Effect of kinetic and configurational thermostats on calculations of the first normal stress coefficient in nonequilibrium molecular dynamics simulations

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Effect of kinetic and configurational thermostats on calculations of the first normal stress coefficient in non-equilibrium molecular dynamics simulations

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Thermostats for homogeneous non-equilibrium molecular dynamics simulations are usually designed to control the kinetic temperature, but it is now possible control any combination of many different types of temperature, including the configurational and kinetic temperatures and their directional components. It is well known that these temperatures can become unequal in homogeneously thermostatted shearing steady states. The microscopic expressions for these temperatures are all derived from equilibrium distribution functions, and it is pertinent to ask, what are the consequences of using these equilibrium microscopic expressions for temperature in thermostats for shearing non-equilibrium steady states? Here we show that the answer to this question depends on which properties are being investigated. We present numerical results showing that the value of the zero shear rate viscosity obtained by extrapolating results of non-equilibrium molecular dynamics simulations of shearing steady states is the same, regardless of the type of temperature that is controlled. It also agrees with the value obtained from the equilibrium stress autocorrelation function via the Green-Kubo relation. However, the values of the limiting zero shear rate first normal stress coefficient obtained from non-equilibrium molecular dynamics simulations of shearing steady states are strongly dependent on the choice of temperature being controlled, They also differ from the value of the first normal stress coefficient that is calculated from the equilibrium stress autocorrelation function. We show that even when all of the directional components of the kinetic and configurational temperatures are simultaneously controlled to the same value, the agreement with the result obtained from the equilibrium stress autocorrelation function is poor.

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I. INTRODUCTION

Homogeneous non-equilibrium molecular dynamics simulations have significant advantages for the determination of transport coefficients. Homogeneity ensures that the whole system is at a single, well-defined state point, that periodic boundary conditions can be applied, that no spurious boundary effects need to be considered, and that a driving force of known strength can be directly and uniformly applied to the whole system [1–3]. However, a completely homogeneous and infinitely periodic system has no temperature gradients and no walls, so heat generated by non-equilibrium processes cannot be conducted away by normal heat conduction. Instead, we use homogeneous synthetic thermostats which remove heat from the system and fix the temperature through the action of additional terms in the equations of motion. These artificial thermostats have been very well studied, and many of their properties are well understood, particularly for equilibrium systems [1].

For non-equilibrium systems, it is well known that linear transport properties such as the viscosity, thermal conductivity and diffusion coefficient are unaffected by the thermostat as long as the system is maintained at the same thermodynamic state. This is a consequence of the fact that the thermostatted linear response is independent of the thermostatting mechanism apart from terms of order $1/N$ where N is the number of particles in the system. For example, it has been proven that the difference between the adiabatic linear response (with no thermostat) and the isokinetic linear response (with a Gaussian constraint isokinetic thermostat) of an arbitrary phase variable differ only by terms of order $1/N$, except when the phase variable is a function of the thermal kinetic energy [1].

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Non-linear rheological properties, such as the normal stress coefficients, are a different matter. In a study of the thermodynamics of steady shear, Daivis [5] used the Green-Kubo relation to calculate the zero shear rate viscosity η_0 and a relationship derived from the retarded motion expansion by Coleman and Markovitz [4] to calculate the zero shear rate limit of the first normal stress coefficient $\Psi_{1,0}$ of a simple liquid from its stress relaxation modulus $G(t)$. These quantities were also computed directly from non-equilibrium molecular dynamics simulations using the sllod [1] algorithm. Although the viscosities calculated by both methods agreed to high precision, the values of the first normal stress coefficient did not. It was suggested that this difference may have been caused by the sensitivity of the normal stress differences to the thermostat. While the shear stress depends on the shear rate linearly at lowest order, the normal stresses are quadratic - i.e. of the same order as the heating effects due to viscous dissipation.

The most commonly used molecular dynamics thermostats only keep the so-called kinetic temperature constant, and consequently, in a system that is far from equilibrium, other degrees of freedom may have different temperatures. Microscopic expressions for the temperatures of these other degrees of freedom are known, and thermostats to control them have been devised. (The concept of temperature in molecular simulations has been concisely reviewed by Powles, Rickayzen and Heyes [8].) Furthermore, it is well-established that the directional components of the kinetic and configurational degrees of freedom can also differ under strongly non-equilibrium conditions. The behaviour of the x, y, and z components of both the kinetic and configurational temperatures for a strongly non-equilibrium system has been studied by Baranyai [7], who concluded that the introduction of a synthetic homogeneous thermostat induces greater temperature anisotropy than is present in a system that is naturally thermostatted by a spatial heat flux. The divergence of the directional kinetic temperatures for an ideal gas in strong shear flow has also been calculated using kinetic theory by Criado-Sancho, Jou and Casas-Vázquez [9]. Hoover [10] has investigated this problem by directly comparing the results of homogeneous shear simulations with those of inhomogeneous, boundary driven shear. In this case, the boundary driven shearing system is not artificially thermostatted, but it has a temperature profile which drives a heat flux to thermostatted regions outside the system of interest. The values of the first normal stresses that were calculated using this method were reported to be substantially higher than the values found by homogeneous shear using the sllod equations of motion with a standard kinetic temperature thermostat.

