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Comparison of thermostatting mechanisms in NVT and NPT simulations of decane under shear

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Nonequilibrium molecular dynamics (NEMD) simulations play a major role in characterizing the rheological properties of fluids undergoing shear flow. However, all previous studies of flows in *molecular* fluids either use an “atomic” thermostat which makes incorrect assumptions concerning the streaming velocity of atoms within their constituent molecules, or they employ a center of mass kinetic (COM) thermostat which only controls the temperature of relatively few degrees of freedom (3) in complex high molecular weight compounds. In the present paper we show how recently developed configurational expressions for the thermodynamic temperature can be used to develop thermostatting mechanisms which avoid both of these problems. We propose a thermostat based on a configurational expression for the temperature and apply it to NEMD simulations of decane undergoing Couette flow at constant volume and at constant pressure. The results so obtained are compared with those obtained using a COM kinetic thermostat. At equilibrium the properties of systems thermostatted in the two different ways are of course equivalent. However, we show that the two responses differ far from equilibrium. In particular, we show that the increase in the potential energy of the internal modes with increasing shear is only observed with a Gaussian isokinetic COM thermostat in both NVT and NPT simulations. There is no such increase with the configurational thermostat, which, unlike the Gaussian isokinetic COM thermostat, correctly accounts for the internal degrees of freedom of the molecular fluid. © 2001 American Institute of Physics.
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I. INTRODUCTION

Nonequilibrium molecular dynamics (NEMD) simulation, particularly the SLLOD algorithm,¹ has been often used over recent years to understand and characterize the rheological properties of fluids undergoing shear flow. The SLLOD algorithm has been applied to determine the shear viscosities of molecular fluids such as alkanes with a statistical precision which is superior to that obtainable from Green–Kubo techniques.^{2–5} Nonequilibrium algorithms like SLLOD enable us to easily study the effects of shear upon the internal rotations and conformations of molecules, something which is extraordinarily difficult using Green–Kubo techniques.

In NEMD, a thermostatting mechanism is required to duplicate the effects of natural thermostatting mechanisms—conduction, convection, and radiation. A comparison between atomic simulations employing thermostatted atomic walls and a homogeneously thermostatted shear flow algorithm⁶ has shown that both methods yield indistinguishable results up to the maximum low rates that are possible in the wall thermostatted system.

Homogeneous thermostats should yield correct equilibrium and linear nonequilibrium regime (i.e., close to equilibrium) properties. Further from equilibrium these fictitious homogeneous thermostats should not exert any net forces or in the case of molecular fluids, torques, on the fluid particles. For atomic fluids in both the linear and weakly nonlinear regimes, Nosé–Hoover and various Gaussian thermostats have been proven to have these properties. In the extreme

nonlinear regime profile unbiased thermostats (PUT) are available.¹ For molecular fluids (both rigid and deformable molecules), the situation is much less satisfactory. The only technique that is known to be valid even in the zero shear rate limit involves thermostatting the center of mass translational peculiar kinetic energy. 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 COM kinetic temperature only monitors 3 out of the possible 3M degrees of freedom per molecule. For molecules of high molecular weight, the unthermostatted degrees of freedom become progressively hotter than the thermostatted 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 COM kinetic thermostat is accurate as the molecular weight is increased.

The second kind of molecular thermostat that has occasionally been used is a molecular thermostat based on an incorrect assumption about the streaming velocity of atoms within molecules which are subject to shear flows. This “atomic” thermostat assumes 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 is located at the position of the atom. Because of the streaming rotation induced in molecules by a shear flow, this assumption is incorrect and the use of “atomic” thermostats for molecular flows is known to exert an average torque on molecules

which in turn restricts the shear induced rotation of the molecules.⁷

In this work, we propose a thermostat based on a configurational expression for the temperature. Recent work has shown that the thermodynamic temperature can be evaluated solely from configurational information.^{8–12} In these configurational expressions, the temperature is computed from the first and the second spatial derivatives of the intermolecular potential energy. The application of a configurational expression to thermostat nonequilibrium systems seems promising since such a thermostat requires no assumption about the streaming velocity of the fluid. Moreover, in the case of molecular fluids, all degrees of freedom are directly taken into account by this approach. In this paper, we present the results of isochoric isothermal (NVT) and isobaric isothermal (NPT) SLLOD simulations of decane undergoing shear flow with two different thermostating mechanisms. First, a commonly used Gaussian molecular kinetic thermostat is applied. Second, simulations are run with a Nose–Hoover configurational temperature thermostat. Results obtained using two types of thermostats are compared with each other.

