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Simulation of electrostatic systems in periodic boundary conditions. I. Lattice sums and dielectric constants

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The effective interactions of ions, dipoles and higher-order multipoles under periodic boundary conditions are calculated where the array of periodic replications forms an infinite sphere surrounded by a vacuum. Discrepancies between the results of different methods of calculation are resolved and some shape-dependent effects are discussed briefly. In a simulation under these periodic boundary conditions, the net Hamiltonian contains a positive term proportional to the square of the net dipole moment of the configuration. Surrounding the infinite sphere by a continuum of dielectric constant ϵ' changes this positive term, the coefficient being zero as $\epsilon' \to \infty$. We report on the simulation of a dense fluid of hard spheres with embedded point dipoles; simulations are made for different values of ϵ', showing how the Kirkwood g-factor and the long-range part of $h_{\Delta}(r)$ depend on ϵ' in a finite simulation. We show how this dependence on ϵ' nonetheless leads to a dielectric constant for the system that is independent of ϵ'. In particular, the Clausius–Mosotti and Kirkwood formulae for the dielectric constant ϵ of the system give consistent values.

1. INTRODUCTION

Monte-Carlo and molecular-dynamic simulations of N particles interacting with a potential $\phi(\boldsymbol{r}_1 - \boldsymbol{r}_2, \Omega_1, \Omega_2)$ under periodic boundary conditions (p.b.c.) may be considered as simulations in the usual minimum image convention (m.i.) but with a Hamiltonian

$$H = \tfrac{1}{2} \sum_{\boldsymbol{n}}{}' \left[\sum_{i=1}^{N} \sum_{j=1}^{N} \phi(\boldsymbol{r}_{ij} + L\boldsymbol{n}, \boldsymbol{\Omega}_i, \boldsymbol{\Omega}_j) \right] \tag{1.1}$$

(Brush *et al.* 1966; Woodcock & Singer 1971; de Leeuw 1978; Valleau & Whittington 1977). In (1.1) the sum over $\boldsymbol{n}$ is a sum over all simple cubic lattice points with integer coordinates $\boldsymbol{n} = (l, m, n)$, and the prime on this sum indicates that if $i = j$, the $\boldsymbol{n} = \boldsymbol{0}$-terms are to be omitted. Here $\boldsymbol{r}_{ij} = \boldsymbol{r}_i - \boldsymbol{r}_j$, $\boldsymbol{\Omega}_i$ and $\boldsymbol{\Omega}_j$ are Euler angles of the particles at $\boldsymbol{r}_i$ and $\boldsymbol{r}_j$ and L is the length of the side of the cubic simulation sample that contains N particles.

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If the potential ϕ satisfies

$$|\phi(\boldsymbol{r}, \Omega_1, \Omega_2)| \leqslant A|\boldsymbol{r}|^{-3-\epsilon} \tag{1.2}$$

for large enough $|\boldsymbol{r}|$ with $A > 0$ and $\epsilon > 0$, then the lattice sums in (1.1) are absolutely convergent and may be readily performed by standard methods (Born & Huang 1968, Appendix 3; Born & Bradbury 1942; Duesbury & Taylor 1977; Duesbury *et al.* 1979). An excellent review of these methods has recently been written by Glasser & Zucker (1979).

If the interacting particles are represented by charge distributions with non-zero charge, dipole- or quadrupole-moments, there are possible interactions of the form

charge–charge $\quad \phi_{\text{c.c.}}(\boldsymbol{r}) = q_i q_j |\boldsymbol{r}_{ij}|^{-1}, \tag{1.3a}$

charge–dipole $\quad \phi_{\text{c.d.}}(\boldsymbol{r}_{ij}) = -q_i \boldsymbol{\mu}_j \cdot \nabla(1/|\boldsymbol{r}_{ij}|), \tag{1.3b}$

dipole–dipole $\quad \phi_{\text{d.d.}}(\boldsymbol{r}_{ij}) = -(\boldsymbol{\mu}_i \cdot \nabla)(\boldsymbol{\mu}_j \cdot \nabla)(1/|\boldsymbol{r}_{ij}|), \tag{1.3c}$

and charge–quadrupole $\quad \phi_{\text{c.q.}}(\boldsymbol{r}_{ij}) = -q_i \boldsymbol{\Theta}_j : \nabla\nabla(1/|\boldsymbol{r}_{ij}|), \tag{1.3d}$

which do not obey inequality (1.2). Our main concern is with the charge–charge potential (1.3*a*). A correct calculation of (1.1) with $\phi = \phi_{\text{c.c.}}$ should (and does) allow the correct calculation of (1.1) with the other potentials in (1.3), by considering the relevant multipoles as limits of charge distributions. With the potential $\phi_{\text{c.c.}}$ the lattice sum in (1.1) is conditionally convergent, but not absolutely convergent. In § 2 we discuss the summing of conditionally convergent series by the use of a convergence factor. We find conditions on the convergence factor that must hold for the result to be correct. We also show how the use of a particular convergence factor in a conditionally convergent lattice sum may correspond to adding up the sum for a sequence of shells of a shape determined by the convergence factor, and find an appropriate convergence factor for adding the series for a sequence of spherical shells. In § 3 we evaluate (1.1) for the charge–charge potential (1.3*a*) and find that if charge neutrality holds, H has the form, when summed for spherical shells,

$$H = \sum_{1 \leqslant i < j \leqslant N} \frac{1}{L} q_i q_j \psi\left(\frac{\boldsymbol{r}_{ij}}{L}\right) + \frac{\xi}{2L} \sum_{i=1}^{N} q_i^2 + \frac{2\pi}{3L^3} \left| \sum_{i=1}^{N} q_i \boldsymbol{r}_i \right|^2. \tag{1.4}$$

In (1.4) the function $\psi(\boldsymbol{r})$ is given by

$$\psi(\boldsymbol{r}) = \sum_{\boldsymbol{n}} \frac{\operatorname{erfc}(\alpha|\boldsymbol{r}+\boldsymbol{n}|)}{|\boldsymbol{r}+\boldsymbol{n}|} + \frac{1}{\pi} \sum_{\boldsymbol{n} \neq 0} |\boldsymbol{n}|^{-2} \exp[2\pi \mathrm{i}\, \boldsymbol{n} \cdot \boldsymbol{r} - \pi^2 |\boldsymbol{n}|^2/\alpha^2], \tag{1.5}$$

in which

$$\operatorname{erfc}(x) = 1 - 2\pi^{-\frac{1}{2}} \int_0^x \mathrm{e}^{-t^2} \mathrm{d}t \tag{1.6}$$

is the complementary error function and

$$\xi = \sum_{\boldsymbol{n} \neq \boldsymbol{0}} \left[\frac{\operatorname{erfc}(\alpha|\boldsymbol{n}|)}{|\boldsymbol{n}|} + \frac{1}{\pi |\boldsymbol{n}|^2} \mathrm{e}^{-\pi^2 \boldsymbol{n}^2/\alpha^2} \right] - \frac{2\alpha}{\pi^{\frac{1}{2}}}. \tag{1.7}$$

We note that

$$\xi = \lim_{|\boldsymbol{r}| \to 0} [\psi(\boldsymbol{r}) - |\boldsymbol{r}|^{-1}]. \tag{1.8}$$

The result (1.4) may be derived in many different ways (Glasser & Zucker 1979) and was first developed in studies of ionic crystals (Ewald 1921; Madelung 1918). However, it is not the same as that used in many simulations, (Brush *et al.* 1966; Woodcock & Singer 1971; Valleau & Whittington 1977). We discuss the methods used in some previous simulation studies and show how they can fail to include the term $(2\pi/3L^3)(\Sigma_{i=1}^{N} q_i \boldsymbol{r}_i)^2$ in terms of our criterion on convergence factors for conditionally convergent sums.

In § 4 we evaluate (1.1) directly for ϕ equal to the dipole–dipole interaction (Smith & Perram 1975) and derive the same result from (1.4) by considering dipoles and limits of charge pairs. We show that other methods used in the literature give different results (Adams & McDonald 1976; Jansoone 1974) by ignoring the problems associated with the conditional convergence of (1.1). We also consider an example for which (1.1) may be evaluated explicitly by adding for spherical shells without using convergence factors. Our result agrees with this known value. In § 5 we use (1.4) to evaluate (1.1) for charge–dipole and charge–quadrupole interactions and in § 6 we compile a list of effective potentials between any two multipoles in p.b.c. and briefly discuss the role of some of the terms in the p.b.c. Hamiltonian in the thermodynamic limit. We emphasize here that the results we obtain are for lattice sums summed for spherical shells, and that the region outside the spherical shells is a vacuum. In § 7 we discuss the effect on the Hamiltonian of surrounding the spherical shells of the lattice sum in (1.1) by a continuum of dielectric constant ϵ'. We derive expressions for the dielectric constant ϵ of the simulation sample for different values of ϵ' (which include the Clausius Mosotti and Kirkwood formulae) in terms of the g-factor of the system under discussion. We illustrate the discussion with a report of Monte-Carlo simulations of 256 hard spherical particles with embedded point dipoles. We show that the various formulae for the dielectric constant will give a consistent picture of the dielectric constant ϵ of a simulation sample if the Hamiltonian appropriate to each formula is used in the simulation. We also show that the long-range part of the function $h_{\Delta}(r)$ introduced by Wertheim (1971) is strongly influenced by the choice of ϵ'.

2. Convergence factors and conditionally convergent series

We consider the conditionally convergent series

$$\sum_{n=1}^{\infty} c_n = l. \tag{2.1}$$

We take a sequence of functions $f(n, s)$ with the properties

$$\left.\begin{aligned}
&\text{(i)}\ f(n,s) \quad \text{continuous on} \quad s \geqslant 0;\\
&\text{(ii)}\ f(n,0) = 1 \quad \text{for all} \quad n;\\
&\text{(iii)}\ f(n+1,s) \leqslant f(n,s) \quad \text{for all} \quad s \geqslant 0 \quad \text{and for all} \quad n;\\
&\text{(iv)}\ 0 \leqslant f(n,s) \leqslant 1 \quad \text{for all} \quad n \quad \text{and for all} \quad s \geqslant 0.
\end{aligned}\right\} \tag{2.2}$$

We now prove that the series

$$\sum_{n=1}^{\infty} c_n f(n,s) \tag{2.3}$$

is uniformly convergent on $s \geqslant 0$. Abel's identity gives

$$\sum_{n=m}^{p} c_n f(n,s) = \sum_{n=m}^{p-1} \left(\sum_{j=m}^{n} c_j \right) [f(n,s) - f(n+1,s)] + \left(\sum_{j=m}^{p} c_j \right) f(p,s).$$

Since $\Sigma_{j=1}^{\infty} c_j$ is convergent, there exists an $N(\epsilon)$ for every $\epsilon > 0$ such that

$$\left| \sum_{j=N}^{\infty} c_j \right| < \epsilon$$

for all $N > N(\epsilon)$. Thus for $p > N(\epsilon)$

$$\left| \sum_{j=N(\epsilon)}^{p} c_j \right| < 2\epsilon.$$

If we note that, from (2.2iii), $f(n,s) - f(n+1,s) \geqslant 0$, we obtain a modification of Abel's identity

$$\left| \sum_{n=N(\epsilon)}^{p} c_n f(n,s) \right| \leqslant \sum_{n=m}^{p-1} 2\epsilon [f(n,s) - f(n+1,s)] + 2\epsilon f(p,s) = 2\epsilon f(n,s) \leqslant 2\epsilon,$$

where we have used (2.2iv) to obtain the last inequality. Thus for every $\epsilon > 0$ and for all $s \geqslant 0$ there exists an $N(\epsilon)$ such that

$$\left| \sum_{j=N(\epsilon)}^{\infty} c_j f(j,s) \right| \leqslant 2\epsilon$$

and so the series (2.3) is a uniformly convergent series of continuous functions on $s \geqslant 0$. Hence the function

$$L(s) = \sum_{n=1}^{\infty} c_n f(n,s)$$

exists, and is continuous on $s \geqslant 0$, and $L(0) = \lim_{s \to 0} L(s) = l$.

If we can evaluate $L(s)$, by any method, we may then evaluate l. The purpose of the 'convergence factors' is to force absolute convergence of the series (2.3). Hence on $s \geqslant k > 0$ we may have absolute and uniform convergence of the series, which allows a wide variety of limit-type operations (such as differentiation, summation, etc.) to be made in any order convenient to the calculation.

We now consider the example when c_n may be written $c_n = a_n + b_n$ and ask what conditions on $f_1(n,s)$ and $f_2(n,s)$ must hold, in addition to (2.2), for

$$\lim_{s \to 0} \sum_{n=1}^{\infty} [a_n f_1(n,s) + b_n f_2(n,s)] = l. \tag{2.4}$$

If we write $f_2(n,s) = f_1(n,s) + [f_2(n,s) - f_1(n,s)]$ we see that a necessary and sufficient condition for (2.4) to hold is that

$$\lim_{s\to 0} \sum_{n=1}^{\infty} b_n [f_2(n,s) - f_1(n,s)] = 0. \tag{2.5}$$

To illustrate these ideas we consider the series

$$\sum_{n=1}^{\infty} \frac{(-1)^n}{n} = \sum_{n=1}^{\infty} \left[\frac{1}{2n} - \frac{1}{(2n-1)}\right] = -\ln 2. \tag{2.6}$$

The series is convergent by the alternating series test. We consider first the convergence factors $f(n,s) = \mathrm{e}^{-sn}$ which obey all the conditions (2.2). Taking the second form of the sum in (2.6) we note that both

$$\sum_{n=1}^{\infty} \frac{1}{2n} \mathrm{e}^{-sn} \quad \text{and} \quad \sum_{n=1}^{\infty} \frac{1}{(2n-1)} \mathrm{e}^{-sn}$$

are uniformly and absolutely convergent on $s \geqslant \epsilon > 0$. Thus

$$\sum_{n=1}^{\infty} \frac{1}{2n} \mathrm{e}^{-sn} = \frac{1}{2} \int_s^{\infty} \mathrm{d}u \frac{\mathrm{e}^{-u}}{1-\mathrm{e}^{-u}}. \tag{2.7}$$

After similar manipulations we may write

$$\sum_{n=1}^{\infty} \frac{1}{2n-1} \mathrm{e}^{-sn} = \mathrm{e}^{-\frac{1}{2}s} \int_0^{\infty} \mathrm{d}t \left[\frac{\mathrm{e}^{-(\frac{1}{2}s+t)}}{1-\mathrm{e}^{-(\frac{1}{2}s+t)}} - \frac{\mathrm{e}^{-(s+2t)}}{1-\mathrm{e}^{-(s+2t)}}\right]$$

$$= \mathrm{e}^{-\frac{1}{2}s} \left[\frac{1}{2} \int_s^{\infty} \mathrm{d}u \frac{\mathrm{e}^{-u}}{1-\mathrm{e}^{-u}} + \int_{\frac{1}{2}s}^{s} \mathrm{d}u \left(\frac{\mathrm{e}^{-u}}{1-\mathrm{e}^{-u}} - \frac{1}{u}\right) + \ln 2\right].$$

Subtracting this from (2.7) we obtain

$$\sum_{n=1}^{\infty} \mathrm{e}^{-sn} \left(\frac{1}{2n} - \frac{1}{2n-1}\right) = \tfrac{1}{2}(1-\mathrm{e}^{-\frac{1}{2}s}) \int_s^{\infty} \mathrm{d}u \frac{\mathrm{e}^{-u}}{1-\mathrm{e}^{-u}}$$

$$- \mathrm{e}^{-\frac{1}{2}s} \int_{\frac{1}{2}s}^{s} \mathrm{d}u \left(\frac{\mathrm{e}^{-u}}{1-\mathrm{e}^{-u}} - \frac{1}{u}\right) - \mathrm{e}^{-\frac{1}{2}s} \ln 2. \tag{2.8}$$

If we now take the limit as $s \to 0$ of the right side of (2.8) we obtain $-\ln 2$. The method of convergence factors works.

