

On the determination of orientational configurational temperature from computer simulation

A. A. Chialvo^{a)}

Chemical and Analytical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6110 and Department of Chemical Engineering, University of Tennessee, Knoxville, Tennessee 37996-2200

J. M. Simonson

Chemical and Analytical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6110

P. T. Cummings

Departments of Chemical Engineering, Chemistry, and Computer Science, University of Tennessee, Knoxville, Tennessee 37996-2200 and Chemical Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6268

P. G. Kusalik

Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, B3H 4J3, Canada

(Received 23 October 2000; accepted 31 January 2001)

A straightforward derivation for the configurational temperature associated with the orientational Ω^N portion of the configurational phase space of the molecules in an open system is presented. Explicit relationships are given for determining the configurational temperatures in classical simulations of molecular liquids, such as water, and their forms and their evaluation discussed.
© 2001 American Institute of Physics. [DOI: 10.1063/1.1357792]

INTRODUCTION

The temperature of an equilibrium system has been almost exclusively studied through the average kinetic energy associated with the translational and rotational degrees of freedom of their molecules.¹ However, the recent publication of Rugh² on the dynamical approach to thermodynamics highlighted alternative ways to define the temperature of a closed system, in terms of configurational properties in the microcanonical ensemble, and opened the door to the development of new tools for the validation and testing of new simulation strategies, and for the interpretation and analysis of systems away from equilibrium.

The distinction between kinetic and configurational temperatures might appear as a mere academic curiosity. However, there are numerous simulation scenarios where either the control or evaluation of the kinetic temperature is not possible,³ or the systems under study are far from equilibrium.⁴ Moreover, there is always the need for new tools to check the validity or self-consistency of simulation algorithms⁵ and the configurational temperature provides one of the few consistency tests available for Monte Carlo simulation.

Typically, the constants of motion are the targets for testing the validity and accuracy of the integration approach in the simulation of dynamical systems. Yet, the conservation of these quantities is not always a necessary or sufficient condition for either accuracy⁶ or correctness⁷ of the algorithm. Nondynamical simulations, such as Monte Carlo techniques, do not involve conserved quantities, and conse-

quently we need tools to test the validity of strategies used not only for the random translational,⁵ but also for orientational moves⁸ regarding the principles of microscopic reversibility⁹ and the most general infinitesimal rotation.¹⁰

A subtler situation may arise when dealing with metastable systems such as supercooled liquids or glasses, for which the configurational/orientational relaxation times become large.¹¹ For these (or any) systems, the most general thermodynamic definition of the temperature will involve the derivative $(\partial E/\partial S)_{V,N}$, where both the entropy, S , and energy, E , will depend on all the microscopic degrees of freedom (kinetic and configurational) of the system. While the motion of individual particles within these systems might be consistent with the desired temperature (the measure of the time-average kinetic energy), the corresponding averages over configurational (translational and orientational) degrees of freedom may not. This scenario might become more complex at low temperature and high density because of the possible coupling between translational and orientational degrees of freedom in supercooled liquids,¹² which might hinder the expected energy equipartition.

Yet, there are other compelling reasons behind our desire to assess the temperature of a system by analyzing average configurational measures rather than averages over the kinetic degrees of freedom. For instance, in the validation of microstructural information from x ray, electron, and neutron scattering spectra by means of reverse Monte Carlo techniques we require ways to diagnose the correctness of the procedure used in the processing and test the internal consistency of the raw data.³ Moreover, many researchers would like to be able to estimate the temperature of a system based

^{a)} Author to whom correspondence should be addressed.

on configurational information gathered from those spectra.¹³

As a first step toward the achievement of these goals, in a recent paper we revived an earlier theoretical development, the so-called *hypervirial theorem* developed by Hirschfelder,¹⁴ as a well-suited tool to make possible the molecular simulation route to *positional and orientational* configurational-temperatures.⁸ We implemented their calculation and reported results for a simple quadrupolar Lennard-Jones system at normal conditions and for the TIP4P water model at low temperature. In the present communication we present an alternative derivation of an expression to determine the orientational configurational temperature for open systems, and discuss its evaluation in a standard computer (MD or MC) simulation of a molecular liquid.

