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Frequency-Dependent Elongational Viscosity by Nonequilibrium Molecular Dynamics[1]

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The elongational viscosity of a liquid describes the response of the liquid to simultaneous stretching and compression in various directions, subject to the restriction that the trace of the rate of the strain tensor is zero (or the density is constant). Despite the growing popularity and usefulness of nonequilibrium molecular dynamics methods in studies of the shear viscosity of simple and complex fluids, the elongational viscosity remains a relatively neglected property in computer simulation studies. This stems from some significant technical difficulties that arise when standard methods such as the constant strain rate SLLOD algorithm are applied to elongational flow. For example, if planar elongational flow with a constant elongation rate is applied in a computer simulation with periodic boundary conditions, the box size in the contracting direction quickly becomes smaller than twice the range of the potential, violating the minimum image convention. The time at which this occurs may be less than the time required for the system to reach a steady state, making it impossible to compute the steady-state elongational viscosity. This difficulty can be avoided by applying an oscillating elongational strain rate to the liquid, and computing frequency dependent elements of the stress tensor, which can then be extrapolated to zero frequency to evaluate the steady-state elongational viscosity. We have used this method to compute the elongational viscosity of a simple atomic liquid and discuss its possible application to a model polymeric liquid.

KEY WORDS: computer simulation; elongational viscosity; frequency dependence.

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1. INTRODUCTION

Recent advances in computer simulation methods and computer power have made it possible to study the rheological properties of a wide variety of liquids, ranging from simple atomic liquids to hydrocarbons and model polymeric liquids at the atomic and molecular level by nonequilibrium molecular dynamics techniques [1, 2]. The vast majority of these studies have been restricted to planar shear flow, and its corresponding transport coefficient, the shear viscosity, because of the relative simplicity of this type of flow, but other flows, along with their respective viscometric variables, are clearly both important and interesting.

The elongational viscosity is a rheological property of industrial importance and theoretical interest [3] that has received limited attention in computer simulation studies [4, 5, and references therein]. An elongational flow can be loosely described as a "stretching" flow. Three types of elongational flow can be defined in three-dimensional systems: planar extension, uniaxial extension, and biaxial extension. In general, the elongational strain-rate tensor takes the following form:

$$\nabla \mathbf{u} = \begin{pmatrix} \dot{\varepsilon}_{xx} & 0 & 0 \\ 0 & \dot{\varepsilon}_{yy} & 0 \\ 0 & 0 & \dot{\varepsilon}_{zz} \end{pmatrix} \tag{1}$$

For constant volume to be maintained, we must have $\mathrm{Tr}(\nabla \mathbf{u}) = 0$. This eliminates the bulk strain from the strain-rate tensor. The various specific types of elongational flow are then generated by specifying $\dot{\varepsilon}_{xx}$, $\dot{\varepsilon}_{yy}$, and $\dot{\varepsilon}_{zz}$, subject to this restriction. Planar elongational flow corresponds to $\dot{\varepsilon}_{xx} = -\dot{\varepsilon}$, $\dot{\varepsilon}_{yy} = \dot{\varepsilon}$, and $\dot{\varepsilon}_{zz} = 0$; uniaxial extension to $\dot{\varepsilon}_{xx} = -\dot{\varepsilon}/2$, $\dot{\varepsilon}_{yy} = \dot{\varepsilon}$, and $\dot{\varepsilon}_{zz} = -\dot{\varepsilon}/2$, and biaxial extension to $\dot{\varepsilon}_{xx} = \dot{\varepsilon}$, $\dot{\varepsilon}_{yy} = \dot{\varepsilon}$, and $\dot{\varepsilon}_{zz} = -2\dot{\varepsilon}$. In this paper, we consider only planar and uniaxial elongational flow.

