Journal of Statistical Physics, Vol. 77, Nos. 1/2, 1994

Calculating the Pressure in Simulations Using Periodic Boundary Conditions

E. R. Smith[1]

Received October 29, 1993; final April 7, 1994

Because it is not immediately clear how to write down a proper Hamiltonian for a system in periodic boundary conditions, particularly with Coulombic interactions, we consider a large, finite array of copies of a basic simulation cell containing N particles with some interaction between them. We also put N independent copy particles in each of the copy cells of the array and write down a constrained Lagrangian for the whole system. Constraints on the velocities of the particles of the whole array together with an appropriate initial condition implement the periodic structure in the cells of the array of copies. We derive a Hamiltonian for the whole system with constraints and then derive the equations of motion and a virial expression for the pressure tensor in terms of the forces on the system. In the limit as the array of cell copies becomes large, the equations of motion become the standard ones used in periodic-boundary-conditions simulations. The method also provides an unequivocal algorithm for the pressure in this limit in terms of a virial expression. Particular attention is paid to the case of Coulombic interactions.

KEY WORDS: Virial theorem; pressure; periodic boundary conditions; computer simulations.

1. INTRODUCTION

Suppose we have a system of N_0 particles with mass m_j and position $\mathbf{r}_j$ in a container Ω of volume V_0. Forces act between the particles and in this paper we shall assume that we have short-ranged forces derived from a potential $\varphi_{SR;j,k}(\mathbf{r}_{jk})$, direct Coulomb forces derived from the pair potential $Q_jQ_k\,|\mathbf{r}_j-\mathbf{r}_k|^{-1}$, where the Q_j, $1\leqslant j\leqslant N$, are the charges on the particles, and "polarization" forces derived from a polarization interaction

[1] Mathematics Department, La Trobe University, Bundoora, Victoria, 3083, Australia. E-mail: MATERS@lure.latrobe.edu.au.

0022-4715/94/1000-0449$07.00/0

$Q_jQ_k\varphi_{\mathrm{POL}}(\mathbf{r}_j, \mathbf{r}_k; \varepsilon')$, where ε' is the dielectric constant of the continuous medium outside Ω. This last interaction arises because a charge Q_j at $\mathbf{r}_j \in \Omega$ polarizes the external dielectric medium and this polarized external medium sets up a potential inside Ω which interacts with Q_k at $\mathbf{r}_k \in \Omega$. We shall describe details of $\varphi_{\mathrm{POL}}(\mathbf{r}_j, \mathbf{r}_k; \varepsilon')$ below. For the moment we note that the polarization force

$$\mathbf{F}_{\mathrm{POL};j}(\mathbf{r}_j, \mathbf{r}_k; \varepsilon') = -Q_jQ_k\nabla_{\mathbf{r}_j}\varphi_{\mathrm{POL}}(\mathbf{r}_j, \mathbf{r}_k; \varepsilon') \tag{1.1}$$

does not in general obey Newton's third law.

The standard way to write down equations of motion and thus carry out a molecular dynamics simulation is to start with the equations of motion. We may write these for our example as

$$m_j\ddot{\mathbf{r}}_j = \sum_{\substack{k=1 \\ k\neq j}}^{N} \mathbf{F}_{\mathrm{SR};jk}(\mathbf{r}_{jk}) + \sum_{\substack{k=1 \\ k\neq j}}^{N} \mathbf{F}_{\mathrm{DC};jk}(\mathbf{r}_{jk}) + \sum_{k=1}^{N} \mathbf{F}_{\mathrm{POL};jk}(\mathbf{r}_j, \mathbf{r}_k; \varepsilon') + \mathbf{F}_{\mathrm{SURF};j}(\mathbf{r}_j) \tag{1.2}$$

where the short-ranged forces are

$$\mathbf{F}_{\mathrm{SR};jk}(\mathbf{r}_{jk}) = -\frac{\mathbf{r}_{jk}}{|\mathbf{r}_{jk}|}\varphi'_{\mathrm{SR};jk}(|\mathbf{r}_{jk}|) \tag{1.3}$$

the direct Coulomb forces are

$$\mathbf{F}_{\mathrm{SR};jk}(\mathbf{r}_{jk}) = -Q_jQ_k\nabla_{\mathbf{r}_j}|\mathbf{r}_{jk}|^{-1} \tag{1.4}$$

and $\mathbf{F}_{\mathrm{SURF};j}(\mathbf{r}_j)$ is the short-ranged force of the container wall $\partial\Omega$ on the particle j.

There are several problems with this scenario when we do standard molecular dynamics. First, how can we define a system in periodic boundary conditions to which we can apply external forces so as to measure response? There is no outside in a really periodic system. Second, how do we calculate the forces in a periodic system, especially with Coulombic interactions? Finally, how do we identify the pressure and in particular, how do we consider polarization interactions? Are they internal or external, do we consider them as internal forces contributing to a virial expression or as surface forces contributing to surface pressure? We answer the problem of identifying the internal pressure in Section 2. In Section 3 we construct a model of a basic simulation cell together with a large, finite array of copies of this simulation system. A Lagrangian is written for the cell–array system with periodicity implemented via velocity constraints and initial conditions. A set of momenta are introduced and the Lagrange multipliers for each of the velocity constraints are determined. In Section 4 we define a Hamiltonian for the large cell–array system and derive equations

of motion for the particles in the basic simulation cell. We also apply the virial expression for the pressure tensor from Section 2 to the cell–array system. In Section 5 we take the limit of the equations of motion and the virial expression of the pressure as the array of copies becomes large. For short-ranged potentials $[|\varphi_{SR;j,k}(|\mathbf{r}|)| \leqslant A\,|\mathbf{r}|^{-4}$ for large enough $|\mathbf{r}|]$ these results are those used in standard simulations. For Coulombic forces we are able to make an unequivocal definition of the polarization forces as internal forces because the large-array limit of these forces in the periodic cell–array takes a form which does obey Newton's third law. The paper concludes with a discussion on implementation in Section 6.

2. MICROCANONICAL DEFINITION OF THE PRESSURE

While it is possible to derive a canonical ensemble expression for the scalar pressure on a statistical mechanical system, if we have no polarization forces present, it is not so simple to derive an expression for the pressure tensor. If we want the scalar pressure, we may consider Ω to be a sphere S_R of radius R. We can then find the derivative of the free energy with respect to the volume V_0 of Ω in the standard treatment[1,2] which involves differentiating potentials $\phi(R\boldsymbol{\rho}_1, R\boldsymbol{\rho}_2)$ with respect to R. However, if we want the pressure tensor, we must know how the polarization potentials change as the sphere is distorted into an ellipsoid. Such calculations involve solutions of Poisson's equation in an ellipsoid and in my opinion are best avoided.

Suppose then that we have the system of Section 1. We introduce a unit vector $\hat{\mathbf{n}}$ of fixed direction and then the region $\omega(\hat{\mathbf{n}}, \zeta)$ where

$$\omega(\hat{\mathbf{n}}, \zeta) = \{\mathbf{r} \in \Omega : \mathbf{r} \cdot \hat{\mathbf{n}} \geqslant \zeta\} \tag{2.1}$$

The region $\omega(\hat{\mathbf{n}}, \zeta)$ has a curved surface $\partial\omega_c(\hat{\mathbf{n}}, \zeta)$ with unit outward normal $\tau(\mathbf{r})$ on $\partial\omega_c(\hat{\mathbf{n}}, \zeta)$. The region $\omega(\hat{\mathbf{n}}, \zeta)$ also has a plane surface

$$D(\hat{\mathbf{n}}, \zeta) = \{\mathbf{r} \in \Omega : \mathbf{r} \cdot \hat{\mathbf{n}} = \zeta\} \tag{2.2}$$

We define

$$Z_-(\hat{\mathbf{n}}, \Omega) = \min_{\mathbf{r} \in \Omega} [\mathbf{r} \cdot \hat{\mathbf{n}}] \qquad \text{and} \qquad Z_+(\hat{\mathbf{n}}, \Omega) = \max_{\mathbf{r} \in \Omega} [\mathbf{r} \cdot \hat{\mathbf{n}}] \tag{2.3}$$

We note that $\omega(\hat{\mathbf{n}}, Z_-) = \Omega$ and $\omega(\hat{\mathbf{n}}, Z_+) = \phi$. To define the pressure we use a method suggested by Hoover.[3] We consider the momentum of the particles in $\omega(\hat{\mathbf{n}}, \zeta)$. This is

$$\mathscr{P}(\hat{\mathbf{n}}, \zeta, t) = \int_{\omega(\hat{\mathbf{n}}, \zeta)} d^3\mathbf{r} \sum_{j=1}^{N} \delta(\mathbf{r} - \mathbf{r}_j(t))\, \mathbf{p}_j(t) \tag{2.4}$$

We may evaluate $\dot{\mathscr{P}}(\hat{\mathbf{n}}, \zeta, t)$ microscopically, in the microcanonical ensemble or equivalently from long-time averages of Hamiltonian dynamics, or we may evaluate $\dot{\mathscr{P}}(\hat{\mathbf{n}}, \zeta, t)$ macroscopically as equal to the pressure forces acting on the surface of $\omega(\hat{\mathbf{n}}, \zeta)$. By equating the microscopic and macroscopic expressions, we can find a virial expression for the internal pressure tensor. This mechanical equivalence serves as a definition of the internal pressure tensor in the microcanonical ensemble. If we imagine an instantaneous internal pressure tensor $\Pi(\mathbf{r}, t)$ in the system (for $\mathbf{r} \in \Omega$) and a surface pressure tensor $\Pi^{S}(\mathbf{r}, t)$ (for $\mathbf{r} \in \partial\Omega$), then we have

$$\dot{\mathscr{P}}(\hat{\mathbf{n}}, \zeta, t) = \int_{D(\hat{\mathbf{n}}, \zeta)} d^2\mathbf{r}\, \hat{\mathbf{n}} \cdot \Pi(\mathbf{r}, t) - \int_{\partial\omega_r(\hat{\mathbf{n}}, \zeta)} d^2\mathbf{r}\, \hat{\boldsymbol{\tau}}(\mathbf{r}) \cdot \Pi^{S}(\mathbf{r}, t) \tag{2.5}$$

To obtain a virial expression, we integrate Eq. (2.5) from $Z_{-}(\hat{\mathbf{n}}, \Omega)$ to $Z_{+}(\hat{\mathbf{n}}, \Omega)$, using Eq. (2.4) for $\mathscr{P}(\hat{\mathbf{n}}, \zeta, t)$ on the left-hand side. This gives, using integration by parts,

$$\begin{aligned} &\hat{\mathbf{n}} \cdot \int_{\Omega} d^3\mathbf{r}\, \Pi(\mathbf{r}, t) + Z_{-}(\hat{\mathbf{n}}, \Omega) \int_{\partial\Omega} d^2\mathbf{r}\, \hat{\boldsymbol{\tau}}(\mathbf{r}) \cdot \Pi^{S}(\mathbf{r}, t) \\ &\quad - \hat{\mathbf{n}} \cdot \int_{\partial\Omega} d^2\mathbf{r}\, \mathbf{r}\hat{\boldsymbol{\tau}}(\mathbf{r}) \cdot \Pi^{S}(\mathbf{r}, t) \\ &= \frac{d}{dt}\left[-Z_{-}(\hat{\mathbf{n}}, \Omega) \sum_{j=1}^{N} \mathbf{p}_j(t) + \hat{\mathbf{n}} \cdot \sum_{j=1}^{N} \mathbf{r}_j(t)\, \mathbf{p}_j(t) \right] \end{aligned} \tag{2.6}$$