ORIENTATIONAL CONFIGURATIONAL TEMPERATURE

As recently indicated by Baranyai,¹⁵ the expression derived by Butler *et al.*⁵ for the configurational (translational) temperature does not apply to open systems (i.e., systems in phase equilibria, etc.), and consequently this author proposed a simpler derivation that fulfilled that condition. In this section we take Baranyai's approach, and derive the corresponding expression for the configurational orientational (as opposed to configurational translational) temperature of an open system, an analysis that parallels the corresponding hypervirial derivation given by Gray and Gubbins.¹⁶

We start with the expression of the instantaneous rotational kinetic temperature of a d -dimensional system, composed of N rigid molecules with $g \equiv dN$ degrees of freedom, i.e.,

$$T_{\text{rot}} \equiv \frac{\sum_{i=1}^N \boldsymbol{\omega}_i \cdot \mathbf{I}_i \cdot \boldsymbol{\omega}_i}{gk} = \frac{\sum_{i=1}^N \mathbf{L}_i \cdot \mathbf{I}_i^{-1} \cdot \mathbf{L}_i}{gk}, \quad (1)$$

where we use the conventional notation k , \mathbf{I}_i , \mathbf{L}_i , and $\boldsymbol{\omega}_i$ to denote Boltzmann constant, the tensor of inertia, the angular momentum, and the angular velocity of molecule i , respectively. By assuming isokinetic conditions, the first and second time derivatives of the instantaneous temperature are

$$\dot{T}_{\text{rot}} = \frac{2 \sum_{i=1}^N \boldsymbol{\omega}_i \cdot \dot{\mathbf{L}}_i}{gk} = 0, \quad (2)$$

and

$$\begin{aligned} \ddot{T}_{\text{rot}} &= \frac{2 \sum_{i=1}^N \dot{\mathbf{L}}_i \cdot \mathbf{I}_i^{-1} \cdot \dot{\mathbf{L}}_i + 2 \sum_{i=1}^N \boldsymbol{\omega}_i \cdot \ddot{\mathbf{L}}_i}{gk} \\ &= \frac{2 \sum_{i=1}^N \boldsymbol{\tau}_i \cdot \mathbf{I}_i^{-1} \cdot \boldsymbol{\tau}_i + 2 \sum_{i=1}^N \boldsymbol{\omega}_i \cdot \dot{\boldsymbol{\tau}}_i}{gk} = 0, \end{aligned} \quad (3)$$

respectively, where $\dot{\mathbf{L}}_i \equiv \boldsymbol{\tau}_i$ is the rotational equation of motion, and the upper dot (dots) over any quantity represents a first (higher) time derivative. The first time-derivative of the instantaneous temperature gives no additional information beyond the well-known fact that the angular velocity and corresponding torque are perpendicular to each other, i.e., not only the summation, but also each term in the summation of Eq. (2) must be identically zero.

The second term on the right-hand side of Eq. (3) can be written explicitly as

$$\begin{aligned} \boldsymbol{\omega}_i \cdot \dot{\boldsymbol{\tau}}_i &= \boldsymbol{\omega}_i \cdot \sum_j \left(\sum_{\alpha=\Omega_x, \Omega_y, \Omega_z} (\partial \boldsymbol{\tau}_i / \partial \alpha_j) \cdot (\partial \alpha_j / \partial t) \right. \\ &\quad \left. + \sum_{\alpha=x, y, z} (\partial \boldsymbol{\tau}_i / \partial \alpha_j) \cdot (\partial \alpha_j / \partial t) \right) \\ &= \boldsymbol{\omega}_i \cdot \left(\sum_j \boldsymbol{\omega}_j \cdot \nabla_{\Omega_j} \boldsymbol{\tau}_i + \mathbf{p}_j \cdot \sum_j \nabla_{r_j} \boldsymbol{\tau}_i \right). \end{aligned} \quad (4)$$