In this paper, we investigate this problem further by applying various combinations of directional thermostats, both kinetic and configurational, to homogeneously sheared systems. We compute the first normal stress coefficients for these systems and compare the results for various thermostats with the predictions of the Coleman-Markovitz equation using the equilibrium shear relaxation modulus.

II. KINETIC AND CONFIGURATIONAL TEMPERATURES

The definition of temperature for a system with a fixed number of particles in classical equilibrium thermodynamics is

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U} \right)_V \tag{1}$$

where V, S and U are the volume, entropy and internal energy. For a system that is out of equilibrium, but obeying local thermodynamic equilibrium, this also defines the temperature at any point in the fluid, provided that we use the values of local thermodynamic variables to define the state.

This definition can be used to obtain a general microscopic expression for the temperature, by following a procedure similar to that outlined by Jepps, Ayton and Evans [12] or Rickayzen and Powles [13], for example. We begin by recalling the microcanonical expression for the entropy, $S = k_B \ln \Omega$ with $\Omega = \int \delta \left(H(\mathbf{\Gamma}) - U \right) d\mathbf{\Gamma}$ where $H(\mathbf{\Gamma})$ is the phase variable for the internal energy. Note that the definition of Ω should strictly include a constant that reduces the right hand side to a dimensionless number, but this constant does not affect the final results, so it is omitted. The entropy can be substituted into the thermodynamic definition of temperature,

$$\frac{1}{T} = \frac{k_B}{\Omega} \left(\frac{\partial \Omega}{\partial U} \right)_V \tag{2}$$

The derivative can be taken when we use the microscopic expression for the entropy

$$\begin{aligned} \frac{\partial \Omega}{\partial U} &= \frac{\partial}{\partial U} \int \delta \left(H(\mathbf{\Gamma}) - U \right) d\mathbf{\Gamma} \\ &= -\int \frac{\partial}{\partial H} \delta \left(H(\mathbf{\Gamma}) - U \right) d\mathbf{\Gamma} \end{aligned} \tag{3}$$

This can be simplified by writing

$$\frac{\partial}{\partial \mathbf{\Gamma}} \delta\left(H(\mathbf{\Gamma}) - U\right) = \frac{\partial H}{\partial \mathbf{\Gamma}} \frac{\partial}{\partial H} \delta\left(H(\mathbf{\Gamma}) - U\right) \tag{4}$$

If we now form the scalar product of both sides of this equation with a vector field $\mathbf{B}(\mathbf{\Gamma})$ this expression can be further simplified, giving

$$\mathbf{B}(\mathbf{\Gamma}) \cdot \frac{\partial}{\partial \mathbf{\Gamma}} \delta\left(H(\mathbf{\Gamma}) - U\right) = \mathbf{B}(\mathbf{\Gamma}) \cdot \frac{\partial H}{\partial \mathbf{\Gamma}} \frac{\partial}{\partial H} \delta\left(H(\mathbf{\Gamma}) - U\right) \tag{5}$$

and the desired derivative is

$$\frac{\partial}{\partial H} \delta\left(H(\mathbf{\Gamma}) - U\right) = \frac{\mathbf{B}(\mathbf{\Gamma})}{\mathbf{B}(\mathbf{\Gamma}) \cdot \frac{\partial H}{\partial \mathbf{\Gamma}}} \frac{\partial}{\partial \mathbf{\Gamma}} \delta\left(H(\mathbf{\Gamma}) - U\right) \tag{6}$$

Finally, if we use this result in the expression for the derivative of the entropy with respect to internal energy and then integrate by parts, noting that the boundary term is zero, we find

