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Rapid calculation of two-dimensional Ewald summation

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Abstract

A computationally efficient method was developed to implement the Ewald summation in calculations for Coulomb interactions in three-dimensional (3D) systems with two-dimensional (2D) periodicity. The computational efficiency and accuracy of this method was evaluated for water systems enclosed in various rectangular parallelepiped boxes (cube, quadratic prism, and slab) and with 2D periodicity. Compared with existing computational methods, this method showed a significant reduction in computational time for all systems examined and was sufficiently accurate for calculating the Coulomb interactions in 3D systems with 2D periodicity, independent of the shape of the simulation box.

1. Introduction

For systems composed of charged particles, the accuracy in the calculation of Coulomb interactions strongly affects the accuracy and computational efficiency of molecular dynamics (MD) simulations and Monte Carlo (MC) simulations [1]. The Ewald summation [2] and related techniques, such as the particle mesh Ewald method [3], have been successfully used for representation of long-range Coulomb interactions for systems with three-dimensional (3D) periodicity. For 3D systems with two-dimensional (2D) periodicity, an accurate formulation of the 2D Ewald summation was first introduced by Parry [4], and the same formulae were independently rederived by Heyes et al. [5] and by Leeuw et al. [6]. For simplicity, we refer to this formulation as the PHL method. However, although elaborate work has been done by Harris [7], the computational burden of the method still remains on the order of N^2, where N is the number of charges in the system. Therefore, the PHL method is sufficiently computationally intensive that its direct use in MD and MC simulations for complex systems with interfacial regions, such as membranes and surfactants, has been limited. Other formulations of the 2D Ewald summation have been proposed [8,9], but the application of these methods has also been limited due to the strict conditions that must be satisfied for the inherent approximations to be valid or due to the long computational time required [9,10]. Recently, other approximation methods have been proposed, in which a correction term is added to the 3D Ewald summation, and good agreement with the simulations using the 2D Ewald

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summation is obtained if the simulation box is sufficiently elongated in the direction of non-periodicity to create large empty spaces outside the system [11–13]. However, in contrast to the PHL method, these methods do not have a sufficiently wide range of applicability.

The purpose of our study was to develop a computationally efficient method for calculating the 2D Ewald summation and which has a similar range of applicability as the PHL method. Section 2 describes an accurate reformulation that we developed for the 2D Ewald summation. Section 3 presents the computational efficiency and accuracy of our method for calculating Coulomb interactions in water systems enclosed in various 3D simulation boxes. To yield a fair comparison of performance, first we determined the optimal conditions for the implementation of our method and of the PHL method. With this optimal set of parameters, the comparison showed that for all systems our method significantly reduces the computational time compared with the PHL method, and that our method is accurate enough to adequately treat Coulomb interactions in 3D systems with 2D periodicity.

2. Computational method

We first describe the original formulae used for the PHL method. We then describe our computationally efficient formulation for calculating Coulomb interactions in 3D systems with 2D periodicity. Similar to a system with 3D periodicity, in a system with 2D periodicity the long-range Coulomb potential energy, V, for N particles with charges $(q_1, q_2, \ldots, q_N)$ satisfying neutrality $(\sum_i q_i = 0)$ can be expressed by the Ewald summation as a sum of rapid convergence series in real and in reciprocal space. For simplicity, we assume that images of a simulation box of rectangular parallelepiped shape are repeated in the (x, y) plane with non-periodicity in the z direction. Extension to simulation using parallelepiped boxes is straightforward.

When a Gaussian charge distribution is used, such as $\rho(\mathbf{r}_i) = q_i\alpha^3\pi^{-3/2}\mathrm{e}^{-\alpha^2|\mathbf{r}_i|^2}$, V can be written as [4–6]

$$V = \frac{1}{2}\sum_{\mathbf{h}_x,\mathbf{h}_y}{}' \sum_{i=1}^{N}\sum_{j=1}^{N}\frac{q_iq_j}{|\mathbf{r}_i - \mathbf{r}_j + \mathbf{h}_x + \mathbf{h}_y|} \approx V^{\mathrm{r}} + V^{\mathrm{k}}_{\mathbf{k}\neq\mathbf{0}} + V^{\mathrm{k}}_{\mathbf{k}=\mathbf{0}} + V^{\mathrm{s}}, \tag{1}$$

where $\mathbf{r}_i$ is a position vector for the ith particle, α is a screening parameter of the charge distribution, $\mathbf{h}_x$ and $\mathbf{h}_y$ are the 2D lattice vectors, and $\mathbf{k}$ is the reciprocal vector. In the first summation in Eq. (1), prime indicates that terms with $i = j$ are omitted when $\mathbf{h}_x + \mathbf{h}_y = \mathbf{0}$. In Eq. (1), V^{r} is the contribution from the real space sum, $V^{\mathrm{k}}_{\mathbf{k}\neq\mathbf{0}}$ and $V^{\mathrm{k}}_{\mathbf{k}=0}$ are contributions from the reciprocal space sums without the $\mathbf{k} = \mathbf{0}$ term and with the $\mathbf{k} = \mathbf{0}$ term, respectively, and V^{s} is the self-correction term. These terms can be expressed as

