

Taming the Ewald Sum in the Computer Simulation of Charged Systems

D. J. ADAMS AND G. S. DUBEY

Department of Chemistry, The University, Southampton, SO9 5NH, United Kingdom

Received May 15, 1986; revised December 12, 1986

The approximation of the Ewald summation for the potential energy of a system of charges with periodic boundary conditions, as used in the computer simulation methods of Monte Carlo and molecular dynamics, is discussed. Isotropic approximations are presented for calculations at low charge density, and systematic approximation using Cubic Harmonics is advanced as the best means for a more accurate approximation. The case of the potential energy of a periodic system of point dipoles is discussed and compared with the reaction-field method and with Ladd's summation. © 1987 Academic Press, Inc

1. INTRODUCTION

Periodic boundary conditions (PBC) are an essential feature of most computer simulation studies of condensed matter using Monte Carlo or molecular dynamics. The PBC remove unwanted surfaces and enable a small number of particles to simulate a portion of an infinitely large system. The presence of charges, whether, for example, as ions or as a charge distribution on a neutral molecule, then presents a problem. The interaction between a pair of charges falls away only as $1/r$ so that more distant periodic images can make a substantial contribution to the net energy of a charge and to the forces acting on it. This problem is acute for dense, highly charged systems such as molten salts and for polar dielectrics. Though a number of ways of summing the charge–charge (or dipole–dipole, etc.) interactions has been proposed, the only satisfactory method has proved to be the Ewald sum [1]. This exploits the periodicity of the lattice of charges, created by the PBC, to obtain an expression for the electrostatic energy in the form of two rapidly convergent summations, one in real space and the other in reciprocal lattice space. There have been many derivations since Ewald's original work, that of Tosi [2] we find particularly clear.

For our purposes it is convenient to express the electrostatic energy per cell of a system of N point charges, $\{q_i\}$, with PBC as

$$U = \frac{1}{2} \sum_{i=1}^N q_i^2 s + \sum_{i=1}^{N-1} q_i \sum_{j>1}^N q_j \psi(\mathbf{r}_{ij}), \quad (1)$$

where $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$.

The term $q_i^2 S$ is the energy of the interaction between charge i and all its own periodic images; S is generally known as the "self term." $\psi(\mathbf{r})$ is an *effective* pair potential which is anisotropic and has the symmetry of the PBC. The Ewald sum gives, where here and throughout this paper \mathbf{r} is expressed in units of cell length:

$$\begin{aligned} \psi(\mathbf{r}) = & \sum_{\mathbf{n}} \frac{\operatorname{erfc}(\alpha |\mathbf{r} - \mathbf{n}|)}{|\mathbf{r} - \mathbf{n}|} - \frac{\pi}{\alpha^2 \Delta} \\ & + \sum_{\mathbf{k} \neq 0} \frac{\exp(-\pi^2 k^2 / \alpha^2)}{\Delta \pi k^2} \cos(2\pi \mathbf{k} \cdot \mathbf{r}). \end{aligned} \quad (2)$$

The $\{\mathbf{n}\}$ are the set of translation vectors of the PBC, Δ is the volume of the periodic cell, and the $\{\mathbf{k}\}$ are the set of reciprocal lattice vectors of the PBC. The effective potential $\psi(\mathbf{r})$ is independent of the adjustable parameter α . In practice α must usually be chosen with care as it determines the rates of convergence of the two summations. The self term is given by

$$S = \lim_{\mathbf{r} \rightarrow 0} \psi(\mathbf{r}) - 1/r. \quad (3)$$

When the system of charges is not neutral overall then the Ewald sum gives the energy of the charges in a uniform, neutralizing background so that, for example, Eqs. (1)–(3) can be used for the one-component plasma (OCP) without modification. Note that when the system *is* neutral then the second term in (2), $-\pi/\alpha^2 \Delta$, cancels out when summed to get U . It is frequently omitted altogether as in, for example, Kittel's [3] derivation of the Ewald sum.

DeLeeuw *et al.* [4] have shown that a careful derivation in which the PBC are constructed layer by layer of cells to form a sphere in vacuum, which is then allowed to become infinitely large, produces another term to add to Eq. (1), $|\sum_{i=1}^N q_i \mathbf{r}_i|^2 2\pi/3\Delta$, which is proportional to the net dipole moment of the periodic cell squared. They show that this term arises in other derivations also if they are performed correctly. This additional term is the extrinsic potential of the periodic system [5].

Equation (1) as given is called the intrinsic potential of the periodic system. It corresponds to the periodic cell being a portion of a sphere of infinite size surrounded by a perfect conductor, the "tin-foil" boundary condition of classical electrostatics.

This paper is concerned with the calculation of $\psi(\mathbf{r})$ and its gradient in Monte Carlo and molecular dynamics computer simulations. Four distinct approaches to implementing the Ewald sum have been used. The most sophisticated is the p^3m method of Hockney and colleagues [6]. This puts the bulk of the calculation into the reciprocal lattice sum which is evaluated by fast Fourier transform. To do this it is first necessary to disperse the charges onto a coarse regular grid. Its most suitable

application is to very large two-dimensional systems such as the simulation of galaxies.

The most popular method is the direct evaluation of the two summations. The real and reciprocal lattice summations are separately evaluated with appropriate truncations. The reciprocal lattice summation is much reduced by the use of the relationship [7]

$$\begin{aligned} \cos(2\pi\mathbf{k} \cdot \mathbf{r}_{ij}) &= \sin(2\pi\mathbf{k} \cdot \mathbf{r}_i) \cos(2\pi\mathbf{k} \cdot \mathbf{r}_j) \\ &\quad - \cos(2\pi\mathbf{k} \cdot \mathbf{r}_i) \sin(2\pi\mathbf{k} \cdot \mathbf{r}_j). \end{aligned} \quad (4)$$

Nevertheless the accuracy of the summation only increases slowly with increasing numbers of reciprocal lattice vectors, and improved accuracy must be balanced, with diminishing returns, against extra computing time. The parameter α has to be set with some care for best accuracy and may need to be adjusted for each individual calculation.

A third method is to interpolate $\psi(\mathbf{r})$ from a three-dimensional table, using the high symmetry of the cube to reduce the size of the table required [7]. Very good accuracy can be achieved [8], and this is a particularly attractive method for Monte Carlo which requires only $\psi(\mathbf{r})$ and not $\nabla\psi(\mathbf{r})$.

The fourth method is to approximate $\psi(\mathbf{r})$ by a three-dimensional polynomial expansion, or some similar function of x , y , and z . As far as we are aware this approach has only been applied to the study of the OCP by Monte Carlo, beginning with the pioneering work of Brush *et al.* [9]. However, it may equally well be applied to other charged systems using either Monte Carlo or molecular dynamics, and also to charge-dipole, dipole-dipole, and other electrostatic interactions.

This paper is devoted to the implementation of the Ewald sum in the form of such expansions. The main reason for our interest was that it offers a simple means of performing the Ewald sum on a parallel processor, in our case the ICL DAP. However, it offers a number of advantages which make it the method of choice for a much wider range of machines. Most obvious are the shortness, the simplicity, and the economy of the code, and also the ease of "vectorization" for such processors as the Cray 1 and Cyber 205. A variety of expressions are available, offering a wide range of closeness-of-fit to the exact Ewald sum. It is a relatively easy matter to choose the appropriate expression as each has a known RMS error; there are no truncation limits or adjustable parameters to be set. Also, because the Ewald sum is expressed in the form of a well-defined pair potential, a problem with the evaluation of the currents required for the correlation functions used in Kubo formulae for transport coefficients is avoided [10].

In the next section we discuss *isotropic* approximations to the Ewald sum, starting with the very simplest and going on to present expressions which compare favourably with any in the literature. Section 3 is devoted to the more accurate approximation of the Ewald potential and its systematic expansion in solutions to Laplace's equation. Once a suitable approximation has been found for the Ewald

potential of a system of charges it is straightforward to obtain, by differentiation, expressions for the forces on charges, for charge-dipole and dipole-dipole interactions, etc. In Section 4 we illustrate this by deriving expressions for the potential of a system of point dipoles.

