Ewald summation of electrostatic interactions in molecular dynamics of a three-dimensional system with periodicity in two directions

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The Poisson summation formula is used to calculate the effective interaction of charged particles in a three-dimensional system with periodicity in two dimensions. The interaction energy expression is identical to that obtained from the Berthaut approach for the Gaussian spreading function, and its correspondence with the results of the Rhee-Halley-Hautman-Rahman method is shown. The formalism based on the Poisson summation formula is used also to calculate the interaction energy of point-dipole moments.

I. INTRODUCTION

Computer simulation techniques often require efficient summation of long-range electrostatic interactions. For three-dimensional periodicity of a system the Ewald summation method is well known and widely used.[1–5] Few years ago Fuchizaki[6] elaborated a generalization of the Ewald method concerning *p*-dimensional space and *p*-dimensional lattice sums of quantities characterized by inverse power law and modulation wave vector. A relatively simple expression was derived for odd-dimensional lattice and for arbitrary power as well as modulation wave vector. However, in many problems of interest in physics and chemistry one encounters systems which are infinite in some directions and finite in others. In simulations of liquid and solid surfaces, membranes, fluid trapped between two walls, adsorption processes on a surface, etc., one needs an extension of the Ewald method for a three-dimensional system with periodicity in two directions only.

In the past, several methods for semi-infinite systems of charges have been developed and tested[7–11] in computer simulations. Heyes and co-workers[7,8] redeveloped the Berthaut method,[12] for a charge spreading function of arbitrary analytical form, to obtain expressions for the electrostatic energy in infinite lamina. Considering the ionic charges over the polar surface of a large piece of rigid ionic crystal Smith[9] found expression for the interaction energy of the charges [Eq. (68) in Ref. 9] which partly coincides with that presented by Heyes and co-workers for the Gaussian spreading function.[7,8] Almost a decade ago Rhee *et al.*[10] proposed another method, called here the Rhee-Halley-Hautman-Rahman (RHHR) method, in which the energy expression was split into sums over the real and reciprocal-space lattices introducing a separation function. The separation function is defined mainly in the reciprocal space and its suitable choice causes both sums to converge at a sufficiently rapid rate. Another approach was presented by Hautman and Klein,[11] who introduced the convergence functions in the real space. The method may be applied to systems in which the size of the periodically replicated cell is larger compared to the extent of the charges in the normal directions. This limitation is due to the fact that the interaction was expanded in a power series in $\Delta z/\Delta\varrho$ where $\Delta\varrho$ and Δz are the components of the distance between particles parallel and perpendicular to the plane of the periodic continuation, respectively.

In this paper, we apply the Poisson summation formula[13] to derive the effective energy expression for long-range Coulomb interactions in molecular dynamics of three-dimensional system with periodicity in two directions. This approach corresponds to the method for systems under periodic boundary conditions in three dimensions,[3] and we analyze singular parts of the energy expression using the convergent factor for a conditionally convergent sum. The obtained results are compared with the energy functions achieved from the other methods, particularly, the extension of the Berthaut method[7,8] and the RHHR method.[10] Therefore the first part of the work constitutes a test of the approach based on the Poisson summation formula for a geometry appropriate for simulation of surfaces and interfaces containing charged particles. Then, considering the same geometry of a system of particles with point-dipole moments we apply the method to find an expression for the dipole-dipole interaction energy.

II. COULOMB INTERACTION

We consider a simulation box in a shape of prism, with a square base $L\times L$ and any height, which contains N charges. The box repeated in the (x,y) plane gives a two-dimensional tetragonal lattice, and in the box centered at $\mathbf{n}=(\mathbf{n}_\varrho,0)$, $\mathbf{n}_\varrho=L(n_x,n_y)$ where n_x and n_y are integers, a charge q_i is located at $\mathbf{r}_i+\mathbf{n}$. The total interaction energy of the basic simulation box has the following form:

$$E_{cc}=\frac{1}{2}\sum_{i,j=1}^{N}{\sum_{\mathbf{n}}}'\frac{q_iq_j}{|\mathbf{r}_{ij}+\mathbf{n}|}. \tag{1}$$

In the above expression $\mathbf{r}_{ij}=\mathbf{r}_i-\mathbf{r}_j$, and the sum over $\mathbf{n}$ is a sum over all tetragonal lattice cells where the prime indicates that for $\mathbf{n}=\mathbf{0}$ the terms with $i=j$ are to be omitted. Taking into account geometry of the system the relative charge position $\mathbf{r}_{ij}$ is expressed by $\mathbf{r}_{ij}=(\varrho_{ij},z_{ij})$. Defining the function $\Phi(\mathbf{r})$ and the factor Φ_0 as

$$\Phi(\mathbf{r})=\sum_{\mathbf{n}}\frac{1}{|\mathbf{r}+\mathbf{n}|},\quad \text{for } \mathbf{r}\neq\mathbf{0},\quad \text{and } \Phi_0=\sum_{\mathbf{n}\neq\mathbf{0}}\frac{1}{|\mathbf{n}|}, \tag{2}$$

the total energy can be expressed by

$$E_{cc}=\frac{1}{2}\sum_{i=1}^{N}\sum_{\substack{j=1\\ j\neq i}}^{N} q_i q_j \Phi(\mathbf{r}_{ij})+\frac{1}{2}\sum_{i=1}^{N} q_i^2 \Phi_0, \tag{3}$$

where the first term represents the interaction of a charge with other charges from the basic simulation box and their images whereas the second term describes interaction of the charge with its own images. To calculate the lattice sums (2) we use the identity basing on the integral representation of the gamma function[14]

$$\frac{1}{x^{2s}}=\frac{1}{\Gamma(s)}\int_0^\infty t^{s-1}e^{-x^2 t}dt \tag{4}$$

for $s=1/2$, and the Poisson summation formula[13] for the two-dimensional space (x,y):

$$\sum_{\mathbf{n}_\varrho} e^{-|\varrho+\mathbf{n}_\varrho|^2 t}=\frac{\pi}{L^2 t}\sum_{\mathbf{G}} e^{i\mathbf{G}\cdot\varrho}\exp\left(-\frac{G^2}{4t}\right). \tag{5}$$