$$V^{\mathrm{r}} = \frac{1}{2}\sum_{\mathbf{h}_x,\mathbf{h}_y}\sum_{i=1}^{N}\sum_{j=1}^{N}\frac{q_iq_j}{|\mathbf{r}_{ij} + \mathbf{h}_x + \mathbf{h}_y|} \times \mathrm{erfc}\left(\alpha|\mathbf{r}_{ij} + \mathbf{h}_x + \mathbf{h}_y|\right), \tag{2}$$

$$V^{\mathrm{k}}_{\mathbf{k}\neq\mathbf{0}} = \frac{\pi}{2|\mathbf{h}_x \times \mathbf{h}_y|}\sum_{\mathbf{k}\neq\mathbf{0}}\sum_{i=1}^{N}\sum_{j=1}^{N} q_iq_j\frac{\cos\left(\mathbf{k}\cdot\mathbf{r}'_{ij}\right)}{|\mathbf{k}|} \times \left[\mathrm{e}^{|\mathbf{k}|z_{ij}}\,\mathrm{erfc}\left(\frac{|\mathbf{k}|}{2\alpha} + \alpha z_{ij}\right) + \mathrm{e}^{-|\mathbf{k}|z_{ij}}\,\mathrm{erfc}\left(\frac{|\mathbf{k}|}{2\alpha} - \alpha z_{ij}\right)\right], \tag{3}$$

$$V^{\mathrm{k}}_{\mathbf{k}=\mathbf{0}} = -\frac{1}{|\mathbf{h}_x \times \mathbf{h}_y|}\sum_{i=1}^{N}\sum_{j=1}^{N} q_iq_j \times \left\{\frac{\sqrt{\pi}}{\alpha}\mathrm{e}^{-(\alpha z_{ij})^2} + \pi z_{ij}\,\mathrm{erf}\left(\alpha z_{ij}\right)\right\}, \tag{4}$$

$$V^{\mathrm{s}} = \frac{-\alpha}{\sqrt{\pi}}\sum_{i=1} q_i^2, \tag{5}$$

where $\mathbf{r}'_i$ indicates the projection of the position vector $\mathbf{r}_i$ onto the (x,y) plane, z_i is the z component of $\mathbf{r}_i$, and erf and erfc represent the error function and the complimentary error function, respectively.

The forces exerted on the ith particle can be expressed as

$$\left(\mathbf{F}_i^{\mathrm{r}}\right)_\lambda = q_i \sum_{\mathbf{h}_x,\mathbf{h}_y} \sum_{j=1}^{N} q_j \frac{(\mathbf{r}_{ij}+\mathbf{h}_x+\mathbf{h}_y)_\lambda}{\left|\mathbf{r}_{ij}+\mathbf{h}_x+\mathbf{h}_y\right|^3} \times \left\{ \operatorname{erfc}[\alpha(\mathbf{r}_{ij}+\mathbf{h}_x+\mathbf{h}_y)] + \frac{2\alpha}{\sqrt{\pi}} \left|\mathbf{r}_{\mathrm{ij}}+\mathbf{h}_x+\mathbf{h}_y\right| \mathrm{e}^{-[\alpha(\mathbf{r}_{ij}+\mathbf{h}_x+\mathbf{h}_y)]^2} \right\}, \quad (\lambda = x,y,z) \tag{6}$$

$$\left(\mathbf{F}^{\mathrm{k}}_{\mathbf{k}\neq\mathbf{0}\ i}\right)_\lambda = \frac{q_i 2\pi}{\left|\mathbf{h}_x \times \mathbf{h}_y\right|} \sum_{\mathbf{k}\neq 0} \sum_{j=1}^{N} q_j \frac{\sin(\mathbf{k}\cdot\mathbf{r}'_{ij})}{|\mathbf{k}|}(\mathbf{k})_\lambda \times \left[\mathrm{e}^{|\mathbf{k}|z_{ij}} \operatorname{erfc}\left(\frac{|\mathbf{k}|}{2\alpha}+\alpha z_{ij}\right) + \mathrm{e}^{-|\mathbf{k}|z_{ij}} \operatorname{erfc}\left(\frac{|\mathbf{k}|}{2\alpha}-\alpha z_{ij}\right)\right], \quad (\lambda = x,y) \tag{7}$$