II. GAUSSIAN ISOKINETIC AND CONFIGURATIONAL TEMPERATURE THERMOSTAT

Two mechanisms were used in this work to thermostat liquid decane undergoing shear flow. First, a Gaussian isokinetic COM thermostat was used to fix the temperature calculated from the momenta of the centers of mass of the decane molecules. In this case, the NVT–SLLOD equations of motion are¹

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

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

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) of the center of mass of molecule i along the y axis, $\mathbf{p}_i$ the momentum of molecule i and ξ the thermostating multiplier.

The thermostating multiplier is determined by applying Gauss' principle of least constraint:¹

$$\xi = \frac{\sum_i (\mathbf{F}_i \cdot \mathbf{p}_i - \gamma \cdot p_{xi} \cdot p_{yi})}{\sum_i \mathbf{p}_i^2}. \quad (2)$$

The constraint forces, which ensure that the bond lengths are constant, are also determined by applying Gauss' principle (the constraint forces are given in the Appendix).

Second, a thermostat based on a configurational expression for the temperature was used to thermostat decane undergoing shear flow. We only briefly present the thermostat-

ting mechanism (full details will be given elsewhere¹³). This thermostat is devised in analogy with the Nose–Hoover thermostat:¹⁴ 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:

$$\dot{\mathbf{r}}_{i\alpha} = \frac{\mathbf{p}_{i\alpha}}{m_\alpha} + \gamma y_i \cdot \mathbf{e}_x + \frac{s}{T_0} \cdot \frac{\partial T_{\text{conf}}}{\partial \mathbf{r}_{i\alpha}} + (\mathbf{R} \cdot \boldsymbol{\xi})_{i\alpha}, \quad (3a)$$

$$\dot{\mathbf{p}}_{i\alpha} = \mathbf{F}_{i\alpha}^N + \mathbf{F}_{i\alpha}^C - \frac{\gamma p_{yi} m_\alpha}{M} \mathbf{e}_x, \quad (3b)$$

$$\dot{s} = -Q_{Tc} \cdot \frac{(T_{\text{conf}} - T_0)}{T_0}, \quad (3c)$$

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 timestep through the following first-order expression:^{12,15}

$$\frac{1}{k_B T_{\text{conf}}} = \sum_i \sum_{\alpha, \alpha' \in i} \left\langle \frac{1}{\Delta} \frac{\partial}{\partial \mathbf{r}_{i\alpha}} \cdot \frac{\partial H_0}{\partial \mathbf{r}_{i\alpha'}} \right\rangle, \quad (4)$$

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

$$\Delta = \sum_i \sum_{\alpha, \alpha' \in i} \frac{\partial H_0}{\partial \mathbf{r}_{i\alpha}} \cdot \frac{\partial H_0}{\partial \mathbf{r}_{i\alpha'}}. \quad (5)$$

Since the thermostating term is not the same for all atoms belonging to the same molecule, one has to add a term, $(\mathbf{R} \cdot \boldsymbol{\xi})_{i\alpha}$, to Eq. (3a) to ensure that the molecular constraints (i.e., a constant bond length) are still satisfied (this term is given in the Appendix). Finally we add that other mechanisms can be used to fix the configurational temperature.¹⁶