Now we consider the pair of convergence factors $f_1(n,s) = (2n)^{-s}$ and $f_2(n,s) = (2n-1)^{-s}$. The condition (2.5) does hold for this pair since

$$f_2(n,s) - f_1(n,s) = (2n)^{-s}[(1-\tfrac{1}{2}n^{-1})^{-s} - 1] = s(2n)^{-(s+1)}[1+O(s)],$$

so that

$$\sum_{n=1}^{\infty} \frac{1}{2n-1} [(2n-1)^{-s} - (2n)^{-s}] = s \sum_{n=1}^{\infty} \frac{1}{2n(2n-1)} + O(s^2).$$

The sum on the right side is absolutely convergent so that the limit of this side as $s \to 0$ is zero and condition (2.5) holds. We now note that

$$\sum_{n=1}^{\infty} (2n)^{-(1+s)} = 2^{-(1+s)} \zeta(1+s), \quad \sum_{n=1}^{\infty} (2n-1)^{-(1+s)}$$

$$= [2^{-(1+s)} - 1] \zeta(1+s), \tag{2.9}$$

where $\zeta(s)$ is the Riemann zeta function (Whittaker & Watson 1958, ch. 13). Since $\zeta(1+s) = s^{-1} + \xi(s)$, where $\xi(s)$ is a function analytic in s in the whole complex s-plane,

$$\lim_{s\to 0} \sum_{n=1}^{\infty} [(2n)^{-s-1} - (2n-1)^{-s-1}] = \lim_{s\to 0} (2^{-s}-1)\frac{1}{s} = -\ln 2.$$

On the other hand, we may consider the pair $f_1(n,s) = (2n)^{-s}$ and $f_2(n,s) = (1+\alpha s^{\gamma})(2n-1)^{-s}$, where α and γ are real numbers with $\gamma > 0$. While this $f_2(n,s)$ does not satisfy (2.2 iv), this condition is not necessary for the proof of uniform convergence and this $f_2(n,s)$ does obey all the other conditions of (2.2). However, condition (2.5) requires

$$\lim_{s\to 0} \sum_{n=1}^{\infty} b_n [f_2(n,s) - f_1(n,s)] = \lim_{s\to 0} [-\tfrac{1}{2}\alpha s^{\gamma-1} + O(s)]$$

to be zero. Thus for $\gamma > 1$ the two factors will satisfy (2.5) and thus give the correct answer; for $\gamma \leqslant 1$, the two factors do not satisfy condition (2.5). For $\gamma = 1$ they will give the sum (2.6) as $-\ln 2 - \frac{1}{2}\alpha$, while for $\gamma < 1$ the two factors give $-\infty\,[\mathrm{sgn}\,(\alpha)]$ for the sum.

We may conclude that while the use of different convergence factors may be permissible, it is far more reliable to use the same convergence factor for all the parts of the sum. If different convergence factors are used, then they must be shown to obey (2.5).

The problem of conditionally convergent lattice sums is a little more complex. We consider a lattice sum $\Sigma_n {}^* a_n = l_*$, where the asterisk implies that a particular order of adding up the lattice sum is to be chosen. We may now choose a convergence factor $f(\boldsymbol{n}, s)$ and ask whether

$$\lim_{s\to 0} [\sum_{n} a_n f(\boldsymbol{n}, s)] = l_*. \tag{2.10}$$

There is no asterisk on the sum in (2.10) since we assume that the convergence factor is 'strong' enough to force absolute convergence of the lattice sum for $s > 0$. Because we study electrostatic problems, and because the electrostatics for spherical samples are rather easier to calculate than those for a sample of any other shape, we calculate the lattice sum over spherical shells. The distance of the cell-centres $\boldsymbol{m}$ from the cell-centre $\mathbf{0}$ may be placed in an ordered sequence:

$D_0 = 0$ (cell $\boldsymbol{m} = (0,0,0)$);
$D_1 = 1$ (cells $\boldsymbol{m} = (\pm 1,0,0),(0,\pm 1,0),(0,0,\pm 1)$);
$D_2 = 2^{\frac{1}{2}}$ (cells $\boldsymbol{m} = (\pm 1,\pm 1,0)$ etc.);
$D_3 = 3^{\frac{1}{2}}$ (cells $\boldsymbol{m} = (\pm 1,\pm 1,\pm 1)$);
$D_4 = 2$ (cells $\boldsymbol{m} = (\pm 2,0,0)$ etc.);
$D_5 = 5^{\frac{1}{2}}$ (cells $\boldsymbol{m} = (\pm 2,\pm 1,0)$ etc.);
$D_6 = 6^{\frac{1}{2}}$ (cells $\boldsymbol{m} = (\pm 2,\pm 1,\pm 1)$ etc.);
$D_7 = 8^{\frac{1}{2}}$ (cells $\boldsymbol{m} = (\pm 2,\pm 2,0)$ etc.);
$D_8 = 3$ (cells $\boldsymbol{m} = (\pm 2,\pm 2,\pm 1)$ etc., $(\pm 3,0,0)$, etc.)

and so on. Thus the lattice sum for spherical shells may be written

$$\sum_{N=0}^{\infty}\left(\sum_{\boldsymbol{n}:\,|\boldsymbol{n}|=D_N} a_{\boldsymbol{n}}\right) = l_{\text{sphere}}, \tag{2.11}$$

which may now be interpreted as a conditionally convergent sum of type (2.1). To this sum we may apply a convergence factor $f(N,s)$. If this convergence factor obeys conditions (2.2), and also makes the resulting lattice sum absolutely convergent for $s > 0$, we have

$$\lim_{s\to 0}\sum_{\boldsymbol{n}} a_{\boldsymbol{n}} f(N(\boldsymbol{n}),s) = l_{\text{sphere}}, \tag{2.12}$$

where $N(\boldsymbol{n})$ is the number of the spherical shell $\boldsymbol{n}$. The calculation of the lattice sum in (2.12) is greatly facilitated if the absolute convergence on $s > 0$ is also uniform on $s \geqslant \epsilon > 0$. Several mathematical techniques involving the intercharge of the order of limiting operations may then be used, after which the limit $s \to 0$ may be taken to obtain l_{sphere}.

We may now consider calculating the lattice sum $\Sigma_{\boldsymbol{n}} a_{\boldsymbol{n}}$ for cubic shells. The Nth cubic shell B_N is made of up those cells centred at $\boldsymbol{m}$ for which

$$\max(|m_x|, |m_y|, |m_z|) = N$$

and the sum over cubes is then

$$\sum_{N=0}^{\infty}\Big(\sum_{\boldsymbol{n}\in B_N} a_{\boldsymbol{n}}\Big) = l_{\text{cube}}. \tag{2.13}$$

If we set $$N_c(\boldsymbol{m}) = \max(|\boldsymbol{m}_x|, |\boldsymbol{m}_y|, |\boldsymbol{m}_z|)$$

then $$\lim_{s\to 0}\sum_{\boldsymbol{m}} a_{\boldsymbol{m}} f(N_c(\boldsymbol{m}),s) = l_{\text{cube}}.$$

However, (2.5) gives a condition for $l_{\text{cube}} = l_{\text{sphere}}$; namely that

$$\lim_{s\to 0}\sum_{N=0}^{\infty}\Big\{\sum_{\boldsymbol{n}\in B_N} a_{\boldsymbol{n}}[f(N(\boldsymbol{n}),s) - f(N_c(\boldsymbol{n}),s)]\Big\} = 0. \tag{2.14}$$

Equation (2.14) may or may not hold, depending on the $a_{\boldsymbol{n}}$. The device of explicitly writing the lattice sum as a one-dimensional sum of contributions from shells of given shape as in (2.12) and (2.13) makes it easier to see how the shape-dependent characteristic of the electrostatics of continuum bodies might arise with lattice sums.

So far we have no convergence factors. We note three possibilities:

(i) $$f(N(\boldsymbol{n}),s) = \mathrm{e}^{-sN(\boldsymbol{n})^2}, \tag{2.15}$$

(ii) $$f(N(\boldsymbol{n}),s) = N(\boldsymbol{n})^{-s}, \tag{2.16}$$

(iii) $$f(\boldsymbol{n},\boldsymbol{\xi}) = \mathrm{e}^{\mathrm{i}\boldsymbol{\xi}\cdot\boldsymbol{n}}. \tag{2.17}$$

In examples (2.15) and (2.16), for sums for spherical shells, we have

$$N(\boldsymbol{n}) = |\boldsymbol{n}|.$$

The two factors obey conditions (2.2) and impose absolute convergence on the electrostatic lattice sums that we wish to investigate, for $s > 0$ for (2.15) and at least for $s > 1$ for (2.16). Example (2.16) does impose fairly formidable technical difficulties, but a variant may be used (Smith & Perram 1975) to give l_{sphere} for dipole–dipole interactions. Example (2.17) has often been used. However, it does not correspond to adding for spherical shells. We shall show how it fails explicitly for ion–ion interactions, in not giving a limit as $|\boldsymbol{\xi}| \to 0$.

3. Methods for ionic systems

We consider a simple cubic lattice of unit spacing. In each cell there are N charges. In the cell centred at $\boldsymbol{m}$ the charges q_i are at $\boldsymbol{r}_i + \boldsymbol{m}$. The total energy of a single cell (the basic simulation cell) may be written as

$$E = \tfrac{1}{2}\sum_{\boldsymbol{n}}{}' \left(\sum_{i=1}^{N}\sum_{j=1}^{N} q_i q_j |\boldsymbol{r}_{ij} + \boldsymbol{n}|^{-1} \right), \tag{3.1}$$

where the prime on the lattice sum indicates, again, that if $\boldsymbol{n} = \boldsymbol{0}$ the $i = j$-terms are to be omitted. The charge neutrality condition

$$\sum_{i=1}^{N} q_i = 0 \tag{3.2}$$

means that for large $|\boldsymbol{n}|$ the actual lattice sum terms are $O(|\boldsymbol{n}|^{-3})$ and that the lattice sum is conditionally convergent. We now calculate (3.1) using convergence factors appropriate to summing for spherical shells.

(a) *The factor* $\mathrm{e}^{-s|\boldsymbol{n}|^2}$

This is the convergence factor of (2.15). It makes the lattice sums (3.1) over spherical shells absolutely and uniformly convergent on $s \geqslant k > 0$. From §2 we know that if we calculate

$$E(s) = \tfrac{1}{2}\sum_{\boldsymbol{n}}{}' \left(\mathrm{e}^{-s|\boldsymbol{n}|^2} \sum_{i=1}^{N}\sum_{j=1}^{N} q_i q_j |\boldsymbol{r}_{ij} + \boldsymbol{n}|^{-1} \right) \tag{3.3}$$

by any correct method and then take the limit as $s \to 0$ we obtain (3.1) for the sum over spherical shells. Since the lattice sums of (3.3) are all absolutely convergent on $s > 0$ we rewrite $E(s)$ in the form (a different order of the sum)

$$E(s) = \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N} q_i q_j \sum_{\boldsymbol{n}}{}' |\boldsymbol{n} + \boldsymbol{r}_{ij}|^{-1} \mathrm{e}^{-s|\boldsymbol{n}|^2} \tag{3.4}$$

for $s > 0$. In the following we develop a representation of

$$\overline{\psi}(\boldsymbol{r}, s) = \sum_{\boldsymbol{n}} |\boldsymbol{r} + \boldsymbol{n}|^{-1} \mathrm{e}^{-s|\boldsymbol{n}|^2} \tag{3.5}$$

that allows us to take the limit as $s \to 0$ of (3.4) correctly.

Before doing this we consider

$$E_2(s) = \tfrac{1}{2}\sum_{\boldsymbol{n}}{}' \left[\sum_{i=1}^{N}\sum_{j=1}^{N} q_i q_j |\boldsymbol{r}_{ij}+\boldsymbol{n}|^{-1} \exp\left(-s|\boldsymbol{r}_{ij}+\boldsymbol{n}|^2\right)\right], \tag{3.6}$$

where the convergence factor changes as $\boldsymbol{r}_{ij}$ changes. From § 2 we may expect this to give the correct answer if and only if

$$\lim_{s\to 0} \sum_{\boldsymbol{n}}{}' \left\{\sum_{i=1}^{N}\sum_{j=1}^{N} q_i q_j |\boldsymbol{r}_{ij}+\boldsymbol{n}|^{-1} \left[\mathrm{e}^{-s|\boldsymbol{n}+\boldsymbol{r}_{ij}|^2} - \mathrm{e}^{-s|\boldsymbol{n}|^2}\right]\right\} = 0. \tag{3.7}$$

We may estimate the size of this limit by considering the contributions at large $|\boldsymbol{n}|$ to the lattice sum. We use

$$\mathrm{e}^{-s|\boldsymbol{n}+\boldsymbol{r}|^2} \approx \mathrm{e}^{-s|\boldsymbol{n}|^2}[1 - 2s\boldsymbol{n}\cdot\boldsymbol{r} - s|\boldsymbol{r}|^2 + O(s^2)]$$

and

$$|\boldsymbol{n}+\boldsymbol{r}|^{-1} \approx |\boldsymbol{n}|^{-1} - (\boldsymbol{r}\cdot\boldsymbol{n})\,|\boldsymbol{n}|^{-3} - \frac{1}{2}\left[\frac{|\boldsymbol{r}|^2}{|\boldsymbol{n}|^3} - \frac{3|\boldsymbol{r}\cdot\boldsymbol{n}|^2}{|\boldsymbol{n}|^5}\right] + \ldots .$$

The left side of (3.7) can then be seen to be approximately

$$\lim_{s\to 0}\left[-\frac{s}{3}\sum_{i=1}^{N}\sum_{j=1}^{N} q_i q_j \boldsymbol{r}_{ij}^2 \sum_{\boldsymbol{n}\neq\boldsymbol{0}} \frac{1}{|\boldsymbol{n}|}\mathrm{e}^{-s|\boldsymbol{n}|^2} + O(s^2)\right]. \tag{3.8}$$

The lattice sum may be approximated by an integral and has the asymptotic form $(A/s)[1+O(s)]$ as $s\to 0$ with $A > 0$. Other terms that might be expected in (3.8) vanish as a result of charge neutrality. Writing $\boldsymbol{r}_{ij} = \boldsymbol{r}_i - \boldsymbol{r}_j$ and using charge neutrality again we obtain, for the limit, $A|\Sigma_{i=1}^{N} q_i \boldsymbol{r}_i|^2$ which is in general non-zero, so that (3.7) does not hold. Thus, using the convergence factors $\exp[-s|\boldsymbol{r}_{ij}+\boldsymbol{n}|^2]$ for the different parts of the lattice sum (3.1) is incorrect and introduces an error proportional to the square of the dipole moment of the configuration concerned. This difficulty also arises with the use of the factor $|\boldsymbol{n}+\boldsymbol{r}_{ij}|^{-s}$. We now return to the evaluation of $\overline{\psi}(\boldsymbol{r}, s)$.

