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Pressure tensor of partial-charge and point-dipole lattices with bulk and surface geometries

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We derive rapidly convergent expressions for the Coulomb component of the pressure tensor of single-charge, partial-charge molecular, and point-dipole lattices in the Ewald formulation for both bulk and surface geometries. In the case of the pressure tensor, a general procedure for generating the series expansions is described. Some of these expressions are simple enough to be suitable for incorporation in molecular-dynamics and Monte Carlo molecular simulation computer programs covering a range of specific polar condensed phases. The surface-geometry formulas are more complicated than the corresponding bulk expressions because of the reduced symmetry.

I. INTRODUCTION

Condensed-phase polar solids and liquids are often represented by unit cells periodically repeated in two and three orthogonal directions for surface and bulk studies, respectively. Each unit cell contains N charged species. The charge distribution of ions is often represented by a series of point charges, molecules by a multipole expansion, or alternatively by a series of discrete "partial" charges distributed at sites within the molecule. These charge interactions decay slowly with distance so that a rapidly converging resummation of the original series is often required for efficient comparison. One of the most important applications for lattice sums is in Monte Carlo (MC) or molecular-dynamics (MD) computer simulation of polar molecular species. We believe some of the expressions derived below could be useful in this area. Some of them (particularly the surface formulas derived below) are possibly a little analytically complicated to be of much use in simulation because of the repetitive nature of the technique. However, there are many nonsimulation applications where the level of complexity of the expression is not such an important issue once they have been coded into the computer because these summations only have to be performed perhaps several times in an application, so the complexity of the formulas is not a serious problem.

One solution to the slow convergence of the original lattice sums is to recast the original slowly converging real-space lattice sum using the Ewald method[1] into two more rapidly converging series. This approach has the advantage that the interaction tends to the original Coulomb form in the thermodynamic limit (i.e., $N\rightarrow\infty$). For a fully periodic three-dimensional lattice, Ewald recast this summation as two series, one in real space and the other in Fourier space (covering the reciprocal lattice).[1] Both of these series can be adjusted to converge rapidly by a suitable choice of an arbitrary inverse distance-scale parameter, κ, which is present in both series. An alternative approach is to curtail artificially the original Coulomb interaction with distance using an arbitrary short-range "switch-off" function. As normally implemented, with a fixed switch-off distance range, this method does not tend to the original system in the thermodynamic limit. The switch-off method can lead to structural artifacts which become manifest in the radial distribution function at pair separations close to the truncation distance.[2] Therefore, the Ewald approach has much to commend it in favor of switch-off functions. The bulk Ewald formulas have been investigated numerous times (see, for example, Refs. 1 and 3–6). The author has derived a range of alternative summations of the general Ewald form for bulk point-charge lattices, concentrating on the potential energy and the forces.[7]

In a polar surface, such as a solid or liquid film, the slowly converging interactions cover a lattice of unit cells repeated to infinity in *two* directions parallel to the surface plane. The lattice is of finite extent in the remaining direction perpendicular to the surface plane. In contrast to the bulk potential, the surface potential and its derivatives has been less well studied by the Ewald route.

Following on from Ewald, Parry[8] adapted the Ewald transformation to apply to laminar and semi-infinite systems. The author has developed these surface formulas for point charges[9–13] and point dipoles,[14] concentrating on the potential energy and the forces, from the perspective of molecular simulation. Subsequently, there have been other contributions to this subject. For example, recently Lekner[15] derived a surface potential formula cast entirely as a Fourier space series. This converges rapidly for charge separations whose components perpendicular to the surface plane are of order or in excess of a typical lattice spacing in a crystal. As the normal separation tends to zero, this formula converges slowly. Hautman and Klein[16] considered a novel expansion procedure, in which the r^{-1} interaction was decomposed into an in-plane component [reformulated as a two-dimensional (2D) Ewald expansion] and an out-of-plane component retained in real space. A completely different method suitable for large-N bulk simulations has been to use a "reduced" multipole reformulation of the Ewald method.[17] In this method, the simulation cell is reduced to an equivalent reduced number of charges with the same lower multipoles as the simulation cell. Replica unit cells are replaced by a unit cell of multipoles, treated again by an Ewald expansion to improve convergence.

The situation for the potential energy and force for point-charge and point-dipole lattices is now well documented and either the conventional Ewald,[3,4] or its surface adaptation, the Parry-Ewald formulas, are suitable and can be generalized to arbitrary multipole distributions.

The purpose of this paper is to develop further the above formulas to consider the *pressure tensor* **P**, which is an important quantity in solid and liquid state statistical mechanics, but has been neglected for a range of idealized polar species lattices. One use for the pressure tensors is in MD simulation of the liquid state. The time correlation functions of the stress tensor using the Green-Kubo expressions give predictions for the viscosity.[6] Without these formulas, Green-Kubo cannot be implemented efficiently.

We extend the Ewald treatment to derive expressions for the pressure tensor of bulk point-charge, partial-charge molecular, and dipole lattices for both bulk and surface geometries. For completeness we also give the expressions for the system and single-species Coulomb potential energy, and the derived forces (the latter being used as a component of the pressure tensor). The formulas for the partial charge systems will be derived in detail, and the point-charge lattice analogous of these expressions will be quoted as special cases. The total energy, force, and pressure tensor for any material will have a number of short-range interaction contributions, but we assume they are sufficiently rapidly decaying with distance to be absolutely convergent and pose no problems when using direct summation over the real lattice. We first consider bulk geometries in the next section.

II. BULK

A. Partial-charge molecules

The long-range nature of the Coulomb interaction necessitates a formal sum over the entire 3D lattice of the replicated simulation ("unit") cells. The vector **n** denoting the position of the unit cell is given by

$$\mathbf{n}=i\hat{\mathbf{x}}L_x+j\hat{\mathbf{y}}L_y+k\hat{\mathbf{z}}L_z \ , \tag{1}$$

where the unit vectors $\hat{\gamma}$ are directed along the γ direction, the corresponding cell sidelengths are L_γ, and the integers i,j,k range over $0,\pm1,\pm2,\ldots,\pm\infty$ to span the entire lattice. Consider N molecules of index i, with n_i charges $q_{i\alpha}$, where α is the site index within the molecule. Each molecule satisfies the electroneutrality condition

$$\sum_{\alpha=1}^{n_i} q_{i\alpha}=0 \ . \tag{2}$$

The total Coulomb interaction energy of the system Φ is

$$2\Phi=\sum_{i=1}^{N}\sum_{\alpha=1}^{n_i} q_{i\alpha}\sum_{j\neq i}^{N}\sum_{\beta=1}^{n_j} q_{j\beta}\sum_{\mathbf{n}'}^{\infty}\frac{1}{r_{\mathbf{n}i\alpha j\beta}} \ , \tag{3}$$

where

$$\mathbf{r}_{\mathbf{n}i\alpha j\beta}=\mathbf{r}_{i\alpha}-\mathbf{r}_{j\beta}+\mathbf{n} \ , \tag{4}$$

and $\mathbf{r}_{i\alpha}$ is the position of partial charge α on molecule i, $q_{i\alpha}$. The prime on the **n** denotes the omission of the $i=j$ term when $\mathbf{n}=0$. An alternative expression for the total electrostatic potential energy is

$$\Phi=\frac{1}{2}\sum_{i}^{N}\phi_i \ , \tag{5}$$

where ϕ_i is the potential energy of molecule i. Partial charges α and β are positioned on molecules i and j, respectively. Therefore we reserve Roman indices for the charged units themselves and the Greek letters for the charge site indices.