We use a Nose–Hoover integral feedback to keep the pressure fixed for both types of thermostats. Since the same barostat mechanism is employed in both cases, we only give the equations of motion for a Gaussian isokinetic COM thermostat. In that case, the NPT–SLLOD equations of motion are²

$$\dot{\mathbf{r}}_{i\alpha} = \frac{\mathbf{p}_{i\alpha}}{m_\alpha} + \gamma y_i \cdot \mathbf{e}_x + \dot{\epsilon} \mathbf{r}_i, \quad (6a)$$

$$\dot{\mathbf{p}}_{i\alpha} = \mathbf{F}_{i\alpha}^N + \mathbf{F}_{i\alpha}^C - \frac{\gamma p_{yi} m_\alpha}{M} \mathbf{e}_x - \frac{\xi m_\alpha}{M} \mathbf{p}_i - \frac{m_\alpha}{M} \dot{\epsilon} \mathbf{p}_i \quad (6b)$$

with the additional equation for the volume,

$$\dot{V} = 3 \epsilon V \quad (6c)$$

and where the multiplier $\dot{\epsilon}$ is found by solving the differential equation:

TABLE I. NVT simulation results using a COM isokinetic Gaussian thermostat (T_{kin} fixed) and a configurational temperature thermostat (T_{conf} fixed) (numbers in the parentheses represent the statistical uncertainty in the least significant digits).

γ^* ($\epsilon/m\sigma^2$) ^{1/2}	T_{conf} (K) (T_{kin} fixed)	T_K (K) (T_{conf} fixed)	P (bar) (T_{kin} fixed)	P (bar) (T_{conf} fixed)	Order parameter (T_{kin} fixed)	Order parameter (T_{conf} fixed)
0.1	475(1)	490(2)	122 (9)	149 (9)	0.07	0.05
0.2	478(1)	489(2)	125 (9)	142 (9)	0.13	0.13
0.3	483(2)	490(2)	138(11)	169 (8)	0.16	0.10
0.5	493(2)	504(2)	175 (9)	200 (7)	0.26	0.22
0.7	506(1)	526(2)	252 (6)	253(12)	0.29	0.27
1	533(2)	556(3)	372 (9)	384(10)	0.33	0.33
1.25	563(1)	596(1)	525 (6)	474(13)	0.37	0.34
1.5	591(1)	630(7)	658 (4)	597(20)	0.35	0.39

$$\ddot{\epsilon} = \frac{(p - p_0)V}{Q_P N k_B T}. \quad (6d)$$

In (6d), p is equal to one-third of the trace of the pressure tensor $\mathbf{P}$, p_0 is the input pressure, V is the volume, and Q_P is a damping constant for the pressure fluctuations ($Q_P = 1/\tau_P^2$ with τ_P the response time of the feedback mechanism). $\mathbf{P}$ is calculated in the molecular representation, in which the molecular momentum density is assumed to be localized at the molecular center of mass.

The thermostat multiplier is obtained by applying Gauss' principle

$$\xi = \frac{\sum_i (\mathbf{F}_i \cdot \mathbf{p}_i - \gamma \cdot p_{xi} \cdot p_{yi})}{\sum_i \mathbf{p}_i^2} - \dot{\epsilon}. \quad (7)$$

Since the barostat term applied on each site is the same, the constraint forces have the same expression as in NVT–SLLOD case.

III. SIMULATION DETAILS

A realistic model used for decane¹⁷ has been shown to predict quantitatively the viscosity of liquid decane.^{3,18,19} 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. Nonbonded interactions take place between two united atoms of different molecules or within the same molecule if the two sites are separated by more than three chemical bonds Lennard-Jones parameters are $\epsilon_{\text{CH}_2} = 47$ K, $\epsilon_{\text{CH}_3} = 114$ K, and $\sigma_{\text{CH}_2} = \sigma_{\text{CH}_3} = 3.93$ Å. Unlike pair potential parameters are determined using the Lorentz–Berthelot combining rules. A spherical cutoff of 9.825 Å is used and the usual tail corrections are added.²⁰

The model also accounts for bond bending and torsion interactions:

$$U^{\text{bend}}(\theta) = \frac{1}{2} k_\theta (\theta - \theta_0)^2, \quad (8)$$

$$U^{\text{tors}}(\phi) = 0.5c_1(1 + \cos \phi) + 0.5c_2(1 - \cos 2\phi) + 0.5c_3(1 + \cos 3\phi), \quad (9)$$

where θ is the angle between the three united atoms, $k_\theta = 62\,500$ K rad⁻² the bending constant, $\theta_0 = 114^\circ$ the equilibrium angle, ϕ the dihedral angle, and $c_1 = 355$ K, $c_2 = 68.19$ K, and $c_3 = 791.3$ K are the torsion parameters. The

