

Ewald summation for systems with slab geometry

In-Chul Yeh and Max L. Berkowitz^{a)}

Department of Chemistry, CB# 3290, University of North Carolina, Chapel Hill, North Carolina 27599

(Received 25 March 1999; accepted 21 May 1999)

We propose a modification in the three-dimensional Ewald summation technique for calculations of long-range Coulombic forces for systems with a slab geometry that are periodic in two dimensions and have a finite length in the third dimension. The proposed method adds a correction term to the standard Ewald summation formula. To test the current method, molecular dynamics simulations on water between Pt(111) walls have been carried out. For a more direct test, the calculation of the pair forces between two point charges has been also performed. An excellent agreement with the results from simulations using the rigorous two dimensional Ewald summation technique were obtained. We observed that a significant reduction in computing time can be achieved when the proposed modification is used. © 1999 American Institute of Physics. [S0021-9606(99)70331-4]

I. INTRODUCTION

An accurate treatment of long-range Coulombic interactions in computer simulations of charged particles is of great importance. For a typical three-dimensionally periodic system, the Ewald summation technique^{1,2} is the most widely used and accepted method for this purpose. Extensive optimization techniques such as the smooth particle mesh Ewald (PME) method^{3,4} have been developed to perform fast and reliable simulations of large systems using Ewald summation.

For a slab geometry which occurs frequently in surface and interfacial systems, the conventional Ewald summation technique cannot be used directly since there is no periodicity in the one of three dimensions (let us say along the z direction). For this type of two-dimensionally periodic (2DP) systems which have a finite length along the third dimension, various methods have been proposed for the treatment of long-range forces.⁵⁻¹⁷ Recently, some of the methods have been compared to each other in terms of computational speed and accuracy.^{16,17} A two-dimensional Ewald summation (EW2D) technique first introduced by Parry⁵ and later independently rederived by Heyes, Barber, and Clarke⁶ and by de Leeuw and Perram⁷ is found to be the most accurate. But the direct use of EW2D formula is known to be computationally very expensive.^{8,16,17} A simple solution to this problem is to use a precalculated table.⁸ The EW2D method with a precalculated table has been successfully applied in our recent simulation studies of water next to metal surfaces.¹⁸⁻²⁰ Another widely used approach is to apply the conventional three-dimensional Ewald summation (EW3D) technique to a simulation cell elongated in z direction so that a sufficiently large empty space between periodic replicas in z direction is created.²¹ The inclusion of empty space into the unit cell is done to avoid an artificial influence from the periodic images in z direction. This method was applied to simulations of various interfacial systems.²²⁻²⁴

Shelley and Patey²¹ studied the effect of boundary con-

ditions for water confined between planar walls. They compared various boundary conditions such as minimum image, spherical and cylindrical cutoffs with the Ewald summation method. The Ewald summation was found to be the safest choice in the calculation. Systems considered in their study were symmetric and, therefore, the possible effect of asymmetry and net polarization of the system on the Ewald summation was not considered. Spohr⁸ compared the results from the simulations that used EW3D method with those from the EW2D method. He concluded that results for EW3D converge to those for EW2D when the length of the simulation cell in z direction (L_z) used in simulations with EW3D was large. At the same time he noticed that even when L_z was five times larger than the length of the simulation cell in x or y directions (L_x or L_y , respectively), the convergence was not satisfactory.

Recently, there has been a renewed interest in the treatment of long-range forces in polar systems or systems carrying a net charge.²⁵⁻²⁹ A better understanding of conditions under which Ewald summation is performed followed from this work. Still one issue that may be important even for some systems that are charged neutral, but have a total dipole moment, remains not clear. The issue is the use of the surface term in the EW3D formula, the term that depends on the shape of the system, its total dipole moment and the dielectric constant of the surrounding medium.^{1,28-31} The surface term is due to the fact that the electrostatic energy of the ionic crystal is composed of two parts. First part is shape-independent but depends on the structure of the crystal lattice concerned and the distribution of ions within a unit cell. Second part depends on the shape of the piece of the crystal and the dipole moment of a unit cell. The expression for the shape-independent part of energy has the same mathematical form as in the regular EW3D formula. Smith³² derived an expression for the shape-dependent part suitable for the slab geometry, which is of particular interest here.

In this study we propose that an EW3D method which includes the shape-dependent correction term introduced by Smith³² can be used for the calculation of the long-range electrostatic forces in simulations of 2DP systems. To distin-

^{a)}Electronic mail: maxb@net.chem.unc.edu

guish it from the regular EW3D method, it will be abbreviated as EW3DC (the three-dimensional Ewald summation with the correction term). This term is similar to the surface term in the standard EW3D formula but has a different proportionality factor and involves only the z component of the total dipole moment. As far as we know, the only attempt to include this correction term was done in a simulation on water between two ideal classical walls performed by Hautman *et al.*¹⁰ No detailed comparison with the rigorous EW2D has been made in that work.

To test the EW3DC method we performed simulations on water next to the charged Pt(111) walls. Recently, we used this system to calculate the dielectric constant of water at high electric fields.¹⁹ The long-ranged forces were treated using the EW2D method in these simulations. Below we compare the results from the simulations performed with the EW3DC method to those obtained with the EW2D method. For more detailed comparison, test calculations involving only two point charges also have been carried out. By adding the extra correction term in the EW3D formula, both accuracy and speed of the calculation are shown to be greatly improved.

II. ELECTROSTATIC INTERACTIONS

Consider a system of N point charges q_i at positions \mathbf{r}_i which satisfy the charge neutrality condition $\sum_i^N q_i = 0$ in a rectangular simulation cell with lengths in x , y , and z directions of L_x , L_y , and L_z , respectively.

