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Pressure calculation in polar and charged systems using Ewald summation: Results for the extended simple point charge model of water

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Ewald summation and physically equivalent methods such as particle-mesh Ewald, kubic-harmonic expansions, or Lekner sums are commonly used to calculate long-range electrostatic interactions in computer simulations of polar and charged substances. The calculation of pressures in such systems is investigated. We find that the virial and thermodynamic pressures differ because of the explicit volume dependence of the effective, resummed Ewald potential. The thermodynamic pressure, obtained from the volume derivative of the Helmholtz free energy, can be expressed easily for both ionic and rigid molecular systems. For a system of rigid molecules, the electrostatic energy and the forces at the atom positions are required, both of which are readily available in molecular dynamics codes. We then calculate the virial and thermodynamic pressures for the extended simple point charge (SPC/E) water model at standard conditions. We find that the thermodynamic pressure exhibits considerably less system size dependence than the virial pressure. From an analysis of the cross correlation between the virial and thermodynamic pressure, we conclude that the thermodynamic pressure should be used to drive volume fluctuations in constant-pressure simulations. © *1998 American Institute of Physics.* [S0021-9606(98)50431-X]

I. INTRODUCTION

Pressure is one of the fundamental thermodynamic variables. The calculation of pressures in fluid systems using computer simulations is generally considered to be a routine task. However, difficulties arise in the presence of long-range interactions. Here, we investigate the calculation of pressures in computer simulations of charged and polar systems, where the long-range Coulomb interactions are commonly treated with Ewald lattice summation[1] or physically equivalent methods like particle-mesh Ewald,[2] kubic-harmonic expansions,[3] or Lekner sums.[4–6] A mechanistic definition of the pressure leads to the standard virial expression. A thermodynamic definition of the pressure is based on the volume dependence of the Helmholtz free energy. When the Coulomb interactions are resummed by using, e.g., the Ewald method, the resulting effective pair interactions depend explicitly on the volume. In addition, self-interactions are present that also depend on the volume. As a consequence, the virial and thermodynamic pressures are not identical for finite Coulomb systems, even though the two pressures are expected to converge in the thermodynamic limit.

The paper is organized as follows: in Sec. II, we derive expressions for the virial and thermodynamic pressures. In Sec. III, we study the pressure in systems with long-range Coulomb interactions. For the thermodynamic pressure, we derive a simple formula that can be readily implemented in standard molecular dynamics or Monte Carlo codes. In Secs. IV and V, we study the system size dependence of the virial and thermodynamic pressures for the extended simple point charge (SPC/E) water model[7] under standard conditions.

II. VIRIAL AND THERMODYNAMIC PRESSURES

A. Virial pressure

The pressure p can be calculated from a mechanistic prescription equating the exterior and interior forces on the container. This leads to the virial expression for the pressure in an atomic system,[8]

$$p_V = \rho k_B T + \frac{1}{3V} \left\langle \sum_i \mathbf{r}_i \cdot \mathbf{F}_i \right\rangle, \tag{1}$$

where ρ is the number density of particles; k_B is Boltzmann's constant; T is the temperature ($k_B T = \beta^{-1}$); and V is the volume. The sum extends over the scalar product betwen particle positions $\mathbf{r}_i$ and forces $\mathbf{F}_i$ exerted on particle i due to other particles in the system. $\langle \cdots \rangle$ denotes a canonical average. For computer simulations under periodic boundary conditions with pair forces, it is convenient to rewrite the virial equation in a form that makes the translational invariance explicit,

$$p_V = \rho k_B T - \frac{1}{3V} \left\langle \sum_{\substack{i,j \\ i<j}} \mathbf{F}_{ij} \cdot \mathbf{r}_{ij} \right\rangle, \tag{2}$$

where $\mathbf{r}_{ij} = \mathbf{r}_j - \mathbf{r}_i$ and $\mathbf{F}_{ij} = -\partial v(\mathbf{r}_{ij})/\partial \mathbf{r}_i = \partial v(\mathbf{r}_{ij})/\partial \mathbf{r}_{ij}$ is the pair force exerted on particle i by particle j, derived from a pair potential $v(\mathbf{r})$; and the sum is over all pairs of particles in the system.

For a system of rigid polyatomic molecules i,j with interaction sites α and β, one obtains an analogous formula

when the forces $\mathbf{F}_{i\alpha j\beta}$ between molecular sites are projected onto a vector $\mathbf{r}_{ij}$ between the ''centers'' of the two molecules (e.g., the center of mass),

$$p_V = \rho k_B T - \frac{1}{3V}\left\langle \sum_{\substack{i,j \\ i<j}} \sum_{\alpha,\beta} \mathbf{F}_{i\alpha j\beta} \cdot \mathbf{r}_{ij} \right\rangle$$

$$= \rho k_B T - \frac{1}{3V}\left\langle \sum_{\substack{i,j \\ i<j}} \mathbf{F}_{ij} \cdot \mathbf{r}_{ij} \right\rangle. \quad (3)$$

Here, $\mathbf{F}_{ij}$ is the net force between two rigid molecules, summed over molecular sites α and β. Otherwise, the constraint forces maintaining the rigidity of the molecules have to be included explicitly in Eq. (3).

