Physica A 176 (1991) 485–498
North-Holland

SUMMATION OF COULOMB FIELDS IN COMPUTER-SIMULATED DISORDERED SYSTEMS

John LEKNER[1]

Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN 55455, USA

Received 7 January 1991

Formulae are derived for the sums over Coulomb forces exerted on a charged particle by other charged particles, the central cell system being repeated to infinity by periodic boundary conditions. Such sums are needed in molecular dynamics simulations involving either ions or neutral molecules represented as bound conglomerates of charges, and in astrophysical simulations of gravitating masses. The derived sums are rapidly convergent, being expressed in terms of Bessel functions $K_\nu(z)$, which decrease exponentially with z. The force expressions are integrated analytically to give the potential function, which may be used in Monte Carlo simulations. The geometries considered are: (i) systems confined between two parallel walls, and (ii) unconfined three-dimensional systems.

1. Introduction

Computer simulations produce configurations of some finite number of atoms, molecules or ions within a central cell. To minimize wall effects, periodic boundary conditions repeat the central cell to infinity. Long-range forces present a problem, because of the slow convergence of the sum over the repetitions of the central cell. The usual procedures of evaluating such sums are based on Ewald's method, developed in the study of ionic crystals to obtain the Madelung energy [1–4]. A discussion of these methods, with further references, may be found in a recent book on computer simulation of liquids [5].

Here we present an alternative method, based on an approach previously used in evaluating dipolar sums [6, 7], using techniques systematized by van der Hoff and Benson [8]. In contrast to the Ewald method, which requires a sum of one or two hundred terms involving the complementary error function and trigonometric functions, the sums we derive usually require the evaluation of ten or twenty terms. The functions which need to be evaluated are tri-

[1]On leave from: Department of Physics, Victoria University, Wellington, New Zealand.

0378-4371/91/$03.50

gonometric functions and Bessel functions of imaginary argument. No arbitrary parameter enters into the evaluation, in contrast to the Ewald method. The Bessel functions may be evaluated by ascending series (see ref. [9], formulae 9.6.10–13), by asymptotic expansions (ref. [9], 9.7.2), or by polynomial approximations (ref. [9], section 9.8). In section 5 we show that the evaluation of the Bessel functions may be avoided, and one sum performed, at the expense of evaluation of a definite integral.

In the next section we will derive expressions for the sum of the charge–charge forces acting in a system confined between two parallel walls. This sum is over a two-dimensional lattice of repetitions of the central simulation cell. The motivation for this section is the current simulation by Davis and collaborators of water and ionic solutions in porous media [10]. In section 3 we will obtain the Coulomb force on a charge in a simulation of a bulk system, where the central cell is repeated to infinity in all three spatial dimensions. In section 4 the force equations are integrated to obtain the potential.

The lattice sums defined below are conditionally convergent, and as such may be summed to give any desired value by a suitable re-arrangement of the terms. (This theorem is due to Riemann; see Knopp [11], section 44.) A given evaluation corresponds to a particular physical configuration of charges, including surface charges. The Ewald method, and the one developed here, give what is known as the intrinsic potential, or the principal value of the potential: see the discussion in refs. [3, 4, 12–15].

2. Systems confined between walls

We consider an assembly of N ions, with charges q_i and positions $\boldsymbol{r}_i$, interacting with Coulomb and other (here unspecified) forces. The molecular dynamics simulation is assumed to be carried out in a central cell, of dimensions L, L, and D in the x, y and z directions, respectively, and the central cell is repeated to infinity in the $\pm x$ and $\pm y$ directions. The containing walls, at (say) $z=0$ and $z=D$, may have arbitrary interaction with the ions; here we will concern ourselves only with the Coulomb interactions between the charged particles. The Ewald method for this geometry has been developed recently [16]. The Coulomb force exerted on particle i by particle j, and by all the repetitions of particle j in the periodic system, is

$$\boldsymbol{F}_i = q_i q_j \sum_{\text{all cells}} \frac{\boldsymbol{r}_i - \boldsymbol{r}_j}{|\boldsymbol{r}_i - \boldsymbol{r}_j|^3} . \tag{1}$$

