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Ewald summation of electrostatic interactions of systems with finite extent in two of three dimensions

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Abstract. The energy of long-range Coulomb and dipole–dipole interactions in three-dimensional systems with periodicity in one direction is derived by an Ewald summation technique. It is found that, in contrast to the case with periodicity in all three directions, no convergence factor is needed to obtain a convergent result.

1. Introduction

Molecular dynamics as well as Monte Carlo simulations have become important tools for the study of classical statistical mechanics of many-body systems. In many models of practical interest it is necessary to consider long-range electrostatic interactions between the particles, such as charge–charge, charge–dipole, dipole–dipole, and charge–quadrupole interactions. These interactions decrease with distance r as $r^{-3+\varepsilon}$ with $\varepsilon > 0$. Hence, when applying periodic boundary conditions for three-dimensional systems, the sum of the energy over the images of the system is only conditionally convergent. To solve this problem, the Ewald summation technique is widely used [1–5]. However, in some cases one may encounter systems, which are infinite in some directions and finite in other directions. For example, in simulations of membranes and other liquid or solid surfaces, one needs to extend the Ewald summation technique to three-dimensional systems with periodicity in two directions only, where the result has been obtained recently [6].

In this paper, an Ewald summation technique is developed to derive the energy of long-range electrostatic interactions in three-dimensional systems with periodicity in one direction. Possible applications include transport of charged particles through channels or wires. In section 2, the energy of charged particles obeying Coulomb interaction is derived. Then, considering the same geometry for particles with point-like dipole moments, the analogous expression for dipole–dipole interaction is obtained in section 3.

2. Coulomb interaction

In the following, a simulation box of size $L \times L' \times L''$ containing N charges is considered. The charges q_u are located at position $\boldsymbol{r}_u$, and the simulation box is assumed to have no net

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charge, $\sum_{u=1}^{N} q_u = 0$. The total energy of the system with periodic boundary conditions in x direction reads as

$$E_1 = \frac{1}{2} \sum_{u,v=1}^{N} \sum_{\boldsymbol{n}}{}' \frac{q_u q_v}{|\boldsymbol{r}_{uv} + \boldsymbol{n}|} \tag{1}$$

with $\boldsymbol{r}_{uv} = \boldsymbol{r}_u - \boldsymbol{r}_v$. The sum over $\boldsymbol{n} = (nL, 0, 0)$ with integer n is the sum over the original and the images of the system, and the prime indicates that for $\boldsymbol{n} = \boldsymbol{0}$ the terms with $u = v$ are to be omitted. Defining the function $\Phi(\boldsymbol{r})$ and the factor Φ_0 as

$$\Phi(\boldsymbol{r}) = \sum_{\boldsymbol{n}} \frac{1}{|\boldsymbol{r} + \boldsymbol{n}|} \qquad \text{for} \quad \boldsymbol{r} \neq 0 \tag{2a}$$

and

$$\Phi_0 = \sum_{\boldsymbol{n} \neq \boldsymbol{0}} \frac{1}{|\boldsymbol{n}|} \tag{2b}$$

one may rewrite equation (1) as

$$E_1 = \tfrac{1}{2} \sum_{\substack{u,v=1 \\ v \neq u}}^{N} q_u q_v \Phi(\boldsymbol{r}_{uv}) + \tfrac{1}{2} \sum_{u=1}^{N} q_u^2 \Phi_0. \tag{3}$$

The first term in equation (3) sums up the contributions from each charge interacting with all other charges, the originals as well as their images, whereas the second term represents the contribution from the interaction of each charge with its own images.

To calculate the sums in equation (2), the identity based on the integral representation of the gamma function $\Gamma(s)$ [7],

$$\frac{1}{x^{2s}} = \frac{1}{\Gamma(s)} \int_0^{\infty} t^{s-1} \exp(-x^2 t)\, \mathrm{d}t \tag{4}$$

is used for $s = 1/2$. Additionally, the Poisson summation formula in one direction,

$$\sum_{n} \exp(-[\rho + n]^2\, t) = \frac{\sqrt{\pi}}{L}\, t^{-1/2} \sum_{G} \exp(\mathrm{i}G\rho) \exp\left(-\frac{G^2}{4t}\right) \tag{5}$$

is applied, where $G = 2\pi k/L$ with k integer denotes the summation index in reciprocal space. Let us start by evaluating the quantity Φ_0. Using equation (4), and noting that $\Gamma(1/2) = \sqrt{\pi}$, the sum for Φ_0 can be written as