$$
\begin{aligned}
\frac{1}{k_B T} &= \frac{1}{\Omega} \int \frac{\partial}{\partial \mathbf{\Gamma}} \cdot \left[\frac{\mathbf{B}(\mathbf{\Gamma})}{\mathbf{B}(\mathbf{\Gamma}) \cdot \frac{\partial H}{\partial \mathbf{\Gamma}}} \right] \delta\left(H(\mathbf{\Gamma}) - U\right) d\mathbf{\Gamma} \\
&= \left\langle \frac{\partial}{\partial \mathbf{\Gamma}} \cdot \left[\frac{\mathbf{B}(\mathbf{\Gamma})}{\mathbf{B}(\mathbf{\Gamma}) \cdot \frac{\partial H}{\partial \mathbf{\Gamma}}} \right] \right\rangle \\
&= \left\langle \frac{\frac{\partial}{\partial \mathbf{\Gamma}} \cdot \mathbf{B}(\mathbf{\Gamma})}{\mathbf{B}(\mathbf{\Gamma}) \cdot \frac{\partial H}{\partial \mathbf{\Gamma}}} \right\rangle - \left\langle \frac{\mathbf{B}(\mathbf{\Gamma}) \cdot \frac{\partial \mathbf{B}(\mathbf{\Gamma})}{\partial \mathbf{\Gamma}} \cdot \frac{\partial H}{\partial \mathbf{\Gamma}} + \mathbf{B}(\mathbf{\Gamma}) \cdot \frac{\partial^2 H}{\partial \mathbf{\Gamma} \partial \mathbf{\Gamma}} \cdot \mathbf{B}(\mathbf{\Gamma})}{\left(\mathbf{B}(\mathbf{\Gamma}) \cdot \frac{\partial H}{\partial \mathbf{\Gamma}}\right)^2} \right\rangle
\end{aligned} \tag{7}
$$

where the second term of the last line usually turns out to be of lower order in N than the first, and is therefore negligible. The vector field $\mathbf{B}$ essentially determines the direction in phase space in which we choose to vary the energy, i.e. the direction in which we move to change the energy when taking the derivative, Eq. (1). The restrictions on $\mathbf{B}$ have been discussed in detail by Jepps, Ayton and Evans [12] and Rickayzen and Powles [13].

Rugh [14] showed that a natural choice for $\mathbf{B}$ is $\mathbf{B}(\mathbf{\Gamma}) = \frac{\partial H}{\partial \mathbf{\Gamma}}$. With this choice, the direction of $\mathbf{B}$ is normal to the energy surface, leading to the name "normal temperature" [12]. The specific cases that are of greatest relevance here are those that lead to the kinetic and configurational temperatures and their directional components. In the first case, we may choose $\mathbf{B}(\mathbf{\Gamma}) = \frac{\partial K}{\partial \mathbf{\Gamma}} = \left(0, \cdots, 0, \frac{\mathbf{p}_1}{m_i} \cdots, \frac{\mathbf{p}_N}{m_N}\right)$, where K is the kinetic energy. Neglecting the second term on the right hand side of Eq. 7, we find

$$\frac{1}{k_B T_K} = \left\langle \frac{\sum \frac{3}{m_i}}{\sum \frac{\mathbf{p}_i^2}{m_i^2}} \right\rangle \tag{8}$$

Specializing to the case where the masses of all particles are equal, we obtain the expression for the kinetic temperature in the microcanonical ensemble

$$\frac{1}{k_B T_K} = 3N \left\langle \frac{1}{\sum \frac{\mathbf{p}_i^2}{m}} \right\rangle \tag{9}$$

which, for sufficiently large N reduces to the usual expression for the kinetic temperature,

$$k_B T_K = \frac{1}{3N} \left\langle \sum \frac{\mathbf{p}_i^2}{m} \right\rangle \tag{10}$$

which we will show later, would be obtained directly in the canonical ensemble. The directional components of the kinetic temperature are obtained by considering $\mathbf{B}(\mathbf{\Gamma}) = \frac{\partial K_x}{\partial \mathbf{\Gamma}} = \left(0, \cdots, 0, \frac{p_{1x}}{m_i}, 0, 0, \cdots, \frac{p_{Nx}}{m_N}, 0, 0\right)$ which leads to

$$\frac{1}{k_B T_K} = \left\langle \frac{\sum \frac{1}{m_i}}{\sum \frac{p_{ix}^2}{m_i^2}} \right\rangle \tag{11}$$

Again, for equal masses and large N this result simplifies to the expression that would be directly obtained in the canonical ensemble

$$k_B T_K = \frac{1}{N} \left\langle \sum \frac{p_{ix}^2}{m} \right\rangle \tag{12}$$

with similar expressions for the y and z components.

The configurational temperature is obtained by considering

$$\mathbf{B}(\mathbf{\Gamma}) = \frac{\partial \Phi}{\partial \mathbf{\Gamma}} = -(\mathbf{F}_1, \cdots, \mathbf{F}_N, 0 \cdots, 0) \tag{13}$$

where $\mathbf{F}_i = -\frac{\partial \Phi}{\partial \mathbf{r}_i}$, which results in

$$\frac{1}{k_B T_C} = -\left\langle \frac{\sum\limits_i \frac{\partial}{\partial \mathbf{r}_i} \cdot \mathbf{F}_i}{\sum\limits_i \mathbf{F}_i^2} + \frac{\sum\limits_j \sum\limits_i \mathbf{F}_i \cdot \frac{\partial \mathbf{F}_j}{\partial \mathbf{r}_i} \cdot \mathbf{F}_j}{\left(\sum\limits_i \mathbf{F}_i^2\right)^2} \right\rangle \tag{14}$$