$$\left(\mathbf{F}^{\mathrm{k}}_{\mathbf{k}\neq\mathbf{0}\ i}\right)_z = \frac{q_i 2\pi}{\left|\mathbf{h}_x \times \mathbf{h}_y\right|} \sum_{\mathbf{k}\neq 0} \sum_{j=1}^{N} q_j \cos(\mathbf{k}\cdot\mathbf{r}'_{ij}) \times \left[\mathrm{e}^{|\mathbf{k}|z_{ij}} \operatorname{erfc}\left(\frac{|\mathbf{k}|}{2\alpha}+\alpha z_{ij}\right) + \mathrm{e}^{-|\mathbf{k}|z_{ij}} \operatorname{erfc}\left(\frac{|\mathbf{k}|}{2\alpha}-\alpha z_{ij}\right) - \frac{2\alpha}{\sqrt{\pi}}\frac{1}{|\mathbf{k}|} \times \left\{ \exp\left[-|\mathbf{k}|z_{ij} - \left(\frac{|\mathbf{k}|}{2\alpha}-\alpha z_{ij}\right)^2\right] - \exp\left[|\mathbf{k}|z_{ij} - \left(\frac{|\mathbf{k}|}{2\alpha}+\alpha z_{ij}\right)^2\right]\right\}\right], \tag{8}$$

$$\left(\mathbf{F}^{\mathrm{k}}_{\mathbf{k}=\mathbf{0}\ i}\right)_\lambda = 0, \quad (\lambda = x,y), \tag{9}$$

$$\left(\mathbf{F}^{\mathrm{k}}_{\mathbf{k}=\mathbf{0}\ i}\right)_z = \frac{2\pi q_i}{\left|\mathbf{h}_x \times \mathbf{h}_y\right|} \sum_{j=1}^{N} q_j \operatorname{erf}(\alpha z_{ij}), \tag{10}$$

where $\mathbf{F}_i^{\mathrm{r}}$, $\mathbf{F}^{\mathrm{k}}_{\mathbf{k}\neq\mathbf{0}\ i}$, and $\mathbf{F}^{\mathrm{k}}_{\mathbf{k}=\mathbf{0}\ i}$ are derived by differentiating V^{r}, $V^{\mathrm{k}}_{\mathbf{k}\neq\mathbf{0}}$, and $V^{\mathrm{k}}_{\mathbf{k}=\mathbf{0}}$, respectively.

Similar to the 3D Ewald summation, the real space sum in Eqs. (2) and (6) can be implemented by using either the naive double-loop or cell-list techniques [14]. For the reciprocal space sum, calculation by using Eqs. (3), (7) and (8) is computationally intensive, and several researchers have proposed techniques to reduce the complexity of the calculations [7,8]. However, even though those proposed methods are computationally efficient compared to the PHL method, the computational burden of the elaborate algorithm developed by Harris [7] still remains on the order of N^2, and application of the computationally efficient method proposed by Hautman [8] has been limited due to its inherent approximation [10].

In this study, we developed a computationally efficient method with a similar range of applicability as the PHL method. The complex product of the exponential function with the complimentary error function in Eqs. (3), (7) and (8) can be re-expressed by using the Fourier integral as [15]

$$\int_{-\infty}^{\infty} \mathrm{d}h\, \mathrm{e}^{\mathrm{i}hz} \frac{1}{|\mathbf{k}|^2+h^2} \exp\left(-\frac{|\mathbf{k}|^2}{4\alpha^2}\right) = \frac{\pi}{2}\frac{1}{|\mathbf{k}|}\exp\left(\frac{|\mathbf{k}|^2}{4\alpha^2}\right)\left[\mathrm{e}^{|\mathbf{k}|z} \operatorname{erfc}\left(\frac{|\mathbf{k}|}{2\alpha}+\alpha z\right) + \mathrm{e}^{-|\mathbf{k}|z} \operatorname{erfc}\left(\frac{|\mathbf{k}|}{2\alpha}-\alpha z\right)\right]. \tag{11}$$

With this relation, $V^{\mathrm{k}}_{\mathbf{k}\neq\mathbf{0}}$ can be written as

$$V^{\mathrm{k}}_{\mathbf{k}\neq\mathbf{0}} = \frac{1}{\left|\mathbf{h}_x \times \mathbf{h}_y\right|} \sum_{\mathbf{k}\neq 0} \sum_{i=1}^{N} \sum_{j=1}^{N} q_i q_j \exp(-\mathrm{i}\mathbf{k}\cdot\mathbf{r}'_{ij}) \times \exp\left(-\frac{|\mathbf{k}|^2}{4\alpha^2}\right) \times \int_{-\infty}^{\infty} \mathrm{d}h\, \mathrm{e}^{\mathrm{i}hz_{ij}} \frac{1}{|\mathbf{k}|^2+h^2} \exp\left(-\frac{h^2}{4\alpha^2}\right). \tag{12}$$

Rearrangement of Eq. (12) yields

$$V^{\mathrm{k}}_{\mathbf{k}\neq\mathbf{0}} = \frac{1}{\left|\mathbf{h}_x \times \mathbf{h}_y\right|} \sum_{\mathbf{k}\neq 0} \int_{-\infty}^{\infty} \mathrm{d}h \frac{1}{|\mathbf{k}|^2+h^2} \times \exp\left[-\frac{1}{4\alpha^2}\left(|\mathbf{k}|^2+h^2\right)\right] |S(\mathbf{k},h)|^2, \tag{13}$$

where $S(\mathbf{k},h)$ is defined as

$$S(\mathbf{k},h) \equiv \sum_{j=1}^{N} q_j \exp\left[\mathrm{i}(\mathbf{k}\cdot\mathbf{r}'_j + hz_j)\right]. \tag{14}$$