(Note that the periodic repetition of particle i itself gives zero force on the charge in the central cell.) We define dimensionless measures of the displacements between charge q_i and charge q_j:

$$x_i - x_j = \xi L , \qquad y_i - y_j = \eta L , \qquad z_i - z_j = \zeta L \tag{2}$$

with $|\xi|, |\eta| \le 1$, and $|\zeta| \le D/L$. The x, y and z components of the force on charge q_i due to charge q_j are then $q_i q_j / L^2$ times the dimensionless functions X, Y and Z, where

$$\begin{aligned} X(\xi, \eta; \zeta) &= \sum_{l,m=-\infty}^{\infty}\sum \frac{\xi + l}{[(\xi + l)^2 + (\eta + m)^2 + \zeta^2]^{3/2}} , \\ Y(\xi, \eta; \zeta) &= \sum_{l,m=-\infty}^{\infty}\sum \frac{\eta + m}{[(\xi + l)^2 + (\eta + m)^2 + \zeta^2]^{3/2}} , \\ Z(\xi, \eta; \zeta) &= \sum_{l,m=-\infty}^{\infty}\sum \frac{\zeta}{[(\xi + l)^2 + (\eta + m)^2 + \zeta^2]^{3/2}} . \end{aligned} \tag{3}$$

Note that $X(-\xi, \eta; \zeta) = -X(\xi, \eta; \zeta)$, etc. Also $Y(\xi, \eta; \zeta) = X(\eta, \xi; \zeta)$, so we need consider only the sums X and Z.

The conversion of these sums to rapidly convergent ones proceeds via three transformations. We first find an integral representation of $[(\xi + l)^2 + (\eta + m)^2 + \zeta^2]^{-3/2}$ using the Euler transformation

$$\frac{1}{x^\nu} = \frac{1}{\Gamma(\nu)} \int_0^\infty \mathrm{d}t\, t^{\nu-1} \mathrm{e}^{-xt} \qquad (\nu > 0) . \tag{4}$$

Since $\Gamma(\frac{3}{2}) = \frac{1}{2}\pi^{1/2}$, this gives

$$\begin{aligned} &[(\xi + l)^2 + (\eta + m)^2 + \zeta^2]^{-3/2} \\ &= \frac{2}{\pi^{1/2}} \int_0^\infty \mathrm{d}t\, t^{1/2} \exp\{-[(\xi + l)^2 + (\eta + m)^2 + \zeta^2]t\} . \end{aligned} \tag{5}$$

The second transformation is based on the Poisson–Jacobi identity (ref. [17], p. 124, exs. 17 and 18)

$$\sum_{-\infty}^{\infty} \exp[-(\xi + l)^2 t] = \left(\frac{\pi}{t}\right)^{1/2} \sum_{-\infty}^{\infty} \exp(-\pi^2 l^2 / t) \cos(2\pi l \xi) . \tag{6}$$

For the Z sum we use (6) directly, evaluate the $l=0$ part separately, and use the third transformation, namely an integral representation of the Bessel function K_ν (from ref. [18], p. 183, eq. (15), and using the fact that $K_{-\nu}(z) = K_\nu(z)$),

$$\int_0^\infty \mathrm{d}t\, t^{\nu-1} \exp(-\pi^2 l^2/t - m^2 t) = 2\left(\pi\left|\frac{l}{m}\right|\right)^\nu K_\nu(2\pi|lm|)\,. \tag{7}$$

to obtain

$$Z(\xi,\eta;\zeta) = \frac{2\pi\sinh(2\pi\zeta)}{\cosh(2\pi\zeta)-\cos(2\pi\eta)} + 8\pi\zeta \sum_1^\infty l\cos(2\pi l\xi) \sum_{-\infty}^\infty [(\eta+m)^2+\zeta^2]^{-1/2} \times K_1(2\pi l[(\eta+m)^2+\zeta^2]^{1/2})\,. \tag{8}$$

The details of this derivation will not be given, since they happen to be the same as given in eqs. (12)–(16) of ref. [7]. (The symmetry $Z(\eta,\xi;\zeta) = Z(\xi,\eta;\zeta)$, not apparent in (8), is also discussed in ref. [7], where an explicitly symmetric expression for a function equal to Z/ζ is obtained.) We note that $Z(\xi,\eta;0)$ is zero, as is evident from (3) or (8): there is no z component of the Coulomb force between particles at the same z.