In these lattice sum evaluations we use the two identities

$$x^{-2s} = \frac{1}{\Gamma(s)}\int_0^\infty t^{s-1}\mathrm{e}^{-tx^2}\,\mathrm{d}t \tag{3.9}$$

and

$$\mathrm{e}^{-t|\boldsymbol{n}+\boldsymbol{r}|^2} = \left(\frac{\pi}{t}\right)^{\frac{3}{2}} \sum_{\boldsymbol{n}} \exp\left[-\pi^2|\boldsymbol{n}|^2/t + 2\pi\mathrm{i}\,\boldsymbol{n}\cdot\boldsymbol{r}\right]. \tag{3.10}$$

Equation (3.9) merely uses the definition of the Γ-function (Whittaker & Watson 1958, ch. 13) while (3.10) is a form of the Jacobi imaginary transformation for θ-functions (Whittaker & Watson 1958, ch. 12; Ewald 1921; Bellman 1961).

We begin the evaluation of $\overline{\psi}(\boldsymbol{r}, s)$ by using (3.9) in (3.5). The result for $s \geqslant k > 0$ is an absolutely and uniformly convergent lattice sum of absolutely and uniformly convergent integrals, which may then be written as an integral of a lattice sum. We obtain

$$\overline{\psi}(\boldsymbol{r}, s) = \frac{1}{\pi^{\frac{1}{2}}}\int_0^\infty t^{-\frac{1}{2}}\,\mathrm{d}t \sum_{\boldsymbol{n}} \exp\left[-s|\boldsymbol{n}|^2 - t|\boldsymbol{r}+\boldsymbol{n}|^2\right]. \tag{3.11}$$

We may expect $\overline{\psi}$ to be singular as $s \to 0$ and we need to know the structure of the singularity. We split the integral in (3.11) into two parts, one on $[\alpha^2, \infty]$ and one on $[0, \alpha^2]$. The parameter α^2 is chosen for computational convenience (Woodcock & Singer (1971), with $N = 216$, found $\alpha = 5.714$ to be appropriate. For the dipolar equivalent of these sums with $N = 256$, which we discuss in § 7, we used $\alpha = 4.7$). The integral on $[\alpha^2, \infty]$ we leave unchanged. It may be written as a very rapidly converging lattice sum of error functions, for $s \geqslant 0$. Hence we may take the limit as $s \to 0$ for this part of the lattice sum without difficulty. For the integral on $[0, \alpha^2]$ we first write

$$-s|\boldsymbol{n}|^2 - t|\boldsymbol{r}+\boldsymbol{n}|^2 = -(s+t)\left|\boldsymbol{n} + \frac{t\boldsymbol{r}}{t+s}\right|^2 - \frac{st|\boldsymbol{r}|^2}{s+t} \tag{3.12}$$

and then use (3.10). We separate the $\boldsymbol{n} = \boldsymbol{0}$-term in this new lattice sum as it contains the singularity as $s \to 0$. This procedure gives

$$\begin{aligned}\overline{\psi}(\boldsymbol{r}, s) = {} & \sum_{\boldsymbol{n}} \frac{1}{\pi^{\frac{1}{2}}} \int_{\alpha^2}^{\infty} t^{-\frac{1}{2}}\, \mathrm{d}t \exp\left[-s|\boldsymbol{n}|^2 - t|\boldsymbol{n}+\boldsymbol{r}|^2\right] \\ & + \sum_{\boldsymbol{n}\neq 0} \pi \int_0^{\alpha^2} \frac{\mathrm{d}t}{\frac{1}{2}[t(t+s)^3]} \exp\left[\frac{-st|\boldsymbol{r}|^2}{s+t} + \frac{2\pi i \boldsymbol{n}\cdot t\boldsymbol{r}}{s+t} - \frac{\pi^2|\boldsymbol{n}|^2}{s+t}\right] \\ & + \pi \int_0^{\alpha^2} \mathrm{d}t\, t^{-\frac{1}{2}}(t+s)^{-\frac{3}{2}} \exp\left(-\frac{st|\boldsymbol{r}|^2}{s+t}\right). \end{aligned} \tag{3.13}$$

The integral in the first lattice sum may be written

$$\frac{1}{\pi^{\frac{1}{2}}} \int_{\alpha^2}^{\infty} t^{-\frac{1}{2}}\, \mathrm{d}t \exp\left[-s\boldsymbol{n}^2 - t|\boldsymbol{n}+\boldsymbol{r}|^2\right] = \frac{\mathrm{e}^{-s|\boldsymbol{n}|^2}}{|\boldsymbol{r}+\boldsymbol{n}|} \operatorname{erfc}(\alpha|\boldsymbol{r}+\boldsymbol{n}|), \tag{3.14}$$

where $\operatorname{erfc}(x)$ is the complementary error function defined in (1.6). An asymptotic expansion of $\operatorname{erfc}(x)$ for large x (Gradshteyn & Ryzhik 1965, p. 931) shows that this first lattice sum is indeed absolutely and uniformly convergent on $s \geqslant 0$ for $\alpha > 0$. Thus we may take the limit $s \to 0$ without difficulty. For the integral in the other lattice sum in (3.13) we substitute $v^2 = t/[s(t+s)]\,|\pi\boldsymbol{n} + is\boldsymbol{r}|^2$ and write it in the form

$$\begin{aligned}\pi \int_0^{\alpha^2} \frac{\mathrm{d}t}{t^{\frac{1}{2}}(s+t)^{\frac{3}{2}}} \exp\left\{-[\pi^2|\boldsymbol{n}|^2 - ts|\boldsymbol{r}|^2 + 2\pi\boldsymbol{n}\cdot t\boldsymbol{r}]/(t+s)\right\} \\ = \frac{2\pi s^{-\frac{1}{2}}\, \mathrm{e}^{-\pi^2|\boldsymbol{n}|^2/s}}{|\pi\boldsymbol{n} + is\boldsymbol{r}|} \int_0^{\omega/s^{\frac{1}{2}}} \mathrm{e}^{v^2}\, \mathrm{d}v \end{aligned} \tag{3.15}$$

with $\omega^2 = \alpha^2|\pi\boldsymbol{n} + is\boldsymbol{r}|^2/(\alpha^2 + s)$. The integral on the right side of (3.15) is essentially Dawson's integral (Abramowitz & Stegun 1965, p. 298) but neither in this reference nor in any other could we find an asymptotic expansion for it). We substitute $v = s^{-\frac{1}{2}}\omega - us^{\frac{1}{2}}/2\omega$ to obtain

$$\int_0^{\omega/s^{\frac{1}{2}}} \mathrm{e}^{v^2}\, \mathrm{d}v = \frac{s^{\frac{1}{2}}\, \mathrm{e}^{\omega^2/s}}{2\omega} \int_0^{2\omega^2/s} \mathrm{d}u\, \mathrm{e}^{-u}\, \mathrm{e}^{su^2/4\omega^2}. \tag{3.16}$$

For small s we may expand $\exp(su^2/4\omega^2)$ as a power series in s and integrate term by term to obtain the representation

$$\int_0^{\omega/s^{\frac{1}{2}}} e^{v^2}\,dv \sim \frac{s^{\frac{1}{2}}\,e^{\omega^2/s}}{2\omega} \sum_{n=0}^{\infty} \frac{(s/4\omega^2)^n}{n!}\left[(2n)! - \Gamma\left(2n+1, \frac{2\omega^2}{s}\right)\right], \tag{3.17}$$

where $\Gamma(a, b)$ is the incomplete gamma function (Gradshteyn & Ryzhik 1965, p. 942) for which

$$\Gamma(2n+1, 2\omega^2/s) \sim (2\omega^2/s)^{2n}\,e^{-2\omega^2/s}.$$

The representation (3.17) can be checked as properly asymptotic (that is the error involved in taking only a finite number of terms tends to zero as $s \to 0$) and we find the asymptotic representation

$$\int_0^{\omega/s^{\frac{1}{2}}} e^{v^2}\,dv \sim \frac{s^{\frac{1}{2}}}{2\omega} e^{\omega^2/s}\left[1 + \frac{s}{2\omega^2} + O(s^2)\right]. \tag{3.18}$$

We may now insert this representation into (3.15) to obtain

$$\pi \int_0^{\alpha^2} \frac{dt}{t^{\frac{1}{2}}(s+t)^{\frac{3}{2}}} \exp\left(-\frac{\pi^2|\boldsymbol{n}|^2}{s+t} - \frac{st|\boldsymbol{r}|^2}{s+t} + \frac{2\pi i\,\boldsymbol{n}\cdot t\boldsymbol{r}}{s+t}\right)$$
$$= \frac{1}{\pi|\boldsymbol{n}|^2} \exp(-\pi^2|\boldsymbol{n}|^2/\alpha^2 + 2\pi i\,\boldsymbol{n}\cdot\boldsymbol{r})[1 + O(s)]. \tag{3.19}$$

The third integral in (3.13) may be transformed by using $u = t/(s+t)$ to give

$$\pi \int_0^{\alpha^2} \frac{t^{-\frac{1}{2}}\,dt}{(t+s)^{\frac{3}{2}}} e^{-st|\boldsymbol{r}|^2/(s+t)} = \frac{\pi}{s} \int_0^{\alpha^2/(\alpha^2+s)} u^{-\frac{1}{2}}\,e^{-s|\boldsymbol{r}|^2 u}\,du. \tag{3.20}$$

This integral diverges as $s \to 0$. There is also an essential singularity at $s = 0$ of the right side of (3.13). This is due to the divergence of the integral in (3.18) as $s \to 0$. However, as $s \to 0$ the contribution of this essential singularity to (3.13) is zero. The divergence of the right side of (3.20) as $s \to 0$ may be displayed by expanding $\exp(-s|\boldsymbol{r}|^2 u)$ as a power series in s and integrating term by term to obtain

$$\frac{\pi}{s} \int_0^{\alpha^2/(\alpha^2+s)} u^{-\frac{1}{2}}\,e^{-s|\boldsymbol{r}|^2 u}\,du = \frac{2\pi}{s}\left(1 + \frac{s}{\alpha^2}\right)^{-\frac{1}{2}} - \frac{2\pi}{3}|\boldsymbol{r}|^2 + O(s). \tag{3.21}$$

This equation shows the singularity of $\overline{\psi}(\boldsymbol{r}, s)$ as $s \to 0$.

The total energy E in (3.1) also contains terms due to the interaction of a charged particle with its own images. If we include the convergence factor these terms are

$$\sum_{n\neq 0} \frac{1}{|\boldsymbol{n}|} e^{-s|\boldsymbol{n}|^2} = \frac{1}{\pi^{\frac{1}{2}}} \int_{\alpha^2}^{\infty} t^{-\frac{1}{2}} \sum_{n\neq 0} e^{-(s+t)|\boldsymbol{n}|^2}\,dt + \frac{1}{\pi^{\frac{1}{2}}} \int_0^{\alpha^2} t^{-\frac{1}{2}} \sum_{n} e^{-(s+t)|\boldsymbol{n}|^2}\,dt - 2\alpha/\pi^{\frac{1}{2}}.$$

This result is obtained by using (3.9), adding an $\boldsymbol{n} = \boldsymbol{0}$-term to the integral on $[0, \alpha^2]$ and then subtracting it separately. The sum in the integral on $[0, \alpha^2]$ is then

transformed by using (3.10). This expression is treated in the same way as $\overline{\psi}(\boldsymbol{r}, s)$ and gives

$$\sum_{\boldsymbol{n}\neq\boldsymbol{0}} |\boldsymbol{n}|^{-1} \mathrm{e}^{-s|\boldsymbol{n}|^2} = \sum_{\boldsymbol{n}\neq\boldsymbol{0}} \left[\frac{\operatorname{erfc}(\alpha|\boldsymbol{n}|)}{|\boldsymbol{n}|} + \frac{\mathrm{e}^{-\pi^2\boldsymbol{n}^2/\alpha^2}}{\pi|\boldsymbol{n}|^2}\right] - \frac{2\alpha}{\pi^{\frac{1}{2}}} + \frac{2\pi}{s}(1+s/\alpha^2)^{-\frac{1}{2}} + O(s)$$

$$= \xi + \frac{2\pi}{s}(1+s/\alpha^2)^{-\frac{1}{2}} + O(s). \quad (3.22)$$

We may now insert (3.14), (3.19) and (3.21) into (3.13), and substitute that result and (3.22) into (3.3). The final result has terms proportional to s^{-1}-, s^0- and $O(s)$-terms. The coefficient of s^{-1} contains the factor $(\Sigma_{i=1}^N q_i)^2$, which is zero, as a result of charge neutrality. Some of the terms from (3.21) make a contribution

$$-\frac{\pi}{3}\sum_{i=1}^N\sum_{j=1}^N q_i q_j |\boldsymbol{r}_{ij}|^2 = \frac{2\pi}{3}\left|\sum_{i=1}^N q_i \boldsymbol{r}_i\right|^2, \quad (3.23)$$

the equality in (3.23) being established by writing $\boldsymbol{r}_{ij} = \boldsymbol{r}_i - \boldsymbol{r}_j$ and by using the condition of charge neutrality. If we let $s \to 0$ in the expression for $E(s)$ we obtain for the energy E of (3.1)

$$E = \sum_{1\leqslant i<j\leqslant N} q_i q_j \psi(\boldsymbol{r}_{ij}) + \tfrac{1}{2}\xi\sum_{i=1}^N q_i^2 + \frac{2\pi}{3}\left|\sum_{i=1}^N q_i \boldsymbol{r}_i\right|^2, \quad (3.24)$$

the function $\psi(\boldsymbol{r})$ being that defined in (1.5). Equation (3.24) constitutes the main result of this section and is the result already quoted in (1.4). We note again that it differs from results often used in simulation studies (Woodcock & Singer 1971) by terms proportional to the square of the dipole moment of the configuration under study.

