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2000 J. Phys.: Condens. Matter 12 4575

(http://iopscience.iop.org/0953-8984/12/21/304)

J. Phys.: Condens. Matter **12** (2000) 4575–4601. Printed in the UK PII: S0953-8984(00)10535-1

A periodic Green function for calculation of coloumbic lattice potentials

Simon L Marshall

Environmental Sciences Division, Oak Ridge National Laboratory,
Oak Ridge National Laboratory, Oak Ridge, TN 37831-6036, USA

Received 23 December 1999, in final form 10 March 2000

Abstract. The modified Green function appropriate for solution of interior boundary value problems of Laplace's equation in a three-dimensional rectangular parallelepiped, subject to periodic boundary conditions, is developed. This allows the determination of the potential due to an arbitrary continuous charge distribution and its periodic replications in three dimensions. Summation of the eigenfunction expansion by application of the Poisson–Jacobi formula gives a Ewald sum, while application of the Poisson summation formula results in a two-dimensional potential that is perturbed by a rapidly converging Fourier cosine series involving K_0 Bessel functions. The latter constitutes a generalization of formulae described by Lekner. Numerical results show that the K_0 expansion is more rapidly convergent than the Ewald sum, and could therefore substantially reduce the computational effort involved in the molecular simulation of ionic and polar fluids. The Green function is also shown to be related to the asymptotic behaviour of lattice sums for the screened Coulomb potential, in the limit as the screening constant tends to zero.

1. Introduction

The evaluation of lattice sums has been of theoretical and practical interest for many years. The mathematical difficulties inherent in this problem originate in the slow decay of the Coulomb potential with distance; as a result, the series that arise are conditionally convergent and are not amenable to treatment by purely numerical convergence-acceleration algorithms. The main focus in previous treatments has therefore been on the construction of analytical transformations.

The development of most of these transformations follows a three-stage pattern: (i) selection of an integral representation for the reciprocal distance (or free-space Green function), $1/4\pi r$; (ii) interchange of the order of summation and integration; and (iii) acceleration of the convergence of the series of integrands. Thus, the well known Ewald (1921) method uses a Gaussian integral, and the van der Hoff–Benson (1953) method and its more recent generations (Lekner 1991, 1998, Grønbech-Jensen *et al* 1997) are based on a gamma-function integral. In both cases the convergence acceleration is realized by application of the Poisson–Jacobi formula for transformation of theta functions (Bellman 1961, p 10), resulting in series of complementary error functions or K_0 Bessel functions, respectively. This result and other properties of theta functions have proved to be of crucial importance in several approaches to lattice summation. For instance, Chaba and Pathria (1974, 1976a, b) integrated the Poisson–Jacobi formula with respect to the theta-function argument to obtain lattice sums for screened Coulomb potentials. Alternatively, the integrals arising in the first two steps of

0953-8984/00/214575+27$30.00

the above-mentioned general scheme can be evaluated as Mellin transforms of theta functions, providing formulae relating lattice sums to the Riemann zeta function and its multidimensional generalizations (Glasser 1973a, b, Zucker, 1974, 1975, 1976). The connection between these zeta functions and lattice sums has been known for many years (Lennard-Jones and Ingham 1925, Topping 1927); an interesting discussion is given by Terras (1985, pp 76–82).

For lattices periodic in two dimensions, $1/r$ is more conveniently represented as an integral involving either the J_0 or K_0 Bessel functions of arguments that depend on the periodic lattice coordinates. In the first case, summation of the J_0 functions over the lattice can then be achieved by reduction to Schlömilch series, as demonstrated by Hautot (1974) and Miller (1995). The sum of K_0 functions arising from the second representation converges rapidly, since these functions decrease exponentially with increasing argument. But this method fails for evaluating the self-energy of an ion in a lattice, because every term in the series becomes singular as the field and source points approach each other. In contrast, the singularity of the J_0-representation is localized in only one term of the transformed series. Both of these approaches have been used in lattice models for adsorbed monolayers (Macdonald and Barlow 1966, Marshall 1986, Marshall and Conway 1992a, b).

Although the earliest work on lattice summation originated from the problem of calculating the cohesive energy of ionic crystals, contemporary interest in this subject is mainly focused on the computer simulation of ionic and polar fluids by the molecular dynamics (MD) or Monte Carlo (MC) methods. Long-range columbic forces acting on the particles in each deterministically or stochastically generated configuration are most commonly estimated by imposing periodic boundary conditions and applying Ewald's method, assuming that the number of particles and the volume of the enclosure are sufficiently large to avoid spurious periodicity effects. Many MC/MD simulation techniques of water and aqueous electrolyte solutions have been described (Chialvo and Cummings 1999).

These simulation techniques have also been applied to gas hydrate crystals (Tse *et al* 1984, Rodger 1990, 1991, Kvamme and Førrisdahl 1996), which are crystalline hydrogen-bonded networks of water molecules that form polyhedral cavities large enough to accommodate small molecules of gases such as carbon dioxide, methane and other light hydrocarbons (Sloan 1998). Methane hydrates occur widely in nature (in particular, on the ocean floor), and are of great importance not only in relation to environmental issues such as global warming (Haq 1998), but also as a potential energy resource (Kvenvolden 1988).

The difficulty in developing an accurate molecular model for gas hydrates appears to reside in ensuring the mutual consistency of the representations of the short- and long-range contributions to the potential. Representing the polarity of the water molecules by a finite quadrupole (Berendsen *et al* 1987, Stillinger and Rahman 1974) and the short-range potential by a Lennard-Jones function is inconsistent: on the one hand, the finite-quadrupole model is a poor representation of the molecular charge distribution at close quarters, and on the other, the Lennard-Jones function implies a spherically-symmetric charge distribution, inherently incompatible with polarity. The resolution of this impasse clearly requires determination of the molecular electronic charge distribution subject not only to the nuclear potentials, but also to the potential resulting from three-dimensional replication of the molecular charge distribution.

Determination of the potential due to an arbitrary periodic charge distribution is of interest primarily in connection with solid-state electronic structure calculations. Crystal wave functions are solutions of an eigenvalue integral equation, in which the kernel is the product of the lattice potential and a periodic Green function for Helmholtz's equation (Jones and March 1973, pp 58–62). While use of the Helmholtz Green function in this context is very well known, a search of the INSPEC database and Science Citation Index since 1970 reveals that surprisingly little use has been made of the Poisson Green function to determine the

electrostatic component of the lattice potential; works by Schadler (1992), Oh *et al* (1992) and Zhang *et al* (1994) are notable exceptions. In contrast, this electrostatic problem is generally solved by multipole expansion within spheres about the atomic nuclei, and construction of a Fourier series representing the potential in the interstitial regions (Weinert 1981, Herzig 1985, Krasovskii *et al* 1999).

The purpose of the present paper is to describe an alternative approach to the construction of rapidly convergent expressions for the periodic Green function of Poisson's equation. The starting point is the plane-wave expansion, which can be transformed into an Ewald sum (by a considerably more direct route than that taken by Oh *et al* 1992) or into a more rapidly converging series of K_0 Bessel functions. These expressions are obtained by application of the Poisson summation formula (PSF), as recently described for two-dimensional modified Green functions (Marshall 1998a, 1999) and other more general Fourier series with coefficient functions defined by various types of power-series expansion (Marshall 1998b). Use of the Green function avoids ambiguous numerical values resulting from conditional convergence of Coulomb potential series, and reduces the determination of the potential to numerical quadrature: resolution of the charge density into multipoles is not necessary.

2. Overview

In the next section, the derivation of the Green function is given. Following this, the results required for the development of rapidly converging representations of the Green function are collected, and applied to the summation of Fourier series representing the periodic Green functions in one, two and three dimensions. The corresponding representation of the Green function as a Ewald sum is then derived. In section 4, numerical results comparing the speed of convergence of these formulae are presented. In section 5, the determination of lattice sums by application of the Green function and by direct summation of the Coulomb potential is compared. Finally, in section 6, the relation between the present work and that of Lekner (1991) is clarified with particular reference to the calculation of the electrostatic potential energy of the unit cell.

3. Analysis

3.1. Relation between periodic potential and charge density

A crystal lattice can be characterized in terms of a charge density $\rho(x, y, z)$ (including 'free' and 'bound' charges) that is spatially periodic

$$\rho(x, y, z) = \rho(x + a, y, z) = \rho(x, y + b, z) = \rho(x, y, z + c) \tag{1}$$

and associated with a periodic electrical potential $V(x, y, z)$:

$$V(x, y, z) = V(x + a, y, z) \qquad \frac{\partial V}{\partial x}(x, y, z) = \frac{\partial V}{\partial x}(x + a, y, z) \tag{2a}$$

$$V(x, y, z) = V(x, y + b, z) \qquad \frac{\partial V}{\partial y}(x, y, z) = \frac{\partial V}{\partial y}(x, y + b, z) \tag{2b}$$

$$V(x, y, z) = V(x, y, z + c) \qquad \frac{\partial V}{\partial z}(x, y, z) = \frac{\partial V}{\partial z}(x, y, z + c). \tag{2c}$$

Lattice potentials can be determined by summing neutral combinations of the single-charge potentials over the entire lattice, but since these series are conditionally convergent, the numerical values of the lattice sums so obtained depend on the manner in which the positive

and negative terms are combined (Whittaker and Watson 1944, p 25). These difficulties can be avoided by first noting that, if the axes defining the unit cell are orthogonal, the charge density can be resolved into Fourier components according to

$$\rho = \sum_{n=-\infty}^{\infty} \sum_{m=-\infty}^{\infty} \sum_{k=-\infty}^{\infty} A_{nmk} \mathrm{e}^{\mathrm{i}\left[\frac{2n\pi x}{a} + \frac{2m\pi y}{b} + \frac{2k\pi z}{c}\right]} \tag{3a}$$

$$A_{nmk} = \frac{1}{abc} \int_0^a \int_0^b \int_0^c \rho(\xi, \eta, \zeta)\, \mathrm{e}^{-\mathrm{i}\left[\frac{2n\pi x}{a} + \frac{2m\pi y}{b} + \frac{2k\pi z}{c}\right]} \mathrm{d}\xi\, \mathrm{d}\eta\, \mathrm{d}\zeta. \tag{3b}$$

The zeroth Fourier component of ρ vanishes for an electrically neutral unit cell:

$$A_{000} = \frac{1}{abc} \int_0^a \int_0^b \int_0^c \rho(\xi, \eta, \zeta)\, \mathrm{d}\xi\, \mathrm{d}\eta\, \mathrm{d}\zeta = 0. \tag{4}$$

If ρ is known, the potential can be determined by solution of Poisson's equation

$$-\nabla^2 V = 4\pi\rho \tag{5}$$

subject to the boundary conditions expressed by equations (2*a*)–(2*c*). If the potential is expanded in the same eigenfunctions as the charge density, the term with $k = m = n = 0$ is found to be a constant, and the remaining terms can be determined by making use of the orthogonality of the eigenfunctions. The potential is thus found to be

$$V = 4\pi \int_0^a \int_0^b \int_0^c \rho(\xi, \eta, \zeta) P_{222}(x, y, z \mid \xi, \eta, \zeta)\, \mathrm{d}\xi\, \mathrm{d}\eta\, \mathrm{d}\zeta \tag{6}$$

where

$$P_{222}(x, y, z \mid \xi, \eta, \zeta) \equiv \frac{1}{abc} \sum_{k,m,n}{}' \frac{1}{(2n\pi/a)^2 + (2m\pi/b)^2 + (2k\pi/c)^2} \mathrm{e}^{\mathrm{i}\left[\frac{2n\pi(x-\xi)}{a} + \frac{2m\pi(y-\eta)}{b} + \frac{2k\pi(z-\zeta)}{c}\right]}$$

is the periodic modified Green function for Poisson's equation within the parallelepiped and the primed summation includes all integral values of k, m and n except $k = m = n = 0$. The three subscripts indicate the number of boundaries in each coordinate. Taking into account the exclusion of the zero eigenvalue, the defining equation is

$$-\nabla^2 P_{222}(x, y, z \mid \xi, \eta, \zeta) = \delta(x - \xi)\delta(y - \eta)\delta(z - \zeta) - \frac{1}{abc} \tag{7}$$

where δ is the Dirac delta function. This shows that P_{222} can be interpreted physically as the potential at the field point (x, y, z), due to a unit point charge at the source point (ξ, η, ζ) and the same quantity of charge of opposite sign distributed uniformly throughout the enclosure. (In section 6, this interpretation is confirmed by deriving the same Fourier series from a lattice sum for the screened Coulomb potential.) The solution for V given by equation (6) is finite throughout the enclosure, provided that the source points are different and the neutrality condition expressed by equation (4) is satisfied. It is also valid for both continuous and discrete charge distributions: for a discrete charge distribution, the potential is given by a sum of values of P_{222}, over the coordinates of the source points, whereas for a continuous charge distribution (such as that obtained from a quantum-chemical calculation) determination of the potential involves a numerical integration of P_{222} times the charge density. The problem of developing a computationally useful expression for the eigenfunction expansion is considered in the next six sections.