C–C bond length is constrained to be equal to 1.54 Å. Masses are $m_{\text{CH}_2} = 14$ g mol⁻¹ and $m_{\text{CH}_3} = 15$ g mol⁻¹. In the remainder of the paper, we give our results in the same system of units as Cui *et al.*:¹⁹ simulation parameters (timestep 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.

NVT–SLLOD simulations with 108 decane molecules are carried out at $T = 480$ K and $\rho = 0.6136$ g cm⁻³. The equilibrium value of the pressure for this state point (112 ± 10 bar) is used as the input pressure in the NPT–SLLOD simulations. We note that this value is in good agreement with the findings of Cui *et al.*¹⁹ (116 ± 6 bar using the atomic formalism and 126 ± 6 bar using the molecular formalism to compute the pressure tensor) and Mundy *et al.*¹⁸ (111 bar using the atomic formalism). The equations of motion are integrated using a reduced timestep of 5×10^{-4} for the Gaussian isokinetic thermostat. In the case of the configurational temperature thermostat, the equations of motion are found to be stiffer because of the large variations of the thermostating term $\partial T_{\text{conf}} / \partial \mathbf{r}_{i\alpha}$ over small distances. A reduced timestep of 1×10^{-4} is used to integrate the equations of motion for a configurational temperature thermostat. The value of the damping constant for the configurational temperature Q_{T_c} is set to 10.0 (i.e., $\tau_{T_c} = 0.316$). The damping constant for the pressure oscillation Q_P was set to 10.0 (i.e., $\tau_P = 0.316$). The results presented in this paper are averaged over runs of about 200 time units at high shear rates (≥ 0.3) and about 400 time units for the lowest shear rates.

IV. RESULTS AND DISCUSSION

The molecular kinetic temperature, when the configurational temperature is fixed, and the configurational temperature, when a Gaussian isokinetic COM thermostat is used, are given in Table I for NVT–SLLOD simulations and in Table II for NPT–SLLOD simulations. As expected, the two definitions for the temperature (and the two thermostating mechanisms) yield similar results at low shear rates. When T_{conf} is fixed, T_{kin} increases monotonically with γ ; conversely when T_{kin} is fixed T_{conf} increases monotonically with γ^* . However, in both cases the differences between the two temperatures is insignificant until $\gamma^* \geq 1.0$. Similar features are observed for the hydrostatic pressure with the two thermostating mechanisms in NVT–SLLOD simulations. The

TABLE II. NPT simulation results using a COM isokinetic Gaussian thermostat (T_{kin} fixed) and a configurational temperature thermostat (T_{conf} fixed) (numbers in the parentheses represent the statistical uncertainty in the least significant digits).

γ^* ($\epsilon/m\sigma^2$) ^{1/2}	T_{conf} (K) (T_{kin} fixed)	T_K (K) (T_{conf} fixed)	V/V_{eq} (T_{kin} fixed)	V/V_{eq} (T_{conf} fixed)	Order parameter (T_{kin} fixed)	Order parameter (T_{conf} fixed)
0.1	477(1)	491(3)	1.005	1.012	0.06	0.05
0.2	479(1)	487(3)	1.008	1.011	0.12	0.12
0.3	480(2)	494(3)	1.009	1.016	0.16	0.17
0.5	494(1)	506(1)	1.038	1.034	0.23	0.21
0.7	506(2)	526(1)	1.045	1.051	0.26	0.23
1	539(1)	551(1)	1.083	1.091	0.27	0.27
1.25	570(1)	582(7)	1.140	1.120	0.28	0.29
1.5	615(2)	620(4)	1.201	1.150	0.27	0.30