(*b*) *The factor* $\mathrm{e}^{\mathrm{i}\xi\cdot\boldsymbol{n}}$

This factor is considered here as it provides an example of the way in which the results of § 2 may not apply if the convergence factor does not obey the conditions required of it. Also, it bears a strong resemblance to the method of long waves used in the theory of dipolar fields in crystals (Born & Huang 1968, ch. V). The requirement (2.2 iii) that the convergence factors decrease as $N(\boldsymbol{n})$ increases does not hold. We may approach the problem in the same way as we did for the convergence factor $\exp(-s\boldsymbol{n}^2)$ and write

$$\sum_{\boldsymbol{n}} |\boldsymbol{r}+\boldsymbol{n}|^{-1} \mathrm{e}^{\mathrm{i}\xi\cdot\boldsymbol{n}} = \frac{2}{\pi^{\frac{1}{2}}}\int_0^\infty t^{-\frac{1}{2}}\,\mathrm{d}t \sum_{\boldsymbol{n}} \exp(-t|\boldsymbol{n}+\boldsymbol{r}|^2 + \mathrm{i}\xi\cdot\boldsymbol{n}) \quad (3.25)$$

We split the integral into an integral on $[0, \alpha^2]$ and one on $[\alpha^2, \infty]$. We transform the integrand on $[0, \alpha^2]$ using (3.10) (the $\boldsymbol{n} = \boldsymbol{0}$-term of the new lattice sum is again the singular term), and it may be written in the form

$$\pi\,\mathrm{e}^{-\mathrm{i}\xi\cdot\boldsymbol{r}}\int_0^{\alpha^2}\frac{\mathrm{d}t}{t^2}\,\mathrm{e}^{-|\xi|^2/4t} = \frac{4\pi}{|\xi|^2}\exp(-\mathrm{i}\xi\cdot\boldsymbol{r} - |\xi|^2/4\alpha^2). \quad (3.26)$$

The singular part of $\Sigma_{n\neq 0}|\boldsymbol{n}|^{-1}\exp(\mathrm{i}\boldsymbol{\xi}\cdot\boldsymbol{n})$ is the same as in (3.26) but with $\boldsymbol{r}=\boldsymbol{0}$. Using charge neutrality we find that the singular parts contribute

$$\frac{2\pi}{|\boldsymbol{\xi}|^2}\left(\boldsymbol{\xi}\cdot\sum_{i=1}^{N}q_i\boldsymbol{r}_i\right)^2$$

to the Hamiltonian. This term does not possess a unique limit as $\boldsymbol{\xi}\to\boldsymbol{0}$. This lack of a unique limit need not surprise us in view of the fact that the conditions for the results of § 2 to hold are not obeyed by this convergence factor. These convergence factors may be useful in calculating the lattice sum for planar slabs perpendicular to $\boldsymbol{\xi}$ when $\boldsymbol{\xi}\to\boldsymbol{0}$, but we have not yet made any detailed examination of this possibility.

(c) *Berthaut's method*

Glasser & Zucker (1979) attribute the following method to Berthaut (1952). The method appears to have been used by many workers to simulate ionic systems (see, for example, Woodcock & Singer (1971); Adams & McDonald (1976)). As used in ionic simulations it consists of writing the charge density $q_i\delta[\boldsymbol{r}-(\boldsymbol{r}_i+\boldsymbol{n})]=p_{i,\boldsymbol{n}}(\boldsymbol{r})$ in the form

$$p_{i,\boldsymbol{n}}(\boldsymbol{r})=p_{1,i,\boldsymbol{n}}(\boldsymbol{r})+p_{2,i,\boldsymbol{n}}(\boldsymbol{r}), \tag{3.27}$$

where
$$p_{1,i,\boldsymbol{n}}(\boldsymbol{r})=q_i\{\delta(\boldsymbol{r}-\boldsymbol{r}_i-\boldsymbol{n})-\alpha^3\pi^{-\frac{3}{2}}\exp[-\alpha^2|\boldsymbol{r}-\boldsymbol{r}_i-\boldsymbol{n}|^2]\} \tag{3.28}$$

and
$$p_{2,i,\boldsymbol{n}}(\boldsymbol{r})=q_i\alpha^3\pi^{-\frac{3}{2}}\exp[-\alpha^2|\boldsymbol{r}-\boldsymbol{r}_i-\boldsymbol{n}|^2]. \tag{3.29}$$

The net energy of a configuration may be written

$$E=\tfrac{1}{2}\sum_{\boldsymbol{n}}{}'\sum_{j=1}^{N}\sum_{k=1}^{N}q_j\int\mathrm{d}^3\boldsymbol{r}(p_{1,k,\boldsymbol{n}}+p_{2,k,\boldsymbol{n}})/|\boldsymbol{r}-\boldsymbol{r}_j|, \tag{3.30}$$

the prime on the lattice sum again indicating that the $k=j$- and the $\boldsymbol{n}=\boldsymbol{0}$-terms are omitted. A little manipulation shows that

$$\int\mathrm{d}^3\boldsymbol{r}\,\frac{p_{1,k,\boldsymbol{n}}(\boldsymbol{r})}{|\boldsymbol{r}-\boldsymbol{r}_j|}=q_k|\boldsymbol{r}_{kj}+\boldsymbol{n}|^{-1}\operatorname{erfc}(\alpha|\boldsymbol{r}_{kj}+\boldsymbol{n}|). \tag{3.31}$$

We now include the $\boldsymbol{n}=\boldsymbol{0}$-term for $i=j$ in the lattice sum over $p_{2,k,\boldsymbol{n}}(\boldsymbol{r})$ and subtract it separately to give

$$E=\frac{1}{2}\sum_{j=1}^{N}\sum_{k=1}^{N}q_jq_k\sum_{\boldsymbol{n}}{}'\frac{\operatorname{erfc}(\alpha|\boldsymbol{r}_{jk}+\boldsymbol{n}|)}{|\boldsymbol{r}_{jk}+\boldsymbol{n}|}-\frac{\alpha}{\pi^{\frac{1}{2}}}\sum_{j=1}^{N}q_j^2$$
$$+\tfrac{1}{2}\sum_{\boldsymbol{n}}\sum_{j=1}^{N}\sum_{k=1}^{N}q_jq_k\frac{\alpha^3}{\pi^{\frac{3}{2}}}\int\mathrm{d}^3\boldsymbol{r}\,\frac{\exp[-\alpha^2|\boldsymbol{r}-\boldsymbol{r}_k-\boldsymbol{n}|^2]}{|\boldsymbol{r}-\boldsymbol{r}_j|}. \tag{3.32}$$

The asymptotic expansion of $\operatorname{erfc}(x)$ for large x shows that the first lattice sum in (3.32) is absolutely convergent. However, if we use (3.31) (with the Dirac δ-function removed from the integrand) to evaluate the integrals in the second lattice sum of (3.32) we obtain a conditionally convergent lattice sum. This conditional convergence may be handled by using the convergence factor $\exp(-s|\boldsymbol{n}|^2)$ and the results

of § 2. As we shall see, this leads to (3.24). A more usual method is to note that the integrals in this second lattice sum of (3.32) are of a convolution type so that we may write

$$\frac{\alpha^3}{\pi^{\frac{3}{2}}}\int \mathrm{d}^3\boldsymbol{r}\,\frac{\exp\left[-\alpha^2|\boldsymbol{r}-\boldsymbol{r}_i-\boldsymbol{n}|^2\right]}{|\boldsymbol{r}-\boldsymbol{r}_j|} = (2\pi)^{-3}\int \mathrm{d}^3\boldsymbol{k}\,\mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_j}F(\boldsymbol{k})\,G_{i,n}(\boldsymbol{k}), \tag{3.33}$$

where

$$F(\boldsymbol{k}) = \int \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}}\frac{1}{|\boldsymbol{r}|}\mathrm{d}^3\boldsymbol{r} \tag{3.34}$$

and

$$G_{i,n}(\boldsymbol{k}) = \alpha^3\pi^{-\frac{3}{2}}\int \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}}\exp\left(-\alpha^2\,|\boldsymbol{r}-\boldsymbol{r}_i-\boldsymbol{n}|^2\right)\mathrm{d}^3\boldsymbol{r}. \tag{3.35}$$

Used uncritically, this process leads apparently to (1.4) but without the terms $(\frac{2}{3}\pi|\Sigma_{i=1}^{N} q_i\boldsymbol{r}_i|^2$. However, the integration in (3.34) is supposed to be taken over all space which means that $F(\boldsymbol{k})$ is given by

$$F(\boldsymbol{k}) = \frac{4\pi}{|\boldsymbol{k}|}\int_0^\infty \sin\left(|\boldsymbol{k}|r\right)\mathrm{d}r, \tag{3.36}$$

and so $F(\boldsymbol{k})$ does not exist. To give $F(\boldsymbol{k})$ a meaning we must either consider the integral in (3.32) over a finite but large region of space, thus introducing unknown edge effects into the convolution integral and so into (3.33), or we must use a convergence factor, for which $\mathrm{e}^{-\mu|\boldsymbol{r}|}$ is normally used, and take the limit as $\mu \to 0$. This second alternative involves the use of a convergence factor of unknown properties with respect to the subsequent lattice sum, as it works while buried inside the integral. Hence we conclude that Berthaut's method may be unreliable if used together with (3.33) since it involves steps that introduce effects about which we know very little.

On the other hand, if we insert the convergence factor $\exp\left(-s\boldsymbol{n}^2\right)$ into the second lattice sum in (3.32), the factor forces rapid enough convergence of the lattice sums to allow an interchange of the lattice sum and the integral. We change the variable in the integral to $\boldsymbol{r}' = \boldsymbol{r}-\boldsymbol{r}_j$ and then use

$$\begin{aligned}-s\boldsymbol{n}^2-\alpha^2|\boldsymbol{r}'-\boldsymbol{r}_{kj}-\boldsymbol{n}|^2 = &-(s+\alpha^2)|\boldsymbol{n}+[\alpha^2/(\alpha^2+s)]\,(\boldsymbol{r}_{kj}-\boldsymbol{r}')|^2\\ &-[\alpha^2 s/(\alpha^2+s)]\,|\boldsymbol{r}_{kj}-\boldsymbol{r}'|^2\end{aligned} \tag{3.37}$$

to convert the resulting lattice sum into a form on which (3.10) may be used. The result is that the second lattice sum in (3.32), with the convergence factor $\exp\left(-s|\boldsymbol{n}|^2\right)$ inserted, may be written in the form

$$\begin{aligned}&\frac{1}{2}\sum_{j=1}^{N}\sum_{k=1}^{N} q_j q_k(1+s/\alpha^2)^{-\frac{3}{2}}\\ &\times\Big\langle\sum_{n\neq 0}\mathrm{e}^{-\pi|n|^2/(s+\alpha^2)}\int\frac{\mathrm{d}^3\boldsymbol{r}}{|\boldsymbol{r}|}\exp-[s|\boldsymbol{r}_{kj}-\boldsymbol{r}|^2-2\pi\mathrm{i}\;\boldsymbol{n}\cdot(\boldsymbol{r}_{kj}-\boldsymbol{r})]/(1+\frac{s}{\alpha^2})\\ &\qquad+\int\frac{\mathrm{d}^3\boldsymbol{r}}{|\boldsymbol{r}|}\exp\left[-\frac{\alpha^2 s}{\alpha^2+s}|\boldsymbol{r}_{kj}-\boldsymbol{r}|^2\right]\Big\rangle.\end{aligned} \tag{3.38}$$

The lattice sum in (3.38) is now absolutely and uniformly convergent on $s \geqslant 0$. Thus we may take $s \to 0$ inside the integrals and use $\int \mathrm{d}^3\boldsymbol{r}[\exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r})]/|\boldsymbol{r}| = 4\pi/k^2$. A little simplification of the final integral then leads to

$$\frac{1}{2}\sum_{j=1}^{N}\sum_{k=1}^{N} q_j q_k \sum_{\boldsymbol{n}\neq\boldsymbol{0}} \frac{1}{\pi|\boldsymbol{n}|^2}\exp(-\pi^2|\boldsymbol{n}|^2/\alpha^2 - 2\pi\mathrm{i}\ \boldsymbol{n}\cdot\boldsymbol{r}_{jk}) + \pi\sum_{j=1}^{N}\sum_{k=1}^{N} q_j q_k \frac{(1+s/\alpha^2)^{-\frac{1}{2}}}{s|\boldsymbol{r}_{kj}|}\int_0^{|r_{kj}|}\exp[-s|\boldsymbol{r}|^2/(1+s/\alpha^2)]\,\mathrm{d}r + O(s) \quad (3.39)$$

in place of (3.38). We may expand the exponential in the integral remaining in (3.39) as a power series in s and integrate term by term. The first term is $O(s^{-1})$ and is zero as a result of charge neutrality. The next term has a finite limit as $s \to 0$ and the rest are all $O(s)$. Putting this result back into (3.32) we find

$$E = \frac{1}{2}\sum_{j=1}^{N}\sum_{k=1}^{N} q_j q_k \psi(\boldsymbol{r}_{jk}) + \tfrac{1}{2}\xi\sum_{k=1}^{N} q_k^2 + \tfrac{2}{3}\pi\left(\sum_{k=1}^{N} q_k \boldsymbol{r}_k\right)^2, \quad (3.40)$$

which is identical to (3.24), but not the same as the result of using the convolution theorem uncritically. It would appear that this method, which uses the convolution theorem and thus, implicitly, the convergence factor $\exp(-\mu|\boldsymbol{r}|)$ in the integral in (3.36), applies a convergence factor that acts differently on different parts of the lattice sum.

We conclude that the correct value for E defined in (3.1) for a sum for spherical shells is given by (3.24). Any method that gives a different answer is thus either explicitly or implicitly using a different convergence factor on the different parts of the lattice sum, or corresponds to adding up (3.1) over non-spherical shapes.