$$\Phi_0 = \frac{1}{\sqrt{\pi}} \sum_{\boldsymbol{n} \neq \boldsymbol{0}} \int_{\alpha^2}^{\infty} t^{-1/2} \exp(-|\boldsymbol{n}|^2 t)\, \mathrm{d}t + \frac{1}{\sqrt{\pi}} \sum_{n} \int_0^{\alpha^2} t^{-1/2} \exp(-n^2 t)\, \mathrm{d}t - \frac{1}{\sqrt{\pi}} \int_0^{\alpha^2} t^{-1/2}\, \mathrm{d}t \tag{6}$$

where the integral over $[0, \infty)$ is split into two intervals, $[0, \alpha^2]$ and $[\alpha^2, \infty)$, with an arbitrary parameter $\alpha > 0$, to separate the singular part of the integral. In the second sum, the term with $n = 0$ is included and afterwards substracted separately. Direct calculation of the integrals in the first sum and in the third term, and applying the Poisson summation formula (5) with $\rho = 0$ to the second sum leads to

$$\Phi_0 = \sum_{\boldsymbol{n} \neq \boldsymbol{0}} \frac{\operatorname{erfc}(\alpha |\boldsymbol{n}|)}{|\boldsymbol{n}|} + \frac{1}{L} \sum_{G} \int_0^{\alpha^2} t^{-1} \exp\left(-\frac{G^2}{4t}\right) \mathrm{d}t - \frac{2\alpha}{\sqrt{\pi}}. \tag{7}$$

A last integration, separately for $G = 0$ and $\neq 0$, yields

$$\Phi_0 = \sum_{\boldsymbol{n}\neq\boldsymbol{0}} \frac{\operatorname{erfc}(\alpha|\boldsymbol{n}|)}{|\boldsymbol{n}|} + \frac{1}{L}[\log(\alpha^2) - \lim_{t\to 0^+} \log(t)] + \frac{1}{L}\sum_{G\neq 0} \Gamma\left(0, \frac{G^2}{4\alpha^2}\right) - \frac{2\alpha}{\sqrt{\pi}} \tag{8}$$

where $\Gamma(s, t)$ denotes the incomplete gamma function. The divergent part, $\log(\alpha^2) - \lim_{t\to 0^+} \log(t)$, resulting from the case $G = 0$ will also appear in identical form in the evaluation of $\Phi(\boldsymbol{r})$ (cf equation (11)) and is hence absent in the final result equation (13) due to the charge neutrality of the sytem.

Analogously, one writes for the function $\Phi(\boldsymbol{r})$

$$\Phi(\boldsymbol{r}) = \frac{1}{\sqrt{\pi}} \sum_{\boldsymbol{n}} \int_{\alpha^2}^{\infty} t^{-1/2} \exp(-|\boldsymbol{r}+\boldsymbol{n}|^2 t)\,\mathrm{d}t + \frac{1}{\sqrt{\pi}} \sum_{n} \int_{0}^{\alpha^2} t^{-1/2} \exp(-[\boldsymbol{r}_x + n]^2 t) \exp(-[\boldsymbol{r}_y^2 + \boldsymbol{r}_z^2]t)\,\mathrm{d}t \tag{9}$$

where $\boldsymbol{r}_x$, $\boldsymbol{r}_y$, and $\boldsymbol{r}_z$ denote the x, y, and z components of $\boldsymbol{r}$. Direct calculation of the integral in the first sum and applying the Poisson summation formula (5) to the second sum leads to

$$\Phi(\boldsymbol{r}) = \sum_{\boldsymbol{n}} \frac{\operatorname{erfc}(\alpha|\boldsymbol{r}+\boldsymbol{n}|)}{|\boldsymbol{r}+\boldsymbol{n}|} + \frac{1}{L}\sum_{G}\int_0^{\alpha^2} t^{-1}\exp(\mathrm{i}G\boldsymbol{r}_x)\exp\left(-\frac{G^2}{4t} - [\boldsymbol{r}_y^2 + \boldsymbol{r}_z^2]t\right)\mathrm{d}t. \tag{10}$$

