JCTC Journal of Chemical Theory and Computation

Article

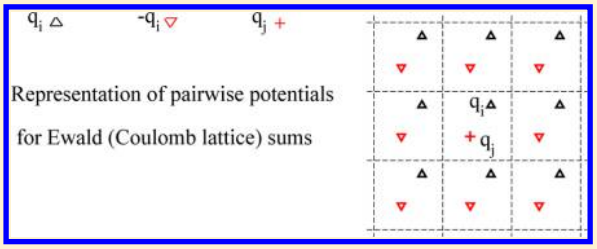
pubs.acs.org/JCTC

Infinite Boundary Terms of Ewald Sums and Pairwise Interactions for Electrostatics in Bulk and at Interfaces

Zhonghan Hu*

State Key Laboratory of Supramolecular Structure and Materials and Institute of Theoretical Chemistry, Jilin University, Changchun 130012, P. R. China

ABSTRACT: We present a unified derivation of the Ewald sum for electrostatics in a three-dimensional infinite system that is periodic in one, two, or three dimensions. The derivation leads to the Ewald3D sum being expressed as a sum of a real space contribution and a reciprocal space contribution, as in previous work. However, the $\mathbf{k} \rightarrow \mathbf{0}$ term in the reciprocal space contribution is analyzed further and found to give an additional contribution that is not part of previous reciprocal space contributions. The transparent derivation provides a unified view of the existing conducting infinite boundary term, the vacuum spherical infinite boundary term and the vacuum planar infinite boundary term for the Ewald3D sum. The derivation further explains that the infinite boundary term is conditional for the Ewald3D sum because it depends on the asymptotic behavior that the system approaches the infinite in 3D but it becomes a definite term for the Ewald2D or Ewald1D sum irrespective of the asymptotic behavior in the reduced dimensions. Moreover, the unified derivation yields two formulas for the Ewald sum in one-dimensional periodicity, and we rigorously prove that the two formulas are equivalent. These formulas might be useful for simulations of organic crystals with wirelike shapes or liquids confined in uniform cylinders. More importantly, the Ewald3D, Ewald2D, and Ewald1D sums are further written as sums of well-defined pairwise potentials overcoming the difficulty in splitting the total Coulomb potential energy into contributions from each individual group of charges. The pairwise interactions with their clear physical meaning of the explicit presence of the periodic images thus can be used to consistently perform analysis based on the trajectories from computer simulations of bulk or interfaces.



1. INTRODUCTION

Modern molecular dynamics (MD) simulations or Monte Carlo techniques deal with a large number of explicit molecules with point charges on their atoms. A typical MD study evaluates the short-ranged intermolecular interaction (e.g., Lennard-Jones (LJ) interaction) in a straightforward way and applies the Ewald sum[1] for the long-ranged Coulomb interaction because simple truncation methods for electrostatics have often introduced unrealistic behavior. Various efficient Ewald algorithms for 3D periodicity (Ewald3D)[2,3] or the so-called particle mesh Ewald (PME) techniques (e.g., refs 4−6) has been developed. These PME techniques interpolate the usual reciprocal (Fourier) space term part of the Ewald3D sum on a grid and then utilizes the computationally $O(N\log N)$ fast Fourier transform technique in spirit close to the much earlier particle−particle−particle mesh method.[7] The implementation of the efficient algorithms in major molecular dynamics simulation packages has largely advanced the field of computational chemistry, computational physics, and computational biochemistry and biophysics and hence has generated more than 10^4 citations for the basic papers.

A successful MD simulation always provides insight for the effect of a particular selected group of particles on another selected group of particles. In principle, it is straightforward to analyze the effect of the LJ interaction within the two groups of particles because we can always obtain the distance between the nearest images of any given two particles, $r_{ij} = |\mathbf{r}_{ij}| \equiv |\mathbf{r}_i - \mathbf{r}_j|$ and then directly evaluate the corresponding LJ potential as a function of r_{ij}.

Unlike the simple pairwise LJ interaction, the complex electrostatic interactions in bulk condensed phase, at 2D planar interfaces and under 1D confinement are often evaluated using the corresponding Ewald sums for the 3D, 2D (Ewald2D), and 1D (Ewald1D) periodicity, respectively. These Ewald sums usually consist of a short-ranged component evaluated in real space ($\mathcal{U}^{\mathrm{R}}$) considering the nearest neighbor charges and a long-ranged component considering all the charges in the simulation box. There are two ways of evaluating the electrostatic contribution from a selected pair of charges (e.g., q_i and q_j). One can easily compute the direct Coulomb potential ($q_iq_j/|\mathbf{r}_{ij}|$) between their nearest images without consideration of the explicit infinite number of images. Alternatively, one can analyze the real space term ($\mathcal{U}^{\mathrm{R}}$) in the Ewald3D sum, which is a short-ranged potential when an appropriate screen factor of the Ewald separation is chosen and totally ignore the presence of the reciprocal (Fourier) space term ($\mathcal{U}^{\mathrm{F}}$) as the Wolf truncation method[8] or the strong coupling approximation in the local molecular field theory[9−11] does for bulk uniform systems.

Received: August 4, 2014

   dx.doi.org/10.1021/ct500704m | J. Chem. Theory Comput. XXXX, XXX, XXX−XXX

Both procedures of splitting the total electrostatic energy into pairs have significant defects. The trajectory to be analyzed is obtained using the Ewald3D sum techniques or its PME alternatives considering both the direct interaction between the two nearest charges q_i and q_j and the indirect effect between all images of q_i and q_j. Therefore, there is an inconsistency between the sum of the electrostatic potential of all pairs evaluated using the direct Coulomb potential $q_iq_j/|\mathbf{r}_{ij}|$ and the total potential energy of the Coulomb lattice sum evaluated using the Ewald3D method. Although the real space term $\mathcal{U}^{\mathrm{R}}$ might contribute significantly compared to the reciprocal space term $\mathcal{U}^{\mathrm{F}}$ for a given relatively small screen factor α, $\mathcal{U}^{\mathrm{R}}$ itself is not well-defined and certainly depends on the value of α when the Ewald sum technique is used. Obviously, one would not have any problem if the total electrostatic potential energy of the system expressed as the Coulomb lattice sum is needed instead of the electrostatic energy of a given pair of charges. However, in general, we are seeking a solution to the problem of exactly rewriting the Ewald sums for a neutral system ($\sum_{j=1}^{N} q_j = 0$) in bulk or at interfaces as sums over pairwise potentials.

Although most papers have regarded the Ewald3D sum or its PME alternatives as the sum of $\mathcal{U}^{\mathrm{R}}$ and $\mathcal{U}^{\mathrm{F}}$,[12] the particular surface term in the Ewald3D sum are important for properties of crystalline energy bands and dielectric response of fluids.[13−16] Indeed, several important research have focused on the shape-dependent surface term inherent with the nature of the conditional convergence of the Coulomb lattice sum in the Ewald3D sum.[17−28] The early seminal derivation by de Leeuw, Perram, and Smith[17] clearly stated that the Ewald3D sum has a special conditional surface or dipole term which might not be fully considered in the original paper by Paul Peter Ewald.[1] This shape-dependent term in the Ewald3D sum mathematically depends on the order in which the Coulomb terms in the series are added up and physically depends on the shape of the macroscopic surface and the surrounding dielectric media for a perfect ionic crystal. Their proof used a convergence factor to transform a divergent series to a uniformly convergent series for the purpose of using rigorous mathematical transformation. Many researchers have thus provided alternative and informative derivations of the Ewald3D sum by addressing the special shape-dependent term either by focusing on the mathematical transform of a finite lattice sum[27] or by expanding the slowly convergent $1/r$ function to higher orders of dipole and quadrupolar contributions.[26,28] Very recently, Ballenegger has made a transparent derivation of the shape-dependent term by subtracting a well chosen conditionally convergent series first and adding the compensation term later.[28]

We now focus on a relatively simple question of an infinite periodic lattice but define its infinite boundary as the asymptotic behavior that the lattice approaches the infinite. This infinite boundary can also be called an asymptotic boundary and it differs from the usual macroscopic but finite realistic boundary. Correspondingly, we define the infinite boundary term as the (perhaps conditional) term arising from the asymptotic behavior that the periodic lattice approaches the infinite. Note that this term does not have to be a small correction term and it could play an important role. Inspired by the original seminal derivation[17−19] and the previous alternative derivations,[20−28] we aim at alternatively deriving the Ewald sums of 3D liquids or crystals with all possibilities of 3D, 2D, and 1D periodicity. Our transparent and unified derivation differs from any existing rigorous derivation that we can find in the literature but still provides a simple and unified view of the existing arguments on the surface or dipole terms of the Ewald3D sum and further illustrates that this infinite boundary term should not be conditional any more in the Ewald2D or Ewald1D sums for the electrostatics at interfaces. Moreover, better understanding of the Ewald sums from the way we derived them immediately suggests a solution to the problem of rewriting the Ewald sum in bulk or at interfaces as a sum over pairwise potentials. To the best of our knowledge, the point of novelty in the present work is 3-fold. First, although the existence and importance of the surface or dipole term was pointed out in more rigorious publications[17−19] many years ago, this is the first time that a relatively simple formal (as opposed to rigorous) analysis is able to give much information about it. Second, our transparent and unified derivation of the Ewald3D, Ewald2D, and Ewald1D sums will clearly explain why the infinite boundary term is only conditional for the 3D periodicity while it goes to a definite term for the 2D or 1D periodicity. The derivation will immediately suggest alternative formulas for the Ewald1D sum. Algorithm development in future based on these formulas might be useful for simulations of wirelike organic crystals and water or organic liquids confined in a uniform nanopore (e.g., carbon nanotubes). Third, we will suggest pairwise potentials for the Ewald3D, Ewald2D, and Ewald1D sums with clear physical meanings to overcome the difficulty of splitting the total electrostatics energies into pairs when analyzing trajectories.

The rest of this paper is organized as follows. In Section 2, we provide the strategy to derive the Ewald3D sum, which does not require any prerequisite knowledge beyond basic calculus and emphasize the particular infinite boundary terms. The derivation and the reformulation of the Ewald3D sum lead to a clear definition of its pairwise potential in Section 3. A straightforward application of the strategy for electrostatics in interfacial systems with 2D periodicity and 1D periodicity are provided in Section 4 and Section 5, respectively. We try to raise questions regarding the existing ambiguity in the Ewald sums in Section 6 and draw conclusions by analyzing the difference and the common terms of the Ewald3D, Ewald2D, and Ewald1D sums in Section 7. We finally provide a brief proof of the Poisson summation formula and a rigorous proof of the equivalence between the two Ewald1D formulas in the appendices.