The electrostatic energy can be written as

$$U = \frac{1}{2} \sum_{\mathbf{n}} \sum_{i=1}^N \sum_{j=1}^N \frac{q_i q_j}{|\mathbf{r}_{ij} + \mathbf{n}|}, \quad (1)$$

where the sum over \mathbf{n} is the sum over all lattice points, $\mathbf{n} = (n_x L_x, n_y L_y, n_z L_z)$ with n_x, n_y, n_z integers. The primed sum indicates the omission of the $i=j$ term when $\mathbf{n} = \mathbf{0}$. The factor $1/(4\pi\epsilon_0)$ is omitted for simplicity (ϵ_0 is the vacuum permittivity). This sum is conditionally convergent, which means that the result depends on the order or the summation geometry in which we add up the terms. The outcome is also dependent on the dielectric constant of the surrounding medium (ϵ_s). The electrostatic energy calculated by the Ewald sum is given by^{1,2,32}

$$U = \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N \sum_{|\mathbf{n}|=0}^{\infty} \frac{q_i q_j \operatorname{erfc}(\alpha|\mathbf{r}_{ij} + \mathbf{n}|)}{|\mathbf{r}_{ij} + \mathbf{n}|} + \frac{1}{2\pi V} \sum_{i=1}^N \sum_{j=1}^N \sum_{\mathbf{k} \neq \mathbf{0}} q_i q_j \left(\frac{4\pi^2}{k^2} \right) \exp\left(-\frac{k^2}{4\alpha}\right) \times \cos(\mathbf{k} \cdot \mathbf{r}_{ij}) - \frac{\alpha}{\sqrt{\pi}} \sum_{i=1}^N q_i^2 + J(\mathbf{M}, P). \quad (2)$$

$J(\mathbf{M}, P)$ is a shape-dependent term and depends on the summation geometry (P).³² \mathbf{M} is the total dipole moment of the unit simulation cell and is given by $\sum_{i=1}^N q_i \mathbf{r}_i$. V is the volume of the unit simulation cell given by $L_x \times L_y \times L_z$ and \mathbf{k} is a reciprocal lattice vector given by $((2\pi n'_x)/L_x, (2\pi n'_y)/L_y, (2\pi n'_z)/L_z)$ with n'_x, n'_y, n'_z inte-

gers. In the calculations α and number of \mathbf{n} and \mathbf{k} vectors are adjustable parameters and are typically chosen for the optimum computational efficiency.

When the spherical geometry is used for summation ($P = S$), $J(\mathbf{M}, S)$ is given by the following relation:^{2,25,32}

$$J(\mathbf{M}, S) = \frac{2\pi}{(2\epsilon_s + 1)V} |\mathbf{M}|^2. \quad (3)$$

If the surrounding medium has an infinite dielectric constant ($\epsilon_s = \infty$, metal), $J(\mathbf{M}, S)$ vanishes. This boundary condition is commonly called conducting ("tinfoil") boundary condition. If ϵ_s has a finite value, this term cannot be simply ignored. In particular, if there is no surrounding medium ($\epsilon_s = 1$, vacuum), this term becomes

$$J(\mathbf{M}, S) = \frac{2\pi}{3V} |\mathbf{M}|^2. \quad (4)$$

The contribution to the force from this term is

$$\mathbf{F}_i = -\nabla_i J(\mathbf{M}, S) = -\frac{4\pi q_i}{3V} \mathbf{M}. \quad (5)$$

Clearly, this term is not necessarily zero especially when there is a net polarization in the simulation cell ($\mathbf{M} \neq \mathbf{0}$). It can be ignored if the system is isotropic, $\mathbf{M} = \mathbf{0}$. Ignoring this term is equivalent to adopting the tinfoil boundary condition. Implications of adopting tinfoil boundary condition in place of vacuum boundary condition for polar systems have been discussed by Roberts and Schnitker.^{30,31}

The total Coulomb energy for a system periodic in two dimensions and finite in the third dimension according to the EW2D method is

$$U = \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N \sum_{|\mathbf{m}|=0}^{\infty} \frac{q_i q_j \operatorname{erfc}(\alpha|\mathbf{r}_{ij} + \mathbf{m}|)}{|\mathbf{r}_{ij} + \mathbf{m}|} + \frac{\pi}{2A} \sum_{i=1}^N \sum_{j=1}^N \sum_{\mathbf{h} \neq \mathbf{0}} q_i q_j \frac{\cos(\mathbf{h} \cdot \mathbf{r}_{ij})}{h} \times \left\{ \exp(hz_{ij}) \operatorname{erfc}\left(\alpha z_{ij} + \frac{h}{2\alpha}\right) + \exp(-hz_{ij}) \operatorname{erfc}\left(-\alpha z_{ij} + \frac{h}{2\alpha}\right) \right\} - \frac{\pi}{A} \sum_{i=1}^N \sum_{j=1}^N q_i q_j \left\{ z_{ij} \operatorname{erf}(\alpha z_{ij}) + \frac{1}{\alpha\sqrt{\pi}} \exp(-\alpha^2 z_{ij}^2) \right\} - \left(\frac{\alpha}{\sqrt{\pi}} \right) \sum_{i=1}^N q_i^2, \quad (6)$$

where \mathbf{m} is a lattice vector for the 2DP system and is given by $(m_x L_x, m_y L_y, 0)$ with m_x, m_y integers. \mathbf{h} is a reciprocal lattice vector for the 2DP system and is given by $((2\pi m'_x)/L_x, (2\pi m'_y)/L_y, 0)$ with m'_x, m'_y integers. A is the area of the unit cell in x and y directions given by $L_x \times L_y$. The primed sum again indicates the omission of the $i=j$ term when $\mathbf{m} = \mathbf{0}$.