Again, the second term is negligible in comparison with the first for large systems, and the configurational temperature can be written as

$$k_B T_C = -\left\langle \frac{\sum\limits_i \mathbf{F}_i^2}{\sum\limits_i \frac{\partial}{\partial \mathbf{r}_i} \cdot \mathbf{F}_i} \right\rangle \tag{15}$$

The configurational temperature can also be resolved into three directional components, as was suggested by Baranyai [7]. In this case, we consider $\mathbf{B}(\mathbf{\Gamma}) = -(F_{1x}, 0, 0, \cdots, F_{Nx}, 0 \cdots, 0)$, with the result

$$k_B T_{Cx} = -\left\langle \frac{\sum\limits_i F_{ix}^2}{\sum\limits_i \frac{\partial F_{ix}}{\partial x_i}} \right\rangle \tag{16}$$

These derivations can also be done in the canonical ensemble. Consider the following integral,

$$\int \frac{\partial}{\partial \mathbf{\Gamma}} \cdot \left(\mathbf{B}(\mathbf{\Gamma}) e^{-\beta H}\right) d\mathbf{\Gamma} = \int \frac{\partial}{\partial \mathbf{\Gamma}} \cdot \mathbf{B}(\mathbf{\Gamma}) e^{-\beta H} d\mathbf{\Gamma} - \beta \int \mathbf{B}(\mathbf{\Gamma}) \cdot \frac{\partial H}{\partial \mathbf{\Gamma}} e^{-\beta H} d\mathbf{\Gamma} \tag{17}$$

This is equal to zero by Gauss's theorem and the fact that the probability density goes to zero at the limits of integration, so we can express the temperature as

$$\frac{1}{k_B T} = \frac{\left\langle \frac{\partial}{\partial \mathbf{\Gamma}} \cdot \mathbf{B}(\mathbf{\Gamma}) \right\rangle}{\left\langle \mathbf{B}(\mathbf{\Gamma}) \cdot \frac{\partial H}{\partial \mathbf{\Gamma}} \right\rangle} \tag{18}$$

Comparing this expression with Eq. (7), we see that they only differ by terms that are of order $1/N$, in that the canonical ensemble expression is a ratio of two ensemble averages whereas the microcanonical one is the ensemble average of a ratio. Jepps et al. [12] have compared them and found that the numerical properties of the canonical (fractional) expression for the configurational temperature,

$$k_B T_{Cf} = -\frac{\left\langle \sum\limits_i \mathbf{F}_i^2 \right\rangle}{\left\langle \sum\limits_i \frac{\partial}{\partial \mathbf{r}_i} \cdot \mathbf{F}_i \right\rangle} \tag{19}$$

are generally superior, so this is the form that we will use. Similarly, the canonical average is used for the kinetic and directional kinetic temperatures.

III. EQUATIONS OF MOTION

A. Equilibrium

The equilibrium simulations were carried out using the equations of motion

$$\dot{\mathbf{r}}_i = \frac{\mathbf{p}_i}{m_i} \tag{20}$$

$$\dot{\mathbf{p}}_i = \mathbf{F}_i - \alpha\mathbf{p}_i \tag{21}$$

where the kinetic temperature is controlled by an isokinetic thermostat derived from Gauss's principle of least constraint [1], which gives

$$\alpha = \frac{\sum\limits_{i=1}^{N} \mathbf{p}_i \cdot \mathbf{F}_i/m_i}{\sum\limits_{i=1}^{N} \mathbf{p}_i^2/m_i} \tag{22}$$

This thermostat keeps the total thermal kinetic energy constant. However, the system is at equilibrium and so all temperatures are equal to the set value, as long as one of them is thermostatted. This was confirmed numerically for our system.

B. Non-equilibrium: kinetic thermostat

The non-equilibrium simulations with a thermostat on the total kinetic temperature were carried out using the sllod algorithm with equations of motion given by

$$\dot{\mathbf{r}}_i = \frac{\mathbf{p}_i}{m_i} + \mathbf{r}_i \cdot \nabla\mathbf{v} \tag{23}$$

$$\dot{\mathbf{p}}_i = \mathbf{F}_i - \mathbf{p}_i \cdot \nabla\mathbf{v} - \alpha\mathbf{p}_i \tag{24}$$

where the velocity gradient tensor for planar shear is $\nabla\mathbf{v} = \mathbf{ji}\dot{\gamma}$. Note that in these equations, $\mathbf{p}$ is now the thermal component of the momentum, i.e. the total momentum minus the streaming component. The thermostat used here constrains the total thermal kinetic energy to a set value, so the individual directional components are allowed to vary as dictated by the dynamics. To control all of the directional components of the kinetic temperature individually, we must use the equations of motion

$$\dot{\mathbf{r}}_i = \frac{\mathbf{p}_i}{m_i} + \mathbf{r}_i \cdot \nabla\mathbf{v} \tag{25}$$

