Generalized approach to Ewald sums

R. E. Johnson
Department of Mathematics and Computer Science, Royal Military College of Canada, Kingston, Ontario, Canada K7K 7B4

S. Ranganathan
Department of Physics, Royal Military College of Canada, Kingston, Ontario, Canada K7K 7B4

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We derive Ewald sum formulas for potential energy and force for a system of point charges interacting with an arbitrary, long-range central potential. The system is made neutral by a uniform background of opposite charge interacting with the same potential. These formulas can be readily used in computer numerical simulations of model physical systems. In particular, expressions for the potential energy and the force have been obtained in both two and three dimensions for Coulomb and other power-law potentials, Yukawa systems, and for an electronic bilayer. We discuss numerical results and their accuracy for various systems and, based on our analysis, suggest values to be used for the parameters that appear in the Ewald sums.

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I. INTRODUCTION

A system of point charged particles embedded in a uniform background of opposite charge (thereby ensuring overall electrical neutrality) has been a subject of research for a number of years. Such systems have been investigated through molecular dynamics (MD) computer simulations in both two and three dimensions and they have proved very successful. However, the MD algorithm that is used for short-range forces such as Lennard Jones is not appropriate: the use of periodic boundary conditions and the minimum imaging criterion works well for short-range potentials since the potential can be truncated at half-the-box length without significant errors, and long-range corrections if required can be formulated. But, if the interparticle force is considered to be long range, as is the case in this study, truncation is no longer an option and the systems require special treatment. The interaction of each particle with all other particles in the basic cell, with all its periodic images and with the uniform neutralizing background charge, must be included. In addition, interaction of a particle with all its periodic images must also be included. Such a treatment is efficiently handled via the Ewald [1] technique. Such evaluations have been performed on systems interacting with a Coulomb potential in both three dimensions (3D) [2,3] and two-dimensions (2D) [4,5], three-dimensional Yukawa potential [6,7], and Coulombic bilayers [8,9]. Various approaches, often involving solutions of Poisson type of partial differential equations, have been used to obtain the Ewald sum expressions for these systems. Here we present a simple mathematical recipe, based only on the error function, with which to derive the Ewald sum that is applicable to any long-range central potential. Expressions for the potential energy and the corresponding forces are obtained for two- and three-dimensional systems. Detailed physical arguments are not required in the derivation of these formulas. The error function approach has been used before in obtaining the Ewald sum, but only to Coulombic systems. Mathematical expressions and numerical results for the special cases of Coulomb potential, other power-law potentials, Yukawa systems, and the electron gas bilayer are presented.

II. EWALD FORMULAS FOR ARBITRARY POTENTIAL

Consider a system of electrons with charge q interacting with a long-range central potential $\phi(r)$; the basic cell is a cube in 3D or a square in 2D with the length of a side L and $\Omega=L^3$ in 3D, L^2 in 2D; there are N electrons in the cell. Let $\vec{p}=L(n_1,n_2,n_3)$, where the n_j are integers with $n_3=0$ for 2D. The potential could be $\phi(r)=q^2r^{-1}e^{-\kappa r}$ with $\kappa=0$ for a Coulomb potential and $\kappa>0$ for a Yukawa potential, or it could be a power-law potential $\phi(r)=q^2r^{-(1+\delta)}$ where $0<\delta<1$. In order to maintain an overall charge neutrality of the system, there is also a uniform background of opposite charge interacting with the same interparticle potential. Due to the long-range nature of the potential, the interaction of each particle with the other $(N-1)$ particles in the basic cell, with all images of the N particles and with the uniform neutralizing background, must all be included. The potential energy of a particle at $\vec{r}_i$ in the basic cell due to another at $\vec{r}_j\neq\vec{r}_i$, all its images, and the uniform background can be written as

$$v(r_{ij})=\sum_{\vec{p}}\phi(|\vec{r}_{ij}+\vec{p}|)-\sum_{\vec{p}}\Omega^{-1}\int_{\vec{p}}d\vec{u}\phi(u), \tag{1}$$

where $\vec{r}_{ij}=\vec{r}_i-\vec{r}_j$. The total potential at $\vec{r}_i$ can be written as a sum of two terms:

$$V(r_i)=V_D(r_i)+V_S, \tag{2}$$

where $V_D(r_i)$ is due to all *other* particles in the basic cell and their respective images, and V_S, the self-energy, is a constant, which is due to all images of $\vec{r}_i$ itself:

$$V_D(r_i)=\sum_{\substack{j\neq i\\ j=1}}^{N}v(r_{ij})$$
$$=\sum_{\substack{j\neq i\\ j=1}}^{N}\sum_{\vec{p}}\phi(|\vec{r}_{ij}+\vec{p}|)-(N-1)\Omega^{-1}\int d\vec{u}\phi(u), \tag{3}$$

$$V_S = v(r_{ii}) = \sum_{\vec{p}\neq 0} \phi(|\vec{p}|) - \Omega^{-1} \int d\vec{u}\phi(u) = \lim_{r\to 0}\left(\sum_{\vec{p}} \phi(|\vec{r}+\vec{p}|) - \phi(r)\right) - \Omega^{-1} \int d\vec{u}\phi(u). \quad (4)$$