The Ewald expression for Eq. (5) involves a summation over the real lattice vectors **n** and also reciprocal lattice vectors **h**. The reciprocal lattice vector is defined by

$$\mathbf{h}=2\pi(i\hat{\mathbf{x}}/L_x+j\hat{\mathbf{y}}/L_y+k\hat{\mathbf{z}}/L_z) \ . \tag{6}$$

Then,

$$\begin{aligned}2\Phi={}&\sum_{i=1}^{N}\sum_{\alpha}^{n_i} q_{i\alpha}\sum_{j\neq i}^{N}\sum_{\beta}^{n_j} q_{j\beta}\sum_{\mathbf{n}'}^{\infty}\operatorname{erfc}(\kappa r_{\mathbf{n}i\alpha j\beta})/r_{\mathbf{n}i\alpha j\beta}+\frac{4\pi}{V}\sum_{\mathbf{h}\neq0}^{\infty}h^{-2}\exp(-h^2/4\kappa^2)\left\|\sum_{i}^{N}\sum_{\alpha}^{n_i} q_{i\alpha}\exp(i\mathbf{h}\cdot\mathbf{r}_{i\alpha})\right\|^2\\&-\sum_{i=1}^{N}\sum_{\alpha=1}^{n_i} q_{i\alpha}^2 2\pi^{-1/2}\kappa-\sum_{i=1}^{N}\sum_{\alpha=1}^{n_i} q_{i\alpha}\sum_{\beta\neq\alpha}^{n_i} q_{i\beta}\operatorname{erf}(\kappa r_{i\alpha i\beta})/r_{i\alpha i\beta} \ .\end{aligned} \tag{7}$$

Therefore the original summation carried out in real space is transformed into two summations, one in real space (over the same real-space lattice) and one in reciprocal space (over the reciprocal lattice). Additional Gaussian charge distributions have been placed on each charge site. The adjustable parameter κ is an arbitrary inverse-length parameter, and erf($\cdots$) and erfc($\cdots$) are the error and complementary error functions, respectively. The value of κ determines the relative emphasis given to the real- and reciprocal-space terms; the reciprocal-space series becomes increasingly more important as κ increases. The volume of the simulation cell equals $V=|\mathbf{L}_x\cdot\mathbf{L}_y\times\mathbf{L}_z|$, where $\mathbf{L}_\alpha=\hat{\mathbf{i}}_\alpha L_\alpha$. Usually, the real- and reciprocal-space series are truncated spherically in each vector space. The last two terms in Eq. (7) specify the self-energy of the molecules in the system. These two expressions correct for the inclusion in the reciprocal-space summation of the interaction energy for the Gaussian spread-out charges on sites α and β, respectively with the point charge $q_{i\alpha}$ in the *same* molecule.

An alternative representation for Φ is to use the definition of Eq. (5) and calculate ϕ_i directly,

$$\phi_i=\sum_{\alpha=1}^{n_i}q_{i\alpha}\sum_{j=1}^{N}\sum_{\beta=1}^{n_j}q_{j\beta}\sum_{\mathbf{n}'}^{\infty}\operatorname{erfc}(\kappa r_{\mathbf{n}i\alpha j\beta})/r_{\mathbf{n}i\alpha j\beta}+\frac{4\pi}{V}\sum_{\mathbf{h}\neq 0}^{\infty}h^{-2}\exp(-h^2/4\kappa^2)\sum_{\alpha=1}^{n_i}q_{i\alpha}\mathrm{Re}[\exp(-\mathbf{h}\cdot\mathbf{r}_{i\alpha})\sum_{j=1}^{N}\sum_{\beta=1}^{n_j}q_{j\beta}\exp(i\mathbf{h}\cdot\mathbf{r}_{j\beta})]$$
$$-\sum_{\alpha=1}^{n_i}q_{i\alpha}^2 2\pi^{-1/2}\kappa-\sum_{\alpha=1}^{n_i}q_{i\alpha}\sum_{\beta\neq\alpha}^{n_i}q_{i\beta}\operatorname{erf}(\kappa r_{i\alpha i\beta})/r_{i\alpha i\beta}\ , \tag{8}$$

where Re denotes the real part of a complex quantity. The force on partial charge on site α on molecule i, $\mathbf{F}_{i\alpha}$ by all charges in the system *including those on the same molecule* is given by

$$\mathbf{F}_{i\alpha}=-\nabla_{i\alpha}\phi_i\ . \tag{9}$$

From the definition of ϕ_i in Eq. (28) we obtain for the electrostatic force on partial charge α,

$$\mathbf{F}_{i\alpha}=\mathbf{F}_{i\alpha}^{\mathrm{I}}+\mathbf{F}_{i\alpha}^{\mathrm{II}}\ . \tag{10}$$

The real-space series contribution to the force is given by $\mathbf{F}_{i\alpha}^{\mathrm{I}}$ and the reciprocal-space series contribution to the force is given by $\mathbf{F}_{i\alpha}^{\mathrm{II}}$. We have

$$\mathbf{F}_{i\alpha}^{\mathrm{I}}=q_{i\alpha}\sum_{j\neq i}^{N}\sum_{\beta=1}^{n_j}q_{j\beta}\sum_{\mathbf{n}'}^{\infty}\left[\frac{2}{\sqrt{\pi}}\kappa r_{\mathbf{n}i\alpha j\beta}\exp(-\kappa^2 r_{\mathbf{n}i\alpha j\beta}^2)+\operatorname{erfc}(\kappa r_{\mathbf{n}i\alpha j\beta})\right]\frac{\mathbf{r}_{\mathbf{n}i\alpha j\beta}}{r_{\mathbf{n}i\alpha j\beta}^3} \tag{11}$$

and

$$\mathbf{F}_{i\alpha}^{\mathrm{II}}=-\frac{4\pi}{V}\sum_{\mathbf{h}\neq 0}^{\infty}\mathbf{h}h^{-2}\exp(-h^2/4\kappa^2)q_{i\alpha}\mathrm{Im}\left[\exp(-i\mathbf{h}\cdot\mathbf{r}_{i\alpha})\sum_{j=1}^{N}\sum_{\beta=1}^{n_j}q_{j\beta}\exp(i\mathbf{h}\cdot\mathbf{r}_{j\beta})\right]\ , \tag{12}$$

where Im denotes the imaginary part of a complex quantity. It is important to note that the Coulomb force on site α for species i, $F_{i\alpha}^{\mathrm{II}}$, contains contributions from partial charges within the molecule. Taking all sites in the molecule into consideration, they do not introduce a net force or torque on the molecule. In any implementation of rigid-molecule dynamics constraint forces or any other geometry-maintaining device (e.g., quaternions) would nullify these forces.

The pressure tensor of a Coulomb system can be written in terms of the virial $-\mathbf{r}\cdot\nabla r^{-1}$. In an atomic description, the pressure tensor is defined solely in terms of the "site-site" pair forces, $\mathbf{F}_{i\alpha j\beta}$,[5]

$$\mathbf{P}V=\sum_{i=1}^{N}m_i\dot{\mathbf{r}}_i\dot{\mathbf{r}}_i+\frac{1}{2}\sum_{i=1}^{N}\sum_{\alpha=1}^{n_i}\sum_{j\neq i}^{N}\sum_{\beta=1}^{n_j}\mathbf{r}_{i\alpha j\beta}\mathbf{F}_{i\alpha j\beta}$$
$$+\frac{1}{2}\sum_{i=1}^{N}\sum_{\alpha=1}^{n_i}\sum_{\beta\neq\alpha}^{n_i}\mathbf{r}_{i\alpha i\beta}\mathbf{F}_{i\alpha i\beta}\ , \tag{13}$$

where $\dot{\mathbf{r}}_i$ is the velocity of the center of mass of molecule i. (The center of mass of molecule i is denoted by $\mathbf{r}_i$). The pair force between site α on molecule i and site β on molecule j is $\mathbf{F}_{i\alpha j\beta}$. In Eq. (13), the first term is the kinetic contribution to the pressure tensor coming from the translational motion only. The second term is the interaction between sites on different molecules only. The last term is the contribution from the intramolecular constraint forces (needed to maintain a rigid unit under motion). In Eq. (13) the nearest-image pair separations and forces are assumed. The forces on the sites that need to be "constrained" come here from charges on other molecules and also from those on the same molecule.

An alternative expression for $\mathbf{P}$ is to use the molecular representation

$$\mathbf{P}V=\sum_{i=1}^{N}m_i\dot{\mathbf{r}}_i\dot{\mathbf{r}}_i+\frac{1}{2}\sum_{i=1}^{N}\sum_{j\neq i}^{N}\mathbf{r}_{ij}\mathbf{F}_{ij}\ , \tag{14}$$

where $\mathbf{r}_{ij}=\mathbf{r}_i-\mathbf{r}_j$. These can be rewritten in a more useful form for computation,

$$\mathbf{P}V=\sum_{i=1}^{N}m_i\dot{\mathbf{r}}_i\dot{\mathbf{r}}_i+\frac{1}{2}\sum_{i=1}^{N}\sum_{\alpha=1}^{n_i}\sum_{j\neq i}^{N}\sum_{\beta=1}^{n_j}\mathbf{r}_{ij}\mathbf{F}_{i\alpha j\beta}\ . \tag{15}$$

