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Correspondence between configurational temperature and molecular kinetic temperature thermostats

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Molecular fluids undergoing shear flow are often modeled using a homogeneous nonequilibrium molecular dynamics algorithm. To reach a steady state, this method must be used in conjunction with a thermostating mechanism which duplicates the heat dissipation in the experimental setup (e.g., by conduction to the shearing boundaries). The most commonly used type of thermostat involves fixing the center of mass kinetic (c.m.) temperature. Though perfectly valid, this approach does not seem to be the most realistic for a *molecular* fluid since heat is removed only through the 3 degrees of freedom of the center of mass for each molecule. The second type of thermostat involves fixing the “atomic” kinetic temperature and therefore takes into account all degrees of freedom. However, since the streaming velocity of atoms within their constituent molecules is unknown, the implementation of such a thermostat is problematic and relies on incorrect assumptions on the streaming velocity of atoms. The recently developed configurational temperature thermostat requires no assumption on the streaming velocity of atoms and takes into account all degrees of freedom. Using a configurational temperature thermostat to thermostat homogeneous shear flow thus seems to be a more realistic approach than the c.m. kinetic thermostat. In this work, we apply this configurational temperature thermostat to the study of linear alkanes (C_{10} and C_{20}) undergoing shear flow. The results so obtained are compared with those obtained using a c.m. kinetic thermostat. Our aims are (1) to test the influence of the total number of degrees of freedom of the system, (2) to make a connection between the results obtained with the two types of thermostats. By carefully examining the energies of the internal modes, we have been able to characterize the loss of accuracy of a c.m. kinetic thermostat at high shear rates and for high molecular weight compounds. Finally, we establish a correspondence between the two types of thermostats by showing that, for the internal modes, a simulation at a fixed c.m. kinetic temperature is equivalent to a simulation at a fixed but higher configurational temperature. © 2002 American Institute of Physics. [DOI: 10.1063/1.1503771]

I. INTRODUCTION

Nonequilibrium molecular dynamics (NEMD) simulation^{1–5} has been often used over recent years to understand and characterize the rheological properties of fluids undergoing shear flow. The homogeneous SLLOD algorithm,⁵ in which the shear rate is introduced in the equations of motion, is now a popular method to determine shear viscosities and to study the effect of shear upon the internal rotation and conformation of molecules in the bulk and in confined liquids.^{5,6,8–19} In homogeneous NEMD, a thermostating mechanism is required to mimic the natural ways by which heat is dissipated—conduction, convection, and radiation—i.e., duplicate the natural thermostating mechanisms. The results obtained by Liem *et al.*⁷ showed the validity of this homogeneous approach to model a fluid undergoing shear flow. They studied an atomic fluid sheared by two thermostated atomic walls and compared the results so obtained to those obtained using a homogeneously thermostated shear flow algorithm. They found that both methods yield indistin-

guishable results up to the maximum flow rates that are possible in a wall thermostated system⁷ and concluded that the homogeneously thermostated SLLOD algorithm was a satisfactory description of atomic fluids undergoing shear flow for low and moderate flow rates.

Thermostating molecular (both rigid and deformable) fluids undergoing shear flow is much more complex. Two mechanisms are commonly used in conjunction with the SLLOD algorithm. The first and only technique that is known to be valid even in the zero shear rate limit involves thermostating the center of mass translational peculiar kinetic energy^{8–14} If local thermodynamic equilibrium is valid, this quantity is clearly related to the local thermodynamic temperature. However, in a system composed of flexible M -atom molecules, the center of mass (c.m.) kinetic temperature only thermostats 3 out of the possible $3M$ degrees of freedom per molecule. For molecules of high molecular weight, the unthermostated degrees of freedom become progressively hotter than the thermostated degrees of freedom as the molecular weight is increased with the strain rate held fixed. This has the effect of reducing the range of shear rates over which the c.m. kinetic thermostat is accurate as the molecular weight is increased. The second kind of thermostat involves