3.2. Integral representation of the free-space Green function

The Green function for any finite three-dimensional region is the total potential due to a point charge and its interaction with the boundaries. For Dirichlet problems, in which the potential is constrained to vanish on the boundaries, this total potential can be represented in terms of a series of image potentials, but for Neumann problems and the periodic boundary conditions that are of interest here, the image potential series do not converge. The convergence of the eigenfunction expansion for the periodic Green function can easily be established, and the PSF can be used to obtain a computationally efficient formula. The required Fourier transforms are best introduced by deriving the well known formula for the free-space Green function in three dimensions. This is the solution of

$$-\nabla^2 G_{000} = \delta(x-\xi)\delta(y-\eta)\delta(z-\zeta). \tag{8}$$

A Fourier integral representation of G_{000} is derived as follows. Assuming that

$$G_{000} = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} A(\lambda,\mu,\nu)\mathrm{e}^{\mathrm{i}(\lambda x+\mu y+\nu z)}\,\mathrm{d}\lambda\,\mathrm{d}\mu\,\mathrm{d}\nu \tag{9}$$

and substituting the appropriate integral representations for the delta functions in each coordinate into equation (8), there results (cf Morse and Feshbach 1953, p 1255)

$$\begin{aligned} G_{000} &= \frac{1}{8\pi^3}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\frac{\mathrm{e}^{\mathrm{i}[\lambda(x-\xi)+\mu(y-\eta)+\nu(z-\zeta)]}}{\lambda^2+\mu^2+\nu^2}\,\mathrm{d}\lambda\,\mathrm{d}\mu\,\mathrm{d}\nu \\ &= \frac{1}{\pi^3}\int_0^{\infty}\int_0^{\infty}\int_0^{\infty}\frac{\cos\lambda(x-\xi)\cos\mu(y-\eta)\cos\nu(z-\zeta)}{\lambda^2+\mu^2+\nu^2}\,\mathrm{d}\lambda\,\mathrm{d}\mu\,\mathrm{d}\nu. \end{aligned} \tag{10}$$

This integral is best evaluated by transformation to polar coordinates, but since rectangular coordinates are of more interest in the present context, it is more conveniently evaluated by use of the following tabulated Fourier cosine transforms:

$$\int_0^{\infty}\frac{\cos XY}{X^2+A^2}\,\mathrm{d}X = \frac{\pi}{2A}\,\mathrm{e}^{-AY} \tag{11}$$

(Erdélyi *et al* 1954, p 8, formula (11));

$$\int_0^{\infty}\frac{\mathrm{e}^{-B\sqrt{x^2+A^2}}}{\sqrt{X^2+A^2}}\cos XY\,\mathrm{d}X = K_0[A\sqrt{B^2+Y^2}] \tag{12}$$

(Erdélyi *et al* 1954, p 17, formula (27)) and

$$\int_0^{\infty}K_0(AX)\cos XY\,\mathrm{d}X = \frac{\pi}{2\sqrt{A^2+Y^2}} \tag{13}$$

(Gray *et al* 1931, p 161; cf Erdélyi *et al* 1954, p 49, formula (40)). Applying these results successively to the integrals over the three coordinates, the required Fourier integral is found to be

$$\begin{aligned} G_{000} &= \frac{1}{\pi^3}\int_0^{\infty}\int_0^{\infty}\cos\mu(y-\eta)\cos\nu(z-\zeta)\frac{\pi\mathrm{e}^{-|x-\xi|\sqrt{\mu^2+\nu^2}}}{2\sqrt{\mu^2+\nu^2}}\,\mathrm{d}\mu\,\mathrm{d}\nu \\ &= \frac{1}{2\pi^2}\int_0^{\infty}\cos\nu(z-\zeta)K_0[\nu\sqrt{(x-\xi)^2+(y-\eta)^2}]\,\mathrm{d}\nu \\ &= \frac{1}{4\pi\sqrt{(x-\xi)^2+(y-\eta)^2+(z-\zeta)^2}}. \end{aligned} \tag{14}$$

3.3. One-dimensional periodic modified Green function

The expansion of the periodic modified Green's function $P_2(x \mid \xi)$ for the line segment $\{x \mid 0 \leqslant x \leqslant a\}$ in the eigenfunctions

$$\phi_n(x) = \mathrm{e}^{\mathrm{i}\lambda_n x} \qquad \lambda_n = \frac{2n\pi}{a} \qquad n = 0, \pm 1, \pm 2, \ldots \tag{15}$$

$$\|\phi_n(x)\|^2 = \int_0^a \phi_n(x)\phi_n^*(x)\,\mathrm{d}x = \int_0^a \mathrm{e}^{\mathrm{i}\frac{2n\pi x}{a}}\mathrm{e}^{-\mathrm{i}\frac{2n\pi x}{a}}\,\mathrm{d}x = a \tag{16}$$

is equal to the sum of the terms in equation (6) for which two indices are equal to zero:

$$P_2(x \mid \xi) = \sum_n{}' \frac{\phi_n(x)\phi_n^*(\xi)}{\|\phi_n(x)\|^2\lambda_n^2} = \frac{2}{a}\sum_{n=1}^{\infty}\frac{\cos(2n\pi/a)(x-\xi)}{(2n\pi/a)^2}. \tag{17}$$

This series can be summed by application of the result

$$\sum_{k=1}^{\infty}\frac{\cos kX}{k^2} = \frac{\pi^2}{6} - \frac{\pi|X|}{2} + \frac{X^2}{4} \tag{18}$$

(Gradshteyn and Ryzhik 1994, p 46), with the identification $X = 2\pi(x-\xi)/a$:

$$P_2(x \mid \xi) = \frac{1}{2a}\left[(x-\xi)^2 - a|x-\xi| + \frac{a^2}{6}\right]. \tag{19}$$

This function is continuous at $x = \xi$, and its derivative

$$\frac{\partial P_2(x \mid \xi)}{\partial x} = \frac{1}{2a}[2(x-\xi) \pm a] \tag{20}$$

(where the '+' and '−' refer respectively to $x < \xi$ and $x > \xi$) satisfies the 'jump' condition

$$\lim_{x\downarrow\xi}\frac{\partial P_2(x \mid \xi)}{\partial x} - \lim_{x\uparrow\xi}\frac{\partial P_2(x \mid \xi)}{\partial x} = \frac{-a}{2a} - \frac{a}{2a} = -1 \tag{21}$$

which is required of one-dimensional Green's functions (Barton 1989, p 48). It can further be verified that the periodic boundary conditions are satisfied by equation (19):

$$\begin{aligned} P_2(0 \mid \xi) &= \frac{1}{2a}\left[\xi^2 - a\xi + \frac{a^2}{6}\right] \\ P_2(a \mid \xi) &= \frac{1}{2a}\left[(a-\xi)^2 - a(a-\xi) + \frac{a^2}{6}\right] = \frac{1}{2a}\left[\xi^2 - a\xi + \frac{a^2}{6}\right]. \end{aligned} \tag{22}$$

This result can also be used to solve the corresponding Dirichlet and Neumann problems for the line segment $\{x \mid 0 \leqslant x \leqslant A\}$, where $A = a/2$ (Stakgold 1967, vol 1, p 86). Thus, addition of the forms of equation (17) appropriate for sources at the points ξ and $-\xi$ gives

$$\begin{aligned} P_2(x \mid \xi) + P_2(x \mid -\xi) &= \frac{4}{a}\sum_{n=1}^{\infty}\frac{\cos(2n\pi x/a)\cos(2n\pi\xi/a)}{(2n\pi/a)^2} \\ &= \frac{2}{A}\sum_{n=1}^{\infty}\frac{\cos(n\pi x/A)\cos(n\pi\xi/A)}{(n\pi/A)^2} \end{aligned} \tag{23}$$

and assuming (without loss of generality) that $x < a/2$, it follows from equation (19) that

$$\begin{aligned} P_2(x \mid \xi) + P_2(x \mid -\xi) = N_2(x \mid \xi) &= \frac{x^2+\xi^2}{2A} - x + \frac{A}{3} \qquad (x > \xi) \\ &= \frac{x^2+\xi^2}{2A} - \xi + \frac{A}{3} \qquad (x < \xi). \end{aligned} \tag{24}$$

The (Dirichlet) Green function can be similarly obtained, either as a Fourier sine series

$$P_2(x \mid \xi) - P_2(x \mid -\xi) = \frac{4}{a}\sum_{n=1}^{\infty}\frac{\sin(2n\pi x/a)\sin(2n\pi\xi/a)}{(2n\pi/a)^2} \tag{25}$$

or as a piecewise linear function of x:

$$\begin{aligned} P_2(x \mid \xi) - P_2(x \mid -\xi) = G_2(x \mid \xi) &= \frac{1}{A}\xi(A-x) \qquad (x > \xi) \\ &= \frac{1}{A}x(A-\xi) \qquad (x < \xi). \end{aligned} \tag{26}$$

3.4. Two-dimensional periodic modified Green function

The analogue of equation (17) for the periodic Green function P_{22} defined for the rectangle $\{(x, y) \mid 0 \leqslant x \leqslant a, 0 \leqslant y \leqslant b\}$ is equal to the sum of terms in equation (6), wherein at most two indices are zero. This can also be obtained by expansion in the eigenfunctions

$$\phi_{nm}(x, y) = \mathrm{e}^{\mathrm{i}(\lambda_n x + \mu_m y)} \qquad \lambda_n = \frac{2n\pi}{a} \qquad \mu_n = \frac{2m\pi}{b} \qquad m, n = 0, \pm 1, \pm 2, \ldots \tag{27}$$

$$\|\phi_{nm}(x, y)\|^2 = \int_0^a \int_0^b \phi_n(x, y)\phi_n^*(x, y)\,\mathrm{d}x\,\mathrm{d}y = ab \tag{28}$$

as

$$P_{22}(x, y \mid \xi, \eta) = \sum_{n,m}{}' \frac{\phi_{nm}(x, y)\phi_{nm}^*(\xi, \eta)}{\|\phi_{nm}(x, y)\|^2(\lambda_n^2 + \mu_m^2)}. \tag{29}$$

After combining the complex exponentials and excluding the term with $n = m = 0$,

$$P_{22}(x, y \mid \xi, \eta) = \frac{4}{ab}\sum_{n=0}^{\infty}\sum_{m=0}^{\infty}\gamma_{nm}\frac{\cos[2n\pi(x-\xi)/a]\cos[2m\pi(y-\eta)/b]}{(2n\pi/a)^2 + (2m\pi/b)^2} \tag{30}$$

where $\gamma_{00} = 0$, $\gamma_{0m} = \gamma_{n0} = 1/2$, and $\gamma_{nm} = 1$ for $n, m > 0$. Suppressing the arbitrary constants that can be added to this expression without affecting the satisfaction of the periodic boundary conditions, two equivalent forms can be derived:

$$P_{22}(x, y \mid \xi, \eta) = \frac{1}{a}P_2(y \mid \eta) + \frac{2}{ab}\sum_{n=1}^{\infty}\cos\frac{2n\pi(x-\xi)}{a}\sum_{m=-\infty}^{\infty}\frac{\cos[2m\pi(y-\eta)/b]}{(2n\pi/a)^2 + (2m\pi/b)^2} \tag{31a}$$

$$P_{22}(x, y \mid \xi, \eta) = \frac{1}{b}P_2(x \mid \xi) + \frac{2}{ab}\sum_{m=1}^{\infty}\cos\frac{2m\pi(y-\eta)}{b}\sum_{n=-\infty}^{\infty}\frac{\cos[2n\pi(x-\xi)/a]}{(2n\pi/a)^2 + (2m\pi/b)^2}. \tag{31b}$$