For systems in equilibrium, the components along the three positional (r_α) and orientational (Ω_α) axes are equivalent, the linear and angular momenta are not correlated, while the positions and orientations are not correlated with their corresponding gradients (forces and torques). Therefore, from Eqs. (3)–(4) we have that

$$0 = \left\langle \sum_{i=1}^N \boldsymbol{\tau}_i \cdot \mathbf{I}_i^{-1} \cdot \boldsymbol{\tau}_i \right\rangle + \left\langle \sum_{i=1}^N \boldsymbol{\omega}_i \cdot \sum_{j=1}^N \boldsymbol{\omega}_j \cdot \nabla_{\Omega_j} \boldsymbol{\tau}_i \right\rangle, \quad (5)$$

which can also be written as

$$0 = \left\langle \sum_{i=1}^N \mathbf{I}_i^{-1} : \boldsymbol{\tau}_i \boldsymbol{\tau}_i \right\rangle + \left\langle \sum_{i=1}^N \sum_{j=1}^N \mathbf{L}_i \mathbf{L}_j : \mathbf{I}_i^{-2} \nabla_{\Omega_j} \boldsymbol{\tau}_i \right\rangle. \quad (6)$$

Note that, for a particular configuration, the only contribution to the average in the second term of Eq. (6) is for $i = j$, because there is no correlation between the angular momenta of different molecules, i.e.,

$$\begin{aligned} 0 &= \langle \mathbf{I}_i^{-1} : \boldsymbol{\tau}_i \boldsymbol{\tau}_i \rangle + kT \langle \mathbf{I}_i : \mathbf{I}_i^{-2} \nabla_{\Omega_i} \boldsymbol{\tau}_i \rangle \\ &= \langle \boldsymbol{\tau}_i \cdot \boldsymbol{\tau}_i \rangle + kT \langle \nabla_{\Omega_i} \boldsymbol{\tau}_i \rangle. \end{aligned} \quad (7)$$

In Eq. (7) we have invoked the fact that the inertia tensor is the same for all molecules, and that $\overline{\mathbf{L}_i \mathbf{L}_i} = kT \mathbf{I}_i$, where the bar indicates an average over all particles for a particular configuration. Finally, from Eq. (7) and the fact that $\boldsymbol{\tau} = -\nabla_{\Omega} \phi$ we obtain the final expression for the orientational configurational temperature,

$$kT_{\text{rot}} = -\langle \boldsymbol{\tau}_i^2 \rangle / \langle \nabla_{\Omega_i} \boldsymbol{\tau}_i \rangle = \langle (\nabla_{\Omega_i} \phi)^2 \rangle / \langle \nabla_{\Omega_i}^2 \phi \rangle, \quad (8)$$

which is precisely the same expression as that derived from Hirschfelder's hypervirial theorem.

SIMULATION IMPLEMENTATION AND FINAL REMARKS

Starting from expression (8), where $\phi(r^N, \Omega^N)$ is a potential depending on distance (r) and orientation (Ω), we have the angular gradient operator $\nabla_{\Omega}(\cdots) \equiv \mathbf{I} \times \nabla_r(\cdots)$, which defines the torque $\boldsymbol{\tau}$,

$$\nabla_{\Omega} \phi \equiv \mathbf{I} \times \nabla_r \phi = -\boldsymbol{\tau}. \quad (9)$$

In Eq. (9) the operator “ \times ” denotes cross-product of two vectors, and $\mathbf{I} = l_x \hat{i} + l_y \hat{j} + l_z \hat{k}$ is the vector position of molecular sites with respect to the corresponding center of mass. Thus, the divergence of the torque becomes

$$\nabla_{\Omega} \cdot \boldsymbol{\tau} = -\nabla_{\Omega} \cdot \nabla_{\Omega} \phi = -\nabla_{\Omega}^2 \phi, \quad (10)$$

where $\nabla_{\Omega}^2(\dots)$ is the angular Laplacian. Consequently, the orientational temperature, Eq. (8), can be represented as

$$\begin{aligned} kT_{\text{rot}} &= \langle \boldsymbol{\tau}^2 \rangle / \langle \nabla_{\Omega}^2 \phi \rangle \\ &= -\langle \boldsymbol{\tau}^2 \rangle / \langle \nabla_{\Omega} \cdot \boldsymbol{\tau} \rangle \\ &= \langle \boldsymbol{\tau}^2 \rangle / \langle (\mathbf{I} \times \nabla_r) \cdot (\mathbf{I} \times \nabla_r \phi) \rangle, \end{aligned} \quad (11)$$

where the angular Laplacian of the intermolecular potential, $\nabla_{\Omega}^2 \phi = (\mathbf{I} \times \nabla_r) \cdot (\mathbf{I} \times \nabla_r \phi)$, can be written more explicitly by solving the two cross-products, as follows:

