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Some comments and corrections regarding the calculation of electrostatic potential derivatives using the Ewald summation technique

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A review of the literature on the calculation of electrostatic potentials, fields, and field gradients in systems consisting of charges and dipoles using the Ewald summation technique is presented. Discrepancies between the previous formulas are highlighted, and an error in the derivation of the reciprocal contributions to the electrostatic field and field gradient is corrected. The new formulas for the field and field gradient are shown to exhibit a termwise identity with the ones for the electrostatic energy. © *2011 American Institute of Physics.* [doi:10.1063/1.3599045]

I. INTRODUCTION

The simulation of bulk systems exhibiting electrostatic (Coulomb and dipole-dipole) interactions is a long-standing issue in physics and chemistry. The reason for this is that intermolecular potentials $v(r)$ that do not decay faster than r^{-3} formally possess an infinite range, in the sense that the integral

$$\int_{r_{cut}}^{\infty} v(r)4\pi r^2 dr, \qquad (1)$$

diverges for all finite values of the cutoff radius r_{cut}. Several solutions to this problem have been proposed, with the most popular one being the lattice-summation technique due to Ewald.[1,2] Within the Ewald formalism, the electrostatic interactions within the simulation box are rendered short-ranged through the addition of a neutralizing Gaussian charge density around each charge, whose width is controlled through the screening parameter α. The contribution from the screening charge distributions are then again subtracted by summing up a collection of Gaussians of opposite sign in reciprocal space. In order to achieve this, one makes an assumption of long-range periodicity, meaning that the primary simulation box is duplicated to generate an infinite primitive cubic lattice.

Apart from calculating electrostatic energies, there is often also a need to calculate electrostatic potentials, fields, and field gradients during the course of a computer simulation. Formulas for these quantities, together with equations describing pressure tensors and forces, in a system composed of charges, dipoles and polarizabilities were derived by Nymand and Linse.[3] These equations were generalized to systems also containing quadrupoles by Aguado and Madden,[4] and subsequently in a slightly different way by Laino and Hutter.[5] The expressions for electrostatic fields were also recently rederived in a contribution by Sala *et al.*[6] We finally note that the (correct) formulas for the electrostatic potential, field, and field gradient in a system consisting of charges, dipoles,

and quadrupoles were given already in 1977 by Weenk and Harwig,[7] although this fact seems to have gone unnoticed to the later authors.

The purpose of this study is to highlight the discrepancies between the equations derived in the above-mentioned papers and correct errors in the expressions describing the spatial potential derivatives.

II. GENERAL THEORY

We consider an infinite periodic system, where the central unit cell is composed of N particles, located at $\{\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N\} \equiv \{\mathbf{r}\}_N$, each one possessing an arbitrary set of electrostatic moments. The potential energy U_{el} of this system can be expressed as

$$U_{el} = \frac{1}{2} {\sum_{\mathbf{n}}}' \left[\sum_{i=1}^{N} \sum_{j=1}^{N} v(\mathbf{r}_{ij} + \mathbf{n}, \boldsymbol{\omega}_i, \boldsymbol{\omega}_j) \right], \qquad (2)$$

where $\mathbf{n} = (n_x L_x, n_y L_y, n_z L_z)$ runs over all lattice points in the primitive cubic lattice, with n_x, n_y, and n_z being integers and L_x, L_y, and L_z are the side lengths of the unit cell. Furthermore, the primed sum indicates that the term with $i = j$ should be excluded for $\mathbf{n} = \mathbf{0}$, and $v(\mathbf{r}_{ij}, \boldsymbol{\omega}_i, \boldsymbol{\omega}_j)$ denotes the (purely electrostatic) intermolecular potential between particles i and j, depending in general on their separation $\mathbf{r}_{ij}$ and orientations $\boldsymbol{\omega}_i$ and $\boldsymbol{\omega}_j$.