As shown by Marshall (1999), a rapidly convergent form of the double series can be obtained by application of the PSF in the form

$$\sum_{m=-\infty}^{\infty} f(m)\cos pm = \sum_{M=-\infty}^{\infty}\int_{-\infty}^{\infty} f(t)\cos(2M\pi + p)t\,\mathrm{d}t \tag{32}$$

where p is a real parameter. Identifying f and p as

$$f(t) \equiv \frac{1}{(2n\pi/a)^2 + (2\pi/b)^2} \qquad p \equiv \frac{2\pi(y-\eta)}{b} \tag{33}$$

and making use of equation (11) produces

$$\sum_{m=-\infty}^{\infty}\frac{\cos[2m\pi(y-\eta)/b]}{(2n\pi/a)^2 + (2m\pi/b)^2} = \frac{ab}{4\pi n}\sum_{M=-\infty}^{\infty}\mathrm{e}^{-\frac{2n\pi}{a}|Mb+y-\eta|}. \tag{34}$$

Therefore

$$H_{ab}(x-\xi, y-\eta) \equiv \sum_{n=1}^{\infty} \cos\frac{2n\pi(x-\xi)}{a} \sum_{m=-\infty}^{\infty} \frac{\cos[2m\pi(y-\eta)/b]}{(2n\pi/a)^2+(2m\pi/b)^2}$$

$$= \frac{ab}{4\pi} \sum_{M=-\infty}^{\infty} \left[\sum_{n=1}^{\infty} \frac{\mathrm{e}^{-\frac{2n\pi|Mb+y-\eta|}{a}}}{n} \cos\frac{2n\pi(x-\xi)}{a} \right]$$

$$= -\frac{ab}{8\pi} \sum_{M=-\infty}^{\infty} \ln\left[1 - 2\mathrm{e}^{-\frac{2\pi|Mb+y-\eta|}{a}} \cos\frac{2\pi(x-\xi)}{a} + \mathrm{e}^{-\frac{4\pi|Mb+y-\eta|}{a}} \right] \tag{35a}$$

where the last step follows by identifying the sum over n as the real part of a complex logarithmic power series. Precisely similar transformations can obviously be applied to the series in the second line of equation (31):

$$H_{ba}(y-\eta, x-\xi) \equiv \sum_{m=1}^{\infty} \cos\frac{2m\pi(y-\eta)}{b} \sum_{n=-\infty}^{\infty} \frac{\cos[2n\pi(x-\xi)/a]}{(2n\pi/a)^2+(2m\pi/b)^2}$$

$$= -\frac{ab}{8\pi} \sum_{N=-\infty}^{\infty} \ln\left[1 - 2\mathrm{e}^{\frac{2\pi|Na+x-\xi|}{b}} \cos\frac{2\pi(y-\eta)}{b} + \mathrm{e}^{\frac{4\pi|Na+x-\xi|}{b}} \right]. \tag{35b}$$

An alternative form of the relation between the functions H_{ab} and H_{ba} can be established by equating the two equivalent rearrangements of the double series

$$\sum_{n=1}^{\infty}\sum_{m=1}^{\infty} \frac{\cos(2n\pi X/a)\cos(2m\pi Y/b)}{(2n\pi/a)^2+(2m\pi/b)^2} = \frac{1}{2}\left[H_{ab}(X,Y) - \sum_{n=1}^{\infty} \frac{\cos(2n\pi X/a)}{(2n\pi/a)^2} \right]$$

$$= \frac{1}{2}\left[H_{ba}(Y,X) - \sum_{m=1}^{\infty} \frac{\cos(2m\pi Y/b)}{(2m\pi/b)^2} \right]. \tag{36}$$

Transposing terms, and making use of equation (18), it follows that

$$H_{ab}(X,Y) - H_{ba}(Y,X) = \sum_{n=1}^{\infty} \frac{\cos(2n\pi X/a)}{(2n\pi/a)^2} - \sum_{m=1}^{\infty} \frac{\cos(2m\pi Y/b)}{(2m\pi/b)^2}$$

$$= \frac{1}{4}\left[\left(X-\frac{a}{2}\right)^2 - \left(Y-\frac{b}{2}\right)^2 + \frac{b^2-a^2}{12} \right]. \tag{37}$$

H_{ab} converges rapidly if $b \gg a$ and H_{ba} converges rapidly for $a \gg b$. Therefore, if the value of the more slowly converging series is needed, equation (37) can be used to express this in terms of the more rapidly converging series, thereby substantially reducing the amount of computation. It is of particular interest to consider the limiting behaviour of the function H_{ab} as its arguments X and Y tend to zero, or equivalently, as the dimensions a and b of the rectangle become infinite. In this limit, the series in equation (35a) will be dominated by the term for which $M = 0$. Expanding the exponentials and the cosine function appearing in the argument of this term to second order produces the approximation

$$1 - 2\mathrm{e}^{-\frac{2\pi|y-\eta|}{a}} \cos\frac{2\pi(x-\xi)}{a} + \mathrm{e}^{-\frac{4\pi|y-\eta|}{a}} = \left(\frac{2\pi}{a}\right)^2 [(x-\xi)^2 + (-\eta)^2] + \cdots \tag{38}$$

$$-\frac{1}{4\pi} \ln\left[1 - 2\mathrm{e}^{-\frac{2\pi|y-\eta|}{a}} \cos\frac{2\pi(x-\xi)}{a} + \mathrm{e}^{-\frac{4\pi|y-\eta|}{a}} \right] = -\frac{1}{2\pi} \ln\sqrt{(x-\xi)^2+(y-\eta)^2} + \cdots. \tag{39}$$

Thus, the logarithmic function correctly reduces to a line-source potential in this limit. Proceeding similarly for the corresponding term with $N = 0$ in the function H_{ba}, it can be concluded that

$$P_{22}(x, y \mid \xi, \eta) = \frac{1}{a} P_2(y \mid \eta) + \frac{2}{ab} H_{ab}(x - \xi, y - \eta) \tag{40a}$$

and

$$P_{22}(x, y \mid \xi, \eta) = \frac{1}{b} P_2(x \mid \xi) + \frac{2}{ab} H_{ba}(y - \eta, x - \xi) \tag{40b}$$

represent the two-dimensional periodic Green's function, and reduce to

$$G_{00} = -\frac{1}{2\pi} \ln \sqrt{(x - \xi)^2 + (y - \eta)^2} \tag{41}$$

in the limit as a and b tend to infinity and the field and source point remain fixed. Finally, the relation between P_{22} and the Neumann function for the rectangle $\{(x, y) \mid 0 \leqslant x \leqslant A, 0 \leqslant y \leqslant B\}$, where $A = a/2$ and $B = b/2$, can be derived. From equation (25),

$$\begin{aligned} P_{22}(x, y \mid \xi, \eta) + P_{22}(x, y \mid \xi, -\eta) + P_{22}(x, y \mid -\xi, \eta) + P_{22}(x, y \mid -\xi, -\eta) \\ = \frac{1}{A} N_2(y \mid \eta) + \frac{1}{2AB} \{F_{AB}(x - \xi, y - \eta) \\ + F_{AB}(x - \xi, y + \eta) + F_{AB}(x + \xi, y - \eta) + F_{AB}(x + \xi, y + \eta)\} \end{aligned} \tag{42}$$

where

$$F_{AB}(X, Y) = \frac{-AB}{2\pi} \sum_{M=-\infty}^{\infty} \ln \left[1 - 2\mathrm{e}^{-\frac{\pi}{A}|2MB+Y|} \cos \frac{\pi X}{A} + \mathrm{e}^{-\frac{2\pi}{A}|2MB+Y|} \right].$$

This agrees, to within a constant, with an earlier result (Marshall 1999).

3.5. Three-dimensional periodic modified Green function

Extending equation (30), the eigenfunction expansion of the three-dimensional periodic Green function is

$$\begin{aligned} P_{222}(x, y, z \mid \xi, \eta, \zeta) = \frac{8}{abc} \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} \sum_{k=0}^{\infty} \gamma_{nmk} \\ \times \frac{\cos[2n\pi(x - \xi)/a] \cos[2m\pi(y - \eta)/b] \cos[2k\pi(z - \zeta)/c]}{(2k\pi/c)^2 + (2m\pi/b)^2 + (2n\pi/a)^2} \end{aligned} \tag{43}$$

where $\gamma_{000} = 0$, $\gamma_{m00} = \gamma_{0m0} = \gamma_{00k} = 1/4$, $\gamma_{0mk} = \gamma_{n0k} = \gamma_{nm0} = 1/2$ and $\gamma_{nmk} = 1$ for n, m and $k > 0$. However, this expression is rather cumbersome; it is much more convenient to construct the three-dimensional Green function by separating the terms for which k is zero from those for which k is nonzero. The sum of the first group (excluding the $n = m = 0$ term) is the two-dimensional Green function considered in the previous section. The second group contains terms with all positive values of k, and positive and zero values of both m and n; since the summands are even functions of m and n, these indices can be considered to assume *all* integral values. Thus, to within an additive constant,

$$\begin{aligned} P_{222}(x, y, z \mid \xi, \eta, \zeta) = \frac{1}{c} P_{22}(x, y \mid \xi, \eta) + \frac{2}{abc} \sum_{k=1}^{\infty} \cos \frac{2k\pi(z - \zeta)}{c} \\ \times \left\{ \sum_{m=-\infty}^{\infty} \sum_{n=-\infty}^{\infty} \frac{\cos[2m\pi(y - \eta)/b] \cos[2n\pi(x - \xi)/a]}{(2k\pi/c)^2 + (2m\pi/b)^2 + (2n\pi/a)^2} \right\}. \end{aligned} \tag{44}$$

Application of the PSF to the sum over n in the curly brackets gives

$$\sum_{n=-\infty}^{\infty} \frac{\cos[2n\pi(x-\xi)/a]}{(2k\pi/c)^2+(2m\pi/b)^2+(2n\pi/a)^2} = \sum_{N=-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{\cos(2N\pi t + 2t\pi(x-\xi)/a)}{(2k\pi/c)^2+(2m\pi/b)^2+(2t\pi/a)^2}\,\mathrm{d}t$$

$$= \frac{a}{2\pi} \sum_{N=-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{\cos(Na+x-\xi)u}{(2k\pi/c)^2+(2m\pi/b)^2+u^2}\,\mathrm{d}u$$

$$= \frac{a}{2} \sum_{N=-\infty}^{\infty} \frac{\mathrm{e}^{-|Na+x-\xi|\sqrt{\left(\frac{2k\pi}{c}\right)^2+\left(\frac{2m\pi}{b}\right)^2}}}{\sqrt{(2k\pi/c)^2+(2m\pi/b)^2}} \tag{45}$$

where the integrals have been evaluated by application of equation (11). The Fourier summation over m can be carried out by a second application of the PSF, in which the Fourier integrals are evaluated by equation (12):

$$\sum_{m=-\infty}^{\infty} \cos\frac{2m\pi(y-\eta)}{b} \sum_{n=-\infty}^{\infty} \frac{\cos[2n\pi(x-\xi)/a]}{(2k\pi/c)^2+(2m\pi/b)^2+(2n\pi/a)^2}$$

$$= \frac{a}{2} \sum_{N=-\infty}^{\infty} \left\{ \sum_{m=-\infty}^{\infty} \frac{\mathrm{e}^{-|Na+x-\xi|\sqrt{\left(\frac{2k\pi}{c}\right)^2+\left(\frac{2m\pi}{b}\right)^2}}}{\sqrt{(2k\pi/c)^2+(2m\pi/b)^2}} \cos\frac{2m\pi(y-\eta)}{b} \right\}$$

$$= \frac{ab}{2\pi} \sum_{N=-\infty}^{\infty} \sum_{M=-\infty}^{\infty} K_0\left[\frac{2k\pi}{c}\sqrt{(Na+x-\xi)^2+(Mb+y-\eta)^2}\right]. \tag{46}$$