In the Ewald summation the interactions are not decomposable solely in terms of pairwise additive interactions because of the reciprocal-space term. In fact, the reciprocal-space term in the Ewald formula is as important as the real-space term because the programs are optimized to truncate the real-space interactions within half the box-sidelength. This necessitates values of $\kappa V^{1/3}>7$, so a major component of the interaction comes from the reciprocal-space term. Typically in a simulation it is found convenient to truncate spherically in real and reciprocal space, where $n<1$ and $h\leq h_{\max}$; for $\alpha V^{1/3}\sim 7$, then $h_{\max} \sim 7$.[18] Therefore, Eq. (15) is only partially applicable (i.e., for the real-space part of the Ewald formula). Our solution to this is to use Eq. (15) for the real-space component of the pressure tensor. For the reciprocal-space component of the pressure tensor we use the form in Eq. (13) directly from Φ which circumvents the periodic boundary problem. A Taylor expression of the interaction energy $\Phi(\epsilon)$ in terms of the strain tensor ϵ leads to a definition of $\mathbf{P}$,

$$\mathbf{P}V = -\frac{\partial \Phi(0)}{\partial \epsilon} . \tag{16}$$

In the case of the diagonal elements, $L_\alpha \rightarrow L_\alpha(1+\epsilon)$ and for the off-diagonal elements, $\epsilon \rightarrow \sin(\theta)$, giving $k_x \rightarrow k_x + \epsilon k_y$ and $k_y \rightarrow \cos(\theta) k_y$. Using the approximation

$$\frac{\partial \Phi(0)}{\partial \epsilon} = \frac{[\Phi(\epsilon) - \Phi(0)]}{\epsilon} \tag{17}$$

in the limit $\epsilon \rightarrow 0$ and carrying out a Taylor expansion in ϵ we have for the Coulombic component of the pressure tensor,

$$\mathbf{P}V = \frac{1}{2} \sum_{i=1}^{N} \sum_{\alpha=1}^{n_i} q_{i\alpha} \sum_{j=1}^{N} \sum_{\beta=1}^{n_j} q_{j\beta} \sum_{\mathbf{n}'}^{\infty} \left[\frac{2}{\sqrt{\pi}} \kappa r_{\mathrm{n}i\alpha j\beta} \exp(-\kappa^2 r^2_{\mathrm{n}i\alpha j\beta}) + \operatorname{erfc}(\kappa r_{\mathrm{n}i\alpha j\beta}) \right] \frac{\mathbf{r}_{\mathrm{n}ij} \mathbf{r}_{\mathrm{n}i\alpha j\beta}}{r^3_{\mathrm{n}i\alpha j\beta}}$$
$$+ \frac{2\pi}{V} \sum_{\mathbf{h}\neq 0}^{\infty} \mathbf{B}(\mathbf{h}) h^{-2} \exp(-h^2/4\kappa^2) \left| \left| \sum_{i=1}^{N} \sum_{\alpha=1}^{n_i} q_{i\alpha} \exp(i \mathbf{h} \cdot \mathbf{r}_{i\alpha}) \right| \right|^2 + \mathbf{E} , \tag{18}$$

where for the $\omega\tau$ component of the tensor $\mathbf{B}$ we have

$$B_{\omega\tau} = \delta_{\omega\tau} - 2h_\omega h_\tau / h^2 - h_\omega h_\tau / 2\kappa^2 , \tag{19}$$

where $\delta_{\omega\tau}$ is the Kronecker delta. The last term in Eq. (18) comes from the final intramolecular component of Eq. (13),

$$\mathbf{E} = -\frac{1}{2n_i} \sum_{i=1}^{N} \sum_{\alpha=1}^{n_i} \sum_{\beta\neq\alpha}^{n_i} \mathbf{r}_{i\alpha i\beta} (\mathbf{F}^{\mathrm{II}}_{i\alpha} - \mathbf{F}^{\mathrm{II}}_{i\beta}) , \tag{20}$$

which can also be written as

$$\mathbf{E} = -\sum_{i=1}^{N} \sum_{\alpha=1}^{n_i} \mathbf{r}_{i\alpha} \mathbf{F}^{\mathrm{II}}_{i\alpha} . \tag{21}$$

To derive Eq. (18) from the expansion of Φ, the trigonometric terms remain the same because $\mathbf{h} \cdot \mathbf{r}_{i\alpha}$ is invariant under the ϵ transformation. An equivalent expression for the pressure tensor has been derived by Nosé and Klein.[19]

The pressure tensor for the corresponding point-charge system is given using the same derivation method,

$$\mathbf{P}V = \frac{1}{2} \sum_{i}^{N} q_i \sum_{j}^{N} q_j \sum_{\mathbf{n}'}^{\infty} \left[\frac{2}{\sqrt{\pi}} \alpha r_{\mathrm{n}ij} \exp(-\alpha^2 r^2_{\mathrm{n}ij}) + \operatorname{erfc}(\alpha r_{\mathrm{n}ij}) \right] \frac{\mathbf{r}_{\mathrm{n}_{ij}} \mathbf{r}_{\mathrm{n}_{ij}}}{r^3_{\mathrm{n}ij}}$$
$$+ \frac{2\pi}{V} \sum_{\mathbf{h}\neq 0}^{\infty} \mathbf{B}(\mathbf{h}) h^{-2} \exp(-h^2/4\alpha^2) \left| \left| \sum_{i=1}^{N} q_i \exp(i \mathbf{h} \cdot \mathbf{r}_i) \right| \right|^2 , \tag{22}$$

where there are N point charges of magnitude q_i in the unit cell. Note the absence of any "self" component for the pressure tensor in the point-charge system.

B. Point-dipole molecules

A point dipole superimposed on a short-range repulsive core is a convenient idealization of polar molecules in certain situations (e.g., Stockmayer molecules).[20] Monte Carlo and molecular-dynamics simulations of such dipolar periodic systems frequently use the Ewald-Kornfeld resummation of this slowly decaying Coulomb interaction,[1,21] to improve the rate of convergence. Consider N model molecules specified by an index i with point dipoles, μ_i charges, on them. These molecules are positioned at $r_{\mathrm{n}i}$. In the case of the dipolar system, the total Coulomb interaction energy is obtained by replacing q_i by the operator $\mu_i \cdot \nabla_i$,

$$2\Phi = -\sum_{i=1}^{N} \sum_{j=1}^{N} \sum_{\mathbf{n}'} \boldsymbol{\mu}_i \mathbf{T}_{\mathrm{n}ij} \cdot \boldsymbol{\mu}_j , \tag{23}$$

where

$$\mathbf{T}_{\mathrm{n}ij} = \frac{1}{r^3_{\mathrm{n}ij}} \left[\frac{3\mathbf{r}_{\mathrm{n}ij} \mathbf{r}_{\mathrm{n}ij}}{r^2_{\mathrm{n}ij}} - \mathbf{I} \right] , \tag{24}$$

$\mathbf{I}$ is the unit dyadic, $r_{\mathrm{n}ij} = |\mathbf{r}_{\mathrm{n}ij}| = |\mathbf{r}_{\mathrm{n}i} - \mathbf{r}_{\mathrm{n}j}|$, and $\mathbf{T}_{ij}$ is the dipole interaction tensor. There is a null entry in Eq. (24) for $i = j$ when $\mathbf{n} = 0$. Using Eq. (5) we have, in the Ewald-Kornfeld formulation of the dipole sum of Eq. (24),

$$2\Phi=\sum_{i=1}^{N}\sum_{j=1}^{N}\sum_{\mathbf{n}'}^{\infty}(\boldsymbol{\mu}_i\cdot\boldsymbol{\mu}_j)B(r_{\mathbf{n}ij})-(\boldsymbol{\mu}_i\cdot\mathbf{r}_{\mathbf{n}ij})(\boldsymbol{\mu}_j\cdot\mathbf{r}_{\mathbf{n}ij})C(r_{\mathbf{n}ij})$$

$$+\frac{4\pi}{V}\sum_{\mathbf{h}\neq 0}^{\infty}h^{-2}\exp(-h^2/4\kappa^2)\left|\left|\sum_{i=1}^{N}\boldsymbol{\mu}_i\cdot\mathbf{h}\exp(i\mathbf{h}\cdot\mathbf{r}_i)\right|\right|^2-\sum_{i=1}^{N}\frac{4\kappa^3\mu_i^2}{3\pi^{1/2}}\ . \tag{25}$$

The quantity κ has the same significance as for Eq. (7),

$$B(r)=\operatorname{erfc}(\kappa r)r^{-3}+2\kappa\pi^{-1/2}\exp(-\kappa^2r^2)r^{-2} \tag{26}$$

and

$$C(r)=3\operatorname{erfc}(\kappa r)r^{-5}+2\kappa\pi^{-1/2}(2\kappa^2+3r^{-2})\exp(-\kappa^2r^2)r^{-2}\ . \tag{27}$$