B. Thermodynamic pressure

The thermodynamic expression for the pressure is derived from the relation between the pressure p_T, the Helmholtz free energy F, and the volume V,

$$p_T = -\left(\frac{\partial F}{\partial V}\right)_{T,N}. \quad (4)$$

The statistical–mechanical relation between the free energy F and the partition function $Q_N(V,T)$ for N identical classical particles in a canonical ensemble is,

$$Q_N(V,T) = e^{-\beta F} = \frac{1}{h^{3N}N!} \int \int e^{-\beta H(\mathbf{r}^N,\mathbf{p}^N)} d\mathbf{r}^N d\mathbf{p}^N, \quad (5)$$

where h is Planck's constant; $H = K + U$ is the Hamiltonian; and the integration extends over the positions $\mathbf{r}^N$ and momenta $\mathbf{p}^N$ of all particles. In taking the volume derivative Eq. (4), the kinetic energy K is independent of the volume. Transforming the positional coordinates into dimensionless form, $V^{-N}\mathbf{r}^N$, and pulling out a factor V^N from the integral, leads to the ideal-gas term $\rho k_B T$ for the pressure. The non-ideal contributions are contained in the volume dependence of the potential energy U,

$$p_T = \rho k_B T - \left\langle \frac{\partial U}{\partial V} \right\rangle. \quad (6)$$

Typically, U does not depend explicitly on the volume. The volume dependence of U then arises from the volume scaling of the particle positions. In the absence of an explicit volume dependence, we can express $\partial U / \partial V$ as

$$\frac{\partial U}{\partial V} = \sum_i \frac{\partial U}{\partial \mathbf{r}_i} \cdot \frac{\partial \mathbf{r}_i}{\partial V} = \frac{1}{3V} \sum_i \frac{\partial U}{\partial \mathbf{r}_i} \cdot \mathbf{r}_i, \quad (7)$$

with $\partial \mathbf{r}_i / \partial V = \mathbf{r}_i / 3V$. By using $\mathbf{F}_i = -\partial U / \partial \mathbf{r}_i$ and combining Eqs. (6) and (7), we find the corresponding thermodynamic pressure to be equivalent to the mechanistic pressure Eq. (1).

III. PRESSURE IN SYSTEMS WITH LONG-RANGE COULOMB INTERACTIONS

A. Thermodynamic pressure in ionic systems

The identity between the virial and thermodynamic pressures, Eqs. (1) and (6), does not hold if the potential depends explicitly on the system volume. Such an explicit volume

dependence arises in computer simulations of charged and polar substances, when the long-range Coulomb interactions are resummed, e.g., by using the Ewald method.[1]

We first split the total potential energy U into a short-range part $U^{(sr)}$ and a long-range Coulomb part $U^{(c)}$,

$$U = U^{(sr)} + U^{(c)}. \quad (8)$$

The pressure $p^{(sr)}$ corresponding to $U^{(sr)}$ contains the ideal-gas term and the contributions from short-range pair interactions,

$$p^{(sr)} = \rho k_B T - \frac{1}{3V} \sum_{\substack{i,j \\ i<j}} \sum_{\alpha,\beta} \mathbf{F}^{(sr)}_{i\alpha j\beta} \cdot \mathbf{r}_{ij}, \quad (9)$$

where the short-range forces $\mathbf{F}^{(sr)}_{i\alpha j\beta}$ are those derived from the short-range part $U^{(sr)}$ of the potential energy. Note that the virial and thermodynamic expressions for $p^{(sr)}$ are equivalent, and therefore the subscripts ''V'' or ''T'' have been omitted in Eq. (9).

Next, we consider the pressure arising from the potential energy $U^{(c)}$ of long-range Coulomb interactions. In Ewald lattice summation, the charges in a periodically replicated simulation box interact with an effective potential. That potential is obtained from a summation over all periodic images. In addition, a self-interaction arises from interactions with a particle's own images. This leads to a Coulomb energy $U^{(c)}$ for a system of partial charges $q_{i\alpha}$ at positions $\mathbf{r}_{i\alpha}$,

$$U^{(c)} = \sum_{\substack{i,j \\ i<j}} \sum_{\alpha,\beta} q_{i\alpha} q_{j\beta} \varphi(\mathbf{r}_{i\alpha j\beta})$$

$$+ \sum_i \sum_{\substack{\alpha,\beta \\ \alpha<\beta}} q_{i\alpha} q_{i\beta} \left[\varphi(\mathbf{r}_{i\alpha i\beta}) - \frac{1}{|\mathbf{r}_{i\alpha i\beta}|} \right]$$

$$+ \frac{1}{2} \sum_i \sum_\alpha q_{i\alpha}^2 \lim_{\mathbf{r}\to 0}\left[\varphi(\mathbf{r}) - \frac{1}{|\mathbf{r}|} \right]. \quad (10)$$