The three-dimensional periodic Green function is therefore

$$P_{222}(x,y,z \mid \xi,\eta,\zeta) = \frac{1}{c}P_{22}(x,y \mid \xi,\eta)$$

$$+\frac{1}{\pi c}\sum_{k=1}^{\infty}\left\{\sum_{N=-\infty}^{\infty}\sum_{M=-\infty}^{\infty} K_0\left[\frac{2k\pi}{c}\sqrt{(Na+x-\xi)^2+(Mb+y-\eta)^2}\right]\right\}$$

$$\times\cos\frac{2k\pi(z-\zeta)}{c}. \tag{47a}$$

The limiting behaviour of this result is best examined in two stages. As a and b tend to infinity, all the K_0 functions vanish except for those corresponding to $N = M = 0$. Since the two-dimensional Green function approaches the line-source potential,

$$P_{002}(x,y,z \mid \xi,\eta,\zeta) \equiv \lim_{a,b\to\infty} P_{222}(x,y,z \mid \xi,\eta,\zeta)$$

$$= -\frac{1}{2\pi c}\ln\sqrt{(x-\xi)^2+(y-\eta)^2} + \frac{1}{\pi c}\sum_{k=1}^{\infty} K_0\left[\frac{2k\pi}{c}\sqrt{(x-\xi)^2+(y-\eta)^2}\right]$$

$$\times\cos\frac{2k\pi(z-\zeta)}{c} \tag{48}$$

which, apart from a trivial difference in nomenclature, is the periodic Green function obtained by Linton (1999) for the region bounded by two parallel planes. As c tends to infinity, the line source term vanishes, and the sum of K_0 functions becomes an integral, which can be evaluated by application of equation (13):

$$\frac{1}{\pi c}\sum_{k=1}^{\infty} K_0\left[\frac{2k\pi}{c}\sqrt{(x-\xi)^2+(y-\eta)^2}\right]\cos\frac{2k\pi(z-\zeta)}{c}$$

$$\to \frac{1}{2\pi^2}\int_0^{\infty} K_0[\nu\sqrt{(x-\xi)^2+(y-\eta)^2}]\cos\nu(z-\zeta)\,\mathrm{d}\nu$$

$$= \frac{1}{4\pi\sqrt{(x-\xi)^2+(y-\eta)^2+(z-\zeta)^2}}. \tag{49}$$

The modified Green function therefore correctly approaches the free-space Green function as the dimensions of the enclosure approach infinity, or equivalently, as the field point and the source point approach each other.

3.6. Ewald representation of the periodic Green function

The coulombic lattice sums that arise in computer simulation of polar fluids are almost exclusively evaluated by applying the Ewald transformation to charge distributions that are represented as neutral collections of point charges. To compare the performance of Ewald summation and the present results, it is necessary to apply the Ewald method to the evaluation of the periodic Green function. This can readily be achieved by a generalization of the derivation given by Leibfried (1955), which is based on an integral representation of the Fourier coefficients of the potential rather than the potential itself:

$$P_{222}(x,y,z\mid\xi,\eta,\zeta) = \frac{1}{abc}\sum_{k,m,n}{}'\int_0^{\infty} \mathrm{e}^{-\left[\left(\frac{2n\pi}{a}\right)^2+\left(\frac{2m\pi}{b}\right)^2+\left(\frac{2k\pi}{c}\right)^2\right]t+\mathrm{i}\left[\frac{2n\pi(x-\xi)}{a}+\frac{2m\pi(y-\eta)}{b}+\frac{2k\pi(z-\zeta)}{c}\right]}\mathrm{d}t$$

$$= \frac{1}{abc}\int_0^{\infty}\left\{\sum_{k,m,n}{}' \mathrm{e}^{-\left[\left(\frac{2n\pi}{a}\right)^2+\left(\frac{2m\pi}{b}\right)^2+\left(\frac{2k\pi}{c}\right)^2\right]t+\mathrm{i}\left[\frac{2n\pi(x-\xi)}{a}+\frac{2m\pi(y-\eta)}{b}+\frac{2k\pi(z-\zeta)}{c}\right]}\right\}\mathrm{d}t. \tag{50}$$

Next, it is observed that the sum of Gaussian functions over all values of k, m and n can be factorized:

$$\sum_{k=-\infty}^{\infty}\sum_{m=-\infty}^{\infty}\sum_{n=-\infty}^{\infty} \mathrm{e}^{-\left[\left(\frac{2n\pi}{a}\right)^2+\left(\frac{2m\pi}{b}\right)^2+\left(\frac{2k\pi}{c}\right)^2\right]t+\mathrm{i}\left[\frac{2n\pi(x-\xi)}{a}+\frac{2m\pi(y-\eta)}{b}+\frac{2k\pi(z-\zeta)}{c}\right]}$$

$$= \left\{\sum_{k=-\infty}^{\infty}\mathrm{e}^{-\left(\frac{2k\pi}{c}\right)^2 t+\mathrm{i}\frac{2k\pi(z-\zeta)}{c}}\right\}\left\{\sum_{m=-\infty}^{\infty}\mathrm{e}^{-\left(\frac{2m\pi}{b}\right)^2 t+\mathrm{i}\frac{2m\pi(y-\eta)}{b}}\right\}$$

$$\times\left\{\sum_{n=-\infty}^{\infty}\mathrm{e}^{-\left(\frac{2n\pi}{a}\right)^2 t+\mathrm{i}\frac{2n\pi(x-\xi)}{a}}\right\}. \tag{51}$$

The convergence of each of these three groups of terms for small values of t can be accelerated by applying the Poisson–Jacobi formula (Bellman 1961, p 10):

$$\sum_{k=-\infty}^{\infty}\mathrm{e}^{-\frac{k^2\pi^2}{u}+2k\pi\mathrm{i}X} = \sqrt{\frac{u}{\pi}}\sum_{K=-\infty}^{\infty}\mathrm{e}^{-(X+K)^2u} \tag{52}$$

where X and u are real parameters. Thus, for example, with $X=(z-\zeta)/c$ and $u=c^2/4t$, the sum over k becomes

$$\sum_{k=-\infty}^{\infty}\mathrm{e}^{-\left(\frac{k\pi}{c}\right)^2 t+\mathrm{i}\frac{2k\pi(z-\zeta)}{c}} = \frac{c}{\sqrt{4\pi t}}\sum_{K=-\infty}^{\infty}\mathrm{e}^{-\frac{(z-\zeta+Kc)^2}{4t}} \tag{53}$$

and proceeding similarly for the other two sums gives

$$\sum_{k=-\infty}^{\infty}\sum_{m=-\infty}^{\infty}\sum_{n=-\infty}^{\infty} \mathrm{e}^{-\left[\left(\frac{2n\pi}{a}\right)^2+\left(\frac{2m\pi}{b}\right)^2+\left(\frac{2k\pi}{c}\right)^2\right]t+\mathrm{i}\left[\frac{2n\pi(x-\xi)}{a}+\frac{2m\pi(y-\eta)}{b}+\frac{2k\pi(z-\zeta)}{c}\right]}$$

$$= \frac{abc}{(4\pi t)^{3/2}}\sum_{K=-\infty}^{\infty}\sum_{M=-\infty}^{\infty}\sum_{N=-\infty}^{\infty} \mathrm{e}^{\frac{-(z-\zeta+Kc)^2+(y-\eta+Mb)^2+(x-\xi+Na)^2}{4t}}. \tag{54}$$

The corresponding form of the primed lattice sum appearing in equation (50) is obtained from equation (54) by subtracting 1 from both sides. Since the right-hand side of equation (54) converges rapidly for small t, and the left-hand side converges rapidly for large t, a rapidly converging expression for P_{222} can be obtained by integrating these respective forms over the two subintervals $[0, \beta]$ and $[\beta, \infty)$, where β is positive. Thus,

$$P_{222}(x, y, z \mid \xi, \eta, \zeta) = \sum_{K=-\infty}^{\infty}\sum_{M=-\infty}^{\infty}\sum_{N=-\infty}^{\infty}\int_0^{\beta}\frac{1}{(4\pi t)^{3/2}}\mathrm{e}^{\frac{-(x-\xi+Na)^2+(y-\eta+Mb)^2+(z-\zeta+Kc)^2}{4t}}\,\mathrm{d}t$$

$$-\frac{\beta}{abc}+\frac{1}{abc}\sum_{k,m,n}{}'\int_{\beta}^{\infty}\mathrm{e}^{-\left[\left(\frac{2n\pi}{a}\right)^2+\left(\frac{2m\pi}{b}\right)^2+\left(\frac{2k\pi}{c}\right)^2\right]t+\mathrm{i}\left[\frac{2n\pi(x-\xi)}{a}+\frac{2m\pi(y-\eta)}{b}+\frac{2k\pi(z-\zeta)}{c}\right]}\,\mathrm{d}t$$

$$= \frac{1}{4\pi}\sum_{K=-\infty}^{\infty}\sum_{M=-\infty}^{\infty}\sum_{N=-\infty}^{\infty}$$

$$\times\frac{\operatorname{erfc}[\sqrt{(x-\xi+Na)^2+(y-\eta+Mb)^2+(z-\zeta+Kc)^2}/2\sqrt{\beta}]}{\sqrt{(x-\xi+Na)^2+(y-\eta+Mb)^2+(z-\zeta+Kc)^2}}$$

$$-\frac{\beta}{abc}+\frac{8}{abc}\sum_{k=0}^{\infty}\sum_{m=0}^{\infty}\sum_{n=0}^{\infty}\gamma_{kmn}\frac{\mathrm{e}^{-\beta\left[\left(\frac{2n\pi}{a}\right)^2+\left(\frac{2m\pi}{b}\right)^2+\left(\frac{2k\pi}{c}\right)^2\right]}}{(2n\pi/a)^2+(2m\pi/b)^2+(2k\pi/c)^2}$$

$$\times\cos\frac{2n\pi(x-\xi)}{a}\cos\frac{2m\pi(y-\eta)}{b}\cos\frac{2k\pi(z-\eta)}{c} \tag{55}$$

where the coefficient γ_{nmk} is as defined following equation (43). The above derivation illustrates why the Ewald method works best for lattices that are periodic in three dimensions: the change of variable that allows the small-t integral in equation (55) to be reducible to a complementary error function is possible only because of the $3/2$ power of t in the denominator, which would not appear if the integrand contained only one or two transformed theta functions.

