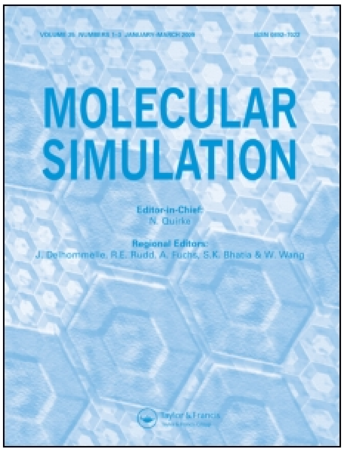

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ON THE RHEOLOGY OF *n*-EICOSANE

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We carry out non-equilibrium molecular dynamics (NEMD) simulations of liquid *n*-eicosane ($C_{20}H_{42}$) undergoing planar Couette flow. We show that a different rheological picture emerges if one uses the standard (but incorrectly formulated) 'atomic' thermostat rather than a thermostat which only couples to the centre of mass translational degrees of freedom. In the latter case eicosane shows shear thinning at low to moderate shear rates and then shear thickening at higher shear rates [G. P. Morriss, P. J. Daivis and Denis J. Evans, *J. Chem. Phys.*, **94**, 7420 (1991)]. However in the atomic thermostatted simulations, eicosane shows only shear thinning across the range of shear rates studied. Moreover in the atomic case, the eicosane molecules are more elongated and spin at a slower rate in the shear plane.

KEY WORDS: Thermostats, alkanes, molecular dynamics, shear.

1 INTRODUCTION

When simulating molecular liquids undergoing a non-equilibrium flow such as planar Couette flow, one must have a mechanism for removing the viscous heat in order to allow relaxation to a non-equilibrium steady state. This can be achieved straightforwardly by appealing to Gauss's principle of least constraint [1]. One adds a frictional term to the equations of motion which is proportional to the peculiar momentum. The constant of proportionality can be determined either by a second application of Gauss's principle of least constraint (differential feedback) [1] or it can be determined by an integral feedback mechanism (the so-called Nosé-Hoover thermostat) [2, 3]. The choice of Gaussian or Nosé-Hoover feedback is purely one of convenience since Evans [4] has proved that the thermostatted nonlinear responses are equivalent for Gaussian and Nosé-Hoover dynamics, arbitrarily far from equilibrium.

An *unbiased* thermostat is a thermostat which does not effect the average streaming velocity (whether translational, rotational or vibrational) of the fluid. This is obviously a desireable property of any thermostat. A second desireable property is that it should thermostat all the degrees of freedom *homogeneously*. If thermostatting is inhomogeneous, the unthermostatted degrees of freedom will, in nonequilibrium systems, become much hotter than the thermostatted degrees of freedom [5] - obviously another undesireable property.

The most difficult aspect of thermostat design is the actual determination of the streaming velocity. For simple fluids undergoing planar Couette flow at low

Reynolds number, the streaming velocity is a linear function of the coordinate parallel to the velocity gradient and therefore the peculiar velocity is trivial to calculate. For molecules, the situation is much more complex. In the past we have frequently thermostatted only the centre of mass translational kinetic energy. The centre of mass streaming velocity is again a simple linear function of the coordinate parallel to the velocity gradient. Thermostatting the centre of mass linear momentum proceeds straightforwardly as for simple atomic fluids. We call this thermostat the centre-of-mass translational (COMT) thermostat. The COMT thermostat is unbiased at low Reynolds number but has the disadvantage of being inhomogeneous. The rotational degrees of freedom are not thermostatted. The problem of inhomogeneity obviously becomes worse as the chain length increases and the relative number of degrees of freedom which are not thermostatted increases.

In the past a number of other authors have employed what has come to be called an atomic thermostat where it is assumed that for planar Couette flow, the streaming velocity of each atom is a linear function of the gradient coordinate, (*i.e.* the streaming velocity evaluated at a site α of molecule i, is simply $\mathbf{i}\gamma z_{i\alpha}$ where γ is the shear rate, $\mathbf{i}$ is a unit vector in the flow direction and $z_{i\alpha}$ is the coordinate of site α of molecule i, in the direction of the velocity gradient).