The first sum is the intermolecular contribution; the second and third sums are the intramolecular contributions, with the self-interactions contained in the third sum. $\varphi(\mathbf{r})$ is the effective, resummed Coulomb potential, with a Fourier representation,[9]

$$\varphi(\mathbf{r}) = \frac{1}{V} \sum_{\substack{\mathbf{k} \\ k\neq 0}} \frac{4\pi}{\mathbf{k}^2} e^{i\mathbf{k}\cdot\mathbf{r}}, \quad (11)$$

where the $\mathbf{k}$ sum extends over the reciprocal lattice corresponding to the lattice vectors $\mathbf{n}$ of periodically replicated simulation boxes. In a kubic lattice of length $L = V^{1/3}$, we have $\mathbf{n} = L(i,j,k)$, and $\mathbf{k} = 2\pi L^{-1}(i,j,k)$, where i, j, and k are integers. It is numerically convenient to partly transform $\varphi(\mathbf{r})$ into real space, leading to its Ewald lattice sum representation,

$$\varphi(\mathbf{r}) = \sum_{\mathbf{n}} \frac{\operatorname{erfc}(\eta|\mathbf{r}+\mathbf{n}|)}{|\mathbf{r}+\mathbf{n}|} + \sum_{\substack{\mathbf{k} \\ k\neq 0}} \frac{4\pi}{Vk^2} e^{-k^2/4\eta^2 + i\mathbf{k}\cdot\mathbf{r}} - \frac{\pi}{V\eta^2}. \quad (12)$$

η is a convergence parameter chosen to accelerate numerical convergence. The value of $\varphi(\mathbf{r})$ is independent of η,[10]

$$\frac{\partial \varphi(\mathbf{r})}{\partial \eta} \equiv 0. \tag{13}$$

The self-interactions in $U^{(c)}$ are given by the interactions of a unit point charge with its periodic images, subtracting the bare self-interaction, $\varphi(\mathbf{r}) - 1/|\mathbf{r}|$, with the appropriate limit taken for $\mathbf{r} \to 0$. For a given box shape, $\varphi(\mathbf{r})$ scales with the box volume V as

$$\varphi(\mathbf{r}) = V^{-1/3} \varphi^*(\mathbf{r}^*), \tag{14a}$$

$$\frac{\partial \varphi(\mathbf{r})}{\partial V} = -\frac{1}{3V} \varphi(\mathbf{r}), \tag{14b}$$

where star superscripts denote volume-independent quantities. This follows from Eq. (11) with volume scaling $\mathbf{r} \sim V^{1/3}$ and $\mathbf{k} \sim V^{-1/3}$. The same scaling is true trivially for the direct $1/|\mathbf{r}|$ interactions. For an ionic system of point charges without bond constraints, Eqs. (6) and (14) immediately lead to an expression for the thermodynamic pressure in terms of the Coulomb energy $U^{(c)}$,

$$p_T = p^{(\mathrm{sr})} + \frac{\langle U^{(c)} \rangle}{3V}. \tag{15}$$

Equation (15) gives the well-known relation between the pressure and energy of an ionic system, for which the Coulomb energy is a homogeneous function of degree -1 in the coordinates.[11]

B. Thermodynamic pressure in systems of rigid polyatomic molecules

For a system of rigid molecules, we find the following volume scaling:

$$\varphi(\mathbf{r}_{i\alpha j\beta}) = V^{-1/3} \varphi^*(\mathbf{r}_{ij}^* + V^{-1/3}\mathbf{d}_{i\alpha j\beta}), \tag{16a}$$

$$\frac{\partial \varphi(\mathbf{r}_{i\alpha j\beta})}{\partial V} = -\frac{1}{3V}\left[\varphi(\mathbf{r}) + \frac{\partial \varphi(\mathbf{r}_{i\alpha j\beta})}{\partial \mathbf{r}_{i\alpha j\beta}} \cdot \mathbf{d}_{i\alpha j\beta} \right], \tag{16b}$$

$$\frac{\partial}{\partial V}\frac{1}{|\mathbf{r}_{i\alpha i\beta}|} = -\frac{1}{3V}\left[\frac{1}{|\mathbf{r}_{i\alpha i\beta}|} + \frac{\partial}{\partial \mathbf{r}_{i\alpha i\beta}}\frac{1}{|\mathbf{r}_{i\alpha i\beta}|} \cdot \mathbf{d}_{i\alpha i\beta} \right] \equiv 0, \tag{16c}$$