3.7. Self-potential

The calculation of lattice sums requires not only the potential experienced by each ion due to the periodic repetitions of all the other ions, but also the potential due to the periodic repetitions of itself. This 'self-potential' is the limit of the nonsingular part of the Green function as the field and source points approach each other (Leibfried 1955, p 135, equation (26.11)):

$$Q_{222}(a, b, c) = \lim_{(x,y,z)\to(\xi,\eta,\zeta)}[P_{222}(x, y, z \mid \xi, \eta, \zeta) - G_{000}(x, y, z \mid \xi, \eta, \zeta)] \tag{56}$$

and is evaluated much more conveniently in the Ewald representation of the Green function than from the K_0 Bessel function expansion. This is because in the former, the singularity is localized in the error-function term with $N = M = K = 0$, while in the latter, the singularity is represented by the combined effect of infinitely many divergent K_0 functions. By use of the

approximation $\operatorname{erfc}(z) \simeq 1 - 2z/\pi^{1/2}$, the Ewald representation of the self-potential Q_{222} can be shown to be:

$$Q_{222}(a,b,c) = -\frac{1}{4\pi\sqrt{\pi\beta}} - \frac{\beta}{abc} + \frac{1}{4\pi}\sum_{K,M,N}{}' \frac{\operatorname{erfc}[\sqrt{(Na)^2+(Mb)^2+(Kc)^2}/2\sqrt{\beta}]}{\sqrt{(Na)^2+(Mb)^2+(Kc)^2}}$$
$$+\frac{1}{abc}\sum_{k,m,n}{}' \frac{\mathrm{e}^{-\beta\left[\left(\frac{2n\pi}{a}\right)^2+\left(\frac{2m\pi}{b}\right)^2+\left(\frac{2k\pi}{c}\right)^2\right]}}{(2n\pi/a)^2+(2m\pi/b)^2+(2k\pi/c)^2}. \tag{57}$$

For semi-infinite regions with rectangular boundaries, Linton (1999) has developed alternatives to Bessel function expansions that converge rapidly when the distance between the field and source points has a small but finite value. His results were obtained by considering the limiting behaviour of the corresponding three-dimensional transient temperature fields, as time tends to infinity. Although Linton's general approach could, in principle, be appropriately modified to produce corresponding representations for P_{222}, it turns out that the counterpart of equation (56) for the K_0 expansion of the Green function can be obtained much more directly by modifying the derivation of the Ewald sum given in the previous section. Substituting the Gaussian-integral representation of K_0, *viz.*,

$$K_0(\lambda R) = \frac{1}{2}\int_0^\infty \frac{1}{t}\mathrm{e}^{-\lambda^2 t - \frac{R^2}{4t}}\,\mathrm{d}t \tag{58}$$

(Watson 1944, p 183) into the double sum of modified Bessel functions results in the integral

$$\frac{1}{2\pi c}\sum_k{}' \mathrm{e}^{\mathrm{i}\frac{2k\pi(z-\zeta)}{c}}\left\{\sum_{N=-\infty}^{\infty}\sum_{M=-\infty}^{\infty} K_0\left[\frac{2k\pi}{c}\sqrt{(x-\xi+Na)^2+(y-\eta+Mb)^2}\right]\right\}$$
$$= \frac{1}{4\pi c}\int_0^\infty \frac{1}{t}\sum_k{}' \mathrm{e}^{-\left(\frac{2k\pi}{c}\right)^2 t + \frac{2k\pi(z-\zeta)}{c}\mathrm{i}}\left\{\sum_{N=-\infty}^{\infty}\sum_{M=-\infty}^{\infty}\mathrm{e}^{-\frac{(x-\xi+Na)^2+(y-\eta+Mb)^2}{4t}}\right\}\mathrm{d}t. \tag{59}$$

The Poisson–Jacobi formula can now be used to transform the summation over k, as in equation (53), and the integration divided into subintervals $[0, \beta]$ and $[\beta, \infty)$ as before. Thus:

$$\frac{1}{2\pi c}\sum_k{}' \mathrm{e}^{\mathrm{i}\frac{2k\pi(z-\zeta)}{c}}\left\{\sum_{N=-\infty}^{\infty}\sum_{M=-\infty}^{\infty} K_0\left[\frac{2k\pi}{c}\sqrt{(x-\xi+Na)^2+(y-\eta+Mb)^2}\right]\right\}$$
$$= \frac{1}{4\pi c}\int_0^\beta \frac{1}{t}\left[\frac{c}{\sqrt{4\pi t}}\sum_{K=-\infty}^{\infty}\mathrm{e}^{-\frac{(z-\zeta+Kc)^2}{4t}} - 1\right]\left\{\sum_{N=-\infty}^{\infty}\sum_{M=-\infty}^{\infty}\mathrm{e}^{\frac{(x-\xi+Na)^2+(y-\eta+Mb)^2}{4t}}\right\}\mathrm{d}t$$
$$+\frac{1}{4\pi c}\int_\beta^\infty \frac{1}{t}\sum_k{}' \mathrm{e}^{-\left(\frac{2k\pi}{c}\right)^2 t + \frac{2k\pi(z-\zeta)}{c}\mathrm{i}}\sum_{n=-\infty}^{\infty}\mathrm{e}^{-\left(\frac{2n\pi}{a}\right)^2 t + \frac{2n\pi(x-\xi)}{a}\mathrm{i}}$$
$$\times\sum_{m=-\infty}^{\infty}\mathrm{e}^{-\left(\frac{2m\pi}{b}\right)^2 t + \frac{2m\pi(y-\eta)}{b}\mathrm{i}}\,\mathrm{d}t. \tag{60}$$

The first part of the first integral results in the same series of error functions that appears in equation (55), and the remaining terms are all readily expressible as exponential integrals:

$$\int_0^\beta \frac{1}{t}\mathrm{e}^{-\frac{R^2}{4t}}\,\mathrm{d}t \xrightarrow{u=1/t} \int_{1/\beta}^\infty \frac{1}{u}\mathrm{e}^{-\frac{R^2 u}{4}}\,\mathrm{d}u \xrightarrow{v=\beta u} \int_1^\infty \frac{1}{v}\mathrm{e}^{-\frac{R^2 v}{4\beta}}\,\mathrm{d}v \equiv E_1\left(\frac{R^2}{4\beta}\right). \tag{61}$$

The final integral on the right-hand side of equation (59) results in an exponential series that differs from its counterpart in equation (55) only in the limits of the summation over k. The alternative representation of the K_0 series is therefore

$$\frac{1}{2\pi c}\sum_{k}{}' \mathrm{e}^{\mathrm{i}\frac{2k\pi(z-\zeta)}{c}}\left\{\sum_{N=-\infty}^{\infty}\sum_{M=-\infty}^{\infty}K_0\left[\frac{2k\pi}{c}\sqrt{(x-\xi+Na)^2+(y-\eta+Mb)^2}\right]\right\}$$

$$=\frac{1}{4\pi}\sum_{K=-\infty}^{\infty}\sum_{M=-\infty}^{\infty}\sum_{N=-\infty}^{\infty}$$

$$\times\frac{\operatorname{erfc}[\sqrt{(x-\xi+Na)^2+(y-\eta+Mb)^2+(z-\zeta+Kc)^2}/2\sqrt{\beta}]}{\sqrt{(x-\xi+Na)^2+(y-\eta+Mb)^2+(z-\zeta+Kc)^2}}$$

$$-\frac{1}{4\pi c}\sum_{N=-\infty}^{\infty}\sum_{M=-\infty}^{\infty}E_1\left[\frac{(x-\xi+Na)^2+(y-\eta+Mb)^2}{4\beta}\right]$$

$$+\frac{2}{abc}\sum_{k=1}^{\infty}\sum_{m=-\infty}^{\infty}\sum_{n=-\infty}^{\infty}\frac{\mathrm{e}^{-\beta\left[\left(\frac{2\pi n}{a}\right)^2+\left(\frac{2\pi m}{b}\right)^2+\left(\frac{2\pi k}{c}\right)^2\right]}}{(2\pi n/a)^2+(2\pi m/b)^2+(2\pi k/c)^2}$$

$$\times\cos\frac{2\pi n(x-\xi)}{a}\cos\frac{2\pi m(y-\eta)}{b}\cos\frac{2\pi k(z-\zeta)}{c}. \tag{62}$$

As a result of the above transformations, the singularity shown by the K_0 series as the field and source points approach each other has been isolated into the error function term with $N=M=K=0$, and the exponential integral with $N=M=0$. However, noting the power series expansion of the exponential integral,

$$E_1(z)=-\gamma-\ln z-\sum_{n=1}^{\infty}\frac{(-z)^n}{nn!} \tag{63}$$

(Abramowitz and Stegun 1964, p 229), it can be seen that the latter singularity will be cancelled by the line-source potential that is approached by P_{22} in this limit:

$$-\frac{1}{2\pi c}\ln\sqrt{(x-\xi)^2+(y-\eta)^2}-E_1\left[\frac{(x-\xi)^2+(y-\eta)^2}{4\beta}\right]$$

$$=\frac{1}{4\pi c}\left\{\gamma-\ln(4\beta)+\sum_{n=1}^{\infty}\frac{(-1/4\beta)^n[(x-\xi)^2+(y-\eta)^2]^n}{nn!}\right\}. \tag{64}$$

Since the limit of the singular complementary error function term is evaluated exactly as in equation (57), the required alternative expression for the self-potential is

$$Q_{222}(a,b,c)=\lim_{(x,y,z)\to(\xi,\eta,\zeta)}[P_{222}(x,y,z\mid\xi,\eta,\zeta)-G_{000}(x,y,z\mid\xi,\eta,\zeta)]$$

$$=\frac{b}{12ac}-\frac{1}{\pi}\sum_{M=1}^{\infty}\ln\left[1-\mathrm{e}^{-\frac{2\pi Mb}{a}}\right]$$

$$+\frac{1}{4\pi c}\left\{\gamma-\ln(4\beta)+\sum_{N,M}{}'E_1\left[\frac{(Na)^2+(Mb)^2}{4\beta}\right]\right\}-\frac{1}{4\pi\sqrt{\pi\beta}}$$

$$+\frac{1}{4\pi}\sum_{K,M,N}{}'\frac{\operatorname{erfc}[\sqrt{(Na)^2+(Mb)^2+(Kc)^2}/2\sqrt{\beta}]}{\sqrt{(Na)^2+(Mb)^2+(Kc)^2}}$$

$$+\frac{2}{abc}\sum_{k=1}^{\infty}\sum_{n=-\infty}^{\infty}\sum_{m=-\infty}^{\infty}\frac{\mathrm{e}^{-\beta\left[\left(\frac{2n\pi}{a}\right)^2+\left(\frac{2m\pi}{b}\right)^2+\left(\frac{2k\pi}{c}\right)^2\right]}}{(n\pi/a)^2+(2m\pi/b)^2+(2k\pi/c)^2}. \tag{65}$$

The mutual consistency of equations (65) and (57) can be established by identifying the double sum of E_1 functions as part of the Ewald expansion of P_{22}, *viz.*

$$P_{22}(x, y \mid \xi, \eta) = \frac{1}{4\pi} \sum_{N=-\infty}^{\infty} \sum_{M=-\infty}^{\infty} E_1 \left[\frac{(x-\xi+Na)^2 + (y-\eta+Mb)^2}{4\beta} \right]$$
$$- \frac{\beta}{ab} + \frac{1}{ab} \sum_{n,m}{}' \frac{e^{-\beta\left[\left(\frac{2n\pi}{a}\right)^2 + \left(\frac{2m\pi}{b}\right)^2\right]}}{(2n\pi/a)^2 + (2m\pi/b)^2} \cos \frac{2n\pi(x-\xi)}{a} \cos \frac{2m\pi(y-\eta)}{b} \qquad (66a)$$

which can readily be derived by adapting the method used to obtain equation (55). Thus,

$$\frac{1}{4\pi} \sum_{N=-\infty}^{\infty} \sum_{M=-\infty}^{\infty} E_1 \left[\frac{(x-\xi+Na)^2 + (y-\eta+Mb)^2}{4\beta} \right] = P_{22}(x, y \mid \xi, \eta) + \frac{\beta}{ab}$$
$$= \frac{1}{ab} \sum_{n,m}{}' \frac{e^{-\beta\left[\left(\frac{2n\pi}{a}\right)^2 + \left(\frac{2m\pi}{b}\right)^2\right]}}{(2n\pi/a)^2 + (2m\pi/b)^2} \cos \frac{2n\pi(x-\xi)}{a} \cos \frac{2m\pi(y-\eta)}{b}. \qquad (66b)$$

It can easily be verified that equation (55) results if equations (62) and (66*b*) are substituted into equation (47*a*).