4. Methods for dipolar systems

(*a*) *The factor* $\mathrm{e}^{-s|\boldsymbol{n}|^2}$

We consider

$$\psi_{\mathrm{d.d.}}(\boldsymbol{r}) = \sum_{\boldsymbol{n}}\left\{\frac{\boldsymbol{\mu}_1\cdot\boldsymbol{\mu}_2}{|\boldsymbol{r}+\boldsymbol{n}|^3} - \frac{3[\boldsymbol{\mu}_1\cdot(\boldsymbol{r}+\boldsymbol{n})][\boldsymbol{\mu}_2\cdot(\boldsymbol{r}+\boldsymbol{n})]}{|\boldsymbol{r}+\boldsymbol{n}|^5}\right\}\mathrm{e}^{-s|\boldsymbol{n}|^2}. \quad (4.1)$$

In the limit $s \to 0$, this lattice sum is conditionally convergent. We could use the convergence factor $\exp(-s|\boldsymbol{r}+\boldsymbol{n}|^2)$ because it leads to slightly simpler analysis, and is the same for the two parts of the conditionally convergent lattice sum. However, $\mathrm{e}^{-s|\boldsymbol{n}|^2}$ gives some continuity with § 3. We treat the sums in (4.1) in exactly the same way as the ionic lattice sums. First, we find

$$\sum_{\boldsymbol{n}}|\boldsymbol{r}+\boldsymbol{n}|^{-3}\mathrm{e}^{-s|\boldsymbol{n}|^2} = \sum_{\boldsymbol{n}}\frac{2}{\pi^{\frac{1}{2}}}\mathrm{e}^{-s|\boldsymbol{n}|^2}\int_{\alpha^2}^{\infty} t^{\frac{1}{2}}\,\mathrm{d}t\,\mathrm{e}^{-t|\boldsymbol{r}+\boldsymbol{n}|^2} + \sum_{\boldsymbol{n}\pm\boldsymbol{0}} 2\pi\,\mathrm{e}^{2\mathrm{i}\pi\boldsymbol{n}\cdot\boldsymbol{r}}\int_{1/\alpha^2}^{\infty}\frac{1}{u}\mathrm{e}^{-\pi^2|\boldsymbol{n}|^2 u}\,\mathrm{d}u + 2\pi\int_0^{\alpha^2}\frac{t^{\frac{1}{2}}}{(t+s)^{\frac{3}{2}}}\,\mathrm{d}t\,\mathrm{e}^{-st|\boldsymbol{r}|^2/(s+t)} + O(s). \quad (4.2)$$

The limit as $s \to 0$ of the two lattice sums in (4.2) added to similar terms from the second part of (4.1) is $-(\boldsymbol{\mu}_1 \cdot \nabla)(\boldsymbol{\mu}_2 \cdot \nabla)\psi(\boldsymbol{r})$. Hence we ignore the lattice sums in (4.2) and concentrate on the singular part, which is the last integral in (4.2). We substitute $v = t/(t+s)$ into this integral, expand the exponential in a power series in s and integrate term by term to obtain

$$2\pi \int_0^{\alpha^2} \frac{t^{\frac{1}{2}}}{(t+s)^{\frac{3}{2}}} \mathrm{d}t \, \mathrm{e}^{-st|\boldsymbol{r}|^2/(s+t)} = -2\pi \ln(s/2\alpha^2) + 2\pi \ln 2 - 4\pi + O(s). \tag{4.3}$$

To evaluate the lattice sum of the other terms in (4.1) we use the identity

$$\sum_{\boldsymbol{n}} |\boldsymbol{r}+\boldsymbol{n}|^{-5} \mathrm{e}^{-s\boldsymbol{n}^2} [\boldsymbol{\mu}_1 \cdot (\boldsymbol{r}+\boldsymbol{n})][\boldsymbol{\mu}_2 \cdot (\boldsymbol{r}+\boldsymbol{n})]$$
$$= -(\boldsymbol{\mu}_1 \cdot \nabla_\xi)(\boldsymbol{\mu}_2 \cdot \nabla_\xi) \sum_{\boldsymbol{n}} |\boldsymbol{r}+\boldsymbol{n}|^{-5} \exp[-s|\boldsymbol{n}|^2 - \mathrm{i}\boldsymbol{\xi} \cdot (\boldsymbol{r}+\boldsymbol{n})]|_{\xi=0}, \tag{4.4}$$

which certainly holds for $s > 0$. We write

$$\sum_{\boldsymbol{n}} |\boldsymbol{r}+\boldsymbol{n}|^{-5} \exp[-s|\boldsymbol{n}|^2 - \mathrm{i}\boldsymbol{\xi} \cdot (\boldsymbol{r}+\boldsymbol{n})]$$
$$= \frac{4}{3\pi^{\frac{1}{2}}} \int_0^\infty t^{\frac{3}{2}} \mathrm{d}t \sum_{\boldsymbol{n}} \exp[-t|\boldsymbol{r}+\boldsymbol{n}|^2 - s|\boldsymbol{n}|^2 - \mathrm{i}\boldsymbol{\xi} \cdot (\boldsymbol{r}+\boldsymbol{n})] \tag{4.5}$$

and then treat the integral in the usual way. The singular part of this integral is found to be the $\boldsymbol{n} = \boldsymbol{0}$-term in the new lattice sum, which results from the transformation of the lattice sum in the integral on $[0, \alpha^2]$, so the singular part is

$$\tfrac{4}{3}\pi \int_0^{\alpha^2} \frac{t^{\frac{3}{2}}}{(t+s)^{\frac{3}{2}}} \mathrm{d}t \exp[-(st|\boldsymbol{r}|^2 + \mathrm{i}s\boldsymbol{r} \cdot \boldsymbol{\xi} + \tfrac{1}{4}\boldsymbol{\xi}^2)/(s+t)]. \tag{4.6}$$

If we now operate on the integral with $-(\boldsymbol{\mu}_1 \cdot \nabla_\xi)(\boldsymbol{\mu}_2 \cdot \nabla_\xi)$ and then set $\boldsymbol{\xi} = \boldsymbol{0}$ as required by (4.4) we obtain

$$\tfrac{2}{3}\pi \boldsymbol{\mu}_1 \cdot \boldsymbol{\mu}_2 \int_0^{\alpha^2} \frac{t^{\frac{3}{2}}}{(t+s)^{\frac{5}{2}}} \mathrm{e}^{-st|\boldsymbol{r}|^2/(s+t)} \mathrm{d}t + \tfrac{4}{3}\pi s^2 (\boldsymbol{\mu}_1 \cdot \boldsymbol{r})(\boldsymbol{\mu}_2 \cdot \boldsymbol{r}) \int_0^{\alpha^2} \frac{t^{\frac{3}{2}}}{(t+s)^{\frac{7}{2}}} \mathrm{e}^{-ts|\boldsymbol{r}|^2/(s+t)} \mathrm{d}t. \tag{4.7}$$

The second integral in (4.7) is $O(s^{-1})$ but carries a factor s^2 so that the term is $O(s)$ as $s \to 0$ and may be ignored. The first integral is evaluated by using the substitution $u = t/(t+s)$, expanding the exponential in a power series in s and integrating term by term to give

$$\tfrac{4}{3}\pi(\boldsymbol{\mu}_1 \cdot \boldsymbol{\mu}_2)[-\tfrac{4}{3} + \tfrac{1}{2}\ln 2 - \tfrac{1}{2}\ln(s/2\alpha^2)] + O(s).$$

If we multiply this expression by -3 and subtract it from the right side of (4.3) multiplied by $\boldsymbol{\mu}_1 \cdot \boldsymbol{\mu}_2$, we are left with the singular part $\frac{4}{3}\pi(\boldsymbol{\mu}_1 \cdot \boldsymbol{\mu}_2)$. The potential $\phi_{\mathrm{d.d.}}$ is then given by

$$\phi_{\mathrm{d.d.}} = \tfrac{4}{3}\pi(\boldsymbol{\mu}_1 \cdot \boldsymbol{\mu}_2) - (\boldsymbol{\mu}_1 \cdot \nabla)(\boldsymbol{\mu}_2 \cdot \nabla)\psi(\boldsymbol{r}) \tag{4.8}$$

in agreement with Smith & Perram (1975), who used the convergence factor $|\boldsymbol{n}+\boldsymbol{r}|^{-2s}$.

We now consider the interaction energy of a dipole with its own lattice of images. We may write this, for a dipole $\boldsymbol{\mu} = (\mu_x, \mu_y, \mu_z)$, in the form

$$\lim_{R\to\infty} \sum_{0<|\boldsymbol{n}|^2\leqslant R} \left[\frac{\boldsymbol{\mu}\cdot\boldsymbol{\mu}}{|\boldsymbol{n}|^3} - \frac{3(\boldsymbol{\mu}\cdot\boldsymbol{n})^2}{|\boldsymbol{n}|^5}\right].$$

The summand in this expression may be rewritten as

$$[\mu_x^2(m^2+n^2-2l^2)+\mu_y^2(l^2+n^2-2m^2)+\mu_z^2(l^2+m^2-2n^2) - 6\mu_x\mu_y lm - 6\mu_x\mu_z ln - 6\mu_y\mu_z mn]|\boldsymbol{n}|^{-5}.$$

The sums over the terms $6\mu_x\mu_y lm$ etc. are zero since if $\boldsymbol{n} = (l, m, n)$ is a term in the sum, then so is $(l, -m, -n)$. The sum over terms like $\mu_x^2(m^2+n^2-2l^2)/|\boldsymbol{n}|^5$ is also zero since we may write for the finite sum

$$\sum_{0<l^2+m^2+n^2\leqslant R} m^2(l^2+m^2+n^2)^{-\frac{5}{2}} = \sum_{0<l^2+m^2+n^2\leqslant R} l^2(l^2+m^2+n^2)^{-\frac{5}{2}}.$$

Thus the terms in the sum cancel with each other to give zero and hence zero limit as $R\to\infty$. This means that we may write the self-energy of a single dipole in p.b.c. as zero.

(*b*) *The factor* $|\boldsymbol{n}+\boldsymbol{r}|^{-2s}$

Details of calculation of $\phi_{\text{d.d.}}$ by using this convergence factor may be found in Smith & Perram (1975). Here we note that the same convergence factor $|\boldsymbol{n}+\boldsymbol{r}|^{-2s}$ is used for the two parts of the conditionally convergent lattice sum (4.1), so that the result of Smith & Perram is correct for addition for spherical shells.

Adams (1978, private communication) has suggested evaluating (4.1) by calculating

$$\lim_{s\to 0} \sum_{\boldsymbol{n}} -(\boldsymbol{\mu}_1\cdot\nabla)(\boldsymbol{\mu}_2\cdot\nabla)|\boldsymbol{r}+\boldsymbol{n}|^{-1-2s}.$$

If we carry out the gradient operations, we obtain

$$\lim_{s\to 0}(1+2s)\left\langle \sum_{\boldsymbol{n}} \left\{\frac{\boldsymbol{\mu}_1\cdot\boldsymbol{\mu}_2}{|\boldsymbol{r}+\boldsymbol{n}|^{3+2s}} - 3(1+\tfrac{2}{3}s)\frac{[\boldsymbol{\mu}_1\cdot(\boldsymbol{r}+\boldsymbol{n})][\boldsymbol{\mu}_2\cdot(\boldsymbol{r}+\boldsymbol{n})]}{|\boldsymbol{r}+\boldsymbol{n}|^{5+2s}}\right\}\right\rangle. \tag{4.9}$$

This suggestion corresponds to using the convergence factors $|\boldsymbol{r}+\boldsymbol{n}|^{-2s}$ on the sum of the first terms and $(1+\frac{2}{3}s)|\boldsymbol{r}+\boldsymbol{n}|^{-2s}$ on the sum of the second terms. From § 2 we know that such a pair of convergence factors can give quite incorrect results. In this case it gives the result

$$\phi_{\text{d.d.}} = -(\boldsymbol{\mu}_1\cdot\nabla)(\boldsymbol{\mu}_2\cdot\nabla)\psi(\boldsymbol{r}),$$

which is missing a term $\frac{4}{3}\pi\boldsymbol{\mu}_1\cdot\boldsymbol{\mu}_2$. This error is due to the use of different convergence factors for the different parts of the lattice sum and is rather similar to that discussed near (3.8), the two convergence factors not obeying the lattice-sum equivalent of (2.5).

(c) *Dipoles as limits of charge pairs*

We consider a configuration of N dipoles at $\boldsymbol{r}_i$, $i = 1, \ldots, N$. We replace the dipole $\boldsymbol{\mu}_i$ at $\boldsymbol{r}_i$ by a pair of charges

$$Q_i = |\boldsymbol{\mu}_i|/2\epsilon \quad \text{at} \quad \boldsymbol{R}_i = \boldsymbol{r}_i + \epsilon\hat{\boldsymbol{\mu}}_i, \quad i = 1, \ldots, N \tag{4.10a}$$

and

$$Q_i = -|\boldsymbol{\mu}_{i-N}|/2\epsilon \quad \text{at} \quad \boldsymbol{R}_i = \boldsymbol{r}_{i-N} - \epsilon\hat{\boldsymbol{\mu}}_{i-N}, \quad i = N+1, \ldots, 2N, \tag{4.10b}$$

$\boldsymbol{\mu}_j$ denoting a unit vector parallel to $\boldsymbol{\mu}_j$. If we take the limit as $\epsilon \to 0$ we regain the set of dipoles $\boldsymbol{\mu}_i$. We may write down the energy of a cubic lattice of such charge configurations by using (3.24). We must subtract the energy

$$\sum_{i=1}^{N} Q_i Q_{i+N} |\boldsymbol{R}_i - \boldsymbol{R}_{i+N}|^{-1}$$

as this is the self-energy of a single charge pair, or dipole. However, we must include the interaction of a charge pair with its own images, since these terms occur naturally in the p.b.c. energy. Using (3.24), we obtain for the energy of a configuration

$$E = \frac{1}{2} \sum_{i=1}^{2N} \sum_{\substack{j=1 \\ j \neq i,\, i \pm N}}^{2N} Q_i Q_j \psi(\boldsymbol{R}_i - \boldsymbol{R}_j) + \tfrac{1}{2}\xi \sum_{i=1}^{2N} Q_i^2 + \xi \sum_{i=1}^{N} Q_i Q_{i+N} + \tfrac{2}{3}\pi \left(\sum_{i=1}^{N} Q_i \boldsymbol{R}_i + Q_{i+N} \boldsymbol{R}_{i+N} \right)^2, \tag{4.11}$$

where the subscript $j \neq i, i \pm N$ indicates that terms for which $i = j$, $i = j + N$ or $j = i + N$ are excluded. If we now take into account the explicit dependence of $\psi(\boldsymbol{R}_i - \boldsymbol{R}_j)$ on ϵ and expand it together with the other terms, to second order in ϵ, use (4.10*a*, *b*) to substitute for the charges Q_i and then take the limit as $\epsilon \to 0$ we obtain

$$E = \sum_{1 \leqslant i < j \leqslant N} [\tfrac{4}{3}\pi \boldsymbol{\mu}_i \cdot \boldsymbol{\mu}_j - (\boldsymbol{\mu}_i \cdot \nabla)(\boldsymbol{\mu}_j \cdot \nabla)\psi(\boldsymbol{r}_{ij})], \tag{4.12}$$

which is in precise agreement with (4.8).