2. SIMPLE, ISOTROPIC APPROXIMATIONS

2.1. Nearest Images and PBC

The exact Ewald $\psi(\mathbf{r})$ has the periodicity of the PBC, but the expressions used to approximate it are not periodic and they will be valid only for \mathbf{r} within a periodic cell centred on the origin. It is therefore necessary to use not \mathbf{r}_{ij} but

$$\mathbf{r}'_{ij} = \mathbf{r}_i - \mathbf{r}_j - \mathbf{n}, \quad (5)$$

where the PBC lattice vector \mathbf{n} is chosen to minimize $|\mathbf{r}'_{ij}|$. This is, of course, the normal procedure in calculating the short-ranged interactions, and \mathbf{r}'_{ij} is called the "nearest-image" or "minimum-image" vector. The leading term in the real-space summation of (2) occurs for the minimum value of $|\mathbf{r} - \mathbf{n}|$ and for $\alpha |\mathbf{r} - \mathbf{n}| \rightarrow 0$ we recover $1/|\mathbf{r} - \mathbf{n}|$, the direct Coulomb potential. The simplest approximation to $\psi(\mathbf{r}_{ij})$ is thus

$$\psi_0(\mathbf{r}_{ij}) = 1/|\mathbf{r}'_{ij}| + S \quad (6)$$

which has the important property that it is exact as $|\mathbf{r}'_{ij}| \rightarrow 0$. When the system of charges is neutral then the self-term makes no net contribution to the total energy and we may use

$$U = \sum_{i=1}^{N-1} q_i \sum_{j>i}^N q_j / |\mathbf{r}'_{ij}|, \quad (7)$$

the conventional form of the nearest-image summation. It is important to note that the summation must be taken over all pairs of charges in the periodic cell and not truncated at some radius, say one-half the cell length, as is commonly done with short-ranged potentials. Equation (7) has been used in the simulation of the restricted primitive model (RPM) with charges and densities appropriate to aqueous electrolyte solutions [11], the results were found to be number dependent. At higher charge densities Eq. (7) produces unphysical liquid structures [9, 12-14].

The problem with Eq. (7) is that it is not merely approximate, it is also biased: it gives values of U close to the true Ewald result for some configurations and very deviant values for other. Thus with simple cubic PBC it gives very good results for the Madelung constant of the *NaCl* lattice, but can be a factor of four out for the Madelung constant of the *CsCl* lattice [15]! Moreover, the improvement with

increasing number of charges in the periodic cell is slight at best [14, 15], and we cannot recommend the use of Eq. (6) or (7) under any circumstances.

Unphysical liquid structures can result from the use of the nearest-image summation because it favours configurations in which the coions around each ion occupy the corners of the periodic cell rather than an isotropic distribution [14]. One approach to this problem with the corners of the cell is to use a more spherical shape than the cube. The best is the truncated octahedral (TO) [16]. As we shall show, the use of TO PBC can have considerable benefits, but for the particular case of Eq. (7) there is no improvement in the RMS deviation between it and the Ewald sum. Using TO PBC rather than a simple cubic with Eq. (7) does give some improvement nevertheless, but not sufficient that we could ever recommend Eq. (7). Another simple way around the cube-corner effect is to modify the potential to

$$\psi_{\text{SCO}}(\mathbf{r}_y) = \begin{cases} 1/|\mathbf{r}'_y| + S, & |\mathbf{r}'_y| < r_c \\ 1/r_c + S, & |\mathbf{r}'_y| > r_c, \end{cases} \quad (8)$$

where r_c is some cut-off radius, such as half the cell length. This does effect a substantial improvement, but we do not recommend its use because there is an equally simple but very much better approximation to the Ewald sum.

2.2. A Simple Approximation

The Ewald $\psi(\mathbf{r})$ contains a term in r^2 , the only component of $\psi(\mathbf{r})$ which does not satisfy Laplace's equation. The r^2 term is a solution of Poisson's equation; it is the contribution of the uniform, neutralizing charge distribution which the Ewald summation puts around each charge [9, 17]. The addition of a term of this form gives

$$\psi_2(\mathbf{r}) = 1/r + S + A_2 r^2, \quad (9)$$

where it is understood that \mathbf{r} is a nearest-image vector. $\psi_2(\mathbf{r})$ is the simplest approximation to the Ewald sum that we consider usable. The coefficient A_2 may be either the exact value [17], $2\pi/3A$, or adjusted to give the best fit of $\psi_2(\mathbf{r})$ to the true $\psi(\mathbf{r})$.

The various approximations were optimized and tested by finding the RMS deviation and maximum error of the approximation as compared to a highly accurate Ewald summation using a set of 100 to 300 vectors randomly distributed within the periodic cell. For both TO and simple cubic (SC) PBC Eq. (9) gave a roughly tenfold decrease in the RMS error over Eq. (6). The RMS error with TO PBC was insensitive to the value of A_2 and the exact coefficient gave a largest error close to the minimum. Exact values of S and A_2 are included in Table I. With SC PBC the adjustment to $A_2 = 1.38306$ gave a twofold improvement over exact value, though the errors were still slightly larger than with TO PBC.

An effective pair potential of similar form to Eq. (9) has been proposed before

TABLE I
Exact Coefficients in Expansion of the Ewald Sum

| | Simple cubic (SC) | Truncated octahedral (TO) | Rhombic dodecahedral |
|------------------------|-------------------|---------------------------|----------------------------|
| Maximum $ \mathbf{r} $ | $\sqrt{3/2}$ | $\sqrt{5/12}$ | 1/2 |
| A | 1 | 1/2 | 1/4 |
| S | -2.837 297 479 | -3.639 233 450 | -4.584 862 074 |
| A_2 | 2.094 395 102 | 4.188 790 205 | 8.377 580 410 |
| A_4 | 7.770 566 707 | -7.766 151 015 | -18.814 228 83 |
| A_6 | 22.073 177 64 | 209.692 430 9 | -1025.443 397 |
| A_8 | 105.927 025 5 | 248.572 698 7 | 2638.559 709 |
| A_{10} | 358.577 283 0 | -3338.632 307 | -541.599 922 4 |
| A_{12} | 1306.319 992 | -201.029 0 | -114373.134 |
| B_{12} | 558.709 501 3 | 149546.461 7 | 4439199.558 |
| A_{14} | 4861.343 067 | 64371.674 05 | -1.228702912×10^6 |
| A_{16} | 18365.067 71 | -501707.801 1 | 3.338552259×10^6 |
| B_{16} | 59.612 73 | 1073231.871 | 6.746060635×10^6 |
| A_{18} | 69319.501 11 | -817007.031 2 | 4.373749572×10^7 |
| B_{18} | -11189.890 02 | 45191429.79 | -5.912420766×10^9 |
| A_{20} | 263204.159 3 | 12155258.42 | 5.810598389×10^8 |
| B_{20} | 927.917 5 | 24158981.17 | 1.921613232×10^9 |

[15], albeit on the basis of a very different argument. This approximation, called SC2 in Ref. [15], was shown to give comparable results to a direct Ewald summation for the Monte Carlo simulation of the RPM at high charge density. SC2 differs from Eq. (9) in that it has a limiting radius as in Eq. (7). Equation (9) gives smaller deviations from the Ewald sum than SC2.

Brush *et al.* [9] reported that the nearest-image summation, Eq. (6), gave a radial distribution function in agreement with the Ewald summation for the OCP with the coupling constant $\Gamma \lesssim 10$. We have made some Monte Carlo calculations for the OCP with 64 charges in the TO periodic cell. The results for the average energy are given in Table II. Equation (6) contains a systematic deviation from the true $\psi(\mathbf{r})$ that cancels in a neutral system; for the OCP it gives results grossly in error. The radial distribution function from Eq. (6) agrees with a more accurate summation at $\Gamma = 10$, is seriously in error at $\Gamma = 40$, and shows a strange, solid-like packing at $\Gamma = 80$ and above. Equation (9) is dramatically better; the radial distribution function is in good agreement with the more accurate results at $\Gamma = 40$ and at larger values of Γ it shows relatively small deviations. The main defect is that the height of the second peak is underestimated.