values taken by the pressure for the two thermostats only differ significantly for the two higher shear rates studied in this work: for $\gamma^* \geq 1.25$, the pressure of the system at T_{kin} fixed is larger than the pressure of the system at T_{conf} fixed by more than 10%. As reported previously,^{2,18} the phenomenon of “shear dilatancy” is observed in NPT simulations as the strain rate is increased: the density of the system decreases in order to keep the pressure constant. This “shear dilatancy” can be described by a power law of the form:

$$\frac{\rho_0 - \rho}{\rho_0} = a \gamma^{*b}, \quad (10)$$

where ρ (respectively, ρ_0) is the density of the system for a shear rate of γ^* (respectively, at equilibrium) and a and b are two fitting parameters. We have fitted this equation to the two sets of data obtained with each type of thermostat: only densities obtained with a significant change of volume, i.e., for $\gamma^* \geq 0.5$, were considered in the fit. We find an exponent $b = 1.78 \pm 0.02$ for the Gaussian isokinetic COM thermostat. This value is in excellent agreement with the findings of Daivis and Evans² ($b = 1.76 \pm 0.04$) for a simplified model of *n*-decane using the Weeks–Chandler–Anderson (WCA) soft spheres to describe intermolecular interaction, i.e., neglecting the attractive interactions. Mundy *et al.*¹⁸ obtained a rather different value of the exponent $b = 1.16$ with the same potential model and the same state point as in this work. They attributed the difference between this value and the value obtained in Ref. 2 to the difference in the potentials. Since we obtain a value of b close to the one of Ref. 2 with the same potential as in Ref. 18, we believe this calculation shows that the difference is not due to differences in potential models as claimed in Ref. 18 but rather to a different algorithm used to compute and maintain pressure: as in Ref. 2, we use a molecular pressure tensor unlike Mundy *et al.*¹⁸ who used an atomic pressure tensor. The exponent b takes a lower value ($b = 1.31 \pm 0.07$) for the configurational temperature thermostat. This is consistent with the NVT–SLLOD results which show that, for a given shear rate ($\gamma^* \geq 1$), the pressure takes lower value when T_{conf} is fixed than when T_{kin} is fixed: the increase in volume to keep the pressure fixed will be less important with a configurational temperature thermostat, resulting in a lower value of the exponent b .

The shear viscosity is plotted against shear rate for the four types of simulation performed in this work in Fig. 1. The shear viscosity is obtained from the following expression:

$$\eta_+ = - \frac{\langle \mathbf{P}_{xy} \rangle + \langle \mathbf{P}_{yx} \rangle}{2\gamma}. \quad (11)$$

We also plot the results obtained by Cui *et al.*¹⁹ using an atomic Nose–Hoover thermostat in a NVT–SLLOD simulation. An atomic thermostat is incorrect and has the spurious effect of exerting a torque on molecules.⁷ However, as pointed out in Ref. 19, this effect is significant only at higher shear rates ($\gamma^* \geq 2$) than those studied in this work: the results of Cui *et al.*¹⁹ can be reliably used to check our NVT results. (Figure 4 shows a good agreement between our NVT results and those of Cui *et al.*¹⁹) Overall, we observe that the thermostatting mechanism has little influence on the shear viscosity: for both NVT and NPT simulations, results obtained using either a thermostat based on T_{kin} or on T_{conf} are within statistical uncertainties for most of the range of shear rates studied in this work and significant differences only for the highest shear rate in the NVT simulation. We also note that both NVT and NPT simulations exhibit shear thinning,

FIG. 1. Shear viscosity vs strain rate. Open squares (respectively, open triangles) are results obtained using a Gaussian isokinetic COM thermostat in NVT simulations (respectively, NPT) and filled squares (respectively, filled triangles) are results obtained using a configurational temperature thermostat in NVT simulations (respectively, NPT). Open circles are NVT–SLLOD results from Ref. 21 obtained using a Nose–Hoover atomic thermostat.