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thermostating the atomic translational peculiar kinetic energy.^{15–19} Such an “atomic” thermostat takes into account all degrees of freedom. However, while the streaming velocity profile of the center of mass is known—that is the imposed linear profile provided that the shear rate is not too extreme⁵—and applying a c.m. kinetic thermostat is straightforward, the streaming velocity profile for each atom within a molecule undergoing shear flow is not known. It is therefore assumed^{15–19} that the streaming velocity of an atom in a molecular flow is the same as the streaming velocity of the center of mass of a molecule which would be located at the position of the atom. Let us consider the example of a rigid diatomic molecule. The streaming velocity of each atom is the sum of the streaming velocity of the center of mass and a contribution due to the streaming angular velocity of the molecule. The difference between the streaming velocities of the two atoms of the same molecule is therefore always perpendicular to the molecular axis. If we assume that each atom has the same linear velocity profile as the center of mass, this difference will be perpendicular to the molecular axis only if the molecule is parallel to the direction of the flow. This example shows that the assumption regarding the streaming velocity of the atoms is incorrect. Such “atomic” kinetic thermostats have the spurious effect of exerting an average torque on molecules which in turn restricts the shear induced rotation of the molecules.¹⁷

Recent work has shown that the thermodynamic temperature can be evaluated solely from configurational information.^{20–24} In these configurational expressions, the temperature is computed from the first and the second spatial derivatives of the intermolecular potential energy. Using a configurational expression for the temperature to thermostat a system under shear allows one to directly take into account all degrees of freedom for a molecule, without making the incorrect assumption mentioned previously about the streaming velocity of the atoms of a molecular fluid, and seems a more realistic way to mimic the heat dissipation.

In previous work,^{25,26} we proposed and applied a Nosé–Hoover thermostating mechanism based on a configurational expression for the temperature. The results so obtained were compared to those obtained using a Gaussian molecular kinetic thermostat based on the center of mass translational peculiar kinetic energy. We showed that both types of thermostats yielded identical system properties at low strain rates, i.e., close to equilibrium. We only observed significant differences far from equilibrium where the values taken by the two expressions for the temperature differ most. Our aims are (1) to test the influence of the total number of degrees of freedom of the system, (2) to make a connection between the results obtained with the two types of thermostats. In this paper, we present the results of isochoric isothermal (NVT) SLLOD simulations of decane and eicosane undergoing shear flow with the two different thermostating mechanisms. We compare the results obtained using the two types of thermostats. In particular, we carefully examine the influence of the thermostating mechanism on the energies of the internal modes for both molecules. We then attempt to make a correspondence between the two thermostating schemes.

II. SIMULATION TECHNIQUE AND MODEL

Since the method and the model used in this work are the same as the ones used in a previous work,²⁶ we only briefly describe the two thermostating mechanisms and the model. First, a Gaussian isokinetic c.m. thermostat was used to fix the temperature calculated from the momenta of the centers of mass of the molecules. In this case, the NVT-SLLOD equations of motion are⁵

$$\dot{\mathbf{r}}_{i\alpha} = \frac{\mathbf{p}_{i\alpha}}{m_\alpha} + \gamma y_i \cdot \mathbf{e}_x, \quad (1a)$$

$$\dot{\mathbf{p}}_{i\alpha} = \mathbf{F}_{i\alpha}^N + \mathbf{F}_{i\alpha}^C - \frac{\gamma p_{yi} m_\alpha}{M} \mathbf{e}_x - \frac{\xi m_\alpha}{M} \mathbf{p}_i, \quad (1b)$$

where $\mathbf{r}_{i\alpha}$ ($\mathbf{p}_{i\alpha}$) stands for the position (respectively, momentum) of center of force α of molecule i , $\mathbf{F}_{i\alpha}^N$ ($\mathbf{F}_{i\alpha}^C$) is the Newtonian force (respectively the constraint force) acting on α , m_α the mass corresponding to the center of force α , γ the imposed strain rate, $\mathbf{e}_x$ is a unit vector, parallel to the direction of the flow, y_i (p_{yi}) the coordinate (respectively, component of the momentum) along the y axis, $\mathbf{p}_i$ the momentum of molecule i and ξ the thermostating multiplier. The thermostating multiplier and the constraint forces are determined by applying Gauss' principle of least constraint.⁵

