i$	$ \Delta/N , \%$	This work	Error, %
1	8	7	-5	71.4	1.5258	-12.7
2	64	81	5	6.2	1.7167	-1.77
3	216	203	-29	14.3	1.7399	-0.44
4	512	485	13	2.7	1.7515	0.22
5	1000	1021	41	4.0	1.7551	0.43
6	1728	1743	31	1.8	1.7543	0.39
7	2744	2777	41	1.5	1.7530	0.31
8	4096	4067	119	2.9	1.7515	0.22
9	5832	5743	55	1.0	1.7493	0.10
10	8000	8025	-31	0.4	1.7480	0.02
Exact ¹ =					1.7476	

main cell. The first column contains the ratio of the size of the cell to the lattice constant, in the second and third columns are reported the numbers of ions in the cell and in the equivalent sphere. The fourth and fifth columns show the actual net charge and the ratio of its magnitude to the number of ions in the cell. The last two columns present the predicted Madelung constants and their deviations from the exact value.¹

It should be noted that even for a spatially nonuniform ionic crystal—that is to say the worst application case for a pre-averaged effective potential essentially devised for spatially uniform ionic fluids—the results are surprisingly positive. The electrostatic energy of the simple cubic NaCl structure predicted by the effective potential is rather good even for small numbers of ions in the main cell. The results are insensitive even to the (practically unavoidable) violation of the electroneutrality condition in the fragment of lattice encompassed by the equivalent sphere. In the case of the examined structure, the method does slightly—but systematically—overestimate the binding energy of the crystal. For a cell containing 1000 ions, the error in the predicted electrostatic energy is lower than 0.5% of the energy value. Nevertheless, in some cases this error may not be acceptable, since its absolute value is comparable with the mean kinetic energy of one ion under ambient conditions. Therefore, particular care should be taken when this method is applied, for instance, to simulation of molten salts near the crystallization temperature. In these cases, if the number of ions in the main cell is not large enough, the calculated transition may occur at temperature higher than one should expect.

A second example showing the relative importance of periodicity effects appearing within Ewald's scheme (but absent in the proposed approach) is produced below. A couple of oppositely charged ions was assumed to be placed in the main cell, and Ewald method was applied to calculate the system energy. The charges will then supposed to be rotating around arbitrary axis. In real uniform systems like molten salts or plasmas there should be no angular dependence of the total energy. This is obviously not the case in this model, and the example shows how important may be the artificial "crystalline field" effects in simulations.

The first nonvanishing angular-dependent term in the se-

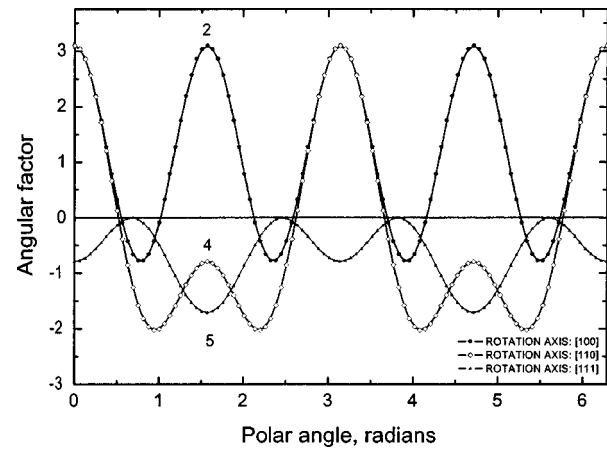


FIG. 3. Angular factor $A(\omega)$ Eq. (10) against the polar angle of rotation about a fixed axis: [100] (black dots), [110] (open squares), [111] (open circles). Points marked by numerals correspond to the curves shown in Fig. 1.