However it is trivial to see that shear induced molecular rotation is incompatible with the form of the streaming velocity assumed in the 'atomic' thermostat. The 'atomic' thermostat is therefore biased and furthermore because of the use of an incorrect assumed form for the streaming velocity, it is also inhomogeneous. The problems related with using either of these thermostats have been discussed in more detail in our earlier work [6]. In that paper an unbiased homogeneous thermostat valid for fluids composed of rigid molecules was proposed and tested. A homogeneous, unbiased thermostatting scheme suitable for flexible molecules has not yet been devised.

In the present paper we study the rheological properties of liquid *n*-eicosane when the simulations are thermostatted using either the unbiased but inhomogeneous. COMT thermostat or the biased and inhomogeneous atomic thermostat. Eicosane is modelled using the potential model of Morriss *et al.* [7] This molecule posseses vibrational as well as rotational degrees of freedom and as mentioned above there is no unbiased but homogeneous thermostat that is presently available for such systems.

A The SLLOD algorithm for molecular shear flow

The molecular representation of the SLLOD algorithm given by Edberg, Morriss and Evans [8] gives an exact description of adiabatic (*i.e.* unthermostatted) shear flow arbitrarily far from equilibrium. The molecular SLLOD equations of motion combined with an atomic thermostat (MSAT) have the following form for the α^{th} site on molecule i

$$\dot{\mathbf{r}}_{i\alpha} = \frac{\mathbf{p}_{i\alpha}}{m_\alpha} + \mathbf{i}\gamma z_i \tag{1}$$

$$\dot{\mathbf{p}}_{i\alpha} = \mathbf{F}^{N}_{i\alpha} + \mathbf{F}^{C}_{i\alpha} - \frac{m_\alpha}{M_i}\mathbf{i}\gamma p_{zi} - \zeta \mathbf{p}_{i\alpha} \tag{2}$$

where $\mathbf{F}^N$ represents the force due to intersite potentials, and $\mathbf{F}^C$ represents the intramolecular constraint forces. In these equations m is the mass of a site, z_i is the z component of the centre-of-mass of molecule i defined by $\mathbf{r}_i = \sum_\alpha m_\alpha \mathbf{r}_{i\alpha}/\sum_\alpha m_\alpha$, M is the mass of the molecule, **i** is the unit vector in the positive x direction, γ is the strain rate, ζ is the thermostatting multiplier, and p_{zi} is the z component of the momentum of molecule i defined by $\mathbf{p}_i = \sum_\alpha \mathbf{p}_{i\alpha}$. The thermostat keeps the assumed total peculiar kinetic energy fixed. .As mentioned earlier the streaming velocity assumed by this thermostat is incorrect and consequently the 'peculiar' kinetic energy that this algorithm fixes, is not really the peculiar kinetic energy at all. We will henceforth refer to this kinetic energy as the *assumed peculiar kinetic energy*. Traivs *et al.* [6] showed that for rigid diatomics, the streaming angular velocity is a complex unknown funtion of the orientation and geometry of the constituent molecules. They also pointed out that the peculiar kinetic energy assumed by the atomic thermostat is an overestimate of the actual peculiar kinetic energy. This is a consequence of the variational principle [1] for determining the streaming velocity, the peculiar kinetic energy and the kinetic temperature.