The total potential energy of the unit cell is then given by

$$U = \frac{1}{2}\sum_{i=1}^{N} V(r_i). \quad (5)$$

$V_D(r_i)$ is the contribution to the potential from distinct particles, while V_S is from each particle with its own periodic images, all in the presence of the uniform neutralizing background charge. It is readily seen that only $V_D(r_i)$ will contribute to the force; therefore, in an MD calculation where the force is required, V_S is not of any consequence. If a calculation of the potential energy is required, one must take into account the self-energy exactly. We consider the entire expression for the total potential energy in our analysis. To keep the formulation as general as possible and applicable to any central potential, we introduce the error function and its complement with two variables, α and μ. Considering $V_D(r_i)$ first, this yields

$$V_D(r_i) = \sum_{\substack{j\neq i \\ j=1}}^{N}\left[\sum_{\vec{p}} \phi(|\vec{r}_{ij}+\vec{p}|)\mathrm{erfc}(\alpha|\vec{r}_{ij}+\vec{p}|^{\mu}) + \sum_{\vec{p}} \phi(|\vec{r}_{ij}+\vec{p}|) \times \mathrm{erf}(\alpha|\vec{r}_{ij}+\vec{p}|^{\mu}) - \Omega^{-1}\int d\vec{u}\phi(u)\right]. \quad (6)$$

The value of the exponent μ should be determined such that V_S [Eq. (4)] can be numerically evaluated [see Eq. (25) in Sec. III]; for instance, the exponent is 1 if the potential has in it an r^{-1} dependence (Coulomb, Yukawa), and $1+\delta$ if the potential has in it a $r^{-(1+\delta)}$ dependence (power law); the value of α, which has the dimensions of $1/L^{\mu}$, will be dictated by the convergence of the infinite series involved. The second term has period L in 2D or 3D and can be replaced by its Fourier series to yield

$$V_D(r_i) = \sum_{\substack{j\neq i \\ j=1}}^{N}\left[\sum_{\vec{p}} \phi(|\vec{r}_{ij}+\vec{p}|)\mathrm{erfc}(\alpha|\vec{r}_{ij}+\vec{p}|^{\mu}) + \sum_{\vec{g}\neq\vec{0}} C(g;\alpha)e^{i\vec{g}\circ\vec{r}_{ij}} + \tilde{C}(0;\alpha)\right], \quad (7)$$

where $\vec{g}=2\pi(\lambda_1,\lambda_2,\lambda_3)/L$, the λ_j are integers, and $\lambda_3=0$ for 2D; then

$$C(g;\alpha) = \Omega^{-1}\int d\vec{u}e^{-i\vec{g}\circ\vec{u}}\phi(u)\mathrm{erf}(\alpha u^{\mu}) \quad \text{if } |\vec{g}| = g > 0,$$

and

$$\tilde{C}(0;\alpha) = C(0;\alpha) - \Omega^{-1}\int d\vec{u}\phi(u) = -\Omega^{-1}\int d\vec{u}\phi(u)\mathrm{erfc}(\alpha u^{\mu}). \quad (8)$$

The first term in Eq. (7) is the real-space series while the second term is the reciprocal-space series. V_S is a constant and independent of the particle configuration; its numerical values for some specific potentials are given in the next section. Note that our system is made up of point charges in the presence of a uniform background of opposite charges; hence, this self-energy is due to the bare potential in the presence of the uniform background.

The Ewald sum expression for the potential energy must be independent of the error function parameter α. This can be shown to be true by taking the derivative of Eq. (7) and using Eq. (8):

$$\frac{\partial V_D(r_i)}{\partial\alpha} = \frac{2}{\sqrt{\pi}}\left[-\sum_{\vec{p}} \phi(|\vec{r}+\vec{p}|)|\vec{r}+\vec{p}|e^{-\alpha^2|\vec{r}+\vec{p}|^2} + \frac{1}{\Omega}\sum_{\vec{g}\neq\vec{0}} e^{i\vec{g}\circ\vec{r}}\int d\vec{u}e^{-i\vec{g}\circ\vec{u}}\phi(u)ue^{-\alpha^2u^2}\right] + \frac{2}{\sqrt{\pi}\Omega}\int d\vec{u}\phi(u)e^{-\alpha^2u^2} = 0, \quad (9)$$

since the Fourier series representation of the first term is precisely the negative of the sum of the second and third terms; μ has been chosen to be 1 and the summation over j has been removed for neatness sake. This independence must be for every type of system and for any configuration of the particles in it. However, in MD calculations one often includes only the $p=0$ terms (with the minimum imaging convention) and truncates the sum on $\vec{g}$; therefore, the total potential energy in such a calculation does depend on α. Then a study of the α independence of the calculated potential energy may be used to determine a range of α for which these approximations are tolerable.