$$(\mathbf{I} \times \nabla_r) = \begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ l_x & l_y & l_z \\ \partial/\partial x & \partial/\partial y & \partial/\partial z \end{vmatrix}, \quad (12)$$

$$\begin{aligned} \mathbf{I} &= l_x \hat{i} + l_y \hat{j} + l_z \hat{k} \\ &= (l_y \partial/\partial z - l_z \partial/\partial y) \hat{i} + (l_z \partial/\partial x - l_x \partial/\partial z) \hat{j} \\ &\quad + (l_x \partial/\partial y - l_y \partial/\partial x) \hat{k}, \end{aligned}$$

and

$$\begin{aligned} (\mathbf{I} \times \nabla_r \phi) &= - \begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ l_x & l_y & l_z \\ f_x & f_y & f_z \end{vmatrix}, \quad \nabla_r \phi = -f_x \hat{i} - f_y \hat{j} - f_z \hat{k}, \\ &= -(l_y f_z - l_z f_y) \hat{i} - (l_z f_x - l_x f_z) \hat{j} - (l_x f_y - l_y f_x) \hat{k}, \end{aligned} \quad (13)$$

where $f_x = -(\partial\phi/\partial x)$ is the x -component of the force \mathbf{f} . Therefore, the denominator of Eq. (11) becomes

$$\begin{aligned} (\mathbf{I} \times \nabla_r) \cdot (\mathbf{I} \times \nabla_r \phi) &= -(l_y \partial/\partial z - l_z \partial/\partial y)(l_y f_z - l_z f_y) - (l_z \partial/\partial x - l_x \partial/\partial z)(l_z f_x - l_x f_z) - (l_x \partial/\partial y - l_y \partial/\partial x)(l_x f_y - l_y f_x) \\ &= -l_y^2(\partial f_z/\partial z + \partial f_x/\partial x) - l_z^2(\partial f_y/\partial y + \partial f_x/\partial x) - l_x^2(\partial f_z/\partial z + \partial f_y/\partial y) + l_x l_z(\partial f_x/\partial z + \partial f_z/\partial x) \\ &\quad + l_y l_z(\partial f_y/\partial z + \partial f_z/\partial y) + l_y l_x(\partial f_y/\partial x + \partial f_x/\partial y) + 2(l_x f_x + l_y f_y + l_z f_z). \end{aligned} \quad (14)$$

For the sake of completeness, we introduce the corresponding positional (translational) configurational temperature, T_{trans} , whose expression has been derived either from the hypervirial theorem⁸ or from Baranyai's approach,¹⁵ i.e.,

$$\begin{aligned} kT_{\text{trans}} &= \langle (\nabla_r \phi)^2 \rangle / \langle \nabla_r^2 \phi \rangle \\ &= -\langle \mathbf{f}^2 \rangle / \langle \nabla_r \cdot \mathbf{f} \rangle, \end{aligned} \quad (15)$$

and

$$\begin{aligned} \nabla_r \cdot \mathbf{f} &= -[(\partial f_x/\partial x) + (\partial f_y/\partial y) + (\partial f_z/\partial z)] \\ &= -2(\partial\phi/\partial r)/r - (\partial^2\phi/\partial r^2). \end{aligned} \quad (16)$$

To make these working expressions more explicit, let us consider the two types of interactions that we might usually find in a typical water model [such as the SPC (Ref. 17) or TIP4P (Ref. 18) model for water], i.e., involving electrostatic and Lennard-Jones potentials. For $\phi(r) = q_i q_j / r_{ij}$, where q_i denotes a point charge on the site i and $r_{ij} = r$ is the distance between the pair of sites i, j ,

$$\begin{aligned} f_x &= q_i q_j x / r^3 \rightarrow \partial f_x / \partial x = -q_i q_j (3x^2 / r^5) + f_x / x \\ &\rightarrow \partial f_x / \partial y = -q_i q_j (3xy / r^5) = \partial f_y / \partial x, \end{aligned} \quad (17)$$

and analogously, for y and z -components. Finally, from Eq. (16),

$$\nabla_r^2 (q_i q_j / r) = 0, \quad (18)$$

and hence this Laplacian will be similarly equal to zero for any multipolar interaction.