Note that Eq. (13) has the same structure as the reciprocal space sum in the 3D Ewald summation as

$$V^{\mathrm{k}}_{\mathrm{3DES}} = \frac{2\pi}{\mathrm{V}} \sum_{\mathbf{k}'\neq\mathbf{0}} \frac{1}{|\mathbf{k}'|^2} \exp\left[-\frac{|\mathbf{k}'|^2}{4\alpha^2}\right] \left|S_{\mathrm{3DES}}(\mathbf{k}')\right|^2, \tag{15}$$

where $\mathbf{k}'$ is the 3D reciprocal vector, V is the volume of the simulation box, and the structure factor $S_{\mathrm{3DES}}(\mathbf{k}')$ is defined as

$$S_{\mathrm{3DES}}(\mathbf{k}') \equiv \sum_{j=1}^{N} q_j \mathrm{e}^{\mathrm{i}\mathbf{k}'\cdot\mathbf{r}_j} \tag{16}$$

A parameter h is used in Eq. (14) instead of the z component of the 3D reciprocal vector $\mathbf{k}'$ used in Eq. (16), and the summation with respect to the z component of the 3D reciprocal vector in Eq. (15) is replaced with an integration with respect to h in Eq. (13). Comparing Eqs. (3) and (13), for a given reciprocal space vector $\mathbf{k}$, the computational burden in Eq. (3) is proportional to N^2, whereas for the evaluation of $S(\mathbf{k},h)$ in Eq. (13), the computational burden for a given pair of $\mathbf{k}$ and h is proportional to N, and integration with respect to h is also required. The increased computational burden of evaluating the additional integral in Eq. (13) is more than compensated by the reduced computational burden of the N-order dependence in Eq. (13) compared with the N^2-dependence in Eq. (3). Therefore, the expression for $V^{\mathrm{k}}_{\mathbf{k}\neq\mathbf{0}}$ in Eqs. (13) and (14) leads to significant reduction of the computational complexity. The simple expression for $\mathbf{F}^{\mathrm{k}}_{\mathbf{k}\neq\mathbf{0}\,i}$ can be derived by differentiating Eqs. (13) and (14) as,

$$\begin{aligned}\left(\mathbf{F}^{\mathrm{k}}_{\mathbf{k}\neq\mathbf{0}\,i}\right)_\lambda = {} & \frac{2q_i}{|\mathbf{h}_x\times\mathbf{h}_y|} \sum_{\mathbf{k}\neq\mathbf{0}} \mathbf{k}_\lambda \int_{-\infty}^{\infty} \mathrm{d}h \frac{1}{|\mathbf{k}|^2+h^2} \\ & \times \exp\left[-\frac{1}{4\alpha^2}\left(|\mathbf{k}|^2+h^2\right)\right] \\ & \times \left[\sin(\mathbf{k}\cdot\mathbf{r}'_i+hz_i)\sum_{j=1}^{N} q_j\cos(\mathbf{k}\cdot\mathbf{r}'_j+hz_j)\right. \\ & \left. -\cos(\mathbf{k}\cdot\mathbf{r}'_i+hz_i)\sum_{j=1}^{N} q_j\sin(\mathbf{k}\cdot\mathbf{r}'_j+hz_j)\right], \\ & (\lambda = x,y)\end{aligned} \tag{17}$$

$$\begin{aligned}\left(\mathbf{F}^{\mathrm{k}}_{\mathbf{k}\neq\mathbf{0}\,i}\right)_z = {} & \frac{2q_i}{|\mathbf{h}_x\times\mathbf{h}_y|} \sum_{\mathbf{k}\neq\mathbf{0}} \int_{-\infty}^{\infty} \mathrm{d}h \frac{h}{|\mathbf{k}|^2+h^2} \\ & \times \exp\left[-\frac{1}{4\alpha^2}\left(|\mathbf{k}|^2+h^2\right)\right] \\ & \times \left[\sin(\mathbf{k}\cdot\mathbf{r}'_i+hz_i)\sum_{j=1}^{N} q_j\cos(\mathbf{k}\cdot\mathbf{r}'_j+hz_j)\right. \\ & \left. -\cos(\mathbf{k}\cdot\mathbf{r}'_i+hz_i)\sum_{j=1}^{N} q_j\sin(\mathbf{k}\cdot\mathbf{r}'_j+hz_j)\right].\end{aligned} \tag{18}$$

These expressions for $\mathbf{F}^{\mathrm{k}}_{\mathbf{k}\neq\mathbf{0}i}$ significantly reduce the computational complexity of Eqs. (7) and (8) in the PHL method.