Since the potential is assumed to be central, the expressions for the Fourier coefficients that appear in $V_D(r_i)$ in Eqs. (7) and (8) can be reduced to single integrals. In 3D the expressions are

$$C(g;\alpha) = \frac{4\pi}{L^3}\frac{1}{g}\int_0^{\infty} duu\phi(u)\sin(gu)\mathrm{erf}(\alpha u^{\mu}) \quad \text{if } g > 0,$$

$$\tilde{C}(0;\alpha) = -\frac{4\pi}{L^3}\int_0^{\infty} duu^2\phi(u)\mathrm{erfc}(\alpha u^{\mu}). \quad (10)$$

In 2D they are

$$C(g;\alpha) = \frac{2\pi}{L^2}\int_0^{\infty} duu\phi(u)J_0(gu)\mathrm{erf}(\alpha u^{\mu}) \quad \text{if } g > 0,$$

$$\tilde{C}(0;\alpha) = -\frac{2\pi}{L^2}\int_0^\infty du u\phi(u)\mathrm{erfc}(\alpha u^\mu). \tag{11}$$

Of course, the model potential must be such that these integrals exist. Depending on the form of the potential, it may be possible to reduce these integrals to simpler analytic expressions. If not, they can be evaluated numerically within an MD calculation, using a Gauss quadrature method for example.

The corresponding Ewald expressions for the force on a particle are needed in MD simulations, and can be obtained from these potential energy formulas. Of course, these do not depend on the self-terms and are also independent of α. The force on particle 1, for example, due to all others is

$$\vec{F}_1(\vec{r}_1) = \sum_{\vec{p}}{}' \sum_{j=1}^{N} \frac{\vec{r}_{1j}+\vec{p}}{|\vec{r}_{1j}+\vec{p}|}\left(-\phi'(|\vec{r}_{1j}+\vec{p}|)\mathrm{erfc}(\alpha|\vec{r}_{1j}+\vec{p}|^\mu) + \frac{2\alpha}{\sqrt{\pi}}\mu|\vec{r}_{1j}+\vec{p}|^{\mu-1}\phi(|\vec{r}_{1j}+\vec{p}|)e^{-\alpha^2|\vec{r}_{1j}+\vec{p}|^{2\mu}}\right) + \sum_{\vec{g}\neq\vec{0}} \vec{g}C(g;\alpha)\sum_{j=2}^{N}\sin(\vec{g}\circ\vec{r}_{1j}). \tag{12}$$

Equations (4), (7), and (12), with supporting Eqs. (10) and (11), are applicable to any central, long-range interparticle potential. These equations constitute the main results of our paper. We now apply these equations for specific potentials.

(1) For the three-dimensional Coulomb potential, $\phi(r) = q^2 r^{-1}$, our formulation yields the well-known result

$$C(g;\alpha) = \frac{4\pi q^2}{L^3}\frac{e^{-g^2/4\alpha^2}}{g^2} \quad \text{if } g>0, \quad \tilde{C}(0;\alpha) = -\frac{\pi q^2}{L^3\alpha^2}. \tag{13}$$

(2) For a three-dimensional power potential, $\phi(r) = q^2 r^{-(1+\delta)}$, it yields

$$C(g;\alpha) = \frac{4\pi q^2}{L^3}\frac{1}{g}\int_0^\infty du u^{-\delta}\sin(gu)\mathrm{erf}(\alpha u^{1+\delta}) \quad \text{if } g>0,$$

$$\tilde{C}(0;\alpha) = -\frac{4\pi q^2}{L^3}\int_0^\infty du u^{1-\delta}\mathrm{erfc}(\alpha u^{1+\delta}) = -\frac{4\pi q^2}{L^3}\frac{\Gamma[3/(2+2\delta)]}{\sqrt{\pi}(2-\delta)\alpha^{(2-\delta)/(1+\delta)}}. \tag{14}$$

(3) For a three-dimensional Yukawa potential, $\phi(r) = q^2 r^{-1} e^{-\kappa r}$, it yields

$$C(g;\alpha) = \frac{4\pi q^2}{L^3}\frac{1}{g}\int_0^\infty du e^{-\kappa u}\sin(gu)\mathrm{erf}(\alpha u) \quad \text{if } g>0,$$

$$\tilde{C}(0;\alpha) = -\frac{4\pi q^2}{L^3}\int_0^\infty du u e^{-\kappa u}\mathrm{erfc}(\alpha u) = -\frac{4\pi q^2}{L^3}\frac{1}{\kappa^2}\left[1-\frac{\kappa}{\sqrt{\pi}\alpha}-e^{\kappa^2/4\alpha^2}\left(1-\frac{\kappa^2}{2\alpha^2}\right)\times\mathrm{erfc}\left(\frac{\kappa}{2\alpha}\right)\right]. \tag{15}$$

(4) For the two-dimensional Coulomb potential, $\phi(r) = q^2 r^{-1}$, it yields the well-known result

$$C(g;\alpha) = \frac{2\pi q^2}{L^2}\frac{\mathrm{erfc}(g/2\alpha)}{g} \quad \text{for } g>0,$$

$$\tilde{C}(0;\alpha) = -\frac{2\sqrt{\pi}q^2}{L^2\alpha}. \tag{16}$$

(5) For a two-dimensional power potential, $\phi(r) = q^2 r^{-(1+\delta)}$, it yields

$$C(g;\alpha) = \frac{2\pi q^2}{L^2}\int_0^\infty du u^{-\delta}J_0(gu)\mathrm{erf}(\alpha u^{1+\delta}) \quad \text{for } g>0,$$

$$\tilde{C}(0;\alpha) = -\frac{2\pi q^2}{L^2}\int_0^\infty du u^{-\delta}\mathrm{erfc}(\alpha u^{1+\delta}) = -\frac{2\pi q^2}{L^2}\frac{\Gamma[1/(1+\delta)]}{\sqrt{\pi}(1-\delta)\alpha^{(1-\delta)/(1+\delta)}}. \tag{17}$$