FIG. 2. Averaged intermolecular energy per molecule vs shear rate. Open squares (respectively, open triangles) are results obtained using a Gaussian isokinetic COM thermostat in NVT simulations (respectively, NPT) and filled squares (respectively, filled triangles) are results obtained using a configurational temperature thermostat in NVT simulations (respectively, NPT). The cross is the energy obtained by equilibrium molecular dynamics.

this phenomenon being more pronounced in the NPT simulations due to the fall in density as the shear rate increases. These findings are consistent with those of Mundy *et al.*¹⁸ Again, in agreement with the shear dilatancy results and most likely because of the different definitions used for pressure, we observe that the NPT simulations performed in this work exhibit less shear thinning than observed in Ref. 18. Finally, we add a comment on the following point: since Mundy *et al.*¹⁸ did not observe the phenomenon of shear thickening in NVT–SLLOD simulations unlike Daivis and Evans,² they suggested that this phenomenon resulted mostly from the use of a Gaussian mechanism instead of a Nose–Hoover mechanism to fix the temperature and not from the differences in potential models. Our results and the comparison of our results with those of Cui *et al.*¹⁹ show that Gaussian and Nose–Hoover mechanisms give the same response: no shear thickening is observed in the range of shear rates investigated in this study whatever thermostatting mechanism is employed.

We now study the effect of the shear rate on the order within the fluid. We first compute the second rank order tensor:

$$\mathbf{S} = \frac{3}{2} \left\langle \frac{1}{N} \sum_i \left(\mathbf{e}_i \cdot \mathbf{e}_i - \frac{1}{3} \mathbf{I} \right) \right\rangle, \quad (12)$$

where $\mathbf{e}_i$ is the unit end-to-end vector of molecule i and $\mathbf{I}$ is the identity second rank tensor. In line with what is usually done for liquid crystals, we define the order parameter as the largest eigenvalue of the order tensor $\mathbf{S}$. The alignment angle can then be defined as the angle between the flow direction and the eigenvector corresponding to the largest eigenvalue of $\mathbf{S}$. Again, no significant difference is observed when a configurational temperature thermostat is used instead of a Gaussian isokinetic COM thermostat. We observe a steady increase of the value of the order parameter in NVT simulations with both thermostats associated with an increased alignment of the fluid with the direction of the shear flow [the alignment angle falls to 19° (respectively, 20°) for the Gaussian (respectively, configurational temperature) thermo-

FIG. 3. Averaged bond-bending potential per molecule vs shear rate (same caption as Fig. 2).

stat at $\gamma^* = 1.5$] and resulting in the phenomenon of shear thinning. The alignment is less important in the NPT simulation [the alignment angle is of 22° (respectively, 24°) for the Gaussian (respectively, configurational temperature) thermostat at $\gamma^* = 1.5$], the fall in density being the most important factor in shear thinning in that case.

Figure 2 shows the variation of the intermolecular energy with the shear rate. The averaged intermolecular energy increases slightly with the shear rate in NVT simulations. When the system is allowed to expand, the increase in the averaged intermolecular energy is much stronger as observed in NPT simulations. Differences between the two thermostatting mechanisms are again only significant far from equilibrium ($\gamma^* = 1.5$).

We then plot in Figs. 3 and 4 the variation of the bending and torsion potential energy, respectively, with the shear rate. Both plots show that for $\gamma^* \geq 0.5$, regardless of the ensemble (NVT or NPT) in which the simulation is performed, using a Gaussian isokinetic COM thermostat yields much higher internal potential energy than at equilibrium whereas using a configurational temperature thermostat approximately maintains the intramolecular potential energy to its equilibrium value. At $\gamma^* = 1.5$, the increase in the bending potential energy is 30% (NVT– T_{kin}) and 32% (NPT– T_{kin}) compared to the equilibrium value. With a configurational temperature thermostat, these values differ from the equilibrium value by, respectively, –2% (NVT– T_{conf})

FIG. 4. Averaged torsion potential energy per molecule vs shear rate (same caption as Fig. 2).

and -3.5% ($\text{NPT}-T_{\text{conf}}$) (the uncertainty being of 3%). This effect can also be monitored by plotting histograms for the bond angle: for a given shear rate ($\gamma^* \geq 0.5$), we observe a broader bond-angle distribution with a Gaussian isokinetic COM thermostat than with a configurational temperature thermostat.