In the above equation $\mathbf{G}$ is a two-dimensional vector in reciprocal lattice and $G=|\mathbf{G}|$; $\mathbf{G}=2\pi(k_x,k_y)/L$ where k_x and k_y are integers.

Using Eq. (4) the function $\Phi(\mathbf{r})$ may be expressed by

$$\Phi(\mathbf{r})=\sum_{\mathbf{n}}\frac{1}{\sqrt{\pi}}\int_{\alpha^2}^\infty t^{-1/2}e^{-|\mathbf{r}+\mathbf{n}|^2 t}dt + \sum_{\mathbf{n}_\varrho}\frac{1}{\sqrt{\pi}}\int_0^{\alpha^2} t^{-1/2}e^{-|\varrho+\mathbf{n}_\varrho|^2 t-z^2 t}dt, \tag{6}$$

where the integral is split into two parts to eliminate singularity which is expected in $\Phi(\mathbf{r})$, and the parameter $\alpha^2(\alpha>0)$ is chosen for computational convenience. Direct calculation of the integral in the first term and application of the Poisson summation formula (5) to the second term of expression (6) gives

$$\Phi(\mathbf{r})=\sum_{\mathbf{n}}\frac{\mathrm{erfc}(\alpha|\mathbf{r}+\mathbf{n}|)}{|\mathbf{r}+\mathbf{n}|}+\frac{2\sqrt{\pi}}{L^2}\sum_{\mathbf{G}\neq\mathbf{0}} e^{i\mathbf{G}\cdot\varrho}\times\int_{1/\alpha}^\infty\exp\left(-\frac{G^2u^2}{4}-\frac{z^2}{u^2}\right)du + \frac{\sqrt{\pi}}{L^2}\int_0^{\alpha^2} t^{-3/2}e^{-z^2 t}dt, \tag{7}$$

where the term for $\mathbf{G}=\mathbf{0}$ in the sum is evaluated separately and the second term is achieved using the substitution $u^2=1/t$. The two integrals appearing in Eq. (7) are known[15] and one obtains the following form of $\Phi(\mathbf{r})$:

$$\Phi(\mathbf{r})=\sum_{\mathbf{n}}\frac{\mathrm{erfc}(\alpha|\mathbf{r}+\mathbf{n}|)}{|\mathbf{r}+\mathbf{n}|}+\frac{\pi}{L^2}\times\sum_{\mathbf{G}\neq\mathbf{0}}\frac{e^{i\mathbf{G}\cdot\varrho}}{G}\left[e^{Gz}\,\mathrm{erfc}\left(\frac{G}{2\alpha}+\alpha z\right)+e^{-Gz}\mathrm{erfc}\left(\frac{G}{2\alpha}-\alpha z\right)\right] - \frac{2\sqrt{\pi}}{L^2}\left[\frac{1}{\alpha}e^{-\alpha^2 z^2}+\sqrt{\pi}z\,\mathrm{erf}(\alpha z)\right]+\frac{2\sqrt{\pi}}{L^2}\lim_{t\to 0^+}\frac{e^{-z^2 t}}{\sqrt{t}}, \tag{8}$$

where the singularity arises from the second integral of expression (7).

The same procedure applied to the evaluation of the factor Φ_0 yields

$$\Phi_0=\sum_{\mathbf{n}\neq\mathbf{0}}\frac{1}{\sqrt{\pi}}\int_{\alpha^2}^\infty t^{-1/2}e^{-|\mathbf{n}|^2 t}dt + \sum_{\mathbf{n}_\varrho}\frac{1}{\sqrt{\pi}}\int_0^{\alpha^2} t^{-1/2}e^{-|\mathbf{n}_\varrho|^2 t}dt-\frac{1}{\sqrt{\pi}}\int_0^{\alpha^2} t^{-1/2}dt \tag{9a}$$

$$=\sum_{\mathbf{n}\neq\mathbf{0}}\frac{\mathrm{erfc}(\alpha|\mathbf{n}|)}{|\mathbf{n}|}+\frac{\sqrt{\pi}}{L^2}\sum_{\mathbf{G}\neq\mathbf{0}}\int_0^{\alpha^2} t^{-3/2}\exp\left(-\frac{G^2}{4t}\right)dt + \frac{\sqrt{\pi}}{L^2}\int_0^{\alpha^2} t^{-3/2}dt-\frac{2\alpha}{\sqrt{\pi}} \tag{9b}$$

$$=\sum_{\mathbf{n}\neq\mathbf{0}}\frac{\mathrm{erfc}(\alpha|\mathbf{n}|)}{|\mathbf{n}|}+\frac{\pi}{L^2}\sum_{\mathbf{G}\neq\mathbf{0}}\frac{1}{G}\,\mathrm{erfc}\left(\frac{G}{2\alpha}\right) - \frac{2\sqrt{\pi}}{\alpha L^2}+\frac{2\sqrt{\pi}}{L^2}\lim_{t\to 0^+}\frac{1}{\sqrt{t}}-\frac{2\alpha}{\sqrt{\pi}}. \tag{9c}$$

To apply the Poisson summation formula in Eq. (9a) the $\mathbf{n}_\varrho=\mathbf{0}$ term is added to the lattice sum with the integral on $[0,\alpha^2]$ and then subtracted separately.