The last term in Eq. (25) subtracts out the self-energy of the dipoles in the system which have been included in the reciprocal-space sum. The potential energy of the point dipole ϕ_i is

$$\phi_i=\sum_{j=1}^{N}\sum_{\mathbf{n}'}^{\infty}(\boldsymbol{\mu}_i\cdot\boldsymbol{\mu}_j)B(r_{\mathbf{n}ij})-(\boldsymbol{\mu}_i\cdot\mathbf{r}_{\mathbf{n}ij})(\boldsymbol{\mu}_j\cdot\mathbf{r}_{\mathbf{n}ij})C(r_{\mathbf{n}ij})$$

$$+\frac{4\pi}{V}\sum_{\mathbf{h}\neq 0}^{\infty}h^{-2}\exp(-h^2/4\kappa^2)\boldsymbol{\mu}_i\cdot\mathbf{h}\,\mathrm{Re}\left[\exp(-i\mathbf{h}\cdot\mathbf{r}_i)\sum_{j}^{N}\boldsymbol{\mu}_i\cdot\mathbf{h}\exp(i\mathbf{h}\cdot\mathbf{r}_j)\right]-\frac{4\kappa^3\mu_i^2}{3\pi^{1/2}}\ . \tag{28}$$

The real-space $\mathbf{F}_{i\alpha}^{\mathrm{I}}$ and reciprocal-space $\mathbf{F}_{i\alpha}^{\mathrm{II}}$ contributions to the forces are determined using Eq. (9).

$$\mathbf{F}_i^{\mathrm{I}}=\sum_{j=1}^{N}\sum_{\mathbf{n}'}^{\infty}(\mathbf{r}_{\mathbf{n}ij}\boldsymbol{\mu}_i\cdot\boldsymbol{\mu}_j+\boldsymbol{\mu}_i\boldsymbol{\mu}_j\cdot\mathbf{r}_{\mathbf{n}ij}+\boldsymbol{\mu}_j\boldsymbol{\mu}_i\cdot\mathbf{r}_{\mathbf{n}ij})C(r_{\mathbf{n}ij})-\frac{\mathbf{r}_{\mathbf{n}ij}}{r_{\mathbf{n}ij}}(\boldsymbol{\mu}_i\cdot\mathbf{r}_{\mathbf{n}ij})(\boldsymbol{\mu}_j\cdot\mathbf{r}_{\mathbf{n}ij})D(r_{\mathbf{n}ij})\ , \tag{29}$$

where

$$D(r)=15\operatorname{erfc}(\kappa r)r^{-6}+18\kappa\pi^{-1/2}\exp(-\kappa^2r^2)r^{-5}+4\kappa^3\pi^{-1/2}(2\kappa^2+3r^{-2})\exp(-\kappa^2r^2)r^{-1}$$

$$+4\kappa\pi^{-1/2}(2\kappa^2+3r^{-2})\exp(-\kappa^2r^2)r^{-3} \tag{30}$$

and

$$\mathbf{F}_i^{\mathrm{II}}=-\frac{4\pi}{V}\sum_{\mathbf{h}\neq 0}^{\infty}\mathbf{h}h^{-2}\exp(-h^2/4\kappa^2)\boldsymbol{\mu}_i\cdot\mathbf{h}\,\mathrm{Im}\left[\exp(-i\mathbf{h}\cdot\mathbf{r}_{i\alpha})\sum_{j=1}^{N}\boldsymbol{\mu}_j\cdot\mathbf{h}\exp(i\mathbf{h}\cdot\mathbf{r}_j)\right]\ . \tag{31}$$

Using the expansion of the Coulomb energy as a route to the pressure tensor [i.e., Eq. (16)] we have for the $\omega\tau$ element,

$$P_{\omega\tau}V=\frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}\sum_{\mathbf{n}}^{\infty}r_{\omega\mathbf{n}ij}\left\{(r_{\tau\mathbf{n}ij}\boldsymbol{\mu}_i\cdot\boldsymbol{\mu}_j+\mu_{i\tau}\boldsymbol{\mu}_j\cdot\mathbf{r}_{\mathbf{n}ij}+\mu_{j\tau}\boldsymbol{\mu}_i\cdot\mathbf{r}_{\mathbf{n}ij})C(r_{\mathbf{n}ij})-r_{\tau\mathbf{n}ij}(\boldsymbol{\mu}_i\cdot\mathbf{r}_{\mathbf{n}ij})(\boldsymbol{\mu}_j\cdot\mathbf{r}_{\mathbf{n}ij})\frac{D(r_{\mathbf{n}ij})}{r_{\mathbf{n}ij}}\right\}$$

$$+\frac{2\pi}{V}\sum_{\mathbf{h}\neq 0}^{\infty}h^{-2}\exp(-h^2/4\kappa^2)\left\{B_{1\omega\tau}(\mathbf{h})\left|\left|\sum_{i=1}^{N}\boldsymbol{\mu}_i\cdot\mathbf{h}\exp(i\mathbf{h}\cdot\mathbf{r}_i)\right|\right|^2+B_{2\omega\tau}\right\}\ , \tag{32}$$

where

$$B_{1\omega\tau}=\delta_{\omega\tau}-2h_\omega h_\tau/h^2-h_\omega h_\tau/2\kappa^2 \tag{33}$$

and

$$B_{2\omega\tau}=2\,\mathrm{Re}\left[\sum_{i=1}^{N}\mu_{i\omega}h_\tau\exp(i\mathbf{h}\cdot\mathbf{r}_i)\sum_{j=1}^{N}\boldsymbol{\mu}_j\cdot\mathbf{h}\exp(i\mathbf{h}\cdot\mathbf{r}_j)\right]\ . \tag{34}$$

Having completed the derivation of the pressure tensor for the three model species, we now derive the corresponding formulas for the surface lamina geometry. A semi-infinite lattice can be constructed one layer of unit cells at a time, positioned adjacent and parallel to each other.

III. SURFACES

A. Partial-charge molecules

The lattice is constructed from layers of unit cells infinite in extent parallel to the surface xy plane. The 2D real-space lattice vector n denoting the position of the unit cell from an origin is given by

$$\mathbf{n}=i\hat{\mathbf{x}}L_x+j\hat{\mathbf{y}}L_y \ , \tag{35}$$

and the reciprocal lattice vector is

$$\mathbf{h}=2\pi(i\hat{\mathbf{x}}/L_x+j\hat{\mathbf{y}}/L_y) \ . \tag{36}$$

The Parry-Ewald reformulation of Eq. (23) is

$$\begin{aligned}2\Phi={}&\sum_{i=1}^{N}\sum_{\alpha=1}^{n_i}q_{i\alpha}\sum_{j=1}^{N}\sum_{\beta=1}^{n_j}q_{j\beta}\sum_{n'}^{\infty}\operatorname{erfc}(\kappa r_{ni\alpha j\beta})/r_{ni\alpha j\beta}+\frac{\pi}{A}\sum_{h}^{\infty}\sum_{i=1}^{N}\sum_{\alpha=1}^{n_i}q_{i\alpha}\sum_{j=1}^{N}\sum_{\beta=1}^{n_j}q_{j\beta}F(\kappa,h,r_{zi\alpha j\beta})\mathrm{Re}[\exp(ih\cdot r_{i\alpha j\beta})]\\&-\sum_{i=1}^{N}\sum_{\alpha=1}^{n_i}q_{i\alpha}^2 2\pi^{-1/2}\kappa-\sum_{i=1}^{N}\sum_{\alpha=1}^{n_i}q_{i\alpha}\sum_{\beta\neq\alpha}^{n_i}q_{i\beta}\operatorname{erf}(\kappa r_{i\alpha i\beta})/r_{i\alpha i\beta} \ ,\end{aligned} \tag{37}$$

where $r_{zi\alpha j\beta}$ is the z or "out-of-plane" component of $r_{i\alpha j\beta}$ (the same for all n). The in-plane area of the unit cell, A, equals $A=|L_x\times L_y|$. The terms in Eq. (37) are as follows:

$$F(\kappa,h,r_{zi\alpha j\beta})=\{\exp(hr_{zi\alpha j\beta})\operatorname{erfc}(h/2\kappa+r_{zi\alpha j\beta}\kappa)+\exp(-hr_{zi\alpha j\beta})\operatorname{erfc}(h/2\kappa-r_{zi\alpha j\beta}\kappa)\}h^{-1} \ , \tag{38}$$

for $h\neq 0$ and,

$$F(\kappa,h=0,r_{zi\alpha j\beta})=-2\{r_{zi\alpha j\beta}\operatorname{erf}(r_{zi\alpha j\beta}\kappa)+\exp[-(r_{zi\alpha j\beta}\kappa)^2]/\kappa\pi^{1/2}\} \ . \tag{39}$$

The existence of a distinct nonzero $h=0$ term is one of the features of the surface formula that distinguishes it from the corresponding bulk Ewald expression,[1] for which the comparable term is equal to zero for an overall charge neutral system. The last term in Eq. (37) again subtracts out the self-energy of the Gaussian charge distributions in the system, just as for the bulk case above.