(6) For a two-dimensional Yukawa potential, $\phi(r) = q^2 r^{-1} e^{-\kappa r}$, it yields

$$C(g;\alpha) = \frac{2\pi q^2}{L^2}\int_0^\infty du e^{-\kappa u}J_0(gu)\mathrm{erf}(\alpha u) \quad \text{for } g>0,$$

$$\tilde{C}(0;\alpha) = -\frac{2\pi q^2}{L^2}\int_0^\infty du e^{-\kappa u}\mathrm{erfc}(\alpha u) = -\frac{2\pi q^2}{L^2}\frac{1}{\kappa}[1-e^{\kappa^2/4\alpha^2}\mathrm{erfc}(\kappa/2\alpha)]. \tag{18}$$

The integrals for $C(g;\alpha)$ in Eqs. (14), (15), (17), and (18) need to be evaluated numerically as required.

There is another version of the Ewald sum for the Yukawa potential in 3D which was obtained by Salin and Caillol [7] starting from the Helmholtz equation. Their formula involves the screening parameter κ in the error function in the real-space sum, while our formulation does not. We have derived the analogous result for two-dimensional Yukawa: it is

$$v(r) = \frac{1}{2}\sum_{\vec{p}} \frac{q^2}{|\vec{r}+\vec{p}|}\left[e^{-\kappa|\vec{r}+\vec{p}|}\,\mathrm{erfc}\left(\alpha|\vec{r}+\vec{p}| - \frac{\kappa}{2\alpha}\right) + e^{\kappa|\vec{r}+\vec{p}|}\,\mathrm{erfc}\left(\alpha|\vec{r}+\vec{p}| + \frac{\kappa}{2\alpha}\right)\right] + \frac{2\pi q^2}{L^2}\left(\sum_{\vec{g}\neq\vec{0}} D(g;\alpha)e^{i\vec{g}\circ\vec{r}} + \tilde{D}(0;\alpha)\right),$$

where

$$D(g{:}\alpha) = \frac{\mathrm{erfc}(\sqrt{g^2+\kappa^2}/2\alpha)}{\sqrt{g^2+\kappa^2}} \quad \text{if } g>0,$$

$$\tilde{D}(0;\alpha) = -\frac{1}{\kappa}[1-\mathrm{erfc}(\kappa/2\alpha)]. \tag{19}$$

(7) In the bilayer problem two parallel layers are separated by distance d. The potential energy at $\vec{r}_i$ in one of the layers due to all particles in both layers and the neutralizing background in both is

$$V(r_i) = V_D(r_i) + V_S + V_{\mathrm{inter}}(r_i), \tag{20}$$

where V_D and V_S for particles in the same plane are given by Eqs. (3) and (4) with Ewald sum expressions (7) and (11). The interlayer potential is

$$V_{\mathrm{inter}}(r_i) = \sum_{j=1}^{N}\sum_{\vec{p}}\left[\phi(|\vec{r}_i-\vec{\rho}_j+\vec{p}|) - \frac{1}{L^2}\int d\vec{u}\,\phi(\sqrt{u^2+d^2})\right] = \sum_{j=1}^{N}\left[\sum_{\vec{p}}\phi(|\vec{r}_i-\vec{\rho}_j+\vec{p}|)\mathrm{erfc}(\alpha|\vec{r}_i-\vec{\rho}_j+\vec{p}|) + \sum_{\vec{g}\neq\vec{0}} B(g;\alpha,d)e^{i\vec{g}\circ\vec{r}} + \tilde{B}(0;\alpha,d)\right], \tag{21}$$

where $r_i=(x_i,y_i,0)$ is in one plane, $\vec{\rho}_j=(\bar{x}_j,\bar{y}_j,d)$ is in the other, and $\vec{p}=L(n_1,n_2,0)$, where n_1,n_2 are integers. The Fourier coefficients in Eq. (21) are

$$B(g;\alpha,d) = \frac{2\pi}{L^2}\int_0^\infty duu\,\phi(\sqrt{u^2+d^2})J_0(gu) \times \mathrm{erfc}(\alpha\sqrt{u^2+d^2}) \quad \text{if } g>0,$$

$$\tilde{B}(g;0,d) = -\frac{2\pi}{L^2}\int_0^\infty duu\,\phi(\sqrt{u^2+d^2})\mathrm{erfc}(\alpha\sqrt{u^2+d^2}). \tag{22}$$

For the Coulomb potential these integrals yield

$$B(g;\alpha,d) = \frac{2\pi}{L^2}\frac{q^2}{2g}\left[e^{-gd}\,\mathrm{erfc}\left(\frac{g}{2\alpha}-\alpha d\right) + e^{gd}\,\mathrm{erfc}\left(\frac{g}{2\alpha}+\alpha d\right)\right] \quad \text{if } g>0,$$

$$\tilde{B}(g;0,d) = -\frac{2\pi q^2}{L^2}\left(\frac{1}{\sqrt{\pi}\alpha}e^{-\alpha^2d^2} + d\,\mathrm{erfc}(\alpha d)\right). \tag{23}$$