$$\dot{\mathbf{p}}_i = \mathbf{F}_i - \mathbf{p}_i \cdot \nabla\mathbf{v} - \alpha_x p_{ix}\mathbf{i} - \alpha_y p_{iy}\mathbf{j} - \alpha_z p_{iz}\mathbf{k} \tag{26}$$

with the thermostat multiplier for the x-kinetic thermostat equal to

$$\alpha_x = \frac{\sum\limits_{i=1}^{N} p_{ix}\left(F_{ix} - (\mathbf{p}_i \cdot \nabla\mathbf{v})_x\right)/m_i}{\sum\limits_{i=1}^{N} p_{ix}^2/m_i} \tag{27}$$

and similar expressions for the y and z multipliers. Note that these thermostats apply constraints to the x, y and z components of the thermal kinetic energy, so the actual number of degrees of freedom for a given directional component is $N - 2$ because the total momentum and thermal kinetic energy of that directional component are both fixed.

C. Non-equilibrium: configurational thermostat

Although other configurational thermostats have been derived [15, 16], we have chosen to use the Nosé-Hoover type of configurational thermostat developed by Braga and Travis [17], because of its superior performance. The equations

of motion implementing this thermostat to control the temperature of the total potential energy are

$$\dot{\mathbf{r}}_i \;=\; \frac{\mathbf{p}_i}{m_i} + \mathbf{r}_i \cdot \nabla \mathbf{v} + \zeta \mathbf{F}_i \tag{28}$$

$$\dot{\mathbf{p}}_i \;=\; \mathbf{F}_i - \mathbf{p}_i \cdot \nabla \mathbf{v} \tag{29}$$

with an additional equation of motion for the thermostat variable

$$\dot{\zeta} = \frac{1}{Q_\zeta}\left(\sum_{i=1}^{N} \mathbf{F}_i{}^2 - k_B T \sum_{i=1}^{N} \frac{\partial}{\partial \mathbf{r}_i} \cdot \mathbf{F}_i \right) \tag{30}$$

and the thermostat inertia Q_ζ which is chosen to give suitable relaxation of the fluctuations in the quantity being controlled. Baranyai [7] has shown that it is also possible to define the directional components of the configurational temperature, given by the fractional form of Eq. (16) so we have adapted the Braga-Travis thermostat to control these temperatures. The equations of motion used for the directional configurational thermostats are

$$\dot{\mathbf{r}}_i \;=\; \frac{\mathbf{p}_i}{m_i} + \mathbf{r}_i \cdot \nabla \mathbf{v} + \zeta_x F_{ix}\mathbf{i} + \zeta_y F_{iy}\mathbf{j} + \zeta_z F_{iz}\mathbf{k} \tag{31}$$

$$\dot{\mathbf{p}}_i \;=\; \mathbf{F}_i - \mathbf{p}_i \cdot \nabla \mathbf{v} \tag{32}$$

and the equations of motion for the thermostat variables are

$$\dot{\zeta}_x = \frac{1}{Q_\zeta}\left(\sum_{i=1}^{N} F_{ix}^2 - k_B T \sum_{i=1}^{N} \frac{\partial F_{ix}}{\partial x_i} \right) \tag{33}$$

$$\dot{\zeta}_y = \frac{1}{Q_\zeta}\left(\sum_{i=1}^{N} F_{iy}^2 - k_B T \sum_{i=1}^{N} \frac{\partial F_{iy}}{\partial y_i} \right) \tag{34}$$

$$\dot{\zeta}_z = \frac{1}{Q_\zeta}\left(\sum_{i=1}^{N} F_{iz}^2 - k_B T \sum_{i=1}^{N} \frac{\partial F_{iz}}{\partial z_i} \right) \tag{35}$$

To ensure that the temperatures of all degrees of freedom were equal, we also ran a set of simulations in which we combined both the directional kinetic and directional configurational thermostats.

IV.   VISCOMETRIC FUNCTIONS

For the velocity gradient tensor $\nabla \mathbf{v} = \mathbf{ji}\dot{\gamma}$ representing planar shear flow, the generalized non-Newtonian shear viscosity is defined as:

$$\eta\left(\dot{\gamma}\right) = -\frac{P_{yx}}{\dot{\gamma}}. \tag{36}$$

with the zero shear rate limit

$$\eta_0 = \lim_{\dot{\gamma}\to 0} \eta\left(\dot{\gamma}\right) \tag{37}$$

and the first normal stress coefficient is defined as

$$\Psi_1(\dot{\gamma}) = \frac{P_{yy} - P_{xx}}{\dot{\gamma}^2} \tag{38}$$

with the zero shear rate limit

$$\Psi_{1,0} = \lim_{\dot{\gamma}\to 0} \Psi_1\left(\dot{\gamma}\right). \tag{39}$$

The above quantities can all be obtained directly from non-equilibrium molecular dynamics simulations [3, 18]. At sufficiently low shear rates, the viscosity and the first normal stress coefficient are both found to be proportional to the square of the shear rate. This was found to be the case for shear rates in the range $0 < \dot{\gamma} < 0.14$. The limiting

zero shear rate values were obtained by plotting the shear rate dependent viscosity and the shear rate dependent first normal stress coefficient against the square of the shear rate at seven equally spaced points and fitting a straight line to the data.