2. EWALD3D SUM AND ITS INFINITE BOUNDARY PROBLEM

The widely accepted Ewald method introduces a screening factor α that divides the basic Coulomb interaction into short and long ranged parts according to the following Ewald separation:

$$\frac{1}{r} \equiv \frac{\mathrm{erfc}(\alpha r)}{r} + \frac{\mathrm{erf}(\alpha r)}{r} \tag{1}$$

where the error function part is proportional to the electrostatic potential arising from a Gaussian charge density, written as a 3D convolution expression

$$\frac{\mathrm{erf}(\alpha r)}{r} = \frac{\alpha^3}{\pi^{3/2}} \int \mathrm{d}\mathbf{r}' \mathrm{e}^{-(\alpha r')^2} \frac{1}{|\mathbf{r} - \mathbf{r}'|} \tag{2}$$

dx.doi.org/10.1021/ct500704m | J. Chem. Theory Comput. XXXX, XXX, XXX−XXX

Therefore, the complementary error function part can be regarded as the electrostatic potential arising from the original point charge distribution plus a screening charge distribution, which is the negative to the Gaussian charge distribution.[2] To efficiently sum the Coulomb interaction between charges and all their periodic images in an ionic crystal, which is a conditionally convergent series, the Ewald sum summs the Gaussian charge distribution in reciprocal space while the original point plus screening charge distribution is summed in real space.

In the past, the Ewald3D formula was derived either rigorously by addressing the subtle issues of the finite boundary of the system at large distances[17−28] or formally by considering an infinite periodic system with no realistic finite boundaries. In the present work, we will use the latter method, but we will be able to identify a contribution to the Ewald3D sum for the infinite periodic system that has not previously been identified and that is closely related to the subtle issues that arise in more rigorous approaches.

2.1. Alternative Derivation. Let us consider a system of N point charges $(q_j, \mathbf{r}_j)$ with $j = 1,...,N$ in a unit cell and their infinite periodic images $(q_j, \mathbf{r}_j + \mathbf{n})$. The unit cell is specified by L_x, L_y, and L_z in the three directions, respectively, and the real space propagation vector $\mathbf{n}$ stands for (n_xL_x, n_yL_y, n_zL_z) with n_x, n_y, and n_z integers. The total electrostatic potential energy per unit cell is the so-called Coulomb lattice sum

$$\mathcal{U} = \frac{1}{2}\sum_{\mathbf{n}}{}' \left(\sum_{i,j=1}^{N} \frac{q_i q_j}{|\mathbf{n} + \mathbf{r}_{ij}|} \right) \tag{3}$$

where $\mathbf{r}_{ij}$ stands for the relative vector between the i-th and the j-th charge. Note that $\mathcal{U}$ is not a constant but depends on the configuration of the charges. The sum over the vector $\mathbf{n}$ is the sum over the infinite images of the N charges in all three directions. The prime indicates that the $i = j$ term is omitted in case of $n_x = n_y = n_z = 0$. For simplicity of notation, we have omitted the prefactor of $1/(4\pi\varepsilon_0)$.

It is well-known that the conditional convergence property of the Coulomb lattice sum depends on the cancellation due to positive and negative values of q_j, and one cannot simply exchange the order of the outside sum over $\mathbf{n}$ and the inside sum over i,j from a rigorous viewpoint of mathematics. Before we proceed to derive the Ewald3D formula for the Coulomb lattice sum, we introduce the basic 3D Fourier transform and the corresponding inverse Fourier transform defined as

$$\hat{f}(\mathbf{k}) \equiv \int d\mathbf{r} f(\mathbf{r}) e^{-i\mathbf{k}\cdot\mathbf{r}} \tag{4}$$

and

$$f(\mathbf{r}) \equiv \frac{1}{(2\pi)^3} \int d\mathbf{k} \hat{f}(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{r}} \tag{5}$$

Knowing the convolution property of the Fourier transform and the convolution expression of the error function part of the Coulomb interaction in eq 2, one can immediately realize an advantage of using Ewald separation is that we can easily obtain the Fourier transform of the error function part as a product of a Gaussian function $e^{-k^2/(4\alpha^2)}$ and $4\pi/k^2$. There is an associated simple mathematical transform for an arbitrary periodic function $f(\mathbf{n} + \mathbf{r})$ called Poisson summation formula

$$\sum_{\mathbf{n}} f(\mathbf{n} + \mathbf{r}) = \frac{1}{L_xL_yL_z} \sum_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}} \hat{f}(\mathbf{k}) \tag{6}$$

where the vector $\mathbf{k} = 2\pi(k_x/L_x, k_y/L_y, k_z/L_z)$ and k_x, k_y, and k_z are all integers. A straightforward proof of the Poisson summation formula is provided in the Appendix.

Rigorously speaking, turning a sum in real space to another sum in reciprocal space in the above Possion summation formula eq 6 requires a strict condition that the series itself is absolutely convergent. Now let us omit all rigorous requirements and just "casually" move forward three steps from the Coulomb lattice sum: (i) removing the prime but accounting for a compensation term, $-\lim_{r\to 0}\sum_{j=1}^{N} q_j^2/(2r)$,

$$\mathcal{U} = \frac{1}{2}\sum_{\mathbf{n}} \left(\sum_{i,j=1}^{N} \frac{q_i q_j}{|\mathbf{n} + \mathbf{r}_{ij}|} \right) - \frac{1}{2}\lim_{r\to 0} \sum_{j=1}^{N} \frac{q_j^2}{r} \tag{7}$$

(ii) exchanging the order of the outside sum over $\mathbf{n}$ and the inside sum over i,j followed by doing the Ewald separation for the Coulomb interaction, $1/|\mathbf{n} + \mathbf{r}_{ij}|$,

$$\mathcal{U} = \frac{1}{2}\sum_{i,j=1}^{N} q_i q_j \left(\sum_{\mathbf{n}} \frac{\mathrm{erfc}(\alpha|\mathbf{n} + \mathbf{r}_{ij}|)}{|\mathbf{n} + \mathbf{r}_{ij}|} \right) - \frac{1}{2}\lim_{r\to 0} \sum_{j=1}^{N} \frac{q_j^2}{r} + \frac{1}{2}\sum_{i,j=1}^{N} q_i q_j \left(\sum_{\mathbf{n}} \frac{\mathrm{erf}(\alpha|\mathbf{n} + \mathbf{r}_{ij}|)}{|\mathbf{n} + \mathbf{r}_{ij}|} \right) \tag{8}$$

and (iii) an immediate application of the Poisson summation formula to the sum over the error function part of the Ewald separation, $\sum_{\mathbf{n}} \mathrm{erf}(\alpha|\mathbf{n} + \mathbf{r}_{ij}|)/|\mathbf{n} + \mathbf{r}_{ij}|$,

$$\mathcal{U} = \frac{1}{2}\sum_{i,j=1}^{N} q_i q_j \left(\sum_{\mathbf{n}} \frac{\mathrm{erfc}(\alpha|\mathbf{n} + \mathbf{r}_{ij}|)}{|\mathbf{n} + \mathbf{r}_{ij}|} \right) - \frac{1}{2}\lim_{r\to 0} \sum_{j=1}^{N} \frac{q_j^2}{r} + \frac{2\pi}{L_xL_yL_z} \sum_{i,j=1}^{N} q_i q_j \sum_{\mathbf{k}} \frac{e^{-k^2/(4\alpha^2)}}{k^2} e^{i\mathbf{k}\cdot\mathbf{r}_{ij}} \tag{9}$$

This three-step procedure in one sentence immediately yields the standard Ewald3D formula for the Coulomb lattice sum

$$\mathcal{U} = \mathcal{U}^{\mathrm{R}} + \mathcal{U}^{\mathrm{F}} + \mathcal{U}^{\mathrm{IB}} \tag{10}$$

where the real space term $\mathcal{U}^{\mathrm{R}}$, the reciprocal space term $\mathcal{U}^{\mathrm{F}}$, and the infinite boundary term $\mathcal{U}^{\mathrm{IB}}$ are explicitly written as

$$\mathcal{U}^{\mathrm{R}} = \frac{1}{2}\sum_{i,j=1}^{N} q_i q_j \sum_{\mathbf{n}}{}' \frac{\mathrm{erfc}(\alpha|\mathbf{r}_{ij} + \mathbf{n}|)}{|\mathbf{r}_{ij} + \mathbf{n}|} - \frac{\alpha}{\sqrt{\pi}} \sum_{j=1}^{N} q_j^2 \tag{11}$$

$$\mathcal{U}^{\mathrm{F}} = \frac{2\pi}{L_xL_yL_z} \sum_{i,j=1}^{N} q_i q_j \sum_{\mathbf{k}\neq 0} \frac{e^{-k^2/(4\alpha^2)}}{k^2} e^{i\mathbf{k}\cdot\mathbf{r}_{ij}} \tag{12}$$

and

$$\mathcal{U}^{\mathrm{IB}} = \frac{2\pi}{L_xL_yL_z} \lim_{\mathbf{k}\to 0} \sum_{i,j=1}^{N} q_i q_j \frac{e^{-k^2/(4\alpha^2)}}{k^2} e^{i\mathbf{k}\cdot\mathbf{r}_{ij}} \tag{13}$$

respectively. The prime in the Coulomb lattice sum is put back to $\mathcal{U}^{\mathrm{R}}$ by taking the limit for the complementary error function part and the compensation term to obtain $-\alpha/(\pi)^{1/2}\sum_{j=1}^{N} q_j^2$ (see eqs 9 and 11), which is also called the self-term (page 159 of ref 2 and page 300 of ref 3). The result from the Poisson

dx.doi.org/10.1021/ct500704m | J. Chem. Theory Comput. XXXX, XXX, XXX−XXX

summation formula is written separately as the sum over $\mathbf{k} \neq \mathbf{0}$ for $\mathcal{U}^{\mathrm{F}}$ in eq 12 and the $\mathbf{k} \to \mathbf{0}$ term for $\mathcal{U}^{\mathrm{IB}}$ in eq 13.