ries expansion of Ewald's potential Eq. (3) in powers of the distance r_{ij} between charges is of the fourth order; hence the pair Coulomb energy can be written as

$$\Phi^{(C)}(r_{ij}, \omega) = \Phi^{(C)}(r_{ij}) \left(1 + A(\omega) \left(\frac{r_{ij}}{L} \right)^5 + \dots \right), \quad (9)$$

where $\Phi^{(C)}(r_{ij})$ is the pre-averaged potential Eq. (6) and $\omega = \{\vartheta, \psi\}$ are two angles determining the orientation of the rotation axis. We performed numerical computations of the angular and distance dependence of Ewald interaction energy and found out that its deviation from the pre-averaged potential Eq. (6), in accordance with Eq. (9), is precisely proportional to the fifth power of distance. Consequently, the distance dependence of the quantity

$$A = \left(\frac{\Phi^{(C)}(r_{ij}, \omega) - \Phi^{(C)}(r_{ij})}{\Phi^{(C)}(r_{ij})} \right) \left(\frac{L}{r_{ij}} \right)^5, \quad (10)$$

is very weak: $A \approx A(\omega)$.

The value of angular factor $A(\omega)$ is shown in Fig. 3 as a function of the polar angle for three directions [100], [110], and [111]. The absolute value of the periodicity artifacts is shown in Fig. 4. For illustration purposes it is more convenient to express the ratio r/L through the number of ions N in the cell, and two reduced quantities: The number density $n^* = a^3(N/L^3)$, and interionic distance $r^* = r/a$, using the characteristic ionic size a

$$\left(\frac{r}{L} \right)^3 = (r^*)^3 \frac{n^*}{N}. \quad (11)$$

If a is the sum of ionic radii, the value of n^* is approximately the same for all molten salts at the melting temperature: $n^* \approx 0.72$. Figure 4 shows the maximum relative deviation

$$\Delta_{\max} = \frac{\Phi^{(C)}(r_{ij}, \omega_{\max}) - \Phi^{(C)}(r_{ij})}{\Phi^{(C)}(r_{ij})}, \quad (12)$$

as a function of N and r^* expressed according to Eqs. (10) and (11). At $r^* = 1$ (approximately the first anion-cation co-

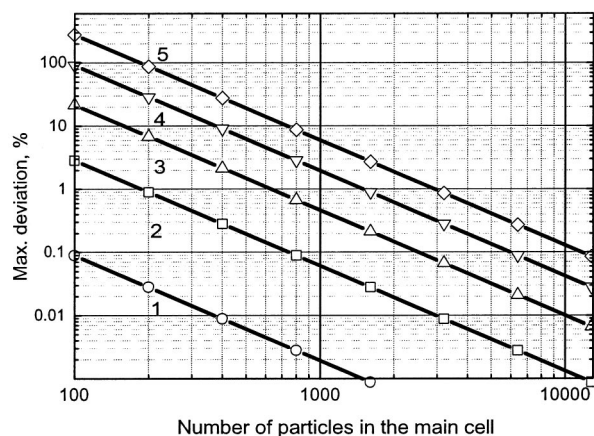


FIG. 4. Effect of periodicity imposed by the Ewald's scheme. Δ_{\max} Eq. (12) at different distances between ions vs the number of ions of the main cell. Numeral labels are interionic distances r^* in units of ionic radii as in Eq. (11).

ordination sphere), the periodicity artifacts are almost negligible even for a relatively small number N of ions in the cell, but at larger distances they become essential for values of N characteristic for real simulations.^{12,13}

IV. CONCLUSION

A method is proposed to simplify the Ewald summation procedure to calculate Coulomb interactions in condensed ionic systems. The method, essentially based on pre-averaging the pair interaction potential over all spatial directions, leads to an energy formulation which is particularly well manageable in computer simulations, avoiding unnecessary computations of nonphysical boundary conditions. Application shows that this method is very effective as well as numerically robust, even for less favorable cases of ionic systems with pronounced nonuniform charge distribution. The dependence of the processor load upon the number of

particles within this approach is the same $O(N^2)$ as in the original Ewald method, but the complexity is incomparably less. We compared the processor time required for computation of the Coulomb energy using the standard Ewald method (convergence parameter: $\delta=4.786$, limit of summation in the reciprocal space: $\max |\mathbf{n}|=30$) to that needed in the proposed approach. A gain factor of approximately 5×10^4 was found. This seems to be large enough to not invoke additional, more sophisticated approaches (see, for instance, Refs. 8 and 9), at least in simulations of Coulomb fluids with a few thousand charged particles in the main cell.

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