(d) *A numerical example*

We now consider a configuration of two dipoles

$$\boldsymbol{\mu}_1 = (1, 1, 1) \quad \text{at} \quad \boldsymbol{r}_1 = (0, 0, 0)$$

and

$$\boldsymbol{\mu}_2 = (1, 1, 1) \quad \text{at} \quad \boldsymbol{r}_2 = (x, 0, 0).$$

The lattice sum over spheres for the effective p.b.c. interaction between these two dipoles is then

$$\lim_{R \to \infty} \sum_{\boldsymbol{n}:\, |\boldsymbol{n}|^2 \leqslant R^2} \frac{3[(l+x)^2 + m^2 + n^2] - 3(l + x + m + n)^2}{[(l+x)^2 + m^2 + n^2]^{\frac{5}{2}}}, \tag{4.13}$$

where $\boldsymbol{n} = (l, m, n)$. The denominator in the summand is independent of the sign of m or n. The numerator, on the other hand, is $-6[(l+x)(m+n) + mn]$. If (l, m, n)

belongs to the set being summed over, then so do $(l, m, -n)$ and $(l, -m, n)$. Thus the sum in (4.13) is zero and, therefore, its limit as $R \to \infty$ is zero. Equation (4.8), for these two dipoles, is equal to

$$4\pi - [(1, 1, 1)\cdot\nabla]^2 \psi(\boldsymbol{r}). \tag{4.14}$$

Evaluation of $[(1, 1, 1).\nabla]^2 \psi(x, 0, 0)$ by the method discussed by Adams & McDonald (1976), and by using the Abramowitz and Stegun (1965, p. 299) approximation for erfc (x) gives 12.566 370 57 for $x = 0.1$, 0.2, 0.3, 0.4 and 0.5 by using double precision C.D.C. computer arithmetic. This differs from 4π by 4×10^{-8}, so (4.14) is zero to 9 significant figures, at least. Hence, for an example for which the answer may be determined independently, as was done here, (4.8) gives the correct answer to at least nine significant figures. The expression $-(\boldsymbol{\mu}_1\cdot\nabla)(\boldsymbol{\mu}_2\cdot\nabla)\psi(\boldsymbol{r})$ used by Adams & McDonald (1976) and Jansoone (1974) is in error, for this particular configurations at least, when the lattice sums are added for spherical shells.

5. The ion–dipole and ion–quadrupole interactions

We consider first the energy of interaction of a set of N charges q_i at $\boldsymbol{r}_i$, $i = 1, \ldots, N$ and M dipoles $\boldsymbol{\mu}_i$ at $\boldsymbol{r}_i$, $i = N+1, \ldots N+M$ under p.b.c. We may write down the p.b.c. charge interaction energy by, (3.24), and the dipole interaction energy, (4.8). To evaluate the ion–dipole energies we replace the dipoles by the $2M$ charges

$$Q_i = |\boldsymbol{\mu}_i|/2\epsilon \quad \text{at} \quad \boldsymbol{R}_i = \boldsymbol{r}_i + \epsilon\hat{\boldsymbol{\mu}}_i, \quad i = N+1, \ldots, N+M$$

and

$$Q_i = -|\boldsymbol{\mu}_{i-M}|/2\epsilon \quad \text{at} \quad \boldsymbol{R}_i = \boldsymbol{r}_{i-M} - \epsilon\hat{\boldsymbol{\mu}}_{i-M}, \quad i = N+M+1, \ldots, N+2M. \tag{5.1}$$

We may now use (3.24) to write down the p.b.c. interaction of these charge pairs with the charges q_i, $i = 1, \ldots, N$. We obtain

$$E_{\text{i.d.}} = \sum_{i=1}^{N} \sum_{j=N+1}^{N+2M} q_i Q_j \psi(\boldsymbol{r}_i - \boldsymbol{R}_j) + \tfrac{4}{3}\pi \left(\sum_{j=1}^{N} q_i \boldsymbol{r}_i \right) \left(\sum_{j=M+1}^{N+M} [Q_j \boldsymbol{R}_j + Q_{j+M} \boldsymbol{R}_{j+M}] \right). \tag{5.2}$$

From (1.5) we note that

$$Q_j \boldsymbol{R}_j + Q_{j+M} \boldsymbol{R}_{j+M} = \boldsymbol{\mu}_j. \tag{5.3}$$

We may expand $\psi(\boldsymbol{r}_i - \boldsymbol{R}_j)$ as

$$\psi(\boldsymbol{r}_i - \boldsymbol{r}_j \mp \epsilon\hat{\boldsymbol{\mu}}_j) = \psi(\boldsymbol{r}_i - \boldsymbol{r}_j) \mp \epsilon\hat{\boldsymbol{\mu}}_j \cdot \nabla\psi(\boldsymbol{r}_i - \boldsymbol{r}_j) + O(\epsilon^2) \tag{5.4}$$

and then use this result into (5.2). Taking the limit as $\epsilon \to 0$, we obtain

$$E_{\text{i.d.}} = -\sum_{i=1}^{N} \sum_{j=n+1}^{N+M} q_i (\boldsymbol{\mu}_j \cdot \nabla) \psi(\boldsymbol{r}_{ij}) + \tfrac{4}{3}\pi \left(\sum_{i=1}^{N} q_i \boldsymbol{r}_i \right) \cdot \left(\sum_{j=N+1}^{N+M} \boldsymbol{\mu}_j \right). \tag{5.5}$$

A further interaction that we must study is the ion–quadrupole interaction. We may write this for a charge q_i at $\boldsymbol{r}_i$ and a quadrupole $\boldsymbol{\Theta}_j$ at $\boldsymbol{r}_j$ in the form

$q_i \boldsymbol{\Theta}_j : \nabla\nabla(1/|\boldsymbol{r}_{ij}|)$, so that the lattice sum we require is, for N charges and M quadrupoles,

$$E_{\text{i.q.}} = \sum_{\boldsymbol{n}}{}' \sum_{i=1}^{N} \sum_{j=N-1}^{N+M} \boldsymbol{\Theta} q_{i\,j} : \nabla\nabla(1/|\boldsymbol{r}|)|_{\boldsymbol{r}=\boldsymbol{r}_{ij}+\boldsymbol{n}}. \tag{5.6}$$

The lattice sum $\Sigma_{\boldsymbol{n}}' \nabla\nabla(1/|\boldsymbol{r}|)|_{\boldsymbol{r}=\boldsymbol{r}_{ij}+\boldsymbol{n}}$ is itself conditionally convergent so we may write (5.6) in the form

$$E_{\text{i.q.}} = \sum_{i=1}^{N} \sum_{j=N+1}^{N+M} q_i \boldsymbol{\Theta}_j : [\sum_{\boldsymbol{n}}{}' \nabla\nabla(1/|\boldsymbol{r}|)|_{\boldsymbol{r}=\boldsymbol{r}+\boldsymbol{n}}]. \tag{5.7}$$

Thus
$$E_{\text{i.q.}} = \sum_{i=1}^{N} \sum_{j=N+1}^{N+M} q_i \boldsymbol{\Theta}_j : [\tfrac{4}{3}\pi \boldsymbol{I} - \nabla\nabla\psi(\boldsymbol{r})|_{\boldsymbol{r}=\boldsymbol{r}_{ij}}],$$

where $\boldsymbol{I}$ is the unit tensor.

This result may be simplified by using charge neutrality so that the terms $(\quad_j : \tfrac{4}{3}\pi \boldsymbol{I}) \sum_{i=1}^{N} q_i$ vanish to give

$$E_{\text{i.q.}} = -\sum_{i=1}^{N} \sum_{j=N+1}^{N+M} q_i \boldsymbol{\Theta}_j : \nabla\nabla\psi(\boldsymbol{r}_{ij}). \tag{5.8}$$

We note that there are no terms in this energy corresponding to the 'extra' ones found in (3.24), (4.8) and (5.5).

Finally we discuss the higher-order multipole–multipole interactions in p.b.c. We consider the interaction of a 2^{l_1} pole, D_{l_1}, at $\boldsymbol{r}_1$ with a 2^{l_2}-pole, D_{l_2}, at $\boldsymbol{r}_2$. The simple interaction (without p.b.c.) may be written in terms of multiple gradients of $|\boldsymbol{r}_{12}|^{-1}$. If we replace the multipoles by discrete charge distributions, use (3.24) for the interaction of these charge distributions under p.b.c. and then take the limit as the charge distributions are collapsed into the appropriate multipoles, we obtain the same energy expression for the interaction without p.b.c., but with $|\boldsymbol{r}_{12}|^{-1}$ replaced by $\psi(\boldsymbol{r}_{12})$. For all multipole interactions apart from those discussed above, the resulting lattice sums are absolutely convergent and hence no discussion of convergence factors is required.

6. Summary of effective interparticle potentials under p.b.c.

We may now consider particles with any type of multipole moments under p.b.c. and with cell-side length equal to L, and write down effective pair potentials that will allow a p.b.c. simulation to proceed, in the normal m.i. convention, with an effective interaction. We start with charge–charge interactions. We add

$$-\tfrac{1}{3}\pi \sum_{i=1}^{N} \sum_{j=1}^{N} q_i q_j (|\boldsymbol{r}_i|^2 + |\boldsymbol{r}_j|^2) = 0$$

to the right side of (3.24) and then identify separate pairwise interactions by the different $\boldsymbol{r}_{ij}$. We obtain

$$\begin{aligned} \phi_{\text{c.c.}}^{\text{p.b.c.}}(q_j, \boldsymbol{r}_j, q_k, \boldsymbol{r}_k) &= L^{-1} q_j q_k [\psi(\boldsymbol{r}_{jk}/L) - \tfrac{2}{3}\pi(\boldsymbol{r}_{jk}/L)^2] \\ &\equiv q_j q_k \psi_{\text{p.b.c.}}(\boldsymbol{r}_{jk}/L); \end{aligned} \tag{6.1}$$

(6.1) defines the function $\psi_{\text{p.b.c.}}(\boldsymbol{r})$.

$$\phi^{\text{p.b.c.}}_{\text{c.d.}}(q_j, \boldsymbol{r}_j, \boldsymbol{\mu}_k, \boldsymbol{r}_k) = -L^{-3} q_j (\boldsymbol{\mu}_k \cdot \nabla)\, \psi(\boldsymbol{r}_{jk}/L) + \tfrac{4}{3}\pi L^{-3} q_j \boldsymbol{\mu}_k \cdot \boldsymbol{r}_{jk} \tag{6.2}$$

and we note that

$$\phi^{\text{p.b.c.}}_{\text{c.d.}}(q_j, \boldsymbol{r}_j, \boldsymbol{\mu}_k, \boldsymbol{r}_k) = -q_j (\boldsymbol{\mu}_k \cdot \nabla)\, \psi_{\text{p.b.c.}}(\boldsymbol{r}_{jk}). \tag{6.3}$$

From (4.8) the dipole–dipole potential is

$$\phi^{\text{p.b.c.}}_{\text{d.d.}}(\boldsymbol{\mu}_j, \boldsymbol{r}_j, \boldsymbol{\mu}_k, \boldsymbol{r}_k) = -L^{-3} (\boldsymbol{\mu}_j \cdot \nabla)(\boldsymbol{\mu}_k \cdot \nabla)\, \psi(\boldsymbol{r}_{jk}/L) + \tfrac{4}{3}\pi L^{-3} \boldsymbol{\mu}_j \cdot \boldsymbol{\mu}_k \tag{6.4}$$

and we note also that

$$\phi^{\text{p.b.c.}}_{\text{d.d.}}(\boldsymbol{\mu}_j, \boldsymbol{r}_j, \boldsymbol{\mu}_k, \boldsymbol{r}_k) = -(\boldsymbol{\mu}_j \cdot \nabla)(\boldsymbol{\mu}_k \cdot \nabla)\, \psi_{\text{p.b.c.}}(\boldsymbol{r}_{jk}). \tag{6.5}$$

Higher-order multipole interactions may be calculated by the methods discussed in § 5. We conclude that any multipole interaction under p.b.c. may be written in exactly the same form as that without p.b.c., that is in terms of contractions of multipole moments by multiple operations of the gradient operator on $|\boldsymbol{r}_{jk}|^{-1}$, but with the function

$$\psi_{\text{p.b.c.}}(\boldsymbol{r}) = L^{-1}[\psi(\boldsymbol{r}/L)) - \tfrac{2}{3}\pi |\boldsymbol{r}/L|^2] \tag{6.6}$$

replacing $|\boldsymbol{r}|^{-1}$.

The charge–charge, charge–dipole and dipole–dipole interactions contain certain terms that have not always been included in simulation studies. One group of simulations (Ladd 1977, 1978) has included them. To consider the energy of a dipole $\boldsymbol{\mu}$ at $\boldsymbol{r}$, Ladd sets up a cube of side L with centre at $\boldsymbol{r}$. The interactions of $\boldsymbol{\mu}$ with all nearest images of the other particles are calculated explicitly. This new cube is also in the centre of a periodic array of replicas of itself. To evaluate the energy of interaction with the non-central cells, Ladd expands the electric field due to the particles in a cell in a multiple expansion about its centre, $\boldsymbol{n}$. All these expansions are convergent at the centre, $\boldsymbol{0}$, of the central cell. The interaction of $\boldsymbol{\mu}$ with the particles in the other periodic replica cells is thus a sum of interactions of a dipole $\boldsymbol{\mu}$ at $\boldsymbol{0}$, in the cell centred at $\boldsymbol{0}$, with a lattice of dipoles, quadrupoles etc. at $\boldsymbol{n}$ in the cell centred at $\boldsymbol{n}$. The only one of these interactions that the considerations of this paper might suggest to be incorrectly calculated is the interaction of a dipole $\boldsymbol{\mu}$ at $\boldsymbol{0}$ in the cell centred at $\boldsymbol{0}$ with a simple cubic lattice of dipoles $\boldsymbol{\mu}^T$. For $L = 1$ (L can be easily scaled in the problem) this interaction may be written as

$$\sum_{\lambda=1}^{3} \mu^\lambda \left[\sum_{\boldsymbol{n} \neq \boldsymbol{0}} \frac{(\mu^T)^\lambda |\boldsymbol{n}|^2 - 3n^\lambda \boldsymbol{\mu}^T \cdot \boldsymbol{n}}{|\boldsymbol{n}|^5} \right], \tag{6.7}$$

where the superfix λ denotes the x-, y- or z-component of a vector. For $\lambda = x$, the summand in (6.7) is

$$\{(\mu^T)^x [(n^y)^2 + (n^z)^2 + (n^x)^2] - 3n^x [-2(\mu^T)^y n^y + (\mu^T)^z n^z]\} / |n|^5. \tag{6.8}$$

Since the x-, y- and z-axes in the lattice are equivalent in a sum over spherical shells, the lattice sum over the first term in (6.8) is zero, and the sum over the second term is zero since the summand is an odd function. Thus for summation

over spherical shells, Ladd's method gives the same results as those obtained in this paper. Ladd has proposed his method because he felt that the computing times necessary to work with the sums in $\psi(\boldsymbol{r})$ were too great.