Inserting expressions (8) and (9c) into Eq. (3), after simple calculations, one obtains the final form of the total interaction energy

$$E_{cc}=\frac{1}{2}\sum_{i,j=1}^{N} q_i q_j {\sum_{\mathbf{n}_\varrho}}' \frac{\mathrm{erfc}[\alpha|(\varrho_{ij}+\mathbf{n}_\varrho,z_{ij})|]}{|(\varrho_{ij}+\mathbf{n}_\varrho,z_{ij})|}+\frac{\pi}{2L^2}\sum_{i,j=1}^{N} q_i q_j \sum_{\mathbf{G}\neq\mathbf{0}}\frac{e^{i\mathbf{G}\cdot\varrho_{ij}}}{G}\left[e^{Gz_{ij}}\,\mathrm{erfc}\left(\frac{G}{2\alpha}+\alpha z_{ij}\right) + e^{-Gz_{ij}}\,\mathrm{erfc}\left(\frac{G}{2\alpha}-\alpha z_{ij}\right)\right]-\frac{\sqrt{\pi}}{L^2}\sum_{i,j=1}^{N} q_i q_j\left[\frac{1}{\alpha}e^{-\alpha^2 z_{ij}^2}+\sqrt{\pi}z_{ij}\,\mathrm{erf}(\alpha z_{ij})\right]-\frac{\alpha}{\sqrt{\pi}}\sum_{i=1}^{N} q_i^2. \tag{10}$$

In the calculations we use charge neutrality of the system, which allows us to eliminate the singularities occurring in expressions (8) and (9). These singular terms give the following contribution to the total energy:

$$\sum_{i,j=1}^{N} q_i q_j \lim_{t\to 0^+} \frac{e^{-z_{ij}^2 t}}{\sqrt{t}} = \sum_{i,j=1}^{N} q_i q_j \lim_{t\to 0^+} \sum_{k=0}^{\infty} \frac{(-z_{ij}^2)^k t^{k-1/2}}{k!}$$
$$= \left(\sum_{i=1}^{N} q_i \right)^2 \lim_{t\to 0^+} \frac{1}{\sqrt{t}}, \tag{11}$$

and it is zero because it contains the factor $(\Sigma_{i=1}^{N} q_i)^2 = 0$.

To analyze the singularities appearing previously we use the approach proposed by de Leeuw, Perram, and Smith[3] introducing the convergence factor $\exp(-s|\mathbf{n}|^2)$ in the lattice sums $\Phi(\mathbf{r})$ and Φ_0

$$\Phi(\mathbf{r}) = \sum_{\mathbf{n}} \frac{e^{-s|\mathbf{n}|^2}}{|\mathbf{r}+\mathbf{n}|}, \text{ for } \mathbf{r}\neq\mathbf{0}, \text{ and } \Phi_0 = \sum_{\mathbf{n}\neq\mathbf{0}} \frac{e^{-s|\mathbf{n}|^2}}{|\mathbf{n}|}. \tag{12}$$

The parameter s is positive and after calculations we take the limit as $s\to 0$. We concentrate on the singular parts introduced by the $\mathbf{G}=\mathbf{0}$ terms which correspond to the last integral in Eq. (7) and the third term in Eq. (9b). For the lattice sum $\Phi(\mathbf{r})$ defined by Eq. (12) the interesting part has the following form:

$$\frac{\sqrt{\pi}}{L^2} \int_0^{\alpha^2} \frac{dt}{\sqrt{t(t+s)}} \exp\left(-\frac{st|\varrho|^2}{t+s} - z^2 t \right)$$
$$= -\frac{\sqrt{\pi}}{L^2\sqrt{s}} e^{s(z^2-|\varrho|^2)} \times \int_1^{s/(\alpha^2+s)} \frac{du}{\sqrt{(1-u)u}} \exp\left(s\left|\varrho\right|^2 u - \frac{sz^2}{u} \right) \tag{13a}$$

$$= -\frac{\sqrt{\pi}}{L^2} e^{s(z^2-|\varrho|^2)} \left\{ \frac{1}{\sqrt{s}} \left[\arcsin\left(\frac{s-\alpha^2}{s+\alpha^2} \right) - \frac{\pi}{2} \right] - \sum_{m=1}^{\infty} (-1)^m \frac{2\alpha^{2m-1} z^{2m}}{(2m-1)m!} + O(s^{1/2}) \right\} \tag{13b}$$

$$= \frac{\sqrt{\pi}}{L^2} e^{s(z^2-|\varrho|^2)} \left[\frac{\pi}{\sqrt{s}} - \frac{2}{\alpha} + \sum_{m=1}^{\infty} (-1)^m \times \frac{2\alpha^{2m-1} z^{2m}}{(2m-1)m!} + O(s^{1/2}) \right] \tag{13c}$$

$$= \frac{\sqrt{\pi}}{L^2} e^{s(z^2-|\varrho|^2)} \left[\frac{\pi}{\sqrt{s}} - \frac{2}{\alpha} e^{-\alpha^2 z^2} - 2\sqrt{\pi} z \,\mathrm{erf}(\alpha z) + O(s^{1/2}) \right]. \tag{13d}$$