For evaluating the reciprocal space sum with the $\mathbf{k}=\mathbf{0}$ term, instead of using Eqs. (4) and (10), using the B-spline interpolation [16] of the Coulomb potential energy and the Coulomb force on a grid in the z direction can lead to a computationally efficient method that is also accurate and of the desired order. The contributions of $V^{\mathrm{k}}_{\mathbf{k}=\mathbf{0}}$ and $(\mathbf{F}^{\mathrm{k}}_{\mathbf{k}=\mathbf{0}\,g})_z$ to the gth grid point ($g=1,\ldots,M$) in the z direction are

$$\begin{aligned}V^{\mathrm{k}}_{\mathbf{k}=\mathbf{0}\,g} = {} & -\frac{1}{|\mathbf{h}_x\times\mathbf{h}_y|}\sum_{j=1}^{N} q_j \left\{\frac{\sqrt{\pi}}{\alpha}\exp\left[-\left(\alpha z_{gj}\right)^2\right]\right. \\ & \left. +\pi z_{gj}\,\mathrm{erf}\left(\alpha z_{gj}\right)\right\},\end{aligned} \tag{19}$$

$$\left(\mathbf{F}^{\mathrm{k}}_{\mathbf{k}=\mathbf{0}\,g}\right)_z = \frac{2\pi}{|\mathbf{h}_x\times\mathbf{h}_y|}\sum_{j=1}^{N} q_j\,\mathrm{erf}\left(\alpha z_{gj}\right). \tag{20}$$

Therefore, the contributions to the Coulomb potential energy and to the force exerted on the ith particle are

$$V^{\mathrm{k}}_{\mathbf{k}=\mathbf{0}} = \sum_{i=1}^{N} q_i B\left[V^{\mathrm{k}}_{\mathbf{k}=\mathbf{0}\,g},\mathbf{r}_i\right], \tag{21}$$

$$\left(\mathbf{F}^{\mathrm{k}}_{\mathbf{k}=\mathbf{0}\,i}\right)_z = q_i B\left[\left(\mathbf{F}^{\mathrm{k}}_{\mathbf{k}=\mathbf{0}\,g}\right)_z,\mathbf{r}_i\right], \tag{22}$$

where $B[f,\mathbf{r}_i]$ is a value of function f at the position of the ith particle, interpolated by using the B-splines. The computational burden of evaluating Eqs. (4) and (10) is proportional to N^2, but through the use of Eqs. (19)–(22), the

computational burden is at most proportional to $N \times M$.

3. Computational efficiency and accuracy

We evaluated the computational efficiency and accuracy of our method and of the PHL method by using a water system in three 3D simulation boxes (cube, quadratic prism, and slab) with 2D periodicity in the (x, y) directions and with non-periodicity in the z direction as shown in Fig. 1. These three boxes are typically used in a wide-range of MD and MC simulations.

The lengths of sides of the simulation box for system 1 were $L_x = L_y = L_z = 3.215$ nm, those of system 2 were $L_x = L_y = 2.229$ nm and $L_z = 6.687$ nm ($= 3 \times L_x$), and those of system 3 were $L_x = L_y = 4.635$ nm and $L_z = 1.545\,\text{nm} = 1/3 \times L_x$). The total number of particles in systems 1, 2, and 3 were 2928, 2955, and 2817, respectively. The TIP3P water model [17] was used in these systems. The intramolecular interactions, such as the 1–2 and the 1–3 interactions, were excluded from the calculations of the real space sum and of the reciprocal space sums with and without the $\mathbf{k} = \mathbf{0}$ term. The initial configurations of the water molecules in the system were randomly generated, and the total energy of each system was minimized by using the steepest-descent algorithm and the conjugate gradient algorithm. The computational efficiency of the PHL method and our method