B *Alkane model*

Our model for eicosane is identical to the one used by Morriss *et al.* [7]. The model alkane molecules are composed of sites which represent the methyl or methylene groups of the *n*-alkane. For simplicity we assume that all sites have the same mass. The distance between neighbouring sites (the bond length) is fixed at 1.53 Å and the bond angles are fixed at 109.47°, using a next-nearest neighbour distance constraint. For this we have used Gauss's principle of least constraint [1]. A torsional or dihedral potential acts between each pair of methyl or methylene groups that are three sites apart on the *n*-alkane chain. To model this we use a potential function that depends on the dihedral angle ϕ, where $\cos\phi = -(\mathbf{r}_i \times \mathbf{r}_{i+1})\cdot(\mathbf{r}_{i+1} \times \mathbf{r}_{i+2})/|(\mathbf{r}_i \times \mathbf{r}_{i+1})|\ |(\mathbf{r}_{i+1} \times \mathbf{r}_{i+2})|$ and $\mathbf{r}_i$, $\mathbf{r}_{i+1}$ and $\mathbf{r}_{i+2}$ are successive bond vectors. We use a simple truncated power series in the cosine of ϕ for the dihedral potential, $\Phi_{\text{dihedral}}(\phi)/k_B = \sum_{i=0}^{5} a_i \cos^i\phi$, where the values of the set of coefficients $\{a_i\}$ are given by $\{1116, 1462, -1578, -368, 3156, -3788\}$. Sites on different molecules, and sites more than three apart on the same molecule, interact through a modified 12-6 Lennard-Jones potential with parameters $\sigma = 3.923$ Å and $\varepsilon/k_B = 72\,\text{K}$. The Lennard-Jones potential is truncated at its minimum $r/\sigma = 2^{1/6}$, and shifted so that the potential is zero at the point of truncation (this also ensures that the force is zero at the cutoff distance, $r/\sigma = 2^{1/6}$). This potential is often referred to as the WCA potential.

2 SIMULATION DETAILS

Here we present results for the 108 molecule Couette flow system with WCA pair interactions, at a reduced temperature $T^* = k_B T/\varepsilon = 5.0$ and a reduced site number density of $\rho^* = \rho\sigma^3 = 1.537$. The simulations were performed using the 4th order Gear algorithm to integrate the equations of motion, with a reduced time step $t^* = t(\sigma(m/\varepsilon)^{1/2})^{-1}$ of 0.001. Henceforth all quantities will be presented in reduced units and we shall drop the asterisk notation. The simulation runs comprised 200 000 time steps at the lowest shear rate down to 150 000 time steps at the highest shear rate.

A Nosé-Hoover thermostat was employed to determine the value of the thermostatting multiplier, ζ. This is done by supplementing the equations of motion for positions and momenta with an extra equation for the time derivative of this multiplier, $\dot{\zeta} = \xi(T_A(t) - T_t)$, where ξ is an integral feedback constant, $T_A(t)$ is the instantaneous atomic temperature and T_t is the target atomic temperature. In these simulations we use a value for ξ of 20.

3 RESULTS AND DISCUSSION

The zero wave vector atomic pressure tensor, $\mathbf{P}^A$ for molecular liquids is given by

$$\mathbf{P}^A V = \sum_i \frac{\mathbf{p}_i \mathbf{p}_i}{M} + \sum_{i,\alpha} \mathbf{r}_{i\alpha} \mathbf{F}_{i\alpha}^{\text{intra}} - \frac{1}{2} \sum_{i,\alpha,j,\beta} \mathbf{r}_{i\alpha j\beta} \mathbf{F}_{i\alpha j\beta}^{\text{inter}}, \tag{3}$$

where $\mathbf{r}_{i\alpha j\beta}$ is defined by $\mathbf{r}_{j\beta} - \mathbf{r}_{i\alpha}$ and $\mathbf{F}_{i\alpha j\beta}^{\text{inter}}$ is the total intermolecular force on site α in molecule i due to site β in molecule j and $\mathbf{F}_{i\alpha}^{\text{intra}}$ is the total intramolecular force acting on site α in molecule i. From this we may define the shear viscosity,

$$\eta(\gamma) = -\frac{\langle \mathbf{P}_{zx}^A \rangle}{\gamma} = -\frac{\langle \mathbf{P}_{xz}^A \rangle}{\gamma}. \tag{4}$$

alternatively, the molecular pressure tensor is given by

$$\mathbf{P}^M V = \sum_{i=1}^{N} \frac{\mathbf{p}_i \mathbf{p}_i}{M} - \frac{1}{2} \sum_{i,j} \mathbf{r}_{ij} \mathbf{F}_{ij}^{\text{inter}} \tag{5}$$

where $\mathbf{r}_{ij}$ is defined as $\mathbf{r}_j - \mathbf{r}_i$ and $\mathbf{F}_{ij}^{\text{inter}}$ is the intermolecular force on molecule i due to molecule j, $\mathbf{F}_{ij}^{\text{inter}} = \Sigma_{\alpha,\beta} \mathbf{F}_{i\alpha j\beta}^{\text{inter}}$. The natural definition of the shear viscosity in a molecular fluid where the molecular pressure tensor is possibly nonsymmetric is,

$$\eta(\gamma) = -\frac{\langle \mathbf{P}_{zx}^M \rangle}{\gamma} \tag{6}$$

This is the natural definition because it is the zx-component of the stress multiplied by the strain rate which gives rise to the dissipation and the entropy production. The corresponding xz-component plays no direct role in the entropy production.