where $\mathbf{r}_{ij}$ is the distance vector between two molecule centers; $\mathbf{d}_{i\alpha} = \mathbf{r}_{i\alpha} - \mathbf{r}_i$ is the vector from the center to site α; and $\mathbf{d}_{i\alpha j\beta} = \mathbf{d}_{j\beta} - \mathbf{d}_{i\alpha}$. Equation (16c) follows from the volume independence of the intramolecular distance vector $\mathbf{r}_{i\alpha i\beta} = \mathbf{d}_{i\alpha i\beta}$. Combining Eqs. (10) and (16), we find for the volume derivative of the Coulomb energy,

$$\frac{\partial U^{(c)}}{\partial V} = -\frac{U^{(c)}}{3V} - \frac{1}{3V}\left\{ \sum_{\substack{i,j \\ i<j}} \sum_{\alpha,\beta} \left[\frac{\partial}{\partial \mathbf{r}_{i\alpha j\beta}} q_{i\alpha} q_{j\beta} \varphi(\mathbf{r}_{i\alpha j\beta}) \right] \right.$$

$$\cdot \mathbf{d}_{i\alpha j\beta} + \sum_i \sum_{\substack{\alpha,\beta \\ \alpha<\beta}} \left[\frac{\partial}{\partial \mathbf{r}_{i\alpha i\beta}} q_{i\alpha} q_{i\beta} \left(\varphi(\mathbf{r}_{i\alpha i\beta}) \right. \right.$$

$$\left. \left. \left. - \frac{1}{|\mathbf{r}_{i\alpha i\beta}|} \right) \right] \cdot \mathbf{d}_{i\alpha i\beta} \right\}. \tag{17}$$

We can simplify $\partial U^{(c)}/\partial V$ further by expressing it in terms of the intermolecular forces $\mathbf{F}_{i\alpha j\beta}^{(\mathrm{inter})}$ exerted by site $j\beta$ onto site $i\alpha$,

$$\mathbf{F}_{i\alpha j\beta}^{(\mathrm{inter})} = \frac{\partial}{\partial \mathbf{r}_{i\alpha j\beta}} q_{i\alpha} q_{j\beta} \varphi(\mathbf{r}_{i\alpha j\beta}) = -\mathbf{F}_{j\beta i\alpha}^{(\mathrm{inter})}, \tag{18}$$

and the intramolecular forces $\mathbf{F}_{i\alpha i\beta}^{(\mathrm{intra})}$,

$$\mathbf{F}_{i\alpha i\beta}^{(\mathrm{intra})} = \frac{\partial}{\partial \mathbf{r}_{i\alpha i\beta}} q_{i\alpha} q_{i\beta}\left[\varphi(\mathbf{r}_{i\alpha i\beta}) - \frac{1}{|\mathbf{r}_{i\alpha i\beta}|} \right] = -\mathbf{F}_{i\beta i\alpha}^{(\mathrm{intra})}. \tag{19}$$

This leads to

$$\frac{\partial U^{(c)}}{\partial V} = -\frac{1}{3V}\left(U^{(c)} + \sum_{\substack{i,j \\ i<j}} \sum_{\alpha,\beta} \mathbf{F}_{i\alpha j\beta}^{(\mathrm{inter})} \cdot \mathbf{d}_{i\alpha j\beta} \right.$$

$$\left. + \sum_i \sum_{\substack{\alpha,\beta \\ \alpha<\beta}} \mathbf{F}_{i\alpha i\beta}^{(\mathrm{intra})} \cdot \mathbf{d}_{i\alpha i\beta} \right). \tag{20}$$

The sums over pairs of sites $i\alpha$ and $j\beta$ can be rewritten as a single sum over all sites. This is possible because the distances $\mathbf{d}_{i\alpha j\beta} = \mathbf{d}_{j\beta} - \mathbf{d}_{i\alpha}$ are intramolecular and are continuous when a particle crosses the box boundary (i.e., $\mathbf{d}_{i\alpha j\beta}$ does not change when the periodic images of the particles i or j are used). This results in

$$\frac{\partial U^{(c)}}{\partial V} = -\frac{1}{3V}\left[U^{(c)} - \sum_i \sum_\alpha (\mathbf{F}_{i\alpha}^{(\mathrm{inter})} + \mathbf{F}_{i\alpha}^{(\mathrm{intra})}) \cdot \mathbf{d}_{i\alpha} \right], \tag{21}$$

where $\mathbf{F}_{i\alpha}^{(\mathrm{inter})}$ is the net intermolecular force on site $i\alpha$,

$$\mathbf{F}_{i\alpha}^{(\mathrm{inter})} = \sum_{\substack{j \\ j\neq i}} \sum_\beta \mathbf{F}_{i\alpha j\beta}^{(\mathrm{inter})}, \tag{22}$$

and $\mathbf{F}_{i\alpha}^{(\mathrm{intra})}$ is the net intramolecular force on site $i\alpha$,

$$\mathbf{F}_{i\alpha}^{(\mathrm{intra})} = \sum_{\substack{\beta \\ \beta\neq\alpha}} \mathbf{F}_{i\alpha i\beta}^{(\mathrm{intra})}. \tag{23}$$