The zero shear rate viscosity and first normal stress coefficient can also be obtained from the equilibrium stress relaxation modulus. This is calculated from the isotropically averaged equilibrium autocorrelation function of the symmetric traceless component of the pressure tensor

$$G\left(t\right) = \frac{V}{10k_BT} \left\langle \mathbf{P}^{0s}\left(t\right) : \mathbf{P}^{0s}\left(0\right) \right\rangle \tag{40}$$

The zero shear rate viscosity follows from the standard Green-Kubo relation

$$\eta_0 = \int_0^\infty G(t)dt \tag{41}$$

The equilibrium stress relaxation modulus can also be used to calculate the limiting zero shear rate normal stress coefficient using the Coleman-Markovitz equation [4]

$$\Psi_{1,0} = 2\int_0^\infty tG(t)dt \tag{42}$$

V. SIMULATIONS

The simulations are conducted on the same system that was studied previously [5], for which there already exists a large body of data for verification. The system consists of $N = 500$ particles interacting via the truncated and shifted Lennard-Jones (LJ) interaction potential given by

$$\phi(r_{ij}) = \begin{cases} 4\epsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^6\right] - \phi_c & r_{ij} \leq r_c \\ 0 & r_{ij} > r_c \end{cases} \tag{43}$$

where r_{ij} is the separation of two interacting atoms, ϵ is the potential well depth and σ is the value of r_{ij} at which the unshifted potential is zero. The shift ϕ_c, which is equal to the value of the unshifted potential at the cutoff $r_{ij} = r_c$, is introduced to eliminate the discontinuity due to truncation of the potential energy. The cutoff point for the potential is the position of the minimum in the LJ potential, $r_c = 2^{1/6}\sigma$. This form of the truncated and shifted LJ potential energy function is usually known as the WCA potential [6]. All simulations are conducted in periodic boundary conditions.

The particle number density is $n = 0.84$ and the temperature is $T = 1.0$. All quantities are given in LJ reduced units using the particle mass m, and the LJ potential energy and distance parameters ϵ, σ as reduction parameters [11].

VI. RESULTS AND DISCUSSION

The equilibrium stress autocorrelation function defined in Eq. (40) was calculated by averaging the results of 10 independent runs, each of 20×10^6 timesteps in duration, with a timestep of 0.002 reduced units, giving a total effective averaging time of 4×10^5 reduced time units.

Fig. 1 shows the result of applying Eq. (41) to the normalized equilibrium stress autocorrelation function. The converged value of the viscosity from the Green-Kubo formula is $\eta = 2.13 \pm 0.01$.

Fig. 2 shows the result for the integral of the time multiplied by the normalized equilibrium stress autocorrelation function. The integral converges to a constant value at around $t = 5$, after which noise in the tail of the stress autocorrelation function becomes dominant. The converged value is $\int tG(t)dt = 0.20 \pm 0.01$ and the value of the first normal stress coefficient obtained from this is $2\int tG(t)dt = 0.40 \pm 0.02$. The uncertainties are obtained by taking the spread of the fluctuations in the integral at lag times between $t = 2$ and $t = 5$, after which the noise dominates. This value for the first normal stress coefficient has recently been confirmed by more precise calculations [23].