However, the results for $\langle U \rangle / NkT$ are still seriously in error with Eq. (9), showing it to be an inadequate approximation for the simulation of the OCP. Equation (9) would, however, be perfectly adequate for neutral systems where the electrostatic interactions do not dominate the structure, such as molecular fluids where the molecules' charge distribution is modelled by a set of point charges. A better

TABLE II
Monte Carlo Results for $\langle U/NkT \rangle$ of the OCP

| Γ | Eq. (6) | Eq. (9) | Eq. (10) | Eq. (18), $l=6$ | Ref. [25] ^a |
|----------|---------|---------|----------|-----------------|------------------------|
| 1.0 | -3.19 | -0.914 | -0.573 | -0.580 | -0.573 |
| 4.0 | -13.39 | -4.277 | -2.909 | -2.941 | -2.927 |
| 10.0 | -34.2 | -11.36 | -7.943 | -8.020 | -7.992 |
| 40.0 | -141. | -47.7 | -34.04 | -34.31 | -34.248 |
| 80.0 | -286. | -96.7 | -70.04 | -69.86 | -69.715 |
| 125.0 | -451. | -151.9 | -112.60 | -110.03 | -109.780 |
| 160.0 | -578. | -195.3 | -144.4 | -141.83 | -141.729 |
| 180.0 | -651. | -220.1 | -165.0 | -159.94 | -159.675 |
| 200.0 | -723. | -244.8 | -183.6 | -178.02 | -177.619 |
| 300.0 | -1086. | -368.1 | -276.8 | -267.94 | -267.243 |

^a Reference [25] calculations used 128 particles with simple cubic PBC, the rest used 64 particles with TO PBC.

approximation is required for strongly polar dielectrics and systems with high charge densities.

2.3. Good, Isotropic Approximations

It has been common in the simulation of ionic glasses, where the charge density is high but the short-ranged interactions may be expected to be more important than the long-ranged part of the Coulombic interaction, to use a simple, isotropic expression in place of the true Ewald summation for reasons of economy. The early, uncritical approach was to use the leading term from the real space sum of Eq. (2) with an arbitrarily chosen value of α [18, 19]. Better attempts at an isotropic approximation to the Ewald summation have since been made [20, 21], with the force set to zero beyond half the (cubic) cell length. Soules [20] has provided separate prescriptions for electrostatic force and energy, suggesting that this approximation would be of general use in molecular dynamics.

Soules's energy approximation returns the best results when used without a truncation at half the cell length and with the correct value of the self term in place of the 0.3049512 factor of his Eq. (4). Even so, it has twice the RMS and maximum deviations of Eq. (9) with optimized A_2 . Optimizing the parameters produced a factor of three improvement, giving as good a fit of an isotropic function to an anisotropic potential as could be expected. A similarly good result was obtained using TO PBC with an RMS error of $\sim \frac{3}{4}$ of that with SC PBC, demonstrating the superiority of the TO periodic cell.

Considerable experimentation was devoted to obtain the best empirical, isotropic expression as an approximation to the Ewald sum, restricting the range of expressions to those which obeyed $\lim_{r \rightarrow 0} \psi(\mathbf{r}) = 1/r + S + O(r^2)$. Our best approximation, balancing closeness-of-fit against brevity, was for TO only

$$\psi(\mathbf{r}) \simeq 1/r + (7.44030r^2 - 19.04297r^6 + S) \exp(r^2). \quad (10)$$

TABLE III
Errors in Various Isotropic Approximations to the Ewald Sum

| Equation | PBC | RMS error | Maximum error |
|--------------------------|-----|-----------|---------------|
| (6) | TO | 0.66 | 1.08 |
| | SC | 0.51 | 0.79 |
| (9), exact A_2 | TO | 0.044 | 0.117 |
| (9), optimum A_2 | SC | 0.061 | 0.193 |
| (10) | TO | 0.0279 | 0.114 |
| (11) | TO | 0.0291 | 0.126 |
| (12) | SC | 0.042 | 0.157 |
| Soules's expression, | TO | 0.0302 | 0.151 |
| Optimized coefficients | SC | 0.041 | 0.149 |
| Soules's expression [20] | SC | 0.131 | 0.416 |

These values of the coefficients apply for the truncated octahedron which fits into a unit cube and thus has a volume of one half. More elaborate expressions gave only marginally better fits. Equation (10) is an improvement over Soules's expression in two ways. First, it is a significantly better fit, as the results in Table III show. Second, it is shorter, requiring only 11 operations as against 16 for Soules's expression. Equation (10) is particularly suitable for the DAP computer which, in matrix mode, computes an exponential or square root in roughly the same time as a simple multiplication [22].

On other machines the exponential is a problem, unless of course Eq. (10) is used in tabulated form. For TO PBC the even shorter expression,

$$\psi(\mathbf{r}) \simeq 1/r + 3.53873r^2 + 8.33958r^4 - 28.51289r^6 + S \quad (11)$$

is also better than the Soules form. With SC PBC the form of Eq. (10) does not give a particularly good fit. The SC PBC version of Eq. (11) is

$$\psi(\mathbf{r}) \simeq 1/r + 2.75022r^2 - 2.94414r^4 + 0.86910r^6 + S. \quad (12)$$

This is only marginally inferior to our optimized version of Soules's expression.

The results in Table II show that Eq. (10) gives good results for the OCP with $\Gamma \lesssim 80$, and is therefore a considerable improvement over Eq. (9). At higher Γ the results with Eq. (10) are not so satisfactory and, particularly in the solid phase, the peaks in $g(r)$ are much higher and narrower than they should be. While Eq. (9) somewhat understates the structure, Eq. (10) considerably overemphasizes it. Thus we may expect Eqs. (10)–(12) to have the same range of application as Eq. (9) but to give a much better approximation to the true Ewald summation in that range. At high enough charge densities a systematic bias may give a substantial distortion of the structure of the simulated material.

The OCP is unusual in having no short-range interactions so that its structure is entirely determined by the electrostatic interactions. A more typical system is the RPM and some Monte Carlo results have been obtained for this, using some of our approximations, for comparison with the results of Larsen [23]. The parameters of this system are the reduced density, $\rho^* = \sigma^3 N/V$, where σ is the ionic diameter and the charge coupling parameter, $\Gamma = q^2/akT$, which is defined exactly as for the OCP, q is the charge and $a = (3V/4\pi N)^{1/3}$. Larsen [23] reported no noticeable number dependence and the present results, obtained with 64 ions in TO PBC and given in Table IV, bear this out. For $\Gamma \leq 10$ the results for $\langle U/NkT \rangle$ using Eq. (10) are not significantly different from those obtained with more accurate approximations, and Eq. (10) is clearly adequate for $\Gamma \leq \sim 20$ for most purposes. The radial distribution functions (RDF's) show that Eq. (10) becomes less adequate with increasing density. At the lowest density, $\rho^* = 0.2861$, all the RDFs show satisfactory agreement with results from an accurate summation, while at the