3.8. Electrostatic energy and Madelung constant

With expressions in hand for both P_{222} and Q_{222}, the general expression for the electrostatic energy E of a neutral unit cell consisting of charges q_i at points (ξ_i, η_i, ζ_i) follows (Leibfried 1955, p 136, equation (27.4)):

$$E = \frac{1}{2} 4\pi \left[\sum_{i \neq j} q_i q_j P_{222}(\xi_i, \eta_i, \zeta_i \mid \xi_j, \eta_j, \zeta_j) + \sum_i q_i^2 Q_{222}(a, b, c) \right]. \qquad (67)$$

For charges of equal magnitude q arranged in a Bravais lattice, all atomic positions are of equivalent symmetry. The Madelung constant is obtained by dividing E by the electrostatic energy of a pair of neighbouring positive and negative charges separated by distance L:

$$Z = -\frac{L}{q^2} E. \qquad (68)$$

4. Numerical results

4.1. Two-dimensional periodic Green function

The difference in the speed of convergence of the logarithmic series in the two equivalent forms of P_{22} can be demonstrated by evaluating them for $(x, y) = (1, 1)$ and $(\xi, \eta) = (1.5, 1.5)$ in a rectangle with $a = 15$ and $b = 4$. An estimate of the value of M required to reduce the leading term of the series in equation (31*a*) to ε can be obtained from the formula

$$M_{max} = \frac{1}{b} \left(|y - \eta| - \frac{a}{2\pi} \ln \frac{\varepsilon}{2} \right). \qquad (69)$$

The terms in the series of equation (31*a*) are as follows:

```
P2 ( 1.0000| 1.5000) =        0.1145833
Mmax =      10
M =  10 ln( 0.9999999) = -0.5960464E-07
M =- 10 ln( 0.9999999) = -0.1192093E-06
M =   9 ln( 0.9999995) = -0.4768373E-06
M =-  9 ln( 0.9999993) = -0.6556513E-06
....
```

```
M =   2 ln( 0.9451995) = -0.5635927E-01
M =-  2 ln( 0.9173283) = -0.8628986E-01
M =   1 ln( 0.7260185) = -0.3201798E+00
M =-  1 ln( 0.6017119) = -0.5079766E+00
M =   0 ln( 0.0711527) = -0.2642928E+01
H    (15.0000, 4.0000,-0.5000,-0.5000) =      8.7044292

P2 ( 1.0000| 1.5000)/15.0000                    =     0.0076389
H    (15.0000, 4.0000, 1.0000, 1.0000)*2/60.0000 =     0.2901476
P22( 1.0000, 1.0000| 1.5000, 1.5000)            =     0.2977865
```

The output resulting from use of equation (31*b*) is:

```
P2 ( 1.0000| 1.5000) =       1.0083333
Mmax =               0
M =   0 ln( 0.5630857) = -0.5743235E+00
H    ( 4.0000,15.0000,-0.5000,-0.5000) =       1.3710963

P2 ( 1.0000| 1.5000)/ 4.0000                    =     0.2520833
H    (15.0000, 4.0000, 1.0000, 1.0000)*2/60.0000 =     0.0457032
P22( 1.0000, 1.0000| 1.5000, 1.5000)            =     0.2977865
```

which confirms that P_{22} can be evaluated very efficiently and that the two representations of this function are indeed equivalent.

4.2. Three-dimensional periodic Green function: K_0 expansion

The highest value of k that is expected to contribute to the Fourier series of modified Bessel functions in P_{222} can be related to the summation tolerance ε by use of the formula

$$k_{max} = \frac{-c \ln \varepsilon}{2\pi\sqrt{(x-\xi)^2 + (y-\eta)^2}} \tag{70}$$

which is obtained by setting $M = N = 0$ in the square root term and approximating K_0 by a simple exponential of its argument. Of course, such an approximation overestimates the number of terms required, since the K_0 function decreases slightly faster with increasing argument:

$$K_0(z) \sim \sqrt{\frac{\pi}{2z}} \mathrm{e}^{-z}. \tag{71}$$

This method is less convenient for determining the highest values of N and M required, because the arguments of the remaining K_0 functions depend on a and b as well as the field and source point coordinates. The summation over N for given values of k and M can be carried out by evaluating the K_0 function only for arguments such that the value of the K_0 function is larger than the error involved in the approximation. For example, the polynomial approximation given by Abramowitz and Stegun (1964, p 378) is stated to have a maximum error of 1.9×10^{-7}, which corresponds to an argument of about 14.3. The double summation is then formed by evaluating the sum over N for $M = 0, \pm 1, \pm 2, \ldots$.

The convergence rate of the series of K_0 functions deteriorates markedly not only as the field point approaches the source point, but more importantly if the x- and y-coordinates of the source points are close. This limit can be dealt with by use of the Ewald-type expression

for the K_0 series derived in section 2.7, but more simply by observing that for a finite three-dimensional region, P_{222} can be written in two other forms besides equation (47*a*):

$$P_{222}(x, y, z \mid \xi, \eta, \zeta) = \frac{1}{a} P_{22}(y, z \mid \eta, \zeta) + \frac{1}{\pi a} \sum_{n=1}^{\infty} \left\{ \sum_{K=-\infty}^{\infty} \sum_{M=-\infty}^{\infty} K_0 \left[\frac{2n\pi}{a} \sqrt{(Kc + z - \zeta)^2 + (Mb + y - \eta)^2} \right] \right\} \times \cos \frac{2n\pi(x - \xi)}{a} \tag{47b}$$

and

$$P_{222}(x, y, z \mid \xi, \eta, \zeta) = \frac{1}{b} P_{22}(z, x \mid \zeta, \xi) + \frac{1}{\pi b} \sum_{m=1}^{\infty} \left\{ \sum_{N=-\infty}^{\infty} \sum_{K=-\infty}^{\infty} K_0 \left[\frac{2m\pi}{b} \sqrt{(Na + x - \xi)^2 + (Kc + z - \zeta)^2} \right] \right\} \times \cos \frac{2m\pi(y - \eta)}{b}. \tag{47c}$$

For example, the value of $P_{222}(0, 0, 0 \mid 0, 0, 1/2)$ cannot be obtained from equation (47*a*), but is obviously the same as $P_{222}(0, 0, 0 \mid 0, 1/2, 0)$ or $P_{222}(0, 0, 0 \mid 1/2, 0, 0)$, which can be obtained without difficulty from equations (47*b*) and (47*c*), respectively. Since, in general, the lengths of the projections of the vector $(x - \xi, y - \eta, z - \zeta)$ on the planes $z = 0$, $x = 0$ and $y = 0$ are

$$r_{xy} = \sqrt{(x - \xi)^2 + (y - \eta)^2} \qquad r_{yz} = \sqrt{(y - \eta)^2 + (z - \zeta)^2} \qquad r_{xz} = \sqrt{(x - \xi)^2 + (z - \zeta)^2} \tag{72}$$

it follows by appropriate modifications of equation (70) that the fastest convergence is expected with equations (47*a*), (47*b*) or (47*c*) depending on whether r_{xy}, r_{yz} or r_{xz} is the greatest of these three quantities, respectively. (The required number of Fourier series terms also depends on the side lengths a, b and c, especially if these lengths are very different. Such a situation is, however, unlikely to be of interest in molecular simulations.)

As an example, let us assume that $a = b = c = 1$ and calculate $P_{222}(0, 0, 0 \mid 1/2, 1/2, 1/2)$, for which equations (47*a*), (47*b*) and (47*c*) are all equivalent. The one- and two-dimensional contributions and the K_0 functions in the Fourier series are as follows:

```
One-dimensional function:
P2 ( 0.0000| 0.5000) =       -0.041667

Two-dimensional function:
Mmax =               3
H    ( 1.0000, 1.0000,-0.5000,-0.5000) =       -0.006746
P22( 0.0000, 0.0000| 0.5000, 0.5000) =       -0.055159
kmax =              3
k =  1              Double Sum = 0.2742429E-01
k =  2              Double Sum = 0.2295795E-03
k =  3              Double Sum = 0.2214305E-05

P222( 0.0000, 0.0000, 0.0000| 0.5000, 0.5000, 0.5000) = -0.063816
Number of K0 evaluations  =          24.
```

4.3. Three-dimensional periodic Green function: Ewald representation

It is of particular interest to repeat the above calculation with the Ewald method, in view of Lekner's (1991) statement that the Ewald summation requires about ten times as many terms as the expansion in K_0 functions. With a convergence parameter, β, equal to 0.072, the sums of error functions corresponding to the first few values of K are

```
K = 0 Sum over M and N =  0.1038852
K = 1 Sum over M and N =  0.1038852
K =-1 Sum over M and N =  0.0000300
K = 2 Sum over M and N =  0.0000300
K =-2 Sum over M and N =  0.0000000
Sum over K =  0.2078303
```

and the terms in the exponential series are

```
K = 0 Sum over M and N = -0.0057329
K = 1 Sum over M and N = -0.0013109
K =-1 Sum over M and N = -0.0013109
K = 2 Sum over M and N =  0.0000001
K =-2 Sum over M and N =  0.0000001
Sum over K = -0.0083547

P222( 0.0000, 0.0000, 0.0000| 0.5000, 0.5000, 0.5000) = -0.063816
Number of erfc evaluations     =             47
Number of exponential terms =             34.
```

The optimal value of β can be expected to depend on the field and source point coordinates; the value of $\beta = 0.072$ was selected by trial and error, so that equal numbers of error function and exponential terms are required in the evaluation of the self-potential term. The self-potential term was chosen for optimizing β because it is the same for all charges in the enclosure, irrespective of their positions, and needs to be evaluated only once in a simulation. The required numbers of error function and exponential terms corresponding to various values of β are presented in table 1, and show that 31 terms are required for a convergent estimate of each series. For example, application of equation (57) gives, for the sum of the error functions,

```
K = 0 Sum over M and N =  0.0341813
K = 1 Sum over M and N =  0.0089684
K =-1 Sum over M and N =  0.0089684
K = 2 Sum over M and N =  0.0000001
K =-2 Sum over M and N =  0.0000001
Sum over K =  0.0521182.
```

For the exponential terms:

```
K = 0 Sum over M and N =  0.0060777
K = 1 Sum over M and N =  0.0016551
K =-1 Sum over M and N =  0.0016551
K = 2 Sum over M and N =  0.0000001
K =-2 Sum over M and N =  0.0000001
Sum over K =  0.0093881

Q222( 1.0000, 1.0000, 1.0000) = -0.225785
Number of erfc evaluations     =          34
Number of exponential terms =          34.
```

Table 1. Optimization of the convergence parameter, β. N_{erfc} and N_{exp} are the number of error function and exponential terms required for convergence, respectively.

β	N_{erfc}	N_{exp}	Total
0.060	25	66	91
0.070	34	42	76
0.071	34	34	68
0.072	34	34	68
0.073	34	34	68
0.074	42	34	76
0.075	42	34	76
0.080	42	34	76
0.090	58	26	84
0.100	66	26	92
0.110	90	25	115
0.120	90	25	115
0.130	90	25	115
0.140	98	21	119

The numerical values just calculated can be used to determine the Madelung constant for CsCl. Since for this body-centred cubic structure, the distance L is equal to $a\sqrt{3}/2$, the Madelung constant is found from application of equation (68) to be $Z = 1.762\,674$, which is in close agreement with the value determined by Lekner (1998): the discrepancy can with confidence be attributed to the errors in the approximate expressions used to evaluate the K_0 and erfc functions. The rate of convergence of equation (65) can be expected to be very similar, considering that the asymptotic behaviour of $E_1(X^2)$ for large arguments X is similar to that of erfc(X).

The calculations presented here show that the convergence acceleration achieved by use of the PSF is extremely effective, and confirm that the K_0 expansion and the Ewald sum converge to the same numerical result. More importantly, they show that the K_0 expansion is considerably more efficient than the Ewald sum, requiring fewer than a third as many terms for a convergent estimate. Although this difference in rate of convergence is not nearly as great as that claimed by Lekner (1991), use of the K_0 expansion in place of Ewald summation could reduce substantially the amount of computation involved in simulation of polar or ionic fluids, assuming that the computational overhead associated with evaluation of the Bessel functions and complementary error functions is comparable. In the present work, these functions were both evaluated by the polynomial-based approximants given by Abramowitz and Stegun (1964); the approximation for K_0 is slightly more complicated (since it involves evaluation of I_0 as well). There is undoubtedly much room for improvement in the calculation of these functions, but comparison of the various methods is beyond the scope of the present paper. One possible improvement involves use of the Fourier integral representation of K_0 to construct an approximation based on the continued-fraction method recently described by Marshall (1998b).