2.2. Infinite Boundary Terms. The above $\mathbf{k} \to \mathbf{0}$ term is related to the surface or dipole term in previous derivations of the Ewald3D sum, and we have called it the infinite boundary term. This special term has attracted attention from early seminal derivations[17−22,29,30] to more recent analysis.[23−28] We now provide a transparent analysis for $\mathcal{U}^{\mathrm{IB}}$, which to the best of our knowledge has not been provided before. Similar analysis will be performed later for the Ewald sums in 2D and 1D periodicity. An immediate power series expansion of $\mathcal{U}^{\mathrm{IB}}$ reads

$$\begin{aligned}\mathcal{U}^{\mathrm{IB}} &= \frac{2\pi}{V}\lim_{\mathbf{k}\to 0}\sum_{i,j=1}^{N} q_i q_j \frac{1 - k^2/(4\alpha^2) + i\mathbf{k}\cdot\mathbf{r}_{ij}}{k^2} \\ &\quad - \frac{\pi}{V}\lim_{\mathbf{k}\to 0}\left(\sum_{i,j=1}^{N} q_i q_j \frac{(\mathbf{k}\cdot\mathbf{r}_{ij})^2}{k^2} + \mathbf{O}(\mathbf{k})\right) \\ &= -\frac{\pi}{V}\lim_{\mathbf{k}\to 0}\sum_{i,j=1}^{N} q_i q_j \frac{(\mathbf{k}\cdot\mathbf{r}_{ij})^2}{k^2}\end{aligned} \tag{14}$$

where we have set the volume of the N charges is $V = L_x L_y L_z$. Here, we have used the capital letter $\mathbf{O}$ for order equal to or larger than, and in general, we use the variational letter O for order of. The validity of the second equality in the above expression is ensured by the removal of the divergence using the electroneutrality condition $\sum_{j=1}^{N} = 0$ and the odd function property when exchanging the indices $\mathbf{k}\cdot\mathbf{r}_{ij} = -\mathbf{k}\cdot\mathbf{r}_{ji}$. Obviously, the final limit in $\mathcal{U}^{\mathrm{IB}}$ is not well-defined but we emphasize that the above procedure actually involves no approximation. The basic problem of the conditional convergence inherent with the Coulomb lattice sum must be *exactly* transferred to this conditional limit in reciprocal space. This observation allows us to find a simple way to analyze the different possibilities and get consistent results with the existing arguments on the surface or dipole term for a finite lattice.

Since the Fourier transform makes a connection between $\mathbf{r}$ in real space and $\mathbf{k}$ in reciprocal space using the Fourier component $e^{i\mathbf{k}\cdot\mathbf{r}}$, we would expect that the $\mathbf{k} \to \mathbf{0}$ term in the above equation is dominated by the behavior of the system at large $\mathbf{r} \to \infty$. We might agree that the term $\mathbf{k} = \mathbf{0}$ mostly or completely depends on $\mathbf{r} = \infty$. If the surrounding media at the infinite boundary has a dielectric constant $\varepsilon_0 = \infty$ in the prefactor, we then expect

$$\mathcal{U}_{\mathrm{T}}^{\mathrm{IB}} = 0 \tag{15}$$

independent of details of the conditional limit. This choice for $\mathcal{U}_{\mathrm{T}}^{\mathrm{IB}}$ is usually called the conducting or tinfoil boundary condition,[17] and we now call it tinfoil (conducting) infinite boundary term. Now let us proceed to discuss the cases of various conditional limits at the vacuum condition with $\varepsilon_0 = 1$, which mathematically reflects the order in which the terms in the Coulomb lattice sum are added up and physically represents the asymptotic behavior that the lattice approaches the infinite. To simplify the discussion, we set the condition $L_x = L_y = L_z = L$ corresponding to a usual simulation setup of the cubic simulation box. The corresponding reciprocal space vector is $\mathbf{k} = 2\pi(k_x, k_y, k_z)/L$.

2.3. Spherical Infinite Boundary Term. The spherical infinite boundary term arises when the infinitely large crystal is built up spherically by filling the azimuthal angle θ and the polar angle ϕ parts first and then extending the radial distance r (e.g., page 157 of ref 2). Correspondingly, the conditional limit of $\mathbf{k} \to 0$ is taken in a particular way such that the angular part of $\mathbf{k}$ is averaged out before taking the limit of $|\mathbf{k}| \to 0$

$$\lim_{\mathbf{k}\to 0}\frac{(\mathbf{k}\cdot\mathbf{r}_{ij})^2}{k^2} = \lim_{|\mathbf{k}|\to 0}\frac{\int \mathrm{d}\Omega (\mathbf{k}\cdot\mathbf{r}_{ij})^2}{k^2 \int \mathrm{d}\Omega} = \frac{r_{ij}^2}{3} \tag{16}$$

where $\int \mathrm{d}\Omega \equiv \int_0^{\pi} \mathrm{d}\theta \sin\theta \int_0^{2\pi} \mathrm{d}\phi$. Given the definition of the dipole moment for the N charges in each direction (e.g., $M_x = \sum_{j=1}^{N} q_j x_j$), immediately we have the spherical infinite boundary term corresponding to the specific spherical path of $\mathbf{k} \to \mathbf{0}$ in reciprocal space:

$$\mathcal{U}_{\mathrm{S}}^{\mathrm{IB}} = \frac{2\pi}{3V}(M_x^2 + M_y^2 + M_z^2) \tag{17}$$

where we have used properties from the electroneutrality condition (e.g., $\sum_{i,j=1}^{N} q_i q_j x_{ij}^2 = -2(\sum_{j=1}^{N} q_j x_j)^2 = -2M_x^2$) to directly expressed the result as the square of the total dipole moment of the N charges. Indeed, this infinite boundary term was also called the dipole term of the Ewald3D formula in the early seminal derivation[17] and discussed frequently in more recent literature.[23−28] Our derivation thus suggests a simple alternative but equivalent way of thinking about this spherical infinite boundary term.

2.4. Planar Infinite Boundary Term. A planar infinite boundary term with the xy plane built up first ($|x| \to \infty$ and $|y| \to \infty$) corresponds to applying the condition $k_x = k_y = 0$ before taking the limit of $k_z \to 0$

$$\lim_{\mathbf{k}\to 0}\frac{(\mathbf{k}\cdot\mathbf{r}_{ij})^2}{k^2} = \lim_{k_z\to 0}\left[\lim_{k_x=k_y=0}\frac{(\mathbf{k}\cdot\mathbf{r}_{ij})^2}{k^2}\right] = z_{ij}^2 \tag{18}$$

Immediately after applying the electroneutrality condition, we have the planar infinite boundary term written as

$$\mathcal{U}_{\mathrm{P}}^{\mathrm{IB}} = \frac{2\pi}{V}\left(\sum_{j=1}^{N} q_j z_j\right)^2 = \frac{2\pi}{V}M_z^2 \tag{19}$$

This dipole term was also known previously[19] and has been used to develop an efficient alternative algorithm for the Ewald sum in a slab geometry with 2D periodicity (Ewald2D) in which a regular Ewald3D method (the real space term plus the reciprocal space term with the conducting infinite boundary term) for the 3D periodic system with a large empty space in the z direction is performed and corrected with an intuitive dipole correction term (Ewald3Dc) equivalent to the above planar infinite boundary term.[31]

Very recently, a unified view of the Ewald2D method, the Ewald3Dc method, and the related other methods are provided via a discussion of the rigorous error bound of the Ewald2D algorithm.[32] We believe that the excellent Ewald3Dc algorithm developed earlier[31] should be interpreted as the correct implementation of the Ewald3D algorithm with the planar infinite boundary term or equivalently "Ewald summation technique with the planar vacuum boundary condition[33]". It is correct but might be misleading to call it "the three-dimensional Ewald summation with the correction term[31]" because the Ewald3D method by itself is associated with certain infinite boundary terms, which can be alternatively obtained from an expansion of the Ewald2D formula.[32] To approximate the Ewald2D formula in a slab geometry using the Ewald3D formula in the special system, which extends the artificial

dx.doi.org/10.1021/ct500704m | J. Chem. Theory Comput. XXXX, XXX, XXX−XXX

periodicity to the direction perpendicular to the slab by adding a large empty space between the adjacent layers of images requires an extra layer correction term accounting for the presence of the artificial layers.[32,34] However, this layer correction term is usually very small and can often be neglected when the empty space is large enough (e.g., three times larger than L_x or L_y).[31,32,34]

The above seemingly casual procedure immediately yields the three infinite boundary terms: $\mathcal{U}_T^{IB}$ in eq 15, $\mathcal{U}_S^{IB}$ in eq 17, $\mathcal{U}_P^{IB}$ in eq 19 consistent with the corresponding results in the literature. In general, one might be tempted to write the infinite boundary terms in Ewald3D simply as the last line of eq 14 (Section 2.2) instead of taking a specific path. However, we have shown that once the divergence irrespective of the position has been removed using the electroneutrality condition, the conditional limit in $\mathcal{U}^{IB}$ depends on the path of taking $\mathbf{k} \to \mathbf{0}$. We will see how an almost identical procedure works for alternative derivations of the Ewald2D and Ewald1D sums.

The present analysis could be generalized to other infinite boundary terms with 3D periodicity using alternate paths in k-space although most present research simply uses $\mathcal{U}_T^{IB} = 0$ for molecular dynamics simulation of liquids in bulk. A more physically relevant but very challenging question is to understand what infinite boundary term is the most appropriate for a given problem, but this is beyond the scope of the present work. Instead, we focus on reformulating the Ewald3D sum using potentials felt by test charges, rewriting the Ewald3D method as a sum over pairwise interactions and doing straightforward extensions to the Ewald2D and Ewald1D sums. These results should be useful whatever the infinite boundary term is.