The total force on particle 1 in one of the layers is

$$\vec{F}_1(\vec{r}_1) = \sum_{\vec{p}}{}'\sum_{j=1}^{N}\frac{\vec{s}_{1j}}{|\vec{s}_{1j}|}\left(-\phi'(|\vec{s}_{1j}|)\mathrm{erfc}(\alpha|\vec{s}_{1j}|) + \frac{2\alpha}{\sqrt{\pi}}\phi(|\vec{s}_{1j}|)e^{-\alpha^2|\vec{s}_{1j}|^2}\right) + \sum_{\vec{p}}\sum_{j=1}^{N}\frac{\vec{r}_1-\vec{\rho}_j+\vec{p}}{|\vec{d}_{1j}|} \times\left(-\phi'(|\vec{d}_{1j}|)\mathrm{erfc}(\alpha|\vec{d}_{1j}|) + \frac{2\alpha}{\sqrt{\pi}}\phi(|\vec{d}_{1j}|)e^{-\alpha^2|\vec{d}_{1j}|^2}\right) + \sum_{\vec{g}\neq\vec{0}}\vec{g}\left(C(g;\alpha)\sum_{j=2}^{N}\sin[\vec{g}\circ(\vec{r}_1-\vec{r}_j)] + B(g;\alpha,d)\sum_{j=1}^{N}\sin[\vec{g}\circ(\vec{r}_1-\vec{\rho}_j)]\right), \tag{24}$$

where $\vec{s}_{1j}=\vec{r}_1-\vec{r}_j+\vec{p}$ and $\vec{d}_{1j}=\vec{r}_1-\vec{\rho}_j+\vec{p}$.

The generalized power law and Yukawa results for 3D and 2D, given by Eqs. (14), (15), (17), and (18) are new to the best of our knowledge. The 3D Coulomb result, given by Eq. (13) and the 2D Coulomb result, given by Eq. (16), are in agreement with published results. The bilayer result, Eq. (21), previously obtained by us [8] using this procedure agrees with that obtained by Weis *et al.* using a different procedure [9].

III. NUMERICAL CONSIDERATIONS

The formulas listed in the previous section are exact. In any application one must select the potential and dimension of the system to be studied along with the thermodynamic state of the system. It should be noted that there are three parameters in any Ewald sum: the vector parameters $\vec{p}$ and $\vec{g}$ associated with the real space and the reciprocal space, respectively, and the scalar parameter α. In what follows, all quantities are dimensionless: distances in units of the Wigner-Seitz radius a, energies in units of q^2/a; a is $(3/4n\pi)^{1/3}$ in 3D and $(1/n\pi)^{1/2}$ in 2D, where n is the particle density. Hence the particle density in dimensionless units is $3/4\pi$ in 3D and $1/\pi$ in 2D. In our calculations, some results of which are presented here, the number of particles is $N=256$ in 3D and 512 in 2D. This gives a box length L of 10.225 in 3D and 40.106 in 2D. Each term in the corresponding expression is evaluated numerically for a chosen value of the Ewald parameter α.

To see that our equations are indeed correct, we first compare our results with those in the literature. We have already established that our exact results are independent of α, as they must be. The one-component plasma system in which the point charges are immersed in a uniform background of opposite charge and interacting with a Coulomb potential has been studied through MD both in 3D and 2D. Using different approaches, Brush *et al.* [2] and Tosi [10] have derived expressions for the total potential energy for such a system in 3D, while Totsuji [4] has done the same for 2D. To make a

full comparison, we need to compute the self-energy V_S. If one uses the same error function formalism, Eq. (4) can be written as

$$V_S = \sum_{\vec{p}\neq 0} \phi(|\vec{p}|)\mathrm{erfc}(\alpha|\vec{p}|^{\mu}) + \sum_{\vec{g}\neq\vec{0}} C(g;\alpha) + \tilde{C}(0;\alpha) + \lim_{p\to 0}\{\phi(p)\mathrm{erfc}(\alpha p^{\mu}) - \phi(p)\}, \quad (25)$$

which is also independent of α. The last term in Eq. (25) yields $-\frac{2\alpha}{\sqrt{\pi}}$ for Coulomb or Yukawa or power law $\phi(r) = q^2 r^{-(1+\delta)}$ with $0<\delta<1$ potentials. V_S is independent of the particle configuration and should be multiplied by $\frac{1}{2}N$ to obtain the total self-energy contribution to the potential energy. In evaluating Eq. (25), the first term can be safely neglected even for αL^{μ} as small as four, since $\mathrm{erfc}(4)<10^{-8}$. Our calculations yield 35.481 for three-dimensional Coulomb and 24.896 for two-dimensional Coulomb, essentially independent of α and particle configuration: these agree very well with published results for the self-energy given by $\frac{N}{2L}\frac{8.913}{\pi}$(=35.479) for 3D [11] and $\frac{N}{2L}$3.900(=24.894) for 2D [4]. Our expressions for $V_D(r_i)$ and hence for the total potential energy U agree exactly with those in literature for both three-dimensional Coulomb [2,10] and two-dimensional Coulomb [4] systems. It should be noted the expression in Allen and Tildesley [12] refers to a system of point charges that is made neutral by point charges of opposite sign and hence differs from our system.