If two particles with charges q_i and q_j are sufficiently apart in z direction and are periodically repeated in x and y directions, the electric field acting on the particle i due to

particle j can be considered as that due to the uniformly charged sheet with a surface charge density $\sigma = q_j / (L_x L_y)$ and is given by^{8,33}

$$E_j = \frac{\sigma}{2\epsilon_0} = \frac{q_j}{2\epsilon_0 L_x L_y} \quad (7)$$

The x , y , and z components of the force are given by the following expression:⁸

$$F_x = F_y = 0, \quad (8)$$

$$F_z = \frac{q_i q_j}{2\epsilon_0 L_x L_y}. \quad (9)$$

By using the EW2D formula, Spohr⁸ found that the above ‘‘parallel plate capacitor’’ approximation can be used with a sufficient accuracy (relative error less than 0.001) if the z separation distance between particles i and j ($|z_{ij}|$) is larger than L_x or L_y . The important feature of this approximation is that no $|z_{ij}|$ distance dependency appears in the formulas. Therefore, if there is an empty space in the EW3D simulation cell along the z direction with a length of at least L_x or L_y , contributions to the forces from the image cells in z direction should be negligible due to the neutrality of the system ($\sum_j^N E_j = (1/2\epsilon_0 L_x L_y) \sum_j^N q_j = 0$). Nevertheless, the comparison between the results from simulations using EW3D and EW2D methods shows that the EW3D method produces unsatisfactory results even when the length of the empty space in z direction is significantly larger than L_x or L_y .⁸ This apparent contradiction suggests that the Ewald summation using tinfoil boundary condition and spherical summation geometry which is commonly used in the Ewald summation may not be suitable for the calculation in the slab geometry.

Smith³² showed that if a geometry of a rectangular plate ($P=R$) or disk which are infinitely thin in z direction are used as a summation geometry in the Ewald summation, then the shape-dependent term $J(\mathbf{M}, R)$ is given by

$$J(\mathbf{M}, R) = \frac{2\pi}{V} M_z^2, \quad (10)$$

where M_z is the z component of the total dipole moment of the simulation cell. This is equivalent to adopting a plane-wise sum method³⁴ (summing x and y directions first then progressing in z direction). The contribution to the force from this term is

$$F_{x,i} = F_{y,i} = 0, \quad (11)$$

$$F_{z,i} = -\frac{\partial J(\mathbf{M}, R)}{\partial z_i} = -\frac{4\pi q_i}{V} M_z. \quad (12)$$

Note that Eqs. (5) and (12) differ by a factor of 3 and that only the z component of the dipole moment appears in Eq. (12). The planewise sum combined with a sufficient empty space in z direction enables us effectively utilize the parallel plate capacitor approximation to eliminate contributions from image cells in z direction which are unwanted in 2DP systems. Therefore, we can use the regular EW3D method but with the correction term given by the Eq. (12) to calculate long-range Coulombic forces for systems which are

periodic in two dimensions and are finite in the third. This constitutes the EW3DC method which as we show in what follows is indeed capable of reproducing the EW2D results.

III. METHODOLOGY

For simulations of water between Pt(111) walls, we use the same interaction potentials that we used in our previous studies,^{18,19,35} namely, the extended simple point charge (SPC/E) model of water³⁶ and water–Pt(111) surface potential.³⁷

A rectangular prism is chosen for the unit cell of the simulations. L_x and L_y of 22.175 and 19.204 Å, respectively, have been used to satisfy the periodicity requirement of Pt(111) surface. Simulations are performed for 512 water molecules in the unit simulation cell. Water molecules are confined in z direction by Pt(111) walls and the density of water at the center of the simulation cell is 1.0 g/cc. This is achieved by changing the value of a parameter z_m in water–Pt(111) potential.³⁷ External electric fields (E_0) of 0–4 V/Å are applied along the z direction.

For the calculation of long-range Coulombic interactions we have used EW2D, EW3D, and EW3DC methods. For EW3D and EW3DC calculations, three-dimensional periodic boundary conditions were applied. L_z was chosen to be 90 Å which is approximately four times larger than L_x . Ewald parameter α of 0.3 Å⁻¹ was used. As customary in the EW3D method, only minimum image ($|\mathbf{n}|=0$) was considered with the real space cut-off radius of 9.5 Å. The reciprocal space cut-off radius of 1.75 Å⁻¹ has been used.

Since the reciprocal space term in the EW2D is computationally very expensive, it is advantageous to have less terms for the reciprocal space part and more terms for the real space part. Therefore, for the EW2D calculation, the parameter α was chosen to be 0.104 Å⁻¹ and the real space terms which satisfy the condition $m_x^2 + m_y^2 \leq 4$ and the reciprocal space terms which satisfy $m_x'^2 + m_y'^2 \leq 9$ have been considered. The direct use of the EW2D formula is so time consuming that a precalculated table of potential energy, forces and second derivatives on a three-dimensional grid with the size of $0.2 \times 0.2 \times 0.2$ Å³ has been constructed as suggested by Spohr.⁸ The EW2D calculations have been performed by interpolation of the table. For smaller distances ($r_{ij} < 3.3$ Å), the exact EW2D formula has been used. For $|z_{ij}| > L_y$, the parallel plate capacitor approximation given in Eqs. (8) and (9) has been utilized.

The Verlet algorithm has been used to propagate the trajectories with a time step of 2.5 fs and SHAKE routine has been used to preserve the rigidity of the water molecules.¹ The coordinates were saved at every 10 time steps for further analysis. The temperature of the run was kept at 300 K by coupling the system to the heatbath using the algorithm of Berendsen *et al.*³⁸ 200 ps run after at least 50 ps equilibration has been used for the analysis.