The remaining integral in the second term reads, for $G = 0$, as

$$\int_0^{\alpha^2} t^{-1}\exp(-[\boldsymbol{r}_y^2 + \boldsymbol{r}_z^2]t)\,\mathrm{d}t = \frac{1}{L}\{\log(\alpha^2) - \lim_{t\to 0^+}\log(t) - \gamma - \Gamma(0, \alpha^2[\boldsymbol{r}_y^2 + \boldsymbol{r}_z^2]) - \log(\alpha^2[\boldsymbol{r}_y^2 + \boldsymbol{r}_z^2])\} \tag{11}$$

where γ denotes Euler's constant. One should note that $\lim_{v\to 0^+} -\gamma - \Gamma(0, v) - \log(v) = 0$. For $G \neq 0$, the integral in equation (10) cannot be obtained in closed form. Hence, the integrand is expanded in powers of $\boldsymbol{r}_y^2 + \boldsymbol{r}_z^2$, and every term is integrated separately, resulting in

$$\int_0^{\alpha^2} t^{-1}\exp\left(-\frac{G^2}{4t} - [\boldsymbol{r}_y^2 + \boldsymbol{r}_z^2]t\right)\mathrm{d}t = \sum_{\kappa=0}^{\infty}\frac{(-1)^\kappa}{4^\kappa \kappa!}G^{2\kappa}[\boldsymbol{r}_y^2 + \boldsymbol{r}_z^2]^\kappa\,\Gamma\left(-\kappa, \frac{G^2}{4\alpha^2}\right). \tag{12}$$

Putting together equations (11) and (12) in (10), and combining with equation (8) using (3) yields the final result

$$\begin{aligned}
E_1 = {} & \frac{1}{2}\sum_{u,v=1}^{N} q_u q_v {\sum_{\boldsymbol{n}}}' \frac{\operatorname{erfc}(\alpha|\boldsymbol{r}_{uv}+\boldsymbol{n}|)}{|\boldsymbol{r}_{uv}+\boldsymbol{n}|} + \frac{1}{2L}\sum_{u,v=1}^{N} q_u q_v \sum_{G\neq 0}\exp(\mathrm{i}G\boldsymbol{r}_{uv,x}) \\
& \times \begin{cases} \displaystyle\sum_{\kappa=0}^{\infty}\frac{(-1)^\kappa}{4^\kappa \kappa!}G^{2\kappa}[\boldsymbol{r}_{uv,y}^2 + \boldsymbol{r}_{uv,z}^2]^\kappa\,\Gamma\left(-\kappa, \frac{G^2}{4\alpha^2}\right) & \text{for} \quad \boldsymbol{r}_{uv,y}^2 + \boldsymbol{r}_{uv,z}^2 \neq 0 \\ \Gamma\left(0, \dfrac{G^2}{4\alpha^2}\right) & \text{for} \quad \boldsymbol{r}_{uv,y}^2 + \boldsymbol{r}_{uv,z}^2 = 0 \end{cases} \\
& + \frac{1}{2L}\sum_{\substack{u,v=1 \\ \boldsymbol{r}_{uv,y}^2 + \boldsymbol{r}_{uv,z}^2 \neq 0}}^{N} q_u q_v\{-\gamma - \Gamma(0, \alpha^2\,[\boldsymbol{r}_{uv,y}^2 + \boldsymbol{r}_{uv,z}^2]) \\
& - \log(\alpha^2[\boldsymbol{r}_{uv,y}^2 + \boldsymbol{r}_{uv,z}^2])\} + \frac{\alpha}{\sqrt{\pi}}\sum_{u=1}^{N} q_u^2
\end{aligned} \tag{13}$$

where $\boldsymbol{r}_{uv,x}$, $\boldsymbol{r}_{uv,y}$, and $\boldsymbol{r}_{uv,z}$ denote the x, y, and z components of $\boldsymbol{r}_{uv}$. The last but one sum can be restricted to charge pairs q_u and q_v for which $\boldsymbol{r}_{uv,y}^2 + \boldsymbol{r}_{uv,z}^2 \neq 0$, because the value in the curly brackets is equal to 0 otherwise.

3. Dipole–dipole interaction

Analogously to the case of Coulomb interaction, in the following a simulation box of size $L \times L' \times L''$ is considered, containing N point-like dipoles $\boldsymbol{\mu}_u$ located at position $\boldsymbol{r}_u$. The total energy of the system with periodic boundary conditions in the x direction reads as

$$E_2 = \frac{1}{2} \sum_{u,v=1}^{N} \sum_{\boldsymbol{n}}{}' \left\{ \frac{\boldsymbol{\mu}_u \cdot \boldsymbol{\mu}_v}{|\boldsymbol{r}_{uv} + \boldsymbol{n}|^3} - \frac{3[\boldsymbol{\mu}_u \cdot (\boldsymbol{r}_{uv} + \boldsymbol{n})][\boldsymbol{\mu}_v \cdot (\boldsymbol{r}_{uv} + \boldsymbol{n})]}{|\boldsymbol{r}_{uv} + \boldsymbol{n}|^5} \right\} \tag{14}$$

where $\boldsymbol{r}_{uv} = \boldsymbol{r}_u - \boldsymbol{r}_v$, the sum is over $\boldsymbol{n} = (nL, 0, 0)$ with integer n, and the prime indicates that for $\boldsymbol{n} = \boldsymbol{0}$ the terms with $u = v$ are to be omitted. Defining the following quantities:

$$\Psi(\boldsymbol{r}) = \sum_{\boldsymbol{n}} \frac{1}{|\boldsymbol{r} + \boldsymbol{n}|^3} \qquad \text{for} \quad \boldsymbol{r} \neq 0 \tag{15a}$$

and

$$\Psi_0 = \sum_{\boldsymbol{n} \neq \boldsymbol{0}} \frac{1}{|\boldsymbol{n}|^3} \tag{15b}$$

as well as

$$\Theta(\boldsymbol{r}, \boldsymbol{\xi}) = \sum_{\boldsymbol{n}} \frac{\exp(-\mathrm{i}\boldsymbol{\xi} \cdot [\boldsymbol{r} + \boldsymbol{n}])}{|\boldsymbol{r} + \boldsymbol{n}|^5} \qquad \text{for} \quad \boldsymbol{r} \neq 0 \tag{16a}$$

and

$$\Theta_0(\boldsymbol{\xi}) = \sum_{\boldsymbol{n} \neq \boldsymbol{0}} \frac{\exp(-\mathrm{i}\boldsymbol{\xi} \cdot \boldsymbol{n})}{|\boldsymbol{n}|^5} \tag{16b}$$

one may rewrite equation (14) as

$$E_2 = \tfrac{1}{2} \sum_{\substack{u,v=1 \\ v \neq u}}^{N} \boldsymbol{\mu}_u \cdot \boldsymbol{\mu}_v \Psi(\boldsymbol{r}_{uv}) + \tfrac{1}{2} \sum_{u=1}^{N} |\boldsymbol{\mu}_u|^2 \Psi_0 + \tfrac{3}{2} \sum_{\substack{u,v=1 \\ v \neq u}}^{N} (\boldsymbol{\mu}_u \cdot \boldsymbol{\nabla}_{\xi})(\boldsymbol{\mu}_v \cdot \boldsymbol{\nabla}_{\xi}) \Theta(\boldsymbol{r}_{uv}, \boldsymbol{\xi})|_{\boldsymbol{\xi}=\boldsymbol{0}}$$
$$+ \tfrac{3}{2} \sum_{u=1}^{N} (\boldsymbol{\mu}_u \cdot \boldsymbol{\nabla}_{\xi})^2 \Theta_0(\boldsymbol{\xi})|_{\boldsymbol{\xi}=\boldsymbol{0}}. \tag{17}$$

To calculate the sums in equations (15) and (16), the integral representation of the gamma function $\Gamma(s)$, equation (4), with $s = 3/2$ and $5/2$ is used, as well as the Poisson summation formula in the following form:

$$\sum_{n} \exp(-[\rho + n]^2 t - \mathrm{i}\xi[\rho + n]) = \frac{\sqrt{\pi}}{L} t^{-1/2} \sum_{G} \exp(\mathrm{i}G\rho) \exp\left(-\frac{[G + \xi]^2}{4t}\right) \tag{18}$$

where $G = 2\pi k/L$ with integer k denotes the summation index in reciprocal space.

Let us start by evaluating Ψ_0 and $\Psi(\boldsymbol{r})$. Using equation (4) with $s = 3/2$, and noting that $\Gamma(3/2) = \sqrt{\pi}/2$, the sums in equation (15) can be written as

$$\Psi_0 = \frac{2}{\sqrt{\pi}} \sum_{\boldsymbol{n} \neq \boldsymbol{0}} \int_{\alpha^2}^{\infty} t^{1/2} \exp(-|\boldsymbol{n}|^2 t)\, \mathrm{d}t + \frac{2}{\sqrt{\pi}} \sum_{n} \int_{0}^{\alpha^2} t^{1/2} \exp(-n^2 t)\, \mathrm{d}t - \frac{2}{\sqrt{\pi}} \int_{0}^{\alpha^2} t^{1/2}\, \mathrm{d}t \tag{19a}$$

and as

$$\Psi(\boldsymbol{r}) = \frac{2}{\sqrt{\pi}} \sum_{\boldsymbol{n}} \int_{\alpha^2}^{\infty} t^{1/2} \exp(-|\boldsymbol{r} + \boldsymbol{n}|^2 t)\, \mathrm{d}t$$
$$+ \frac{2}{\sqrt{\pi}} \sum_{n} \int_{0}^{\alpha^2} t^{1/2} \exp(-[r_x + n]^2 t) \exp(-[r_y^2 + r_z^2] t)\, \mathrm{d}t. \tag{19b}$$