Before considering the effect of the extra terms on simulations, we consider briefly their effect on the thermodynamic limit. For non-polarized systems, their effect on the free energy density in the thermodynamic limit appears to be zero (Smith & Perram 1976). However, for a system with uniform polarization $\boldsymbol{p}$ per unit volume they add an energy $\frac{2}{3}\pi p^2 V^2$ to the Hamiltonian, where V is the volume of the sample. This suggests that if an infinite system polarizes under p.b.c., it does so by forming a large number of domains. At present it is not possible to study large enough samples to obtain many domains in simulations. This suggests that for a system to undergo a transition to a state that has a net polarization (as in a ferroelectric), the simple periodic boundary conditions discussed so far in this paper may be unsuitable.

7. Simulation of the hard sphere dipole fluid in periodic boundary conditions

Many computer simulations have been reported for systems with electrostatic interactions, almost none of them (the work of Ladd being the exception) using the potentials of § 6 for p.b.c. For ionic systems especially, the agreement with experiment has nonetheless been quite good (Woodcock & Singer 1971; De Leeuw 1978). For dipolar systems, the internal energy and radial distribution function are relatively insensitive to the boundary conditions (m.i., p.b.c. or reaction field) (Adams & McDonald 1976; Jansoone 1974; Levesque *et al.* 1977). However, those quantities, such as dielectric constant, angular correlation functions and specific heat; that depend on angular dipole correlation functions, are often strongly affected by boundary conditions (Adams & McDonald 1976; Levesque *et al.* 1977). Since we know of no simulations of ionic systems in which the dielectric response was analysed, we decided to concentrate on the polar system. Although a number of simulations of substances, such as water, that have a large permanent dipole moment have been reported, we have decided to examine the properties of the hard sphere dipole fluid where dipole interactions are the only source of orientational correlations.

Before discussing the results of these simulations, we should be clear as to what we are simulating and why we are simulating it. The key to these questions is our result (3.24), where we found the p.b.c. lattice sums for an infinite sphere of periodic replications of the cubic simulation sample. This establishes the geometry of our periodic system, which is rather more difficult to do for simulations in m.i., cutoff and the normal reaction field boundary conditions. Thus in our simulation, which uses the p.b.c. potential of (6.5), we are simulating a very large sphere of periodic replications of the central cubic sample.

In simulating this system, we are seeking to establish its orientational correlation functions, thermodynamic functions and dielectric constant. In understanding the

behaviour of these quantities, it turns out to be crucial to discuss first the dielectric constant or, if the system does not possess spherical symmetry, the dielectric tensor.

We begin by considering the response of a large sphere of radius a containing N_0 polar particles in vacuo to an externally applied electric field $\boldsymbol{E}$. Let $\rho^{(1)}(1;\boldsymbol{E})$ be the one-particle distribution function for this system, which has a Hamiltonian H_0 in the absence of the field. We have, quite generally,

$$\rho^{(1)}(1;\boldsymbol{E}) = \frac{\frac{1}{(N-1)!}\int \mathrm{d}(2)\ldots\int \mathrm{d}(N)\exp\left[-\beta H_0+\beta\sum_{i=1}^{N_0}\boldsymbol{\mu}(i)\cdot\boldsymbol{E}\right]}{\frac{1}{N!}\int \mathrm{d}(1)\ldots\int \mathrm{d}(N)\exp\left[-\beta H_0+\beta\sum_{i=1}^{N_0}\boldsymbol{\mu}(i)\cdot\boldsymbol{E}\right]}, \tag{7.1}$$

where $\int \mathrm{d}(i)$ represents integration over the position of the ith particle, integration over its angular coordinates and multiplication by a factor $\frac{1}{4\pi}$. For small fields $\boldsymbol{E}$, $\rho^{(1)}(1;\boldsymbol{E})$ may be expanded in a Taylor series about $\rho^{(1)}(1;\boldsymbol{0})$. We obtain

$$\rho^{(1)}(1;\boldsymbol{E}) = \rho^{(1)}(1;\boldsymbol{0})+\beta\boldsymbol{E}\cdot\left\{\boldsymbol{\mu}(1)\rho^{(1)}(1;\boldsymbol{0})+\int \mathrm{d}(2)\,\boldsymbol{\mu}(2)\left[\rho^{(2)}(1,2;\boldsymbol{0})-\rho^{(1)}(1;\boldsymbol{0})\rho^{(1)}(2;\boldsymbol{0})\right]\right\}+O(|\boldsymbol{E}^2|), \tag{7.2}$$

where $\rho^{(2)}(1,2;\boldsymbol{E})$ is the two-particle distribution function. The induced polarization per particle is then

$$\begin{aligned}\boldsymbol{P} &= N_0^{-1}\int \mathrm{d}(1)\rho^{(1)}(1;\boldsymbol{E})\,\boldsymbol{\mu}(1)\\ &= N_0^{-1}\int \mathrm{d}(1)\rho^{(1)}(1;\boldsymbol{0})\,\boldsymbol{\mu}(1)+N_0^{-1}\beta\boldsymbol{E}\cdot\left\{\int \mathrm{d}(1)\,\boldsymbol{\mu}(1)\,\boldsymbol{\mu}^{(1)}\rho^{(1)}(1;0)\right.\\ &\quad\left.+\int \mathrm{d}(1)\int \mathrm{d}(2)\,\boldsymbol{\mu}(1)\,\boldsymbol{\mu}(2)\left[\rho^{(2)}(1,2;\boldsymbol{0})-\rho^{(1)}(1;\boldsymbol{0})\rho^{(1)}(2;\boldsymbol{0})\right]\right\}+O(|\boldsymbol{E}^2|).\end{aligned} \tag{7.3}$$

It is then normally assumed that this quantity is approximated by evaluating it over the fundamental cell of side-length L of the simulation that contains N particles, where

$$N/L^3 = 3N_0/4\pi a^3. \tag{7.4}$$

The specific polarization $\boldsymbol{P}$ is conveniently written as

$$\boldsymbol{P} = \langle\boldsymbol{M}\rangle/N+\beta\boldsymbol{E}\cdot(\langle\boldsymbol{MM}\rangle-\langle\boldsymbol{M}\rangle\langle\boldsymbol{M}\rangle)/N, \tag{7.5}$$

where

$$\boldsymbol{M} = \sum_{i=1}^{N}\boldsymbol{\mu}(i), \tag{7.6}$$

μ is the magnitude of the dipole $\boldsymbol{\mu}(i)$ and angle brackets indicates an ensemble average.

To compute the dielectric tensor $\boldsymbol{\varepsilon}$ of this system, we must compute the response

of a sphere of dielectric material characterized by this tensor to the same applied field. The result is

$$\boldsymbol{P} = \boldsymbol{P}_0 + \frac{\boldsymbol{E}}{N_0} \cdot \int \mathrm{d}\boldsymbol{r}\, \boldsymbol{X}(\boldsymbol{r}), \tag{7.7}$$

where the integral is over the sphere and $\boldsymbol{X}(\boldsymbol{r})$ is the susceptibility tensor. Comparing (7.7) and (7.5) and taking the limit as $|\boldsymbol{E}| \to 0$ we find the integral of the susceptibility tensor:

$$\int \boldsymbol{X}(\boldsymbol{r})\, \mathrm{d}\boldsymbol{r} = \frac{N_0}{N} \beta(\langle \boldsymbol{M}\boldsymbol{M} \rangle - \langle \boldsymbol{M} \rangle \langle \boldsymbol{M} \rangle). \tag{7.8}$$

If the dielectric is assumed isotopic,

$$\boldsymbol{X}(\boldsymbol{r}) = \boldsymbol{I} \cdot \frac{3}{4\pi} \left(\frac{\epsilon - 1}{\epsilon + 2} \right). \tag{7.9}$$

where $\boldsymbol{I}$ is the unit tensor and ϵ is the dielectric constant. Inserting (7.9) into (7.8) and taking the trace, we find

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi\rho\mu^2}{9kT} \left(\frac{\langle \boldsymbol{M}^2 \rangle - \langle \boldsymbol{M} \rangle^2}{N\mu^2} \right) \tag{7.10}$$

which is the equation of Clausius Mosotti. It is usual to denote $4\pi\rho\mu^2/9kT$ by y and $(\langle |\boldsymbol{M}|^2 \rangle - \langle \boldsymbol{M} \rangle^2)/N\mu^2$ by g, the latter being the g-factor. We shall in fact denote the g-factor as $g(\epsilon')$, where ϵ' is the dielectric constant of the region exterior to the sphere. In this notation (7.10) becomes

$$(\epsilon - 1)/(\epsilon + 2) = yg(1). \tag{7.11}$$

We may now repeat the above calculation when the large sphere, of radius a, of periodic replications of the simulation cell is enclosed within a much larger spherical shell, of outer radius $b \gg a$, of uniform material of dielectric constant ϵ'. The larger sphere is subject to an applied external field $\boldsymbol{E}$ and we compute the response of the inner sphere to $\boldsymbol{E}$ via both macroscopic electrostatics and the Taylor series expansion, (7.2). We find for the dielectric constant of the inner sphere, in the limit $(b/a) \to \infty$,

$$(\epsilon - 1)(2\epsilon' + 1)/3(\epsilon + 2\epsilon') = yg(\epsilon'). \tag{7.12}$$

Setting $\epsilon' = 1$, we recover (7.11) and setting $\epsilon' = \epsilon$ we obtain the formula of Kirkwood,

$$(\epsilon - 1)(2\epsilon + 1)/9\epsilon = yg(\epsilon). \tag{7.13}$$

It is reasonable to expect that the formulae (7.11)–(7.13) should all produce the same value of the dielectric constant from a computer simulation, if the Hamiltonian appropriate to the composition of the surrounding medium of dielectric constant ϵ' is used. If the simulation cell has a polarization $\boldsymbol{P}$, then the sphere of replications polarizes the external medium which then reacts with the simulation cell. This interaction may be calculated by standard methods for the calculation of Onsager

reaction fields. If we let $H(\epsilon')$ be the appropriate Hamiltonian when the external shell has dielectric constant ϵ', then $H(1)$ is given by

$$H(1) = \sum_{1 \leqslant i < j \leqslant N} -[\boldsymbol{\mu}(i)\cdot\nabla][\boldsymbol{\mu}(j)\cdot\nabla]\psi_{\text{p.b.c.}}(\boldsymbol{r}_{ij}) \tag{7.14}$$

and

$$H(\epsilon') = H(1) - \frac{6kTy(\epsilon'-1)}{N\mu^2(2\epsilon'+1)} \sum_{1 \leqslant i < j \leqslant N} \boldsymbol{\mu}(i)\cdot\boldsymbol{\mu}(j). \tag{7.15}$$

In the next paper in this series we show that an exact calculation of ϵ for a system with one value of ϵ' in the limit $L \to \infty$, $N \to \infty$, $N/L^3 = \rho$ gives the same value of ϵ as a calculation with a different value of ϵ', denoted by ϵ''.

Equation (7.12) can be rearranged to give

$$\epsilon = [2\epsilon' + 1 + 6\epsilon' yg(\epsilon')]/[2\epsilon' + 1 - 3yg(\epsilon')]. \tag{7.16}$$

In part II we show that

$$g(\epsilon'') = g(\epsilon')\,[1 - \tfrac{1}{3}\lambda(\epsilon', \epsilon'')\,g(\epsilon')]^{-1}, \tag{7.17}$$

where

$$\lambda(\epsilon', \epsilon'') = 6y\left(\frac{\epsilon''-1}{2\epsilon''+1} - \frac{\epsilon'-1}{2\epsilon'+1}\right). \tag{7.18}$$

If we attempt to calculate ϵ from (7.16) by using $g(\epsilon'')$ and ϵ'', and substitute (7.17) for $g(\epsilon'')$, and (7.12) for $g(\epsilon')$, we obtain the value of ϵ calculated from (7.16) by using $g(\epsilon')$ and ϵ'. Thus changes in ϵ' modify the Hamiltonian in such a way that the g-factor changes (even in the thermodynamic limit) and gives a value to ϵ from (7.16) that is independent of ϵ'.

We have performed Monte-Carlo simulations for 256 particles by using the pair potential of (6.4) at a density of $\rho\sigma^3 = 0.8$, and values of the reduced temperature $\sigma^3 kT/\mu^2$ of 1.5, 1.0 and 0.5. The system was equilibrated from a lattice and averages taken for between 10^6 and 2×10^6 configurations. The values of $g(1)$ and ϵ, calculated from

$$\epsilon = [2yg(1) + 1]/[1 - yg(1)] \tag{7.19}$$

are shown in table 1.

Figures 1–3 show the projections of the pair correlation function $g^{(2)}(1, 2)$ onto the usual angular functions $1, \Delta(1, 2)$ and $D(1, 2)$ (Wertheim 1971) at the lowest temperature ($\sigma^3 kT/\mu^2 = 0.5$). We see clearly the negative region in the function $h_\Delta(1, 2)$, which was also observed in the m.i. simulations of Levesque *et al.* (1977). For these boundary conditions, as T decreases to zero (or a ferroelectric critical temperature) $yg(1)$ must evidently approach unity so the formula (7.19) may grossly magnify errors in $g(1)$, calculated from the simulation. While $\epsilon' = 1$ suppresses dipole-moment fluctuations in the simulation more effectively than any other value of ϵ', the error magnification caused by the formula (7.19) forces us to view the result $\epsilon = 14.9$ at the lowest temperature with some suspicion. This lowest temperature corresponds to $y = 2.23$. As the value of y for water at 273 K, with a gas phase dipole moment of $1.84D$, is 4.1, it may be that the error magnification caused by the formula (7.19) is so large as to preclude use of this boundary condition for such

large values of y. Another feature of these results is that $h_\Delta(r)$ does not tend quickly to zero as predicted by both the mean spherical model (Wertheim 1971) and perturbation theory that uses the angle-averaged Boltzmann factor (Perram & White 1974). We discuss this behaviour of $h_\Delta(r)$ in part II.