In our previous work¹⁹ where we determined the dielectric constant of water as a function of the electric field we performed simulations on water lamina embedded between two surfaces. To find the value of the dielectric constant we needed to calculate the total electric field inside the lamina.

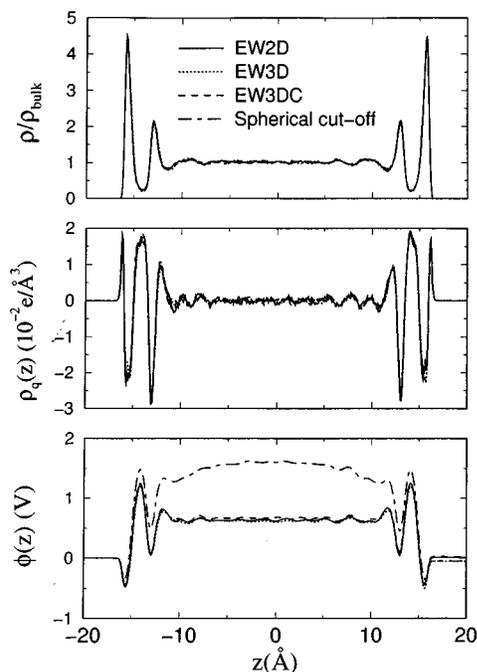


FIG. 1. Comparison of simulation results for water between Pt(111) walls at zero external electric field obtained by using different methods to treat the long-range forces. Top: Oxygen density distributions. Middle: Charge density distributions. Bottom: Electrostatic potential.

This total electric field [$E(z)$] was obtained using the following relation:

$$E(z) = E_0 + E_p(z), \quad (13)$$

where $E_p(z)$ is the electric field due to orientational polarization of water sample and is given by the following expression:^{39,40}

$$E_p(z) = \frac{\int_{-L_z}^z \rho_q(z') dz'}{\epsilon_0}, \quad (14)$$

where $\rho_q(z)$ is a charge density distribution.

The relative permittivity (dielectric constant ϵ) of water in the external electric field E_0 and the total electric field E can be obtained from the following equation:

$$\epsilon = \frac{E_0}{E}. \quad (15)$$

To find the permittivity we calculated the total field in the vicinity of the center of the slab. In previous simulation studies on water–Pt interface it was found that the influence of the walls on the orientational distributions of water is almost absent for water about 10 Å away from the closest approach of the water molecule to the Pt wall.^{18,35} Therefore, it is expected that water–wall interaction has no influence on the estimate of E when using the current method. To estimate the total electric field E around the center of the sample cell, 10 Å interval averages have been taken across the sample cell in the z direction. Then to eliminate any local fluctuation of the electric field around the center, further 5 Å interval averages were taken. The resulting average electric field at

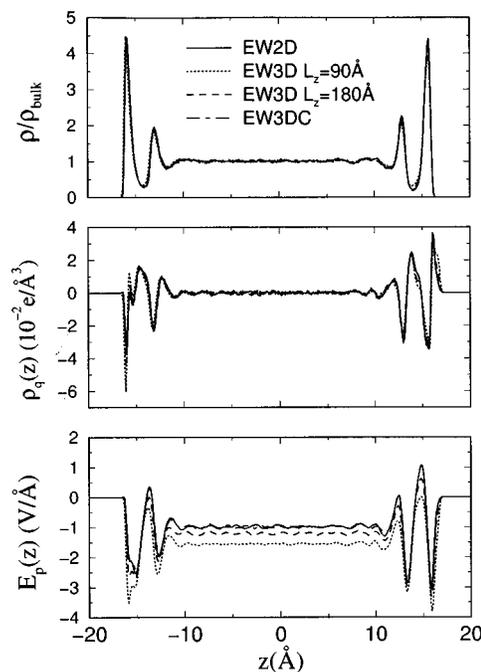


FIG. 2. Comparison of simulation results for water between Pt(111) walls at E_0 of 1.0 V/Å calculated by different Ewald methods. Top: Oxygen density distributions. Middle: Charge density distributions. Bottom: Electric field E_p calculated by Eq. (14).

$z=0$ (the center of the simulation cell) is taken to be the total electric field E that enters the equation determining the dielectric constant.

The electrostatic potential (ϕ) has been calculated by the following equation:

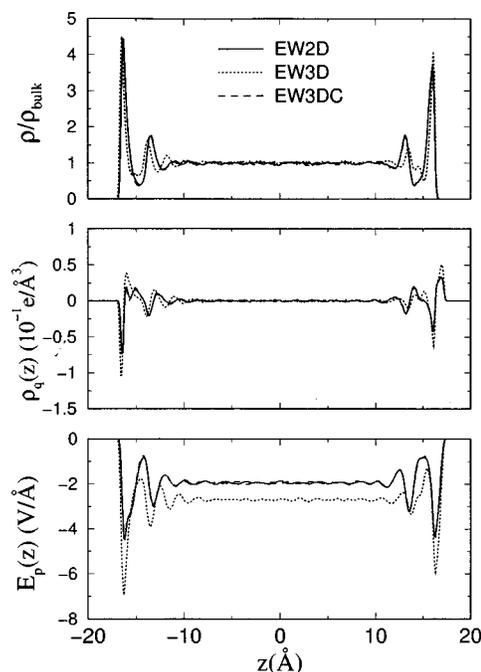


FIG. 3. Comparison of simulation results for water between Pt(111) walls at E_0 of 2.0 V/Å calculated by different Ewald methods. Top: Oxygen density distributions. Middle: Charge density distributions. Bottom: Electric field E_p calculated by Eq. (14).