TABLE IV
Monte Carlo Results for $-\langle U/NkT \rangle$ of the RPM

| ρ^* | Γ | Eq. (10) | Eq. (18), $l=6$ | Eq. (13) | Ref. [23] ^a |
|----------|----------|----------|-----------------|----------|------------------------|
| 0.2861 | 2.0 | 0.838 | 0.841 | 0.843 | 0.839 |
| | 5.0 | 2.471 | 2.457 | 2.468 | 2.467 |
| | 10.0 | 5.487 | 5.451 | 5.443 | 5.465 |
| | 20.0 | 12.09 | 11.96 | 12.00 | 11.95 |
| | 50.0 | 33.8 | 33.33 | 33.3 | 33.62 |
| | 100.0 | 70.00 | 68.5 | 68.66 | 70.16 |
| 0.4788 | 2.0 | 0.770 | 0.771 | 0.769 | 0.783 |
| | 5.0 | 2.236 | 2.245 | 2.235 | 2.226 |
| | 10.0 | 4.946 | 4.897 | 4.910 | 4.876 |
| | 20.0 | 10.78 | 10.565 | 10.595 | 10.53 |
| | 50.0 | 30.73 | 28.82 | 28.75 | 28.61 |
| | 100.0 | 62.73 | 60.13 | 60.06 | 59.91 |
| 0.66902 | 2.0 | 0.736 | 0.748 | 0.722 | 0.756 |
| | 5.0 | 2.109 | 2.10 | 2.087 | 2.114 |
| | 10.0 | 4.594 | 4.58 | 4.53 | 4.601 |
| | 20.0 | 10.4 | 10.00 | 9.88 | 9.87 |
| | 50.0 | 27.5 | 26.55 | 26.44 | 26.54 |
| | 100.0 | 56.9 | 54.88 | 54.71 | 54.93 |
| 0.75344 | 2.0 | 0.726 | 0.751 | 0.713 | 0.711 |
| | 5.0 | 2.076 | 2.073 | 2.058 | 2.067 |
| | 10.0 | 4.44 | 4.60 | 4.410 | 4.511 |
| | 20.0 | 10.63 | 10.12 | 9.67 | 9.58 |
| | 50.0 | 27.42 | 26.08 | 25.82 | 25.71 |
| | 100.0 | 55.1 | 53.6 | 53.21 | 53.26 |

^a Reference [23] calculations used 216 ions with simple cubic PBC, the rest used 64 ions with TO PBC.

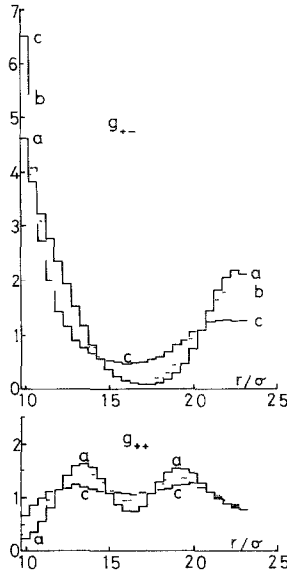


FIG. 1. Radial distribution functions for the RPM with $\rho^* = 0.7534$, $\Gamma = 20$. These show the largest deviations of all the state points covered in Table IV: (a) Eq. (10), (b) Eq. (18), $l = 6$; (c) Eq. (13)—an accurate summation.

highest density, $\rho^* = 0.7534$, the RDFs are satisfactory only for $\Gamma = 5$, and 10. Note that the error does not necessarily increase monotonically with Γ , the worst RDFs were at $\rho^* = 0.7534$, $\Gamma = 20$. These are shown in Fig. 1.

3. ACCURATE APPROXIMATIONS

There is a clear need in many applications for a more accurate approximation than that provided by Eqs. (10)–(12). To obtain this $\psi(\mathbf{r})$ must be approximated by functions of cubic symmetry. An expansion of $\psi(\mathbf{r})$ in powers of r in any given direction converges rapidly, at least with TO PBC, and truncation at r^{12} gives an RMS error of only $\sim 10^{-8}$. The coefficients in this expansion depend on the direction of \mathbf{r} and can be approximated by angular functions of cubic symmetry, such as

$$\begin{aligned} (x^k + y^k + z^k)/r^k, & \quad k \geq 4, \\ (xyz)^k/r^{3k}, & \quad k \geq 4, \end{aligned}$$

and

$$(x^k y^k + y^k z^k + z^k x^k)/r^{2k}, \quad k \geq 8,$$

where x , y , and z are the Cartesian components of \mathbf{r} . Thus an empirical form for $\psi(\mathbf{r})$ might be

$$\psi(\mathbf{r}) \simeq 1/r + S + A_2 r^2 + \sum_{n=4,6}^{12} \sum_{k=0,1}^{k_n} A_{nk} F_k r^n, \quad (13)$$

where the F_k are angular functions such as those given above and $F_0 = 1$.

An approximation of this form was made and sets of coefficients A_{nk} were optimised for each value of n . With 53 coefficients the RMS error was $\sim 2 \times 10^{-5}$. This approximation was used to obtain one of the sets of results given in Table IV and in Fig. 1. Much the same accuracy, however, can be obtained with a considerably shorter expression and we do not recommend the approach of Eq. (13).

Apart from the early work of Brush *et al.* [9] there have been two anisotropic approximations to $\psi(\mathbf{r})$ reported: that of Hansen [24] and that of Slattery *et al.* [25]. Hansen split $\psi(\mathbf{r})$ into an isotropic part and a part with cubic symmetry. The isotropic part was given by the leading term of the real-space sum in Eq. (2) with $\alpha = \pi^{1/2}$. With this particular value of α Hansen's approximation contains the exact value of A_2 . Slattery *et al.* [25] mistakenly claim the $A_2 r^2$ term to be missing in Hansen's approximation. Hansen's program evaluated the isotropic part by table look-up, but this can be replaced by an accurate approximation to the complementary error function [26] when a vectorizable code is required. The part with cubic symmetry Hansen describes as "an 'optimised' expansion in Kubic harmonics," He used the first three nontrivial angular functions multiplied by terms such as $e^{-\pi r^2} (d_8 r^8 + d_{10} r^{10} + d_{12} r^{12})$ with a total of 15 optimised coefficients and the exact self term.

Using a 5-coefficient approximation for the complementary error function we obtain an RMS error of 7×10^{-4} and a maximum error of 1.6×10^{-3} . The optimization of Hansen's approximation for TO boundary conditions has not been done, but there can be little doubt that rather smaller errors would be obtained.

Hansen's approach is an efficient one, with a small error for the length of the computer code. However, an even better approach is that provided by Slattery *et al.* [25], who used a summation over solutions to Laplace's equation with cubic symmetry. This approach is superior for two reasons, one practical and the other aesthetic. First, it gives even smaller errors for a given length of code and, second, it provides a $\psi(\mathbf{r})$ which, apart from the $A_2 r^2$ term, is an exact solution of Laplace's equation.

To find all the cubic solutions of Laplace's equation of a given power, n , a methodical search was made. All terms of the form $x^a y^b z^c r^p$ were considered where a , b , c , and p are zero or positive even integers and $n = a + b + c + p$. Polynomials of cubic symmetry were constructed by linear combination of these, for example $(x^2 y^4 + y^2 z^4 + z^2 x^4 + x^4 y^2 + y^4 z^2 + z^4 x^2)$. Then substitution using $r^2 = x^2 + y^2 + z^2$ was used to eliminate those polynomials which were linear combinations of others, for example,

$$(xyz)^2 = \frac{1}{6} r^6 - \frac{1}{2} r^2 T_4 + \frac{1}{3} T_6 \quad (14)$$

where

$$T_n = x^n + y^n + z^n. \quad (15)$$

Those polynomials requiring the least computation were chosen as the minimum set. Finally, combinations of the minimum set were constructed to satisfy Laplace's equation. Table V lists a complete basis set up to $n = 20$, these are the α -set of the Cubic Harmonics of Von der Lage and Bethe [27]. For $n < 12$ there is one solution to Laplace's equation for each n . For $n = 12$ there are *two* solutions of Laplace's equation and both are needed. One, like the lower order solutions, is a combination of Legendre polynomials, $P_{12}(x) + P_{12}(y) + P_{12}(z)$. For a second solution Slattery *et al.* [25] used

$$\begin{aligned} & \text{Re}[(x + iy)^{12} + (y + iz)^{12} + (z + ix)^{12}] \\ &= 2T_{12} - 66(x^{10}(y^2 + z^2) + y^{10}(z^2 + x^2) + z^{10}(x^2 + y^2)) \\ & \quad + 495(x^8(y^4 + z^4) + y^8(z^4 + x^4) + z^8(x^4 + y^4)) \\ & \quad - 924(x^6y^6 + y^6z^6 + z^6x^6). \end{aligned} \quad (16)$$

This must have made a substantial contribution to the computing time of their calculations, particularly as the calculation of these cross terms could not take full advantage of the parallelism of the floating point systems processor they used. The second solution that we have obtained, KHb_{12} of Table V, is far more computationally convenient as the only term in it additional to those needed for KH_{12} is simply $(xyz)^4$. KHb_{12} is not a new, independent solution of Laplace's equation but is related by

$$\begin{aligned} & \text{Re}[(x + iy)^{12} + (y + iz)^{12} + (z + ix)^{12}] \\ &= 1025(KH_{12}) - 7128(KHb_{12}) \end{aligned} \quad (17)$$

There are two solutions each to Laplace's equation at $n = 16, 18$, and 20 . We have not explored beyond $n = 20$. Slattery *et al.* [25] did not use any other second solutions, but for simple cubic PBC their contribution to the Ewald summation is very small.