2.5. Reformulation of the Ewald3D Formula. The Coulomb lattice sum discussed in this section can be regarded as the sum of the electrostatic potential felt by N test charges in the periodic lattice of the N source charges

$$\mathcal{U} = \frac{1}{2}\sum_{i=1}^{N} \Phi(q_i, \mathbf{r}_i; N) - \frac{1}{2}\sum_{j=1}^{N} \lim_{\mathbf{r}\to\mathbf{r}_j} \frac{q_j^2}{|\mathbf{r} - \mathbf{r}_j|} \tag{20}$$

with the electrostatic potential felt by one test charge specified by $(q,\mathbf{r})$ defined as

$$\Phi(q, \mathbf{r}; N) \equiv q \sum_{\mathbf{n}} \sum_{j=1}^{N} \frac{q_j}{|\mathbf{n} + (\mathbf{r} - \mathbf{r}_j)|} \tag{21}$$

where we have explicitly denoted the dependence of $\Phi(q,\mathbf{r};N)$ on N, the number of source charges in the periodic lattice. This particular view has been taken as early as in the original paper,[35] was considered later in the development of the Ewald2D sum,[36] and was also used more recently by other researchers (e.g., refs 3 and 37). By applying the three-step casual mathematics described in the preceding section: exchanging the order of the outside and inside sum, doing the Ewald separation, and transforming the error function part of the real space sum to the reciprocal space sum using the Poisson summation formula to evaluate $\Phi(q, \mathbf{r};N)$, we immediately obtain the Ewald3D formula for the electrostatic potential of the test charge $(q,\mathbf{r})$ in the periodic lattice of the N source charges:

$$\Phi(q, \mathbf{r}; N) = \Phi^R(q, \mathbf{r}; N) + \Phi^F(q, \mathbf{r}; N) + \Phi^{IB}(q, \mathbf{r}; N) \tag{22}$$

with the real space term Φ^R, the reciprocal space term Φ^F, and the infinite boundary term Φ^{IB} written as

$$\Phi^R(q, \mathbf{r}; N) = q\sum_{j=1}^{N} q_j \sum_{\mathbf{n}} \frac{\mathrm{erfc}(\alpha|\mathbf{r} - \mathbf{r}_j + \mathbf{n}|)}{|\mathbf{r} - \mathbf{r}_j + \mathbf{n}|} \tag{23}$$

$$\Phi^F(q, \mathbf{r}; N) = q\frac{4\pi}{V}\sum_{j=1}^{N} q_j \sum_{\mathbf{k}\neq 0} \frac{e^{-k^2/(4\alpha^2)}}{k^2} e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}_j)} \tag{24}$$

and

$$\Phi^{IB}(q, \mathbf{r}; N) = q\frac{-2\pi}{V}\sum_{j=1}^{N} q_j \lim_{\mathbf{k}\to 0} \frac{[\mathbf{k}\cdot(\mathbf{r} - \mathbf{r}_j)]^2}{k^2} \tag{25}$$

respectively. Obviously, the previous results of the Ewald3D formula in eqs 11−13 for the Coulomb lattice sum in a neutral system can be easily reproduced using the above equations. We have not specified the particular path to further simplify the infinite boundary term because at present we think that eq 25 is the general way of writing it. This reformulation using $\Phi(q,\mathbf{r};N)$ suggests that the divergence in the electrostatic potential felt by the test charge can be removed as well via the electroneutrality condition. Therefore, one should be able to obtain a well-defined potential as long as the potential is defined in a neutral system. The role of the explicit presence of images can be related to neutralize the charge of the image cells. We show in the next section that the use of $\Phi(q,\mathbf{r};N)$ is crucial to rewrite the Ewald3D formula *exactly* as the sum over an effective pairwise potential.

3. PAIRWISE POTENTIAL FOR THE EWALD3D SUM

Here, we show that the total Coulomb energy in eq 10 from the lattice sum of eq 3 with 3D periodicity can be exactly rewritten as a sum of effective pairwise additive interactions $u(\mathbf{r}_i,\mathbf{r}_j)$ between the N source charge sites located only in the primary unit cell:

$$\mathcal{U} = \frac{1}{2}\sum_{1\le i\neq j\le N} u(\mathbf{r}_i, \mathbf{r}_j) \equiv \sum_{1\le i<j\le N} u(\mathbf{r}_i, \mathbf{r}_j) \tag{26}$$

We can anticipate that the difficulty in obtaining a unique form of $u(\mathbf{r}_i, \mathbf{r}_j)$ for each individual pair q_i and q_j is that it is challenging to split the reciprocal space term and the infinite boundary term exactly into pairs. Considering the neutral system of N charges in the unit cell ($q_1 + q_2 + \cdots + q_N = 0$), the first charge $(q_1,\mathbf{r}_1)$ and its images $(q_1,\mathbf{r}_1 + \mathbf{n})$ together interact with the rest $N-1$ charges. In order to separate the effect of all images of q_1 into $N-1$ pieces such that each piece is combined to one of q_2, q_3, ⋯, q_N to yield a well-defined pairwise interaction, one can simply rewrite $q_1 = -q_2 - q_3 - \cdots - q_N$ from the electroneutrality condition and then $-q_2$ with coordinates $\mathbf{r}_1 + \mathbf{n}$ is assigned to $(q_2,\mathbf{r}_2)$, $-q_3$ with coordinates $\mathbf{r}_1 + \mathbf{n}$ is assigned to $(q_3,\mathbf{r}_3)$, ⋯, $-q_N$ with coordinates $\mathbf{r}_1 + \mathbf{n}$ is assigned to $(q_N,\mathbf{r}_N)$. Therefore, we successfully divide the total effect of the images of $(q_1,\mathbf{r}_1)$ into $N - 1$ pieces. Such a division should be able to yield the pairwise interaction for any given pair of charges, $(q_i,\mathbf{r}_i)$ and $(q_j,\mathbf{r}_j)$. This argument is helpful to understand the equivalence between the sum of the pairwise

dx.doi.org/10.1021/ct500704m | J. Chem. Theory Comput. XXXX, XXX, XXX−XXX

interactions and the Ewald sum, and we now rigorously show that the pairwise form is exact.

The above discussion suggests considering the following special two-charge system shown in Figure 1a in which the two

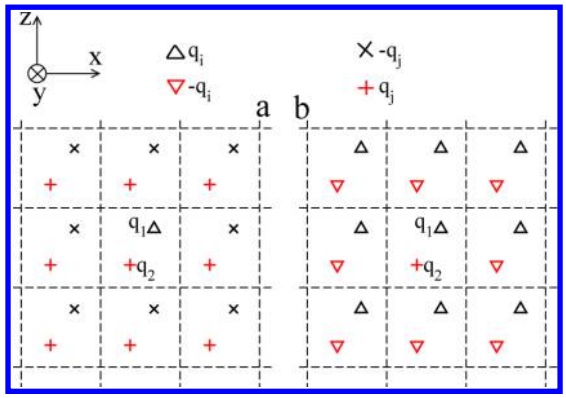


Figure 1. Representation of the special two-charge system in three-dimensional real space for an arbitrary pair of charges $(q_i,\mathbf{r}_i)$ and $(q_j,\mathbf{r}_j)$. The two charges in the central cell are ($\mathbf{r}_1 = \mathbf{r}_i$, $q_1 = q_i(\Delta)$) and ($\mathbf{r}_2 = \mathbf{r}_j$, $q_2 = q_j$ (+)), respectively. However, the charge of all images of q_1 is replaced by $-q_j$ (×) (a) or the charge of all images of q_2 is replaced by $-q_i$ (▽) (b). Given the same infinite boundary term, the electrostatic energy (the Coulomb lattice sum) felt by q_1 in the central cell of part a is identical to that felt by q_2 in the central cell of part b. The infinite number of images are explicitly plotted in the two dimensions but implicit in the other dimension pointing into the paper/screen for the 3D periodicity. One can image the corresponding similar representations for the 2D or 1D periodicity. These representations define $u(\mathbf{r}_i,\mathbf{r}_j)$, $u^{2D}(\mathbf{r}_i,\mathbf{r}_j)$, and $u^{1D}(\mathbf{r}_i,\mathbf{r}_j)$ between any pair of charges: $(q_i,\mathbf{r}_i)$ and $(q_j,\mathbf{r}_j)$ subject to 3D, 2D, or 1D periodicity, respectively. See eq 27.

particles $(q_1,\mathbf{r}_1) = (q_i,\mathbf{r}_i)$ and $(q_2,\mathbf{r}_2) = (q_j,\mathbf{r}_j)$ are duplicated in all three dimensions using the same periodicity as the N-charge system but where the charge of all images of q_1 is reset to $-q_j$. Regarding $(q_i,\mathbf{r}_i)$ as a test charge located inside and overlapping $(q_1,\mathbf{r}_1)$ of the infinite and neutral periodic lattice, we are able to compute the electrostatic potential felt by q_i in the special infinite lattice formed by $(q_1,\mathbf{r}_1)$ and $(q_2,\mathbf{r}_2)$

$$u(\mathbf{r}_i,\mathbf{r}_j) = \Phi(q_i,\mathbf{r}_i;2) - \lim_{\mathbf{r}\to\mathbf{r}_i}\frac{-q_iq_j}{|\mathbf{r}-\mathbf{r}_i|} = q_iq_j[v^{R}(\mathbf{r}_i,\mathbf{r}_j) + v^{F}(\mathbf{r}_i,\mathbf{r}_j) + v^{IB}(\mathbf{r}_i,\mathbf{r}_j)] \quad (27)$$

where Φ is defined as in eq 21 and computed as in eqs 23−25. Thus, we obtain the real space term v^R, the reciprocal space term v^F, and the infinite boundary term v^{IB} in 3D periodicity written as

$$v^{R}(\mathbf{r}_i,\mathbf{r}_j) = \sum_{\mathbf{n}}\frac{\operatorname{erfc}(\alpha|\mathbf{r}_{ij}+\mathbf{n}|)}{|\mathbf{r}_{ij}+\mathbf{n}|} - \sum_{\mathbf{n}}{}'\frac{\operatorname{erfc}(\alpha|\mathbf{n}|)}{|\mathbf{n}|} + \frac{2\alpha}{\sqrt{\pi}} \quad (28)$$

$$v^{F}(\mathbf{r}_i,\mathbf{r}_j) = \frac{4\pi}{V}\sum_{\mathbf{k}\neq 0}\frac{e^{-k^2/(4\alpha^2)}e^{i\mathbf{k}\cdot\mathbf{r}_{ij}}}{k^2} - \frac{4\pi}{V}\sum_{\mathbf{k}\neq 0}\frac{e^{-k^2/(4\alpha^2)}}{k^2} \quad (29)$$

and

$$v^{IB}(\mathbf{r}_i,\mathbf{r}_j) = -\frac{2\pi}{V}\lim_{\mathbf{k}\to 0}\frac{(\mathbf{k}\cdot\mathbf{r}_{ij})^2}{k^2} \quad (30)$$

respectively. Using a rewrite of the electroneutrality condition

$$\Big(\sum_{j=1}^{N}q_j\Big)^2 = 0 \leftrightarrow -\sum_{1\le i<j\le N}q_iq_j = \frac{1}{2}\sum_{j=1}^{N}q_j^2 \quad (31)$$

we can immediately prove that the sum over each term of the pairwise form of the Ewald3D formula is equivalent to the corresponding term of the Ewald3D formula in the preceding section

$$\sum_{1\le i<j\le N}q_iq_jv^{R}(\mathbf{r}_i,\mathbf{r}_j) = \mathcal{U}^{R} \quad (32)$$

$$\sum_{1\le i<j\le N}q_iq_jv^{F}(\mathbf{r}_i,\mathbf{r}_j) = \mathcal{U}^{F} \quad (33)$$

and

$$\sum_{1\le i<j\le N}q_iq_jv^{IB}(\mathbf{r}_i,\mathbf{r}_j) = \mathcal{U}^{IB} \quad (34)$$