It is advantageous to add the intra- and intermolecular forces because in common Ewald-sum implementations the Fourier term already contains the sum of both inter- and intramolecular contributions which are thus not easily separated. We define the net Coulomb force $\mathbf{F}_{i\alpha}^{(c)}$ on site $i\alpha$ as the sum of the inter- and intramolecular forces,

$$\mathbf{F}_{i\alpha}^{(c)} = \mathbf{F}_{i\alpha}^{(\mathrm{inter})} + \mathbf{F}_{i\alpha}^{(\mathrm{intra})} = -\frac{\partial U^{(c)}}{\partial \mathbf{r}_{i\alpha}}. \tag{24}$$

We then find for the thermodynamic pressure of a system of rigid molecules,

$$p_T = p^{(\mathrm{sr})} + \frac{1}{3V}\left(\langle U^{(c)} \rangle - \left\langle \sum_i \sum_\alpha \mathbf{F}_{i\alpha}^{(c)} \cdot \mathbf{d}_{i\alpha} \right\rangle \right). \tag{25}$$

Thus the presence of intramolecular constraints in rigid polyatomic molecules results in a force term to be subtracted from the pressure of the purely ionic system, Eq. (15). Note that the forces $\mathbf{F}_{i\alpha}^{(c)}$ in Eq. (25) are derived from the Coulomb energy $U^{(c)}$ alone. Additional ideal-gas and short-range contributions to the pressure are reflected in $p^{(\mathrm{sr})}$.

C. Tin-foil boundary conditions and reaction-field correction

The infinite Ewald lattice is implicitly embedded in a conducting medium with dielectric constant $\epsilon_{\text{rf}}=\infty$, corresponding to ''tin-foil'' boundary conditions. This is the appropriate choice for a conducting medium. However, for a polar substance it can be advantageous to use a reaction-field dielectric constant ϵ_{rf} similar to that of the bulk medium.[12] The resulting correction to the Coulomb energy $U^{(\text{c})}(\epsilon_{\text{rf}}=\infty)$ is[13]

$$U^{(\text{rf})}=U^{(\text{c})}(\epsilon_{\text{rf}})-U^{(\text{c})}(\epsilon_{\text{rf}}=\infty)=\frac{2\pi}{(2\epsilon_{\text{rf}}+1)V}\mathbf{M}^2. \quad (26)$$

$\mathbf{M}$ is the instantaneous dipole moment of the simulation volume arising from the dipole moments $\mathbf{m}_i$ of individual molecules,

$$\mathbf{M}=\sum_i \mathbf{m}_i=\sum_i \sum_\alpha q_{i\alpha}\mathbf{d}_{i\alpha}. \quad (27)$$

For rigid molecules the $\mathbf{m}_i$ do not change with volume. The reaction-field correction, Eq. (26), thus scales as V^{-1},

$$\frac{\partial U^{(\text{rf})}}{\partial V}=-\frac{U^{(\text{rf})}}{V}. \quad (28)$$

The forces derived from the reaction-field correction are

$$\mathbf{F}_{i\alpha}^{(\text{rf})}=-\frac{\partial U^{(\text{rf})}}{\partial \mathbf{r}_{i\alpha}}=-\frac{4\pi q_{i\alpha}}{(2\epsilon_{\text{rf}}+1)V}\mathbf{M}. \quad (29)$$

By using Eq. (27), we can express the sum of reaction-field forces projected onto the intramolecular distance vectors in terms of the reaction-field energy $U^{(\text{rf})}$,

$$\sum_{i,\alpha} \mathbf{F}_{i\alpha}^{(\text{rf})}\cdot\mathbf{d}_{i\alpha}=-2U^{(\text{rf})}. \quad (30)$$

Accordingly, the volume derivative of the reaction-field energy $U^{(\text{rf})}$ can be written as

$$-\frac{\partial U^{(\text{rf})}}{\partial V}=\frac{1}{3V}\left[U^{(\text{rf})}-\sum_{i,\alpha} \mathbf{F}_{i\alpha}^{(\text{rf})}\cdot\mathbf{d}_{i\alpha}\right]. \quad (31)$$