We now define the average internal pressure tensor by

$$\bar{\Pi}(t) = \frac{1}{V_0} \int_{\Omega} d^3\mathbf{r}\, \Pi(\mathbf{r}, t) \tag{2.7}$$

the total external force on the system by

$$\mathbf{F}_{EX}(t) = -\int_{\partial\Omega} d^2\mathbf{r}\, \hat{\boldsymbol{\tau}}(\mathbf{r}) \cdot \Pi^{S}(\mathbf{r}, t) \tag{2.8}$$

and the total momentum of the system by

$$\mathbf{P}_{T}(t) = \sum_{j=1}^{N} \mathbf{p}_j(t) \tag{2.9}$$

Notice that we do not assume at this stage any particular relation between the internal pressure $\Pi(\mathbf{r}, t)$ and the surface pressure $\Pi^{S}(\mathbf{r}, t)$, nor shall we do so below. We may then rearrange Eq. (2.6), writing $\dot{\mathbf{p}}_j(t)$ in terms of

the short-range, direct Coulomb, polarization, and surface forces. For all directions $\hat{\mathbf{n}}$ we obtain

$$\begin{aligned}\hat{\mathbf{n}}\cdot\bar{\Pi}(t)\,V_0 = \hat{\mathbf{n}}\cdot\Bigg\{&\sum_{j=1}^{N}\dot{\mathbf{r}}_j(t)\,\mathbf{p}_j(t)\\&+\sum_{j=1}^{N}\sum_{k=1}^{N}\mathbf{r}_j(t)[\mathbf{F}_{\mathrm{SR};jk}(\mathbf{r}_{jk})+\mathbf{F}_{\mathrm{DC};jk}(\mathbf{r}_{jk})]\\&+\sum_{j=1}^{N}\sum_{k=1}^{N}\mathbf{r}_j\mathbf{F}_{\mathrm{POL};j}(\mathbf{r}_j,\mathbf{r}_k;\varepsilon')\\&+\sum_{j=1}^{N}\mathbf{r}_j(t)\,\mathbf{F}_{\mathrm{SURF};j}(\mathbf{r}_j)+\int_{\partial\Omega}d^2\mathbf{r}\,\mathbf{r}\hat{\mathbf{t}}(\mathbf{r})\cdot\Pi^{\mathrm{S}}(\mathbf{r},t)\Bigg\}\\&+Z_{-}(\hat{\mathbf{n}},\Omega)[\mathbf{F}_{\mathrm{EX}}(t)-\dot{\mathbf{P}}_{\mathrm{T}}(t)]\end{aligned}\tag{2.10}$$

Next we introduce the notion of a long-time average of a variable X as

$$\langle X\rangle=\lim_{t_0\to\infty}\frac{1}{t_0}\int_0^{t_0}X(t)\,dt\tag{2.11}$$

and define the internal pressure as

$$\Pi=\langle\bar{\Pi}(t)\rangle\tag{2.12}$$

Now any change of total system momentum must be driven by the external forces, that is, by the surface pressure, so that $\mathbf{F}_{\mathrm{EX}}(t)=\dot{\mathbf{P}}_{\mathrm{T}}(t)$ and so we have

$$\begin{aligned}\Pi V_0=&\left\langle\sum_{j=1}^{N}\dot{\mathbf{r}}_j(t)\,\mathbf{p}_j(t)\right\rangle+\frac{1}{2}\left\langle\sum_{j=1}^{N}\sum_{k=1}^{N}\mathbf{r}_{jk}[\mathbf{F}_{\mathrm{SR};jk}(\mathbf{r}_{jk})+\mathbf{F}_{\mathrm{DC};jk}(\mathbf{r}_{jk})]\right\rangle\\&+\left\langle\sum_{j=1}^{N}\sum_{k=1}^{N}\mathbf{r}_j(t)\,\mathbf{F}_{\mathrm{POL};j}(\mathbf{r}_j,\mathbf{r}_k;\varepsilon')\right\rangle\\&+\left\langle\sum_{j=1}^{N}\mathbf{r}_j(t)\,\mathbf{F}_{\mathrm{SURF};j}(\mathbf{r}_j)+\int_{\partial\Omega}d^2\mathbf{r}\,\mathbf{r}\hat{\mathbf{t}}(\mathbf{r})\cdot\Pi^{\mathrm{S}}(\mathbf{r},t)\right\rangle\end{aligned}\tag{2.13}$$

In the normal course of events, we should be able to identify the last expectation on the right-hand side of Eq. (2.13) as zero: the surface forces give rise to the surface pressure. However, let us consider Ω to be a spherical

container of radius R and define $\varphi_{LM}(\mathbf{r}) = r^L Y_{LM}(\hat{\mathbf{r}})$, where the $Y_{LM}(\hat{\mathbf{r}})$ are spherical harmonics in standard notation.[4 6] We then have

$$\varphi_{\mathrm{POL}}(\mathbf{r}_j, \mathbf{r}_k; \varepsilon') = -\sum_{L=0}^{\infty} \sum_{M=-L}^{L} \frac{4\pi}{2L+1} \frac{(L+1)(\varepsilon'-1)}{\varepsilon'(L+1)+L} \times R^{-(2L+1)} \varphi_{LM}(\mathbf{r}_j)\, \varphi^*_{LM}(\mathbf{r}_k) \tag{2.14}$$

Notice, for example, the self-interaction

$$\varphi_{\mathrm{POL}}(\mathbf{r}_j, \mathbf{r}_k; \varepsilon') = -\sum_{L=0}^{\infty} \frac{(L+1)(\varepsilon'-1)}{\varepsilon'(L+1)+L} R^{-1} \left(\frac{\mathbf{r}_j^2}{R^2}\right)^L \tag{2.15}$$

This looks for all the world like an external interaction which we should include in the surface forces in the last expectation in Eq. (2.13). In general the polarization forces on j due to k and on k due to j do not obey Newton's third law, because of their origin in interactions of both particles with the external dielectric medium. However, we shall see below that in the periodic boundary condition structure that we establish, these pairwise polarization forces do obey Newton's third law and so it is entirely appropriate to include them in the internal forces. When we ignore the last expectation of Eq. (2.13) as described above, we then obtain a virial expression from Eq. (2.13).

3. THE LARGE CELL ARRAY AND ITS CONSTRAINED LAGRANGIAN

We consider first a simulation cell $\Gamma(\mathbf{0}) = \{\mathbf{r}: -L/2 \leqslant \mathbf{r} \cdot \mathbf{a}_\alpha \leqslant L/2, \alpha = 1, 2, 3\}$, where the $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ are three noncoplanar vectors with which we generate a lattice $\Lambda = \{\mathbf{n} = \sum_{\alpha=1}^{3} n_\alpha L\mathbf{a}_\alpha, (n_1, n_2, n_3) \in \mathbb{Z}^3\}$. The volume of this central simulation cell is $V_\Lambda = L^3 |\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3|$. There are N point particles of mass m_j at $\mathbf{r}_j \in \Gamma(\mathbf{0})$. We assume that pair interactions $\phi_{jk}(\mathbf{r}_{jk})$ act between the particles. We then construct a large but finite array of copies $\Gamma(\mathbf{n})$ of $\Gamma(\mathbf{0})$. The copies $\Gamma(\mathbf{n})$ are $\{\mathbf{r}: \mathbf{r} - \mathbf{n} \in \Gamma(\mathbf{0})\}$ with $\mathbf{n} = \sum_{\alpha=1}^{3} n_\alpha L\mathbf{a}_\alpha$, and so the copies also have volume V_Λ. The set C_R is a finite but large array of vectors $\mathbf{n} \in \Lambda$, and we shall also use C_R to refer to the region contained in the cells $\Gamma(\mathbf{n})$ for which $\mathbf{n} \in C_R$. The linear dimensions of this region will be assumed to grow linearly with R. We shall generally use the region $S_R(\Lambda)$, which is all the vectors $\mathbf{n} \in \Lambda$ for which $|\mathbf{n}| \leqslant R$, but other shapes are possible. In each cell $\Gamma(\mathbf{n})$ of the array C_R we put N copy particles of mass m_j at $\mathbf{R}(j, \mathbf{n})$, $1 \leqslant j \leqslant N$. We define $\mathbf{R}(j, \mathbf{0}) = \mathbf{r}_j$. The potentials ϕ_{jk} act between all the particles in the entire array. It is convenient to introduce $r(\alpha, j, \mathbf{n})$ via

$$\mathbf{R}(j, \mathbf{n}) = \sum_{\alpha=1}^{3} \hat{\mathbf{e}}_\alpha r(\alpha, j, \mathbf{n}) \tag{3.1}$$

so that $\{r(\alpha, j, \mathbf{n}), 1 \leqslant \alpha \leqslant 3, 1 \leqslant j \leqslant N, \mathbf{n} \in C_R\}$ are the coordinates of all the particles in the entire finite large array of copies of the original simulation cell. We also assume that there is a short-ranged single-particle surface potential $\phi_{1j}(\mathbf{r}_j)$ acting on each particle.

The unconstrained Lagrangian for the whole system is

$$\begin{aligned}\mathscr{L} = &\tfrac{1}{2} \sum_{\alpha=1}^{3} \sum_{j=1}^{N} \sum_{\mathbf{n} \in C_R} m_j \dot{r}(\alpha, j, \mathbf{n})^2 \\ &- \tfrac{1}{2} \sum_{j=1}^{N} \sum_{\mathbf{n}_1 \in C_R} \sum_{k=1}^{N} {\sum_{\mathbf{n}_2 \in C_R}}^{*} \phi_{jk}(\mathbf{R}(j, \mathbf{n}_1), \mathbf{R}(k, \mathbf{n}_2)) \\ &- \sum_{j=1}^{N} \sum_{\mathbf{n} \in C_R} \phi_{1j}(\mathbf{R}(j, \mathbf{n}))\end{aligned} \tag{3.2}$$

and the asterisk on the sum means we omit singular self-interactions. To implement the periodic boundary conditions, we introduce $D_R = C_R \backslash \{\mathbf{0}\}$ and then insist on the constraints

$$\begin{aligned}f(\alpha, j, \mathbf{n}) = &\, r(\alpha, j, \mathbf{n}) - r(\alpha, j, \mathbf{0}) \\ &- \mathbf{n} \cdot \hat{\mathbf{e}}_\alpha = 0, \qquad 1 \leqslant \alpha \leqslant 3, \quad 1 \leqslant j \leqslant N, \quad \mathbf{n} \in D_R\end{aligned} \tag{3.3}$$

In the analysis below the techniques of De Leeuw *et al.*[7] are adapted directly to these "periodic" constraints. We replace these constraints by the velocity constraints

$$\begin{gathered}\frac{d}{dt} f(\alpha, j, \mathbf{n}) = \sum_{\beta=1}^{3} \sum_{k=1}^{N} \sum_{\mathbf{n}' \in C_R} \dot{r}(\beta, k, \mathbf{n}') \frac{\partial f(\alpha, j, \mathbf{n})}{\partial r(\beta, k, \mathbf{n}')} = 0 \\ \text{for} \quad 1 \leqslant \alpha \leqslant 3, \quad 1 \leqslant j \leqslant N, \quad \mathbf{n} \in D_R\end{gathered} \tag{3.4}$$

together with the requirement that in the initial conditions for the whole system, the constraints of Eq. (3.3) hold.