In the absence of applied external torques, the steady state time averaged molecular pressure tensor should however be symmetric. In previous work [6] we found that the MSAT which is biased and inhomogenous has the spurious property of applying an average torque to the molecules comprising the fluid. This induces an antisymmetric molecular stress on fluids undergoing planar Couette flow. Figure 1 shows a plot of the zx component of the atomic stress tensor and for comparison,

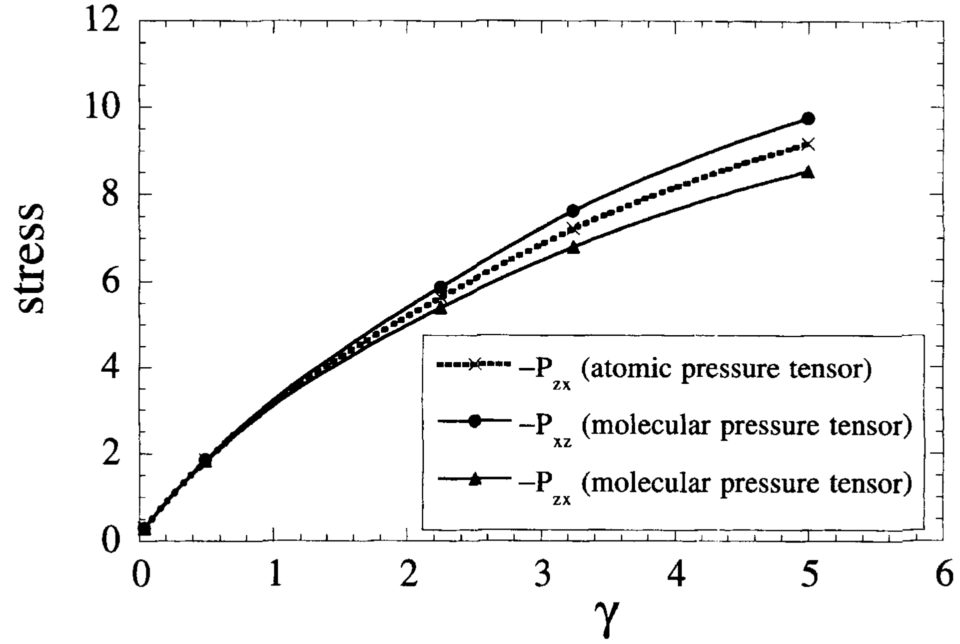

Figure 1 Comparison of molecular and atomic stress obtained from the atomic thermostatted simulations. Error bars are typically smaller than the plot symbols. Smooth curves connecting the data are for guidance only.

the *xz* and *zx* elements of the molecular pressure tensor. The quantities $\mathbf{P}_{zx}^{M}$ and $\mathbf{P}_{xz}^{M}$ are not equal to the *zx* element of the atomic pressure tensor. In fact the mean of $\mathbf{P}_{zx}^{M}$ and $\mathbf{P}_{xz}^{M}$ is within statistical uncertainties, equal to $\mathbf{P}_{zx}^{A}$. Figure 1 shows that for eicosane the atomic thermostat has the spurious property of generating a nonsymmetric pressure tensor, at least at high strain rates.

Figure 2 shows a plot of shear viscosity versus strain rate obtained from our MSAT simulations. We also show the previously published results of Morriss *et al.* [7] which were obtained using the COMT thermostat, for comparison. We see that whereas the molecular thermostatted simulations yield shear thickening beyond a shear rate of unity, the MSAT results show only shear thinning across the range of shear rates studied. Daivis and Evans [9] found that shear thickening in *n*-decane simulations at constant volume vanishes when the simulations are carried out at constant pressure (1/3 Tr(**P**)). Our results show that shear thickening can also vanish when the method of heat removal is changed from a centre-of-mass to a site based thermostat. It seems that high shear rate rheology is still essentially unknown, because of sensitivity to the thermostat.