The correction Eq. (26) for a finite reaction-field dielectric constant ϵ_{rf} then leads to an expression for the thermodynamic pressure analogous to Eq. (25),

$$p_T=p^{(\text{sr})}+\frac{1}{3V}\left[\langle U^{(\text{c})}(\epsilon_{\text{rf}})\rangle-\left\langle \sum_i \sum_\alpha \mathbf{F}_{i\alpha}^{(\text{c},\epsilon_{\text{rf}})}\cdot\mathbf{d}_{i\alpha}\right\rangle\right]. \quad (32)$$

Here, the forces $\mathbf{F}_{i\alpha}^{(\text{c},\epsilon_{\text{rf}})}$ are derived from the Coulomb energy $U^{(\text{c})}(\epsilon_{\text{rf}})$

$$\mathbf{F}_{i\alpha}^{(\text{c},\epsilon_{\text{rf}})}=-\frac{\partial U^{(\text{c})}(\epsilon_{\text{rf}})}{\partial \mathbf{r}_{i\alpha}}, \quad (33)$$

and contain the reaction-field contribution $\mathbf{F}_{i\alpha}^{(\text{rf})}$ defined in Eq. (29).

D. General considerations

We emphasize the simplicity of the pressure expressions Eqs. (25) and (32) for systems of rigid molecules. The Cou-

lomb energy contribution $\langle U^{(\text{c})}\rangle/3V$ to the pressure is analogous to that of the corresponding ionic system, Eq. (15), but corrected for the presence of constraint forces. A more or less equivalent expression for the pressure in Coulombic systems treated with Ewald summation was derived before by Smith,[14] and similarly by Boulougouris et al.[15] However, in those derivations the volume derivative was carried out explicitly for the Ewald energy. Also, the derivations start from an approximate expression for the Ewald energy that does not include the full real-space lattice sum and self terms. Therefore, the derivations did not arrive at a closed expression and the simplicity of the results given here was masked.

Expressions for the pressure tensor $\mathbf{P}$ for Ewald summation were derived previously by Nosé and Klein,[16] and Heyes,[17] as discussed by Alejandre et al.,[18] as well as by others.[19–22] However, the tensor character does not lend itself easily to a compact notation for the bulk pressure $p=\text{Tr}(\mathbf{P})$ in a homogeneous system. Equations (15), (25), and (32) have the advantage of being independent of the specific method used to evaluate the energies and forces. All that is needed is the total Coulomb energy and forces at all sites that are consistent with that energy. Molecular dynamics codes normally produce this information at no additional cost. The Coulomb interactions can then be evaluated by using conventional Ewald sums,[1,23] particle-mesh Ewald,[2] kubic-harmonic expansion,[3] or Lekner sums.[4–6] For approximate Coulomb energy calculations such as reaction-field[24,25] or generalized reaction-field methods,[26] Eqs. (15), (25), and (32) suggest an evaluation of the pressure that is formally consistent with that of Ewald sums and physically equivalent methods.

IV. COMPUTER SIMULATIONS

To investigate the quantitative differences between the virial and thermodynamic pressures, we study a model of water at standard conditions (298 K temperature, 997.07 kg m^{-3} mass density corresponding to a number density of $\rho=33.33$ nm^{-3}). We use the SPC/E model of water,[7] formed by a Lennard-Jones (LJ) center on the oxygens,

$$v_{\text{LJ}}(r)=\frac{A}{r^{12}}-\frac{B}{r^6}, \quad (34)$$

where $A=0.3428^{12}$ kJ nm^{12}/mol and $B=0.371\,22^6$ kJ nm^6/mol. In addition, the SPC/E model carries three partial charges. The hydrogen and oxygen sites carry charges $q_H=0.4238e$ and $q_O=-2q_H$, respectively, where e is the elementary charge. The oxygen–hydrogen bond length is 0.1 nm, the hydrogen–oxygen–hydrogen bond angle is $\cos^{-1}(-1/3)\approx 109.47$ deg.

We use Metropolis Monte Carlo simulations for the canonical sampling,[23] where the translational and rotational move widths are chosen to give an acceptance rate of about 40%. Ewald summation is used for the electrostatic interactions, with $\eta=5.6/L$ where $L=V^{1/3}$ is the length of the kubic box. A spherical cutoff of $L/2$ is used for the real-space interactions (charge and Lennard-Jones). The real-space potentials are shifted by a constant, such that they are zero at the cutoff. The Fourier space sum is truncated at $\mathbf{k}^2$

TABLE I. Characteristics and results of the Monte Carlo simulations of SPC/E water. Statistical errors are one estimated standard deviation of the mean. Also included are the cross-correlation coefficient r and the absolute deviation Δ, as defined in Eq. (35).