We now consider $X(\xi,\eta;\zeta)$: use of (5) transforms this sum to

$$X(\xi,\eta;\zeta) = \frac{2}{\pi^{1/2}} \sum\sum_{-\infty}^{\infty} (\xi+l) \int_0^\infty \mathrm{d}t\, t^{1/2} \times \exp\{-[(\xi+l)^2+(\eta+m)^2+\zeta^2]t\}\,. \tag{9}$$

On transforming the m sum using (6), this becomes

$$X(\xi,\eta;\zeta) = 2\sum\sum_{-\infty}^{\infty} (\xi+l)\cos(2\pi m\eta) \times \int_0^\infty \mathrm{d}t \exp\{-\pi^2 m^2/t - [(\xi+l)^2+\zeta^2]t\}\,. \tag{10}$$

The $m=0$ part of this sum is (compare eqs. (13)–(15) of ref. [7])

$$2\sum_{-\infty}^{\infty} \frac{\xi+l}{(\xi+l)^2+\zeta^2} = \sum_{-\infty}^{\infty}\left(\frac{1}{\xi+l-\mathrm{i}\zeta} + \frac{1}{\xi+l+\mathrm{i}\zeta}\right) = \pi\cot[\pi(\xi-\mathrm{i}\zeta)] + \pi\cot[\pi(\xi+\mathrm{i}\zeta)] = \frac{2\pi\sin(2\pi\xi)}{\cosh(2\pi\zeta)-\cos(2\pi\xi)}\,. \tag{11}$$

In the remaining part of the sum we use (7) to express the integral in terms of the Bessel function K_1. The final result is

$$X(\xi,\eta;\zeta) = \frac{2\pi\sin(2\pi\xi)}{\cosh(2\pi\zeta)-\cos(2\pi\xi)} + 8\pi\sum_{-\infty}^{\infty}\frac{\xi+l}{[(\xi+l)^2+\zeta^2]^{1/2}}\sum_1^\infty m\cos(2\pi m\eta) \times K_1(2\pi m[(\xi+l)^2+\zeta^2]^{1/2})\,. \tag{12}$$

Another way of evaluating X is to transform the l sum by means of an identity obtained from (6) by differentiation with respect to ξ:

$$\sum_{-\infty}^{\infty}(\xi+l)\exp[-(\xi+l)^2 t] = \left(\frac{\pi}{t}\right)^{3/2}\sum_{-\infty}^{\infty} l\sin(2\pi l\xi)\exp(-\pi^2 l^2/t)\,. \tag{13}$$

Using of (7) then gives

$$X(\xi,\eta;\zeta) = 8\pi\sum_1^\infty l\sin(2\pi l\xi)\sum_{-\infty}^{\infty} K_0(2\pi l[(\eta+m)^2+\zeta^2]^{1/2})\,. \tag{14}$$

If the two charges under consideration have the same x coordinate in the central cell, there is no x component of the Coulomb force. Thus $X=0$ if $\xi=0$ or ± 1. Also $X(\pm\frac{1}{2},\eta;\zeta)=0$, because of the symmetry of such configurations.

3. Unconfined three-dimensional systems

We again consider a system with N charges in the central cell, so that there are $\frac{1}{2}N(N-1)$ forces to be calculated, with three components for each force. The force on charge q_i due to charge q_j is as given by (1), where now the sum over cells is over a three-dimensional repetition of the central cell. If the central cell is a cube of side L, and ξ, η and ζ are as defined in (2), the force on charge q_i due to charge q_j has components $L^{-2}q_i q_j(X,Y,Z)$, where

$$X(\xi,\eta,\zeta) = \sum_l\sum_m\sum_n{}_{-\infty}^{\infty} \frac{\xi+l}{[(\xi+l)^2+(\eta+m)^2+(\zeta+n)^2]^{3/2}} \tag{15}$$

and Y or Z are sums with the same denominator and $\eta+m$ or $\zeta+n$ in the numerator. Because of the x, y, z symmetry we now need consider only one component of the force. Note that we do not preceed ζ with a semicolon, since z is not a special direction, as it was in the previous section.

Application of (5) transforms (15) to

$$X(\xi,\eta,\zeta)=\frac{2}{\pi^{1/2}}\sum\sum_{-\infty}^{\infty}\sum(\xi+l)$$
$$\times\int_0^\infty \mathrm{d}t\, t^{1/2}\exp\{-[(\xi+l)^2+(\eta+m)^2+(\zeta+n)^2]t\}\,. \tag{16}$$

We may rewrite the sum over l using (13), to obtain

$$X(\xi,\eta,\zeta)=8\pi\sum_1^\infty l\sin(2\pi l\xi)\sum\sum_{-\infty}^{\infty}K_0(2\pi l[(\eta+m)^2+(\zeta+n)^2]^{1/2})\,. \tag{17}$$

As in the wall-confined case, the x component of the force is zero when $\xi=0$, ±1 and $\pm\frac{1}{2}$.