The systematic expansion of the Ewald sum is thus

$$\begin{aligned} \psi_l(\mathbf{r}) &= 1/r + S + A_2 r^2 \\ & \quad + \sum_{n=4,6}^l (A_n KH_n(\mathbf{r}) + B_n KHb_n(\mathbf{r})) \end{aligned} \quad (18)$$

for $4 \leq l \leq 20$, l even, and $B_n = 0$ except for $n = 12, 16, 18$, and 20 . Successive terms get longer and it is necessary to weigh the required accuracy against the computing time required. As a rough measure of this a count has been made of the number of binary operations in the Fortran code for each value of l . The exact coefficients in

TABLE V
 Cubic Harmonic Solutions to Laplace's Equation:
 A Complete Basis Set Up to $n=20$

| | |
|------------|---|
| KH_4 | $T_4 - \frac{3}{5}r^4$ |
| KH_6 | $T_6 - \frac{15}{11}r^2T_4 + \frac{39}{77}r^6$ |
| KH_8 | $T_8 - \frac{28}{13}r^2T_6 + \frac{14}{13}r^4T_4 - \frac{7}{39}r^8$ |
| KH_{10} | $T_{10} - \frac{45}{19}r^2T_8 + \frac{630}{323}r^4T_6 - \frac{210}{323}r^6T_4 + \frac{252}{3553}r^{10}$ |
| KH_{12} | $T_{12} - \frac{66}{23}r^2T_{10} + \frac{495}{161}r^4T_8 - \frac{660}{257}r^6T_6 + \frac{2475}{7429}r^4T_4 - \frac{2475}{96577}r^{12}$ |
| KHb_{12} | $(xyz)^4 + \frac{6}{115}r^2T_{10} - \frac{41}{322}r^4T_8 + \frac{128}{1311}r^6T_6 - \frac{160}{7429}r^8T_4 - \frac{2629}{2897310}r^{12}$ |
| KH_{14} | $T_{14} - \frac{91}{27}r^2T_{12} + \frac{1001}{225}r^4T_{10} - \frac{1001}{345}r^6T_8 + \frac{1001}{1035}r^8T_6 - \frac{1001}{6555}r^{10}T_4 + \frac{286}{32775}r^{14}$ |
| KH_{16} | $T_{16} - \frac{120}{31}r^2T_{14} + \frac{5460}{899}r^4T_{12} - \frac{40040}{8091}r^6T_{10} + \frac{2002}{899}r^8T_8 - \frac{56056}{103385}r^{10}T_6$ $+ \frac{4004}{62031}r^{12}T_4 - \frac{1001}{351509}r^{16}$ |
| KHb_{16} | $(x^8y^8 + y^8z^8 + z^8x^8) + \frac{4}{31}r^2T_{14} - \frac{84}{29}r^4(xyz)^4 - \frac{182}{896}r^4T_{12}$ $- \frac{1316}{4495}r^6T_{10} + \frac{700}{899}r^8T_8 - \frac{9996}{20677}r^{10}T_6 - \frac{1190}{20677}r^{12}T_4 + \frac{23701}{1757545}r^{16}$ |
| KH_{18} | $T_{18} - \frac{153}{35}r^2T_{16} + \frac{612}{77}r^4T_{14} - \frac{2652}{341}r^6T_{12} + \frac{3978}{899}r^8T_{10} - \frac{1326}{899}r^{10}T_8$ $+ \frac{6188}{22475}r^{12}T_6 - \frac{2652}{103385}r^{14}T_4 + \frac{1768}{1964315}r^{16}$ |
| KHb_{18} | $(xyz)^0 - \frac{3}{56}r^2(x^8y^8 + y^8z^8 + z^8x^8) + \frac{3}{112}r^2T_{16} - \frac{9}{77}r^4T_{14} + \frac{3}{31}r^6(xyz)^4$ $+ \frac{133}{682}r^6T_{12} - \frac{657}{4495}r^8T_{10} + \frac{275}{7192}r^{10}T_8 + \frac{56}{13485}r^{12}T_6 - \frac{8}{20677}r^{14}T_4 - \frac{71423}{94287120}r^{18}$ |
| KH_{20} | $T_{20} - \frac{190}{39}r^2T_{18} + \frac{4845}{481}r^4T_{16} - \frac{38760}{3367}r^6T_{14} + \frac{3230}{407}r^8T_{12}$ $- \frac{3876}{1147}r^{10}T_{10} + \frac{29070}{33265}r^{12}T_8 - \frac{12920}{99789}r^{14}T_6 + \frac{323}{33265}r^{16}T_4 - \frac{323}{1164205}r^{20}$ |
| KHb_{20} | $(x^{10}y^{10} + y^{10}z^{10} + z^{10}x^{10}) + \frac{50}{13}r^2(xyz)^6 - \frac{5}{39}r^2T_{18} - \frac{825}{962}r^4(x^8y^8 + y^8z^8 + z^8x^8)$ $+ \frac{1335}{1924}r^4T_{16} - \frac{5370}{3367}r^6T_{14} + \frac{525}{481}r^8(xyz)^4 + \frac{9980}{5291}r^8T_{12} - \frac{15627}{14911}r^{10}T_{10} + \frac{35595}{432419}r^{12}T_8$ $+ \frac{54660}{432419}r^{14}T_6 - \frac{8199}{864838}r^{16}T_4 - \frac{1492591}{181615980}r^{20}$ |

the expansion of $\psi(\mathbf{r})$ have been calculated for SC, TO, and rhombic dodecahedral PBC to nine significant figures and these are given in Table I. These coefficients are for \mathbf{r} measured in units of cell length, so that for all three boundary conditions $|x|$, $|y|$, and $|z| < \frac{1}{2}$, and the expansions are rapidly convergent despite the high values of the coefficients. Additionally, values of coefficients have been adjusted to improve the RMS error and selected tables of these optimized coefficients are given in Tables VI and VII. For SC PBC the improvement on optimization is very considerable. Slattery *et al.* [25] took their optimized expansion up to $l = 22$ and so it is both longer and more accurate than any of our results in Fig. 2. Note that Hansen's approximation [24] lies slightly above the line of optimized expansions and also that the best isotropic approximations, Eqs. (10)–(12), are considerably more economic than $\psi_4(\mathbf{r})$ with comparable accuracy.