TABLE I. The “effective” external electric field E'_0 and total electric field E for water between Pt(111) walls calculated by the EW3D method. Units of $\langle E_p \rangle$ and $(4\pi\langle M_z \rangle)/V$ are V/Å. Errors in parentheses are estimated from standard deviations of the results of four consecutive 50 ps runs.

E_0 (V/Å)	L_z (Å)	$\langle E_p \rangle$	$(4\pi\langle M_z \rangle)/V$	$E'_0 = E_0 + (4\pi\langle M_z \rangle)/V$	$E = E'_0 + \langle E_p \rangle$
1	180	-1.2060(±0.0006)	0.2257(±0.0004)	1.2257(±0.0004)	0.020(±0.001)
1	90	-1.5535(±0.0054)	0.5860(±0.0009)	1.5860(±0.0009)	0.032(±0.006)
2	90	-2.7025(±0.0032)	1.0511(±0.0005)	3.0511(±0.0005)	0.349(±0.004)
3	90	-2.9429(±0.0008) ^a	1.1535(±0.0005)	4.1535(±0.0005)	1.211(±0.001)

^aThe average is taken over the 10.6 Å interval to take into account the periodic structure in z direction introduced by the phase transition.

$$\phi(z) = -\frac{1}{\epsilon_0} \int_{-L_z/2}^z \rho_q(z')(z-z') dz', \quad (16)$$

where ρ_q is the charge density.

IV. RESULTS AND DISCUSSION

A. Water–Pt(111) interface

Oxygen density profiles, charge density distributions, and electrostatic potential profiles for water between Pt(111) walls at zero external electric field calculated with different methods to treat the long-ranged Coulombic forces (EW2D, EW3D, EW3DC, and the spherical cutoff) are compared in Fig. 1. For the spherical cutoff method, all the interactions with the distance larger than the cutoff radius of 9.5 Å are ignored. Oxygen density profiles and charge density distributions are almost identical regardless of methodology. But the value of the electrostatic potential at the center of the lamina calculated with spherical cutoff is significantly larger than when other methods are used. This is consistent with the results from previous simulation studies.^{8,24} This result shows that the spherical cutoff should be avoided even for a symmetric system. Therefore the spherical cutoff results are not considered any longer in the following comparisons. The electrostatic potential profiles calculated with EW2D is in good agreement with those obtained by EW3D and EW3DC. The correction term has very little influence on the calculation results since the system is symmetric in z direction and there is no net dipole moment in z direction ($M_z = 0$). From Fig. 1 we also notice that for the value of $L_z = 90$ Å an empty spacing with a length in z direction of at least 56 Å exists in the system, which is about 2.5 L_x .

Figure 2 shows oxygen density profiles, charge density distributions, electric field profiles for water between Pt(111) walls at $E_0 = 1$ V/Å when we use EW2D, EW3D, and EW3DC methods. For the EW3D calculations, two different values of L_z (90 and 180 Å) have been used to see the effect of the value of L_z . Oxygen density profiles show very little difference. The charge density distribution in the water lamina obtained from simulations with the EW3D method are significantly different from those obtained by EW2D and EW3DC methods. A good agreement between the results by EW2D and EW3DC methods has been found. Due to the difference in the charge density distributions obtained from simulations that use EW2D and EW3D methods, the corresponding $E_p(z)$ distributions are also different. From the figure we notice that around bulk region ($-5 \text{ Å} < z < 5 \text{ Å}$), the

field E' , which is the sum of two components $E' = E_p + E_0$, has a negative value when EW3D method is used. While in simulations of the lamina using EW2D method E' would be the total field, since it is negative in simulations with EW3D it indicates that overcompensation of the external field E_0 occurred in this case. This type of overcompensation of the electric field in thermodynamically stable system is highly unlikely and it is a consequence of an improper treatment of electrostatic forces using the EW3D method without considering the slab geometry. Imposing tinfoil boundary condition and thus neglecting the correction term seem to introduce an extra external electric field contribution in addition to the initially assigned value of E_0 . As a matter of fact, using Eq. (12) the external field E'_0 that molecules of water experience in simulations which employ the EW3D method can be estimated by the following relation:

$$E'_0 = E_0 + \frac{4\pi\langle M_z \rangle}{V}, \quad (17)$$

where $\langle M_z \rangle$ is the average of the z -component of the dipole moment of the sample. The second term in this equation is the contribution due to images of the lamina from the central cell. Figure 3 shows results similar to the one from Fig. 2, but for E_0 of 2 V/Å. Again, the result from EW3D without the correction term deviates significantly from that of EW2D, while the result from EW3DC agrees well with that from EW2D.

Simulations at E_0 of 3 and 4 V/Å have been also carried out. In our recent simulations on water–Pt(111) interface, a phase transition to proton ordered cubic ice was observed when E_0 was somewhere between 3 and 4 V/Å with the EW2D method^{18,19} and between 2 and 3 V/Å with the EW3D method.³⁵ In this study, a phase transition to a proton ordered cubic ice has been observed in a region between 3 and 4 V/Å with EW3DC. This again confirms that water feels stronger “effective” external electric field when EW3D is used, resulting in a lower critical E_0 for a phase transition. Table I presents a summary of the results for the calculations done on water lamina in the external electric field when EW3D is used. This table shows that the data are consistent with the previously obtained results. Thus, for example, in calculations with EW3D when the external field E_0 is 3 V/Å the effective external field E'_0 is actually ~ 4.15 V/Å and the total field E is 1.21 V/Å. As our previous simulations showed,¹⁹ for water to undergo the transition, the total field is supposed to be somewhat smaller than 1 V/Å. This is why

TABLE II. The dielectric constant ϵ and $\langle \cos \theta_{\mu, \mathbf{E}_0} \rangle$ for water between Pt(111) walls. $\theta_{\mu, \mathbf{E}_0}$ is the angle between a water dipole μ and the direction of the external electric field \mathbf{E}_0 . Errors in parentheses are estimated from standard deviations of the results of four consecutive 50 ps runs.