The constrained Lagrangian is then

$$\begin{aligned}\mathscr{L}^* = &\tfrac{1}{2} \sum_{\alpha=1}^{3} \sum_{j=1}^{N} \sum_{\mathbf{n} \in C_R} m_j \dot{r}(\alpha, j, \mathbf{n})^2 - U(\{r(\alpha, j, \mathbf{n})\}) \\ &+ \sum_{\beta=1}^{3} \sum_{k=1}^{N} \sum_{\mathbf{n}' \in D_R} \gamma(\beta, k, \mathbf{n}') \\ &\times \sum_{\alpha=1}^{3} \sum_{j=1}^{N} \sum_{\mathbf{n} \in C_R} \dot{r}(\alpha, j, \mathbf{n}) \frac{\partial f(\beta, k, \mathbf{n}')}{\partial r(\alpha, j, \mathbf{n})}\end{aligned} \tag{3.5}$$

where

$$U(\{r(\alpha, j, \mathbf{n})\}) = \tfrac{1}{2} \sum_{j=1}^{N} \sum_{\mathbf{n}_1 \in C_R} \sum_{k=1}^{N} {\sum_{\mathbf{n}_2 \in C_R}}^{*} \phi_{jk}(\mathbf{R}(j, \mathbf{n}_1), \mathbf{R}(k, \mathbf{n}_2)) + \sum_{j=1}^{N} \sum_{\mathbf{n} \in C_R} \phi_{1j}(\mathbf{R}(j, \mathbf{n})) \tag{3.6}$$

We can simplify this constrained Lagrangian using

$$\frac{\partial f(\beta, k, \mathbf{n}')}{\partial r(\alpha, j, \mathbf{n})} = \delta_{\alpha\beta}\delta_{jk}\{\delta_{\mathbf{n},\mathbf{n}'}[1 - \delta_{\mathbf{n},\mathbf{0}}] - \delta_{\mathbf{n},\mathbf{0}}\} \tag{3.7}$$

so that

$$\mathscr{L}^* = \tfrac{1}{2} \sum_{\alpha=1}^{3} \sum_{j=1}^{N} \sum_{\mathbf{n} \in C_R} m_j \dot{r}(\alpha, j, \mathbf{n})^2 - U(\{r(\alpha, j, \mathbf{n})\}) + \sum_{\alpha=1}^{3} \sum_{j=1}^{N} \sum_{\mathbf{n} \in D_R} \gamma(\alpha, j, \mathbf{n})\{\dot{r}(\alpha, j, \mathbf{n}) - \dot{r}(\alpha, j, \mathbf{0})\} \tag{3.8}$$

To begin exact implementation of the constraints in a simpler system of equations, we define momenta in the standard way:

$$p(\alpha, j, \mathbf{n}) = \partial \mathscr{L}^* / \partial \dot{r}(\alpha, j, \mathbf{n}) \tag{3.9}$$

This gives

$$p(\alpha, j, \mathbf{n}) = m_j \dot{r}(\alpha, j, \mathbf{n}) + \gamma(\alpha, j, \mathbf{n})[1 - \delta_{\mathbf{n},\mathbf{0}}] - \delta_{\mathbf{n},\mathbf{0}} \sum_{\mathbf{n}' \in D_R} \gamma(\alpha, j, \mathbf{n}') \tag{3.10}$$

which we may reorganize as

$$\dot{r}(\alpha, j, \mathbf{n}) = \frac{1}{m_j}\left\{ p(\alpha, j, \mathbf{n}) - \gamma(\alpha, j, \mathbf{n})[1 - \delta_{\mathbf{n},\mathbf{0}}] + \delta_{\mathbf{n},\mathbf{0}} \sum_{\mathbf{n}' \in D_R} \gamma(\alpha, j, \mathbf{n}') \right\} \tag{3.11}$$

We can use this result and Eq. (3.7) to rewrite the velocity constraint equations in the form

$$p(\alpha, j, \mathbf{n}) - p(\alpha, j, \mathbf{0}) = \sum_{\mathbf{n}' \in D_R} \mathsf{M}(\mathbf{n}, \mathbf{n}')\, \gamma(\alpha, j, \mathbf{n}') \tag{3.12}$$

where

$$\mathsf{M}(\mathbf{n}, \mathbf{n}') = 1 + \delta_{\mathbf{n},\mathbf{n}'} \tag{3.13}$$

We now define $\mathcal{N}_R$ as the number of cells in the large array, so that D_R has $\mathcal{N}_R - 1$ members. Thus we may show that

$$\mathsf{M}^{-1}(\mathbf{n}, \mathbf{n}') = \delta_{\mathbf{n},\mathbf{n}'} - \frac{1}{\mathcal{N}_R} \tag{3.14}$$

by a simple matrix multiplication. Equation (3.12) then gives

$$\gamma(\alpha, j, \mathbf{n}) = p(\alpha, j, \mathbf{n}) - \frac{1}{\mathcal{N}_R} \sum_{\mathbf{n}' \in C_R} p(\alpha, j, \mathbf{n}')$$
$$\text{for} \quad 1 \leqslant \alpha \leqslant 3, \quad 1 \leqslant j \leqslant N, \quad \text{and} \quad \mathbf{n} \in D_R \tag{3.15}$$

With minor differences for $\mathbf{n} \neq \mathbf{0}$ and $\mathbf{n} = \mathbf{0}$, we may then use Eq. (3.11) to find

$$\dot{r}(\alpha, j, \mathbf{n}) = \frac{1}{m_j \mathcal{N}_R} \sum_{\mathbf{n}' \in C_R} p(\alpha, j, \mathbf{n}') \quad \text{for } 1 \leqslant \alpha \leqslant 3, \ 1 \leqslant j \leqslant N, \text{ and } \mathbf{n} \in D_R \tag{3.16}$$

We note then that $\dot{r}(\alpha, j, \mathbf{n}) = \dot{r}(\alpha, j, \mathbf{0})$ for all (α, j) and for $\mathbf{n} \in D_R$. This, together with the initial condition, implements the periodic boundary condition.

4. THE HAMILTONIAN, EQUATIONS OF MOTION, AND PRESSURE

Here we continue to follow the constraint dynamics techniques of De Leeuw *et al.*[7] We define the Hamiltonian in the standard way as

$$\mathscr{H} = \sum_{\alpha=1}^{3} \sum_{j=1}^{N} \sum_{\mathbf{n} \in C_R} \dot{r}(\alpha, j, \mathbf{n})\, p(\alpha, j, \mathbf{n}) - \mathscr{L} \tag{4.1}$$

We use the Lagrangian $\mathscr{L}$ here rather than the constrained Lagrangian $\mathscr{L}^*$ since we shall eliminate the $\dot{r}(\alpha, j, \mathbf{n})$ from the Hamiltonian using Eqs. (3.16). When Eq. (3.16) holds we have $\mathscr{L} = \mathscr{L}^*$. The Hamiltonian reduces to

$$\mathscr{H} = \sum_{\alpha=1}^{3} \sum_{j=1}^{N} \frac{1}{2m_j \mathcal{N}_R} \left[\sum_{\mathbf{n} \in C_R} p(\alpha, j, \mathbf{n}) \right]^2 - U(\{r(\alpha, j, \mathbf{n})\}) \tag{4.2}$$

The initial conditions for the dynamics defined by this Hamiltonian are: At $t = 0$

$$r(\alpha, j, \mathbf{n}) - r(\alpha, j, \mathbf{0}) - \mathbf{n} \cdot \hat{\mathbf{e}}_\alpha = 0, \qquad 1 \leqslant \alpha \leqslant 3, \quad 1 \leqslant j \leqslant N, \quad \mathbf{n} \in D_R \tag{4.3}$$

First we obtain, for $1 \leqslant \alpha \leqslant 3$, $1 \leqslant j \leqslant N$, and $\mathbf{n} \in C_R$,

$$\dot{r}(\alpha, j, \mathbf{n}) = \frac{\partial \mathscr{H}}{\partial p(\alpha, j, \mathbf{n})} = \frac{1}{m_j \mathscr{N}_R} \sum_{\mathbf{n} \in C_R} p(\alpha, j, \mathbf{n}) \tag{4.4}$$

Thus the Hamiltonian dynamics from Eq. (4.2) indeed implies

$$\dot{r}(\alpha, j, \mathbf{n}) = \dot{r}(\alpha, j, \mathbf{0}) \tag{4.5}$$

We may integrate these equations and apply the initial condition to obtain

$$r(\alpha, j, \mathbf{n}) - r(\alpha, j, \mathbf{0}) - \mathbf{n} \cdot \hat{\mathbf{e}}_\alpha = 0, \quad 1 \leqslant \alpha \leqslant 3, \ 1 \leqslant j \leqslant N, \ \mathbf{n} \in D_R \text{ for } t \geqslant 0 \tag{4.6}$$

The Hamiltonian with $\mathscr{L}$ in Eq. (4.1) thus gives a dynamical evolution in which the periodic boundary conditions are implemented. Equation (4.4) brings with it the appealing physical picture of each particle j in the original simulation cell $\Gamma(\mathbf{0})$ behaving as though it had mass $m_j \mathscr{N}_R$, the mass of all the copies of j in the whole array.