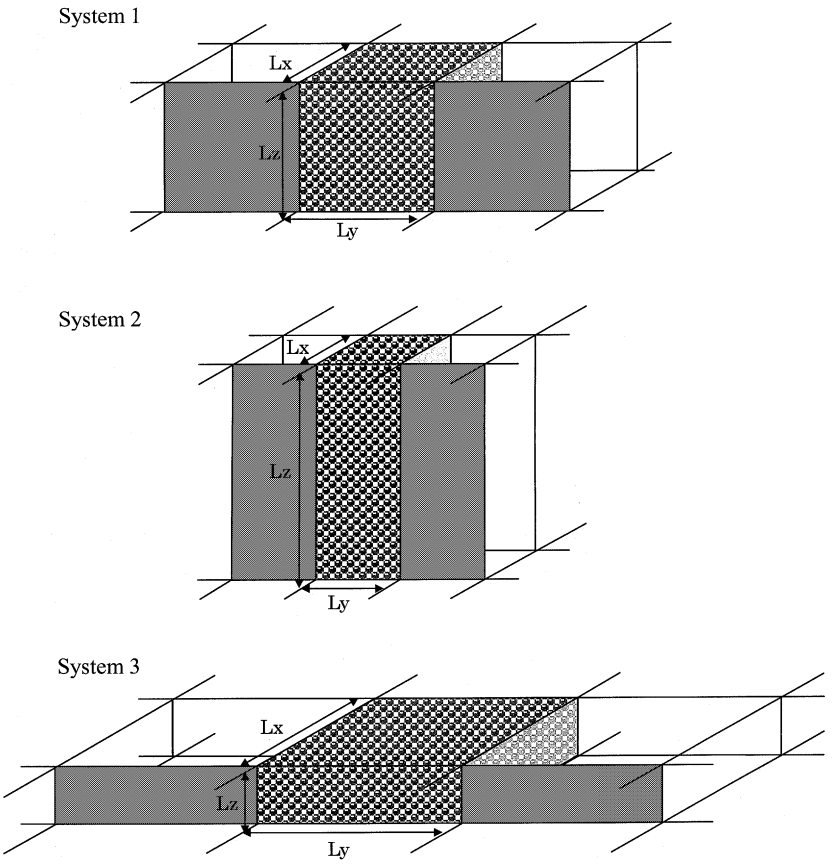

Fig. 1. Three types of 3D simulation boxes with 2D periodicity. Original particles are contained in the central box. L_x, L_y, and L_z are lengths of sides of the box in the x, y, and z directions, respectively. Images of the central box are repeated in the (x, y) plane with non-periodicity in the z direction.

depends on the required accuracy and the set of parameters used. An optimal set of parameters to minimize the CPU time while retaining a given accuracy should be used to make a fair comparison of the performance of the methods. The optimal sets of parameters were determined as follows.

3.1. Optimal set of parameters for the real space sum

The maximum error in the calculation of the force is defined as

$$\Delta\mathbf{F}^{\mathrm{r}}_{\max} = \underset{i=1,\ldots,N}{\mathrm{Max}} \left\{ \underset{\lambda=x,y,z}{\mathrm{Max}} \left[\left| \left(\mathbf{F}^{\mathrm{r}}_i\right)_\lambda - \left(\mathbf{F}^{*\mathrm{r}}_i\right)_\lambda \right| \right] \right\}, \tag{23}$$

and was used to evaluate an optimal set of parameters for the real space sum. In Eq. (23), $\mathbf{F}^{*\mathrm{r}}_i$ is a reference force arising from the real space sum, with a $L_{xy}/2$ cutoff length, where L_{xy} is the length of the sides of simulation box in the x and y directions ($L_{xy} \equiv L_x = L_y$). Parameters affecting Eq. (23) are α and cutoff length in the real space sum, R^{Cutoff}. For each α (increasing from 1.0 to 9.0, in increments of 1.0), R^{Cutoff} (in increments of 0.05 nm) was determined as the minimum value such that $\Delta\mathbf{F}^{\mathrm{r}}_{\max} < 0.4184$ kJ mol^{-1} nm^{-1} ($= 0.01$ kcal mol^{-1} Å^{-1}). If $\Delta\mathbf{F}^{\mathrm{r}}_{\max} \geqslant 0.4184$ kJ mol^{-1} nm^{-1} for a given α, even when the cutoff length was increased to $L_{xy}/2 - 0.05$ nm, α was excluded from the list of optimal pairs of parameters (blank entries in Table 1), because $\mathbf{F}^{*\mathrm{r}}_i$ was not sufficiently accurate to be used as a reference force in the error estimation.

3.2. Optimal set of parameters for reciprocal space sum without $\mathbf{k} = \mathbf{0}$ term

The set of parameters required to evaluate Eqs. (7) and (8) in the PHL method are α and cutoff length in the reciprocal space sum, K^{Cutoff}_{xy} ($\equiv K^{\mathrm{Cutoff}}_x = K^{\mathrm{Cutoff}}_y$) whereas those required to evaluate Eqs. (17) and (18) in our method are α, K^{Cutoff}_{xy}, h^{Cutoff}, and dh, where h^{Cutoff} and dh are the boundary and step-size of the integration in terms of h, respectively. The maximum error in the force from the reciprocal space sum without the $\mathbf{k} = \mathbf{0}$ term is defined as

$$\Delta\mathbf{F}^{\mathrm{k}}_{\mathbf{k}\neq\mathbf{0}\max} = \underset{i=1,\ldots,N}{\mathrm{Max}} \left\{ \underset{\lambda=x,y,z}{\mathrm{Max}} \left[\left| \left(\mathbf{F}^{\mathrm{k}}_{\mathbf{k}\neq\mathbf{0}\,i}\right)_\lambda - \left(\mathbf{F}^{*\mathrm{k}}_{\mathbf{k}\neq\mathbf{0}\,i}\right)_\lambda \right| \right] \right\}, \tag{24}$$