As a starting point for deriving expressions describing electrostatic fields and field gradients from the expression for U_{el}, we introduce an infinitesimal test charge δq located at $\mathbf{r}$ and define the electrostatic potential $\phi(\mathbf{r})$ as

$$\phi(\mathbf{r}) \equiv \lim_{\delta q \to 0} \frac{\partial U_{el}}{\partial(\delta q)}. \qquad (3)$$

The Cartesian components $E_\alpha(\mathbf{r})$ of the electrostatic field and $E_{\alpha\beta}(\mathbf{r})$ of the electrostatic field gradient are similarly defined

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by the relations

$$E_\alpha(\mathbf{r}) \equiv -\frac{\partial \phi(\mathbf{r})}{\partial r_\alpha} \quad (\mathbf{r} \notin \{\mathbf{r}\}_N), \tag{4a}$$

$$E_\alpha(\mathbf{r}_i) \equiv \lim_{\mathbf{r} \to \mathbf{r}_i} E_\alpha(\mathbf{r}) \quad (\mathbf{r}_i \in \{\mathbf{r}\}_N), \tag{4b}$$

and

$$E_{\alpha\beta}(\mathbf{r}) \equiv \frac{\partial E_\alpha(\mathbf{r})}{\partial r_\beta} \quad (\mathbf{r} \notin \{\mathbf{r}\}_N), \tag{5a}$$

$$E_{\alpha\beta}(\mathbf{r}_i) \equiv \lim_{\mathbf{r} \to \mathbf{r}_i} E_{\alpha\beta}(\mathbf{r}) \quad (\mathbf{r}_i \in \{\mathbf{r}\}_N). \tag{5b}$$

In a periodic system, the definitions given in Eqs. (4a) and (5a) hold only as long as the derivative is evaluated in a point where no particle is located. This is due to the fact that in a periodic system, the potential at the location $\mathbf{r}_i$ of particle i depends on the positions of all the periodic images of i. A direct evaluation of the spatial derivatives in $\mathbf{r}_i$ would thus correspond to an unphysical shift of the positions of all the periodic images of i, rather than just shifting the point where the potential is evaluated. Thus, to evaluate potential derivatives at the location of a particle, we use the complementary definitions given in Eqs. (4b) and (5b), whereby we avoid changing the particle positions when performing the derivative. We also add that for $\mathbf{n} = \mathbf{0}$ and $\mathbf{r} \in \{\mathbf{r}\}_N$, the infinite contributions coming from the particle in the evaluation point need to be subtracted from Eqs. (3), (4b) and (5b) in order to obtain finite values of the respective quantities. Henceforth, we will use the simplified notations $\phi_i = \phi(\mathbf{r}_i)$, $E_{i,\alpha} = E_\alpha(\mathbf{r}_i)$, and $E_{i,\alpha\beta} = E_{\alpha\beta}(\mathbf{r}_i)$.

An alternative route to obtaining expressions for the electrostatic potential and its derivatives is to identify them from an expression for the electrostatic energy of the system. In general, the total electrostatic energy U_{el} can be written as a multipole expansion of the charge distributions of the particles, in the form[8]

$$U_{\text{el}} = \frac{1}{2} \sum_{i=1}^{N} \left[q_i \phi_i - \mu_{i,\alpha} E_{i,\alpha} - \frac{1}{3} \Theta_{i,\alpha\beta} E_{i,\alpha\beta} + \dots \right], \tag{6}$$

where the Einstein summation convention has been used, and q_i, $\mu_{i,\alpha}$ and $\Theta_{i,\alpha\beta}$ denote the charge and the Cartesian dipole and quadrupole components, respectively, of particle i. The use of this strategy may in some cases be easier than directly using the definitions stated in Eqs. (3)–(5), and one also avoids the problems discussed above with performing spatial derivatives. On the other hand, Eq. (6) cannot be used to derive expressions for the electrostatic functions in any points outside of $\{\mathbf{r}\}_N$, so this strategy is less general.

In the following, we will consider systems consisting of only charges and dipoles, although quadrupoles sometimes need to be introduced in order to identify electrostatic field gradients using Eq. (6). We will furthermore assume that the system is charge neutral, i.e., $\sum_i q_i = 0$.

III. EWALD SUMMATION

The electrostatic energy of an infinite periodic system calculated using the Ewald summation technique involves a partitioning of the energy into four different contributions:

1. A real space energy U_{real} coming from the short-range Gaussian screened interaction between particles in the central box.
2. A reciprocal space energy U_{rec} coming from the summation of the interactions between the complementary Gaussian charge distributions.
3. A self-energy U_{self}, correcting for the inclusion of the interaction between each particle and its own Gaussian charge cloud.
4. A surface energy U_{surf}, coming from the solvation of the infinite lattice, which depends on the dielectric constant ε_{sur} of the surrounding medium. This contribution can be identified as coming from the $\mathbf{k} = \mathbf{0}$ term in the reciprocal space sum.[9]

In Subsections III A–III D, we will treat the four contributions to the potential, field, and field gradient one at a time highlighting some discrepancies and errors in the equations previously given in the literature.