E_0 (V/Å)	Method	ϵ	$\langle \cos \theta_{\mu, \mathbf{E}_0} \rangle$
1	EW2D	59.9(± 11)	0.330(± 0.001)
1	EW3DC	67.5(± 7.1)	0.329(± 0.001)
2	EW2D	38.1(± 1.3)	0.664(± 0.002)
2	EW3DC	37.1(± 1.7)	0.664(± 0.002)
3	EW2D	9.2(± 0.1)	0.905(± 0.001)
3	EW3DC	9.3(± 0.1)	0.907(± 0.002)

the phase transition was observed in a field with E_0 below 3 V/Å when the EW3D method was used.

We also calculated ϵ by Eq. (15) and average $\cos \theta_{\mu, \mathbf{E}_0}$ ($\langle \cos \theta_{\mu, \mathbf{E}_0} \rangle$) where $\theta_{\mu, \mathbf{E}_0}$ is the angle between a water dipole μ and the direction of the external electric field \mathbf{E}_0 . Values for ϵ and $\langle \cos \theta_{\mu, \mathbf{E}_0} \rangle$ obtained by using EW2D and EW3DC have been compared in Table II. An excellent agreement has been observed.

B. Forces between two particles

Calculation of the pair forces is the most direct and accurate measure to compare different methods for the treatment of long-range forces.^{8,16,17} Spohr⁸ compared the pair forces calculated by EW2D and EW3D. He attributed the deviations of the EW3D results from the EW2D results to the coupling between the periodic replicas of the interface.

The same geometry of the simulation cell used in Spohr's work has been used here ($L_x = L_y = 18$ Å and $L_z = 3 \times L_x$ or $5 \times L_x$). α of 0.45 Å⁻¹ and the reciprocal space cut off radius of 5.0 Å⁻¹ have been used. The parameters have been chosen for better accuracy because we want to eliminate any unwanted error due to numerical artifacts when we compare the results for the EW2D and EW3D. The choice of parameters could be relaxed for better computational efficiency. For the EW2D calculation, the parameter α was chosen to be 0.111 Å⁻¹ and the real space terms which

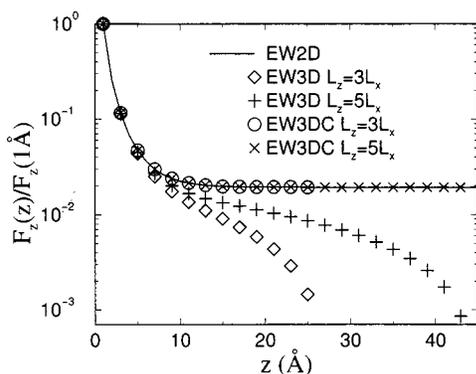


FIG. 4. Comparison of the z component of the force acting on the unit point charge at $(0,0,z)$ by another oppositely charged unit point charge fixed at $(0,0,0)$ in two-dimensionally periodic systems calculated by different Ewald methods. The logarithmic scale is used for better comparison with the result in Spohr's work (Ref. 8).

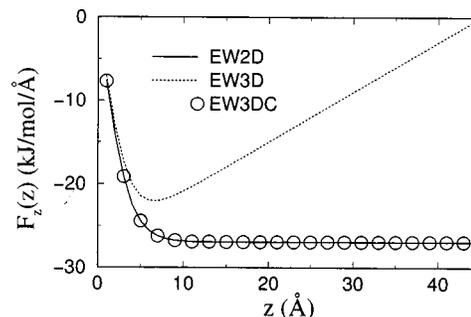


FIG. 5. Comparison of the z component of the force acting on the unit point charge at $(4.5$ Å, 4.5 Å, $z)$ by another oppositely charged unit point charge fixed at $(0,0,0)$ in two-dimensionally periodic systems calculated by different Ewald methods.

satisfy the condition $m_x^2 + m_y^2 \leq 4$ and the reciprocal space terms which satisfy $m_x'^2 + m_y'^2 \leq 9$ have been considered.

We calculated the pair forces between two oppositely charged unit point charges at $(0,0,0)$ and $(0,0,z)$ using EW2D, EW3D, and EW3DC methods. z changes from 0 to about $L_z/2$ in our tests. This type of arrangement of charges is also used in Spohr's work⁸ and creates a dipole moment in z direction. The results are shown in Fig. 4. The deviations of the EW3D results without the correction term from the EW2D results reported in Spohr's work⁸ have been reproduced. At the same time the results from the EW3DC are almost identical to the EW2D results. It is to be noted that there are empty spaces with lengths of at least $1.5 \times L_x$ and $2.5 \times L_x$ in z direction for L_z of $3 \times L_x$ and $5 \times L_x$, respectively, for the results shown in Fig. 4. This clearly shows that to use EW3D in 2DP systems, the empty space need not be huge but the correction term should be included.

Figure 5 shows the pair forces experienced by two oppositely charged unit point charges at $(0,0,0)$ and $(4.5$ Å, 4.5 Å, $z)$. For EW3D and EW3DC calculations, L_z of $5 \times L_x$ (90 Å) has been used. z again changes from 0 to $L_z/2$. This type of arrangement of charges creates a dipole moment not only in z direction but also in x and y directions. The z components of forces are shown and an excellent agreement between EW2D and EW3DC results is evident. Note that even for the cases when M_x and M_y are not zero, the correction term [Eq. (12)] which involves only M_z is sufficient.