The molecule ϕ_i from Eq. (5) is

$$\begin{aligned}\phi_i={}&\sum_{\alpha=1}^{n_i}q_{i\alpha}\sum_{j\neq i}^{N}\sum_{\beta=1}^{n_j}q_{j\beta}\sum_{\mathbf{n}'}^{\infty}\operatorname{erfc}(\kappa r_{\mathrm{n}i\alpha j\beta})/r_{\mathrm{n}i\alpha j\beta}+\frac{\pi}{A}\sum_{\mathbf{h}}^{\infty}\sum_{\alpha=1}^{n_i}q_{i\alpha}\sum_{j=1}^{N}\sum_{\beta}^{n_j}q_{j\beta}F(\kappa,h,r_{zi\alpha j\beta})\mathrm{Re}[\exp(i\mathbf{h}\cdot\mathbf{r}_{i\alpha j\beta})]\\&-\sum_{\alpha=1}^{n_i}q_{i\alpha}^2 2\pi^{-1/2}\kappa-\sum_{\alpha=1}^{n_i}q_{i\alpha}\sum_{\beta\neq\alpha}^{n_i}q_{i\beta}\operatorname{erf}(\kappa r_{i\alpha i\beta})/r_{i\alpha i\beta} \ .\end{aligned} \tag{40}$$

We have for the x, y, and z components of $\mathbf{F}_i^{\mathrm{I}}$, the expression given in Eq. (11), with the sum over n covering the two-dimensional lattice in this case. For $\mathbf{F}_i^{\mathrm{II}}$ we have for the x and y components a distinct formula from the z component, reflecting the inequivalence between in-plane and out-of-plane expressions,

$$\mathbf{F}_i^{\mathrm{II}}=\frac{\pi}{A}\sum_{\mathbf{h}}^{\infty}\sum_{\alpha=1}^{n_i}q_{i\alpha}\sum_{j\neq i}^{N}\sum_{\beta=1}^{n_j}q_{j\beta}F(\kappa,h,r_{zi\alpha i\beta})\mathbf{h}\,\mathrm{Im}[\exp(i\mathbf{h}\cdot\mathbf{r}_{i\alpha i\beta})] \ . \tag{41}$$

For the z component of the force we have

$$\begin{aligned}\mathbf{F}_i^{\mathrm{II}}={}&-\frac{\pi}{A}\sum_{\mathbf{h}}^{\infty}\sum_{\alpha=1}^{n_i}q_{i\alpha}\sum_{j\neq i}^{N}\sum_{\beta}^{n_j}q_{j\beta}\{\exp(hr_{zi\alpha j\beta})\operatorname{erfc}(h/2\kappa+r_{zi\alpha j\beta}\kappa)-\exp(-hr_{zi\alpha j\beta})\operatorname{erfc}(h/2\kappa-r_{zi\alpha j\beta}\kappa)\\&+2\exp(-hr_{zi\alpha j\beta})\exp[-(h/2\kappa-r_{zi\alpha j\beta}\kappa)^2]\kappa/\pi^{1/2}h\\&-2\exp(hr_{zi\alpha j\beta})\exp[-(h/2\kappa+r_{zi\alpha j\beta}\kappa)^2]\kappa/\pi^{1/2}h\}\mathrm{Re}[\exp(i\mathbf{h}\cdot\mathbf{r}_{i\alpha j\beta})]\end{aligned} \tag{42}$$

for $h\neq 0$ and

$$\mathbf{F}_i^{\mathrm{II}}=\frac{2\pi}{A}\sum_{\alpha=1}^{n_i}q_{i\alpha}\sum_{j\neq i}^{N}\sum_{\beta=1}^{n_j}q_{j\beta}\operatorname{erf}(r_{zi\alpha j\beta}\kappa) \tag{43}$$

for $h=0$. The surface pressure tensor is a more complicated expression than for the bulk Ewald system, because the surface geometry breaks the formal equivalence between the three Cartesian directions. In the notation of this work, the x and y directions are equivalent in the formal expressions, whereas the z direction is quite distinct in its analytic behavior. For the Coulombic component of the stress tensor (including both real- and reciprocal-space series) we have for the xx, xy, yx, and yy components,

$$P_{\omega\tau}V=\frac{1}{2}\sum_{i=1}^{N}\sum_{\alpha=1}^{n_i}q_{i\alpha}\sum_{j=1}^{N}\sum_{\beta=1}^{n_j}q_{j\beta}\sum_{\mathbf{n}'}^{\infty}\left[\frac{2}{\sqrt{\pi}}\kappa r_{\mathbf{n}i\alpha j\beta}\exp(-\kappa^2 r_{\mathbf{n}i\alpha j\beta}^2)+\operatorname{erfc}(\kappa r_{\mathbf{n}i\alpha j\beta})\right]\frac{\mathbf{r}_{\omega\mathbf{n}ij}\mathbf{r}_{\tau\mathbf{n}i\alpha j\beta}}{r_{\mathbf{n}i\alpha j\beta}^3}$$
$$+\frac{\pi}{2A}\sum_{\mathbf{h}}^{\infty}\sum_{i=1}^{N}\sum_{\alpha=1}^{n_i}q_{i\alpha}\sum_{j=1}^{N}\sum_{\beta=1}^{n_j}q_{j\beta}B_{\omega\tau}\operatorname{Re}[\exp(i\mathbf{h}\cdot\mathbf{r}_{i\alpha j\beta})]+E_{\omega\tau}\ . \tag{44}$$

For $h\neq 0$, we have

$$B_{\omega\tau}=\delta_{\omega\tau}F(\kappa,h,r_{zi\alpha j\beta})+h_\omega h_\tau h^{-2}\{(r_{zi\alpha j\beta}-h^{-1})\exp(hr_{zi\alpha j\beta})\operatorname{erfc}(h/2\kappa+r_{zi\alpha j\beta}\kappa)$$
$$-(r_{zi\alpha j\beta}+h^{-1})\exp(-hr_{zi\alpha j\beta})\operatorname{erfc}(h/2\kappa-r_{zi\alpha j\beta}\kappa)$$
$$-\exp(hr_{zi\alpha j\beta})\exp[-(h/2\kappa+r_{zi\alpha j\beta}\kappa)^2]/\kappa\pi^{1/2}$$
$$-\exp(-hr_{zi\alpha j\beta})\exp[-(h/2\kappa-r_{zi\alpha j\beta}\kappa)^2]/\kappa\pi^{1/2}\}\ , \tag{45}$$

and for $h=0$ there is

$$B_{\omega\tau}=\delta_{\omega\tau}F(\kappa,h=0,r_{zi\alpha j\beta})\ . \tag{46}$$

For the *zz* component of the stress tensor,

$$P_{zz}V=\frac{1}{2}\sum_{i=1}^{N}\sum_{\alpha=1}^{n_i}q_{i\alpha}\sum_{j=1}^{N}\sum_{\beta=1}^{n_j}q_{j\beta}\sum_{\mathbf{n}'}^{\infty}\left[\frac{2}{\sqrt{\pi}}\kappa r_{\mathbf{n}i\alpha j\beta}\exp(-\kappa^2 r_{\mathbf{n}i\alpha j\beta}^2)+\operatorname{erfc}(\kappa r_{\mathbf{n}i\alpha j\beta})\right]\mathbf{r}_{z\mathbf{n}ij}\frac{\mathbf{r}_{z\mathbf{n}i\alpha j\beta}}{r_{\mathbf{n}i\alpha j\beta}^3}$$
$$-\frac{\pi}{2A}\left[\sum_{\mathbf{h}\neq 0}^{\infty}\sum_{i=1}^{N}\sum_{\alpha=1}^{n_i}q_{i\alpha}\sum_{j=1}^{N}\sum_{\beta=1}^{n_j}q_{j\beta}\{\exp(hr_{zi\alpha j\beta})\operatorname{erfc}(h/2\kappa+r_{zi\alpha j\beta}\kappa)-\exp(-hr_{zi\alpha j\beta})\operatorname{erfc}(h/2\kappa-r_{zi\alpha j\beta}\kappa)\right.$$
$$+2\exp(-hr_{zi\alpha j\beta})\exp[-(h/2\kappa-r_{zi\alpha j\beta\kappa})^2]\kappa/\pi^{1/2}h$$
$$\left.-2\exp(hr_{zi\alpha j\beta})\exp[-(h/2\kappa+r_{zi\alpha j\beta}\kappa)^2]\kappa/\pi^{1/2}h\}r_{zi\alpha j\beta}\operatorname{Re}[\exp(i\mathbf{h}\cdot\mathbf{r}_{i\alpha j\beta})]\right]$$
$$+\frac{\pi}{A}\sum_{i=1}^{N}\sum_{\alpha}^{n_i}q_{i\alpha}\sum_{j=1}^{N}\sum_{\beta}^{n_j}q_{j\beta}r_{zi\alpha j\beta}\operatorname{erf}(r_{zi\alpha j\beta}\kappa)+E_{zz}\ . \tag{47}$$