Another version of the X sum can be obtained by transforming (for example) the sum over n by means of (6). This gives

$$X(\xi,\eta,\zeta)=2\sum_{-\infty}^{\infty}(\xi+l)\sum_{-\infty}^{\infty}\sum_{-\infty}^{\infty}\cos(2\pi n\zeta)$$
$$\times\int_0^\infty \mathrm{d}t\exp\{-[(\xi+l)^2+(\eta+m)^2]t-\pi^2n^2/t\}\,. \tag{18}$$

The $n=0$ part of this sum is

$$2\sum\sum_{-\infty}^{\infty}\frac{\xi+l}{(\xi+l)^2+(\eta+m)^2}$$
$$=\sum\sum_{-\infty}^{\infty}\{[\xi+l+\mathrm{i}(\eta+m)]^{-1}+[\xi+l-\mathrm{i}(\eta+m)]^{-1}\}\,. \tag{19}$$

The sum over l is known from (11), so the $n=0$ part reduces to

$$2\pi\sin(2\pi\xi)\sum_{-\infty}^{\infty}\{\cosh[2\pi(\eta+m)]-\cos(2\pi\xi)\}^{-1}\,. \tag{20}$$

The $n\neq0$ part of (18) is transformed via (7) to

$$8\pi\sum_{-\infty}^{\infty}(\xi+l)\sum_{-\infty}^{\infty}[(\xi+l)^2+(\eta+m)^2]^{-1/2}$$
$$\times\sum_1^\infty n\cos(2\pi n\zeta)\,K_1(2\pi n[(\xi+l)^2+(\eta+m)^2]^{1/2})\,. \tag{21}$$

The force calculated from (17) and (20), (21) is in agreement with the numerical values quoted in ref. [4], as is the potential to be derived in the next section.

4. Potential energy functions

We noted in conjunction with eq. (1) that the periodic self-replication of a particle gives zero force on that particle. (This holds by symmetry for any central pairwise interaction.) The Coulomb potential due to these repetitions is however infinite. In a neutral system ($\Sigma_i q_i=0$ in any cell), the total potential at any point is finite, because of cancellation of such infinities. In the Ewald method this cancellation of infinites is taken care of by omission of the $k=0$ term in the Fourier expansion of the potential: for overall neutrality the zeroth Fourier component of the charge density is zero, and the potential and density components are related through the Poisson equation by $\psi_k=4\pi\rho_k/k^2$. (The problem of division of one zero by another is usually not discussed.) Here we have no explicit device for cancellation of the infinities (see however the comment regarding the Laplacian at the end of this section), but we can obtain the potential energy function

$$U_{ij}\equiv\frac{q_iq_j}{L}V \tag{22}$$

by integration of the force $\boldsymbol{F}_i$, so that

$$-\nabla_iU_{ij}=\boldsymbol{F}_i\,,\qquad -\frac{\partial V}{\partial\xi}=X\,,\qquad \text{etc.} \tag{23}$$

4.1. Systems confined between walls

Since $\mathrm{d}K_0(z)/\mathrm{d}z=-K_1(z)$, the x component of force as given by (12) can be written as minus the derivative with respect to ξ of

$$4\sum_{l=-\infty}^{\infty}\sum_{m=1}^{\infty}\cos(2\pi m\eta)\,K_0(2\pi m[(\xi+l)^2+\zeta^2]^{1/2})$$
$$-\log[\cosh(2\pi\zeta)-\cos(2\pi\xi)]\,. \tag{24}$$

The z component of force, eq. (8), can be written as minus the derivative with respect to ζ of

$$4\sum_{l=1}^{\infty}\sum_{m=-\infty}^{\infty}\cos(2\pi l\xi)\,K_0(2\pi l[(\eta+m)^2+\zeta^2]^{1/2})$$
$$-\log[\cosh(2\pi\zeta)-\cos(2\pi\eta)]\,. \tag{25}$$