5. Direct summation of Coulomb potentials

In the previous section the performances of the representations of the Green function as a Ewald sum and a Bessel function expansion were compared. Another comparison of interest is between the values of lattice sums determined by use of the Green function and those obtained by application of the PSF to summation of the Coulomb potentials. The potential at the point

(x, y, z) due to a unit positive charge at (x_1, y_1, z_1) and a unit negative charge at (x_2, y_2, z_2), assumed to be infinitely repeated in three dimensions, is

$$S = \sum_{n=-\infty}^{\infty}\sum_{m=-\infty}^{\infty}\sum_{k=-\infty}^{\infty}\left\{\frac{1}{\sqrt{\rho_1^2+(kc+z-z_1)^2}}-\frac{1}{\sqrt{\rho_2^2+(kc+z-z_2)^2}}\right\} \tag{73}$$

where

$$\rho_{1,2}^2 = (na+x-x_{1,2})^2+(mb+y-y_{1,2})^2.$$

As observed by Chaba and Pathria (1976a), the three-dimensional PSF cannot be applied to this series, but application of the one-dimensional PSF to the sum over k gives

$$\sum_{n=-\infty}^{\infty}\sum_{m=-\infty}^{\infty}\sum_{k=-\infty}^{\infty}\left\{\frac{1}{\sqrt{\rho_1^2+(kc+z-z_1)^2}}-\frac{1}{\sqrt{\rho_2^2+(kc+z-z_2)^2}}\right\}$$
$$= F(0)+2\sum_{K=1}^{\infty}F(2K\pi) \tag{74}$$

where for $K > 0$,

$$F(2K\pi) = \int_{-\infty}^{\infty}\left\{\frac{1}{\sqrt{\rho_1^2+(tc+z-z_1)^2}}-\frac{1}{\sqrt{\rho_2^2+(tc+z-z_2)^2}}\right\}\cos(2K\pi t)\,\mathrm{d}t$$
$$= \frac{2}{c}\left\{\cos\frac{2K\pi(z-z_1)}{c}K_0\left(\frac{2K\pi\rho_1}{c}\right)-\cos\frac{2K\pi(z-z_2)}{c}K_0\left(\frac{2K\pi\rho_2}{c}\right)\right\} \tag{75}$$

(Erdélyi *et al* 1954, p 11, formula (7)) and

$$F(0) = \int_{-\infty}^{\infty}\left\{\frac{1}{\sqrt{\rho_1^2+(tc+z-z_1)^2}}-\frac{1}{\sqrt{\rho_2^2+(tc+z-z_2)^2}}\right\}\mathrm{d}t = \frac{2}{c}\ln\frac{\rho_2}{\rho_1}. \tag{76}$$

The sum over k is therefore

$$\sum_{k=-\infty}^{\infty}\left\{\frac{1}{\sqrt{\rho_1^2+(kc+z-z_1)^2}}-\frac{1}{\sqrt{\rho_2^2+(kc+z-z_2)^2}}\right\} = \frac{1}{c}\ln\frac{\rho_2^2}{\rho_1^2}$$
$$+\frac{4}{c}\sum_{K=1}^{\infty}\left\{\cos\frac{2K\pi(z-z_1)}{c}K_0\left(\frac{2K\pi\rho_1}{c}\right)\right.$$
$$\left.-\cos\frac{2K\pi(z-z_2)}{c}K_0\left(\frac{2K\pi\rho_2}{c}\right)\right\}. \tag{77}$$

This series can be expected to converge rapidly when summed with respect to n and m as well as K; to proceed further it is necessary to develop a rapidly converging representation of the sum of logarithmic terms. Application of the theory of residues (as described in the appendix) leads to the result

$$\sum_{n=-\infty}^{\infty}\ln\frac{(n+\alpha_2)^2+\beta_2^2}{(n+\alpha_1)^2+\beta_1^2} = \ln\frac{\cosh 2\pi\beta_2-\cos 2\pi\alpha_2}{\cosh 2\pi\beta_1-\cos 2\pi\alpha_1} = \ln\frac{\cosh^2\pi\beta_2-\cos^2\pi\alpha_2}{\cosh^2\pi\beta_1-\cos^2\pi\alpha_1}$$
$$= \ln\frac{\sinh^2\pi\beta_2+\sin^2\pi\alpha_2}{\sinh^2\pi\beta_1+\sin^2\pi\alpha_1} \tag{78}$$

where

$$\alpha_{1,2} = \frac{x - x_{1,2}}{a} \qquad \beta_{1,2} = \frac{mb + y - y_{1,2}}{a}.$$

The summation with respect to m can be carried out directly. The transformed lattice sum is therefore

$$\begin{aligned} S = \frac{1}{c}\sum_{m=-\infty}^{\infty} \ln \frac{\cosh[2\pi(y - y_2 + mb)/a] - \cos[2\pi(x - x_2)/a]}{\cosh[2\pi(y - y_1 + mb)/a] - \cos[2\pi(x - x_1)/a]} \\ + \frac{4}{c}\sum_{K=1}^{\infty}\left(\sum_{n=-\infty}^{\infty}\sum_{m=-\infty}^{\infty} K_0\left[\frac{2K\pi}{c}\sqrt{(na + x - x_1)^2 + (mb + y - y_1)^2}\right]\right) \\ \times \cos\frac{2K\pi(z - z_1)}{c} \\ - \frac{4}{c}\sum_{K=1}^{\infty}\left(\sum_{n=-\infty}^{\infty}\sum_{m=-\infty}^{\infty} K_0\left[\frac{2K\pi}{c}\sqrt{(na + x - x_2)^2 + (mb + y - y_2)^2}\right]\right) \\ \times \cos\frac{2K\pi(z - z_2)}{c}. \end{aligned} \tag{79}$$

The procedure by which the above expression for S was obtained is essentially equivalent to Lekner's (1991) method, but operated in reverse: Lekner summed the expressions for the field components and obtained the potential by integration, adjusting the integration constants to produce the correct values of Madelung constants. Alternatively, in terms of the Green function, the potential within this lattice of charges is

$$\begin{aligned} V &= 4\pi[P_{222}(x, y, z \mid x_1, y_1, z_1) - P_{222}(x, y, z \mid x_2, y_2, z_2)] \\ &= \frac{4\pi}{c}[P_{22}(x, y \mid x_1, y_1) - P_{22}(x, y \mid x_2, y_2)] \\ &\quad + \frac{4}{c}\sum_{k=1}^{\infty}\left(\sum_{N=-\infty}^{\infty}\sum_{M=-\infty}^{\infty} K_0\left[\frac{2k\pi}{c}\sqrt{(Na + x - x_1)^2 + (Mb + y - y_1)^2}\right]\right) \\ &\quad \times \cos\frac{2k\pi(z - z_1)}{c} \\ &\quad - \frac{4}{c}\sum_{k=1}^{\infty}\left(\sum_{N=-\infty}^{\infty}\sum_{M=-\infty}^{\infty} K_0\left[\frac{2k\pi}{c}\sqrt{(Na + x - x_2)^2 + (Mb + y - y_2)^2}\right]\right) \\ &\quad \times \cos\frac{2k\pi(z - z_2)}{c}. \end{aligned} \tag{80}$$

The sums of K_0 functions appearing here are identical to those in equation (47a), but the relation between the remaining terms in equation (79) and the corresponding parts of the Green function is less obvious. Taking into account the definition of the two-dimensional Green function in equations (35a) and (40a), one obtains

$$\begin{aligned} &\frac{4\pi}{c}[P_{22}(x, y \mid x_1, y_1) - P_{22}(x, y \mid x_2, y_2)] \\ &\qquad = \frac{4\pi}{c}\left[P_2(y \mid y_1) - P_2(y \mid y_2)\right. \\ &\qquad\quad \left. + \frac{1}{4\pi}\sum_{M=-\infty}^{\infty} \ln \frac{1 - 2\mathrm{e}^{-\frac{2\pi}{a}|Mb+y-y_2|}\cos[2\pi(x - x_2)/a] + \mathrm{e}^{-\frac{4\pi}{a}|Mb+y-y_2|}}{1 - 2\mathrm{e}^{-\frac{2\pi}{a}|Mb+y-y_1|}\cos[2\pi(x - x_1)/a] + \mathrm{e}^{-\frac{4\pi}{a}|Mb+y-y_1|}}\right]. \end{aligned} \tag{81}$$

Assuming for the sake of definiteness that the quantities within the absolute value signs are positive, and noting that

$$1 - 2e^{-\frac{2\pi}{a}(Mb+y-y_2)}\cos\frac{2\pi(x-x_2)}{a} + e^{-\frac{4\pi}{a}(Mb+y-y_2)}$$
$$= 2e^{-\frac{2\pi}{a}(Mb+y-y_2)}\left[\cosh\frac{2\pi}{a}(Mb+y-y_2) - \cos\frac{2\pi(x-x_2)}{a}\right] \tag{82}$$

it follows that

$$\frac{1}{c}\sum_{M=-\infty}^{\infty}\ln\frac{1-2e^{-\frac{2\pi}{a}|Mb+y-y_2|}\cos[2\pi(x-x_2)/a]+e^{-\frac{4\pi}{a}|Mb+y-y_1|}}{1-2e^{-\frac{2\pi}{a}|Mb+y-y_1|}\cos[2\pi(x-x_1)/a]+e^{-\frac{4\pi}{a}|Mb+y-y_1|}}$$
$$= \frac{2\pi(y_2-y_1)}{ac} + \frac{1}{c}\sum_{M=-\infty}^{\infty}\ln\frac{\cosh[2\pi(Mb+y-y_2)/a]-\cos[2\pi(x-x_2)/a]}{\cosh[2\pi(Mb+y-y_1)/a]-\cos[2\pi(x-x_1)/a]} \tag{83}$$

which is to be compared with the second form of equation (78). The difference in the one-dimensional Green functions is thus found to be

$$\frac{4\pi}{ac}[P_2(y \mid y_1) - P_2(y \mid y_2)] = \frac{2\pi}{abc}(y_1^2 - y_2^2) - \frac{2\pi}{ac}(y_1 - y_2) \tag{84}$$

which, when inserted into equation (81), yields

$$V = S + \frac{2\pi}{abc}(y_1^2 - y_2^2). \tag{85}$$

Thus, the potentials obtained from the Green function and summing over the lattice differ by a constant that depends on the coordinates of the source points. From the mathematical viewpoint, this difference can be understood as a consequence of the conditional convergence: the numerical value obtained depends on the manner in which the positive and negative terms of the individually divergent series are combined. For crystal lattice sums, Redlack and Grindlay (1975) pointed out that Ewald sums and the direct addition of Coulomb potentials produce different results for some crystal structures, notably the CsCl lattice, and De Leeuw *et al* (1980) showed that a similar discrepancy arises when spherical shells of charges about a given lattice point are summed. Equation (84) is clearly consistent with this observation, noting the difference in the y coordinates of the Cs and Cl positions. Redlack and Grindlay (1975) identified two components of the potential: a *principal* or *intrinsic* part (which they showed to be identical to that given by Ewald's method) and an *extrinsic* part, depending on the size and shape of the lattice and equal to the difference between the Ewald potential and the direct sum of Coulomb terms. The distinction resides in the uniform neutralizing charge that is implied in the differential equation defining the Green function, but not in the direct summation methods—interestingly, Lekner (1991) showed that this uniform neutralizing charge was also implied in his results. Physically, the extrinsic potential depends on how the effects of the positive and negative charges cancel out at the boundary, or in other words, on the normal component of the dipole moment of the unit cell. In general, depolarization corrections must be applied to direct potential sums in order to recover the intrinsic potentials. Euwema and Surratt (1975) and Stuart (1978) showed how these corrections could be obtained from the second moment tensor of the charge cluster used in direct summation methods.

6. Relation to Lekner's results

The application of the Green function as described gives results that are, apart from minor differences in notation and the selection of coordinate variables, equivalent to Lekner's (1991,

1998) formulae. But a more substantial difference appears to reside in the manner in which the electrostatic energy E of the unit cell is calculated: Lekner (1998, equation (22)) expresses this as a sum of pairwise electrostatic potentials, while equation (67) of the present work contains contributions from single ions as well as pairs. The succinct explanation of this difference is that Lekner's electrostatic pair potential contains the self-energy terms that are written out separately in equation (67); pairwise decomposition followed by electroneutrality (as expressed by Lekner's equation (20)). More importantly, Lekner's electrostatic pair potential is given as the difference between two divergent lattice sums, while the functions P_{222} and Q_{222} that appear in equation (67) are both individually convergent. It is, however, of interest to consider the relation between the two approaches in more detail. By doing so, it is not only possible to prove that they are completely equivalent, but also to gain valuable insights into the physical significance of the mathematical functions appearing in the present work and in Lekner's papers.