Reducing the RMS error by a factor of ten increases the computing time for $\psi(\mathbf{r})$ by about two and a half times. A highly accurate approximation can therefore be expensive. For many purposes ψ_6 with TO PBC or ψ_8 with SC PBC should be adequate. Some Monte Carlo calculations have been made for both the OCP and RPM using ψ_6 with 64 charges in TO PBC, the results are in Tables II and IV and in Fig. 1. Except for the most precise work ψ_6 is shown to be perfectly adequate over the whole range of these data. Where great precision does seem required, for example, in the location of the phase transition of the OCP [8, 25] then, obviously, a more accurate expansion is required. However, there is no point in using so accurate an expression that its errors are dwarfed by those inherent in the use of

TABLE VI
Optimized Coefficients for Eq. (18) Using Simple Cubic PBC

| l | 8 | 10 | 12 | 16 | 20 |
|--------------|----------------------|----------------------|----------------------|----------------------|----------------------|
| A_2 | 2.094395 | 2.094395 | 2.094395 | 2.094395 | 2.0943951 |
| A_4 | 7.511320 | 7.704548 | 7.749439 | 7.770567 | 7.7705667 |
| A_6 | 17.07159 | 20.56331 | 21.58047 | 22.07318 | 22.073178 |
| A_8 | 60.53989 | 86.42400 | 97.44609 | 105.9270 | 105.92703 |
| A_{10} | | 181.0800 | 265.0164 | 352.1079 | 358.57728 |
| A_{12} | | | 510.8133 | 1247.168 | 1292.8374 |
| B_{12} | | | 1917.2538 | 138.637 | 590.2863 |
| A_{14} | | | | 3462.959 | 4736.2504 |
| A_{16} | | | | 8003.836 | 15877.120 |
| B_{16} | | | | 5424.535 | -362.617 |
| A_{18} | | | | | 48768.946 |
| B_{18} | | | | | -164519.278 |
| A_{20} | | | | | 95717.5750 |
| B_{20} | | | | | -32.0248 |
| RMS Error | 2.4×10^{-3} | 6.2×10^{-4} | 2.2×10^{-4} | 3.2×10^{-5} | 5.2×10^{-6} |

TABLE VII
Optimized Coefficients for Eq. (18) Using Truncated Octahedral PBC

| l | 6 | 8 | 10 | 14 | 18 |
|-----------|--------------------|----------------------|----------------------|----------------------|----------------------|
| A_2 | 4.188790 | 4.188790 | 4.188790 | 4.188790 | 4.188790 |
| A_4 | -7.762017 | -7.595989 | -7.77621 | -7.766151 | -7.7661510 |
| A_6 | 194.329 | 199.285 | 207.362 | 209.692 | 209.6924 |
| A_8 | | 208.641 | 251.058 | 248.573 | 248.5727 |
| A_{10} | | | -2680.16 | -3273.93 | -3335.138 |
| A_{12} | | | | -274.149 | -192.134 |
| B_{12} | | | | 132597.592 | 148881.138 |
| A_{14} | | | | 49612.06 | 62622.301 |
| A_{16} | | | | | -438790.41 |
| A_{18} | | | | | -551456.9 |
| B_{18} | | | | | 33332228.2 |
| RMS error | 4×10^{-3} | 1.3×10^{-3} | 3.3×10^{-4} | 2.5×10^{-5} | 1.9×10^{-6} |

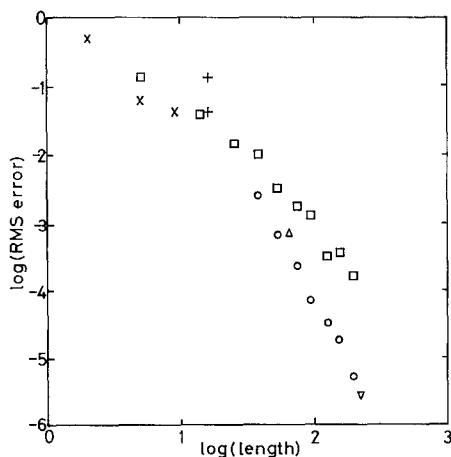


FIG. 2. Log-log plot of error vs length of expression (as number of binary operations) for various approximations using simple cubic periodic boundary conditions: +, Soules's approximation [20]; Δ , Hansen's approximation [24]; \times , isotropic approximations, Eqs. (6), (9), and (12); \square , expansion in Kubic Harmonics with exact coefficients; \circ , expansion in Kubic Harmonics with optimized coefficients; ∇ , Slater *et al.* expansion [25].

periodic boundary conditions: it is not the periodic system that is the ultimate goal but the ordinary bulk material. It is precisely in such cases as the location of the solid/liquid phase transition that the periodic cell, its volume, its shape, and the exact number of particles can have a strong influence on the results. In such cases it is invariably better to use a large number of particles, even at the sacrifice of having to use a less accurate expression for $\psi(\mathbf{r})$.

A comparison of Figs. (2) and (3) shows the advantage of using TO boundary conditions over simple cubic. In most cases the extras involved in calculating the nearest-image vector are easily defrayed by improved precision of the approximation to $\psi(\mathbf{r})$. The RMS errors are those found in the calculation of the energy of a pair of unit charges placed randomly in the periodic cell. When comparing TO with SC one should compare two cells of the same volume, and the TO errors are then reduced by a factor of $2^{1/3}$. The exact expansion of $\psi(\mathbf{r})$ with rhombic dodecahedral PBC is comparable in accuracy to that with TO PBC, and the more complicated rhombic dodecahedral PBC are unlikely to give any worthwhile improvement over truncated octahedral.

When using any of the approximations in this paper with molecules, every charge on each molecule should interact with the nearest image of every other charge in the system. The alternative strategy of computing nearest-image distances based on the distance between molecular centres is not likely to introduce severe errors though. The direct, $1/r$, interaction between each charge and the other charges on the same molecule may be subtracted to obtain the intramolecular interaction: the interaction of a molecule with its own images is then correctly included as an intramolecular interaction. Additional considerations apply with polar molecules and this is discussed at the end of the next section.

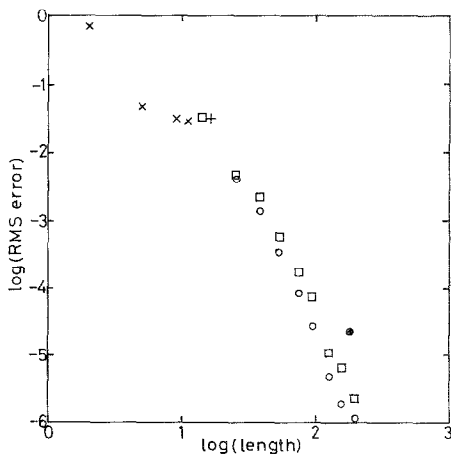


FIG. 3. Log-log plot of error vs length of expression for various approximations using truncated octahedral periodic boundary conditions: same key as for Fig. 2, with ●, Eq. (13) with 53 coefficients and x, isotropic approximations, Eqs. (6), (9), (10), and (11).

4. DIPOLE-DIPOLE INTERACTIONS

It is a most useful feature of all the approximations for $\psi(\mathbf{r})$ advanced in this paper, Eqs. (9)–(12) and (18), that they are readily differentiated to obtain expressions for the forces between the ions needed for molecular dynamics simulation. If the potential of a charge, q , placed at the origin is $q\psi(\mathbf{r})$, then the electric field at \mathbf{r} is $-\nabla q(\psi(\mathbf{r}))$. The energy of a point dipole in an electric field is $-\boldsymbol{\mu} \cdot \mathbf{E}$, so the energy between one dipole, $\boldsymbol{\mu}$, and one charge, q , in a periodic system and separated by vector \mathbf{r} is $\boldsymbol{\mu} \cdot \nabla q\psi(\mathbf{r})$. Likewise, the torque on the dipole is $-\boldsymbol{\mu} \times \nabla q\psi(\mathbf{r})$ and the translational force on the dipole is $-\nabla(\boldsymbol{\mu} \cdot \nabla q\psi(\mathbf{r}))$. The charge experiences an equal and opposite force, hence the electric field due to a point dipole must be $\nabla \boldsymbol{\mu} \cdot \nabla \psi(\mathbf{r})$ and the potential energy per cell between a pair of dipoles with PBC is $-(\boldsymbol{\mu}_1 \cdot \nabla)(\boldsymbol{\mu}_2 \cdot \nabla) \psi(\mathbf{r}'_{12})$. With unit vectors \mathbf{u}_j , given by $\boldsymbol{\mu}_j = |\boldsymbol{\mu}_j| \mathbf{u}_j$, the potential energy of a periodic system of point dipoles, $\{\boldsymbol{\mu}_i\}$, is given by

$$U_{DD} = \frac{1}{2} \sum_{i=1}^N \boldsymbol{\mu}_i^2 S_{DD} + \sum_{i=1}^{N-1} |\boldsymbol{\mu}_i| \sum_{j>i}^N |\boldsymbol{\mu}_j| \phi(\mathbf{u}_i, \mathbf{u}_j, \mathbf{r}_{ij}), \quad (19)$$

where the effective pair potential for dipoles is

$$\phi(\mathbf{u}_1, \mathbf{u}_2, \mathbf{r}) = -(\mathbf{u}_1 \cdot \nabla)(\mathbf{u}_2 \cdot \nabla) \psi(\mathbf{r}). \quad (20)$$