The second set of Hamiltonian evolution equations are

$$\dot{p}(\alpha, j, \mathbf{n}) = -\frac{\partial \mathscr{H}}{\partial r(\alpha, j, \mathbf{n})} = -\frac{\partial U}{\partial r(\alpha, j, \mathbf{n})} \tag{4.7}$$

so that

$$\sum_{\mathbf{n} \in C_R} \dot{p}(\alpha, j, \mathbf{n}) = -\sum_{\mathbf{n} \in C_R} \frac{\partial U}{\partial r(\alpha, j, \mathbf{n})} \tag{4.8}$$

Using Eq. (4.4) then gives

$$m_j \ddot{r}(\alpha, j, \mathbf{n}) = m_j \ddot{r}(\alpha, j, \mathbf{0}) = -\frac{1}{\mathscr{N}_R} \sum_{\mathbf{n} \in C_R} \frac{\partial U}{\partial r(\alpha, j, \mathbf{n})} \tag{4.9}$$

Using $\mathbf{r}_j = \sum_{\alpha=1}^{3} \hat{\mathbf{e}}_\alpha r(\alpha, j, \mathbf{0})$, we can then write

$$m_j \ddot{\mathbf{r}}_j = \mathbf{F}_{\mathrm{SURF};j}(\mathbf{r}_j) + \sum_{k=1}^{N}{}^{*} \mathbf{F}_{jk}(\mathbf{r}_j, \mathbf{r}_k) \tag{4.10}$$

where

$$\mathbf{F}_{\mathrm{SURF};j}(\mathbf{r}_j) = -\frac{1}{\mathscr{N}_R} \sum_{\mathbf{n} \in C_R} \nabla \phi_{1j}(\mathbf{n} + \mathbf{r}_j) \tag{4.11}$$

$$\mathbf{F}_{jk}(\mathbf{r}_j, \mathbf{r}_k) = -\frac{1}{\mathscr{N}_R} \sum_{\mathbf{n}_1 \in C_R} \sum_{\mathbf{n}_2 \in C_R} \phi_{jk}(\mathbf{n}_1 + \mathbf{r}_j, \mathbf{n}_2 + \mathbf{r}_k) \tag{4.12}$$

and the asterisk on the sum in Eq. (4.10) means we omit singular self-interaction terms when $j=k$ and $\mathbf{n}_1=\mathbf{n}_2$ from the double lattice sum in Eq. (4.12). Using these representations for $\mathbf{F}_{\mathrm{SURF};j}(\mathbf{r}_j)$ and $\mathbf{F}_{jk}(\mathbf{r}_j, \mathbf{r}_k)$, we have that Eq. (4.10) represents the equation of motion for the finite but large periodic cell–array. We shall see below that the equations of motion reduce to rather standard forms in the limit as the array becomes large.

We may now turn to the pressure of the large array, remembering that the surface forces $-\nabla\phi_{1j}(\mathbf{n}+\mathbf{r}_j)$ tend to zero quickly as the distance on $\mathbf{n}$ from the boundary of the cell–array becomes large. We note that $V_0 = N_R V_A\{1+O(1/R)\}$, where V_0 is the volume of the whole region Ω containing the cell array, N_R is the number of cells in the array, and V_A is the volume of one cell. With the notation $\mathbf{p}(j,\mathbf{n}) = \sum_{\alpha=1}^{N} \hat{\mathbf{e}}_\alpha p(\alpha, j, \mathbf{n})$, Eq. (2.13) becomes

$$
\begin{aligned}
\Pi N_R V_A
&= \left\langle \sum_{j=1}^{N} \sum_{\mathbf{n}\in C_R} \dot{\mathbf{r}}(j,\mathbf{n})\,\mathbf{p}(j,\mathbf{n}) \right\rangle \\
&\quad -\frac{1}{2}\left\langle \sum_{j=1}^{N}\sum_{k=1}^{N} \sum_{\mathbf{n}_1\in C_R} \sum_{\mathbf{n}_2\in C_R}{}^{*} (\mathbf{n}_1-\mathbf{n}_2+\mathbf{r}_{jk})\,\nabla_{\mathbf{r}_j}\phi_{\mathrm{SR};jk}(\mathbf{n}_1-\mathbf{n}_2+\mathbf{r}_{jk}) \right\rangle \\
&\quad -\frac{1}{2}\left\langle \sum_{j=1}^{N}\sum_{k=1}^{N} \sum_{\mathbf{n}_1\in C_R} \sum_{\mathbf{n}_2\in C_R}{}^{*} (\mathbf{n}_1-\mathbf{n}_2+\mathbf{r}_{jk})\,\nabla_{\mathbf{r}_j} Q_j Q_k\,|\mathbf{n}_1-\mathbf{n}_2+\mathbf{r}_{jk}|^{-1} \right\rangle \\
&\quad +\left\langle \sum_{j=1}^{N}\sum_{k=1}^{N} \sum_{\mathbf{n}_1\in C_R} \sum_{\mathbf{n}_2\in C_R} (\mathbf{n}_1+\mathbf{r}_j)\,\mathbf{F}_{\mathrm{POL};j}(\mathbf{n}_1+\mathbf{r}_j, \mathbf{n}_2+\mathbf{r}_k; \varepsilon') \right\rangle \\
&\quad +\left\langle \sum_{j=1}^{N} \sum_{\mathbf{n}\in C_R} (\mathbf{n}+\mathbf{r}_j)\,\mathbf{F}_{\mathrm{SURF};j}(\mathbf{n}+\mathbf{r}_j) + \int_{\partial\Omega} d^2\mathbf{r}\,\mathbf{r}\hat{\mathbf{t}}(\mathbf{r})\cdot\Pi^{\mathrm{S}}(\mathbf{r},t) \right\rangle
\end{aligned}
\tag{4.13}
$$

We may find the scalar pressure Π by taking one-third of the trace of both sides of Eq. (4.13). There are five expectations on the right-hand side of Eq. (4.13) and we identify them in turn as $\Pi_{\mathrm{kin}} N_R V_A$, the kinetic energy contribution, $\Pi_{\mathrm{SR}} N_R V_A$, the short-ranged force contribution, $\Pi_{\mathrm{DC}} N_R V_A$, the direct Coulomb interaction contribution, $\Pi_{\mathrm{POL}} N_R V_A$, the polarization force contribution, and a contribution from the surface forces and surface pressure. Note that we do not yet have a way of deciding how to allot the Π_{POL} contribution between internal pressure $\Pi(\mathbf{r}, t)$ and external pressure on the surface, $\Pi^{\mathrm{S}}(\mathbf{r}, t)$, because the forces $\mathbf{F}_{\mathrm{POL};j}(\mathbf{n}_1+\mathbf{r}_j, \mathbf{n}_2+\mathbf{r}_k; \varepsilon')$ giving rise to Π_{POL} do not obey Newton's third law.

5. THE LIMIT AS THE ARRAY BECOMES LARGE

First we look at the equations of motion given in Eq. (4.10). Equation (4.10) shows the surface force as

$$\mathbf{F}_{\mathrm{SURF};j}(\mathbf{r}_j) = -\frac{1}{\mathcal{N}_R} \sum_{\mathbf{n} \in C_R} \nabla \phi_{1j}(\mathbf{n} + \mathbf{r}_j) \tag{5.1}$$

From here on we shall consider C_R to be the sphere S_R with center $\mathbf{0}$ and radius R. As the array becomes large we have $R \to \infty$ and we also have $V_0 = \mathcal{N}_R V_\Lambda [1 + O(1/R)]$. We consider the one-particle surface potential $\phi_{1j}(\mathbf{r})$ to be of the form $\psi_j(R\hat{\mathbf{r}} - \mathbf{r})$ with ψ_j independent of R and $\psi_j(\boldsymbol{\rho}) \to 0$ as $|\boldsymbol{\rho}| \to \infty$, so that we may indeed interpret $\phi_{1j}(\mathbf{r})$ as a surface interaction. In Eq. (5.1), the factor $1/\mathcal{N}_R$ is $O(R^{-3})$ while the sum of surface forces is proportional to the surface of S_R and so is $O(R^2)$. Thus $\mathbf{F}_{\mathrm{SURF};j}(\mathbf{r}_j)$ vanishes in the limit $R \to \infty$. The equation of motion for $\mathbf{r}_j$ [Eq. (4.10)] has no surface force term in the limit $R \to \infty$.

The pair force $\mathbf{F}_{jk}(\mathbf{r}_j, \mathbf{r}_k)$ is derived from short-ranged interactions, polarization interactions, and direct Coulomb interactions. The short-ranged force is

$$\mathbf{F}_{\mathrm{SR};jk}(\mathbf{r}_j, \mathbf{r}_k) = -\frac{1}{\mathcal{N}_R} \nabla_{\mathbf{r}_j} \sum_{\mathbf{n}_1 \in S_R} \sum_{\mathbf{n}_2 \in S_R} \phi_{\mathrm{SR};jk}(\mathbf{n}_1 - \mathbf{n}_2 + \mathbf{r}_{jk}) \tag{5.2}$$

Now if the potentials $\phi_{\mathrm{SR};jk}(\mathbf{r})$ are "short-ranged," they are $O(|\mathbf{r}|^{-4})$ as $|\mathbf{r}| \to \infty$. Thus we may substitute $\mathbf{n}$ for $\mathbf{n}_1 - \mathbf{n}_2$ and sum over $\mathbf{n}$ over the whole of the lattice Λ, also summing later over $\mathbf{n}_1 \in S_R$, which gives a factor $\mathcal{N}_R$, this procedure having an error which is $O(R^{-1})$ compared with the result. We thus have, in the limit $R \to \infty$,

$$\psi_{\mathrm{SR};jk}(\mathbf{r}_{jk}) = \sum_{\mathbf{n} \in \Lambda} \phi_{\mathrm{SR};jk}(\mathbf{n} + \mathbf{r}_{jk}) \tag{5.3}$$

and

$$\mathbf{F}_{\mathrm{SR};jk}(\mathbf{r}_j, \mathbf{r}_k) = -\nabla_{\mathbf{r}_j} \psi_{\mathrm{SR};jk}(\mathbf{r}_{jk}) = -\sum_{\mathbf{n} \in \Lambda} \nabla_{\mathbf{r}_j} \phi_{\mathrm{SR};jk}(\mathbf{n} + \mathbf{r}_{jk}) \tag{5.4}$$

The total polarization force on particle j may be written using Eq. (2.14) as

$$\begin{aligned}
\mathbf{F}_{\mathrm{POL};j} = {} & \frac{3V_\Lambda}{4\pi R^5} \sum_{L=0}^{\infty} \frac{4\pi}{2L+1} \frac{(L+1)(\varepsilon' - 1)}{\varepsilon'(L+1) + L} \\
& \times \sum_{M=-L}^{L} \left[\sum_{\mathbf{n}_1 \in S_R} Q_j \nabla \varphi_{LM}(\mathbf{n}_1 + \mathbf{r}_j)\, R^{(L-1)} \right] \\
& \times \left\{ \sum_{k=1}^{N} \sum_{\mathbf{n}_2 \in S_R} Q_k [\varphi_{LM}(\mathbf{n}_2 + \mathbf{r}_k) - \varphi_{LM}(\mathbf{n}_2)]\, R^{-L} \right\}^* \\
& \times \left[1 + O\left(\frac{1}{R}\right) \right]
\end{aligned} \tag{5.5}$$