The radius of gyration provides a useful measure of the average size of a flexible molecule. It is conveniently expressed in terms of the inertia tensor

$$\mathbf{I}_i = \sum_{\alpha=1}^{n_s} m_a(R_{i\alpha}^2\mathbf{1} - \mathbf{R}_{i\alpha}\mathbf{R}_{i\alpha}), \tag{7}$$

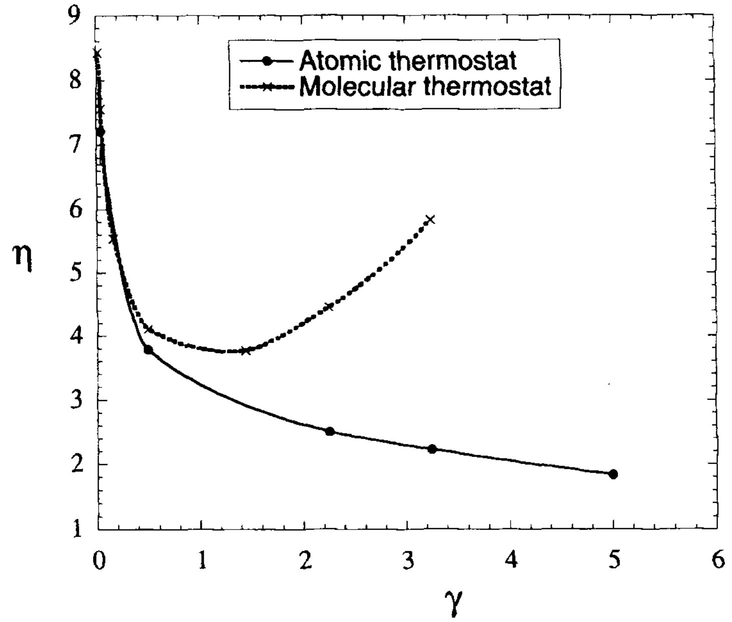

Figure 2 Plot of shear viscosity versus shear rate. The filled circles are the results obtained in this work using the atomic thermostatting scheme while the crosses represent the previously published results of Morriss, Daivis and Evans using a molecular thermostatting scheme. Smooth curves connecting the data are for guidance only.

by

$$s_i^2 = \mathrm{Tr}(\mathbf{I}_i)/(2\sum m_\alpha). \qquad (8)$$

In the above expressions R is the position of a site relative to the centre-of-mass, $\mathbf{R}_{i\alpha} = \mathbf{r}_{i\alpha} - \mathbf{r}_i$.

Figure 3 shows a plot of the percentage of *trans* conformers and the mean square radius of gyration of the molecules. We also show the Morriss *et al.* [7] results for comparison. For the MSAT results we observe an increase in the % *trans* conformers and a parallel increase in the mean square radius of gyration, as the strain rate increases. Contrast this with the COMT results: both quantities *decrease* with increasing strain rate. Clearly the eicosane molecules are more elongated in the atomic thermostatted fluids than they are in the molecular thermostatted fluids.

We note that with a COMT thermostat the translational temperature must be very much less than the rotational temperature. For an atomic thermostat the translational temperature stays relatively close to its COMT value.

4 CONCLUSIONS

In this work we have shown that two thermostatting schemes-atomic and molecular, can yield contrasting rheological pictures of a realistic flexible molecule, *n*-eicosane.