The last term in Eq. (47) comes from the $h=0$ component of the Fourier space term. For the $xz(=zx)$ component of the stress tensor (and yz, by index swap, $x\rightarrow y$) we have

$$P_{zx}V=\frac{1}{2}\sum_{i=1}^{N}\sum_{\alpha=1}^{n_i}q_{i\alpha}\sum_{j=1}^{N}\sum_{\beta=1}^{n_j}q_{j\beta}\sum_{\mathbf{n}'}^{\infty}\left[\frac{2}{\sqrt{\pi}}\kappa r_{\mathbf{n}i\alpha j\beta}\exp(-\kappa^2 r_{\mathbf{n}i\alpha j\beta}^2)+\operatorname{erfc}(\kappa r_{\mathbf{n}i\alpha j\beta})\right]\frac{\mathbf{r}_{z\mathbf{n}ij}\mathbf{r}_{x\mathbf{n}i\alpha j\beta}}{r_{\mathbf{n}i\alpha j\beta}^3}$$
$$+\frac{\pi}{2A}\left\{\sum_{\mathbf{h}\neq 0}^{\infty}h_x\sum_{i=1}^{N}\sum_{\alpha=1}^{n_i}q_{i\alpha}\sum_{j=1}^{N}\sum_{\beta=1}^{n_j}q_{j\beta}r_{zi\alpha j\beta}F(\kappa,h,r_{zi\alpha j\beta})\operatorname{Im}[\exp(i\mathbf{h}\cdot\mathbf{r}_{i\alpha j\beta})]\right\}+E_{zx}\ . \tag{48}$$

The $h=0$ term for S_{xx} (and S_{zx}, S_{yz}, and S_{zy}) is equal to zero. The corresponding point-charge expressions are obtained by setting $n_i=1$, for all i and $\mathbf{E}=\mathbf{0}$.

B. Point dipoles

If we replace q_i by the operator $\mu_i\cdot\nabla_i$ in the point-charge simplification of Eq. (37) then the Parry-Ewald reformulation of Eq. (23) for a lamellar periodic lattice is

$$2\Phi=\sum_{i=1}^{N}\sum_{j=1}^{N}\sum_{\mathbf{n}'}^{\infty}(\boldsymbol{\mu}_i\cdot\boldsymbol{\mu}_j)B(r_{\mathbf{n}ij})-(\boldsymbol{\mu}_i\cdot\mathbf{r}_{\mathbf{n}ij})(\boldsymbol{\mu}_j\cdot\mathbf{r}_{\mathbf{n}ij})C(r_{\mathbf{n}ij})$$
$$+\frac{\pi}{A}\sum_{\mathbf{h}}^{\infty}\sum_{i=1}^{N}\sum_{i=j}^{N}\{\operatorname{Re}[\exp(i\mathbf{h}\cdot\mathbf{r}_{ij})][F(\kappa,h,r_{zij})(\boldsymbol{\mu}_i\cdot\mathbf{h})(\boldsymbol{\mu}_j\cdot\mathbf{h})-\mu_{zi}\mu_{zj}K(\kappa,\mathbf{h},r_{zij})]$$
$$+\operatorname{Im}[\exp(i\mathbf{h}\cdot\mathbf{r}_{ij})][\mu_{zi}(\boldsymbol{\mu}_j\cdot\mathbf{h})+\mu_{zj}(\boldsymbol{\mu}_i\cdot\mathbf{h})]H(\kappa,h,r_{zij})\}-\sum_{i=1}^{N}\frac{4\kappa^3\mu_i^2}{3\pi^{1/2}}\ , \tag{49}$$

where the functions B and C are given by Eq. (26) and Eq. (27), respectively. The functions in the reciprocal series term involve F, given by Eqs. (38) and (39). There are two new functions required, which are

$$H=\frac{\partial F}{\partial r_{zij}}=\exp(hr_{zij})\mathrm{erfc}(h/2\kappa+r_{zij}\kappa)-\exp(-hr_{zij})\mathrm{erfc}(h/2\kappa-r_{zij}\kappa)$$
$$+2\exp(-hr_{zij})\exp[-(h/2\kappa-r_{zij}\kappa)^2]\kappa/\pi^{1/2}h-2\exp(hr_{zij})\exp[-(h/2\kappa+r_{zij}\kappa)^2]\kappa/\pi^{1/2}h \tag{50}$$

for $h\neq 0$,

$$H=-2\,\mathrm{erf}(r_{zij}\kappa) \tag{51}$$

for $h\neq 0$,

$$K=\frac{\partial^2 F}{\partial r_{zij}^2}=h\,\exp(hr_{zij})\mathrm{erfc}(h/2\kappa+r_{zij}\kappa)+h\,\exp(-hr_{zij})\mathrm{erfc}(h/2\kappa-r_{zij}\kappa)$$
$$-4\{\exp(hr_{zij})\exp[-(h/2\kappa+r_{zij}\kappa)^2]+\exp(-hr_{zij})\exp[-(h/2\kappa-r_{zij}\kappa)^2]\}\kappa/\pi^{1/2}$$
$$+4\{\exp(hr_{zij})(h/2\kappa+r_{zij}\kappa)\exp[-(h/2\kappa+r_{zij}\kappa)^2]$$
$$+\exp(-hr_{zij})(h/2\kappa-r_{zij}\kappa)\exp[-(h/2\kappa-r_{zij}\kappa)^2]\}\kappa^2/\pi^{1/2}h \tag{52}$$

for $h\neq 0$, and

$$K=-4\exp[-(r_{zij}\kappa)^2]\kappa\pi^{-1/2}\;. \tag{53}$$

We have for the x, y, and z components of $\mathbf{F}_i^{\mathrm{I}}$, Eq. (29), with the sum over $\mathbf{n}$ covering the two-dimensional lattice in this case. Again for $\mathbf{F}_i^{\mathrm{II}}$ the x, y, and z components are represented by analytically distinct expressions, reflecting the inequivalence between in-plane and out-of-plane directions. For the in-plane (x,y) forces,

$$\mathbf{F}_i^{\mathrm{II}}=\frac{\pi}{A}\sum_{\mathbf{h}}^{\infty}\sum_{j\neq i}^{N}\mathbf{h}\{\mathrm{Im}[\exp(i\mathbf{h}\cdot\mathbf{r}_{ij})][F(\kappa,h,r_{zij})(\boldsymbol{\mu}_i\cdot\mathbf{h})(\boldsymbol{\mu}_j\cdot\mathbf{h})-\mu_{zi}\mu_{zj}K(\kappa,h,r_{zij})]$$
$$-\mathrm{Re}[\exp(i\mathbf{h}\cdot\mathbf{r}_{ij})][\mu_{zi}(\boldsymbol{\mu}_j\cdot\mathbf{h})+\mu_{zj}(\boldsymbol{\mu}_i\cdot\mathbf{h})]H(\kappa,h,r_{zij})\}\;. \tag{54}$$