Equation (13a) is obtained by using the substitution $u = s/(t+s)$. In the right integral of Eq. (13a) the exponential function only is dependent on the parameter s, and expanding this function in a power series in s and integrating term by term one obtains Eq. (13b). We are interested in very small values of the parameter s, and hence representing the arcsine function by the Maclaurin series with respect to s the expression (13c) is achieved. The final form (13d) may be obtained using the Maclaurin series for the exponential function and error function.[14] Similar procedure applied to the singular part of the lattice sum Φ_0 gives

$$\frac{\sqrt{\pi}}{L^2} \int_0^{\alpha^2} \frac{dt}{\sqrt{t(t+s)}} = -\frac{\sqrt{\pi}}{L^2\sqrt{s}} \int_1^{s/(\alpha^2+s)} \frac{du}{\sqrt{(1-u)u}}$$
$$= -\frac{\sqrt{\pi}}{L^2\sqrt{s}} \left[\arcsin\left(\frac{s-\alpha^2}{s+\alpha^2} \right) - \frac{\pi}{2} \right]$$
$$= \frac{\sqrt{\pi}}{L^2} \left[\frac{\pi}{\sqrt{s}} - \frac{2}{\alpha} + O(s^{1/2}) \right]. \tag{14}$$

Combining Eqs. (13d) and (14) one obtains the following contribution to the total energy:

$$-\frac{\sqrt{\pi}}{L^2} \sum_{i,j=1}^{N} q_i q_j e^{s(z_{ij}^2 - |\varrho_{ij}|^2)} \left[\frac{1}{\alpha} e^{-\alpha^2 z_{ij}^2} + \sqrt{\pi} z_{ij} \mathrm{erf}(\alpha z_{ij}) \right] + \frac{\sqrt{\pi}}{2L^2} \left[\frac{\pi}{\sqrt{s}} + O(s^{1/2}) \right] \left(\sum_{i=1}^{N} q_i \right)^2. \tag{15}$$

Because of charge neutrality the second term vanishes and taking the limit as $s\to 0$ the expression (15) tends to the third term of Eq. (10). The above calculations indicate that the convergence factor $\exp(-s|\mathbf{n}|^2)$ for conditionally convergent sums does not introduce any additional term to the total-energy function described by Eq. (10).

Heyes and co-workers[7,8] using the Berthaut method[12] derived expression for the Coulomb potential of infinite lamina point-charge lattice. They considered different spherically symmetric charge spreading functions. Among others they used Gaussian function where the charge density at a distance u from the lattice site j was given by $q_j \alpha^3 \exp(-u^2 a^2)/\pi^{3/2}$, and application of the function leads to the energy expression[7,8] identical to that given by Eq. (10).

One must note that the approach proposed by Smith[9] used the integral representation (4) and the identity (26) in Ref. 9, which corresponds to the Poisson summation formula (5). Therefore the Smith's method is similar to that presented here and the first two terms of Eq. (68) in Ref. 9 are identical to the first, second, and fourth terms of Eq. (10) when $\alpha = \eta/L$ and $\mathbf{G} = 2\pi\boldsymbol{\mu}/L$. The third term of Eq. (68) in Ref. 9 represents contributions to the energy expression for $\mathbf{G}=\mathbf{0}$. In the Smith's method the $\mathbf{G}=\mathbf{0}$ term was calculated in different manner and it is defined by the function $\Psi_3(\mathbf{r})$ [Eq. (63) in Ref. 9]. It is easy to see that the first term in the function $\Psi_3(\mathbf{r})$, for a net charge of a simulation cell assumed in the method, diverges as the thermodynamic limit $K\to\infty$ is taken, and it corresponds to the singular parts of Eqs. (8) and (9c) that are removed due to the charge neutrality condition. The remaining terms in the function $\Psi_3(\mathbf{r})$ should give the third term of Eq. (10), but because of approximations made in the Smith's calculations we fail to prove exact equality of these terms.

Rhee *et al.*[10] proposed a different method for the treatment of the long-range Coulomb interactions when the system is finite in one of three dimensions. The method, starting from the charge density and solution of the Poisson equation,

introduces a function $f(\alpha,G,z)$ which allows us to separate the electrostatic energy into a sum on lattice vectors $\mathbf{n}_\varrho$ and a sum on reciprocal-lattice vectors $\mathbf{G}$. The separation function must hold $f(\alpha,0,z)=1$, where the parameter α determines how fast the function approaches zero for large G. For the symbols introduced previously the total energy[10] has the following form:

$$E_{cc}=\frac{1}{2}\sum_{i,j=1}^{N} q_i q_j {\sum_{\mathbf{n}_\varrho}}' F(\alpha,z_{ij},\varrho_{ij}+\mathbf{n}_\varrho)+\frac{\pi}{L^2}\sum_{i,j=1}^{N} q_i q_j \sum_{\mathbf{G}\neq\mathbf{0}} \frac{e^{-G|z_{ij}|}}{G} f(\alpha,G,z_{ij}) e^{-i\mathbf{G}\cdot\varrho_{ij}} - \frac{\pi}{L^2} \times \sum_{i,j=1}^{N} q_i q_j \left[|z_{ij}| - \left.\frac{\partial f(\alpha,G,z_{ij})}{\partial G}\right|_{G=0}\right] - \frac{1}{2}\sum_{i=1}^{N} q_i^2 \int_0^\infty f(\alpha,G,0)\,dG, \tag{16}$$