Obviously, the modified Coulomb interaction $v(\mathbf{r}_i,\mathbf{r}_j) \equiv v^R(\mathbf{r}_i,\mathbf{r}_j) + v^F(\mathbf{r}_i,\mathbf{r}_j) + v^{IB}(\mathbf{r}_i,\mathbf{r}_j)$ is independent of the screening factor α because it equals the negative to the Coulomb lattice sum of a system of one cation ($q = 1$) and one anion ($q = -1$) both with the unit charge in the same periodicity subject to the same infinite boundary term. Therefore, we have successfully obtained the pairwise potential $u(\mathbf{r}_i,\mathbf{r}_j) = q_iq_jv(\mathbf{r}_i,\mathbf{r}_j)$ for any given pair of charges q_i and q_j in a N-charge system with electroneutrality accounting for the effect of the infinite periodic images subject to a certain infinite (asymptotic) boundary. The physical meaning of $u(\mathbf{r}_i,\mathbf{r}_j)$ is that $u(\mathbf{r}_i,\mathbf{r}_j)$ represents the potential energy felt by the test charge q_i in the specially designed two-charge system explained in Figure 1a or the potential energy felt by the test charge q_j in the corresponding system plotted in Figure 1b. Although the pairwise potential does not directly produce any efficient algorithm for the purpose of computation, the clear physical meaning of the pairwise form helps us to interpret the Coulomb contribution from any group of charges based on the molecular simulation trajectory using the efficient Ewald3D method or equivalently the PME method.

Further analysis and use of the modified Coulomb interaction $v(\mathbf{r}_i,\mathbf{r}_j)$ might be very fruitful. $v(\mathbf{r}_i,\mathbf{r}_j)$ clearly depends only on the nearest relative vector between all images of the two charges $(q_i,\mathbf{r}_i)$ and $(q_j,\mathbf{r}_j)$ subject to a given periodic boundary condition and the chosen infinite boundary term. $u(\mathbf{r}_i,\mathbf{r}_j)$ is well-defined as the Coulomb lattice energy of the unit cell consisting of two charges $(q_i,\mathbf{r}_i)$ and $(q_j,\mathbf{r}_j)$ in a periodic lattice of all their images with the charge of all images of one charge $(q_i,\mathbf{r}_i)$ set to $-q_j$ (Figure 1a) or the other charge $(q_j,\mathbf{r}_j)$ set to $-q_i$ (Figure 1b) subject to a given infinite (asymptotic) boundary.

Clearly, $v(\mathbf{r}_i,\mathbf{r}_j)$ can be written as either the form of the Coulomb lattice sum or the form of the Ewald3D sum. All discussions on the conditional infinite boundary term of the Ewald3D sum can be recast and extended by means of the corresponding term of $v(\mathbf{r}_i,\mathbf{r}_j)$. $v(\mathbf{r}_i,\mathbf{r}_j)$ itself is directional when the three orthogonal directions are defined, but as $V\to\infty$ in a very large simulation box, for the scaled distance $\alpha|\mathbf{r}_{ij}|$ (α is the screening factor of the Ewald separation) much smaller than 1, $v(\mathbf{r}_i,\mathbf{r}_j) \to 1/|\mathbf{r}_i - \mathbf{r}_j|$, which is the usual Coulomb interaction.

dx.doi.org/10.1021/ct500704m | J. Chem. Theory Comput. XXXX, XXX, XXX−XXX

4. EWALD2D SUM FOR ELECTROSTATICS AT INTERFACES AND THE PAIRWISE FORM

The above transparent derivation immediately suggests that it is straightforward as well to derive the Ewald2D sum for electrostatics in slab geometry as long as one can determine the corresponding 2D Fourier transform of the error function part of the Ewald separation, eq 1. Therefore, we are looking for the 2D Fourier transform $\hat{f}(\mathbf{m})$ satisfying

$$\frac{\mathrm{erf}(\alpha r)}{r} = \frac{1}{(2\pi)^2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \mathrm{d}m_1\mathrm{d}m_2 \hat{f}(\mathbf{m}) \mathrm{e}^{i\mathbf{m}\cdot\mathbf{r}} \tag{35}$$

where the 2D Fourier space vector is $\mathbf{m} = (m_1,m_2,0)$. We have emphasized that the Gaussian function in the convolution expression of the error function part of Ewald separation in eq 2 helps to obtain the 3D Fourier transform. Similarly, by transferring the Gaussian functions in x and y in the definition of the error function, we can find the corresponding 2D Fourier transform

$$\begin{aligned}\hat{f}(\mathbf{m}) &= \frac{2}{\sqrt{\pi}}\int_0^{\alpha} \mathrm{d}\tau \left(\frac{\sqrt{\pi}}{\tau}\right)^2 \mathrm{e}^{-(m_1^2+m_2^2)/(4\tau^2)} \\ &\quad \times \frac{1}{2\pi}\int_{-\infty}^{\infty} \frac{\sqrt{\pi}}{\tau} \mathrm{e}^{-u^2/(4\tau^2)} \mathrm{e}^{iuz}\,\mathrm{d}u \\ &= \frac{1}{2\pi}\int_{-\infty}^{\infty} \mathrm{d}u \frac{4\pi}{m^2+u^2} \mathrm{e}^{-(u^2+m^2)/(4\alpha^2)} \mathrm{e}^{iuz}\end{aligned} \tag{36}$$

where m is the module of vector ($m = |\mathbf{m}| = (m_1^2 + m_2^2)^{1/2}$). With the above 2D Fourier transform, we apply the previous transparent procedure and then immediately obtain the first two terms of the Ewald2D formula

$$\mathcal{U}^{\mathrm{R-2D}} = \frac{1}{2}\sum_{i,j=1}^{N} q_i q_j \sum_{\mathbf{n}}{}' \frac{\mathrm{erfc}(\alpha|\mathbf{r}_{ij}+\mathbf{n}|)}{|\mathbf{r}_{ij}+\mathbf{n}|} - \frac{\alpha}{\sqrt{\pi}}\sum_{j=1}^{N} q_j^2 \tag{37}$$

and

$$\mathcal{U}^{\mathrm{F-2D}} = \sum_{i,j=1}^{N} q_i q_j \sum_{\mathbf{h}\neq 0} \frac{\mathrm{e}^{i\mathbf{h}\cdot\mathbf{r}_{ij}}}{L_x L_y}\int_{-\infty}^{\infty} \mathrm{d}u \frac{\mathrm{e}^{-(h^2+u^2)/(4\alpha^2)}}{h^2+u^2} \mathrm{e}^{iuz_{ij}} \tag{38}$$

where $\mathbf{h} = 2\pi(h_x/L_x,h_y/L_y,0)$ and the 2D real space vector $\mathbf{n} = (n_xL_x,n_yL_y,0)$. The reciprocal space term is a form of 2D Fourier transform[38] and can be written alternatively as

$$\begin{aligned}\mathcal{U}^{\mathrm{F-2D}} = \frac{\pi}{2A}\sum_{i,j} q_i q_j \sum_{\mathbf{h}\neq 0} \frac{\mathrm{e}^{i\mathbf{h}\cdot\mathbf{r}_{ij}}}{h}\Bigg[&\mathrm{e}^{-hz_{ij}}\,\mathrm{erfc}\left(\frac{h}{2\alpha} - \alpha z_{ij}\right) \\ &+ \mathrm{e}^{hz_{ij}}\,\mathrm{erfc}\left(\frac{h}{2\alpha} + \alpha z_{ij}\right)\Bigg]\end{aligned}$$

where we have set the unit area $A = L_xL_y$. Following the identical procedure that we simplified $\mathcal{U}^{\mathrm{IB}}$, we have

$$\begin{aligned}\mathcal{U}^{\mathrm{IB-2D}} &= \frac{\pi}{2A}\lim_{\mathbf{h}\to 0}\sum_{i,j=1}^{N} q_i q_j \frac{1 + i\mathbf{h}\cdot\mathbf{r}_{ij} + \mathbf{O}(h^2)}{h} \\ &\quad \times \left[2 - 2h\left(z_{ij}\mathrm{erf}(\alpha z_{ij}) + \frac{\mathrm{e}^{-(\alpha z_{ij})^2}}{\alpha\sqrt{\pi}}\right) + \mathbf{O}(h^2)\right] \\ &= \frac{-\pi}{A}\sum_{i,j=1}^{N} q_i q_j \left[z_{ij}\mathrm{erf}(\alpha z_{ij}) + \frac{\mathrm{e}^{-(\alpha z_{ij})^2}}{\alpha\sqrt{\pi}}\right]\end{aligned} \tag{39}$$

Clearly, in the Ewald2D case, the limit in the infinite boundary term exists and is independent of the orientation chosen for h. The above Ewald2D sum was originally derived in different fashions by Parry,[39] Heyes, Barber, and Clarke,[40] and de Leeuw and Perram.[36] It is interesting to note that the Ewald2D sum was actually done in a few years earlier than the work on the Ewald3D sum by de Leeuw, Perram, and Smith[17] although the development of efficient algorithms for Ewald2D sum at present lags far behind that for the Ewald3D sum (see, e.g., ref 32). Recent progress made by Lindbo and Tornberg[41] via approximating the above eqs 38 and 39 seems very promising. However, it might be useful to think about the role of the extra periodicity in the Ewald3D sum and how these developments for the Ewald2D sum can be made more efficient than or as efficient as the usual PME algorithms for the case of 3D periodicity.[42]