and was used to evaluate an optimal set of parameters, where $\mathbf{F}^{*\mathrm{k}}_{\mathbf{k}\neq\mathbf{0}\,i}$ is a reference force exerted on the ith particle and is calculated for a given α by using the PHL method (i.e., Eqs. (7) and (8)) with a sufficiently large cutoff length in the reciprocal space sum to converge within machine precision. The optimal K^{Cutoff}_{xy} for a given α was determined as the minimum cutoff length such that $\Delta\mathbf{F}^{\mathrm{k}}_{\mathbf{k}\neq\mathbf{0}\max} < 0.4184$ kJ mol^{-1} nm^{-1}, where $\mathbf{F}^{\mathrm{k}}_{\mathbf{k}\neq\mathbf{0}\,i}$ was calculated by using Eqs. (7) and (8). In the search for the optimal set of parameters used in Eqs. (17) and (18), for the given optimal pair of α and K^{Cutoff}_{xy} obtained above, first, h^{Cutoff} was determined as the minimum value such that $\Delta\mathbf{F}^{\mathrm{k}}_{\mathbf{k}\neq\mathbf{0}\max} < 0.418605$ kJ mol^{-1} nm^{-1} for each dh (0.75, 0.50, 0.25, and 0.01, in units of $2\pi/L_z$). Then, for each set of parameters (i.e., α, K^{Cutoff}_{xy}, and h^{Cutoff}), the optimal dh for minimizing the CPU time was determined.

3.3. Optimal set of parameters for the reciprocal space sum with $\mathbf{k} = \mathbf{0}$ term

In the reciprocal space sum with the $\mathbf{k} = \mathbf{0}$ term, the x and y components of the force are zero. Therefore, in the search for the optimal set of parameters, the maximum error in the force was defined as

$$\Delta\mathbf{F}^{\mathrm{k}}_{\mathbf{k}=\mathbf{0}\max} = \underset{i=1,\ldots,N}{\mathrm{Max}} \left[\left| \left(\mathbf{F}^{\mathrm{k}}_{\mathbf{k}=\mathbf{0}\,i}\right)_z - \left(\mathbf{F}^{*\mathrm{k}}_{\mathbf{k}=\mathbf{0}\,i}\right)_z \right| \right]. \tag{25}$$

In Eq. (25), the term $\left(\mathbf{F}^{*\mathrm{k}}_{\mathbf{k}=\mathbf{0}\,i}\right)_z$ was calculated by using Eq. (10) with no cutoff, and the term $\left(\mathbf{F}^{\mathrm{k}}_{\mathbf{k}=\mathbf{0}\,i}\right)_z$ was calculated by using Eqs. (20) and (22). The set of parameters used in Eqs. (20) and (22) were α, the number of grid points in the z direction N_g, and the order of the B-spline interpolation M_{B}. For a given α, first, an optimal pair of N_g and M_{B} was determined to minimize the CPU time while the required accuracy was maintained. Then, a set of parameters (i.e., α, N_g, and M_{B}) yielding a minimum CPU time was chosen as the optimal set.

Table 1 lists the optimal set of parameters for a given system. Blank entries indicate that no

Table 1
Set of parameters to minimize the CPU time with our method, while retaining a given accuracy[a] in the real space sum, and in the reciprocal space sums with and without the $k = 0$ term

α (nm^{-1})	R^{Cutoff} (nm)	$K_{xy}^{Cutoff}/(2\pi/L_{xy})$	$h^{Cutoff}/(2\pi/L_z)$	$dh/(2\pi/L_z)$	N_g	M_B	Total CPU time[b] (s)
System 1							
1.0		3	4	0.5	10	4	
2.0	1.45	5	9	0.5	20	3	2.38[c]
3.0	1.00	8	15	0.5	40	3	5.60
4.0	0.75	12	22	0.5	40	3	16.42
5.0	0.60	15	28	0.5	80	3	33.14
6.0	0.55	19	34	0.5	80	3	68.08
7.0	0.45	21	40	0.5	80	3	90.82
8.0	0.4	25	46	0.5	80	5	148.02
9.0	0.35	28	52	0.5	80	5	210.36
System 2							
1.0		2	6	0.5	20	5	
2.0		4	18	0.5	40	5	
3.0	1.00	6	30	0.5	80	5	6.52[c]
4.0	0.75	8	48	0.5	80	7	16.64
5.0	0.60	11	60	0.5	160	3	38.22
6.0	0.55	13	72	0.5	160	3	63.49
7.0	0.45	15	83	0.5	160	5	97.48
8.0	0.40	17	95	0.5	160	9	141.46
9.0	0.35	19	108	0.5	320	3	202.05
System 3							
1.0		3	3	0.25	10	3	
2.0	1.45	7	8	0.25	10	5	2.86[c]
3.0	1.00	12	14	0.25	20	3	10.53
4.0	0.75	17	20	0.25	20	5	32.79
5.0	0.60	22	26	0.25	40	3	69.29
6.0	0.55	26	33	0.25	40	5	110.71
7.0	0.45	30	37	0.25	40	7	182.37
8.0	0.40	35	43	0.25	80	3	252.90
9.0	0.35	41	50	0.25	80	3	466.69

[a] Maximum error in force was less than 0.4184 kJ mol^{-1} nm^{-1} (= 0.01 kcal $mol^{-1}Å^{-1}$).
[b] CPU time on Compaq Alpha Station XP1000 (Alpha21264 667 MHz).
[c] Optimal set of parameters to minimize total CPU time for each system.

parameters met the error criterion (i.e., maximum error in the forces was less than 0.4184 kJ mol^{-1} nm^{-1}). Forces from the real space sum with $\alpha = 1.0$ for system 1, with $\alpha = 1.0$ and 2.0 for system 2, and with $\alpha = 1.0$ for system 3 did not meet our error criterion. This degradation of the accuracy was due to the simulation box being too small to yield sufficient accuracy. Note that our method used to calculate the reciprocal space sum, i.e., Eqs. (17), (18), (20), and (22), yielded forces sufficiently accurate to meet the error criterion over the entire range of α for all three systems, independent of the shape of the simulation box. Over the entire range of α, the Coulomb potential energies calculated by using our method had the same accuracy as those calculated by using the PHL method.