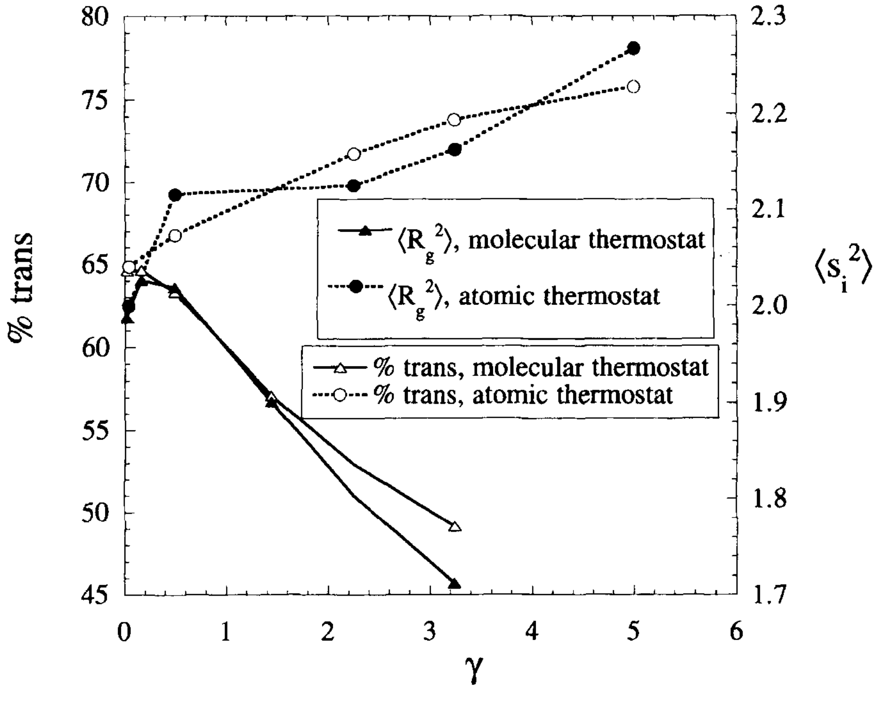

Figure 3 Plot of the percentage of *trans* conformers (left hand axis) and the mean square radius of gyration (right hand axis) against shear rate. Filled and open circles represent the mean square radius of gyration and % *trans* data respectively from this work (obtained using an atomic thermostatting scheme). While the filled and open triangles is the data from the earlier work by Morriss, Daivis and Evans which employed molecular thermostatting.

Where an erroneous atomic thermostat is employed, *n*-eicosane shows shear thinning and molecular elongation across a wide range of shear rates. When a centre-of-mass translational thermostat is instead used *n*-eicosane shows both shear thickening and shear thinning where the former effect correlates with a *decrease* in molecular size with increasing shear rate. Although COMT is preferred to atomic because it does not exert an average torque on molecules, it still suffers from a defect that that it is inhomogeneous. This inhomogeneity increases as the chain length increases. Unfortunately there is no thermostat which is known for flexible molecular fluids which is both unbiased and homogeneous. This unsatisfactory state of affairs means that the nonlinear rheological properties of long chain molecules are presently unaccessible to thermostatted nonequilibrium molecular dynamics computer simulation.

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References

[1] D. J. Evans and G. P. Morris, *Statistical Mechanics of Nonequilibrium Liquids*, (Academic Press, London, 1990).

[2] S. Nosé, "A unified formulation of the constant temperature molecular dynamics methods.", *J. Chem. Phys.*, **81**, 511 (1984).

[3] W. G. Hoover, "Canonical dynamics: Equilibrium phase-space distributions.", *Phys. Rev. A.*, **31**, 1695 (1985).

[4] D. J. Evans and S. Sarman, "Equivalence of thermostatted nonlinear responses", *Phys. Rev. E.*, **48**, 65 (1993).

[5] K. P. Travis, P. J. Daivis and D. J. Evans, "Computer simulation algorithms for molecules undergoing planar Couette flow: A non-equilibrium molecular dynamics study.", *J. Chem. Phys.*, **103**, 1109 (1995).

[6] K. P. Travis, P. J. Daivis and D. J. Evans, "Thermostats for molecular fluids undergoing shear flow: Application to liquid chlorine", *J. Chem. Phys.*, **103**, 10638 (1995).

[7] G. P. Morriss, P. J. Daivis and D. J. Evans, "The rheology of *n*-alkanes: Decane and eicosane", *J. Chem. Phys.*, **94**, 7420 (1991).

[8] R. Edberg, G. P. Morriss and D. J. Evans, "Rheology of *n*-alkanes by nonequilibrium molecular dynamics", *J. Chem. Phys.*, **86**, 4555 (1987).

[9] P. J. Daivis and D. J. Evans, "Comparison of constant pressure and constant volume nonequilibrium simulations of sheared model decane", *J. Chem. Phys.*, **100**, 541 (1994).