For the z direction we have

$$\mathbf{F}_i^{\mathrm{II}}=-\frac{\pi}{A}\sum_{\mathbf{h}}^{\infty}\sum_{j\neq i}^{N}\{\mathrm{Re}[\exp(i\mathbf{h}\cdot\mathbf{r}_{ij})][H(\kappa,h,r_{zij})(\boldsymbol{\mu}_i\cdot\mathbf{h})(\boldsymbol{\mu}_j\cdot\mathbf{h})-\mu_{zi}\mu_{zj}G(\kappa,h,r_{zij})]$$
$$+\mathrm{Im}[\exp(i\mathbf{h}\cdot\mathbf{r}_{ij})][\mu_{zi}(\boldsymbol{\mu}_j\cdot\mathbf{h})+\mu_{zj}(\boldsymbol{\mu}_i\cdot\mathbf{h})]K(\kappa,h,r_{zij})\}\;, \tag{55}$$

where

$$G=\frac{\partial^3 F}{\partial r_{zij}^3}=\{h^3\exp(hr_{zij})\mathrm{erfc}(h/2\kappa+r_{zij}\kappa)-6h^2\exp(hr_{zij})\exp[-(h/2\kappa+r_{zij}\kappa)^2]\kappa\pi^{-1/2}$$
$$+12h\,\exp(hr_{zij})(h/2\kappa+r_{zij}\kappa)\kappa^2\exp[-(h/2\kappa+r_{zij}\kappa)^2]\pi^{-1/2}+4\exp(hr_{zij})\kappa^3\exp[-(h/2\kappa+r_{zij}\kappa)^2]\pi^{-1/2}$$
$$-8\exp(hr_{zij})(h/2\kappa+r_{zij}\kappa)^2\kappa^3\exp[-(h/2\kappa+r_{zij}\kappa)^2]\pi^{-1/2}$$
$$-h^3\exp(-hr_{zij})\mathrm{erfc}(h/2\kappa-r_{zij}\kappa)+6h^2\exp(-hr_{zij})\exp[-(h/2\kappa-r_{zij}\kappa)^2]\kappa\pi^{-1/2}$$
$$-12h\,\exp(-hr_{zij})(h/2\kappa-r_{zij}\kappa)\kappa^2\exp[-(h/2\kappa-r_{zij}\kappa)^2]\pi^{-1/2}$$
$$-4\exp(-hr_{zij})\kappa^3\exp[-(h/2\kappa-r_{zij}\kappa)^2]\pi^{-1/2}$$
$$+8\exp(-hr_{zij})(h/2\kappa-r_{zij}\kappa)^2\kappa^3\exp[-(h/2\kappa-r_{zij}\kappa)^2]\pi^{-1/2}\}/h \tag{56}$$

for $h\neq 0$, and

$$G=24r_{zij}\kappa^3\exp[-(r_{zij}\kappa)^2]\pi^{-1/2}+16r_{zij}^3\kappa^5\exp[-(r_{zij}\kappa)^2]\pi^{-1/2}-16(r_{zij}+r_{zij}^3\kappa^2)\pi^{-1/2}\kappa^3\exp[-(r_{zij}\kappa)^2] \tag{57}$$

for $h=0$.

For the Coulombic component of the stress tensor (including both real- and reciprocal-space series) we have for the xx, xy, yx, and yy components,

$$
\begin{aligned}
P_{\omega\tau}V=\frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}\sum_{\mathbf{n}'}^{\infty} r_{\omega\mathbf{n}ij}\left\{(r_{\tau\mathbf{n}ij}\boldsymbol{\mu}_i\cdot\boldsymbol{\mu}_j+\mu_{i\tau}\boldsymbol{\mu}_j\cdot\mathbf{r}_{\mathbf{n}ij}+\mu_{j\tau}\boldsymbol{\mu}_i\cdot\mathbf{r}_{\mathbf{n}ij})C(r_{\mathbf{n}ij})-r_{\tau\mathbf{n}ij}(\boldsymbol{\mu}_i\cdot\mathbf{r}_{\mathbf{n}ij})(\boldsymbol{\mu}_j\cdot\mathbf{r}_{\mathbf{n}ij})\frac{D(r_{\mathbf{n}ij})}{r_{\mathbf{n}ij}}\right\}& \\
+\frac{\pi}{2A}\sum_{\mathbf{h}'}^{\infty}\sum_{i=1}^{N}\sum_{j=1}^{N}\delta_{\omega\tau}\{\mathrm{Re}[\exp(i\mathbf{h}\cdot\mathbf{r}_{ij})][F(\kappa,h,r_{zij})(\boldsymbol{\mu}_i\cdot\mathbf{h})(\boldsymbol{\mu}_j\cdot\mathbf{h})-\mu_{zi}\mu_{zj}K(\kappa,\mathbf{h},r_{zij})]& \\
+\mathrm{Im}[\exp(i\mathbf{h}\cdot\mathbf{r}_{ij})][\mu_{zi}(\boldsymbol{\mu}_j\cdot\mathbf{h})+\mu_{zj}(\boldsymbol{\mu}_i\cdot\mathbf{h})]H(\kappa,h,r_{zij})\}& \\
+\frac{\pi}{2A}\sum_{\mathbf{h}'}^{\infty}\sum_{i=1}^{N}\sum_{j=1}^{N}\{\mathrm{Re}[\exp(i\mathbf{h}\cdot\mathbf{r}_{ij})](F(\kappa,h,r_{zij})h_{\tau}[\mu_{\omega i}(\boldsymbol{\mu}_j\cdot\mathbf{h})+(\boldsymbol{\mu}_i\cdot\mathbf{h})\mu_{\omega j}]& \\
+(\boldsymbol{\mu}_i\cdot\mathbf{h})(\boldsymbol{\mu}_j\cdot\mathbf{h})F^{E}(\kappa,h,r_{zij})h_{\omega}h_{\tau}h^{-2}-\mu_{zi}\mu_{zj}K^{E}(\kappa,h,r_{zij})h_{\omega}h_{\tau}h^{-2})& \\
+\mathrm{Im}[\exp(i\mathbf{h}\cdot\mathbf{r}_{ij})](h_{\tau}(\mu_{zi}\mu_{\omega j}+\mu_{zj}\mu_{\omega i})H(\kappa,h,r_{zij})& \\
+[\mu_{zi}(\boldsymbol{\mu}_j\cdot\mathbf{h})+\mu_{zj}(\boldsymbol{\mu}_i\cdot\mathbf{h})]H^{E}(\kappa,h,r_{zij})h_{\omega}h_{\tau}h^{-2})\}\ .& \qquad (58)
\end{aligned}
$$

For the *zz* component of the stress tensor,

$$
\begin{aligned}
P_{zz}V=\sum_{i}^{N}\sum_{j}^{N}\sum_{\mathbf{n}}^{\infty}\frac{1}{2}r_{z\mathbf{n}ij}\left\{(r_{z\mathbf{n}ij}\boldsymbol{\mu}_i\cdot\boldsymbol{\mu}_j+\mu_{iz}\boldsymbol{\mu}_j\cdot\mathbf{r}_{\mathbf{n}ij}+\mu_{jz}\boldsymbol{\mu}_i\cdot\mathbf{r}_{\mathbf{n}ij})C(r_{\mathbf{n}ij})-r_{z\mathbf{n}ij}(\boldsymbol{\mu}_i\cdot\mathbf{r}_{\mathbf{n}ij})(\boldsymbol{\mu}_j\cdot\mathbf{r}_{\mathbf{n}ij})\frac{D(r_{\mathbf{n}ij})}{r_{\mathbf{n}ij}}\right\}& \\
-\frac{\pi}{2A}\sum_{\mathbf{h}}^{\infty}\sum_{i=1}^{N}\sum_{j=1}^{N}\{\mathrm{Re}[\exp(i\mathbf{h}\cdot\mathbf{r}_{ij})][H(\kappa,h,r_{zij})(\boldsymbol{\mu}_i\cdot\mathbf{h})(\boldsymbol{\mu}_j\cdot\mathbf{h})-\mu_{zi}\mu_{zj}G(\kappa,h,r_{zij})]& \\
+\mathrm{Im}[\exp(i\mathbf{h}\cdot\mathbf{r}_{ij})]r_{zij}[\mu_{zi}(\boldsymbol{\mu}_j\cdot\mathbf{h})+\mu_{zj}(\boldsymbol{\mu}_i\cdot\mathbf{h})]K(\kappa,\mathbf{h},r_{zij})\}\ .& \qquad (59)
\end{aligned}
$$