In the last large bracket in Eq. (5.5) we have inserted an extra term independent of k, a manipulation which does not change the result because we always assume a charge neutrality condition

$$\sum_{k=1}^{N} Q_k = 0 \tag{5.6}$$

without which we cannot define electrostatic interactions in the array in the limit $R \to \infty$. Now

$$\sum_{k=1}^{N} \sum_{\mathbf{n}_2 \in S_R} Q_k [\varphi_{LM}(\mathbf{n}_2 + \mathbf{r}_k) - \varphi_{LM}(\mathbf{n}_2)] R^{-L}$$
$$= \frac{R^3}{V_A} \sum_{k=1}^{N} \sum_{\boldsymbol{\rho}(\mathbf{n}) \in S_1} Q_k \left[\varphi_{LM}\left(\boldsymbol{\rho}(\mathbf{n}) + \frac{\mathbf{r}_k}{R}\right) - \varphi_{LM}(\boldsymbol{\rho}(\mathbf{n})) \right] \frac{V_A}{R^3} \tag{5.7}$$

where $\boldsymbol{\rho}(\mathbf{n}) = \mathbf{n}/R$ and S_1 is a sphere of radius 1 with center $\mathbf{0}$. The right-hand side of Eq. (5.7) contains a sum approximation to a Riemann integral over S_1 and so we have

$$\sum_{k=1}^{N} \sum_{\mathbf{n}_2 \in S_R} Q_k [\varphi_{LM}(\mathbf{n}_2 + \mathbf{r}_k) - \varphi_{LM}(\mathbf{n}_2)] R^{-L}$$
$$= \frac{R^2}{V_A} \mathbf{M} \cdot \int_{S_1} d^3\mathbf{r}\, \nabla \varphi_{LM}(\mathbf{r}) [1 + O(R^{-1})] \tag{5.8}$$

where

$$\mathbf{M} = \sum_{k=1}^{N} Q_k \mathbf{r}_k \tag{5.9}$$

is the total dipole moment of the particles of the original simulation cell $\Gamma(\mathbf{0})$. If we introduce the "spherical basis"[4] $\hat{\mathbf{e}}_1 = -\frac{1}{\sqrt{2}}(1, -i, 0)$, $\hat{\mathbf{e}}_0 = (0, 0, 1)$, and $\hat{\mathbf{e}}_{-1} = \frac{1}{\sqrt{2}}(1, i, 0)$, we then have

$$\int_{S_1} d^3\mathbf{r}\, \nabla \varphi_{LM}(r) = \left(\frac{4\pi}{3}\right)^{1/2} \delta_{L,1} \hat{\mathbf{e}}_M^* \tag{5.10}$$

and similarly we have

$$\sum_{\mathbf{n}_1 \in S_R} \nabla \varphi_{LM}(\mathbf{n}_1 + \mathbf{r}_j) R^{-(L-1)}$$
$$= \frac{R^2}{V_A} \int_{S_1} d^3\mathbf{r}\, \nabla \varphi_{LM}(r) [1 + O(R^{-1})]$$
$$= \left(\frac{4\pi}{3}\right)^{1/2} \frac{R^2}{V_A} \delta_{L,1} \hat{\mathbf{e}}_M^* [1 + O(R^{-1})] \tag{5.11}$$

Thus in the limit $R \to \infty$ we have

$$\mathbf{F}_{\mathrm{POL};j} = \frac{4\pi}{3V_\Lambda} \frac{2(\varepsilon' - 1)}{2\varepsilon' + 1} Q_j \sum_{k=1}^{N} Q_k \mathbf{r}_k \tag{5.12}$$

and the apparent failure of the polarization forces to obey Newton's third law is particularly clear. However, because of the charge neutrality constraint [Eq. (5.6)] we can write

$$\mathbf{F}_{\mathrm{POL};j} = -\frac{4\pi}{3V_\Lambda} \frac{2(\varepsilon' - 1)}{2\varepsilon' + 1} Q_j \sum_{k=1}^{N} Q_k \mathbf{r}_{jk} \tag{5.13}$$

and so identify pair polarization forces

$$\mathbf{F}_{\mathrm{POL};jk}(\mathbf{r}_j, \mathbf{r}_k; \varepsilon') = -\frac{4\pi}{3V_\Lambda} \frac{2(\varepsilon' - 1)}{2\varepsilon' + 1} Q_j Q_k \mathbf{r}_{jk} \tag{5.14}$$

Thus we have a pair polarization force in the central cell of periodic boundary conditions (and indeed in any other cell) for which Newton's third law holds. We shall see below that similar considerations hold for the polarization force contribution to the virial expression for the pressure.

The remaining force term in the equations of motion is due to the direct Coulomb interactions. We may derive this force from the direct Coulomb energy of the whole array, namely

$$U_{\mathrm{DC}}(\{\mathbf{r}_1, \ldots, \mathbf{r}_N\}) = \tfrac{1}{2} \sum_{j=1}^{N} \sum_{k=1}^{N} \sum_{\mathbf{n}_1 \in S_R} \sum_{\mathbf{n}_2 \in S_R}^{*} Q_j Q_k \, |\mathbf{n}_1 - \mathbf{n}_2 + \mathbf{r}_{jk}|^{-1} \tag{5.15}$$

To evaluate this double lattice sum, we note the identity

$$\frac{1}{|\mathbf{r}|} = \frac{\operatorname{erfc}(\alpha |\mathbf{r}|)}{|\mathbf{r}|} + \frac{1}{\pi} \int_{\mathbb{R}^3} d^3\mathbf{u} \, \frac{e^{-\pi^2 \mathbf{u}^2/\alpha^2}}{\mathbf{u}^2} e^{2\pi i \mathbf{u} \cdot \mathbf{r}} \tag{5.16}$$

which may be reasonably easily established.[8] We then introduce the lattice $\mathscr{R}$ reciprocal to Λ with lattice vectors $\mathbf{m}$ such that $\exp(2\pi i \mathbf{m} \cdot \mathbf{n}) = 1$, and we introduce the cells $\gamma(\mathbf{m})$ of the reciprocal lattice. With $\mathbf{m} = \sum_{\alpha=1}^{3} m_\alpha \mathbf{A}_\alpha$ and $\mathbf{A}_1 = L^2 \mathbf{a}_2 \times \mathbf{a}_3 / V_\Lambda$ etc., we have

$$\gamma(\mathbf{0}) = \{\mathbf{u} \in \mathbb{R}^3 : -\tfrac{1}{2} \leqslant \mathbf{u} \cdot \mathbf{A}_\alpha \leqslant \tfrac{1}{2}, \alpha = 1, 2, 3\} \tag{5.17a}$$

and

$$\gamma(\mathbf{m}) = \{\mathbf{u} \in \mathbb{R}^3 : \mathbf{u} - \mathbf{m} \in \gamma(\mathbf{0})\} \tag{5.17b}$$

We may then split the integral in Eq. (5.16) into a sum of integrals over the $\gamma(\mathbf{m})$, in each $\gamma(\mathbf{m})$ substituting $\mathbf{u}=\mathbf{m}+\mathbf{v}$ with $\mathbf{v}\in\gamma(\mathbf{0})$. We then obtain

$$\frac{1}{|\mathbf{r}|}=\frac{\operatorname{erfc}(\alpha|\mathbf{r}|)}{|\mathbf{r}|}+\sum_{\substack{\mathbf{m}\in\mathscr{M}\\ \mathbf{m}\neq\mathbf{0}}}\frac{1}{\pi}\int_{\gamma(\mathbf{0})}d^3\mathbf{v}\,\frac{e^{-\pi^2(\mathbf{m}+\mathbf{v})^2/\alpha^2}}{(\mathbf{m}+\mathbf{v})^2}e^{2\pi i\mathbf{v}\cdot\mathbf{r}}e^{2\pi i\mathbf{m}\cdot\mathbf{r}}$$
$$+\frac{1}{\pi}\int_{\gamma(\mathbf{0})}d^3\mathbf{v}\,\frac{e^{-\pi^2\mathbf{v}^2/\alpha^2}}{\mathbf{v}^2}e^{2\pi i\mathbf{v}\cdot\mathbf{r}} \tag{5.18}$$

When we insert this rather complicated expression for $|\mathbf{n}_1-\mathbf{n}_2+\mathbf{r}_{jk}|^{-1}$ into Eq. (5.15), several interesting things happen. The sum of complementary error functions may be estimated by setting $\mathbf{n}_1-\mathbf{n}_2=\mathbf{n}$: the double sum is then $\mathscr{N}_R$ times a sum on $\mathbf{n}\in\Lambda$ with an error which is $O(1/R)$ because the summand is absolutely and rapidly summable on Λ. The sum of Fourier-series-like terms with $\mathbf{m}\neq\mathbf{0}$ may be estimated by noting that if used in an integral for which the rest of the integrand is smoothly varying in the components of $\mathbf{v}$, then

$$\sum_{\mathbf{n}\in S_R}\exp(2\pi i\mathbf{n}\cdot\mathbf{v})=\frac{1}{V_\Lambda}\delta(\mathbf{v})\left[1+O\left(\frac{1}{R}\right)\right] \tag{5.19}$$

on $\gamma(\mathbf{0})$. We can then do the sum over $\mathbf{n}_2$ using this formula and then the sum on $\mathbf{n}_1$ to obtain

$$U_{\mathrm{DC}}(\{\mathbf{r}_1,\ldots,\mathbf{r}_N\})=\frac{1}{2}\mathscr{N}_R\sum_{j=1}^{N}{\sum_{k=1}^{N}}^{*}Q_jQ_k\psi_{\mathrm{Ewald}}(\mathbf{r}_{jk})\left[1+O\left(\frac{1}{R}\right)\right]$$
$$-\frac{\alpha}{\sqrt{\pi}}\mathscr{N}_R\sum_{j=1}^{N}Q_j^2$$
$$+\frac{1}{2\pi}\sum_{j=1}^{N}\sum_{k=1}^{N}Q_jQ_k\int_{\gamma(\mathbf{0})}d^3\mathbf{v}\,\frac{e^{-\pi^2\mathbf{v}^2/\alpha^2}}{\mathbf{v}^2}e^{-2\pi i\mathbf{v}\cdot\mathbf{r}_{jk}}$$
$$\times\sum_{\mathbf{n}_1\in S_R}e^{2\pi i\mathbf{n}_1\cdot\mathbf{v}}\sum_{\mathbf{n}_2\in S_R}e^{-2\pi i\mathbf{n}_2\cdot\mathbf{v}} \tag{5.20}$$

where

$$\psi_{\mathrm{Ewald}}(\mathbf{r})=\sum_{\mathbf{n}\in\Lambda}\frac{\operatorname{erfc}(\alpha|\mathbf{n}+\mathbf{r}|)}{|\mathbf{n}+\mathbf{r}|}+\sum_{\substack{\mathbf{m}\in\mathscr{M}\\ \mathbf{m}\neq\mathbf{0}}}\frac{e^{-\pi^2\mathbf{m}^2/\alpha^2}}{\pi\mathbf{m}^2V_\Lambda}\exp(2\pi i\mathbf{m}\cdot\mathbf{r}) \tag{5.21}$$