Second, a thermostat based on a configurational expression for the temperature was used to thermostat decane undergoing shear flow. This thermostat is devised in analogy with the Nosé–Hoover thermostat²⁷ (full details are given elsewhere²⁵): An extended system, with an additional degree of freedom s , is considered and the configurational temperature is maintained using an integral feedback mechanism. However, since the configurational temperature is evaluated from the positions and not from the momenta, the thermostating term is included in the $\dot{\mathbf{r}}_{i\alpha}$ equation instead of the $\dot{\mathbf{p}}_{i\alpha}$ equation. We have the following NVT-SLLOD equations of motion:^{25,26}

$$\dot{\mathbf{r}}_{i\alpha} = \frac{\mathbf{p}_{i\alpha}}{m_\alpha} + \gamma y_i \cdot \mathbf{e}_x + \frac{s}{T_0} \cdot \frac{\partial T_{\text{conf}}}{\partial \mathbf{r}_{i\alpha}} + (\mathbf{R} \cdot \xi)_{i\alpha}, \quad (2a)$$

$$\dot{\mathbf{p}}_{i\alpha} = \mathbf{F}_{i\alpha}^N + \mathbf{F}_{i\alpha}^C - \frac{\gamma p_{yi} m_\alpha}{M} \mathbf{e}_x, \quad (2b)$$

$$\dot{s} = -Q_{Tc} \cdot \frac{(T_{\text{conf}} - T_0)}{T_0}, \quad (2c)$$

where T_0 is the input temperature, T_{conf} the configurational temperature and Q_{Tc} a damping constant [$Q_{Tc} = \sigma^2 / \tau_{Tc}^2$ with τ_{Tc} the response time of the feedback mechanism]. T_{conf} is evaluated at each time step through the following first-order expression:²³

$$\frac{1}{k_B T_{\text{conf}}} = \sum_i \sum_{\alpha, \alpha' \in i} \left\langle \frac{1}{\Delta} \frac{\partial}{\partial \mathbf{r}_{i\alpha}} \cdot \frac{\partial H_0}{\partial \mathbf{r}_{i\alpha'}} \right\rangle, \quad (3)$$

where k_B is the Boltzmann constant, H_0 the internal energy of the system, α and α' label the two atoms belonging to the same molecule i and Δ is defined as

FIG. 1. Deviation from the equilibrium value of the averaged intermolecular energy per molecule vs shear rate. Open squares (respectively, open triangles) are results obtained using a Gaussian isokinetic c.m. thermostat for decane (respectively, eicosane) and closed squares (respectively, closed triangles) are results obtained using a configurational temperature thermostat for decane (respectively, eicosane).

$$\Delta = \sum_i \sum_{\alpha, \alpha' \in i} \frac{\partial H_0}{\partial \mathbf{r}_{i\alpha}} \cdot \frac{\partial H_0}{\partial \mathbf{r}_{i\alpha'}}. \quad (4)$$

Since the thermostating term is not the same for all atoms belonging to the same molecule, one has to add a term, $(\mathbf{R} \cdot \xi)_{i\alpha}$, to Eq. (2a) to ensure that the molecular constraints (i.e., a constant bond length) are still satisfied (this term is given in Ref. 26). Finally we add that other mechanisms can be used to fix the configurational temperature.²⁸

Simulations are carried out for systems of 108 molecules. The simulated state point is ($T=298$ K, $\rho=0.7246$ g cm⁻³) for decane and ($T=333$ K, $\rho=0.773$ g cm⁻³) for eicosane. The model²⁹ used in this work has been shown to predict quantitatively the viscosity of liquid decane, hexadecane, and tetracosane.^{15,16} It is an united atom model, i.e., methyl and methylene groups are treated as single Lennard-Jones interaction sites located at the center of carbon atoms. A spherical cutoff of 9.825 Å is used and usual tail corrections are added.³⁰ The intramolecular interactions consist of nonbonded Lennard-Jones interactions, bond angle bending, and torsion potentials. Nonbonded Lennard-Jones interactions take place between two united atoms within the same molecule if they are separated by more than three chemical bonds. The bond angle bending potential is a harmonic function of the bond angle and the torsion potential is a Fourier series of the dihedral angle. In the remainder of the paper, simulation parameters (time step and shear rate) are given in reduced units with respect to the parameters of the CH₂ group and simulation results are given in real units. The equations of motion are integrated using a reduced time step of 5×10^{-4} in all cases. The value of the damping constant for the configurational temperature Q_{Tc} is set to 10.0 (i.e., $\tau_{Tc}=0.316$).

III. RESULTS AND DISCUSSION

We showed in previous work^{25,26} that both types of thermostats yielded identical system properties at low strain rates, i.e., close to equilibrium. We also observed that the shear viscosity and the shear alignment angle remained identical within statistical uncertainties until very far from equilibrium ($\gamma^* \geq 1.5$). However, we showed that the various con-

tributions to the total interaction energy were much more sensitive to the type of thermostat used:²⁶ significant differences can be observed for shear rates $\gamma^* \geq 0.5$. In this section, we focus on the influence of the thermostating mechanism on the various contributions to the total interaction energy as the shear rate increases.