By abbreviating the first integrals in equation (19) as

$$B(\alpha, \boldsymbol{r}) = \frac{2}{\sqrt{\pi}} \int_{\alpha^2}^{\infty} t^{1/2} \exp(-|\boldsymbol{r}|^2 t)\, \mathrm{d}t = \frac{\operatorname{erfc}(\alpha|\boldsymbol{r}|)}{|\boldsymbol{r}|^3} + \frac{2\alpha \exp(-\alpha^2|\boldsymbol{r}|^2)}{\sqrt{\pi}|\boldsymbol{r}|^2} \tag{20}$$

and using the Poisson summation formula (5) for the second integrals, this yields

$$\Psi_0 = \sum_{\boldsymbol{n} \neq \boldsymbol{0}} B(\alpha, \boldsymbol{n}) + \frac{2}{L} \sum_{G} \int_0^{\alpha^2} \exp\left(-\frac{G^2}{4t}\right) \mathrm{d}t - \frac{4\alpha^3}{3\sqrt{\pi}} \tag{21a}$$

and

$$\Psi(\boldsymbol{r}) = \sum_{\boldsymbol{n}} B(\alpha, \boldsymbol{r} + \boldsymbol{n}) + \frac{2}{L} \sum_{G} \int_0^{\alpha^2} \exp\left(-\frac{G^2}{4t} - [\boldsymbol{r}_y^2 + \boldsymbol{r}_z^2]t\right) \mathrm{d}t. \tag{21b}$$

Analogously, using equation (4) with $s = 5/2$, and noting that $\Gamma(5/2) = 3\sqrt{\pi}/4$, the sums in equation (16) can be written as

$$\begin{aligned}\Theta_0(\boldsymbol{\xi}) = {} & \frac{4}{3\sqrt{\pi}} \sum_{\boldsymbol{n} \neq \boldsymbol{0}} \exp(-\mathrm{i}\boldsymbol{\xi} \cdot \boldsymbol{n}) \int_{\alpha^2}^{\infty} t^{3/2} \exp(-|\boldsymbol{n}|^2 t)\, \mathrm{d}t \\ & + \frac{4}{3\sqrt{\pi}} \sum_{n} \exp(-\mathrm{i}\boldsymbol{\xi}_x n) \int_0^{\alpha^2} t^{3/2} \exp(-n^2 t)\, \mathrm{d}t - \frac{4}{3\sqrt{\pi}} \int_0^{\alpha^2} t^{3/2}\, \mathrm{d}t\end{aligned} \tag{22a}$$

and as

$$\begin{aligned}\Theta(\boldsymbol{r}, \boldsymbol{\xi}) = {} & \frac{4}{3\sqrt{\pi}} \sum_{\boldsymbol{n}} \exp(-\mathrm{i}\boldsymbol{\xi} \cdot [\boldsymbol{r} + \boldsymbol{n}]) \int_{\alpha^2}^{\infty} t^{3/2} \exp(-|\boldsymbol{r} + \boldsymbol{n}|^2 t)\, \mathrm{d}t \\ & + \frac{4}{3\sqrt{\pi}} \sum_{n} \exp(-\mathrm{i}\boldsymbol{\xi}_x [\boldsymbol{r}_x + n] - \mathrm{i}[\boldsymbol{\xi}_y y + \boldsymbol{\xi}_z z]) \\ & \times \int_0^{\alpha^2} t^{3/2} \exp(-[\boldsymbol{r}_x + n]^2 t) \exp(-[\boldsymbol{r}_y^2 + \boldsymbol{r}_z^2] t)\, \mathrm{d}t\end{aligned} \tag{22b}$$

where $\boldsymbol{\xi}_x, \boldsymbol{\xi}_y, \boldsymbol{\xi}_z$ denote the x, y, and z components of $\boldsymbol{\xi}$. By abbreviating the first integrals in equation (22) as

$$\begin{aligned}C(\alpha, \boldsymbol{r}) & = \frac{4}{3\sqrt{\pi}} \int_{\alpha^2}^{\infty} t^{3/2} \exp(-|\boldsymbol{r}|^2 t)\, \mathrm{d}t \\ & = \frac{\operatorname{erfc}(\alpha|\boldsymbol{r}|)}{|\boldsymbol{r}|^5} + \frac{2\alpha \exp(-\alpha^2|\boldsymbol{r}|^2)}{\sqrt{\pi}|\boldsymbol{r}|^2} \left(\frac{2}{3}\alpha^2 + \frac{1}{|\boldsymbol{r}|^2}\right)\end{aligned} \tag{23}$$

and using the Poisson summation formula in the form of equation (18) for the second integrals, one obtains