is the standard Ewald potential.[8] The asterisk on the double sum of the Ewald potential in Eq. (5.20) means that when $\mathbf{r}=\mathbf{0}$, the $\mathbf{n}=\mathbf{0}$ term in the sum of complementary error functions in ψ_{Ewald} must be replaced by

$$\lim_{r\to 0}\frac{\operatorname{erfc}(\alpha r)}{r}-\frac{1}{r}=-\frac{2\alpha}{\sqrt{\pi}} \tag{5.22}$$

to exclude the direct self-interaction of a charge with itself but include the interactions of charges with their own periodic copies. To evaluate the last integral terms in Eq. (5.20), we expand the factor $\exp(-\pi^2\mathbf{v}^2/\alpha^2 + 2\pi i\mathbf{v}\cdot\mathbf{r}_{jk})$ in powers of $\mathbf{v}$. The zeroth- and first-order terms are divergent as $R\to\infty$, but vanish by charge neutrality. Third-order and higher terms give a smooth integrand, zero at $\mathbf{v}=\mathbf{0}$, for which the representation (5.19) may be used for the sum on $\mathbf{n}_2$, giving a total which is $O(\mathcal{N}_R/R)$. The second-order terms may be evaluated using the symmetry arguments of refs. 8 and 9. The final result is

$$U_{\mathrm{DC}}(\{\mathbf{r}_1,\ldots,\mathbf{r}_N\}) = \mathcal{N}_R\left(\frac{1}{2}\sum_{j=1}^{N}\sum_{k=1}^{N}{}^{*}Q_jQ_k\psi_{\mathrm{Ewald}}(\mathbf{r}_{jk}) - \frac{\alpha}{\sqrt{\pi}}\sum_{j=1}^{N}Q_j^2 + \frac{2\pi}{3V_A}\mathbf{M}^2\right)\times\left[1+O\left(\frac{1}{R}\right)\right] \tag{5.23}$$

We thus find in the limit $R\to\infty$

$$\mathbf{F}_{\mathrm{DC}}(\mathbf{r}_j,\mathbf{r}_k) = -\sum_{\substack{k=1\\k\neq j}}^{N}Q_jQ_k\nabla\psi_{\mathrm{Ewald}}(\mathbf{r}_{jk}) - \frac{4\pi}{3V_A}Q_j\mathbf{M} \tag{5.24}$$

In the limit $R\to\infty$, the equations of motion are then

$$m_j\ddot{\mathbf{r}}_j = -\sum_{\substack{k=1\\k\neq j}}^{N}\left[\nabla\psi_{\mathrm{SR};jk}(\mathbf{r}_{jk}) + Q_jQ_k\nabla\psi_{\mathrm{Ewald}}(\mathbf{r}_{jk})\right] + \sum_{k=1}^{N}\mathbf{F}_{\mathrm{MAC}}(\mathbf{r}_j,\mathbf{r}_k) \tag{5.25}$$

where

$$\mathbf{F}_{\mathrm{MAC}}(\mathbf{r}_j,\mathbf{r}_k) = \frac{4\pi}{V_A(2\varepsilon'+1)}Q_jQ_k(\mathbf{r}_j-\mathbf{r}_k) \tag{5.26}$$

This completes the description of molecular dynamics in periodic boundary conditions with Coulombic interactions. We now turn to the pressure tensor.

The kinetic energy contribution to the pressure tensor is then, using $\mathbf{r}(j,\mathbf{n}) = \mathbf{r}(j,\mathbf{0})$,

$$\Pi_{\mathrm{kin}}\mathcal{N}_RV_A = \left\langle\sum_{j=1}^{N}\sum_{\mathbf{n}\in C_R}\dot{\mathbf{r}}(j,\mathbf{n})\,\mathbf{p}(j,\mathbf{n})\right\rangle \tag{5.27}$$

Using Eq. (4.4) to first replace $\mathbf{r}(j, \mathbf{n})$ by $\mathbf{r}(j, \mathbf{0})$ and then replace the sum of momenta, we find

$$\Pi_{\text{kin}} V_\Lambda = \left\langle \sum_{j=1}^{N} m_j \dot{\mathbf{r}}(j, \mathbf{0})\, \dot{\mathbf{r}}(j, \mathbf{0}) \right\rangle \tag{5.28}$$

We may also write

$$\Pi_{\text{kin}} V_\Lambda = \left\langle \sum_{j=1}^{N} \frac{1}{m_j} \left(\frac{1}{\mathcal{N}_R} \sum_{\mathbf{n} \in C_R} \mathbf{p}(j, \mathbf{n}) \right) \left(\frac{1}{\mathcal{N}_R} \sum_{\mathbf{n} \in C_R} \mathbf{p}(j, \mathbf{n}) \right) \right\rangle \tag{5.29}$$

but Eq. (5.28) seems physically more transparent. Note that we do not have $\mathbf{p}(j, \mathbf{n}) = m_j \dot{\mathbf{r}}(j, \mathbf{n})$, the canonical momenta for the limiting periodic system being more complicated. In deriving Eq. (5.28) we have used $V_0 = \mathcal{N}_R V_\Lambda [1 + O(1/R)]$, so that Eq. (5.28) holds exactly in the limit $R \to \infty$.

The short-ranged potential contribution to the pressure tensor is

$$\Pi_{\text{SR}} V_\Lambda \mathcal{N}_R = -\frac{1}{2} \left\langle \sum_{j=1}^{N} \sum_{k=1}^{N} \sum_{\mathbf{n}_1 \in S_R} \sum_{\mathbf{n}_2 \in S_R}^{*} (\mathbf{n}_1 - \mathbf{n}_2 + \mathbf{r}_{jk})\, \nabla \phi_{\text{SR};jk}(\mathbf{n}_1 - \mathbf{n}_2 + \mathbf{r}_{jk}) \right\rangle \tag{5.30}$$

Because $\mathbf{n} \nabla \phi_{\text{SR};jk}(\mathbf{n})$ is absolutely summable on $\mathbf{n} \neq \mathbf{0}$ (basically the definition of a short-ranged potential), we can write the sum on $\mathbf{n}_1$ and $\mathbf{n}_2$ as $\mathcal{N}_R$ times a sum on $\mathbf{n} = \mathbf{n}_1 - \mathbf{n}_2 \in \Lambda$ with an $O(1/R)$ error, giving in the limit $R \to \infty$

$$\Pi_{\text{SR}} V_\Lambda = -\frac{1}{2} \left\langle \sum_{j=1}^{N} \sum_{k=1}^{N} \sum_{\mathbf{n} \in \Lambda}^{*} (\mathbf{n} + \mathbf{r}_{jk})\, \nabla \phi_{\text{SR};jk}(\mathbf{n} + \mathbf{r}_{jk}) \right\rangle \tag{5.31}$$

The polarization interaction contribution to the pressure tensor is

$$\begin{aligned} \Pi_{\text{POL}} V_\Lambda \mathcal{N}_R = & \left\langle \sum_{j=1}^{N} \sum_{k=1}^{N} Q_j Q_k \sum_{\mathbf{n}_1 \in S_R} \sum_{\mathbf{n}_2 \in S_R} (\mathbf{n}_1 + \mathbf{r}_j)\, R^{-1} \sum_{L=0}^{\infty} \sum_{M=-L}^{L} \frac{4\pi}{2L+1} \right. \\ & \left. \times \frac{(\varepsilon' - 1)(L+1)}{\varepsilon'(L+1) + L} R^{-L} \nabla_{\mathbf{r}_j} \varphi_{LM}(\mathbf{n}_1 + \mathbf{r}_j)\, R^{-L} \varphi_{LM}^{*}(\mathbf{n}_2 + \mathbf{r}_k) \right\rangle \end{aligned} \tag{5.32}$$

We may simplify this in the same manner as the polarization force, replacing the sums by integrals to obtain the leading-order behavior in R with $O(1/R)$ corrections. From Eqs. (5.8) and (5.11) we find an expression for

the sum on k and $\mathbf{n}_2$ in Eq. (5.32) which contains a factor $\delta_{L,1}$. Thus we have

$$\Pi_{\mathrm{POL}} V_\Lambda \mathcal{N}_R = \frac{R}{V_\Lambda}\left(\frac{4\pi}{3}\right)^{3/2}\left\langle \sum_{M=-1}^{1} \mathbf{M}\cdot\hat{\mathbf{e}}_M \frac{2(\varepsilon'-1)}{2\varepsilon'+1} \times \sum_{\mathbf{n}\in S_R}\sum_{j=1}^{N} Q_j\{(\mathbf{n}+\mathbf{r}_j)\nabla\varphi_{1M}(\mathbf{n}+\mathbf{r}_j) - \mathbf{n}\nabla\varphi_{1M}(\mathbf{n})\}\left[1+O\left(\frac{1}{R}\right)\right]\right\rangle \tag{5.33}$$

To evaluate this, we require

$$\int_{S_1} d^3\mathbf{r}\,\mathbf{M}\nabla\varphi_{1M}(\mathbf{r}) + \mathbf{r}\mathbf{M}\cdot\nabla\nabla\varphi_{1M}(\mathbf{r}) = \left(\frac{4\pi}{3}\right)^{1/2}\mathbf{M}\mathbf{e}^*_M \tag{5.34}$$

We show this by noting that the integrand is $\underline{\mathbf{M}}\cdot\nabla[\mathbf{r}\nabla\varphi_{1M}(\mathbf{r})]$, using Gauss' divergence theorem, noting that $\hat{\mathbf{r}}\hat{\mathbf{r}} = \frac{1}{3}\sqrt{(4\pi)}\,\mathsf{I}Y_{00}(\hat{\mathbf{r}})$ plus $Y_{LM}(\hat{\mathbf{r}})$ terms with $L=2$ (here I is the unit tensor) and calculating the remaining integral. We then have, in the limit $R\to\infty$,

$$\Pi_{\mathrm{POL}} V_\Lambda = \frac{4\pi}{3V_\Lambda}\frac{2(\varepsilon'-1)}{2\varepsilon'+1}\langle \mathbf{M}\mathbf{M}\rangle \tag{5.35}$$

We may now answer the question which we raised earlier, whether to treat this contribution as that of an internal force in the virial expression for the pressure tensor, or as that of an external force which should be included in the last expectation of Eq. (2.13). That expectation is a balance of the time average of contributions of the moment of the microscopic surface forces with the moment of the macroscopic surface pressure force contributions. We use charge neutrality to write

$$\Pi_{\mathrm{POL}} V_\Lambda = \frac{1}{2}\left\langle \sum_{j=1}^{N}\sum_{k=1}^{N} \mathbf{r}_{jk}\mathbf{F}_{\mathrm{POL};jk}(\mathbf{r}_j,\mathbf{r}_k;\varepsilon')\right\rangle \tag{5.36}$$

where the forces $\mathbf{F}_{\mathrm{POL};jk}(\mathbf{r}_j,\mathbf{r}_k;\varepsilon')$ are precisely those identified in Eq. (5.14) as giving the polarization pair force in the final equations of motion, and which obey Newton's third law. This means that we should include all of $\Pi_{\mathrm{POL}} V_\Lambda$ in the internal pressure tensor. It appears that there may still be polarization force contributions to Eq. (2.13) about which it seems difficult to decide whether they should be considered as internal or external forces. The point turns out to be unimportant, for their contribution is $O(1/R)$ in Eq. (2.13) and so the problem goes away in the limit $R\to\infty$.