A. Real space contributions

As was originally pointed out by Smith,[10] the real-space part of the electrostatic energy is conveniently obtained by replacing $r^{-(2n+1)}$, where r is the interparticle separation, in the standard (unscreened) formulas for the electrostatic energy, potential, field, and field gradient by its screened counterpart $\widehat{r^{-(2n+1)}}$. Although there does not seem to be any real controversy about these formulas, there are some typographic errors present in the literature. This was pointed out by Laino and Hutter,[5] who corrected for a missing double factorial in the formulas due to Nymand and Linse[3] and Aguado and Madden.[4] However, they instead introduced a new typo in the enumerator of the recursion formula. Thus, for completeness, the correct formulas for $\widehat{r^{-(2n+1)}}$ should read

$$\widehat{\frac{1}{r}} = \frac{\text{erfc}(\alpha r)}{r}, \tag{7a}$$

$$\widehat{\frac{1}{r^{(2n+1)}}} = r^{-2} \left[\widehat{\frac{1}{r^{(2n-1)}}} + \frac{(2\alpha^2)^n}{\sqrt{\pi}\alpha(2n-1)!!} e^{-\alpha^2 r^2} \right], \tag{7b}$$

in accordance with the expressions given by Sala *et al.*[6] In the above equations, erfc is the complementary error function, α is the Ewald screening parameter and !! denotes a double factorial.

B. Reciprocal space contributions

The expression for the reciprocal space energy U_{rec} of a system consisting of charges and permanent dipoles has been given several times in the literature and reads

$$U_{\text{rec}} = \frac{2\pi}{V} \sum_{\mathbf{k} \neq \mathbf{0}} A_k |\rho_N(\mathbf{k})|^2, \tag{8}$$

where $V = L_x L_y L_z$ is the volume of the unit cell,

$$A_k = \frac{e^{-k^2/4\alpha^2}}{k^2}, \tag{9}$$

and the generalized k-space charge density $\rho_N(\mathbf{k})$ is given by

$$\rho_N(\mathbf{k}) = \sum_{i=1}^{N} \left[q_i + \iota(\boldsymbol{\mu}_i \cdot \mathbf{k}) \right] e^{\iota \mathbf{k} \cdot \mathbf{r}_i}, \tag{10}$$

where the sum runs over all particles in the primary box. In the above equations, the vector $\mathbf{k}$ is defined as

$$\mathbf{k} = 2\pi(n_x/L_x, n_y/L_y, n_z/L_z), \tag{11}$$

and ι denotes the imaginary unit.

Insertion of the expression for $\rho_N(\mathbf{k})$ into Eq. (8) followed by a direct application of Eq. (3) now gives the following expression for the reciprocal space contribution to the electric potential at $\mathbf{r}$:

$$\phi^{\text{rec}}(\mathbf{r}) = \frac{4\pi}{V} \sum_{\mathbf{k} \neq \mathbf{0}} A_k \operatorname{Re}\left[e^{\iota \mathbf{k} \cdot \mathbf{r}} \rho_N^*(\mathbf{k}) \right] \tag{12}$$

where * denotes complex conjugation. For $\mathbf{r} = \mathbf{r}_i$, this trivially reduces to the expression for the electric potential ϕ_i^{rec} at the position of particle i already given in the literature,[3–5,7] namely,

$$\phi_i^{\text{rec}} = \frac{4\pi}{V} \sum_{\mathbf{k} \neq \mathbf{0}} A_k \operatorname{Re}\left[e^{\iota \mathbf{k} \cdot \mathbf{r}_i} \rho_N^*(\mathbf{k}) \right]. \tag{13}$$

The component $E_\alpha^{\text{rec}}(\mathbf{r})$ of the electrostatic field is straightforwardly retrieved from a direct application of Eq. (4a) to Eq. (12), and the result is

$$E_\alpha^{\text{rec}}(\mathbf{r}) = -\frac{4\pi}{V} \sum_{\mathbf{k} \neq \mathbf{0}} A_k k_\alpha \operatorname{Re}\left[\iota e^{\iota \mathbf{k} \cdot \mathbf{r}} \rho_N^*(\mathbf{k}) \right]. \tag{14}$$