Similar features are observed for the torsion potential energy. At $\gamma^* = 1.5$, the increase in the torsion potential energy is 10% ($\text{NVT}-T_{\text{kin}}$) and 11% ($\text{NPT}-T_{\text{kin}}$) compared to the equilibrium value. With a configurational temperature thermostat, these values differ from the equilibrium value by, respectively, $+2\%$ ($\text{NVT}-T_{\text{conf}}$) and $+1\%$ ($\text{NPT}-T_{\text{conf}}$) (the uncertainty being of 2%). 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. At $\gamma^* = 1.5$, the increase in the nonbonded intramolecular energy is 8% ($\text{NVT}-T_{\text{kin}}$) and 8% ($\text{NPT}-T_{\text{kin}}$) compared to the equilibrium value. With a configurational temperature thermostat, these values differ from the equilibrium value by, respectively, $+3\%$ ($\text{NVT}-T_{\text{conf}}$) and $+2\%$ ($\text{NPT}-T_{\text{conf}}$) (the uncertainty being of 2%). We have checked for the highest shear rate ($\gamma^* = 1.5$) that integrating the NVT-SLLOD equations of motion for a Gaussian isokinetic COM thermostat with a timestep of 1×10^{-4} gave results within statistical uncertainties of those compared with a timestep of 5×10^{-4} . Therefore, the differences observed in the potential energy of the internal—and of high frequency—modes between the results obtained using the two types of thermostats are not due to the higher value of the timestep but are a genuine effect of the choice of the expression of the temperature used to thermostat the system. A Gaussian isokinetic COM thermostat only takes into account the translational degrees of freedom of the molecule. At low shear rates, the system is close enough to equilibrium and the equipartition principle is obeyed. As the shear rate increases, the system is taken further from equilibrium and the equipartition principle breaks down: the internal degrees of freedom heat up allowing molecules to access higher intramolecular potential energies. On the contrary, a configurational temperature thermostat takes into account all degrees of freedom, prevents the internal degrees of freedom from heating up and maintains the intramolecular potential energy of the system under shear close to its equilibrium value. 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.

V. CONCLUSIONS

We have applied two different thermostating schemes to decane undergoing shear flow in NVT-SLLOD and NPT-SLLOD simulations. First, we have used a Gaussian isokinetic thermostat to fix the COM kinetic. 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. We show that for both NVT and NPT simulations, the results (viscosity, shear alignment and intermolecular energy) 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. Whereas the Gaussian isokinetic thermostat yields to a significant increase in the intramolecular potential energy, using a configurational temperature thermostat allows to avoid this effect and ensures that the intramolecular potential energy of the system under shear remains close to its equilibrium value.

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APPENDIX: EXPRESSION OF THE CONSTRAINT TERMS

We first give the expressions of the constraints forces. Let us consider the example of a butane molecule with bond constraints (i.e., three constraints). The constraint forces are given by

$$\mathbf{F}_{i\alpha}^C = \sum_{\alpha'} M_{\alpha\alpha'} \cdot \lambda_{\alpha} \mathbf{r}_{i\alpha' \alpha' + 1}, \quad (\text{A1})$$

where $\mathbf{r}_{i\alpha\alpha} = \mathbf{r}_{i\alpha\alpha} - \mathbf{r}_{i\alpha}$, and $\mathbf{M}$ is the following matrix:

$$\mathbf{M} = \begin{bmatrix} -1 & 0 & 0 \\ 1 & -1 & 0 \\ 0 & 1 & -1 \end{bmatrix}. \quad (\text{A2})$$