The direct Coulomb interaction contribution to Eq. (2.13) is

$$\Pi_{\mathrm{DC}} V_{\Lambda} \mathcal{N}_R = -\frac{1}{2}\left\langle \sum_{j=1}^{N}\sum_{k=1}^{N}\sum_{\mathbf{n}_1 \in S_R}{\sum_{\mathbf{n}_2 \in S_R}}^{*} Q_j Q_k (\mathbf{n}_1 - \mathbf{n}_2 + \mathbf{r}_{jk}) \times \nabla |\mathbf{n}_1 - \mathbf{n}_2 + \mathbf{r}_{jk}|^{-1} \right\rangle \tag{5.37}$$

To deal with this cumbersome object we use the identity (5.16). The complementary error function term then gives a "real-space" contribution to Π_{DC} which is, in the limit $R \to \infty$,

$$\Pi_{\mathrm{DC;Real}} V_{\Lambda} = \frac{1}{2}\left\langle \sum_{j=1}^{N}\sum_{k=1}^{N}\sum_{\mathbf{n}\in\Lambda} \frac{(\mathbf{n}+\mathbf{r}_{jk})(\mathbf{n}+\mathbf{r}_{jk})}{(\mathbf{n}+\mathbf{r}_{jk})^2} \times \left\{ \frac{\operatorname{erfc}(\alpha |\mathbf{n}+\mathbf{r}_{jk}|)}{|\mathbf{n}+\mathbf{r}_{jk}|} + \frac{2\alpha}{\sqrt{\pi}} \exp[-\alpha^2 (\mathbf{n}+\mathbf{r}_{jk})^2] \right\} \right\rangle \tag{5.38}$$

The remaining part is more complicated, but is treated along the lines analogous to those used for the direct Coulomb forces in the equation of motion. We have

$$\Pi_{\mathrm{DC;Fourier}} V_{\Lambda} \mathcal{N}_R = -\frac{1}{2}\left\langle \sum_{j=1}^{N}\sum_{k=1}^{N}\sum_{\mathbf{n}_1 \in S_R}\sum_{\mathbf{n}_2 \in S_R} Q_j Q_k (\mathbf{n}_1 - \mathbf{n}_2 + \mathbf{r}_{jk}) \times \frac{1}{\pi} \nabla_{\mathbf{r}_j} \int_{\mathbb{R}^3} d^3\mathbf{u}\, \frac{e^{-\pi^2 \mathbf{u}^2/\alpha^2}}{\mathbf{u}^2} e^{2\pi i \mathbf{u}\cdot(\mathbf{n}_1 - \mathbf{n}_2 + \mathbf{r}_{jk})} \right\rangle \tag{5.39}$$

There is no asterisk on the sum here because the summand is zero for $j = k$, $\mathbf{n}_1 = \mathbf{n}_2$. We may write

$$(\mathbf{n}_1 - \mathbf{n}_2 + \mathbf{r}_{jk}) \nabla_{\mathbf{r}_j} \exp[2\pi i \mathbf{u}\cdot(\mathbf{n}_1 - \mathbf{n}_2 + \mathbf{r}_{jk})] = \nabla_{\mathbf{u}} \{\exp[2\pi i \mathbf{u}\cdot(\mathbf{n}_1 - \mathbf{n}_2 + \mathbf{r}_{jk})]\}\mathbf{u} \tag{5.40}$$

and then use Green's theorem on the integral. This is not entirely straightforward, because of the singularity in the integrand at $\mathbf{u} = \mathbf{0}$. If we excise a small sphere about $\mathbf{u} = \mathbf{0}$ before using Green's theorem, it is easy to show that the singularity does not contribute. We then use the stratagem we introduced earlier of dividing $\mathbb{R}^3$ into cells $\gamma(\mathbf{m})$ with $\mathbf{m} \in \mathcal{M}$. For the $\mathbf{m} \neq \mathbf{0}$ terms we use Eq. (5.19) for the sum on $\mathbf{n}_2$. We then obtain

$$\Pi_{\text{DC:Fourier}} V_A, V_R = \frac{1}{2} \cdot V_R \left\langle \sum_{j=1}^{N} \sum_{k=1}^{N} Q_j Q_k \sum_{\substack{\mathbf{m} \in \mathcal{M} \\ \mathbf{m} \neq \mathbf{0}}} \left(I - \frac{2\pi^2 \mathbf{mm}}{\alpha^2} - \frac{2\mathbf{mm}}{\mathbf{m}^2} \right) \right.$$
$$\times \frac{e^{-\pi^2 \mathbf{m}^2/\alpha^2}}{\pi \mathbf{m}^2 V_A} \exp(2\pi i \mathbf{m} \cdot \mathbf{r}_{jk}) \left[1 + O\left(\frac{1}{R}\right) \right] \Big\rangle$$
$$+ \Pi_{\text{Macro}} V_A, V_R \tag{5.41}$$

where

$$\Pi_{\text{Macro}} V_A, V_R = \frac{1}{2\pi} \left\langle \sum_{j=1}^{N} \sum_{k=1}^{N} Q_j Q_k \sum_{\mathbf{n}_1 \in S_R} \sum_{\mathbf{n}_2 \in S_R} \int_{\gamma(\mathbf{0})} d^3\mathbf{v} \right.$$
$$\times \frac{e^{-\pi^2 \mathbf{v}^2/\alpha^2}}{\mathbf{v}^2} e^{2\pi i \mathbf{v} \cdot \mathbf{r}_{jk}}$$
$$\left. \times \left(I - \frac{2\pi^2 \mathbf{vv}}{\alpha^2} - \frac{2\mathbf{vv}}{\mathbf{v}^2} \right) e^{2\pi i \mathbf{v} \cdot (\mathbf{n}_1 - \mathbf{n}_2 + \mathbf{r}_{jk})} \right\rangle \tag{5.42}$$

To evaluate this final contribution for large R, we expand $\exp(-\pi^2 \mathbf{v}^2/\alpha^2 + 2\pi i \mathbf{v} \cdot \mathbf{r}_{jk})$ in powers of $\mathbf{v}$ with only quadratic powers giving an $O(R^0)$ contribution, as with the forces. In the expansion, only the term $+4\pi^2(\mathbf{v} \cdot \mathbf{r}_j)(\mathbf{v} \cdot \mathbf{r}_k)$ survives to $O(R^0)$. After we convert the sums on $\mathbf{n}_1$ and $\mathbf{n}_2$ to integrals, and replace $\gamma(\mathbf{0})$ as the range of integration by $\mathbb{R}^3$ [processes which cause an error which is $O(1/R)$ with respect to the result], we obtain

$$\Pi_{\text{Macro}} V_A = -\frac{1}{2} \left\langle \frac{3}{4\pi V_A} \int_{S_1} d^2\boldsymbol{\rho}_1 \, [\mathbf{M} \cdot \nabla_{\boldsymbol{\rho}_1}][\mathbf{M} \cdot \nabla_{\boldsymbol{\rho}_1}] \int_{S_1} d^2\boldsymbol{\rho}_2 \right.$$
$$\times \frac{1}{(2\pi)^3} \int_{\mathbb{R}^3} d^3\mathbf{v} \left[\frac{8\pi}{\mathbf{v}^2} (I - \hat{\mathbf{v}}\hat{\mathbf{v}}) - \frac{4\pi}{\mathbf{v}^2} \right]$$
$$\left. \times e^{i\mathbf{v} \cdot (\boldsymbol{\rho}_1 - \boldsymbol{\rho}_2)} \left[1 + O\left(\frac{1}{R}\right) \right] \right\rangle \tag{5.43}$$

The Fourier transforms which appear here are standard and this expression then reduces in the limit $R \to \infty$ to

$$\Pi_{\text{Macro}} V_A = \left\langle \frac{3}{8\pi V_A} \int_{S_1} d^2\boldsymbol{\rho}_1 \, [\mathbf{M} \cdot \nabla_{\boldsymbol{\rho}_1}][\mathbf{M} \cdot \nabla_{\boldsymbol{\rho}_1}] \right.$$
$$\left. \times \int_{S_1} d^2\boldsymbol{\rho}_2 \, (\boldsymbol{\rho}_1 - \boldsymbol{\rho}_2) \nabla_{\boldsymbol{\rho}_1} |\boldsymbol{\rho}_1 - \boldsymbol{\rho}_2|^{-1} \right\rangle \tag{5.44}$$

Using the standard spherical harmonic expansions of $|\boldsymbol{\rho}_1 - \boldsymbol{\rho}_2|^{-1}$ and the result[4]

$$\hat{\boldsymbol{\rho}} = \left(\frac{4\pi}{3}\right)^{1/2} \sum_{\mu=-1}^{1} \mathbf{e}_\mu Y_{1\mu}(\hat{\boldsymbol{\rho}}) \tag{5.45}$$

we amy, with a little effort, evaluate these integrals to find

$$\Pi_{\text{Macro}} V_\Lambda = \frac{2\pi}{5V_\Lambda} \langle \mathbf{M}^2 \rangle \mathbf{I} - \frac{8\pi}{15V_\Lambda} \langle \mathbf{MM} \rangle \tag{5.46}$$

We can now write the direct Coulomb and polarization contributions to the virial expression in the limit $R \to \infty$ as

$$\begin{aligned} \Pi_{\text{Coul}} V_\Lambda = {} & \frac{1}{2} \left\langle \sum_{j=1}^{N} \sum_{k=1}^{N} Q_j Q_k \mathsf{G}_{\text{Ewald}}(\mathbf{r}_{jk}) \right\rangle \\ & - \frac{2\pi}{15V_\Lambda} (4\langle \mathbf{MM} \rangle - 3\langle \mathbf{M}^2 \rangle \mathbf{I}) \\ & - \frac{4\pi}{V_\Lambda(2\varepsilon' + 1)} \langle \mathbf{MM} \rangle \end{aligned} \tag{5.47}$$

where

$$\begin{aligned} \mathsf{G}_{\text{Ewald}}(\mathbf{r}) = {} & \sum_{\mathbf{n} \in \Lambda} \frac{(\mathbf{n}+\mathbf{r})(\mathbf{n}+\mathbf{r})}{(\mathbf{n}+\mathbf{r})^2} \\ & \times \left\{ \frac{\operatorname{erfc}(\alpha |\mathbf{n}+\mathbf{r}_{jk}|)}{|\mathbf{n}+\mathbf{r}_{jk}|} + \frac{2\alpha}{\sqrt{\pi}} \exp[-\alpha^2 (\mathbf{n}+\mathbf{r}_{jk})^2] \right\} \\ & + \sum_{\substack{\mathbf{m} \in \mathscr{M} \\ \mathbf{m} \neq \mathbf{0}}} \left(I - \frac{2\pi^2 \mathbf{mm}}{\alpha^2} - \frac{2\mathbf{mm}}{\mathbf{m}^2} \right) \\ & \times \frac{e^{-\pi^2 \mathbf{m}^2/\alpha^2}}{\pi \mathbf{m}^2 V_\Lambda} \exp(2\pi i \mathbf{m} \cdot \mathbf{r}) \end{aligned} \tag{5.48}$$