This is the Ewald-Kornfeld summation [28], similar expressions involving point quadrupoles have been derived [4, 28]. The term $\boldsymbol{\mu}_i^2 S_{DD}$ is the interaction of dipole i with its own periodic images, $S_{DD} = -4\pi/3A$ [29]. Substituting ψ_0 , Eq. (6), into (20) one obtains

$$\phi_0 = \frac{\mathbf{u}_1 \cdot \mathbf{u}_2}{r^3} - \frac{3(\mathbf{u}_1 \cdot \mathbf{r})(\mathbf{u}_2 \cdot \mathbf{r})}{r^5}, \quad (21)$$

the energy of a pair of dipoles without PBC. Substituting ψ_2 , Eq. (9), into (20) produces

$$\phi_2 = \phi_0 - 2A_2 \mathbf{u}_1 \cdot \mathbf{u}_2. \quad (22)$$

This may be compared to the reaction-field expression of Barker and Watts [30]:

$$\phi_{RF} = \begin{cases} \phi_0 - \frac{2(\epsilon_c - 1)}{a^3(2\epsilon_c + 1)} \mathbf{u}_1 \cdot \mathbf{u}_2, & r \leq a, \\ 0, & r > a. \end{cases} \quad (23)$$

The approximation here is that a sphere of radius a is considered around each dipole. Within it, all dipole-dipole interactions are summed exactly. The dipoles outside the sphere are approximated by a dielectric continuum, of dielectric con-

stant ϵ_c , which is polarized by the dipoles within the sphere. Letting $\epsilon_c \rightarrow \infty$, which is appropriate for the Ewald summation, the two expressions (22) and (23) will be the same for $r < a$ when a is the radius of a sphere of the same volume as the periodic cell, and the exact value of A_2 is used.

Substitution of Eq. (10), our best isotropic approximation, into Eq. (20) produces a rather clumsy expression, but Eqs. (11) and (12) provide simple isotropic approximations. For TO PBC,

$$\begin{aligned} \phi(\mathbf{u}_1, \mathbf{u}_2, \mathbf{r}) \simeq & (\mathbf{u}_1 \cdot \mathbf{u}_2)[1/r^3 - 7.07746 - 33.35832r^2 + 171.0773r^4] \\ & + (\mathbf{u}_1 \cdot \mathbf{r})(\mathbf{u}_2 \cdot \mathbf{r})[-3/r^5 - 66.71664 + 684.3094r^2], \end{aligned} \quad (24)$$

and for SC PBC,

$$\begin{aligned} \phi(\mathbf{u}_1, \mathbf{u}_2, \mathbf{r}) \simeq & (\mathbf{u}_1 \cdot \mathbf{u}_2)[1/r^3 - 5.50044 + 11.7766r^2 - 5.2146r^4] \\ & + (\mathbf{u}_1 \cdot \mathbf{r})(\mathbf{u}_2 \cdot \mathbf{r})[-3/r^5 + 23.55312 - 20.8584r^2]. \end{aligned} \quad (25)$$

These approximations are isotropic in the sense that they depend only on the angles between \mathbf{u}_1 , \mathbf{u}_2 , and \mathbf{r} and not on their directions relative to the coordinate system defined by the PBC.

Such angle-dependent terms do arise, of course, when the Kubic Harmonic expansion, Eq. (18), is used. Thus

$$\begin{aligned} \phi_4(\mathbf{u}_1, \mathbf{u}_2, \mathbf{r}) = & \phi_0 - 2A_2\mathbf{u}_1 \cdot \mathbf{u}_2 \\ & + \frac{12}{5}A_4\{(\mathbf{u}_1 \cdot \mathbf{u}_2)r^2 + 2(\mathbf{u}_1 \cdot \mathbf{r})(\mathbf{u}_2 \cdot \mathbf{r}) \\ & - 5\mathbf{u}_1 \cdot \mathbf{R}^{(2)} \cdot \mathbf{u}_2\}, \end{aligned} \quad (26)$$

where $\mathbf{R}^{(n)}$ is a diagonal, dyadic tensor given by

$$\begin{aligned} R_{\alpha\alpha}^{(n)} &= \alpha^n \\ R_{\alpha\beta}^{(n)} &= 0, \quad \alpha \neq \beta \end{aligned} \quad (27)$$

This is because

$$-(\mathbf{u}_2 \cdot \nabla)(\mathbf{u}_1 \cdot \nabla) T_n = -n(n-1)\mathbf{u}_1 \cdot \mathbf{R}^{(n-2)} \cdot \mathbf{u}_2. \quad (28)$$

Higher terms rapidly become more involved. The next is

$$\begin{aligned} \phi_6 = & \phi_4 + A_6\{-30\mathbf{u}_1 \cdot \mathbf{R}^{(4)} \cdot \mathbf{u}_2 \\ & + \frac{15}{11}[2\mathbf{u}_1 \cdot \mathbf{u}_2 T_4 + 8(\mathbf{u}_1 \cdot \mathbf{r})(\mathbf{u}_2 \cdot \mathbf{R}^{(3)} \cdot \mathbf{I}) \\ & + 8(\mathbf{u}_2 \cdot \mathbf{r})(\mathbf{u}_1 \cdot \mathbf{R}^{(3)} \cdot \mathbf{I}) + 12r^2\mathbf{u}_1 \cdot \mathbf{R}^{(2)} \cdot \mathbf{u}_2] \\ & - \frac{30}{77}[6r^4\mathbf{u}_1 \cdot \mathbf{u}_2 + 24r^2(\mathbf{u}_1 \cdot \mathbf{r})(\mathbf{u}_2 \cdot \mathbf{r})]\} \end{aligned} \quad (29)$$

where $\mathbf{I} = (1, 1, 1)$.

Ladd [31] has proposed an alternative to the Ewald–Kornfeld summation for systems with point dipoles and quadrupoles; only dipoles are discussed here. Each dipole in turn is considered to be at the centre of its periodic cell. It interacts with all the other dipoles in the periodic cell, i.e., nearest-image summation, and the dipoles in the periodically repeating cells outside are replaced by multipole expansions at their cell centres. The lattice sums have only to be done once for each order of multipole. The first non-zero contribution from the multipoles is the dipole–octopole term. This and higher terms can be written as effective pair potentials [32]. It has been recognized that Ladd’s approach is equivalent to the Ewald sum [4]. It is important to realize further that Ladd’s expression is identical, *term by term*, with the expressions given by $-(\mathbf{u}_2 \cdot \nabla)(\mathbf{u}_1 \cdot \nabla)\psi_i(\mathbf{r})$, except that Ladd’s approximation does not include the “reaction field” term, $-(4\pi/3\mathcal{A})\mathbf{u}_1 \cdot \mathbf{u}_2$ [4]. For example, with a little reorganization it is found that the dipole–octopole term given by Ladd [32] is exactly the same as the term in ϕ_4 extra to ϕ_2 . The value of the coefficient given by Ladd [32] for this term is in precise agreement with the value of A_4 for SC PBC given in Table I.