The results of the non-equilibrium molecular dynamics computations of the viscosity are shown in Table I. Row 1 shows the results for the usual isokinetic thermostat, which keeps the total thermal kinetic energy, and therefore the kinetic temperature, constant. This procedure does not guarantee that any one of the directional temperatures
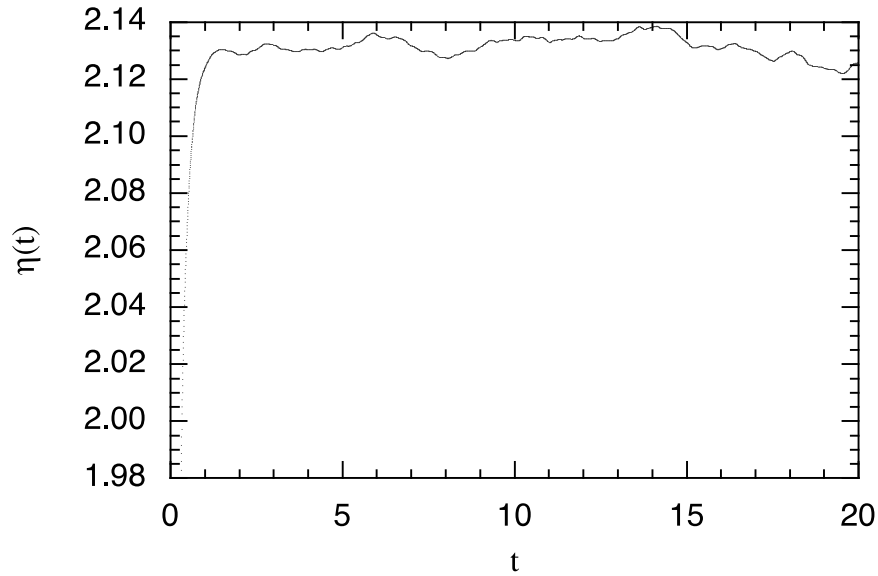
FIG. 1: Integral of the normalized stress relaxation modulus, showing the convergence of the Green-Kubo integral for the viscosity. The converged value is $\eta = 2.13 \pm 0.01$. Note that the vertical scale has been truncated and expanded to emphasise the small statistical error.
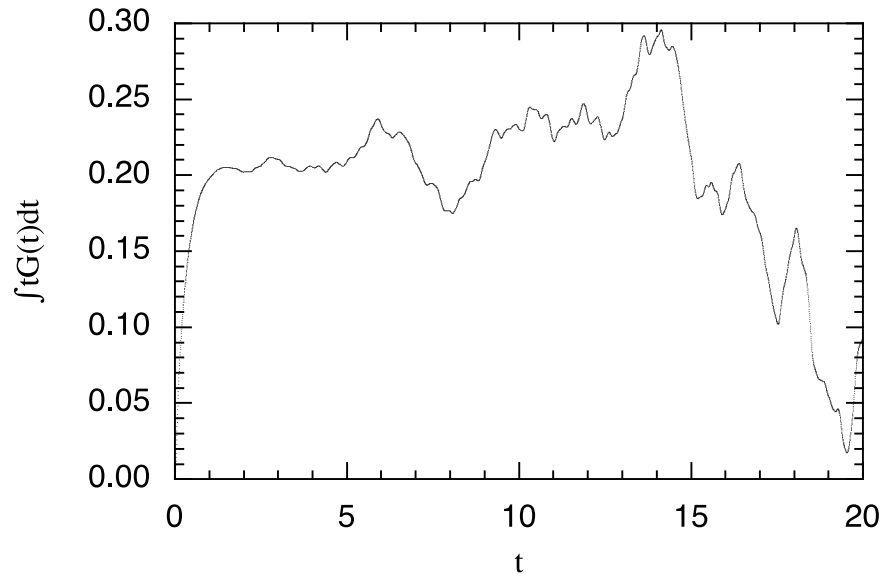

FIG. 2: Integral of $tG(t)$, showing the convergence of the Coleman-Markovitz integral for the first normal stress coefficient. The converged value is $\int tG(t)dt = 0.20 \pm 0.01$. The value of the first normal stress coefficient obtained from this is $2\int tG(t)dt = 0.40 \pm 0.02$.

is precisely equal to the set temperature except at equilibrium, because each of the directional temperatures is free to change according to the dynamics of the system. Row 2 shows similar data, but for the total configurational temperature. Row 3 shows the results when all of the directional kinetic temperatures are separately fixed to the set value, and row 4 likewise for the directional configurational temperatures. Row 5 shows the results when all of the kinetic and configurational directional temperatures are individually fixed. The viscosity is consistently found to be constant within the uncertainties and the average value of the NEMD results, 2.119 ± 0.005 agrees very well with the value found from the Green-Kubo calculation, 2.13 ± 0.01.

The values of the first normal stress coefficient, on the other hand, vary strongly with the type of thermostat applied. The largest value is found for the directional kinetic thermostat, while the smallest is found for the non-

TABLE I: Zero shear rate viscosities and first normal stress coefficients calculated by NEMD for various thermostats.

temperatures fixed	η_0	error	$\Psi_{1,0}$	error
T_K	2.119	0.001	0.206	0.004
T_C	2.118	0.002	0.193	0.009
$T_{K\alpha}, \alpha = x, y, z$	2.124	0.006	0.27	0.03
$T_{C\alpha}, \alpha = x, y, z$	2.115	0.002	0.205	0.009
$T_{K\alpha}, T_{C\alpha}, \alpha = x, y, z$	2.120	0.003	0.24	0.02

directional configurational thermostat. In general, it appears that the directional kinetic thermostat tends to give a larger value of the first normal stress coefficient, while the non-directional kinetic and the configurational thermostats tend to give smaller values. All of the NEMD results for the first normal stress coefficients are much smaller than the value obtained from the Coleman-Markovitz equation. This is similar to the result obtained by Hoover [10], who found that the first normal stress coefficient calculated from homogeneous non-equilibrium molecular dynamics simulations with a non-directional kinetic thermostat was significantly lower than the value found from boundary driven and thermostatted shear simulations. Experimental tests of the Coleman-Markovitz equation on polymer melts, for example, show that it accurately predicts the first normal stress coefficient found from direct measurements (e.g. Table 5.3-1 of Bird et al. [19] or section 1.G.1 of Ferry [20]). These experimental tests are performed on systems that are naturally thermostatted with temperature gradients that remain very small in the linear viscoelastic regime.