Note that, if we use a reaction field approach for the electrostatic interactions, with a reaction field dielectric ϵ_{rf} and a cut-off radius r_c , i.e.,

$$\phi(r) = q_i q_j (1/r - (\epsilon_{rf} - 1)r^2 / (2\epsilon_{rf} + 1)r_c^3),$$

then

$$\begin{aligned} f_x &= q_i q_j x (1/r^3 + 2(\epsilon_{rf} - 1)/(2\epsilon_{rf} + 1)r_c^3) \\ &\rightarrow \partial f_x / \partial x = -q_i q_j (3x^2 / r^5) + f_x / x \\ &\rightarrow \partial f_x / \partial y = -q_i q_j (3xy / r^5), \end{aligned} \quad (19)$$

and Eq. (18) becomes automatically satisfied if we recall that the molecule's electroneutrality is implicitly fulfilled, i.e., $\sum_{\alpha, \beta} q_{\alpha}^{\alpha} q_{\beta}^{\beta} = 0$. Obviously, the corresponding Ewald sum expressions might be determined in a straightforward manner.

Otherwise, for the Lennard-Jones potential $\phi(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$ we have that,

$$\begin{aligned} f_x &= \epsilon[48(\sigma^{12}/r^{14}) - 24(\sigma^6/r^8)]x \\ &\rightarrow \partial f_x / \partial x = -\epsilon[672(\sigma^{12}/r^{16}) - 192(\sigma^6/r^{10})]x^2 + f_x / x \\ \partial f_x / \partial y &= -\epsilon[672(\sigma^{12}/r^{16}) - 192(\sigma^6/r^{10})]xy = \partial f_y / \partial x, \end{aligned} \quad (20)$$

and

$$\nabla_r^2 \phi(r) = \epsilon[528(\sigma^{12}/r^{14}) - 120(\sigma^6/r^8)]. \quad (21)$$

Note that according to Eqs. (17)–(21), only short-ranged (nonharmonic) potentials contribute to the positional Laplacian, and consequently, to the definition of the positional configurational temperature [Eq. (15)]. In contrast, both short- and long-ranged potentials contribute to the angular Laplacian in the definition of the orientational configurational temperature [Eq. (8)]. This feature, in principle, suggests that the translational and orientational configurational temperatures would exhibit different dependence on the range of the inter-

molecular potential acting on the molecules of the system. Consequently, we might also expect they would exhibit different relaxation behavior.⁸

According to the previous analysis [Eqs. (8) and (15)] both configurational temperatures are defined in terms of the ratio between two independent averages. These averages are taken over the number of particles and over the trajectory in the phase space. Yet, we can define an instantaneous temperature, average only over the N -particles constituting the system.¹⁶ Finally we can average that instantaneous temperature as usual, over the phase space trajectory. This means that we can replace the ratio of two averages by the average of the ratio, i.e.,

$$T = \frac{\langle \xi \rangle_{N,t}}{\langle \zeta \rangle_{N,t}} \rightarrow T = \left\langle \frac{\xi}{\zeta} \right\rangle_t \quad (22)$$

by invoking the following identity in the thermodynamic limit;¹⁹

$$\left\langle \frac{1}{\zeta} \right\rangle = \frac{\left\langle \frac{1}{1 + \delta\zeta} \right\rangle}{\langle \zeta \rangle} \approx \frac{\langle 1 - \delta\zeta + (\delta\zeta)^2 \dots \rangle}{\langle \zeta \rangle} \quad (23)$$

with $\delta\zeta = (\zeta - \langle \zeta \rangle) / \langle \zeta \rangle$, where $\langle \xi \rangle_{N,t}$ and $\langle \zeta \rangle_{N,t}$ are the numerator and k -times the denominator of the right-hand side of either Eq. (8) or (15) for a finite system of size N . Therefore, Eq. (23) reduces to

$$\left\langle \frac{\xi}{\zeta} \right\rangle = \left\langle \frac{1}{\zeta} \right\rangle \langle \xi \rangle \quad (24)$$

by assuming that the numerator and denominator are not correlated (independent). Thus, according to Eqs. (23)–(24),