where we use the explicit expressions for $c_1(\alpha,\{z_{ij}\})$ and $c_2(\alpha)$ derived in Appendix A of Ref. 10. The functions $F(\alpha,z,\varrho)$ and $f(\alpha,G,z)$ are related through two-dimensional Fourier transform as follows [Eq. (A1) in Ref. 10]:

$$\frac{1}{2\pi}\int_{\Omega(\varrho)} F(\alpha,z,\varrho) e^{-i\mathbf{G}\cdot\varrho} d^2\varrho = \frac{e^{-G|z|}}{G}[1-f(\alpha,G,z)], \tag{17}$$

where $\Omega(\varrho)$ denotes an whole infinite two-dimensional real space.

It is easy to see that expression (16) has the same structure as Eq. (10). We must note that the functions appearing in the second and third sums of Eq. (10) are even functions with respect to z_{ij} and Eq. (10) may be rewritten replacing z_{ij} by $|z_{ij}|$. Therefore comparing Eqs. (16) and (10) one has two identities:

$$f(\alpha,G,z)=\frac{1}{2}\left[e^{2G|z|}\,\mathrm{erfc}\left(\frac{G}{2\alpha}+\alpha|z|\right)+\mathrm{erfc}\left(\frac{G}{2\alpha}-\alpha|z|\right)\right], \tag{18a}$$

$$F(\alpha,z,\varrho)=\frac{\mathrm{erfc}(\alpha|(\varrho,z)|)}{|(\varrho,z)|}, \tag{18b}$$

where the function (18a) equals one for $G=0$. First of all one must check that the functions f and F are related through Eq. (17). The Fourier transform of the function $F(\alpha,z,\varrho)$ may be expressed as follows:

$$\frac{1}{2\pi}\int_{\Omega(\varrho)} F(\alpha,z,\varrho) e^{-i\mathbf{G}\cdot\varrho} d^2\varrho$$

$$= \frac{1}{\sqrt{\pi}}\int_{\alpha^2}^\infty dt\, e^{-z^2 t} t^{-\frac{1}{2}} \int_0^\infty d\varrho\,\varrho\, e^{-t\varrho^2} J_0(G\varrho) \tag{19a}$$

$$= \frac{1}{G}\int_0^{G/2\alpha} u \exp\left(-\frac{u^2}{2}-\frac{G^2z^2}{4u^2}\right)\left[I_{-\frac{1}{2}}\left(\frac{u^2}{2}\right)-I_{\frac{1}{2}}^{1}\left(\frac{u^2}{2}\right)\right] du \tag{19b}$$

$$= \frac{e^{-G|z|}}{2G}\left[2-e^{2G|z|}\,\mathrm{erfc}\left(\frac{G}{2\alpha}+\alpha|z|\right)-\mathrm{erfc}\left(\frac{G}{2\alpha}-\alpha|z|\right)\right]. \tag{19c}$$

In the calculations we introduce the polar coordinate system (ϱ,φ), where φ is an angle between the vector ϱ and a space fixed vector $\mathbf{G}$, and integration with respect to φ on the interval $[0,2\pi]$ gives the Bessel function of the first kind J_0. The integral representation[14] of the right side of Eq. (18b) and the change of the integral order give Eq. (19a). The integral with respect to ϱ may be performed[14] to give Eq. (19b) where the substitution $u^2=G^2/4t$ is used. $I_{1/2}$ and $I_{-1/2}$ are the hyperbolic Bessel functions which can be expressed by the hyperbolic sine and cosine functions,[14] respectively, and one has the known integral[15] which gives Eq. (19c). Finally, using the explicit form of the function $f(\alpha,G,z)$ one obtains the right side of Eq. (17). Moreover, it is easy to prove that using Eq. (18a) in the two last sums of Eq. (16) gives the corresponding sums in Eq. (10).

III. DIPOLE-DIPOLE INTERACTION

For N dipoles located in the rectangular simulation box and periodic boundary conditions applied to the box in the plane (x,y) the total interaction energy of the basic simulation box has the following form:

$$E_{dd}=\frac{1}{2}\sum_{i,j=1}^{N}{\sum_{\mathbf{n}}}' \left\{ \frac{\boldsymbol{\mu}_i\cdot\boldsymbol{\mu}_j}{|\mathbf{r}_{ij}+\mathbf{n}|^3} - 3\frac{[\boldsymbol{\mu}_i\cdot(\mathbf{r}_{ij}+\mathbf{n})][\boldsymbol{\mu}_j\cdot(\mathbf{r}_{ij}+\mathbf{n})]}{|\mathbf{r}_{ij}+\mathbf{n}|^5}\right\} \tag{20}$$

where the symbols have the same meaning as in Sec. II, and $\boldsymbol{\mu}_i$ denotes a dipole moment which is located at $\mathbf{r}_i+\mathbf{n}$ in the box centered at $\mathbf{n}$. Introducing the lattice sums $\Psi(\mathbf{r})$, Ψ_0, $\Theta(\mathbf{r},\boldsymbol{\xi})$, and $\Theta_0(\boldsymbol{\xi})$ and defining