To obtain $E_{i,\alpha}^{\text{rec}}$, we merely take the limit $\mathbf{r} \to \mathbf{r}_i$, as given in Eq. (4b), leading to

$$E_{i,\alpha}^{\text{rec}} = -\frac{4\pi}{V} \sum_{\mathbf{k} \neq \mathbf{0}} A_k k_\alpha \operatorname{Re}\left[\iota e^{\iota \mathbf{k} \cdot \mathbf{r}_i} \rho_N^*(\mathbf{k}) \right]. \tag{15}$$

This expression differs from the those previously given by Nymand and Linse,[3] Laino and Hutter,[5] and Sala et al.[6] by a term

$$\frac{4\pi}{V} \sum_{\mathbf{k} \neq \mathbf{0}} A_k k_\alpha (\boldsymbol{\mu}_i \cdot \mathbf{k}), \tag{16}$$

although it is equivalent to the expression given by Weenk and Harwig.[7] The term in Eq. (16) can be identified as the derivative

$$\frac{4\pi}{V} \sum_{\mathbf{k} \neq \mathbf{0}} A_k \operatorname{Re}\left[e^{\iota \mathbf{k} \cdot \mathbf{r}_i} \frac{\partial}{\partial r_{i,\alpha}} \rho_N^*(\mathbf{k}) \right], \tag{17}$$

which indicates that the source of this spurious term is the use of Eq. (4a) rather than Eq. (4b) when evaluating the spatial derivative at $\mathbf{r}_i$, corresponding to an unwanted shift of the positions of the image particles as discussed in Sec. II.

Following the same procedure as above, we apply Eq. (5b) to Eq. (14) to obtain the following expression for $E_{i,\alpha\beta}^{\text{rec}}$:

$$E_{i,\alpha\beta}^{\text{rec}} = \frac{4\pi}{V} \sum_{\mathbf{k} \neq \mathbf{0}} A_k k_\alpha k_\beta \operatorname{Re}\left[e^{\iota \mathbf{k} \cdot \mathbf{r}_i} \rho_N^*(\mathbf{k}) \right]. \tag{18}$$

This expression again differs from that given by Nymand and Linse[3] and Laino and Hutter[5] by a spurious term

$$-\frac{4\pi}{V} \sum_{\mathbf{k} \neq \mathbf{0}} A_k k_\alpha k_\beta q_i, \tag{19}$$

the rationale behind which is totally analogous to the reasoning behind the extra term in the expression for the electrostatic field.

We finally note that Aguado and Madden[4] do not provide any explicit expressions for $E_{i,\alpha}^{\text{rec}}$ or $E_{i,\alpha\beta}^{\text{rec}}$. However, they state that these quantities were derived through an identification using Eq. (6), whereby the differentiation problems discussed above are avoided. Sala et al.[6] do not provide any expressions for the field gradients.

C. Self contributions

The correction U_{self} for the inclusion of the interaction between each particle and its own screening charge distribution in a system with charges, dipoles, and quadrupoles is given by[1,3–5]

$$U_{\text{self}} = -\sum_{i=1}^{N} \left[\frac{\alpha}{\sqrt{\pi}} q_i^2 + \frac{2\alpha^3}{3\sqrt{\pi}} \mu_i^2 - \frac{4\alpha^3}{9\sqrt{\pi}} q_i \operatorname{Tr}(\boldsymbol{\Theta}_i) \right]. \tag{20}$$

The contributions to the potential, field, and field gradient can readily be obtained using the identity in Eq. (6). A straightforward comparison yields the following expressions for ϕ_i^{self}, $E_{i,\alpha}^{\text{self}}$, and $E_{i,\alpha\beta}^{\text{self}}$, in accordance with Aguado and Madden,[4] Weenk and Harwig,[7] and Sala et al.:[6]

$$\phi_i^{\text{self}} = -\frac{2\alpha}{\sqrt{\pi}} q_i, \tag{21}$$

$$E_{i,\alpha}^{\text{self}} = \frac{4\alpha^3}{3\sqrt{\pi}} \mu_{i,\alpha}, \tag{22}$$

$$E_{i,\alpha\beta}^{\text{self}} = -\frac{4\alpha^3}{3\sqrt{\pi}} q_i \delta_{\alpha\beta}, \tag{23}$$

where $\delta_{\alpha\beta}$ is the Kronecker delta.