Following the previous transparent procedure to derive the pairwise form of the Ewald3D sum, it is also straightforward to write down the corresponding pairwise form of the Ewald2D sum with its physical meaning shown by the picture in Figure 1

$$\begin{aligned}u^{\mathrm{2D}}(\mathbf{r}_i,\mathbf{r}_j) = q_i q_j[&v^{\mathrm{R-2D}}(\mathbf{r}_i,\mathbf{r}_j) + v^{\mathrm{F-2D}}(\mathbf{r}_i,\mathbf{r}_j) \\ &+ v^{\mathrm{IB-2D}}(\mathbf{r}_i,\mathbf{r}_j)]\end{aligned} \tag{40}$$

with the real space term $v^{\mathrm{R-2D}}$, the reciprocal space term $v^{\mathrm{F-2D}}$, and the infinite boundary term $v^{\mathrm{IB-2D}}$ in 2D periodicity written as

$$v^{\mathrm{R-2D}}(\mathbf{r}_i,\mathbf{r}_j) = \sum_{\mathbf{n}} \frac{\mathrm{erfc}(\alpha|\mathbf{r}_{ij}+\mathbf{n}|)}{|\mathbf{r}_{ij}+\mathbf{n}|} - \sum_{\mathbf{n}}{}' \frac{\mathrm{erfc}(\alpha|\mathbf{n}|)}{|\mathbf{n}|} + \frac{2\alpha}{\sqrt{\pi}} \tag{41}$$

$$\begin{aligned}v^{\mathrm{F-2D}}(\mathbf{r}_i,\mathbf{r}_j) = \frac{\pi}{A}\sum_{\mathbf{h}\neq 0} \frac{\mathrm{e}^{i\mathbf{h}\cdot\mathbf{r}_{ij}}}{h}\Bigg[&\mathrm{e}^{-hz_{ij}}\,\mathrm{erfc}\left(\frac{h}{2\alpha} - \alpha z_{ij}\right) \\ &+ \mathrm{e}^{hz_{ij}}\mathrm{erfc}\left(\frac{h}{2\alpha} + \alpha z_{ij}\right)\Bigg] - \frac{2\pi}{A}\sum_{\mathbf{h}\neq 0}\frac{1}{h}\,\mathrm{erfc}\left(\frac{h}{2\alpha}\right)\end{aligned} \tag{42}$$

and

$$v^{\mathrm{IB-2D}}(\mathbf{r}_i,\mathbf{r}_j) = \frac{-2\pi}{A}\left[z_{ij}\,\mathrm{erf}(\alpha z_{ij}) + \frac{\mathrm{e}^{-(\alpha z_{ij})^2}}{\alpha\sqrt{\pi}} - \frac{1}{\alpha\sqrt{\pi}}\right] \tag{43}$$

respectively.

5. EWALD1D SUM FOR ELECTROSTATICS AT INTERFACES AND THE PAIRWISE FORM

There is also no difficulty in obtaining the Ewald1D sum. Again, we first focus on the 1D Fourier transform in z direction of the error function part of the Ewald separation in eq 2.

dx.doi.org/10.1021/ct500704m | J. Chem. Theory Comput. XXXX, XXX, XXX−XXX

Following the same procedure we obtain the 2D Fourier transform, we have

$$\hat{f}(q) = \int\int_{-\infty}^{+\infty} \mathrm{d}u\mathrm{d}v \frac{\mathrm{e}^{-(u^2+v^2+q^2)/(4\alpha^2)}}{\pi(u^2+v^2+q^2)} \mathrm{e}^{i(ux+vy)} \tag{44}$$

Note that notation q is the variable in one-dimensional reciprocal space in this section, which should not be confused with the previous notation for the test charge. If we use this 1D Fourier transform, we will arrive at the Ewald1D sum identical to the previous result by Smith[27] expressing the reciprocal space term and the infinite boundary term as complicated double integrals. According to our notation, we write the Ewald1D formula:

$$\mathcal{U}^{1D} = \mathcal{U}^{R-1D} + \mathcal{U}^{F-1D} + \mathcal{U}^{IB-1D} \tag{45}$$

where the real space term $\mathcal{U}^{R-1D}$, the reciprocal space term $\mathcal{U}^{F-1D}$, and the infinite boundary term $\mathcal{U}^{IB-1D}$ are explicitly written as

$$\mathcal{U}^{R-1D} = \frac{1}{2}\sum_{i,j=1}^{N} q_i q_j {\sum_{\mathbf{n}}}' \frac{\mathrm{erfc}(\alpha|\mathbf{r}_{ij}+\mathbf{n}|)}{|\mathbf{r}_{ij}+\mathbf{n}|} - \frac{\alpha}{\sqrt{\pi}}\sum_{j=1}^{N} q_j^2 \tag{46}$$

$$\mathcal{U}^{F-1D} = \frac{1}{2}\sum_{i,j=1}^{N} q_i q_j \sum_{q\neq 0} \frac{\mathrm{e}^{iqz_{ij}}}{L_z} \int\int_{-\infty}^{+\infty} \mathrm{d}u\mathrm{d}v \frac{\mathrm{e}^{-(u^2+v^2+q^2)/(4\alpha^2)}}{\pi(u^2+v^2+q^2)} \mathrm{e}^{i(ux_{ij}+vy_{ij})} \tag{47}$$

and

$$\mathcal{U}^{IB-1D} = \lim_{q\to 0}\frac{1}{2}\sum_{i,j=1}^{N} q_i q_j \frac{\mathrm{e}^{iqz_{ij}}}{L_z} \int\int_{-\infty}^{+\infty} \mathrm{d}u\mathrm{d}v \frac{\mathrm{e}^{-(u^2+v^2+q^2)/(4\alpha^2)}\,\mathrm{e}^{i(ux_{ij}+vy_{ij})} - 1}{\pi(u^2+v^2+q^2)} \tag{48}$$

where the propagation vector in 1D periodicity is $\mathbf{n} = (0,0,nL_z)$. q is taken as $2\pi/L_z$ multiplied by an integer analogous to $\mathbf{h}$ for 2D periodicity and $\mathbf{k}$ for 3D periodicity. The above Ewald1D expression in eqs 46 and 47 is identical to the formula derived rigorously by Smith (see the first two terms of eq 43 of ref 27). Smith further manipulated the surface term (the third term of eq 43 of ref 27), but we simply write the term as the infinite boundary term of eq 48.

Alternatively, we have the following 1D Fourier transform

$$\hat{f}(q) = \int_{-\infty}^{+\infty} \mathrm{d}z \frac{\mathrm{erf}(\alpha r)}{r} \mathrm{e}^{-iqz} = 2\int_0^{\alpha} \mathrm{d}\tau \frac{\mathrm{e}^{-q^2/(4\tau^2)}}{\tau} \mathrm{e}^{-(x^2+y^2)\tau^2} \tag{49}$$

which seems a simpler expression than the previous 1D Fourier transform of eq 44. Using this alternative 1D Fourier transform and following the transparent procedure in the previous sections, we obtain the alternative Ewald1D sum formula in which the real space term is identical to eq 46 but the reciprocal space term $\mathcal{U}^{F-1D}$ and the infinite boundary term $\mathcal{U}^{IB-1D}$ have the following explicit expressions

$$\mathcal{U}^{F-1D} = \sum_{i,j=1}^{N} q_i q_j \sum_{q\neq 0} \frac{\mathrm{e}^{iqz_{ij}}}{L_z} \int_0^{\alpha} \mathrm{d}\tau \frac{\mathrm{e}^{-q^2/(4\tau^2)}}{\tau} \mathrm{e}^{-(x_{ij}^2+y_{ij}^2)\tau^2} \tag{50}$$

and

$$\mathcal{U}^{IB-1D} = \lim_{q\to 0}\sum_{i,j=1}^{N} q_i q_j \frac{\mathrm{e}^{iqz_{ij}}}{L_z} \int_0^{\alpha} \mathrm{d}\tau \frac{\mathrm{e}^{-q^2/(4\tau^2)}}{\tau} \mathrm{e}^{-(x_{ij}^2+y_{ij}^2)\tau^2} \tag{51}$$

respectively. By removing the constant divergence associated with the infinite boundary term, we have

$$\mathcal{U}^{IB-1D} = \frac{1}{L_z}\sum_{i,j=1}^{N} q_i q_j \int_0^{\alpha} \mathrm{d}\tau \frac{\mathrm{e}^{-(x_{ij}^2+y_{ij}^2)\tau^2} - 1}{\tau} \tag{52}$$

In the Appendix, we rigorously prove the equivalence between the two Ewald1D formula of eqs 47 and 48 and that of eqs 50 and 52 subject to the electroneutrality condition. Correspondingly, the pairwise form of the Ewald1D formula is

$$u^{1D}(\mathbf{r}_i, \mathbf{r}_j) = q_i q_j [v^{R-1D}(\mathbf{r}_i, \mathbf{r}_j) + v^{F-1D}(\mathbf{r}_i, \mathbf{r}_j) + v^{IB-1D}(\mathbf{r}_i, \mathbf{r}_j)] \tag{53}$$

with the real space term v^{R-1D}, the reciprocal space term v^{F-1D}, and the infinite boundary term v^{IB-1D} written as

$$v^{R-1D}(\mathbf{r}_i, \mathbf{r}_j) = \sum_{\mathbf{n}} \frac{\mathrm{erfc}(\alpha|\mathbf{r}_{ij}+\mathbf{n}|)}{|\mathbf{r}_{ij}+\mathbf{n}|} - {\sum_{\mathbf{n}}}' \frac{\mathrm{erfc}(\alpha|\mathbf{n}|)}{|\mathbf{n}|} + \frac{2\alpha}{\sqrt{\pi}} \tag{54}$$

$$v^{F-1D}(\mathbf{r}_i, \mathbf{r}_j) = \sum_{q\neq 0} \frac{2\mathrm{e}^{iqz_{ij}}}{L_z} \int_0^{\alpha} \mathrm{d}\tau \frac{\mathrm{e}^{-q^2/(4\tau^2)}}{\tau} \mathrm{e}^{-(x_{ij}^2+y_{ij}^2)\tau^2} - \frac{2}{L_z}\sum_{q\neq 0}\int_0^{\alpha} \mathrm{d}\tau \frac{\mathrm{e}^{-q^2/(4\tau^2)}}{\tau} \tag{55}$$

and

$$v^{IB-1D}(\mathbf{r}_i, \mathbf{r}_j) = \frac{2}{L_z}\int_0^{\alpha} \mathrm{d}\tau \frac{\mathrm{e}^{-(x_{ij}^2+y_{ij}^2)\tau^2} - 1}{\tau} \tag{56}$$

Now it is very clear that the conditional property of the infinite boundary term depending on the asymptotic behavior that the periodic system approaches the infinite in the present work is specific and only inherent to the Ewald3D formula and does not occur in the Ewald2D and Ewald1D formula. The underlying mathematical reason is that the divergence is only partially removed in the Ewald3D sum by the electroneutrality condition but is completely removed in the Ewald2D and Ewald1D sums. The present analysis focusing on the simpler infinite periodic lattice does not directly suggest whether the ambiguity exists or not when considering a macroscopic but finite system that is periodic in one and two dimensions. We present some preliminary discussion about the nature of ambiguities in Ewald sums in the next section.