The corrections to the Hamiltonian caused by surrounding the infinite sphere of

TABLE 1. VALUES OF y, $g(1)$ AND ϵ FOR $\rho\sigma^3 = 0.8$, $\sigma^3 kT/\mu^2 = 0.5$, 1.0 AND 1.5

$\sigma^3 kT/\mu^2$	y	$g(1)$	ϵ
1.5	0.745	0.714	4.4
1.0	1.117	0.612	7.5
0.5	2.234	0.368	14.9

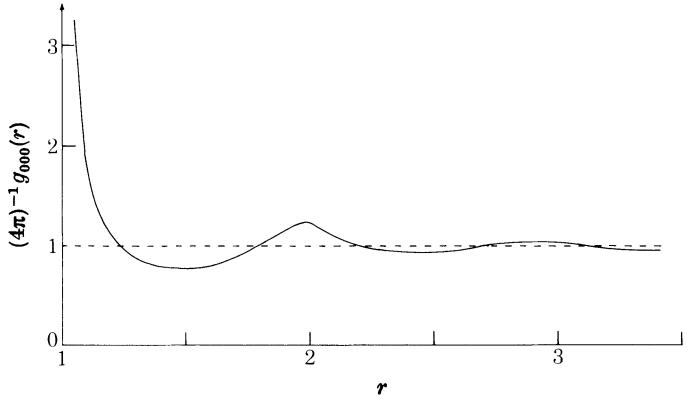

FIGURE 1. Plot of simulation results for $g_{000}(r)$ with $\rho\sigma^3 = 0.8$, $\sigma^3 kT/\mu^2 = 0.5$ and $\epsilon' = 1$.

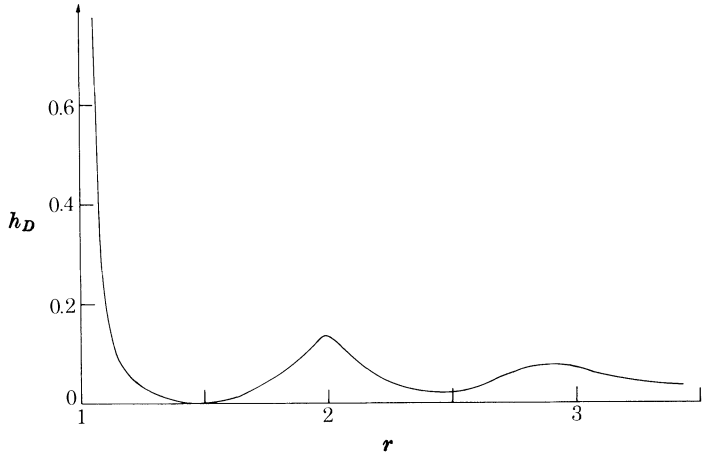

FIGURE 2. Plot of simulation results for $h_D(r)$ with $\rho\sigma^3 = 0.8$, $\sigma^3 kT/\mu^2 = 0.5$ and $\epsilon' = 1$.

replicas of the simulation cell by a medium of dielectric constant ϵ', given in (7.15), correspond to a change in the effective pair potential $\Delta\psi(1,2)$ which may be computed as

$$\Delta\phi(1,2) = \psi_{\epsilon'}(1,2) - \psi_1(1,2) = -\tfrac{8}{3}\pi \frac{\boldsymbol{\mu}(1)\cdot\boldsymbol{\mu}(2)}{L^3} \frac{\epsilon'-1}{2\epsilon'+1}, \tag{7.20}$$

Adams & McDonald (1976) have reported simulations of face-centred cubic and simple cubic lattices of freely rotating permanent dipoles that use a potential

$$\psi_{\mathrm{d}}(1,2) = -[\boldsymbol{\mu}(1)\cdot\nabla][\boldsymbol{\mu}(2)\cdot\nabla]\psi_{\mathrm{p.b.c.}}(\boldsymbol{r}_{12}) - \frac{4}{3}\frac{\pi}{L^3}\boldsymbol{\mu}(1)\cdot\boldsymbol{\mu}(2). \tag{7.21}$$

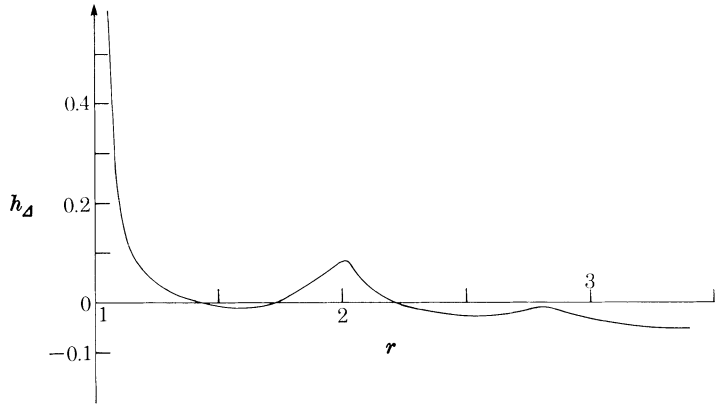

FIGURE 3. Plot of simulation results for $h_\Delta(r)$ with $\rho\sigma^3 = 0.8$, $\sigma^3 kT/\mu^2 = 0.5$ and $\epsilon' = 1$. For large r, $h_\Delta(r) \simeq -0.053$.

TABLE 2. AVERAGE POLARIZATION COMPONENTS, g-FACTOR AND DIELECTRIC CONSTANT (ϵ) FOR $\epsilon^T \to \infty$ AND $\epsilon' = 1$, $\sigma^3 kT/\mu^2 = 0.5$, $\rho\sigma^3 = 0.8$

	$\langle M_x\rangle$	$\langle M_y\rangle$	$\langle M_z\rangle$	$g(\epsilon')$	ϵ
$\epsilon' = 1$	−0.915	−0.647	0.056	0.368	14.9
$\epsilon' \to \infty$	1.541	−10.097	−15.657	3.239	22.7

This corresponds to the use of (4.8) with the first term omitted. We see that this potential corresponds (via (7.20)) to the case $\epsilon' \to \infty$. For this, (7.12) gives

$$\epsilon = 1 + 3yg(\infty), \tag{7.22}$$

which magnifies errors in $yg(\infty)$ by a factor of only 3.

We repeated the simulation at $kT\sigma^3/\mu^2 = 0.5$ with the effective pair potential (7.21), equilibrating and performing averages over 2×10^6 configurations. Table 2 shows the values of $g(\infty)$ obtained, as well as the averages of the three components of the dipole moment of the cell. The corresponding results for the first simulations are also shown, and it is not surprising to note the much lower average polarization for the first simulation. Equation (7.22) gives the value $\epsilon = 22.7$ which is at variance

with the result $\epsilon = 14.9$ obtained by the first simulations at $kT\sigma^3/\mu^2 = 0.5$. While the magnification of errors involved in (7.22) is much less than that involved in (7.19), the much larger fluctuations in the net dipole moment of the cell as $\epsilon' \to \infty$ (i.e. potential (7.21)) allow the possibility that the error in $g(\infty)$ from a finite simulation may be much larger than the error in $g(1)$.

TABLE 3. SUBAVERAGES OF POLARIZATION COMPONENTS, SQUARE OF POLARIZATION, AND g-FACTOR OVER FIVE BLOCKS OF 10^5 CONFIGURATIONS AT THE END OF THE $\epsilon' = 1$ and $\epsilon' \to \infty$ RUNS FOR $kT\sigma^3/\mu^2 = 0.5$, TOGETHER WITH ϵ CALCULATED FROM THE g-FACTORS

	configurations/10^6	M_x/μ	M_y/μ	M_z/μ	M^2/μ^2	g	ϵ
$\epsilon' = 1$	$1.3 \to 1.4$	6.672	−2.458	−1.885	117.716	0.396	24.0
	$1.4 \to 1.5$	−3.490	−2.427	−1.931	98.732	0.300	7.1
	$1.5 \to 1.6$	−0.608	−2.632	1.234	116.284	0.420	46.6
	$1.6 \to 1.7$	−5.031	0.843	1.677	72.783	0.172	2.9
	$1.7 \to 1.8$	−1.608	0.431	−4.222	86.221	0.256	5.0
$\epsilon' \to \infty$	$1.5 \to 1.6$	−5.176	−15.924	1.207	460.51	0.698	5.7
	$1.6 \to 1.7$	10.375	12.230	5.551	671.10	1.496	11.0
	$1.7 \to 1.8$	4.196	−7.316	−19.011	867.72	1.700	12.4
	$1.8 \to 1.9$	−6.304	−26.612	−0.210	949.88	0.789	6.3
	$1.9 \to 2.0$	−19.686	−14.776	−20.775	1411.61	1.461	10.8

To investigate this possibility we averaged M_x, M_y, M_z and $|M|^2$ over the last five blocks of 10^5 configurations, for $\epsilon' = 1$ and $\epsilon' \to \infty$ at $kT\sigma^3/\mu^2 = 0.5$, and calculated $g(\epsilon')$ and ϵ from these sub-averages. The results are presented in table 3. We can see from the table that for both simulations the maximum and minimum values of the g-factors vary by a factor of about 2.4. The calculated values of ϵ are widely scattered, and bear only slight relation to the averages over all the 2×10^6 configurations presented earlier. Since table 3 is concerned with the last quarter of each run, so that the sub-averages listed are over about 5% of the run each, the table suggests that runs with a higher acceptance rate (it was approximately 6% in the runs reported here) or more configurations must be tried. The scatter in the values of ϵ shown in table 3 shows that the estimate $\epsilon = 14.9$ from the $\epsilon' = 1$ run and the estimate $\epsilon = 22.7$ from the $\epsilon' \to \infty$ run are not inconsistent. Further, even these extremely noisy data gave $\epsilon > 1$ for all the estimates and did not give any estimates that were excessively large.

The low acceptance rate in these simulations was primarily due to the method used for randomly orienting the dipoles. This used an algorithm due to Massaglia (1972), that gives a method for choosing randomly distributed points on a sphere. This method gives large changes in orientation, but does not give a biased distribution. To improve the acceptance rate, it is necessary to construct an algorithm that yields much smaller increments, but is not biased in a particular direction. To do this, we rotate a dipole by first choosing a random cartesian axis system and then rotating the dipoles by a small, random amount about each axis. The algorithm

was tested and found to give a satisfactory distribution of orientations. Using this algorithm, we repeated the $\epsilon' = \infty$ run using an acceptance rate of 25% and averaging over 1.4×10^6 configurations. The individual average dipole moments were now much lower, and a value of $\epsilon = 15.5$ was observed.

In figure 4 we present the $h_{\Delta}(r)$ calculated in the two simulations. Whereas $h_{\Delta}(r)$ is negative at large r for $\epsilon' = 1$, it is positive at large r for $\epsilon' \to \infty$ and we must ask

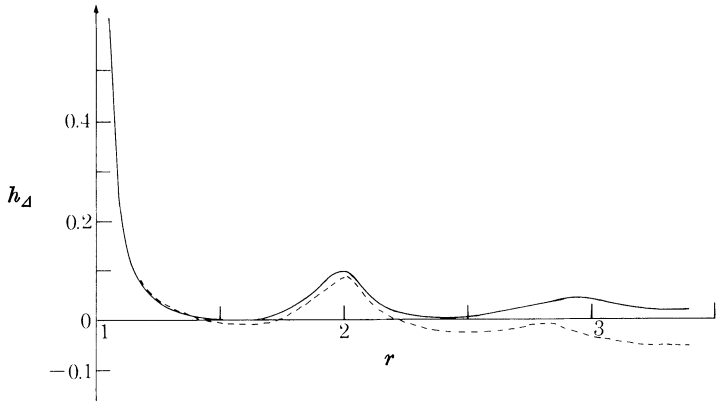

FIGURE 4. Plot of simulation results for $h_{\Delta}(r)$ with $\rho\sigma^3 = 0.8$, $\sigma^3 kT/\mu^2 = 0.5$. ——, $\epsilon' = \infty$; – – –, $\epsilon' = 1$. For $\epsilon' = \infty$, $h_{\Delta}(r) \simeq 0.015$ for large r.

why this is so. Neumann & Steinhauser (1979) have shown that macroscopic electrostatics could ensure that $h_{\Delta}(r)$ was negative at large r. We may also argue from (7.11) noting that

$$g = 1 + \tfrac{1}{3}\rho \int \mathrm{d}^3\boldsymbol{r} h_{\Delta}(\boldsymbol{r})$$

so that (7.11) becomes

$$\frac{\epsilon - 1}{\epsilon + 2} = y\left[1 + \tfrac{4}{3}\pi\rho \int_0^{\infty} r^2 h_{\Delta}(r)\,\mathrm{d}r\right]. \tag{7.23}$$

For $y > 1$, the right side of (7.23) can only be less than unity if the integral is negative, which will only occur if $h_{\Delta}(r)$ is negative over much of its range for $\epsilon' = 1$. We notice that for $\epsilon' \to \infty$, $h_{\Delta}(r)$ is positive. Based upon these observations and the expectation that $h_{\Delta}(r)$ should go to zero as $r \to \infty$ in an infinite system, we expect that the long tail of $h_{\Delta}(r)$ should disappear if we choose $\epsilon' = \epsilon$. This is rather difficult, since we do not know ϵ in advance, although (7.16) (or more particularly (7.19) and (7.22)) allows calculation of ϵ without taking care of the long-ranged tail in $h_{\Delta}(r)$. In Part II we show explicitly how the long-range tail of $h_{\Delta}(r)$ will change as ϵ' is changed from 1 to $+\infty$. The change is caused by the change in Hamiltonian in (7.15) which can be treated exactly, by perturbation theory to order N^{-1}. The perturbation theory explains the change in the tail of $h_{\Delta}(r)$ qualitatively.

We may conclude that there are many forms for the effective pair interaction of dipoles under p.b.c., the form depending on ϵ'. For each value of ϵ' chosen, there is

but one route to the dielectric constant. For fairly short runs the choices $\epsilon' = 1$ and $\epsilon' \to \infty$ give values of the dielectric constant that are consistent with one another. Different values of ϵ' give quite different values of the g-factor in a simulation.

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Note added in proof, 24 *July* 1980. Following equation (7.23), it is conjectured that $h_\Delta(r)$ is short-ranged if $\epsilon' = \epsilon$. Further simulations for $y = 2.234$, using the value of ϵ computed here as ϵ' confirm this conjecture (de Leeuw, Perram & Quirke, to be published).

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