For the *zx* component of the stress tensor (and *zy*, by index swap, $x\rightarrow y$) we have

$$
\begin{aligned}
P_{zx}V=\frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}\sum_{\mathbf{n}'}^{\infty}r_{z\mathbf{n}ij}\left\{(r_{x\mathbf{n}ij}\boldsymbol{\mu}_i\cdot\boldsymbol{\mu}_j+\mu_{ix}\boldsymbol{\mu}_j\cdot\mathbf{r}_{\mathbf{n}ij}+\mu_{jx}\boldsymbol{\mu}_i\cdot\mathbf{r}_{\mathbf{n}ij})C(r_{\mathbf{n}ij})-r_{x\mathbf{n}ij}(\boldsymbol{\mu}_i\cdot\mathbf{r}_{\mathbf{n}ij})(\boldsymbol{\mu}_j\cdot\mathbf{r}_{\mathbf{n}ij})\frac{D(r_{\mathbf{n}ij})}{r_{\mathbf{n}ij}}\right\}& \\
+\frac{\pi}{2A}\sum_{\mathbf{h}}^{\infty}\sum_{i=1}^{N}\sum_{j=1}^{N}h_x r_{zij}\{\mathrm{Im}[\exp(i\mathbf{h}\cdot\mathbf{r}_{ij})][F(\kappa,h,r_{zij})(\boldsymbol{\mu}_i\cdot\mathbf{h})(\boldsymbol{\mu}_j\cdot\mathbf{h})-\mu_{zi}\mu_{zj}K(\kappa,h,r_{zij})]& \\
-\mathrm{Re}[\exp(i\mathbf{h}\cdot\mathbf{r}_{ij})][\mu_{zi}(\boldsymbol{\mu}_j\cdot\mathbf{h})+\mu_{zj}(\boldsymbol{\mu}_i\cdot\mathbf{h})]H(\kappa,h,r_{zij})\}\ ,& \qquad (60)
\end{aligned}
$$

where

$$
\begin{aligned}
F^{E}=\{hr_{zij}\exp(hr_{zij})\mathrm{erfc}(h/2\kappa+r_{zij}\kappa)-\exp(hr_{zij})\pi^{-1/2}\exp[-(h/2\kappa+r_{zij}\kappa)^2]h/\kappa& \\
-hr_{zij}\exp(-hr_{zij})\mathrm{erfc}(h/2\kappa-r_{zij}\kappa)-\exp(-hr_{zij})\pi^{-1/2}\exp[-(h/2\kappa-r_{zij}\kappa)^2]h/\kappa& \\
-\exp(hr_{zij})\mathrm{erfc}(h/2\kappa+r_{zij}\kappa)+\exp(-hr_{zij})\mathrm{erfc}(h/2\kappa-r_{zij}\kappa)\}/h\ .& \qquad (61)
\end{aligned}
$$

The quantity H^{E} is

$$H^{E}=H_1^{E}+H_2^{E}\ , \qquad (62)$$

where

$$
\begin{aligned}
H_1^{E}=h\exp(hr_{zij})\mathrm{erfc}(h/2\kappa+r_{zij}\kappa)+h^2r_{zij}\exp(hr_{zij})\mathrm{erfc}(h/2\kappa+r_{zij}\kappa)& \\
-h^2\exp(hr_{zij})\pi^{-1/2}\exp[-(h/2\kappa+r_{zij}\kappa)^2]/\kappa-2hr_{zij}\exp(hr_{zij})\pi^{-1/2}\exp[-(h/2\kappa+r_{zij}\kappa)^2]\kappa& \\
+2\exp(hr_{zij})\pi^{-1/2}(h/2\kappa+r_{zij}\kappa)h\exp[-(h/2\kappa+r_{zij}\kappa)^2]& \\
-h\exp(-hr_{zij})[1+\mathrm{erf}(-h/2\kappa+r_{zij}\kappa)]+h^2r_{zij}\exp(-hr_{zij})\mathrm{erfc}(h/2\kappa-r_{zij}\kappa)& \\
+h^2\exp(-hr_{zij})\pi^{-1/2}\exp[-(h/2\kappa-r_{zij}\kappa)^2]/\kappa-2hr_{zij}\exp(-hr_{zij})\pi^{-1/2}\exp[-(-h/\kappa/2+r_{zij}\kappa)^2]\kappa& \\
+2\exp(-hr_{zij})\pi^{-1/2}(-h/2\kappa+r_{zij}\kappa)h\exp[-(h/\kappa/2-r_{zij}\kappa)^2]/h\ ,& \qquad (63)
\end{aligned}
$$

$$
\begin{aligned}
H_2^{E}=(-\{h\exp(hr_{zij})\mathrm{erfc}(h/2\kappa+r_{zij}\kappa)-2\exp(hr_{zij})\pi^{-1/2}\exp[-(h/2\kappa+r_{zij}\kappa)^2]\kappa& \\
-h\exp(-hr_{zij})\mathrm{erfc}(h/2\kappa-r_{zij}\kappa)+2\exp(-hr_{zij})\pi^{-1/2}\exp[-(-h/2\kappa+r_{zij}\kappa)^2]\kappa\})/h\ .& \qquad (64)
\end{aligned}
$$

The quantity K^E is

$$K^E = K_1^E + K_2^E \ , \tag{65}$$

where

$$\begin{aligned}
K_1^E = \{ & 2h^2 \exp(hr_{zij}) \operatorname{erfc}(h/2\kappa + r_{zij}\kappa) + h^3 r_{zij} \exp(hr_{zij}) \operatorname{erfc}(h/2\kappa + r_{zij}\kappa) \\
& - h^3 \exp(hr_{zij}) \pi^{-1/2} \exp[-(h/2\kappa + r_{zij}\kappa)^2]/\kappa - 2h \exp(hr_{zij}) \pi^{-1/2} \exp[-(h/2\kappa + r_{zij}\kappa)^2]\kappa \\
& - 4h^2 r_{zij} \exp(hr_{zij}) \pi^{-1/2} \exp[-(h/2\kappa + r_{zij}\kappa)^2]\kappa \\
& + 4h^2 \exp(hr_{zij}) \pi^{-1/2} (h/2\kappa + r_{zij}\kappa) \exp[-(h/2\kappa + r_{zij}\kappa)^2] \\
& + 4h r_{zij} \exp(hr_{zij}) \pi^{-1/2} (h/2\kappa + r_{zij}\kappa)\kappa^2 \exp[-(h/2\kappa + r_{zij}\kappa)^2] \\
& - 4 \exp(hr_{zij}) \pi^{-1/2} (h/2\kappa + r_{zij}\kappa)^2 \kappa h \exp[-(h/2\kappa + r_{zij}\kappa)^2] \\
& + 2h^2 \exp(-hr_{zij}) \operatorname{erfc}(h/2\kappa - r_{zij}\kappa) - h^3 r_{zij} \exp(-hr_{zij}) \operatorname{erfc}(h/2\kappa - r_{zij}\kappa) \\
& - h^3 \exp(-hr_{zij}) \pi^{-1/2} \exp[-(h/2\kappa - r_{zij}\kappa)^2]/\kappa - 2h \exp(-hr_{zij}) \pi^{-1/2} \exp[-(h/2\kappa - r_{zij}\kappa)^2]\kappa \\
& + 4h^2 r_{zij} \exp(-hr_{zij}) \pi^{-1/2} \exp[-(h/2\kappa - r_{zij}\kappa)^2]\kappa \\
& + 4h^2 \exp(-hr_{zij}) \pi^{-1/2} (h/2\kappa - r_{zij}\kappa) \exp[-(h/2\kappa - r_{zij}\kappa)^2] \\
& - 4h r_{zij} \exp(-hr_{zij}) \pi^{-1/2} (h/2\kappa - r_{zij}\kappa)^2 \kappa^2 \exp[-(h/2\kappa - r_{zij}\kappa)^2] \\
& - 4 \exp(-hr_{zij}) \pi^{-1/2} (h/2\kappa - r_{zij}\kappa)^2 \kappa h \exp[-(h/2\kappa - z\kappa)^2] \} / h \ ,
\end{aligned} \tag{66}$$

$$\begin{aligned}
K_2^E = -\{ & h^2 \exp(hr_{zij}) \operatorname{erfc}(h/2\kappa + r_{zij}\kappa) - 4h \exp(hr_{zij}) \pi^{-1/2} \exp[-(h/2\kappa + r_{zij}\kappa)^2]\kappa \\
& + 4 \exp(hr_{zij}) \pi^{-1/2} (h/2\kappa + r_{zij}\kappa)\kappa^2 \exp[-(h/2\kappa + r_{zij}\kappa)^2] \\
& + h^2 \exp(-hr_{zij}) \operatorname{erfc}(h/2\kappa - r_{zij}\kappa) - 4h \exp(-hr_{zij}) \pi^{-1/2} \exp[-(h/2\kappa - r_{zij}\kappa)^2]\kappa \\
& + 4 \exp(-hr_{zij}) \pi^{-1/2} (h/2\kappa - r_{zij}\kappa)\kappa^2 \exp[-(h/2\kappa - r_{zij}\kappa)^2] \} / h \ .
\end{aligned} \tag{67}$$

The F^E, H^E, and K^E are zero for $h=0$.

IV. CONCLUSIONS

In this paper we have filled in a number of gaps in the formulas for the electrostatic potential, force, and pressure tensor for partial-charge molecule and point-dipole lattices. The geometries we have considered are both bulk and surface. Clearly, the formulas become more complicated in the case for the surface geometry. Also the complexity increases on going from potential through force to pressure tensor. All the formulas were confirmed numerically on lattices containing randomly filled unit cells.

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