$$\Theta_0(\boldsymbol{\xi}) = \sum_{\boldsymbol{n} \neq \boldsymbol{0}} \exp(-\mathrm{i}\boldsymbol{\xi} \cdot \boldsymbol{n}) C(\alpha, \boldsymbol{n}) + \frac{4}{3L} \sum_{G} \int_0^{\alpha^2} \exp\left(-\frac{[G + \boldsymbol{\xi}_x]^2}{4t}\right) \mathrm{d}t - \frac{8\alpha^5}{15\sqrt{\pi}} \tag{24a}$$

and

$$\begin{aligned}\Theta(\boldsymbol{r}, \boldsymbol{\xi}) = {} & \sum_{\boldsymbol{n}} \exp(-\mathrm{i}\boldsymbol{\xi} \cdot [\boldsymbol{r} + \boldsymbol{n}]) C(\alpha, \boldsymbol{r} + \boldsymbol{n}) + \frac{4}{3L} \sum_{G} \exp(\mathrm{i}G\boldsymbol{r}_x - \mathrm{i}[\boldsymbol{\xi}_y y + \boldsymbol{\xi}_z z]) \\ & \times \int_0^{\alpha^2} \exp\left(-\frac{[G + \boldsymbol{\xi}_x]^2}{4t} - [\boldsymbol{r}_y^2 + \boldsymbol{r}_z^2]t\right) \mathrm{d}t.\end{aligned} \tag{24b}$$

The remaining integrals in equations (21*b*) and (24*b*) cannot be obtained in closed form. Thus, the integrand is expanded in powers of $\boldsymbol{r}_y^2 + \boldsymbol{r}_z^2$, and every term is integrated separately, resulting in

$$\int_0^{\alpha^2} \exp\left(-\frac{[G+\boldsymbol{\xi}_x]^2}{4t} - [\boldsymbol{r}_y^2 + \boldsymbol{r}_z^2]t\right) \mathrm{d}t$$
$$= \sum_{\kappa=0}^{\infty} \frac{(-1)^\kappa}{4^{\kappa+1}\kappa!}[G+\boldsymbol{\xi}_x]^{2(\kappa+1)}[\boldsymbol{r}_y^2+\boldsymbol{r}_z^2]^\kappa\,\Gamma\left(-(\kappa+1), \frac{[G+\boldsymbol{\xi}_x]^2}{4\alpha^2}\right). \tag{25}$$

One should note that equation (25) contains also, as special cases with $\boldsymbol{r}_y^2+\boldsymbol{r}_z^2 = 0$, the integrals in equations (21*a*), (24*a*),

$$\int_0^{\alpha^2} \exp\left(-\frac{[G+\boldsymbol{\xi}_x]^2}{4t}\right) \mathrm{d}t = \frac{1}{4}[G+\boldsymbol{\xi}_x]^2\,\Gamma\left(-1, \frac{[G+\boldsymbol{\xi}_x]^2}{4\alpha^2}\right). \tag{26}$$

For the case $\boldsymbol{\xi}_x = 0$ in equations (25), (26), being equivalent to the integrals in (21), the abbreviation

$$D(\alpha, G, \boldsymbol{r}) = \frac{2}{L}\begin{cases} \dfrac{1}{4}G^2\Gamma\left(-1, \dfrac{G^2}{4\alpha^2}\right) & \text{for} \quad \boldsymbol{r}_y^2+\boldsymbol{r}_z^2 = 0 \\ \displaystyle\sum_{\kappa=0}^{\infty}\frac{(-1)^\kappa}{4^{\kappa+1}\kappa!}G^{2(\kappa+1)}[\boldsymbol{r}_y^2+\boldsymbol{r}_z^2]^\kappa\,\Gamma\left(-(\kappa+1), \dfrac{G^2}{4\alpha^2}\right) & \text{for} \quad \boldsymbol{r}_y^2+\boldsymbol{r}_z^2 \neq 0 \end{cases} \tag{27}$$

is used, including the factor $2/L$. One should note the special case $G = 0$ in equation (27), $D(\alpha, 0, \boldsymbol{r}) = \alpha^2$ for $\boldsymbol{r}_y^2 + \boldsymbol{r}_z^2 = 0$ and $D(\alpha, 0, \boldsymbol{r}) = [1 - \exp(-\alpha^2[\boldsymbol{r}_y^2+\boldsymbol{r}_z^2])]/[\boldsymbol{r}_y^2+\boldsymbol{r}_z^2]$ for $\boldsymbol{r}_y^2+\boldsymbol{r}_z^2 \neq 0$.