Figure 6 considers a rather extreme case when there is a

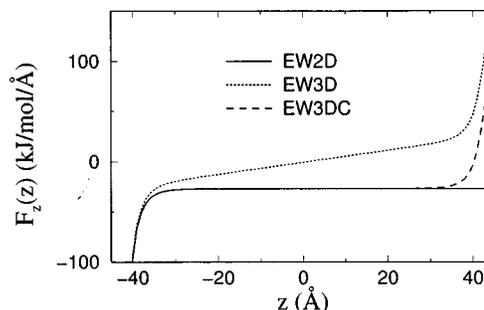


FIG. 6. Comparison of the z component of the force acting on the unit point charge at $(0,0,z)$ by another oppositely charged unit point charge fixed at $(0,0,-44$ Å) in two-dimensionally periodic systems calculated by different Ewald methods.

TABLE III. Comparison of computing times per time step calculated by EW2D and EW3DC methods.

Method	Time (s)
EW2D	59.9
EW2D (optimized)	18.1
EW2D (table)	7.52
EW3DC	0.71

very little empty space between periodic replicas in z direction. Forces between two oppositely charged unit point charges at $(0,0,-44 \text{ \AA})$ and $(0,0,z)$ are calculated. z is changed from -43 to 44 \AA . L_z used in EW3D and EW3DC is 90 \AA , which means that one of the charges is fixed near the end of the simulation cell in z direction at $(0,0,-44 \text{ \AA})$. Figure 6 shows that the result from EW3D without the correction term deviates from the EW2D result in almost the entire range of z values. The result from EW3DC agrees well with EW2D result for z values up to $\sim 28 \text{ \AA}$ where interaction with the adjacent charges in periodic replicas in z direction are beginning to dominate the interaction force. At $z = 28 \text{ \AA}$, an empty space with a length of L_x in z direction is present in the box. This shows that to get good numerical results, there should be an empty space at least with a length of L_x or L_y even when EW3DC is used.

C. Speed and accuracy

Computational speeds of the direct use of the EW2D formula, the EW2D method with a precalculated table and the EW3DC calculations have been checked for water–Pt(111) system. Only interactions between water molecules have been considered for more direct comparisons. Calculations have been carried out on a Silicon Graphics Origin 2000 workstation. The geometry of the simulation cell and the Ewald parameters are the same as the ones used in this work for water–Pt(111) systems. Since the actual computing time may strongly depend on the number of particles, the choice of Ewald parameters, the machine used, and the degree of the optimization, the numbers given here should be interpreted with caution.

Computational time per time step has been estimated for each Ewald method and is summarized in Table III. Since the value of α is small, a reciprocal space term with $\mathbf{h} \neq 0$ [the second term in Eq. (6)] could be neglected with very little error as suggested by the previous studies.^{6,16} This optimization of the EW2D method results in a significant reduction of the computing time in the direct use of EW2D formula as shown in Table III, but does not reduce the computing time significantly in the EW2D calculation with the table. The inclusion of the correction term into the EW3D formula (EW3DC) hardly introduces any difference in the computing time compared with EW3D. The computing time for the EW3DC is ~ 10 times faster than the time for EW2D with the table.

We also compared the accuracy of the calculations. The components of forces acting on randomly selected atoms calculated by EW2D, EW2D with the table, and EW3DC from a given configuration of 512 water molecules have been

compared. We found that EW3DC shows better accuracy than the EW2D with the precalculated table compared with the direct EW2D calculation. We think that an accumulation of errors introduced by the interpolation of the table and the parallel plate capacitor approximation results in a loss of accuracy when the EW2D method with the precalculated table is used.

V. CONCLUSION

In this study, Ewald summation techniques for systems periodic in two dimensions with a finite length in the third dimension have been tested. In terms of speed and accuracy, the usual three-dimensional Ewald method with a correction term for the slab geometry (EW3DC) seems to be the best choice. The inclusion of the correction term does not introduce any significant computational difficulty and can be easily incorporated in the standard EW3D program. Various optimization techniques available for the EW3D technique could be readily applicable to the EW3DC.^{3,4}

Recently, there have been considerable interests in the application of the first-principles simulations using the Car–Parrinello scheme⁴¹ to the interfacial systems such as water–metal interfaces.⁴² This very promising approach may play an important role in the future simulations of various interfacial systems. The correct treatment of long-range forces in this approach is required to come to any reliable conclusions from the first-principles simulations, especially on charged systems. The EW3D with the correction term can be conveniently used for the calculation of long-range forces in the first-principles simulations.

In this study, we clearly demonstrated how simulations of interfacial systems using the EW3D method without the correction term can lead to erroneous results. Numerous simulation studies on interfacial systems in the literature have been carried out by using the EW3D method without considering the correction term. We do not know how serious the errors are for each studied system and which properties are most likely to be affected by the negligence of the correction term. More careful studies need to be done to resolve this matter and we plan to carry out further simulation studies in this direction. The safest and economical choice for the calculation of the long-range forces in most of simulations of interfacial systems seems to be the EW3D with the correction term.

ACKNOWLEDGMENT

We are grateful to the Office of Naval Research for the support.

¹M. P. Allen and D. J. Tildesley, *Computer Simulations of Liquids* (Oxford University, New York, 1987).

²S. W. de Leeuw, J. W. Perram, and E. R. Smith, *Proc. R. Soc. London, Ser. A* **373**, 27 (1980); **388**, 177 (1983).