$$\Psi(\mathbf{r})=\sum_{\mathbf{n}}\frac{1}{|\mathbf{r}+\mathbf{n}|^3},\quad \text{for } \mathbf{r}\neq\mathbf{0},\quad \text{and } \Psi_0=\sum_{\mathbf{n}\neq\mathbf{0}}\frac{1}{|\mathbf{n}|^3}, \tag{21a}$$

$$\Theta(\mathbf{r},\boldsymbol{\xi})=\sum_{\mathbf{n}}\frac{e^{-i\boldsymbol{\xi}\cdot(\mathbf{r}+\mathbf{n})}}{|\mathbf{r}+\mathbf{n}|^5},\quad \text{for } \mathbf{r}\neq\mathbf{0},$$

$$\text{and } \Theta_0(\boldsymbol{\xi})=\sum_{\mathbf{n}\neq\mathbf{0}}\frac{e^{-i\boldsymbol{\xi}\cdot\mathbf{n}}}{|\mathbf{n}|^5}, \tag{21b}$$

the total energy (20) can be expressed by

$$E_{dd}=\frac{1}{2}\sum_{i=1}^{N}\sum_{\substack{j=1\\ j\neq i}}^{N}\boldsymbol{\mu}_i\boldsymbol{\mu}_j\Psi(\mathbf{r}_{ij})+\frac{1}{2}\sum_{i=1}^{N}|\boldsymbol{\mu}_i|^2\Psi_0 + \frac{3}{2}\sum_{i=1}^{N}\sum_{\substack{j=1\\ j\neq i}}^{N}(\boldsymbol{\mu}_i\cdot\boldsymbol{\nabla}_{\boldsymbol{\xi}})(\boldsymbol{\mu}_j\cdot\boldsymbol{\nabla}_{\boldsymbol{\xi}})\Theta(\mathbf{r}_{ij},\boldsymbol{\xi})\Big|_{\boldsymbol{\xi}=\mathbf{0}} + \frac{3}{2}\sum_{i=1}^{N}(\boldsymbol{\mu}_i\cdot\boldsymbol{\nabla}_{\boldsymbol{\xi}})(\boldsymbol{\mu}_i\cdot\boldsymbol{\nabla}_{\boldsymbol{\xi}})\Theta_0(\boldsymbol{\xi})\Big|_{\boldsymbol{\xi}=\mathbf{0}}. \tag{22}$$

In the above equation the first and third terms describe interaction of a dipole moment with other dipole moments from the simulation box and their images whereas the second and fourth terms represent interaction of the dipole moment with its own images. Similarly as in the previous section each vector is represented by its components parallel and perpendicular to the plane (x,y) and $\boldsymbol{\xi}=(\boldsymbol{\xi}_\varrho,\xi_z)$.

We calculate the sums (21a) in exactly the same way as for the Coulomb interaction lattice sums, and the identity (4) for $s=3/2$ and the Poisson summation formula (5) lead to

$$\Psi(\mathbf{r})=\frac{2}{\sqrt{\pi}}\sum_{\mathbf{n}}\int_{\alpha^2}^{\infty}t^{1/2}e^{-|\mathbf{r}+\mathbf{n}|^2t}dt + \frac{2\sqrt{\pi}}{L^2}\sum_{\mathbf{G}}e^{i\mathbf{G}\cdot\varrho}\int_0^{\alpha^2}t^{-1/2}\exp\left(-z^2t-\frac{G^2}{4t}\right)dt, \tag{23a}$$

$$\Psi_0=\frac{2}{\sqrt{\pi}}\sum_{\mathbf{n}\neq\mathbf{0}}\int_{\alpha^2}^{\infty}t^{1/2}e^{-|\mathbf{n}|^2t}dt + \frac{2\sqrt{\pi}}{L^2}\sum_{\mathbf{G}}\int_0^{\alpha^2}t^{-1/2}\exp\left(-\frac{G^2}{4t}\right)dt-\frac{4\alpha^3}{3\sqrt{\pi}}. \tag{23b}$$

In the case of the sums (21b) we use the identity (4) for $s=5/2$ and the Poisson summation formula[13] in the following form:

$$\sum_{\mathbf{n}_\varrho}e^{-[t|\varrho+\mathbf{n}_\varrho|^2+i\boldsymbol{\xi}_\varrho\cdot(\varrho+\mathbf{n}_\varrho)]}=\frac{\pi}{L^2t}\sum_{\mathbf{G}}e^{i\mathbf{G}\cdot\varrho}\times\exp\left(-\frac{|\mathbf{G}+\boldsymbol{\xi}_\varrho|^2}{4t}\right), \tag{24}$$

and the sums are given as follows:

$$\Theta(\mathbf{r},\boldsymbol{\xi})=\frac{4}{3\sqrt{\pi}}\sum_{\mathbf{n}}e^{-i\boldsymbol{\xi}\cdot(\mathbf{r}+\mathbf{n})}\int_{\alpha^2}^{\infty}t^{3/2}e^{-|\mathbf{r}+\mathbf{n}|^2t}dt + \frac{4\sqrt{\pi}}{3L^2}\sum_{\mathbf{G}}e^{i\mathbf{G}\cdot\varrho-i\xi_zz}\times\int_0^{\alpha^2}t^{-1/2}\exp\left(-z^2t-\frac{|\mathbf{G}+\boldsymbol{\xi}_\varrho|^2}{4t}\right)dt, \tag{25a}$$

$$\Theta_0(\boldsymbol{\xi})=\frac{4}{3\sqrt{\pi}}\sum_{\mathbf{n}\neq\mathbf{0}}e^{-i\boldsymbol{\xi}\cdot\mathbf{n}}\int_{\alpha^2}^{\infty}t^{3/2}e^{-|\mathbf{n}|^2t}dt + \frac{4\sqrt{\pi}}{3L^2}\sum_{\mathbf{G}}\int_0^{\alpha^2}t^{-1/2}\exp\left(-\frac{|\mathbf{G}+\boldsymbol{\xi}_\varrho|^2}{4t}\right)dt-\frac{4\alpha^5}{3\sqrt{\pi}}. \tag{25b}$$