6. DISCUSSION

The infinite boundary in this work refers to the way that the periodic system approaches the infinite, and hence, the infinite boundary term arises from the asymptotic boundary of the system, different from the usual macroscopic boundary at a large but finite distance. We have provided a simple analysis based on the $\mathbf{k} \to 0$ term, which yields an explicit expression for

the infinite boundary terms. As far as the author of the present work understands, ambiguity might still exist when one deals with a very large but finite system. For example, we might consider a neutral system of a cubic unit cell consisting of 2 point charges and its N (N is a large but finite number) periodic replica in 3D, 2D, or 1D dimension. What is the difference between the Coulomb energy felt by the central unit cell for $N \simeq 10^{10}$ and that for $N \simeq 10^{23}$? If the value of the difference between the two Coulomb energies is nonnegligible, how does it change when we arrange the replica differently corresponding to different macroscopic shapes?

We denote the dipole moment in the unit cell is $\mathbf{d}$, the dipole moment contribution to the difference of Coulomb lattice sum, Δ^{1D} in one-dimensional periodicity can be written as

$$\Delta^{1D} = \sum_{m=10^{10}}^{10^{23}} \frac{\mathbf{d}\cdot\mathbf{d}}{(mL)^3} \simeq \frac{\mathbf{d}\cdot\mathbf{d}}{L^3}\int_{10^{10}}^{10^{23}} dx \frac{1}{x^3} \simeq 10^{-20}\frac{\mathbf{d}\cdot\mathbf{d}}{L^3} \tag{57}$$

Similarly, one can estimate the order of the dipole moment contribution to Δ^{2D} in case that the macroscopic boundary is a flat cylinder.

$$\begin{aligned}\Delta^{2D} &= \sum_{n=10^5}^{10^{12}}\sum_{m=10^5}^{10^{12}} \frac{\mathbf{d}\cdot\mathbf{d}}{(m^2+n^2)^{3/2}L^3} \\ &\simeq \frac{\mathbf{d}\cdot\mathbf{d}}{L^3}\int_{10^5}^{10^{12}}\int_{10^5}^{10^{12}} dxdy \frac{1}{(x^2+y^2)^{3/2}} \\ &\simeq 10^{-5}\frac{\mathbf{d}\cdot\mathbf{d}}{L^3}\end{aligned} \tag{58}$$

Furthermore, when the macroscopic shape is a sphere, one can estimate the order of the dipole moment contribution to Δ^{3D}

$$\begin{aligned}\Delta^{3D} &= \sum_{n=10^3}^{10^8}\sum_{m=10^3}^{10^8}\sum_{p=10^3}^{10^8} \frac{\mathbf{d}\cdot\mathbf{d}}{(m^2+n^2+p^2)^{3/2}L^3} \\ &\simeq \frac{\mathbf{d}\cdot\mathbf{d}}{L^3}\int_{10^3}^{10^8}\int_{10^3}^{10^8}\int_{10^3}^{10^8} dxdydz \frac{1}{(x^2+y^2+z^2)^{3/2}} \\ &\simeq 20\pi \ln 10 \frac{\mathbf{d}\cdot\mathbf{d}}{L^3}\end{aligned} \tag{59}$$

Because Δ^{1D} and Δ^{2D} are relatively small values compared to the electrostatic energy of the single cell (the gas phase energy) or $\mathbf{d}\cdot\mathbf{d}/L^3$, both Δ^{1D} and Δ^{2D} might weakly depend on the macroscopic shape of the crystal. However, Δ^{3D} is a very large value, and we expect that it should strongly depend on the macroscopic shape of the finite crystal. This discussion is more or less consistent with the observation that the infinite boundary term of the Ewald2D or Ewald1D sum is not conditional. However, we are aware of that this discussion is far from an ultimate rigorous analysis because we have neglected the effect of the quadrupole and higher order moments and replaced the discrete sums by the corresponding continuous integrals. Nonetheless, we hope that the present work and this discussion will stimulate investigation of new and more rigorous analysis.

7. CONCLUSION

We have given new derivations of the Ewald3D, Ewald2D, and Ewald1D sums for the relatively simple system of infinite lattice subject to a infinite (asymptotic) boundary using a transparent three-step procedure. We systematically analyze the infinite boundary terms consistent with a number of existing arguments. The transparent and unified derivations help to understand how the divergence in the Coulomb lattice sum can be completely removed using the electroneutrality condition for systems with 2D and 1D periodicity. However, the divergence in the Ewald3D sum cannot be completely removed because it couples with the coordinates of charges. Therefore, the infinite boundary term in the Ewald3D sum is conditional because it explicitly depends on the asymptotic behavior that the system approaches the infinite. However, we obtain the definite infinite boundary terms regardless of the asymptotic behavior in the 2D and 1D periodicity.

Although the previous works[17−19] have pointed out the existence and importance of the surface or dipole terms in 3D periodicity long time ago, we have shown that a very simple formal analysis of the $\mathbf{k} \to \mathbf{0}$ term is able to give very fruitful information about it. We hope that our plausible analysis about how to deal with the ambiguity might be at least useful to stimulate investigation of new and more rigorous analysis.

Moreover, when starting from the alternative 1D Fourier transform of the error function part of the Ewald separation, we have obtained the alternative Ewald1D formula. A rigorous proof is provided to confirm that the two Ewald1D formulas are equivalent. In the future, we plan to present further analysis of the two Ewald1D formula regarding their efficiency for computer simulation of liquids under 1D uniform confinement or wirelike organic crystals.

Using a physically transparent method that accounts for the explicit presence of the periodic images, we have derived pairwise potentials for the Ewald3D, Ewald2D, and Ewald1D sums, respectively. These pairwise potentials depend on the periodic boundary conditions and have the same real space term but quite different reciprocal space terms and infinite boundary terms reflecting the effect of the explicit presence of the images. The developed pair potentials with their clear physical meanings should be useful for consistent analysis of the contributions from selected group of charges when computer simulations of bulk or interfaces use the Ewald sums for the electrostatics.

APPENDIX A: AN ELEMENTARY PROOF OF THE POISSON SUMMATION FORMULA

We give in this appendix a simple proof of the Poisson summation formula eq 6 used in the main text. The 1D Poisson summation formula relates the periodic series of an arbitrary function $f(x)$ to a sum over its continuous Fourier transform $\hat{f}(k)$. Given that $f(x)$ is integrable over the region $[-P/2,P/2]$, we then expand each function $f(nP + x)$ by its discrete Fourier series:

$$f(nP+x) \equiv g(x) = \sum_{m=-\infty}^{\infty} C_{m,n}\, e^{i2m\pi x/P} \tag{A1}$$

where the discrete Fourier coefficient is written as

dx.doi.org/10.1021/ct500704m | J. Chem. Theory Comput. XXXX, XXX, XXX−XXX

$$C_{m,n} = \frac{1}{P}\int_{-P/2}^{P/2} \mathrm{d}t g(t) \mathrm{e}^{-i2m\pi t/P} = \frac{1}{P}\int_{-P/2}^{P/2} \mathrm{d}t f(nP + t) \mathrm{e}^{-i2m\pi t/P} = \frac{1}{P}\int_{-P/2+nP}^{P/2+nP} \mathrm{d}t f(t) \mathrm{e}^{-i2m\pi t/P} \tag{A2}$$

Clearly, the sum over all n gives the continuous Fourier transform

$$\sum_{n=-\infty}^{\infty} C_{m,n} = \frac{1}{P}\int_{-\infty}^{\infty} \mathrm{d}t f(t) \mathrm{e}^{-i2m\pi t/P} \tag{A3}$$

Therefore, the 1D Poisson summation formula reads

$$\sum_n f(nP + x) = \sum_m \mathrm{e}^{i2\pi mx/P} \frac{1}{P}\int_{-\infty}^{\infty} \mathrm{d}t f(t) \mathrm{e}^{-i2m\pi t/P} = \frac{1}{P}\sum_m \hat{f}\left(\frac{2\pi m}{P}\right) \mathrm{e}^{i2\pi mx/P} \tag{A4}$$

where the 1D Fourier transform is defined as

$$\hat{f}(q) = \int_{-\infty}^{\infty} \mathrm{d}t f(t) \mathrm{e}^{-iqt} \leftrightarrow f(t) = \frac{1}{2\pi}\int_{-\infty}^{\infty} \mathrm{d}q f(q) \mathrm{e}^{iqt} \tag{A5}$$

Extension of the 1D formula to 2D or 3D is straightforward. For example, the 3D Poisson summation formula of eq 6 in the main text reads

$$\sum_{n_1,n_2,n_3} f(\mathbf{n}\cdot\mathbf{P} + \mathbf{r}) = \frac{1}{P_1P_2P_3}\sum_{k_1,k_2,k_3} \hat{f}(\mathbf{k}) \mathrm{e}^{i\mathbf{k}\cdot\mathbf{r}} \tag{A6}$$

where the real space vectors $\mathbf{P}$, and $\mathbf{n}$ and the reciprocal space vector $\mathbf{k}$ are (P_1,P_2,P_3), (n_1,n_2,n_3), and $2\pi(k_1/P_1,k_2/P_2,k_3/P_3)$, respectively. Clearly, the real space propagation vector $\mathbf{n}$ in the Poisson summation formula in the main text resembles (n_1P_1,n_2P_2,n_3P_3) here.