N	Passes [10^3]	$\langle U/N \rangle$ [kJ/mol]	p_V [MPa]	p_T [MPa]	r	Δ [MPa]
16	500	-46.95 ± 0.10	1061 ± 15	-7 ± 17	0.90	114
32	900	-46.67 ± 0.04	274.9 ± 6.0	-28.6 ± 5.6	0.95	51
64	2100	-46.82 ± 0.03	52.9 ± 2.4	-4.1 ± 2.4	0.98	24
128	3000	-46.83 ± 0.02	2.8 ± 1.6	-5.9 ± 1.6	0.990	12
256	1200	-46.79 ± 0.02	-3.8 ± 1.5	-5.5 ± 1.5	0.995	6
512	540	-46.82 ± 0.02	-4.1 ± 1.7	-4.4 ± 1.7	0.997	3

$\leq 38(2\pi/L)^2$, leading to 2×510 **k** vectors being considered. A reaction-field dielectric constant of $\epsilon_{rf} = 65$ is used in all simulations. Standard finite-size corrections are applied to the Lennard-Jones contributions to pressure and potential energy.[23]

System sizes of $N = 16, 32, 64, 128, 256,$ and 512 water molecules are studied. Starting from random configurations, these systems are equilibrated for at least 250 000 Monte Carlo passes. (One pass corresponds to one attempted move for each of the N particles.) In the production runs, the energy as well as the virial and thermodynamic pressures are calculated every tenth pass.

V. RESULTS FOR SPC/E WATER

Table I contains the simulation characteristics, as well as results for the virial and thermodynamic pressures. The thermodynamic pressure is calculated using Eq. (32). The virial pressure is calculated using Eq. (3), where the pair forces are derived from the total potential energy $U = U^{(sr)} + U^{(c)}$. Also included in Table I are results for the average potential energy per particle. (To compare with the experimental energy, one has to add a polarization correction of 5.22 kJ/mol.)[7] Errors are obtained from a block analysis,[23] plotting calculated standard deviations of the mean as a function of the number of blocks used. The reported error is then the plateau value reached in the limit of long blocks with typically more than about 10 000 Monte Carlo passes.

The system size dependence of the virial and thermodynamic pressure is shown in Fig. 1. From Table I and Fig. 1, we find that p_V and p_T converge to the same value of about -5 MPa (1 MPa=10 bar) for large system sizes, with a statistical error of about 2 MPa. This convergence is expected, as the thermodynamic and virial pressure should be identical in the thermodynamic limit. However, the thermodynamic pressure exhibits a considerably weaker system size dependence than the virial pressure. The thermodynamic pressure for as few as 64 SPC/E water molecules is in agreement with large system sizes. The virial pressure, on the other hand, scales as roughly $1/N^2$ for small to intermediate system sizes, with its value off by about one order of magnitude for $N = 64$. We emphasize that for typical system sizes of $N \geq 256$, the virial and thermodynamic pressures are identical within statistical errors for SPC/E water under standard conditions.

Figure 2 shows the radial distribution functions of water oxygens and hydrogens, which were calculated also in the

corners of the kubic simulation box with appropriate weights. We find that the radial distribution functions for $N \geq 64$ water molecules are practically indistinguishable, whereas the $N=16$ and $N=32$ simulations are somewhat more structured beyond the first peaks. These slight structural differences could explain the deviations of the thermodynamic pressure for those small system sizes. We caution that these are results for the specific thermodynamic state (room temperature and standard density) studied here, and we expect more pronounced finite-size effects, e.g., for low densities.

In constant pressure simulations,[27,28] the box volume is rescaled according to the ''instantaneous pressure'' obtained from individual configurations by omitting the canonical average $\langle \cdots \rangle$ in the pressure formulas above. It is therefore important that not only the average but also the instantaneous pressure driving the volume fluctuations be correct. As measures of discrepancy between the virial and thermodynamic pressures p_V and p_T, we use the correlation coefficient r and the average absolute deviation minus the deviation of the averages, Δ,

$$r = \frac{\langle (p_T - \langle p_T \rangle)(p_V - \langle p_V \rangle) \rangle}{\langle (p_T - \langle p_T \rangle)^2 \rangle^{1/2} \langle (p_V - \langle p_V \rangle)^2 \rangle^{1/2}}, \tag{35a}$$

$$\Delta = \langle |p_T - \langle p_T \rangle - p_V + \langle p_V \rangle| \rangle, \tag{35b}$$