Inserting the identities (23) and (25) into Eq. (22) and performing required calculations the total energy of the dipole-dipole interaction is given by

$$E_{dd}=\frac{1}{\sqrt{\pi}}\sum_{i,j=1}^{N}{\sum_{\mathbf{n}}}'\left\{(\boldsymbol{\mu}_i\cdot\boldsymbol{\mu}_j)\int_{\alpha^2}^{\infty}t^{1/2}e^{-|\mathbf{r}_{ij}+\mathbf{n}|^2t}dt-2[\boldsymbol{\mu}_i\cdot(\mathbf{r}_{ij}+\mathbf{n})][\boldsymbol{\mu}_j\cdot(\mathbf{r}_{ij}+\mathbf{n})]\int_{\alpha^2}^{\infty}t^{3/2}e^{-|\mathbf{r}_{ij}+\mathbf{n}|^2t}dt\right\}$$

$$+\frac{\sqrt{\pi}}{L^2}\sum_{i,j=1}^{N}\sum_{\mathbf{G}}e^{i\mathbf{G}\cdot\varrho_{ij}}(\mu_i^z\mu_j^z)\left\{\int_0^{\alpha^2}t^{-1/2}\exp\left(-z_{ij}^2t-\frac{G^2}{4t}\right)dt-2z_{ij}^2\int_0^{\alpha^2}t^{1/2}\exp\left(-z_{ij}^2t-\frac{G^2}{4t}\right)dt\right\}$$

$$+i\frac{\sqrt{\pi}}{L^2}\sum_{\substack{i,j=1\\ i\neq j}}^{N}\sum_{\mathbf{G}\neq\mathbf{0}}e^{i\mathbf{G}\cdot\varrho_{ij}}[\mu_i^z(\boldsymbol{\mu}_j^\varrho\cdot\mathbf{G})+(\boldsymbol{\mu}_i^\varrho\cdot\mathbf{G})\mu_j^z]z_{ij}\int_0^{\alpha^2}t^{-1/2}\exp\left(-z_{ij}^2t-\frac{G^2}{4t}\right)dt+\frac{\sqrt{\pi}}{2L^2}\sum_{i,j=1}^{N}\sum_{\mathbf{G}\neq\mathbf{0}}e^{i\mathbf{G}\cdot\varrho_{ij}}(\boldsymbol{\mu}_j^\varrho\cdot\mathbf{G})$$

$$\times(\boldsymbol{\mu}_i^\varrho\cdot\mathbf{G})\int_0^{\alpha^2}t^{-3/2}\exp\left(-z_{ij}^2t-\frac{G^2}{4t}\right)dt-\frac{2\alpha^3}{3\sqrt{\pi}}\sum_{i=1}^{N}|\boldsymbol{\mu}_i|^2, \tag{26}$$

where the components of the dipole moment parallel and perpendicular to the plane (x,y) are denoted by $\boldsymbol{\mu}^\varrho$ and μ^z, respectively. The integrals in Eq. (26) may be performed[14,15] to give the final expression of the dipole-dipole interaction energy:

$$E_{dd}=\frac{1}{2}\sum_{i,j=1}^{N}{\sum_{\mathbf{n}_\varrho}}'\{(\boldsymbol{\mu}_i\cdot\boldsymbol{\mu}_j)B[\alpha,|(\varrho_{ij}+\mathbf{n}_\varrho,z_{ij})|]-[\boldsymbol{\mu}_i\cdot(\varrho_{ij}+\mathbf{n}_\varrho,z_{ij})][\boldsymbol{\mu}_j\cdot(\varrho_{ij}+\mathbf{n}_\varrho,z_{ij})]C[\alpha,|(\varrho_{ij}+\mathbf{n}_\varrho,z_{ij})|]\}$$
$$+\frac{\pi}{2L^2}\sum_{i,j=1}^{N}\sum_{\mathbf{G}}(\mu_i^z\mu_j^z)\cos(\mathbf{G}\cdot\varrho_{ij})\{E(\alpha,G,z_{ij})-G[D(\alpha,G,z_{ij})+D(\alpha,G,-z_{ij})]\}+\frac{\pi}{2L^2}\sum_{i,j=1}^{N}\sum_{\mathbf{G}\neq\mathbf{0}}[\mu_i^z(\boldsymbol{\mu}_j^\varrho\cdot\mathbf{G})$$
$$+(\boldsymbol{\mu}_i^\varrho\cdot\mathbf{G})\mu_j^z]\sin(\mathbf{G}\cdot\varrho_{ij})[D(\alpha,G,z_{ij})-D(\alpha,G,-z_{ij})]+\frac{\pi}{2L^2}\sum_{i,j=1}^{N}\sum_{\mathbf{G}\neq\mathbf{0}}(\boldsymbol{\mu}_i^\varrho\cdot\mathbf{G})(\boldsymbol{\mu}_j^\varrho\cdot\mathbf{G})\frac{\cos(\mathbf{G}\cdot\varrho_{ij})}{G}[D(\alpha,G,z_{ij})$$
$$+D(\alpha,G,-z_{ij})]-\frac{2\alpha^3}{3\sqrt{\pi}}\sum_{i=1}^{N}|\boldsymbol{\mu}_i|^2 \tag{27}$$