We note that Eqs. (22) and (23) differ from those given by Nymand and Linse,[3] who instead provide the expressions

$$E_{i,\alpha}^{\text{self}} = \frac{4\pi}{3V} \mu_{i,\alpha} \quad \text{(Nymand and Linse)}, \tag{24}$$

$$E_{i,\alpha\beta}^{\text{self}} = -\frac{4\pi}{3V} q_i \delta_{\alpha\beta} \quad \text{(Nymand and Linse)}, \tag{25}$$

although these were formally included into U_{rec} rather than into U_{self}. These terms were introduced somewhat *ad hoc*, but as will be shown in Sec. IV the difference between the expressions for the self contributions present in the literature is intimately connected with the error in the k-space contributions highlighted in Subsection III B. In fact, the use of Eqs. (24) and (25) instead of Eqs. (22) and (23) almost exactly corrects for the error introduced by using Eqs. (4a) and (5a) rather than Eqs. (4b) and (5b) when deriving the k-space contributions to the potential derivatives.

D. Surface contributions (k = 0)

The so-called surface contribution, corresponding to the **k = 0** term, to the electrostatic energy is given by[1,9]

$$U_{\text{surf}} = \frac{2\pi}{(2\varepsilon_{\text{sur}} + 1)V} \left[\left(\sum_{i=1}^{N} q_i \mathbf{r}_i \right)^2 \right.$$
$$\left. + 2 \left(\sum_{i=1}^{N} q_i \mathbf{r}_i \right) \cdot \left(\sum_{i=1}^{N} \boldsymbol{\mu}_i \right) + \left(\sum_{i=1}^{N} \boldsymbol{\mu}_i \right)^2 \right], (26)$$

where ε_{sur} is the dielectric constant of the surroundings. A straightforward application of Eqs. (3), (4b), and (5b) leads to

$$\phi_i^{\text{surf}} = \frac{4\pi}{(2\varepsilon_{\text{sur}} + 1)V} \mathbf{r}_i \cdot \sum_{j=1}^{N} (q_j \mathbf{r}_j + \boldsymbol{\mu}_j), \qquad (27)$$

$$E_{i,\alpha}^{\text{surf}} = -\frac{4\pi}{(2\varepsilon_{\text{sur}} + 1)V} \sum_{j=1}^{N} (q_j r_{j,\alpha} + \mu_{j,\alpha}), \qquad (28)$$

$$E_{i,\alpha\beta}^{\text{surf}} = 0, \qquad (29)$$

where we should again highlight the importance of following the procedure of Eqs. (4b) and (5b) rather than that of Eqs. (4a) and (5a) when deriving the electrostatic fields and field gradients in the positions of the particles. Equations (27)–(29) agree with those provided by Nymand and Linse[3] and Sala *et al.*[6] Weenk and Harwig,[7] Aguado and Madden,[4] and Laino and Hutter[5] do not treat the surface term, corresponding to an implicit assumption of conducting boundaries, i.e., $\varepsilon_{\text{sur}} = \infty$.

We finally note that Laino and Hutter[5] and Sala *et al.*[6] provide, without any clear motivation, additional **k = 0** terms for both energy, fields and field gradients (only Laino and Hutter[5]), in addition to the self and surface terms treated above. However, since the energy expressions given in Eqs. (7), (8), and (20) (with $\boldsymbol{\Theta}_i = 0$), and (26) (with $\varepsilon_{\text{sur}} = 1$) were shown by Nymand and Linse[3] to yield identical (to at least 8 significant digits) results compared to a direct summation using Eq. (2), we argue that these extra **k = 0** terms are spurious.

IV. NUMERICAL RESULTS

In order to verify the equations derived in the present work and to compare with results obtained using the expressions derived by Nymand and Linse,[3] we will calculate the electrostatic energy for a dipolar system using the three different approaches outlined below.

Method 1: Calculation of U_{rec}, U_{self}, and U_{surf} directly using the energy expressions given by Eqs. (8), (20), and (26).