Finally, from eq. (14) we deduce that

$$V(\xi,\eta;\zeta)=4\sum_{l=1}^{\infty}\sum_{m=-\infty}^{\infty}\cos(2\pi l\xi)\,K_0(2\pi l[(\eta+m)^2+\zeta^2]^{1/2})+\phi(\eta;\zeta)\,, \tag{26}$$

where ϕ is some arbitrary function. Comparison of (25) with (26) indicates that, up to a constant,

$$\phi(\eta;\zeta)=-\log[\cosh(2\pi\zeta)-\cos(2\pi\eta)]\,. \tag{27}$$

With this choice of ϕ, the three expressions (24), (25) and (26) are all equivalent, because of the hidden ξ,η symmetry implicit in the equality of (24) and (25). Thus

$$\begin{aligned}V(\xi,\eta;\zeta)&=4\sum_{l=1}^{\infty}\cos(2\pi l\xi)\sum_{m=-\infty}^{\infty}K_0(2\pi l[(\eta+m)^2+\zeta^2]^{1/2})\\&\quad-\log[\cosh(2\pi\zeta)-\cos(2\pi\eta)]\\&=4\sum_{m=1}^{\infty}\cos(2\pi m\eta)\sum_{l=-\infty}^{\infty}K_0(2\pi m[(\xi+l)^2+\zeta^2]^{1/2})\\&\quad-\log[\cosh(2\pi\zeta)-\cos(2\pi\xi)]\,.\end{aligned} \tag{28}$$

The unknown constant C_2 to be added to V can be determined as follows: when $\xi=\pm\frac{1}{2}$, $\eta=\pm\frac{1}{2}$, $\zeta=0$, and the two charges in each cell are $\pm q$, the potential energy per cell is

$$-\frac{q^2}{L}[V(\pm\tfrac{1}{2},\pm\tfrac{1}{2};0)+C_2]=-\frac{q^2}{L/\sqrt{2}}M_s\,, \tag{29}$$

where $M_s=1.61554\ldots$ is the Madelung constant for a square lattice of ±1 alternating charges, with unit distance between nearest neighbours,

$$M_s=\sum_{\substack{l,m=-\infty\\ l^2+m^2\neq0}}^{\infty}\sum(-)^{l+m+1}(l^2+m^2)^{-1/2}\,. \tag{30}$$

This sum may be obtained by a limiting process from table II of ref. [8]. We find

$$M_s=2\log2+8\sum_{l=1}^{\infty}\sum_{m=0}^{\infty}(-)^{l+1}K_0(\pi l(2m+1))\,, \tag{31}$$

where we have used the fact that the Riemann zeta function $\zeta(s)$ diverges to infinity at $s=1$ as $(s-1)^{-1}$, so that

$$\lim_{s\to1}(1-2^{1-s})\zeta(s)=\log2\,. \tag{32}$$

From (28) and (31) we have

$$\begin{aligned}V(\pm\tfrac{1}{2},\pm\tfrac{1}{2};0)&=8\sum_{l=1}^{\infty}\sum_{m=0}^{\infty}(-)^{l}K_0(\pi l(2m+1))-\log2\\&=\log2-M_s\end{aligned} \tag{33}$$

and thus the constant to be added to the potential function (28) is

$$C_2=\sqrt{2}\,M_s-V(\tfrac{1}{2},\tfrac{1}{2};0)=(1+\sqrt{2})M_s-\log2=3.20711\ldots \tag{34}$$

The Laplacian $\nabla^2V=-(\partial X/\partial\xi+\partial Y/\partial\eta+\partial Z/\partial\zeta)$ is zero, as may be verified by calculating $\partial X/\partial\xi$ and $\partial Y/\partial\eta$ from (14), and $\partial Z/\partial\zeta$ from (8). We note in passing that since

$$\frac{\partial Z}{\partial\zeta}=\frac{\partial}{\partial\zeta}(\zeta F)=-S\,, \tag{35}$$

where $F(\xi,\eta;\zeta)$ and $S(\xi,\eta;\zeta)$ are functions defined in eqs. (7) and (8) of ref. [7], the fact that the Laplacian is zero gives a new expression for S:

$$\begin{aligned}S(\xi,\eta;\zeta)&=16\pi^2\sum_{l=1}^{\infty}l^2\cos(2\pi l\xi)\sum_{m=-\infty}^{\infty}K_0(2\pi l[(\eta+m)^2+\zeta^2]^{1/2})\\&\quad+16\pi^2\sum_{m=1}^{\infty}m^2\cos(2\pi m\eta)\sum_{l=-\infty}^{\infty}K_0(2\pi m[(\xi+l)^2+\zeta^2]^{1/2})\,.\end{aligned} \tag{36}$$