Lekner (1998, equation (11)) expresses E in terms of lattice sums S and T which give, respectively, the potential experienced by one ion due to another ion and its infinite repetitions, and the potential experienced by the ion due to its own infinite repetitions. Since S and T are obviously infinite, they are obtained as limits of the corresponding lattice sums for the screened Coulomb potential. By an ingenious but rather involved argument, Lekner showed that these screened Coulomb lattice sums diverge as $1/s$, where $s^{1/2}$ is the screening constant, and that the nonsingular part consists of one function that vanishes as s tends to zero, and another function can be identified as the K_0 expansion of the Green function obtained in the present work. However, the reason why the Green function appears in this asymptotic result can be understood much more easily by applying some of the ideas described in the work of Chaba and Pathria (1976a) concerning the evaluation of lattice sums for the screened Coulomb potential. Subtracting the $k = m = n = 0$ term (i.e., 1) from both sides of the Poisson–Jacobi formula (equation (54)), and integrating from 0 to t with respect to t gives

$$-\sum_{k,m,n}{}' \frac{\mathrm{e}^{-\left[\left(\frac{2n\pi}{a}\right)^2+\left(\frac{2m\pi}{b}\right)^2+\left(\frac{2k\pi}{c}\right)^2\right]t+\mathrm{i}\left[\frac{2n\pi(x-\xi)}{a}\,\frac{2m\pi(y-\eta)}{b}+\frac{2k\pi(z-\zeta)}{c}\right]}}{(2n\pi/a)^2+(2m\pi/b)^2+(2k\pi/c)^2}+abcP_{222}(x,y,z\mid\xi,\eta,\zeta)$$
$$=\frac{abc}{4\pi}\sum_{K=-\infty}^{\infty}\sum_{M=-\infty}^{\infty}\sum_{N=-\infty}^{\infty}$$
$$\times\frac{\operatorname{erfc}[\sqrt{(x-\xi+Na)^2+(y-\eta+Mb)^2+(z-\zeta+Kc)^2}/2\sqrt{t}]}{\sqrt{(x-\xi+Na)^2+(y-\eta+Mb)^2+(z-\zeta+Kc)^2}}-t; \qquad (86)$$

the periodic Green function corresponds to the lower limit of the integral. Taking Laplace transforms with respect to t with parameter s (Erdélyi *et al* 1954, p 133, formulae (1) and (3); p 143, formula (1); p 177, formula (11)):

$$-\sum_{k,m,n}{}' \frac{\mathrm{e}^{\mathrm{i}\left[\frac{2n\pi(x-\xi)}{a}+\frac{2m\pi(y-\eta)}{b}+\frac{2k\pi(z-\zeta)}{c}\right]}}{[(2n\pi/a)^2+(2m\pi/b)^2+(2k\pi/c)^2][s+(2n\pi/a)^2+(2m\pi/b)^2+(2k\pi/c)^2]}$$
$$+\frac{abc}{s}P_{222}(x,y,z\mid\xi,\eta,\zeta)=\frac{abc}{4\pi}\sum_{K=-\infty}^{\infty}\sum_{M=-\infty}^{\infty}\sum_{N=-\infty}^{\infty}$$
$$\times\frac{\mathrm{e}^{-s^{1/2}\sqrt{(x-\xi+Na)^2+(y-\eta+Mb)^2+(z-\zeta+Kc)^2}}}{s\sqrt{(x-\xi+Na)^2+(y-\eta+Mb)^2+(z-\zeta+Kc)^2}}-\frac{1}{s^2}. \qquad (87)$$

The required lattice sum follows after transposing terms and multiplying by $4\pi s/abc$:

$$S_s = \sum_{K=-\infty}^{\infty}\sum_{M=-\infty}^{\infty}\sum_{N=-\infty}^{\infty}\frac{\mathrm{e}^{-s^{1/2}\sqrt{(x-\xi+Na)^2+(y-\eta+Mb)^2+(z-\zeta+Kc)^2}}}{s\sqrt{(x-\xi+Na)^2+(y-\eta+Mb)^2+(z-\zeta+Kc)^2}}$$
$$= \frac{4\pi}{abcs} + 4\pi P_{222}(x, y, z \mid \xi, \eta, \zeta)$$
$$-s\sum_{k,m,n}{}' \mathrm{e}^{\mathrm{i}\left[\frac{2n\pi(x-\xi)}{a}+\frac{2m\pi(y-\eta)}{b}+\frac{2k\pi(z-\zeta)}{c}\right]}\{[(2n\pi/a)^2+(2m\pi/b)^2+(2k\pi/c)^2]$$
$$\times[s+(2n\pi/a)^2+(2m\pi/b)^2+(2k\pi/c)^2]\}^{-1}. \tag{88}$$

The result for T_s follows by subtracting the free-space Green function (cf section 3.7):

$$T_s = \frac{4\pi}{abcs} + 4\pi Q_{222}(a, b, c) + \mathrm{O}(s). \tag{89}$$

Forming the electrostatic energy E from Lekner's (1998) equation (11),

$$E = \sum_{i<j} q_i q_j S_s(\xi_i, \eta_i, \zeta_i, \xi_j, \eta_j, \zeta_j) + \frac{T_s}{2}\sum_i q_i^2$$
$$= \frac{1}{2}\left[\frac{4\pi}{abcs}\left(\sum_i q_i\right)^2 + 4\pi\sum_{i\neq j} q_i q_j P_{222}(\xi_i, \eta_i, \zeta_i \mid \xi_j, \eta_j, \zeta_j)\right.$$
$$\left.+4\pi Q_{222}(a, b, c)\sum_i q_i^2 + \mathrm{O}(s)\right] \tag{90}$$

and noting that the algebraic sum of charges is zero, equation (67) is obtained by taking the limit as s tends to zero. Applying Lekner's equation (20), this can clearly be written as

$$E = \sum_{i<j} V_{ij} \qquad \text{where } V_{ij} = 4\pi q^2[P_{222}(\xi_i, \zeta_i, \eta_i \mid \xi_j, \eta_j, \zeta_j) - Q_{222}(a, b, c)] \tag{91}$$

is an effective 'pairwise' electrostatic potential (that in fact includes an infinite number of contributions from repetitions of the unit cell). The essential difference between the present work and Lekner's is expressed by the first step in the above derivation, which corresponds physically to the neutralization of the positive point charge by a uniform negative charge density, thereby ensuring the convergence of P_{222} and Q_{222}.

7. Conclusions

It has been shown in this paper that the intrinsic values of lattice sums for arbitrary periodic charge distributions can be obtained by use of the periodic modified Green function for Poisson's equation. Computationally efficient representations of this function as expansions in complementary error functions and K_0 Bessel functions were derived from the triple Fourier series by application of Ewald's method, or the PSF, respectively. The application of these formulae to simple ionic crystal lattices gives results equivalent to those recently derived by Lekner (1991, 1998), but the Green function is more general, being applicable to both discrete and continuous periodic charge distributions. The K_0 function expansion is more efficient, requiring about a third as many terms for convergent estimates as the Ewald sum. Depending on the relative efficiency of the algorithms used in the evaluation of K_0 and complementary error functions, use of the K_0 expansion in place of the more usual Ewald summation could result in reductions of more than 50% in the computational effort involved in computer simulations of ionic/polar fluids.

Acknowledgments

The present work was carried out as part of an interdisciplinary research project on the properties and behaviour of methane hydrates in ocean-floor sediments, recently established in the Environmental Sciences Division of Oak Ridge National Laboratory (ORNL), and supported by the Laboratory Director's Research and Development fund. I am grateful to Dr J G Blencoe, of the Chemical and Analytical Sciences Division, for many helpful comments on the present manuscript, and to Professor J Lekner for sending me copies of his work. I also appreciate the constructive criticisms offered by an anonymous referee.

Appendix. Derivation of equation (78)

The evaluation of the series

$$T = \sum_{m=-\infty}^{\infty} \ln \frac{(m+\alpha_2)^2 + \beta^2}{(m+\alpha_1)^2 + \beta^2} \tag{A1}$$

can be achieved by techniques similar to those used to establish the Mittag–Leffler expansion and Weierstass factorization theorems (see Whittaker and Watson 1944, pp 134–9). To apply these results it is convenient to consider first the function

$$S(\zeta) = \sum_{m=-\infty}^{\infty} \ln \frac{(m+\alpha_2)^2 + (\beta\zeta)^2}{(m+\alpha_1)^2 + (\beta\zeta)^2} \tag{A2}$$

where ζ is a real parameter having values in the range [0, 1]. Termwise differentiation of S with respect to ζ produces the series

$$S'(\zeta) = 2\beta^2\zeta \sum_{m=-\infty}^{\infty} \left[\frac{1}{(m+\alpha_2)^2 + (\beta\zeta)^2} - \frac{1}{(m+\alpha_1)^2 + (\beta\zeta)^2} \right] \tag{A3}$$

which can be readily evaluated by standard techniques of residue theory. The result is

$$\sum_{m=-\infty}^{\infty} \frac{1}{(m+\alpha)^2 + (\beta\zeta)^2} = \frac{\pi}{\beta\zeta} \frac{\sinh(\pi\beta\zeta)\cosh(\pi\beta\zeta)}{\cosh^2(\pi\beta\zeta) - \cos^2\pi\alpha} \tag{A4}$$

where α stands for either α_1 or α_2. But since

$$\sinh(\pi\beta\zeta)\cosh(\pi\beta\zeta) = \frac{1}{2\beta\pi} \frac{\partial}{\partial\zeta} \{\cosh^2(\pi\beta\zeta)\} \tag{A5}$$

the right-hand side of equation (A4) can be written

$$\frac{\pi}{\beta\zeta} \frac{\sinh(\pi\beta\zeta)\cosh(\pi\beta\zeta)}{\cosh^2(\pi\beta\zeta) - \cos^2\pi\alpha} = \frac{1}{2\beta^2\zeta} \frac{\partial}{\partial\zeta} \ln[\cosh^2(\pi\beta\zeta) - \cos^2(\pi\alpha)] \tag{A6}$$

so that

$$\frac{\partial S}{\partial\zeta} = \frac{\partial}{\partial\zeta} \ln[\cosh^2(\beta\pi\zeta) - \cos^2\pi\alpha_2] - \frac{\partial}{\partial\zeta} \ln[\cosh^2(\beta\pi\zeta) - \cos^2\pi\alpha_2]. \tag{A7}$$

Integration with respect to ζ from $\zeta = 0$ to $\zeta = 1$ now results in

$$S(1) - S(0) = \sum_{m=-\infty}^{\infty} \ln \frac{(m+\alpha_2)^2 + \beta^2}{(m+\alpha_1)^2 + \beta^2} - \sum_{m=-\infty}^{\infty} \ln \frac{(m+\alpha_2)^2}{(m+\alpha_1)^2}$$
$$= \ln \frac{\cosh^2(\beta\pi\zeta) - \cos^2\pi\alpha_2}{\cosh^2(\beta\pi\zeta) - \cos^2\pi\alpha_1} - \ln \frac{\sin^2\pi\alpha_2}{\sin^2\pi\alpha_1}. \tag{A8}$$

The second series on the left-hand side of equation (A8) can be evaluated as follows:

$$\sum_{m=-\infty}^{\infty} \ln \frac{(m+\alpha_2)^2}{(m+\alpha_1)^2} = 2\ln\frac{\alpha_2}{\alpha_1} + 2\sum_{m=1}^{\infty} \ln \frac{m^2 - \alpha_2^2}{m^2 - \alpha_1^2} = \ln \frac{\sin^2\pi\alpha_2}{\sin^2\pi\alpha_1} \tag{A9}$$

where use has been made of the infinite product

$$\frac{\sin z}{z} = \prod_{m=1}^{\infty} \left[1 - \left(\frac{z}{m\pi}\right)^2\right]. \tag{A10}$$

With appropriate simplification, the final result is

$$\sum_{m=-\infty}^{\infty} \ln \frac{(m+\alpha_2)^2 + \beta^2}{(m+\alpha_1)^2 + \beta^2} = \ln \frac{\cosh^2\pi\beta - \cos^2\pi\alpha_2}{\cosh^2\pi\beta - \cos^2\pi\alpha_1} = \ln \frac{\sinh^2\pi\beta + \sin^2\pi\alpha_2}{\sinh^2\pi\beta + \sin^2\pi\alpha_1}. \tag{A11}$$

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