Method 2: Calculation of $E_{i,\alpha}^{\text{rec}}$, $E_{i,\alpha}^{\text{self}}$, and $E_{i,\alpha}^{\text{surf}}$ using the field equations (14), (22), and (28), together with Eq. (6) (with $q_i = \boldsymbol{\Theta}_i = 0$) to calculate electrostatic energies. This method is mathematically equivalent to Method 1.

TABLE I. U_{rec}, U_{self}, and U_{surf} calculated using the three methods described in the text. Energies are given in reduced units with $4\pi\varepsilon_0 = 1$, charges in units of e and lengths in units of Å. A cutoff of $n_{\text{cut}} = 20$ was used in reciprocal space.

	Method 1	Method 2	Method 3
U_{rec}	0.196805948	0.196805947	−1.251893333
U_{self}	−1.458226117	−1.458226117	−0.009526838
U_{surf}	0.001386998	0.001386998	0.001386998
Sum	−1.260033172	−1.260033172	−1.260033172

Method 3: As Method 2, but adding the extra term of Eq. (16) to $E_{i,\alpha}^{\text{rec}}$ and using Eq. (24) rather than Eq. (22) for $E_{i,\alpha}^{\text{self}}$. This corresponds to the expressions prescribed by Nymand and Linse.[3]

All energies were calculated for a single configuration of 1000 Stockmayer particles ($\mu = 0.344e$ Å) in a typical equilibrium liquid-state configuration with $L_x = L_y = L_z = 29.629$ Å and $\alpha = 0.32$ Å^{-1}. The surface terms were calculated using vacuum boundary conditions, corresponding to $\varepsilon_{\text{sur}} = 1$. Since the formulas for the real-space electrostatic energies and fields are well-established, these were not included into the analysis.

Values of U_{rec}, U_{self}, and U_{surf} calculated using the three different methods are given in Table I. From these we make the observations that (i) the formulas for $E_{i,\alpha}$ used in Method 2 gives a termwise identity with a direct application of the energy formulas used in Method 1, (ii) the formulas for $E_{i,\alpha}$ used in Method 3 do not agree on a termwise level with the energy formulas, and (iii) the three methods yield identical, to at least 10 significant digits, energies when the three energy contributions are summed. We thus note that using Method 3 corresponds to a repartitioning of the field (as compared to the energy) between the reciprocal and self contributions, which leads to that the electrostatic field converges in a different way than the energy. This property is highlighted in Fig. 1, where the same energies as in Table I are given as a function of the cutoff n_{cut} in reciprocal space. It is clear that (i) the convergence properties of
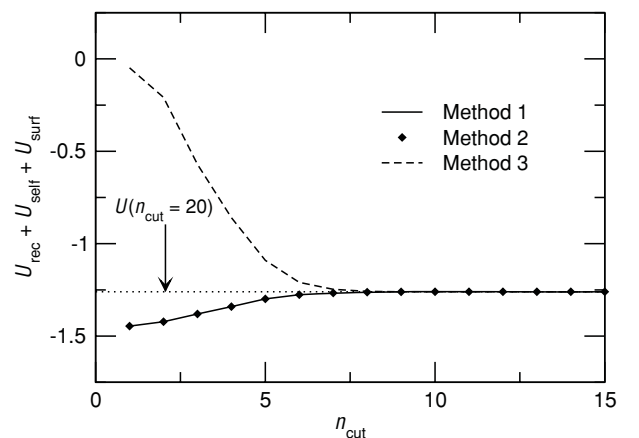

FIG. 1. Electrostatic energy $U_{\text{rec}} + U_{\text{self}} + U_{\text{surf}}$ obtained using three different methods as a function of the cutoff n_{cut} in reciprocal space. Units as in Table I.

the formulas provided by Nymand and Linse[3] are distinctly different from those provided in this contribution and (ii) the formulas for $E_{i,\alpha}$ provided in this contribution exhibit identical convergence properties compared to a direct application of the energy formulas, just as expected. We finally mention that, although $U_{\rm rec} + U_{\rm self} + U_{\rm sur}$ calculated using Methods 1 and 2 seem to exhibit a faster convergence than the one calculated using Method 3, our tests indicate that the relative convergence speed of the two methods is configuration dependent.

We do not show explicitly any numerical results describing the different routes to obtaining $E_{i,\alpha\beta}$, as the qualitative correspondence with the results given above for the electrostatic field is obvious.