For a bilayer, our expressions for the total potential energy and for the self-energy agree with those of Weis *et al.* [9], though the approaches are different. Thus our results can be applied with confidence to any three-dimensional and two-dimensional long-range central potentials.

One needs to truncate the infinite series in both real space and reciprocal space in order to obtain numerical values for the force (or potential energy) that are needed in any computer simulation. The real-space sum truncation would then involve another parameter R_{cut}, the real-space forces cutoff, defined by $|\vec{r}_{ij}+\vec{p}L|<R_{\mathrm{cut}}$. But in MD simulations, one often uses the minimum imaging criterion and this implies R_{cut} be equal to half the boxlength. Since any other value of R_{cut} would introduce further complexities in the MD program and place large demands on computer processing, we have followed the usual procedure of including only the basic cell (i.e., $\vec{p}=\vec{0}$ term only) when evaluating the real-space contribution; this term is dominant in the real-space sum, more so for larger α and hence one must choose α that is not too small. On the other hand, α should be small enough so that the sum of the infinite series in the g space can be approximated well by including as few terms as possible. We seek a range of α for which both requirements are met.

It is not difficult to determine acceptable values of α. This can be done by studying the α independence of the potential energy numerically. To do this we created various particle configurations and evaluated each term of the potential energy expressions for selected values of α. We studied $U_D = \Sigma_{i=1}^{N} V_D(r_i)$ with $V_D(r_i)$ given by Eq. (7). This was done for the Coulomb, power law, and Yukawa potentials in both 2D and 3D; these calculations require Eqs. (13)–(18). For the bilayer we have studied the Coulomb potential for selected values of the layer separation distance d; this requires Eqs. (20)–(23). We truncated the g-space series using a safe value for the largest magnitude of λ ($g=2\pi\lambda/L$), 8 for 3D, and 16 for 2D. Typical results are shown in Fig. 1(a) for a three-dimensional Coulomb potential, Fig. 1(b) for a 3D $r^{-(1+\delta)}$ with $\delta=0.4$ power-law potential and Fig. 1(c) for a two-dimensional Yukawa potential with $\kappa=0.5$. An equilibrium

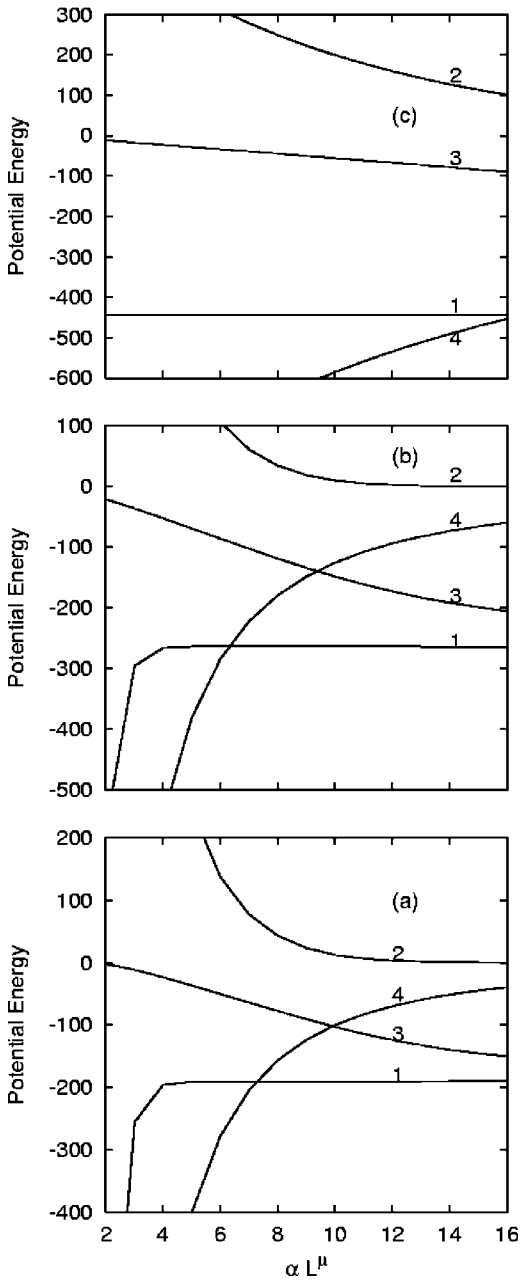

FIG. 1. Potential energy terms as a function of the Ewald parameter αL^{μ} for a typical equilibrium particle configuration in (a) 3D with Coulomb interaction, (b) 3D with a power-law potential, $r^{-(1+\delta)}$ with $\delta=0.4$ and (c) two-dimensional Yukawa potential with $\kappa=0.5$: $U_D=\Sigma_{i=1}^{N} V_D(r_i)$ is labeled (1); $V_D(r_i)$ given by Eq. (7) is the sum of three terms: the real-space contribution to U_D is (2), the reciprocal space is (3), and the $\tilde{C}(0,\alpha)$ is (4). $\vec{p}=0$ and $\lambda_{\mathrm{max}}=8$ for 3D and 16 for 2D.