Figure 1 shows the variation of the intermolecular energy with the shear rate. The averaged intermolecular energy increases slightly and steadily with the shear rate. At a given shear rate $\gamma^*=1.5$ and with a Gaussian isokinetic c.m. thermostat, the increase is 6.4% for decane and 13.4% for eicosane compared to the equilibrium value. With a configurational temperature thermostat, these values differ from the equilibrium value by, respectively, 5.8% for decane and 8% for eicosane (the uncertainty being of 0.5%). Differences between the two thermostating mechanisms are only significant far from equilibrium ($\gamma^* \geq 0.7$) for eicosane and farther from equilibrium for decane ($\gamma^* \geq 1.25$). We then plot in Figs. 2 and 3 the variation of the bending and torsion potential energy, respectively, with the shear rate. Both plots show that for $\gamma^* > 0.5$, regardless of the alkane studied, using a Gaussian isokinetic c.m. thermostat yields much higher internal potential energy than at equilibrium whereas using a configurational temperature thermostat maintains the intramolecular potential energy closer to its equilibrium value. At $\gamma^*=1.5$, the increase in the bending potential energy is 43% for decane and 98% for eicosane compared to the equilibrium value. With a configurational temperature thermostat, these values differ from the equilibrium value by, respectively, 1% for decane and 15% for eicosane (the uncertainty being of 2%). Similar features are observed for the torsion potential energy. At $\gamma^*=1.5$, the increase in the torsion potential energy is 19% for decane and 36% for eicosane compared to the equilibrium value. With a configurational temperature thermostat, these values differ from the equilibrium value by, respectively, 11% for decane and 16% for eicosane (the uncertainty being of 1%). We finally add that we also observe similar features for the third type of intramolecular energy, i.e., the nonbonded Lennard-Jones interactions between united atoms more than three bonds apart within the same molecule. For instance, for eicosane, at $\gamma^*=1.5$, the increase in the non-

FIG. 2. Deviation from the equilibrium value of the averaged bending energy per molecule vs shear rate. Same legend as in Fig. 1.

bonded intramolecular energy is 9% (T_{kin} fixed) and 3% (T_{conf} fixed) compared to the equilibrium value.

In a nonequilibrium system entropy production occurs in all the degrees of freedom. However a Gaussian thermostat only extracts heat from the three center of mass translational degrees of freedom in each molecule. These translational degrees of freedom are thermostated at the correct temperature. The temperature of all the other degrees of freedom is controlled by the rate at which energy in those modes can migrate to the three center of mass translational degrees of freedom. The noncenter of mass degrees of freedom will be hotter than the center of mass degrees of freedom. The temperature difference will increase if the molecular weight of the molecules is increased keeping all other intensive properties fixed. On the other hand, the configurational thermostat removes heat from all the degrees of freedom in a molecular fluid. Thus there is no opportunity for large temperature differences in different degrees of freedom to occur. This is expected to be much closer to what happens in nature where heat conduction, for example, will be expected to remove heat from all degrees of freedom and not simply from the c.m. translational degrees of freedom. At low shear rates ($\gamma^* \leq 0.5$ for eicosane and $\gamma^* \leq 0.7$ for decane) there are no

differences between the results obtained using the two different types of thermostating mechanisms. The global heating rates which asymptotically are quadratic functions of the shear rate are sufficiently low that temperature inhomogeneities in the c.m. thermostating method do not have a chance to develop.

We now attempt to establish a correspondence between the two types of thermostating mechanisms. We first consider one of the systems we have studied in the first part of this section: eicosane at a given shear rate $\gamma^* = 1.5$ with a c.m. kinetic temperature fixed at $T_{\text{kin}} = 333$ K (experiment 1). We measure for this system the averaged configurational temperature $T_{\text{conf}} = 565$ K. We then perform a simulation of the same system—eicosane at a shear rate $\gamma^* = 1.5$ —using a configurational temperature thermostat set with an input temperature $T_0 = 565$ K (experiment 2). The resulting bond angle and the dihedral angle distributions are plotted in Figs. 4 and 5. We also plot in Figs. 4 and 5 the distributions obtained using a configurational temperature thermostat set with an input temperature $T_0 = 333$ K for the same system (experiment 3). Accordingly with the results plotted in Figs. 2 and 3, both angle distributions obtained using the two types of thermostats set with the same input temperature $T_0 = 333$ K

FIG. 3. Deviation from the equilibrium value of the averaged torsion energy per molecule vs shear rate. Same legend as in Fig. 1.