As a corollary of the apparent equivalence between Methods 2 and 3 in the limit $n_{\rm cut} \to \infty$, the k-space sums in Eqs. (16) and (19) are suggested to be equal to the difference between the two different forms of the self contribution, i.e.,

$$\frac{4\pi}{V} \sum_{\mathbf{k}\neq\mathbf{0}} A_k k_\alpha (\boldsymbol{\mu}_i \cdot \mathbf{k}) \simeq \mu_{i,\alpha} \left[\frac{4\alpha^3}{3\sqrt{\pi}} - \frac{4\pi}{3V} \right], \qquad (30)$$

$$-\frac{4\pi}{V} \sum_{\mathbf{k}\neq\mathbf{0}} A_k k_\alpha k_\beta q_i \simeq q_i \delta_{\alpha\beta} \left[-\frac{4\alpha^3}{3\sqrt{\pi}} + \frac{4\pi}{3V} \right]. \qquad (31)$$

After considering some symmetry properties of the lattice sums, both these expressions reduce to

$$\sum_{\mathbf{k}\neq\mathbf{0}} e^{-k^2/4\alpha^2} \simeq \frac{\alpha^3 V}{\pi^{3/2}} - 1. \qquad (32)$$

By a comparison with the 3-dimensional version of the Poisson summation formula (see, for example, Eq. (4) of Chaba and Pathria[11]), Eq. (32) can be shown to hold in the limit $\alpha^2 L_{\rm min}^2 \gg 1$, where $L_{\rm min}$ is the smallest of the box lengths L_x, L_y, and L_z. With the parameters used in the present study, corresponding to $\alpha^2 L_{\rm min}^2 \approx 90$, Eq. (32) becomes tremendously accurate, with a relative difference between the right- and left-hand sides of $\sim 10^{-39}$. Thus, the formulas provided by Nymand and Linse[3] give essentially correct values of the field and field gradient for all reasonable choices of α and $L_{\rm min}$ used in practical applications.

V. CONCLUSIONS

In summary, we have shown that the correct formulas corresponding to the electrostatic energy of Eq. (2) are given by Eqs. (14), (22), and (28) (electrostatic fields) and Eqs. (18), (23), and (29) (electrostatic field gradients), combined with Eq. (7) for the real-space contributions. These equations constitute the main results of this study, although we again want to stress the fact that the formulas presented here are, apart from the missing surface term, identical to the equations due to Weenk and Harwig.[7] Furthermore, we have shown that an incorrect differentiation procedure explains the erroneous forms of the reciprocal and self contributions to the spatial potential derivatives present in the litera-

ture. Our corrected formulas were also shown to yield results that are termwise identical to those calculated from a direct application of the Ewald formulas for the electrostatic energy.

Although we have shown that some of the formulas present in the literature are formally incorrect, it is also clear that using the formulas prescribed by Nymand and Linse[3] leads to numerically negligible errors for the field and field gradient, as long as the proper self terms are added. They, however, still lead to an inappropriate partitioning between the reciprocal and self terms, which can be unwanted in certain situations. For example, when performing Ewald summation using unit cells that do not pack as a primitive cubic lattice, Eq. (32) does not hold anymore, possibly leading to errors in the electrostatic field and field gradient.

Furthermore, the use of the incorrect formulas for the reciprocal contributions together with the correct forms [i.e., Eqs. (22) and (23)] of the self contributions, as was prescribed by Laino and Hutter[5] and Sala et al.,[6] leads to incorrect values of the calculated quantities also in the limit $n_{\rm cut} \to \infty$. Since the self terms are constant for particles possessing fixed charge distributions, this does not lead to any change in the structural properties of the simulated system. It does, however, lead to erroneous results when comparing the magnitudes of electrostatic and non-electrostatic (e.g., Lennard-Jones) energies. Also, for systems containing polarizable particles the use of incorrect (with respect to the choice of k-space expressions) self terms leads to an unphysical stabilization or destabilization of the induced dipoles, corresponding to an unwanted shift of the particle polarizabilities.

We finally note that expressions for forces and pressure tensors do not suffer from the problems with the incorrect differentiation procedures discussed in this work, as these quantities are defined as derivatives with respect to particle positions. The formulas already provided in the literature[3–5] are therefore expected to be correct.

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