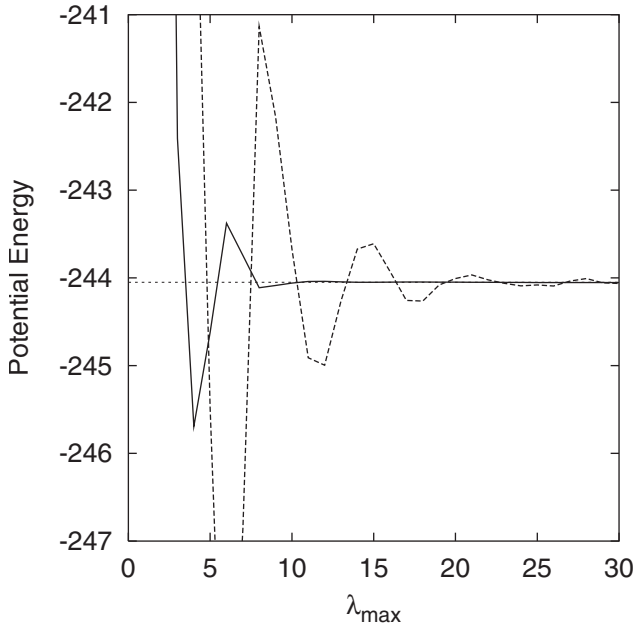

FIG. 2. Potential energy U_D as a function of λ_{max} for a three-dimensional power-law potential, $r^{-(1+\delta)}$ with $\delta=0.3$. $\vec{p}=0$ and $\alpha L^{\mu}=6$. Solid line and dashed line using modified and normal error function, respectively.

configuration of the particles, corresponding to a given thermodynamic state, was chosen. The figures show potential energy contributions from the real-space term (line 2), the reciprocal-space term (line 3), and the $\tilde{C}(0,\alpha)$ term (line 4), along with their sum, the U_D contribution to the total potential energy (line 1) as a function of αL^{μ}. In all cases, excellent agreement confirming the α independence of the results for a certain range of α was obtained. Since the real-space terms contain α, the accuracy of our results justifies the neglect of the $\vec{p}\neq\vec{0}$ terms. Since one cannot deduce the accuracy of the constancy of our results from the graph, we present the actual numbers; the variation in U_D is from -190.70 to -190.68 in $6<\alpha L<10$ for three-dimensional Coulomb, from -263.81 to -264.02 in $6<\alpha L^{1+\delta}<10$ for three-dimensional power and from -442.95 to -442.96 in $2<\alpha L<16$ for two-dimensional Yukawa. These errors agree with the order-of-magnitude analysis of Perram *et al.* [13] for three-dimensional Coulomb systems, where they show that α and λ_{max} should be chosen so that $\varepsilon\approx\exp(-\alpha^2L^2/4)$ and $\varepsilon\approx\exp(-\pi^2\lambda_{max}^2/\alpha^2L^2)$, where ε is the error estimate; the choice of $\alpha L=6$ and $\lambda_{max}=6$ would give $\varepsilon\approx10^{-4}$, consistent with our numerical findings. Although our results indicate that a range of α would be acceptable in a MD calculation, our conclusion is that recommended values for αL^{μ} are 6 in 3D and 8 in 2D, given that a smaller α is preferred, since it then requires fewer terms in the g-space sum.

Having chosen $\vec{p}$ and α, we then analyzed the results for various choices of $\vec{g}$ in the reciprocal-space term. The problem of determining an acceptable set of $\vec{g}$ terms is considerably more difficult for some potentials, although it is simple for Coulomb systems. We studied the choice of g by considering $C(g,\alpha)$ as given by Eqs. (10) and (11) as sequences on integer λ where $g=2\pi\lambda/L$. For the Coulomb potential it is obvious that the sequences corresponding to Eqs. (13) and (16) converge to 0 rapidly and conclude that λ_{max} of 6 would be sufficient.

However, for non-Coulomb potentials, the integrals in Eqs. (10) and (11) must be studied carefully. We considered two non-Coulomb potentials in both 2D and 3D to analyze consistency in our results: Yukawa, $r^{-1}e^{-\kappa r}$ for κ in $[0,1]$ and power law, $r^{-(1+\delta)}$ for δ in $[0,1)$. The $C(g,\alpha)$ integrals in Eqs. (14), (15), (17), and (18) are best evaluated numerically using erfc rather than erf according to

$$\int_0^\infty dx e^{-\kappa x}\sin(gx)\mathrm{erf}(\alpha x) = \frac{g}{g^2+\kappa^2} - \int_0^\infty dx e^{-\kappa x}\sin(gx)\mathrm{erfc}(\alpha x), \tag{26}$$

$$\int_0^\infty dx e^{-\kappa x}J_0(gx)\mathrm{erf}(\alpha x) = \frac{1}{\sqrt{g^2+\kappa^2}} - \int_0^\infty dx e^{-\kappa x}J_0(gx)\mathrm{erfc}(\alpha x), \tag{27}$$

for Yukawa potential, and

TABLE I. U_D contribution to the total potential energy for Yukawa potential in 3D and 2D for various values of κ. $\vec{p}=0$ and $\alpha L=6$ for 3D (8 for 2D). Third (sixth) and fourth (seventh) columns indicate the minimum values of λ_{max} needed to guarantee an error in the total potential energy of no more than 1% and 0.1%, respectively.