FIG. 4. Distribution of the bond angle for eicosane undergoing shear flow at a given shear rate of $\gamma^*=1.5$. Open triangles (respectively, closed triangles) are results obtained using a Gaussian isokinetic c.m. thermostat (respectively, a configurational temperature thermostat) at a fixed temperature of 333 K. The dotted line is the distribution obtained using a configurational temperature thermostat at a fixed temperature of 565 K.

(experiments 1 and 3) significantly differ. When using a Gaussian c.m. isokinetic thermostat, the internal degrees of freedom heat up considerably allowing molecules to access higher intramolecular potential energies as shown by the broader bond angle distribution (Fig. 4) and by the dihedral angle distribution (Fig. 5) than when using a configurational temperature thermostat. Figures 4 and 5 also show that the bond angle and the dihedral angle distributions obtained using a c.m. kinetic thermostat at $T_0=333$ K (experiment 1) are in excellent agreement with the ones obtained using a configurational temperature thermostat at $T_0=565$ K (experiment 2). As experiments 1 and 2 have the same effect on the internal degrees of freedom of the molecules, performing a simulation at a fixed c.m. kinetic temperature can be interpreted as performing a simulation at a fixed—and higher—configurational temperature. Moreover, this higher value of the configurational temperature is known: it is the actual configurational temperature of the system when run at a fixed c.m. kinetic temperature. This result enables us to draw two conclusions. First, this result shows the loss of accuracy of the c.m. kinetic thermostat as the shear rate increases since the internal degrees of freedom are much hotter than the desired temperature. This is due to the few degrees of free-

FIG. 5. Distribution of the dihedral angle for eicosane undergoing shear flow at a given shear rate of $\gamma^*=1.5$. Same legend as in Fig. 4.

dom such a thermostat actually controls. It should be noted that this problem will become progressively worse as the molecular weight increases. Second, it enables us to establish a correspondence between the results obtained using a c.m. kinetic thermostat and those obtained using a configurational temperature thermostat. This correspondence is imperfect since it is limited to the internal degrees of freedom (as in c.m. kinetic thermostated systems, the 3 thermostated degrees of freedom are maintained to the desired—much lower—temperature). However, we expect this correspondence to become more and more exact as the molecular weight increases—making the effect of thermostating 3 degrees of freedom per molecule negligible.

IV. CONCLUSIONS

We have applied two different thermostating schemes to decane and eicosane undergoing shear flow in *NVT-SLLOD* simulations. First, we have used a Gaussian isokinetic thermostat to fix the c.m. kinetic temperature. Such a thermostat assumes that solely thermostating the center of mass translational degrees of freedom is satisfactory. Second, we have applied a configurational temperature thermostat to this system. The configurational temperature is evaluated from the first and second derivatives of the potential energy and accounts for internal as well as translational degrees of freedom. Intuitively, we expect that this should be a closer approximation to a real experiment where heat conduction to remote boundaries removes heat from all degrees of freedom of a molecule—not just from the center of mass translational degrees of freedom. We show that for both molecules, the results obtained using the two thermostats are very similar to each other for the low shear rates. However, as soon as the shear rate is higher than 0.5, the response of the internal degrees of freedom strongly depends on the thermostating mechanism. Using Gaussian isokinetic thermostat yields to a significant increase in the intramolecular potential energy, this effect being even more significant and appearing for lower shear rates as the total number of degrees of freedom of the molecules increases. This increase in the temperature disparity between the internal modes and the c.m. kinetic temperature is not surprising since c.m. kinetic thermostats only remove heat from the c.m. modes. All the other modes become increasingly hotter as either the shear rate or the molecular weight increase. A configurational temperature thermostat removes heat from all the internal degrees of freedom, leading to greatly reduced increases. Finally, by showing that a simulation run at T_{kin} fixed gives very similar results for the internal modes as a simulation run with T_{conf} fixed—where $T_{\text{conf}} \gg T_{\text{kin}}$!—we have been able to quantify the loss of accuracy of the c.m. kinetic thermostat at high shear rates and to establish a correspondence between the results obtained using a c.m. kinetic thermostat and those obtained using a configurational temperature thermostat.