In addition to the problem of its bias the NI summation presents another difficulty when used in the molecular dynamics simulation of systems of point-dipoles: there is an upward drift in the total energy [33]. This drift arises because the NI summation does not have the periodicity of the boundary conditions. Some approximations to the Ewald sum could also suffer from drift, in particular all isotropic approximations, Eqs. (22), (24), and (25). There is no corresponding problem with free charges.

A most important consideration is the connection between the approximation used and the appropriate formulae for the dielectric properties. Neumann and Steinhauser [34] obtained the formula

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{4\pi}{9VkT} \left\langle \left(\sum_{i=1}^N \boldsymbol{\mu}_i \right)^2 \right\rangle \left[1 \frac{\varepsilon - 1}{\varepsilon + 2} \mathbf{Q} \right] \quad (30)$$

for the static dielectric constant. Extension to the dynamic properties is straightforward [35]. Though in practice a scalar, \mathbf{Q} is related to the integral of the dipole–dipole tensor (with the singularity at $\mathbf{r} = 0$ removed) taken over the periodic cell,

$$\mathbf{Q} = \frac{3}{4\pi} \int_{PC} dv \nabla \nabla \psi(\mathbf{r}). \quad (31)$$

For Eq. (21) we have $\mathbf{Q} = 0$ and for the reaction field, Eq. (23),

$$\mathbf{Q} = \frac{2(\varepsilon_c - 1)}{2\varepsilon_c + 1} \quad (32)$$

when the integral is taken over $r < a$. The exact Ewald summation corresponds to the “tin foil” case where $\mathbf{Q} = 1$. It is an important result of Neumann and

Steinhauser [34] that for the Ewald–Kornfeld summation evaluated by the direct method

$$\mathbf{Q} = \int (\alpha/\pi^{1/2})^3 \exp(-\alpha^2 r^2) d\mathbf{r}, \quad (33)$$

where the integral is taken over the range of evaluation of the real-space summation. Small deviations of \mathbf{Q} from 1 significantly alter the dielectric constant obtained from Eq. (30). This accounts for the reported sensitivity of the computed dielectric constant to the accuracy with which the Ewald–Kornfeld summation was evaluated [36].

There are thus two considerations when dielectric properties are required. First, the summation must be sufficiently good that the correct local structure is produced and, second, the correct value of Q is put into Eq. (30). The first requirement seems easily met; even Eq. (21) may be adequate provided TO PBC are used [37]. The best solution to the second point is to ensure that $\mathbf{Q} = 1$ exactly.

If $F(\mathbf{r})$ satisfies Laplace's equation, so that $\nabla \cdot \nabla F(\mathbf{r}) = 0$ for all \mathbf{r} , it follows that the contribution of F to each of the diagonal components of \mathbf{Q} will also be zero, when F has the symmetry of the cube. Thus, if the expansion of the Ewald sum in Cubic Harmonics is used, only the $A_2 r^2$ term contributes to \mathbf{Q} , and we have

$$\mathbf{Q} = \frac{3}{4\pi} \int_{PC} 2A_2 dv = 1. \quad (34)$$

This condition is fulfilled for point dipoles by using ϕ_2 , ϕ_4 , ϕ_6 , or some yet higher approximation with the correct, unoptimized value of A_2 . All the sets of coefficients in Tables VI and VII satisfy this condition. Similarly for finite dipoles Eq. (18) should be used with the correct value of A_2 . If an isotropic approximation is used then its \mathbf{Q} will have to be determined from Eq. (31).

ACKNOWLEDGMENTS

D.J.A. is an S.E.R.C. Advanced Fellow. We thank S.E.R.C. for financial support for G.S.D. and acknowledge the assistance of the DAP Support Unit at Queen Mary College, University of London. We thank W. L. Slattery for supplying us with additional information regarding the calculations reported in Ref. [25].

REFERENCES

1. P. P. EWALD, *Ann. Phys. (Leipzig)* **64**, 253 (1921).
2. M. P. TOSI, *Solid State Phys.* **16**, 1, Appendix A (1964).
3. C. KITTEL, *Introduction to Solid State Physics*, 2nd ed., (Wiley, New York, 1956), Appendix A.
4. S. W. DE LEEUW, J. W. PERRAM, AND E. R. SMITH, *Proc. R. Soc. London A* **373**, 27 (1980).
5. S. N. STUART, *J. Comput. Phys.* **29**, 127 (1978).

6. R. W. HOCKNEY AND J. W. EASTWOOD, *Computer Simulation Using Particles* (McGraw-Hill, Maidenhead, NJ, 1981).
7. M. J. L. SANGSTER AND M. DIXON, *Adv. Phys.* **25**, 247 (1976).
8. H. L. HELFER, R. L. MCCRORY, AND H. M. VAN HORN, *J. Stat. Phys.* **37**, 577 (1984).
9. S. G. BRUSH, H. L. SAHLIN, AND E. TELLER, *J. Chem. Phys.* **45**, 2102 (1966).
10. J. P. HANSEN, I. R. McDONALD, AND E. L. POLLOCK, *Phys. Rev. A* **11**, 1025 (1975).
11. J. C. RASAIHA, D. N. CARD, AND J. P. VALLEAU, *J. Chem. Phys.* **56**, 248 (1972).
12. J. KROGH-MOE, T. ØSTVOLD, AND T. FORLAND, *Acta Chem. Scand.* **23**, 2421 (1969).
13. L. V. WOODCOCK AND K. SINGER, *Trans. Faraday Soc.* **67**, 12 (1971).
14. D. J. ADAMS, *Chem. Phys. Lett.* **62**, 329 (1979).
15. D. J. ADAMS, *J. Chem. Phys.* **78**, 2585 (1983).
16. D. J. ADAMS, *Proceedings, 9th NRCC*; Lawrence Berkeley Laboratory, University of California Report LBL-10634, 1980, p. 13.
17. J. C. SLATER AND P. DE CICCO, MIT Solid State and Molecular Theory Group Quarterly Progress Report 50, 1963, p. 46.
18. T. F. SOULES, *J. Chem. Phys.* **71**, 4570 (1979).
19. S. BRAWER, *J. Chem. Phys.* **73**, 4032 (1980).
20. T. F. SOULES, *J. Chem. Phys.* **72**, 6314 (1980).
21. S. A. BRAWER AND M. J. WEBER, *J. Chem. Phys.* **75**, 3522 (1981).
22. R. W. HOCKNEY AND C. R. JESSHOPE, *Parallel Computers*, (Hilger, Bristol, 1981).
23. B. LARSEN, *Chem. Phys. Lett.* **27**, 47 (1974).
24. J. P. HANSEN, *Phys. Rev. A* **8**, 3096 (1973).
25. W. L. SLATTERY, G. D. DOOLEN, AND H. E. DEWITT, *Phys. Rev. A* **21**, 2087 (1980).
26. M. ABRAMOWITZ AND I. A. STEGUN, *Handbook of Mathematical Functions* (Dover, New York, 1964), p. 299.
27. F. C. VON DER LAGE AND H. A. BETHE, *Phys. Rev.* **71**, 612 (1947).
28. H. KORNFELD, *Z. Phys.* **22**, 27 (1924).
29. V. M. JANSOONE, *Chem. Phys.* **3**, 78 (1974).
30. J. A. BARKER AND R. O. WATTS, *Mol. Phys.* **26**, 789 (1973).
31. A. J. C. LADD, *Mol. Phys.* **33**, 1039 (1977).
32. A. J. C. LADD, *Mol. Phys.* **36**, 463 (1978).
33. D. J. ADAMS, E. M. ADAMS, AND G. J. HILLS, *Mol. Phys.* **38**, 387 (1979).
34. M. NEUMANN AND O. STEINHAUSER, *Chem. Phys. Lett.* **95**, 417 (1983).
35. M. NEUMANN AND O. STEINHAUSER, *Chem. Phys. Lett.* **102**, 508 (1983).
36. D. J. ADAMS, *Mol. Phys.* **40**, 1261 (1980).
37. D. J. ADAMS AND E. M. ADAMS, *Mol. Phys.* **42**, 907 (1981).