The vector of multipliers λ is obtained by solving the following system of equations:

$$\begin{bmatrix} \mathbf{r}_{i12}^2 \left(\frac{1}{m_1} + \frac{1}{m_2} \right) & -\frac{\mathbf{r}_{i12} \cdot \mathbf{r}_{i23}}{m_2} & 0 \\ -\frac{\mathbf{r}_{i12} \cdot \mathbf{r}_{i23}}{m_2} & \mathbf{r}_{i23}^2 \left(\frac{1}{m_2} + \frac{1}{m_3} \right) & -\frac{\mathbf{r}_{i23} \cdot \mathbf{r}_{i34}}{m_3} \\ 0 & -\frac{\mathbf{r}_{i23} \cdot \mathbf{r}_{i34}}{m_3} & \mathbf{r}_{i34}^2 \left(\frac{1}{m_3} + \frac{1}{m_4} \right) \end{bmatrix} \times \begin{bmatrix} \lambda_{i1} \\ \lambda_{i2} \\ \lambda_{i3} \end{bmatrix} = \begin{bmatrix} -(\dot{\mathbf{r}}_{i12})^2 - \mathbf{r}_{i12} \cdot \left(\frac{F_{i2}^N}{m_2} - \frac{F_{i1}^N}{m_1} \right) \\ -(\dot{\mathbf{r}}_{i23})^2 - \mathbf{r}_{i23} \cdot \left(\frac{F_{i3}^N}{m_3} - \frac{F_{i2}^N}{m_2} \right) \\ -(\dot{\mathbf{r}}_{i34})^2 - \mathbf{r}_{i34} \cdot \left(\frac{F_{i4}^N}{m_4} - \frac{F_{i3}^N}{m_3} \right) \end{bmatrix}. \quad (\text{A3})$$

When the configurational temperature thermostat is used, the thermostating term takes a different value for each

atom. A constraint term, $(\mathbf{R} \cdot \boldsymbol{\xi})_{i\alpha}$, is added to Eq. (3a) to ensure that the bonding constraints are still satisfied.

The multiplier vector $\boldsymbol{\xi}$ is determined by expressing the constraint condition for all atoms α ($\alpha \leq 3$) belonging to molecule i :

$$(\mathbf{r}_{i\alpha+1} - \mathbf{r}_{i\alpha}) \cdot (\dot{\mathbf{r}}_{i\alpha+1} - \dot{\mathbf{r}}_{i\alpha}) = 0 \quad (\text{A4})$$

which can be written as

$$\begin{aligned} & \left[\begin{array}{l} \mathbf{r}_{i12} \cdot \left(\left(\frac{\mathbf{p}_{i2}}{m_2} - \frac{\mathbf{p}_{i1}}{m_1} \right) + \frac{s}{T_0} \left(\frac{\partial T_{\text{conf}}}{\partial \mathbf{r}_{i2}} - \frac{\partial T_{\text{conf}}}{\partial \mathbf{r}_{i1}} \right) \right) \\ \mathbf{r}_{i23} \cdot \left(\left(\frac{\mathbf{p}_{i3}}{m_3} - \frac{\mathbf{p}_{i2}}{m_2} \right) + \frac{s}{T_0} \left(\frac{\partial T_{\text{conf}}}{\partial \mathbf{r}_{i3}} - \frac{\partial T_{\text{conf}}}{\partial \mathbf{r}_{i2}} \right) \right) \\ \mathbf{r}_{i34} \cdot \left(\left(\frac{\mathbf{p}_{i4}}{m_4} - \frac{\mathbf{p}_{i3}}{m_3} \right) + \frac{s}{T_0} \left(\frac{\partial T_{\text{conf}}}{\partial \mathbf{r}_{i4}} - \frac{\partial T_{\text{conf}}}{\partial \mathbf{r}_{i3}} \right) \right) \end{array} \right] \\ & + \left[\begin{array}{lll} 2(\mathbf{r}_{i12})^2 & -\mathbf{r}_{i12} \cdot \mathbf{r}_{i23} & 0 \\ -\mathbf{r}_{i12} \cdot \mathbf{r}_{i23} & 2(\mathbf{r}_{i23})^2 & -\mathbf{r}_{i23} \cdot \mathbf{r}_{i34} \\ 0 & -\mathbf{r}_{i23} \cdot \mathbf{r}_{i34} & 2(\mathbf{r}_{i34})^2 \end{array} \right] \cdot \left[\begin{array}{l} \xi_{i12} \\ \xi_{i23} \\ \xi_{i34} \end{array} \right] = 0. \end{aligned} \quad (\text{A5})$$

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