Finally, one needs to evaluate $(\boldsymbol{\mu}_u \cdot \boldsymbol{\nabla}_\xi)(\boldsymbol{\mu}_v \cdot \boldsymbol{\nabla}_\xi)\Theta_0(\boldsymbol{\xi})|_{\boldsymbol{\xi}=\boldsymbol{0}}$ and $(\boldsymbol{\mu}_u \cdot \boldsymbol{\nabla}_\xi)(\boldsymbol{\mu}_v \cdot \boldsymbol{\nabla}_\xi)\Theta(\boldsymbol{r}, \boldsymbol{\xi})|_{\boldsymbol{\xi}=\boldsymbol{0}}$. Denoting $\boldsymbol{\mu}_{u,x}$, $\boldsymbol{\mu}_{u,y}$, and $\boldsymbol{\mu}_{u,z}$ as the x, y, and z components of $\boldsymbol{\mu}_u$, one obtains

$$(\boldsymbol{\mu}_u \cdot \boldsymbol{\nabla}_\xi)(\boldsymbol{\mu}_v \cdot \boldsymbol{\nabla}_\xi)\Theta_0(\boldsymbol{\xi})|_{\boldsymbol{\xi}=\boldsymbol{0}} = -\sum_{\boldsymbol{n}\neq\boldsymbol{0}}(\boldsymbol{\mu}_u\cdot\boldsymbol{n})(\boldsymbol{\mu}_v\cdot\boldsymbol{n})C(\alpha,\boldsymbol{n}) + \sum_G \boldsymbol{\mu}_{u,x}\boldsymbol{\mu}_{v,x}\boldsymbol{F}_{xx}(\alpha, G, \boldsymbol{0}) \tag{28}$$

and

$$(\boldsymbol{\mu}_u \cdot \boldsymbol{\nabla}_\xi)(\boldsymbol{\mu}_v \cdot \boldsymbol{\nabla}_\xi)\Theta(\boldsymbol{r}, \boldsymbol{\xi})\big|_{\boldsymbol{\xi}=\boldsymbol{0}} = -\sum_{\boldsymbol{n}}(\boldsymbol{\mu}_u\cdot[\boldsymbol{r}+\boldsymbol{n}])(\boldsymbol{\mu}_v\cdot[\boldsymbol{r}+\boldsymbol{n}])C(\alpha,\boldsymbol{r}+\boldsymbol{n})$$
$$+\sum_G \sum_{\substack{\omega_1\in\{x,y,z\}\\ \omega_2\in\{x,y,z\}}} \boldsymbol{\mu}_{u,\omega_1}\boldsymbol{\mu}_{v,\omega_2}\boldsymbol{G}_{\omega_1}(G,\boldsymbol{r})\boldsymbol{G}_{\omega_2}(G,\boldsymbol{r})\boldsymbol{F}_{\omega_1\omega_2}(\alpha, G, \boldsymbol{r}). \tag{29}$$

The summation over ω_1 and ω_2 runs over all three coordinates x, y, and z, and $\boldsymbol{G}_x(G, \boldsymbol{r})$, $\boldsymbol{G}_y(G, \boldsymbol{r})$, and $\boldsymbol{G}_z(G, \boldsymbol{r})$ denote the x, y, and z components of the vector $\boldsymbol{G}(G, \boldsymbol{r})$, which is defined as $\boldsymbol{G}(G, \boldsymbol{r}) = (1, \mathrm{i}G\boldsymbol{r}_y, \mathrm{i}G\boldsymbol{r}_z)$. The nine components of the tensor $\boldsymbol{F}(\alpha, G, \boldsymbol{r})$ are given by

$$\boldsymbol{F}_{xx}(\alpha, G, \boldsymbol{r}) = \frac{4}{3L}\exp(\mathrm{i}G\boldsymbol{r}_x)$$

$$\times \begin{cases} \left[1-\frac{2\alpha^2}{G^2}\right]\exp\left(-\frac{G^2}{4\alpha^2}\right)+\frac{1}{2}\Gamma\left(-1,\frac{G^2}{4\alpha^2}\right) & \text{for} \quad r_y^2+r_z^2=0 \\ \sum_{\kappa=0}^{\infty}\frac{(-1)^\kappa}{4^{\kappa+1}\kappa!}[r_y^2+r_z^2]^\kappa & \\ \times\left\{4^{\kappa+1}\alpha^{2\kappa}\left[1-(2\kappa+1)\frac{2\alpha^2}{G^2}\right]\exp\left(-\frac{G^2}{4\alpha^2}\right)\right. & \\ \left.-2G^{2\kappa}(2\kappa+1)(\kappa+1)\Gamma\left(-(1+\kappa),\frac{G^2}{4\alpha^2}\right)\right\} & \text{for} \quad r_y^2+r_z^2\neq 0 \end{cases} \tag{30}$$