with

$$B(\alpha,r)=\mathrm{erfc}(\alpha r)/r^3+(2\alpha/\sqrt{\pi})\exp(-\alpha^2r^2)/r^2,$$

$$C(\alpha,r)=3\,\mathrm{erfc}(\alpha r)/r^5+(2\alpha/\sqrt{\pi})(2\alpha^2+3/r^2)\times\exp(-\alpha^2r^2)/r^2,$$

$$D(\alpha,G,z)=\exp(Gz)\mathrm{erfc}(G/2\alpha+\alpha z),$$

$$E(\alpha,G,z)=(4\alpha/\sqrt{\pi})\exp(-G^2/4\alpha^2-\alpha^2z^2).$$

In practice, taking into account the fact that for typical values of the parameter $\alpha\cong 5/L$ the functions $B(\alpha,r)$ and $C(\alpha,r)$ decay quickly to zero with increasing r, the real-space sum is truncated by omitting contributions from pairs for which $r_{ij}>L/2$. In other words, the real-space sum is restricted to the basic simulation box, i.e., $\mathbf{n}_\varrho=(0,0)$ and the normal minimum image convention is applied, and it is calculated in the same way as in a case of a system with periodicity in three dimensions.[4,5] Moreover, it is easy to prove that apart from the last sum the expression (27) can be obtained from Eq. (10) replacing q_iq_j by $-(\boldsymbol{\mu}_i\cdot\boldsymbol{\nabla}_{\mathbf{r}_i})(\boldsymbol{\mu}_j\cdot\boldsymbol{\nabla}_{\mathbf{r}_j})$.

IV. CONCLUSIONS

Using the Poisson summation formula we redevelop an Ewald method for the Coulomb interactions in systems with periodicity in two directions and finite extent in the third direction. We show that the convergence factor, proposed by de Leeuw, Perram, and Smith,[3] introduced in the two-dimensional lattice sums allows to eliminate the singular part in elegant way but does not give any additional term, particularly a term proportional to the square of the net dipole moment of the configuration which was achieved for a three-dimensional system.[3]

The method based on the Poisson summation formula gives the same expression for the electrostatic energy as the Berthaut method with the Gaussian charge spreading function.[7,8] We prove also that the RHHR method[10] for the separation function defined by Eq. (18a) gives the energy function identical to that obtained from the method based on the Poisson summation formula and/or the Berthaut method. In that sense the three methods are equivalent. The Berthaut method allows us to modify the charge spreading function in the real space whereas the RHHR method gives possibility to change the separation function, which depend on the vector $\mathbf{G}$ in the two-dimensional reciprocal space and may depend on the variable z in the real space. Our results indicate that for a given charge spreading function one may find corresponding separation function in the RHHR method, e.g., for the Gaussian spreading function applied to charges the separation function is given by Eq. (18a). Of course, a given separation function is associated with a certain charge spreading function, however, the calculation may be hard or even impossible.

From the physical point of view the Berthaut approach is the most instructive method; the energy function is derived from first principles and the method illustrates the physical ideas. However, the method may be hardly applied to interactions of higher electrostatic multipoles and in those cases the Poisson summation formula should be a helpful tool, which we show for the dipole-dipole interactions.

At the end we would like to comment shortly numerical implications of the obtained results. Because of the double sum over all distinct pairs of particles in the reciprocal space, appearing in Eqs. (10) and (27), the direct use of the two-dimensional Ewald summation formula is computationally expensive. To improve efficiency of the summation of the Coulomb interactions two modifications were proposed. Spohr[16] suggested the use of a precalculated table of potential energy, forces, etc., and the calculations may be performed by interpolation of the table. The other approach[7,17] makes possible to neglect the reciprocal sum with $\mathbf{G}\neq\mathbf{0}$ by diminishing the parameter α value and including the contribution from the first layer of image cells in the real space summation. A significant reduction of the computing time is given by the calculations with a precalculated table, however, the calculations are still slower than those using the conventional three-dimensional Ewald summation (compare data in Ref. 18).

We should point out that the regular three-dimensional Ewald technique was applied also in case of systems periodic in two directions including an empty space into the basic simulation box to avoid an artificial influence from the periodic images in the third direction (see Refs. 16, 18, and references cited therein). Recently, Yeh and Berkowitz[18] showed that even large height of the simulation box, i.e., large size of the empty space, does not eliminate the coupling between the periodic replicas of the interface, and simulations of interfacial systems using that method can lead

to erroneous results. Therefore they included the shape-dependent correction term, suitable for the slab geometry, proposed by Smith.[19] The modified approach,[18] i.e., the three-dimensional Ewald method with a correction term, is computationally efficient and accurate, however, to get good numerical results, the simulation box must also contain an empty space.

Finally, we must stress that the two-dimensional Ewald summations given by Eqs. (10) and (27) as well as the RHHR approach[10] treat correctly long-range interactions in system of finite thickness. Therefore, although the calculations are rather slow, the results of simulation using the method proposed here may be used to test other techniques, as it was done in Refs. 16 and 18.

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