	3D			2D		
		λ_{max} for error in U_D of			λ_{max} for error in U_D of	
κ	$-U_D$	1%	0.1%	$-U_D$	1%	0.1%
0	190.70	4	5	534.59	3	5
0.1	189.25	4	8	525.2	6	15
0.2	185.16	5	10	506.0	9	24
0.3	179.05	5	10	484	9	25
0.4	171.64	7	10	463	11	27
0.5	163.55	7	10	443	13	33

TABLE II. Same as Table I, except for the power potential, for various values of δ.

	3D			2D		
		λ_{max} for error in U_D of			λ_{max} for error in U_D of	
δ	$-U_D$	1%	0.1%	$-U_D$	1%	0.1%
0	190.70	4	5	534.59	3	5
0.1	207.95	4	6	600.0	3	6
0.2	225.6	4	7	678.2	4	8
0.3	244.0	4	7	776	4	20
0.4	263.5	4	8	906	5	35
0.5	284.3	4	8	1085	5	70

$$\int_0^\infty dx x^{-\delta} \sin(gx)\mathrm{erf}(\alpha x^{1+\delta}) = \frac{\Gamma(1-\delta)}{g^{1-\delta}} \sin\frac{\pi(1-\delta)}{2} - \int_0^\infty dx x^{-\delta} \sin(gx)\mathrm{erfc}(\alpha x^{1+\delta}), \tag{28}$$

$$\int_0^\infty dx x^{-\delta} J_0(gx)\mathrm{erf}(\alpha x^{1+\delta}) = \frac{\Gamma[(1-\delta)/2]}{2^\delta g^{1-\delta}\Gamma[(1+\delta)/2]} - \int_0^\infty dx x^{-\delta} J_0(gx)\mathrm{erfc}(\alpha x^{1+\delta}). \tag{29}$$

for the power potential. The four integrals containing erfc can be evaluated accurately using Gauss quadrature with a combination of Legendre and Laguerre abscissas and weights. We evaluated $C(g,\alpha)$ using Eqs. (14), (15), (17), and (18) for selected values of κ and δ for various values of λ. In every case, these sequences are positive, monotone decreasing, and convergent to 0. The potential energy U_D is then computed as a function of λ_{max}. The number of $\vec{g}$ vectors is determined by letting the x component of λ take on values from 0 to λ_{max}, while the y and z components take on values from $-\lambda_{max}$ to λ_{max}, subject to the constraint that the magnitude of λ not exceedλ_{max}. A typical plot of U_D as a function λ_{max} is shown in Fig. 2 for a 3D $r^{-(1+\delta)}$ with $\delta=0.3$ power-law potential. The parameter $\vec{p}$ is set at 0 and αL^μ at 6. U_D for this potential can be obtained by using the regular or the modified error function ($\mu=1$ or $1+\delta$): the two results are shown by the dashed and solid lines, respectively. It is clearly seen that the use of the modified error function is vastly superior. This is true for all values of δ and for 3D and 2D. In general, potential energy exhibits damped oscillations before settling to a constant value. The smaller the δ, the smaller are the oscillations and the quicker is the approach to the constant value. Thus one truncates the g-space terms depending on the accuracy needed. For example, for a three-dimensional power-law potential with $\delta=0.3$, an error of 1% in the total potential energy can be achieved if one chooses $\lambda_{max}=4$, but $\lambda_{max}=7$ is required for a 0.1% error, assuming the use of the modified error function. We have done similar analysis for Yukawa potential and have incorporated our results in Tables I and II. These provide the exact values of U_D obtained from their constant values at large λ_{max}, and λ_{max} values that are required to obtain an accuracy of 1% and 0.1%. Table I is for selected values of κ for Yukawa potential in both 3D and 2D; α was chosen as $6/L$ in 3D and $8/L$ in 2D. Table II gives the same for the power potential as a function of δ.

It is seen that each sequence for 3D converges much faster than the corresponding sequence for 2D. This is fortunate since there are many more $\vec{g}$ vectors for a given λ in 3D than in 2D. The infinite series which appear in Eq. (7) for potential energy and Eq. (12) for the interparticle force are Fourier series and have partial sum sequences which are not monotone: consequently, these series do converge faster than the corresponding absolute value series. It should be stressed that numerical checks on the accuracy and errors in the potential energy and the force should be carried out for each system before beginning the computer simulation.

IV. CONCLUSIONS

We have formulated a universal approach, based on the error function, to the derivation of the Ewald sum for an arbitrary long-range central interparticle potential in both three and two dimensions. The appropriate expressions for the total potential and the force have been obtained. We have applied the formalism to a number of specific potentials that include Coulomb, Yukawa, and power-law potentials and done a study of the numerical considerations, since choice of parameters and truncations of infinite series are involved. Based on our analysis, we have suggested values to be used for the parameters and truncation in the various Ewald sums.

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