$$F_{xy}(\alpha,G,r)=F_{yx}(\alpha,G,r)=F_{xz}(\alpha,G,r)=F_{zx}(\alpha,G,r)=\frac{4}{3L}\exp(\mathrm{i}Gr_x)$$

$$\times \begin{cases} \frac{2\alpha^2}{G^2}\exp\left(-\frac{G^2}{4\alpha^2}\right)+\frac{1}{2}\Gamma\left(-1,\frac{G^2}{4\alpha^2}\right) & \text{for} \quad r_y^2+r_z^2=0 \\ \sum_{\kappa=0}^{\infty}\frac{(-1)^\kappa}{4^{\kappa+1}\kappa!}[r_y^2+r_z^2]^\kappa & \\ \times\left\{4^{\kappa+1}\alpha^{2\kappa}\frac{2\alpha^2}{G^2}\exp\left(-\frac{G^2}{4\alpha^2}\right)\right. & \\ \left.-2G^{2\kappa}(\kappa+1)\Gamma\left(-(1+\kappa),\frac{G^2}{4\alpha^2}\right)\right\} & \text{for} \quad r_y^2+r_z^2\neq 0 \end{cases} \tag{31}$$

and

$$F_{yy}(\alpha,G,r)=F_{zz}(\alpha,G,r)=\frac{4}{3L}\exp(\mathrm{i}Gr_x)$$

$$\times \begin{cases} \Gamma\left(-1,\frac{G^2}{4\alpha^2}\right) & \text{for} \quad r_y^2+r_z^2=0 \\ \sum_{\kappa=0}^{\infty}\frac{(-1)^\kappa}{4^{\kappa+1}\kappa!}[r_y^2+r_z^2]^\kappa\Gamma\left(-(1+\kappa),\frac{G^2}{4\alpha^2}\right) & \text{for} \quad r_y^2+r_z^2\neq 0. \end{cases} \tag{32}$$

Putting all the above together, one obtains the final result

$$\begin{aligned} E_2 = \tfrac{1}{2}\sum_{u,v=1}^{N}\sum_{n}{}' & \mu_u\cdot\mu_v B(\alpha, r_{uv}+n) \\ & -3(\mu_u\cdot[r_{uv}+n])(\mu_v\cdot[r_{uv}+n])C(\alpha, r_{uv}+n) \\ & +\tfrac{1}{2}\sum_{u,v=1}^{N}\sum_{G}\mu_u\cdot\mu_v D(\alpha,G,r_{uv}) \\ & -3\sum_{\substack{\omega_1\in\{x,y,z\}\\ \omega_2\in\{x,y,z\}}}\mu_{u,\omega_1}\mu_{v,\omega_2}G_{\omega_1}(G,r_{uv})G_{\omega_2}(G,r_{uv})F_{\omega_1\omega_2}(\alpha,G,r_{uv}) \\ & -\frac{2\alpha^3}{3\sqrt{\pi}}\sum_{u=1}^{N}|\mu_u|^2. \end{aligned} \tag{33}$$

One should note that the same result, apart from the last term $-2\alpha^3/(3\sqrt{\pi})\sum_{u=1}^{N}|\mu_u|^2$, can be obtained by replacing $q_u q_v \to -(\mu_u\cdot\nabla_{r_u})(\mu_v\cdot\nabla_{r_v})$ in equation (13) and evaluating the ∇ operators, similar to the cases of periodicity in two of three dimensions [6] and periodicity in all three dimensions [4].

4. Conclusion

Using the integral representation of the gamma function and the Poisson summation formula an Ewald summation technique is developed for long-range electrostatic interactions in systems that are periodic in one direction and have a finite extent in the two other directions. A convergence factor, proposed for the summation with periodicity in all three directions [4], is not needed. Hence, for the case of charges, a term proportional to the square of the net dipole moment of the system, which has been achieved for three-dimensional systems as a consequence of the convergence factor [4], does not exist for the present geometry. This result is similar to the case of three-dimensional systems with periodicity in two directions [6].

Concerning the usage of equations (13), (33) in practical applications, one should note that the parameter α is usually chosen quite large, so that, for both charges and dipoles, the sum in real space can be truncated by omitting contributions from pairs (u, v) for which $|\boldsymbol{r}_{uv}| > L/2$. This means that the real-space sum is restricted to the original simulation box by applying the minimum image convention. Typically, one uses $\alpha \cong 5/L$ and includes about 100–200 wavevectors in the sums in reciprocal space.

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