4.2. *Three-dimensional repetition of the central cell*

The integration of the force equations to obtain a potential $V(\xi,\eta,\zeta)$ such that $-\partial V/\partial\xi=X$, etc., is more difficult in the fully three-dimensional case. Eq. (17) is easy to integrate:

$$\begin{aligned}V(\xi,\eta,\zeta)&=4\sum_{l=1}^{\infty}\cos(2\pi l\xi)\sum_{m,n=-\infty}^{\infty}\sum K_0(2\pi l[(\eta+m)^2+(\zeta+n)^2]^{1/2})\\&\quad+\Phi(\eta,\zeta)\,.\end{aligned} \tag{37}$$

An integral of (20) and (21) is

$$V(\xi,\eta,\zeta)=4\sum_{n=1}^{\infty}\cos(2\pi n\zeta)\sum_{l,m=-\infty}^{\infty}\sum K_0(2\pi n[(\xi+l)^2+(\eta+m)^2]^{1/2})$$
$$-\log\lim_{M\to\infty}\prod_{-M}^{M}\frac{\cosh[2\pi(\eta+m)]-\cos(2\pi\xi)}{\cosh(2\pi m)}+\Psi(\eta,\zeta)\,. \quad (38)$$

(The specification of how the product is to be taken is necessary, since the product converges only if $+m$ and $-m$ terms occur together.) A clue to the form of the unknown functions Φ and Ψ can be found by summing the conditionally convergent series (19) in a different way:

$$2\sum_{l,m=-\infty}^{\infty}\sum\frac{\xi+l}{(\xi+l)^2+(\eta+m)^2}$$
$$=\mathrm{i}^{-1}\sum_{l,m=-\infty}^{\infty}\sum\{[\eta+m-\mathrm{i}(\xi+l)]^{-1}-[\eta+m+\mathrm{i}(\xi+l)]^{-1}\}$$
$$=\frac{\pi}{\mathrm{i}}\sum_{l=-\infty}^{\infty}(\cot\{\pi[\eta-\mathrm{i}(\xi+l)]\}-\cot\{\pi[\eta+\mathrm{i}(\xi+l)]\})$$
$$=2\pi\sum_{l=-\infty}^{\infty}\frac{\sinh[2\pi(\xi+l)]}{\cosh[2\pi(\xi+l)]-\cos(2\pi\eta)}\,. \quad (39)$$

This sum converges (and rapidly) if the $+l$ and $-l$ terms are taken together, that is, if the sum is interpreted as the limit of $M\to\infty$ of the sum from $l=-M$ to $+M$. It is larger than the absolutely convergent sum (20) by $4\pi\xi$, and is the derivative with respect to ξ of

$$\log\left(\lim_{M\to\infty}\prod_{-M}^{M}\frac{\cosh[2\pi(\xi+m)]-\cos(2\pi\eta)}{\cosh(2\pi m)}\right). \quad (40)$$

We are thus led to postulate that the function of ξ and η to be added to the sum over Bessel functions in (38) is

$$f(\xi,\eta)=2\pi\xi^2-\log\left(\lim_{M\to\infty}\prod_{-M}^{M}\frac{\cosh[2\pi(\xi+m)]-\cos(2\pi\eta)}{\cosh(2\pi m)}\right)$$
$$=2\pi\eta^2-\log\left(\lim_{M\to\infty}\prod_{-M}^{M}\frac{\cosh[2\pi(\eta+m)]-\cos(2\pi\xi)}{\cosh(2\pi m)}\right). \quad (41)$$

The interchange symmetry $f(\xi,\eta)=f(\eta,\xi)$ follows from the identity

$$\lim_{M\to\infty}\prod_{-M}^{M}\frac{\cosh[2\pi(\eta+m)]-\cos(2\pi\xi)}{\cosh[2\pi(\xi+m)]-\cos(2\pi\eta)}=\exp[2\pi(\eta^2-\xi^2)]\,. \quad (42)$$

The first expression for f is clearly periodic in η, and by the interchange symmetry f is periodic in both ξ and η.