The total CPU time was a summation of that required for calculating the real space sum and reciprocal space sums with and without the $\mathbf{k} = \mathbf{0}$ term. The overall performance was most affected by the performance of the reciprocal space sum without the $\mathbf{k} = \mathbf{0}$ term. Significant reduction of the CPU time was obtained mainly by decreasing the CPU time required for calculating the reciprocal space sum without the $\mathbf{k} = \mathbf{0}$ term. Although

Table 2
CPU time to calculate the Coulomb interactions for the systems by using the PHL method and our method with the optimal sets of parameters[a,b]

	System 1	System 2	System 3
Number of particles	2928	2955	2817
$L_x = L_y$ (nm)	3.215	2.229	4.635
L_z (nm)	3.215	6.687	1.545
PHL method (s)	1098.29	1455.58	1828.77
Our method (s)	2.38	6.52	2.86

[a] CPU time on Compaq Alpha Station XP1000 (Alpha21264 667 MHz).
[b] Optimal set of parameters for the PHL method (i.e., α, R^{Cutoff}, and K_{xy}^{Cutoff}) was a subset of the optimal set of parameters for our method in Table 1.

the contributions to the Coulomb potential energy and forces from the real space sum and the reciprocal space sum with the $\mathbf{k} = \mathbf{0}$ term were not negligible, the CPU time for these calculations was small compared with that required for calculations of the reciprocal space sum without the $\mathbf{k} = \mathbf{0}$ term. The minimum CPU time to calculate the Coulomb interactions with the given accuracy was determined by taking the set of parameters for which the accuracy of the real space sum first met the error criterion.

Table 2 shows the total CPU time required to implement both the PHL method and our method with the optimal sets of parameters obtained above. For all the systems examined, our method reduced the computational time by an average of 99.73%. The advantage of our method for reducing the computational effort becomes significant when the size of the systems increases. For MD simulations of systems with 2D periodicity and using isobaric ensembles, our method is effective because either the pressure or the virial coefficients can be calculated in a straightforward manner. Furthermore, our formulation of the 2D Ewald summation can be applied to the periodic fast multipole method [18,19] for systems with 2D periodicity.

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References

[1] M.P. Allen, D.J. Tildesley, Computer Simulation of Liquids, Oxford University Press, Oxford, 1989.
[2] P. Ewald, Ann. Phys. Leipzig 64 (1921) 253.
[3] U. Essmann, L. Perera, M.L. Berkowitz, T. Darden, H. Lee, L.G. Pedersen, J. Chem. Phys. 103 (1995) 8577.
[4] D.E. Parry, Surf. Sci. 49 (1975) 433.
[5] D.M. Heyes, M. Barber, J.H.R. Clarke, J. Chem. Soc. Faraday Trans. II 73 (1977) 1485.
[6] S.W. de Leeuw, J.W. Perram, Mol. Phys. 37 (1979) 1313.
[7] F.E. Harris, Int. J. Quantum Chem. 68 (1998) 385.
[8] J. Hautman, M.L. Klein, Mol. Phys. 75 (1992) 379.
[9] S.Y. Liem, H.H.R. Clarke, Mol. Phys. 92 (1997) 19.
[10] A.H. Widmann, D.B. Adolf, Comp. Phys. Commun. 107 (1997) 167.
[11] E. Spohr, J. Chem. Phys. 107 (1997) 6342.
[12] I. Yeh, M.L. Berkowitz, J. Chem. Phys. 111 (1999) 3155.
[13] P.S. Crozier, R.L. Rowley, E. Spohr, D. Henderson, J. Chem. Phys. 112 (2000) 9253.
[14] R.W. Hockney, J.W. Eastwood, Computer Simulation Using Particles, IOP Publishing Ltd, London, 1989.
[15] A. Erdelyi, Tables of Integral Transforms, vol. I, McGraw-Hill Book Company, New York, 1954.
[16] L.L. Schumaker, Spline functions: Basic theory, Krieger Publishing Company, Florida, 1993.
[17] W.L. Jorgensen, J. Chandrasekhar, J.D. Madura, R.W. Impey, M.L. Klein, J. Chem. Phys. 79 (1983) 926.
[18] L. Greengard, V.I. Rokhlin, J. Comp. Phys. 73 (1987) 325.
[19] F. Figueirido, R.M. Levy, R. Zhou, B.J. Berne, J. Chem. Phys. 106 (1997) 9835.