While there is good experimental evidence for the validity of the Coleman-Markovitz equation for complex fluids such as polymer melts, where the viscous relaxation time is expected to be much greater than the thermal relaxation time, there is less evidence of its validity for simple fluids in which the two relaxation times are comparable. We have used the Coleman-Markovitz equation to compute the first normal stress coefficient of a simple liquid as a function of density, and we find that the value of the first normal stress coefficient that we obtain in the low density limit agrees with the prediction of kinetic theory [23].

The disparity between the first normal stress coefficients obtained from NEMD simulations on homogeneously thermostatted systems and the value obtained from the equilibrium stress relaxation function has several possible causes.

An obvious relationship between an isokinetic thermostat and the first normal stress coefficient is that the normal components of the kinetic part of the pressure tensor are trivially related to the directional kinetic temperatures, e.g. $P_{xx} = (1/V) \sum p_{ix}^2/m_i$ and similarly for the yy and zz components. This means that constraining all of the kinetic temperatures to the same value also constrains the kinetic parts of the normal stress differences to zero. In the dilute gas limit, this will obviously lead to a first normal stress coefficient of zero, which is at odds with the results of kinetic theory [24]. This point was also made by Hoover [10]. The effect of a directional kinetic thermostat on the configurational part of the pressure tensor, which is dominant in the liquid state, is less well understood.

In an equilibrium simulation, controlling one temperature still allows the others to fluctuate naturally around the mean value. As long as the temperature being controlled is not trivially related to the quantity being calculated, the calculations should be unaffected by the details of the thermostat. In a homogeneously thermostatted non-equilibrium simulation, work is done on some degrees of freedom, and heat is removed from some degrees of freedom, not necessarily the same ones. This leads to temperature differences between the different degrees of freedom of quadratic order in the shear rate. Linear transport coefficients should remain unaffected by these differences. This indeed what we find for the viscosity. However, non-linear properties are sensitive to these differences. In this case, we might expect that thermostatting all of the temperatures to the same value should improve the agreement between the equilibrium and non-equilibrium calculations. This is what seems to be implied in the discussion by Baranyai [7] for example. However, we see that this is not the case. Simply equalizing all of the directional kinetic and directional configurational temperatures does not improve the agreement.

An obvious shortcoming of the usual derivations of microscopic expressions for the temperature is that they are based on equilibrium distribution functions. This would be satisfactory if we could verify that the local equilibrium hypothesis is valid, but this does not apply to the non-linear properties. It has already been proposed that the thermodynamic temperature for a shearing steady state should include a term that is quadratic in the stress (or the shear rate) [21]. This is of the same order as the divergence of the temperatures of different degrees of freedom. Therefore, both effects need be investigated in order to understand the behaviour of non-linear properties such as the normal stress coefficients in homogeneously thermostatted simulations. A preliminary thermodynamic analysis of these effects has been presented by Daivis and Jou [22].

VII. CONCLUSIONS

We have calculated the first normal stress coefficient of a dense simple fluid in the limit of zero shear rate by equilibrium and non-equilibrium molecular dynamics simulations. In the equilibrium simulations, the Coleman-Markovitz equation was used to obtain the first normal stress coefficient from the shear relaxation modulus, which is proportional to the equilibrium stress autocorrelation function. In the non-equilibrium simulations, several different homogeneous thermostats were used; kinetic, configurational, directional kinetic, directional configurational and a combination of directional kinetic and directional configurational. The first normal stress coefficient was found to be sensitive to the thermostat, while the viscosity was not. In all cases, the value of the first normal stress coefficient obtained from the non-equilibrium simulations was significantly lower than the value obtained from the equilibrium simulations. This is similar to the result found by Hoover et al. when they compared the first normal stress coefficient from homogeneous shear non-equilibrium molecular dynamics to that found from boundary driven shear simulations. We suggest that there are two main reasons for the difference between the predictions of the Coleman-Markovitz equation and the results of the homogeneously thermostatted non-equilibrium simulations. One is that the normal stresses depend on the thermodynamic temperature and this is quadratically dependent on the shear rate. The other is that, although the temperatures of different degrees of freedom may all depend quadratically on the shear rate, each of these may have a different coefficient, leading to differences in the temperatures of the different degrees of freedom (e.g. x, y and z kinetic and x, y and z configurational) that grow quadratically with shear rate. A thermostat that is designed for computing non-linear properties as well as the linear ones by homogeneous non-equilibrium molecular dynamics must correctly reproduce the boundary driven system in both of these respects. Work in this direction is currently in progress.

Acknowledgments

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