APPENDIX B: A RIGOROUS PROOF OF THE EQUIVALENCE BETWEEN THE TWO EWALD1D FORMULAS

We give a rigorous proof the equivalence between the reciprocal space term and the infinite boundary term of the two Ewald1D formulas in the main text. The infinite boundary term eqs 48 or 52 differs from the reciprocal space term eq 47 or eq 50 in that an infinite constant multiplied by $\sum_{i,j=1}^{N} q_iq_j$ is added to remove the divergence. Therefore, it is enough to prove the following identity for any $q \neq 0$,

$$\int_0^{\alpha} \mathrm{d}\tau \frac{\mathrm{e}^{-q^2/(4\tau^2)}}{\tau} \mathrm{e}^{-(x^2+y^2)\tau^2} = \frac{1}{2\pi}\iint_{-\infty}^{\infty} \mathrm{d}u\mathrm{d}v \frac{\mathrm{e}^{-(u^2+v^2+q^2)/(4\alpha^2)}}{u^2+v^2+q^2} \mathrm{e}^{i(ux+vy)} \tag{B1}$$

Although the Ewald sum formulas in the present work are all derived formally on an ad hoc basis, we show here that there is no ambiguity for the correctness of the above equality (eq B1). Using the inverse 2D Fourier transform of the Gaussian function $\mathrm{e}^{-(x^2+y^2)\tau^2}$, the left-hand side of eq B1 is written as

$$\text{l.h.s.} = \int_0^{\alpha} \mathrm{d}\tau \frac{\mathrm{e}^{-q^2/(4\tau^2)}}{\tau} \frac{1}{4\pi\tau^2} \iint_{-\infty}^{\infty} \mathrm{d}u\mathrm{d}v \, \mathrm{e}^{-(u^2+v^2)/(4\tau^2)} \mathrm{e}^{i(ux+vy)} = \frac{1}{2\pi}\int_0^{\alpha} \mathrm{d}\tau \iint_{-\infty}^{\infty} \mathrm{d}u\mathrm{d}v \frac{\mathrm{e}^{-(u^2+v^2+q^2)/(4\tau^2)}}{2\tau^3} \mathrm{e}^{i(ux+vy)} \tag{B2}$$

Because both the integration over $\mathrm{d}u\mathrm{d}v$ and the total integral absolutely converge for any finite value of q, we can exchange the order of the integral to perform the integration over $\mathrm{d}\tau$ first

$$\text{l.h.s.} = \frac{1}{2\pi}\iint_{-\infty}^{\infty} \mathrm{d}u\mathrm{d}v \, \mathrm{e}^{i(ux+vy)} \int_0^{\alpha} \mathrm{d}\tau \frac{\mathrm{e}^{-(u^2+v^2+q^2)/(4\tau^2)}}{2\tau^3} = \frac{1}{2\pi}\iint_{-\infty}^{\infty} \mathrm{d}u\mathrm{d}v \, \mathrm{e}^{i(ux+vy)} \int_{1/(4\alpha^2)}^{\infty} \mathrm{d}t \mathrm{e}^{-(u^2+v^2+q^2)t} = \frac{1}{2\pi}\iint_{-\infty}^{\infty} \mathrm{d}u\mathrm{d}v \, \mathrm{e}^{i(ux+vy)} \frac{\mathrm{e}^{-(u^2+v^2+q^2)/(4\alpha^2)}}{u^2+v^2+q^2} \equiv \text{r.h.s.} \tag{B3}$$

where we have used the substitute $t = 1/(4\tau^2)$ and hence $\mathrm{d}t = -1/(2\tau^3)\mathrm{d}\tau$ in the second equality of the above equation. We thus complete the rigorous proof of the equality (eq B1) for any $q \neq 0$.

AUTHOR INFORMATION

Corresponding Author

*E-mail: zhonghanhu@jlu.edu.cn.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by National Natural Science Foundation of China (grant nos. 91127015 and 21103063). I am indebted to Prof. Hans C. Andersen and Prof. John D. Weeks for their many useful comments and criticisms. I also acknowledge the anonymous reviewers for their comments to the first version of the draft that helps to significantly improve the quality of the present work. Finally, I acknowledge Prof. Yiqin Gao, Prof. Yi Wang, Prof. Jhih-Wei Chu, Prof. Hao Hu, Prof. Jiushu Shao, Prof. Yanting Wang, and Prof. Christopher Jarzynski for their helpful discussions and reading the manuscript.

REFERENCES

(1) Ewald, P. P. *Ann. Phys. Leipzig* **1921**, *64*, 253−87.
(2) Allen, M. P.; Tildesley, D. J. *Computer Simulation of Liquids*, 1st ed.; Oxford University Press Inc.: New York, 1987.
(3) Frenkel, D.; Smit, B. *Understanding Molecular Simulation: From Algorithms to Applications*, 2nd ed.; Academic Press, Inc.: San Diego, 2002.
(4) Darden, T.; York, D.; Pedersen, L. *J. Chem. Phys.* **1993**, *98*, 10089−10092.
(5) Essmann, U.; Perera, L.; Berkowitz, M. L.; Darden, T.; Lee, H.; Pedersen, L. G. *J. Chem. Phys.* **1995**, *103*, 8577−8593.
(6) Deserno, M.; Holm, C. *J. Chem. Phys.* **1998**, *109*, 7678−7693.
(7) Hockney, R.; Eastwood, J. *Computer Simulation Using Particles*; McGraw-Hill: NewYork, 1981.
(8) Wolf, D.; P, S.; Keblinski, P.; Eggebrecht, J. *J. Chem. Phys.* **1999**, *110*, 8254.
(9) Rodgers, J. M.; Weeks, J. D. *Proc. Natl. Acad. Sci. U.S.A.* **2008**, *105*, 19136−19141.
(10) Hu, Z.; Weeks, J. D. *Phys. Rev. Lett.* **2010**, *105*, 140602.

(11) Rodgers, J. M.; Hu, Z.; Weeks, J. D. *Mol. Phys.* **2011**, *109*, 1195−1211.
(12) Sagui, C.; Darden, T. A. *Annu. Rev. Biophys. Biomol. Struct.* **1999**, *28*, 155−79.
(13) Euwema, R. N.; Surratt, G. T. *J. Phys. Chem. Solids* **1975**, *36*, 67.
(14) Neumann, M.; Steinhauser, O.; Pawley, G. *Mol. Phys.* **1984**, *52*, 97.
(15) Boresch, S.; Steinhauser, O. *Berichte der Bunsengesellschaft für physikalische Chemie* **1997**, *101*, 1019.
(16) Ballenegger, V.; Hansen, J. P. *Mol. Phys.* **2004**, *102*, 599.
(17) de Leeuw, S. W.; Perram, J. W.; Smith, E. R. *Proc. R. Soc. London, Ser. A* **1980**, *373*, 27−56.
(18) de Leeuw, S. W.; Perram, J. W.; Smith, E. R. *Proc. R. Soc. London, Ser. A* **1980**, *373*, 57−66.
(19) Smith, E. R. *Proc. R. Soc. London, Ser. A* **1981**, *375*, 475.
(20) de Leeuw, S. W.; Perram, J. W.; Smith, E. R. *Proc. R. Soc. London, Ser. A* **1983**, *388*, 177−193.
(21) Hansen, J.-P. In *Molecular Dynamics Simulation of Statistical Mechanical System*; Proceeding of the International School of Physics "Enrico Fermi", North-Holland Amsterdam; Ciccotti, G., Hoover, W. G., Eds.; Wiley: New York, 1986; pp 89−129.
(22) Smith, E. *Mol. Phys.* **1988**, *65*, 1089−1104.
(23) Hunenberger, P. H. *AIP Conf. Proc.* **1999**, *492*, 17−83.
(24) Kantorovich, L. N.; Tupitsyn, I. I. *J. Phys.: Cond. Matter* **1999**, *11*, 6159.
(25) Heinz, T. N.; Hunenberger, P. H. *J. Chem. Phys.* **2005**, *123*, 034107.
(26) Herce, H. D.; Garcia, A. E.; Darden, T. *J. Chem. Phys.* **2007**, *126*, 124106.
(27) Smith, E. R. *J. Chem. Phys.* **2008**, *128*, 174104.
(28) Ballenegger, V. *J. Chem. Phys.* **2014**, *140*, 161102.
(29) Redlack, A.; Grindlay, J. *Can. J. Phys.* **1972**, *50*, 2815−2825.
(30) Redlack, A.; Grindlay, J. *J. Phys. Chem. Solids* **1975**, *36*, 73−82.
(31) Yeh, I.-C.; Berkowitz, M. L. *J. Chem. Phys.* **1999**, *111*, 3155−3162.
(32) Pan, C.; Hu, Z. *J. Chem. Theory Comput.* **2014**, *10*, 534−542.
(33) Yeh, I.-C.; Wallqvist, A. *J. Chem. Phys.* **2011**, *134*, 055109.
(34) Arnold, A.; de Joannis, J.; Holm, C. *J. Chem. Phys.* **2002**, *117*, 2496−2502.
(35) See the first two equations in the original 1921 paper by Paul Peter Ewald.
(36) De Leeuw, S. W.; Perram, J. W. *Mol. Phys.* **1979**, *37*, 1313−1322.
(37) Hummer, G.; Gro/nbech-Jensen, N.; Neumann, M. *J. Chem. Phys.* **1998**, *109*, 2791−2797.
(38) *Tables of Integral Transforms*; Erdelyi, A., Ed.; McGraw-Hill: New York, 1954; Vol. *I*.
(39) Parry, D. *Surf. Sci.* **1975**, *49*, 433−440.
(40) Heyes, D. M.; Barber, M.; Clarke, J. H. R. *J. Chem. Soc., Faraday Trans. II: Mol. Chem. Phys.* **1977**, *73*, 1485−1496.
(41) Lindbo, D.; Tornberg, A.-K. *J. Chem. Phys.* **2012**, *136*, 164111.
(42) Hu, Z. *Chem. Commun.* **2014**, *50*, 14397−14400.