We now return to consider (37) and (38). Interchange of ξ and ζ in (38) makes the sum over Bessel functions the same as in (37). Thus both equations, and the requirements of symmetry and periodicity, are satisfied by the potential function

$$V(\xi,\eta,\zeta)=4\sum_{l=1}^{\infty}\cos(2\pi l\xi)\sum_{m,n=-\infty}^{\infty}\sum K_0(2\pi l[(\eta+m)^2+(\zeta+n)^2]^{1/2})$$
$$+2\pi\eta^2-\log\left(\lim_{M\to\infty}\prod_{-M}^{M}\frac{\cosh[2\pi(\eta+m)]-\cos(2\pi\zeta)}{\cosh(2\pi m)}\right). \quad (43)$$

It remains to evaluate the constant C_3 to be added to V. When ξ,η,ζ take any combination of the values $\pm\frac{1}{2},\pm\frac{1}{2},\pm\frac{1}{2}$, and the two charges in each cell are $+q$ and $-q$, the potential energy per cell is

$$-\frac{q^2}{L}[V(\pm\tfrac{1}{2},\pm\tfrac{1}{2},\pm\tfrac{1}{2})+C_3]=-\frac{q^2}{\sqrt{3}\,L/2}M_c\,, \quad (44)$$

where $M_c=1.76267\ldots$ is the Madelung constant for the CsCl structure, in which each positive ion is at the centre of a cube with negative ions at the corners, and vice versa. From (43) we find $V(\frac{1}{2},\frac{1}{2},\frac{1}{2})=-1.1560\ldots$ and so $C_3=3.1913\ldots$.

The Laplacian of V, i.e. $-(\partial X/\partial\xi+\partial Y/\partial\eta+\partial Z/\partial\zeta)$, is 4π. This shows that the method developed here for transforming conditionally and slowly convergent sums into absolutely and rapidly convergent sums has introduced a neutralizing uniform background charge. The same is true of the Ewald summation method: see the comments by Hasimoto [19] following his equation (2.22).

5. Discussion

We have obtained resummations of the Coulomb force sums required in molecular dynamics simulations of systems involving charged particles. The resummations are rapidly convergent, since they are expressed in terms of Bessel functions of imaginary argument, which have the asymptotic behaviour $K_\nu(z)\sim(\pi/2z)^{1/2}\,\mathrm{e}^{-z}$. We can use this asymptotic form to estimate the number of terms required for a given accuracy. In the case of a system confined between walls, the sums are over l and m with either $l = 0$ or $m = 0$ excluded, and for moderately large $|l|$ and $|m|$ the argument of the Bessel functions is approximately $2\pi|lm|$. Thus for part-per-million accuracy it is sufficient to include terms up to $|lm| = 2$. For a sum where l is positive and m takes either sign, as in (14), there are six terms with $|lm| \leq 2$. To these we need to add another three or four of the $m = 0$ terms, making about ten terms to be evaluated in the entire series. In the fully three-dimensional case the argument of K_0 in (17) is approximately $2\pi l\sqrt{m^2+n^2}$ for $|m|$, $|n| \geq 1$, with $l = 0$ excluded. The number of terms with m, n not both zero and $l\sqrt{m^2+n^2} \leq 2$ is 16, to which we need to add another three or four of the $m = 0 = n$ terms, making about 20 terms to be evaluated for part-per-million accuracy. Since the number of terms to be evaluated in the Ewald summation is an order of magnitude greater, we expect the method presented here to be faster, provided fast algorithms are used for the Bessel functions, such as polynomial approximations.

There is a way of avoiding the Bessel functions, and at the same time performing one of the sums, but at the expense of evaluating a definite integral. This approach, outlined below, also verifies the r^{-1} divergence of the potential as two particles get close together. We use the integral representation (ref. [9], 9.6.24; ref. [18], section 6.22)

$$K_0(z) = \int_0^\infty dt\, e^{-z\cosh t} \tag{45}$$

in the expressions (28) or (43). The sum over l in both cases takes the form

$$I(\alpha, \beta) = \sum_{l=1}^{\infty} \cos(\alpha l)\, K_0(\beta l) \tag{46}$$

with $\alpha = 2\pi\xi$, $\beta = 2\pi[(\eta+m)^2 + (\zeta+n)^2]^{1/2}$. (In the case of replication of the central cell in the x and y directions only, $n = 0$.) On using (45) in (46) we obtain the series

$$\sum_{l=1}^{\infty} \cos(\alpha l)\, e^{-\gamma l} = \mathrm{Re}\left(\sum_{l=1}^{\infty} e^{-(\gamma+i\alpha)l}\right) = \frac{e^{\gamma}\cos\alpha - 1}{e^{2\gamma} - 2e^{\gamma}\cos\alpha + 1}, \tag{47}$$

where $\gamma = \beta\cosh t$. Thus

$$I(\alpha, \beta) = \int_0^\infty dt\, \frac{e^{\beta\cosh t}\cos\alpha - 1}{e^{2\beta\cosh t} - 2e^{\beta\cosh t}\cos\alpha + 1}$$

$$= \int_1^\infty \frac{dx}{\sqrt{x^2-1}}\, \frac{e^{\beta x}\cos\alpha - 1}{e^{2\beta x} - 2e^{\beta x}\cos\alpha + 1}. \tag{48}$$