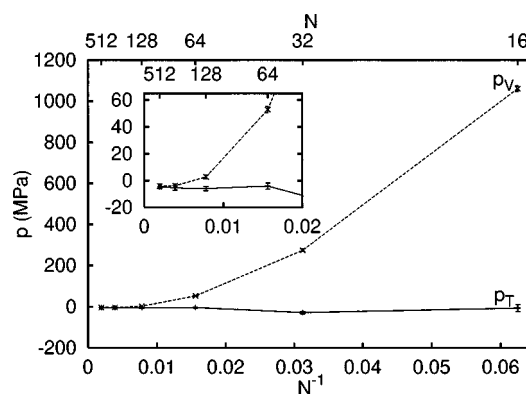

FIG. 1. Pressure of SPC/E water as a function of the inverse number of water molecules, $1/N$. Cross symbols and dashed lines correspond to the virial pressure p_V. Plus symbols and solid lines show the results for the thermodynamic pressure p_T. The inset highlights results for larger system sizes, $N \geq 64$. Error bars indicate one standard deviation of the mean, estimated from a block error analysis.
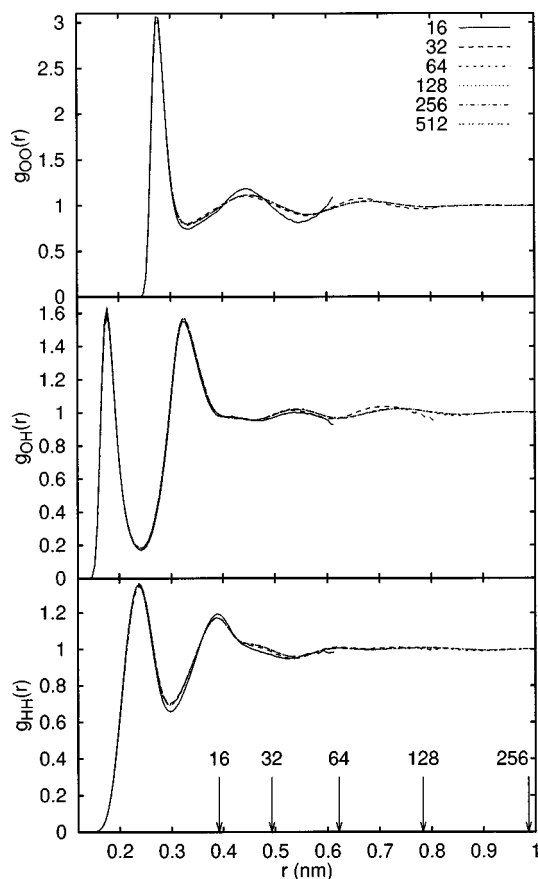
FIG. 2. Radial distribution functions of water atoms. Oxygen–oxygen (top panel), oxygen–hydrogen (middle panel), and hydrogen–hydrogen (bottom panel) radial distribution functions are shown for different numbers of water molecules. Arrows indicate half the box length, $r = L/2$, for different system sizes. The radial distribution functions were calculated for distances beyond $L/2$ using appropriate weights.

where instantaneous pressures p_T and p_V are used. Results for r and Δ are listed in Table I. The cross-correlation coefficient r indicates strong correlation, with r values between 0.90 and 0.997 for $N = 16$ to $N = 512$. However, the average absolute deviation Δ between the two pressures is significant even for systems of 512 water molecules, scaling approximately as $\Delta \sim 1/N$. Therefore, in constant pressure simulations, the use of the thermodynamic pressure appears advantageous.

In an earlier study of pressure effects on the stability of hydrophobic aggregates in water,[29] we determined the thermodynamic pressure of SPC water[30] as a function of density using Eq. (32). For the temperature and density studied here ($T = 298$ K, $\rho = 33.33$ nm^{-3}), we found a pressure of about 37 ± 6 MPa for SPC water. From the density dependence of the pressure, we determined a compressibility factor $\rho k_B T \chi_T \approx 0.06$ for SPC water, where χ_T is the isothermal compressibility. That compressibility factor is in excellent agreement with the experimental value of 0.062.

VI. CONCLUSIONS

We have derived a simple, compact expression for the Coulomb contribution to the thermodynamic pressure in a system treated with Ewald lattice summation. For a system

of point ions, we recover the well-known relation between the pressure and potential energy. We then derive an expression for the pressure in a system of rigid molecules carrying point charges. The pressure in such a system can be calculated from the total energy and the forces at each site alone. This makes the implementation of that pressure formula trivial, because both energy and forces are produced routinely in molecular dynamics codes. Moreover, these formulas are entirely independent of the particular method used to resum the Coulomb interactions. Ewald summation, particle-mesh Ewald,[2] kubic-harmonic expansions,[3] and Lekner sums[4–6] can be used readily. For approximate reaction-field methods,[24–26] expressions for the pressure are suggested by analogy.

We have compared the thermodynamic pressure, obtained from the volume dependence of the Helmholtz free energy, with the mechanistic virial pressure. We find that for rigid SPC/E water at standard conditions, the two pressures are approximately equal (within errors of about 2 MPa) for systems larger than $N = 256$ water molecules. For smaller systems, the virial pressure exhibits a pronounced system-size dependence, whereas the thermodynamic pressure can be calculated accurately by using as few as 64 SPC/E water molecules.

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