³U. Essmann, L. Perera, M. L. Berkowitz, T. Darden, H. Lee, and L. G. Pedersen, *J. Chem. Phys.* **103**, 8577 (1995).

⁴A. Y. Toukmaji and J. A. Board Jr., *Comput. Phys. Commun.* **95**, 73 (1996).

⁵D. E. Parry, *Surf. Sci.* **49**, 433 (1975); **54**, 195 (1976).

⁶D. M. Heyes, M. Barber, and J. H. R. Clarke, *J. Chem. Soc., Faraday Trans. II* **73**, 1485 (1977).

- ⁷S. W. de Leeuw and J. W. Perram, *Mol. Phys.* **37**, 1313 (1979).
- ⁸E. Spohr, *J. Chem. Phys.* **107**, 6342 (1997).
- ⁹F. E. Harris, *Int. J. Quantum Chem.* **68**, 385 (1998).
- ¹⁰J. Hautman, J. W. Halley, and Y.-J. Rhee, *J. Chem. Phys.* **91**, 467 (1989).
- ¹¹Y.-J. Rhee, J. W. Halley, J. Hautman, and A. Rahman, *Phys. Rev. B* **40**, 36 (1989).
- ¹²E. Wasserman, J. R. Rustad, A. R. Felmy, B. P. Hay, and J. W. Halley, *Surf. Sci.* **385**, 217 (1997).
- ¹³J. Hautman and M. L. Klein, *Mol. Phys.* **75**, 379 (1992).
- ¹⁴G. Aloisi, M. L. Foresti, R. Guidelli, and P. Barnes, *J. Chem. Phys.* **91**, 5592 (1989).
- ¹⁵J. Lekner, *Physica A* **176**, 485 (1991).
- ¹⁶S. Y. Liem and J. H. R. Clarke, *Mol. Phys.* **92**, 19 (1997).
- ¹⁷A. H. Widmann and D. B. Adolf, *Comput. Phys. Commun.* **107**, 167 (1997).
- ¹⁸M. L. Berkowitz, I.-C. Yeh, and E. Spohr, to appear in *Interfacial Electrochemistry: Theory, Experiment, and Applications*, edited by A. Wieckowski (Marcel Dekker, New York) in press.
- ¹⁹I.-C. Yeh and M. L. Berkowitz, *J. Chem. Phys.* **110**, 7935 (1999).
- ²⁰I.-C. Yeh and M. L. Berkowitz, *Chem. Phys. Lett.* **301**, 81 (1999).
- ²¹J. C. Shelley and G. N. Patey, *Mol. Phys.* **88**, 385 (1996).
- ²²J. Alejandre, D. J. Tildesly, and G. A. Chapela, *J. Chem. Phys.* **102**, 4574 (1995).
- ²³J. C. Shelley, G. N. Patey, D. R. Bérard, and G. M. Torrie, *J. Chem. Phys.* **107**, 2122 (1997).
- ²⁴S. E. Feller, R. W. Pastor, A. Rojnuckarin, S. Bogusz, and B. R. Brooks, *J. Phys. Chem.* **100**, 17011 (1996).
- ²⁵G. Hummer, N. Grønbech-Jensen, and M. Neumann, *J. Chem. Phys.* **109**, 2791 (1998).
- ²⁶G. Hummer, L. R. Pratt, and A. E. García, *J. Phys. Chem. A* **102**, 7885 (1998).
- ²⁷P. H. Hünenberger and J. A. McCammon, *J. Chem. Phys.* **110**, 1856 (1999).
- ²⁸S. Boresch and O. Steinhauser, *Ber. Bunsenges. Phys. Chem.* **101**, 1019 (1997).
- ²⁹S. Bogusz, T. E. Cheatham III, and B. R. Brooks, *J. Chem. Phys.* **108**, 7070 (1998).
- ³⁰J. E. Roberts and J. Schnitker, *J. Chem. Phys.* **101**, 5024 (1994).
- ³¹J. E. Roberts and J. Schnitker, *J. Phys. Chem.* **99**, 1322 (1995).
- ³²E. R. Smith, *Proc. R. Soc. London, Ser. A* **375**, 475 (1981).
- ³³R. P. Feynman, R. B. Leighton, and M. Sands, *The Feynman Lectures on Physics* (Addison-Wesley, Reading, 1964), Vol. 2.
- ³⁴J. A. Hernando, *Phys. Rev. A* **44**, 1228 (1991).
- ³⁵I.-C. Yeh and M. L. Berkowitz, *J. Electroanal. Chem.* **450**, 313 (1998).
- ³⁶H. J. C. Berendsen, J. R. Grigera, and T. P. Straatsma, *J. Phys. Chem.* **91**, 6269 (1987).
- ³⁷K. Raghavan, K. Foster, K. Motakabbir, and M. Berkowitz, *J. Chem. Phys.* **94**, 2110 (1991).
- ³⁸H. J. C. Berendsen, J. P. M. Postma, W. van Gunsteren, A. DiNola, and J. R. Haak, *J. Chem. Phys.* **81**, 3684 (1984).
- ³⁹M. A. Wilson, A. Pohorille, and L. R. Pratt, *J. Phys. Chem.* **91**, 4873 (1987).
- ⁴⁰J. N. Glosli and M. R. Philpott, *Electrochim. Acta* **41**, 2145 (1996).
- ⁴¹R. Car and M. Parrinello, *Phys. Rev. Lett.* **55**, 2471 (1985).
- ⁴²J. W. Halley, A. Mazzolo, Y. Zhou, and D. Price, *J. Electroanal. Chem.* **450**, 273 (1998).