$$\left\langle \frac{\xi}{\zeta} \right\rangle = \frac{\langle 1 - \delta\zeta + (\delta\zeta)^2 \dots \rangle \langle \xi \rangle}{\langle \zeta \rangle} = \frac{\langle 1 + (\delta\zeta)^2 \dots \rangle \langle \xi \rangle}{\langle \zeta \rangle} \quad (25)$$

since $\langle \delta\zeta \rangle = 0$, and finally,

$$T = \frac{\langle \xi \rangle}{\langle \zeta \rangle} \left(\frac{\langle \zeta^2 \rangle}{\langle \zeta \rangle^2} + \dots \right) = \frac{\langle \xi \rangle}{\langle \zeta \rangle} + O(N^{-1}). \quad (26)$$

In the thermodynamic limit,

$$\lim_{N \rightarrow \infty} \frac{\langle \xi \rangle_{N,t}}{\langle \zeta \rangle_{N,t}} = \left\langle \frac{\xi}{\zeta} \right\rangle_t. \quad (27)$$

ACKNOWLEDGMENTS

This research was sponsored by the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences, and by the Environmental Management Science Program (TTP OR17-SP22), under Contract No. DE-AC05-00OR22725 with Oak Ridge National Laboratory, managed and operated by UT-Battelle, LLC. P.T.C. was supported by the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences, U.S. Department of Energy. P.G.K. acknowledges the financial support of the Natural Sciences and Engineering Research Council of Canada. A.A.C. acknowledges fruitful discussions with Dr. Andras Baranyai during the visit to the Department of Theoretical Chemistry at Eötvös University (Budapest, September 2000).

¹D. A. McQuarrie, *Statistical Mechanics* (Harper and Row, New York, 1976).

²H. H. Rugh, *J. Phys. A* **31**, 7761 (1998).

³G. Tóth and A. Baranyai, *Mol. Phys.* **97**, 339 (1999).

⁴G. Ayton, O. G. Jepps, and D. J. Evans, *Mol. Phys.* **96**, 915 (1999).

⁵B. D. Butler, G. Ayton, O. G. Jepps, and D. J. Evans, *J. Chem. Phys.* **109**, 6519 (1998).

⁶D. Greenspan, *J. Comput. Phys.* **91**, 490 (1990).

⁷A. R. Tindell, D. J. Tildesley, and J. Walton, *CCP5 Newsletter* **4**, 26 (1982).

⁸A. A. Chialvo, J. M. Simonson, P. G. Kusalik, and P. T. Cummings, in *Proceedings of Foundations of Molecular Modeling and Simulation (FOMMS 2000)*, *AICHE Symposium Series* (to be published).

⁹M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Oxford University Press, Oxford, 1987).

¹⁰V. J. Menon, *Eur. J. Phys.* **21**, 91 (2000).

¹¹S. Sastry, P. G. Debenedetti, F. H. Stillinger, T. B. Schröder, J. C. Dyre, and S. C. Glotzer, *Physica A* **270**, 301 (1999).

¹²C. Theis and R. Schilling, *Phys. Rev. E* **60**, 740 (1999).

¹³H. Heinze, P. Borrmann, H. Stamerjohanns, and E. R. Hilf, *Z. Phys. D: At., Mol. Clusters* **40**, 190 (1997).

¹⁴J. O. Hirschfelder, *J. Chem. Phys.* **33**, 1462 (1960).

¹⁵A. Baranyai, *J. Chem. Phys.* **112**, 3964 (2000).

¹⁶C. G. Gray and K. E. Gubbins, *Theory of Molecular Fluids* (Oxford University Press, Oxford, 1985).

¹⁷H. J. C. Berendsen, J. P. M. Postma, W. F. van Gunsteren, and J. Hermans, in *Intermolecular Forces: Proceedings of the Fourteenth Jerusalem Symposium on Quantum Chemistry and Biochemistry*, edited by B. Pullman (Reidel, Dordrecht, 1981), pp. 331–342.

¹⁸W. L. Jorgensen, J. Chandrasekhar, J. D. Madura, R. W. Impey, and M. L. Klein, *J. Chem. Phys.* **79**, 926 (1983).

¹⁹E. M. Pearson, T. Halicioglu, and W. A. Tiller, *Phys. Rev. A* **32**, 3030 (1985).