We may now conclude by writing the total virial expression for the pressure tensor as

$$\begin{aligned} \Pi V_\Lambda = {} & \left\langle \sum_{j=1}^{N} m_j \dot{\mathbf{r}}(j,0)\, \dot{\mathbf{r}}(j,0) \right\rangle \\ & - \frac{1}{2} \left\langle \sum_{j=1}^{N} \sum_{k=1}^{N} {\sum_{\mathbf{n} \in \Lambda}}^{*} [(\mathbf{n}+\mathbf{r}_{jk}) \nabla \phi_{\text{SR};jk}(\mathbf{n}+\mathbf{r}_{jk}) - Q_j Q_k \mathsf{G}_{\text{Ewald}}(\mathbf{r}_{jk})] \right\rangle \\ & - \frac{2\pi}{5V_\Lambda} (3\langle \mathbf{MM} \rangle - \langle \mathbf{M}^2 \rangle \mathbf{I}) + \frac{2\pi(2\varepsilon' - 1)}{V_\Lambda(2\varepsilon' + 1)} \langle \mathbf{MM} \rangle \end{aligned} \tag{5.49}$$

In writing this final expression, the periodic virial theorem, we have assumed that in our periodic-boundary-condition array construction the surface pressure Π^S is entirely due to the short-ranged forces, so that the last long-time averages in Eqs. (2.13) and (4.13) are zero. This virial theorem in Eq. (5.49) finally provides us with an unequivocal algorithm for the internal pressure tensor from a molecular dynamics simulation.

6. DISCUSSION

One problem which has not been mentioned so far is the problem of point dipoles. If we have a point $\boldsymbol{\mu}_j$ on particle j, then the pressure tensor is that in Eq. (5.49) with Q_j replaced by $Q_j + \boldsymbol{\mu}_j \cdot \nabla_{\mathbf{r}_j}$ and the $Q_j \mathbf{r}_j$ contribution to $\mathbf{M}$ is increased by $\boldsymbol{\mu}_j$. Similar appropriate changes must be made to the kinetic energy contribution and the equations of motion must be extended by the same considerations so that they will also describe the rotational motion of the dipolar molecules. Implementation with polarizable molecules will be rather more complicated if point polarizability models are used. Other problems also arise with extended molecules because of the possibility that a molecule may be part in $\Gamma(\mathbf{0})$ and part in one of its nearest neighbors. These last questions are not discussed in this paper, but the framework for settling them has been provided.

In implementing this algorithm for the pressure, the normal methods[1] for choosing the parameter α for optimal numerical performance should be followed in the dynamics and in evaluating the expectations of $G_{\text{Ewald}}(\mathbf{r}_{jk})$. For the short-ranged force contribution we should recall that the dynamics is normally implemented via the minimum image convention and accordingly it seems appropriate to use $\bar{\mathbf{r}}_{jk} \nabla \phi_{\text{SR};jk}(\bar{\mathbf{r}}_{jk})$ in place of the lattice sum of short-range interaction contributions in Eq. (5.49). Here $\bar{\mathbf{r}}_{jk}$ is the minimum image form of $\mathbf{r}_{jk}$. That is, $\bar{\mathbf{r}}_{jk} = \mathbf{n}_0 + \mathbf{r}_{jk}$, where $\mathbf{n}_0$ is that lattice vector which makes $|\bar{\mathbf{r}}_{jk}|$ minimum.

We may now consider the scalar pressure $\Pi = \frac{1}{3}$ trace Π. First we look at the short-ranged force contribution. For potentials $\phi_{\text{SR};jk}(\mathbf{r}_{jk})$ which depend only on $|\mathbf{r}_{jk}|$, we have

$$(\mathbf{n} + \mathbf{r}_{jk}) \cdot \nabla \phi_{\text{SR};jk}(\mathbf{n} + \mathbf{r}_{jk}) = r \frac{\partial}{\partial r} \phi_{\text{SR};jk}(r) \Big|_{r = |\mathbf{n} + \mathbf{r}_{jk}|} \tag{6.1}$$

This gives a fairly simple lattice sum for any such potential, especially simple when the lattice sum is replaced by its minimum image term. For potentials $A_{jk} |\mathbf{r}_{jk}|^{-p}$ with $p \geqslant 4$, we may define the short-ranged energy

$$U_p(\{\mathbf{r}_1, \ldots, \mathbf{r}_N\}) = \frac{1}{2} \sum_{j=1}^{N} \sum_{k=1}^{N} {\sum_{\mathbf{n} \in \Lambda}}^{*} A_{jk} |\mathbf{n} + \mathbf{r}_{jk}|^{-p} \tag{6.2}$$

and then we have

$$-\frac{1}{2}\left\langle \sum_{j=1}^{N}\sum_{k=1}^{N}\sum_{\mathbf{n}\in\Lambda}^{*}(\mathbf{n}+\mathbf{r}_{jk})\cdot\nabla_{\mathbf{r}_j}A_{jk}\,|\mathbf{n}+\mathbf{r}_{jk}|^{-p}\right\rangle$$
$$=p\langle U_p(\{\mathbf{r}_1,\ldots,\mathbf{r}_N\})\rangle \tag{6.3}$$

which is a particularly convenient form for Lennard-Jones interactions. For the Coulomb interaction we have

$$\text{trace}\,G_{\text{Ewald}}(\mathbf{r})=\psi_{\text{Ewald}}(\mathbf{r})+\frac{2\alpha}{\sqrt{\pi}}\sum_{\mathbf{n}\in\Lambda}\exp[-\alpha^2(\mathbf{n}+\mathbf{r}_{jk})^2]$$
$$-\frac{2\pi^2}{\alpha^2 V_\Lambda}\left[\sum_{\mathbf{m}\in\mathscr{R}}\exp\frac{-\pi^2\mathbf{m}^2}{\alpha^2}\exp(2\pi i\mathbf{m}\cdot\mathbf{r})-1\right] \tag{6.4}$$

We may ignore the -1 in the last bracket here by charge neutrality. The sum on $\mathbf{m}\in\mathscr{R}$ is well defined and absolutely convergent and uniformly convergent in $\mathbf{r}$. This is quite unlike the case of lattice sums with factors $1/\mathbf{m}^2$, for which we may not use the Poisson summation formula directly. For the sum in Eq. (6.4), we may use the Poisson summation formula. It then exactly cancels the sum on $\mathbf{n}$ in Eq. (6.4). We also note that $3\mathbf{MM}-\mathbf{M}^2\mathbf{I}$ is traceless. Thus the scalar pressure virial theorem reads

$$\Pi V_\Lambda=\frac{1}{3}\left\langle\sum_{j=1}^{N}m_j\dot{\mathbf{r}}(j,\mathbf{0})^2\right\rangle-\frac{1}{6}\left\langle\sum_{j=1}^{N}\sum_{k=1}^{N}\bar{\mathbf{r}}_{jk}\cdot\nabla_{\mathbf{r}_j}\phi_{\text{SR};jk}(\bar{\mathbf{r}}_{jk})\right\rangle$$
$$+\frac{1}{6}\left\langle\sum_{j=1}^{N}\sum_{k=1}^{N}Q_jQ_k\psi_{\text{Ewald}}(\mathbf{r}_{jk})\right\rangle+\frac{2\pi(2\varepsilon'-1)}{3V_\Lambda(2\varepsilon'+1)}\langle\mathbf{M}^2\rangle \tag{6.5}$$

Finally we must consider the value of ε' to be used. It usually makes sense to take the limit $\varepsilon'\to\infty$, for then the equations of motion have no square dipole term. Also, the equation for the scalar pressure becomes simpler. For some simulations, particularly of dipolar systems, where the mean square dipole moment is needed accurately for dielectric constant estimation, it appears that it is sometimes useful to use a finite value of ε'. This may improve the rate at which the time-averaged mean square dipole moment converges to its long-time limit. In either case we must use the full catastrophe of Eq. (6.5) and an equation of motion [see Eqs. (5.25) and (5.26)] which contains forces proportional to $\mathbf{M}$ if ε' is finite. The $\mathbf{M}$ we use in both the dynamics and the pressure averages must be the dipole moment of those particles which were in $\Gamma(\mathbf{0})$ at the start of the simulation. Only by doing this can we avoid discontinuities in the forces when a particle moves out of one face of $\Gamma(\mathbf{0})$ and reenters by the opposite face. That

is simply a computing time cost that we must pay to avoid excessively slow convergence of the square dipole moment averages. What this tells us about the original dynamics is that the particles do not stay inside their respective copy cells $\Gamma(\mathbf{n})$, but stay "associated" with it.

This mean square dipole moment term which remains in the pressure tensor of Eq. (5.49) in the limit $\varepsilon' \to \infty$ is very interesting. It is the only example I know where the mean square dipole moment terms inherent in the conditionally convergent lattice sums which arise in periodic-boundary-condition simulations cannot be induced to go away by some construction or another when we use a spherical lattice sum summation order. It should be noticed, however, that no amount of fiddling with the external medium will make such terms vanish if we use plane-slab-shaped summation order.[8] Thus the fact that such terms arise in the pressure tensor, which measures response to shear, is not perhaps as surprising as it might first seem.

ACKNOWLEDGMENT

I thank Oliver Penrose for his training in applied mathematics and statistical mechanics.

REFERENCES

1. M. A. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Clarendon Press, Oxford, 1987).
2. S. A. Rice and P. Gray, *The Statistical Mechanics of Simple Liquids* (Interscience, New York, 1965).
3. W. G. Hoover, *Computational Statistical Mechanics* (Elsevier, Amsterdam, 1991), pp. 143–144.
4. D. A. Varshalovich, A. N. Moskalev, and V. K. Khersonskii, *Quantum Theory of Angular Momentum* (World Scientific, Singapore, 1988), Chapter 5.
5. M. Abramowitz and I. A. Stegun, eds., *Handbook of Mathematical Functions* (Dover, New York, 1972).
6. A. Erdelyi, ed., *Higher Transcendental Functions*, Vols. 1 and 2 (McGraw-Hill, New York, 1955).
7. S. W. De Leeuw, J. W. Perram, and H. G. Petersen, *J. Stat. Phys.* **61**:1203–1222 (1990).
8. E. R. Smith, *Proc. R. Soc. Lond. A* **375**:475–504 (1981).
9. S. W. De Leeuw, J. W. Perram, and E. R. Smith, *Proc. R. Soc. Lond. A* **373**:27–56 (1980).