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- ¹A. W. Lees and S. F. Edwards, J. Phys. Ser. C **5**, 1921 (1972).
²W. T. Ashurst and W. G. Hoover, Phys. Rev. A **11**, 658 (1975).
³G. Ciccotti and A. Tenenbaum, J. Stat. Phys. **23**, 767 (1980); A. Tenenbaum, G. Ciccotti, and R. Gallico, Phys. Rev. A **25**, 2778 (1982).
⁴K. Singer, J. V. L. Singer, and D. Fincham, Mol. Phys. **40**, 515 (1980).
⁵D. J. Evans and G. P. Morriss, Phys. Rev. A **30**, 1528 (1984).
⁶D. J. Evans and G. P. Morriss, *Statistical Mechanics of Nonequilibrium Liquids* (Academic, London, 1990), <http://rsc.anu.edu.au/~evans/evansmorrissbook.htm>.
⁷S. Y. Liem, D. Brown, and J. H. R. Clarke, Phys. Rev. A **45**, 3706 (1992).
⁸R. Edberg, G. P. Morriss, and D. J. Evans, J. Chem. Phys. **86**, 4555 (1987).
⁹S. Chynoweth, U. C. Klomp, and Y. Michopoulos, J. Chem. Phys. **95**, 3024 (1991).
¹⁰A. Berker, S. Chynoweth, U. C. Klomp, and Y. Michopoulos, J. Chem. Soc., Faraday Trans. **88**, 1719 (1992).
¹¹P. Padilla and S. Toxvaerd, J. Chem. Phys. **97**, 7687 (1992).
¹²P. J. Davis and D. J. Evans, J. Chem. Phys. **100**, 541 (1994).
¹³W. Allen and R. L. Rowley, J. Chem. Phys. **106**, 10273 (1997).
¹⁴R. Khare, J. de Pablo, and A. Yethiraj, J. Chem. Phys. **107**, 6956 (1997).
¹⁵C. J. Mundy, J. I. Siepmann, and M. L. Klein, J. Chem. Phys. **103**, 10192 (1995).
¹⁶S. T. Cui, P. T. Cummings, and H. D. Cochran, J. Chem. Phys. **104**, 255 (1996).
¹⁷K. P. Travis, P. J. Davis, and D. J. Evans, J. Chem. Phys. **103**, 10638 (1995); **105**, 3893 (1996); K. P. Travis and D. J. Evans, Mol. Simul. **17**, 157 (1996).
¹⁸S. T. Cui, S. A. Gupta, P. T. Cummings, and H. D. Cochran, J. Chem. Phys. **105**, 1214 (1996).
¹⁹M. J. Stevens, M. Mondello, G. S. Grest, S. T. Cui, H. D. Cochran, and P. T. Cummings, J. Chem. Phys. **106**, 7303 (1997).
²⁰H. H. Rugh, Phys. Rev. Lett. **78**, 772 (1997); J. Phys. A **31**, 7761 (1998).
²¹B. D. Butler, G. Ayton, O. G. Jepps, and D. J. Evans, J. Chem. Phys. **109**, 6519 (1998); G. Ayton, O. G. Jepps, and D. J. Evans, Mol. Phys. **96**, 915 (1998).
²²O. G. Jepps, G. Ayton, and D. J. Evans, Phys. Rev. E **62**, 4757 (2000).
²³L. Lue and D. J. Evans, Phys. Rev. E **62**, 4764 (2000).
²⁴J. Delhommelle and D. J. Evans, J. Chem. Phys. **114**, 6229 (2001); **114**, 6236 (2001).
²⁵L. Lue, O. G. Jepps, J. Delhommelle, and D. J. Evans, Mol. Phys. **14**, 2387 (2002).
²⁶J. Delhommelle and D. J. Evans, J. Chem. Phys. **115**, 43 (2001); Mol. Phys. **99**, 1825 (2001).
²⁷W. G. Hoover, Phys. Rev. A **31**, 1695 (1985).
²⁸O. G. Jepps (private communication).
²⁹B. Smit, S. Karaborni, and J. I. Siepmann, J. Chem. Phys. **102**, 2126 (1995).
³⁰M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Oxford University Press, Oxford, 1987).