In close approach, $|\xi|$, $|\eta|$ and $|\zeta|$ are all small, and the dominant terms in the potential sum are those with $m, n = 0$. Then α and β are both small, and

$$I(\alpha, \beta) \to \beta \int_0^1 \frac{dy}{(\beta^2 + \alpha^2 y^2)\sqrt{1-y^2}} = \beta \int_0^{\pi/2} \frac{d\theta}{\beta^2 + \alpha^2\sin^2\theta} = \frac{\pi/2}{\sqrt{\alpha^2+\beta^2}}. \tag{49}$$

The potentials $V(\xi, \eta; \zeta)$ and $V(\xi, \eta, \zeta)$ then both diverge as $(\xi^2 + \eta^2 + \zeta^2)^{-1/2}$, as expected.

In the Ewald method, and the one presented here, no distinction is made between pairs of particles that are near or far apart (in the central cell). For N particles there are $\frac{1}{2}N(N-1)$ interactions, and the cost of computation increases as N^2. For large N it is more efficient to lump together groups of particles that are far from a given particle, and to treat the interaction of the particle with the group by a multipole expansion. The computational cost of these methods increases as $N \log N$ or as N, and is thus ultimately lower than that of the direct summation methods. A description of these "hierarchichal" and "fast multipole" methods, and further references, may be found in ref. [20].

Acknowledgement

It is a pleasure to thank Professor H. Ted Davis for his warm hospitality, and for discussions concerning computer simulations of water and ionic solutions, which motivated this work.

References

[1] M. Born and K. Huang, Dynamical Theory of Crystal Lattices (Clarendon, Oxford, 1954) sec. 30 and app. II.
[2] F. Berthaut, J. Phys. Radium 13 (1952) 499; J. Phys. Chem. Solids 39 (1978) 97.
[3] S.W. de Leeuw, J.W. Perram and E.R. Smith, Proc. R. Soc. London A 373 (1980) 27.
[4] D.M. Heyes, J. Chem. Phys. 74 (1981) 1924.
[5] M.P. Allen and D.J. Tildesley, Computer Simulation of Liquids (Clarendon, Oxford, 1987) sec. 5.5.
[6] J. Lekner and P.J. Castle, Physica A 101 (1980) 89.
[7] J. Lekner, Physica A 157 (1989) 826.

[8] B.M.E. van der Hoff and G.C. Benson, Can. J. Phys. 31 (1953) 1087.
[9] F.W.J. Olver, Handbook of Mathematical Functions, NBS Applied Mathematics Series, vol. 55, M. Abramomitz and I.A. Stegun, eds. (U.S. Government Printing Office, Washington, 1965) ch. 9.
[10] H.T. Davis and L. Zhang, to be published.
[11] K. Knopp, Theory and Application of Infinite Series (Blackie, London, 1951).
[12] A. Redlack and J. Grindlay, J. Phys. Chem. Solids 36 (1975) 73.
[13] R.N. Euwema and G.T. Surratt, J. Phys. Chem. Solids 36 (1975) 67.
[14] S.N. Stuart, J. Comput. Phys. 29 (1978) 127.
[15] D.J. Epstein and A.C. Smith, Am. J. Phys. 47 (1979) 99.
[16] J.W. Halley, J. Hautman, A. Rahman and Y-J. Rhee, Phys. Rev. B 40 (1989) 36.
[17] E.T. Whittaker and G.N. Watson, A Course of Modern Analysis, 4th ed. (Cambridge Univ. Press, Cambridge, 1963).
[18] G.N. Watson, Theory of Bessel Functions, 2nd ed. (Cambridge Univ. Press, Cambridge, 1944).
[19] H. Hasimoto, J. Fluid Mech. 5 (1959) 317.
[20] L. Greengard and V. Rokhlin, Chem. Scr. 29A (1989) 139.