In all of the nonequilibrium molecular dynamics studies of elongational flow so far reported, steady elongational flow has been studied. In steady elongation simulations, one dimension of the simulation box is extended, while one or more of the other dimensions contract at a constant strain rate. However, the smallest dimension of the simulation box must never be less than twice the cutoff radius of the potential energy function if the minimum image convention is to be satisfied. Thus, there exists a fundamental restriction on the maximum possible length of a simulation. If the response to the elongational strain does not reach its steady-state value within this interval, it becomes almost impossible to obtain the steady-state elongational viscosity from the transient elongational viscosity because no adequate procedure to extrapolate from the transient to the steady-state elongational viscosity exists.

Two methods of overcoming this difficulty have previously been proposed. The time available to reach the steady-state can be increased by beginning with a simulation box that is maximally contracted in the direction that is to be expanded [4]. Baranyai and Cummings [5] have proposed another technique for extending the length of the experiment in which the basic simulation box is doubled to include the original set of particles plus one set of randomly perturbed periodic images of these particles when the minimum dimension is reached. After a time determined by the maximum Lyapunov exponent of the system, this composite system becomes uncorrelated with the original replicated system. However, if the strain rate is high, insufficient time is available for the divergence of the trajectories and anomalous results are obtained. These techniques, while partially successful, are not totally satisfactory. This has led us to propose an alternative simulation method in which an oscillatory strain rate of a given frequency is applied, and the results are extrapolated to zero frequency to give the steady shear limit. This method has been investigated and the zero frequency extrapolated results have been discussed in another publication [9]. The purpose of this paper is to elaborate on the frequency dependence of the elongational viscosity obtained by this technique, and in particular to investigate the agreement with the zero-shear-rate, frequency-dependent shear viscosity obtained by other methods.

2. THEORY

For a system undergoing steady planar elongation in the geometry defined above, the elongational viscosity is defined by the constitutive equation,

$$\eta_{\mathrm{EP}}=\frac{P_{xx}-P_{yy}}{4\dot{\varepsilon}} \tag{2}$$

while for steady uniaxial elongational flow, we define

$$\eta_{\mathrm{EU}}=\frac{1/2(P_{xx}-P_{zz})-P_{yy}}{3\dot{\varepsilon}} \tag{3}$$

where $P_{\alpha\alpha}$ represent elements of the pressure tensor and $\dot{\varepsilon}$ is the elongational strain rate. By analogy with the generalized strain-rate-dependent shear viscosity, the elongational viscosities may also be strain rate dependent. Note that the definitions given above differ slightly from those found in standard rheology texts [3] because we have included numerical factors in the denominator so that the limits of these coefficients have a particularly simple form. Defined in this way, the elongational viscosities have the property that they approach the Newtonian shear viscosity η in the limit of zero strain rate, i.e.,

$$\lim_{\dot{\varepsilon} \to 0} \eta_{\mathrm{EP}}(\dot{\varepsilon}) = \lim_{\dot{\varepsilon} \to 0} \eta_{\mathrm{EU}}(\dot{\varepsilon}) = \lim_{\dot{\gamma} \to 0} \eta(\dot{\gamma}) \tag{4}$$

This relationship is perhaps clearer when we realize that the Newtonian viscosity is in general terms, the transport coefficient relating the symmetric traceless part of the strain rate tensor to the symmetric traceless part of the stress tensor, i.e.,

$$\overset{\mathrm{os}}{\mathbf{P}} = -2\eta(\overset{\mathrm{os}}{\nabla \mathbf{u}}) \tag{5}$$

and since Eq. (1) is already in traceless symmetric form, the corresponding pressure tensor must also be a symmetric traceless tensor (for an isotropic material), giving the relationship Eq. (4). Equation (5) can be generalized to arbitrary time-dependent strain rates in the small strain rate, small deformation limit as

$$\overset{\mathrm{os}}{\mathbf{P}}(t) = -2 \int_0^t G(t-s)(\overset{\mathrm{os}}{\nabla \mathbf{u}}(s))\, ds \tag{6}$$

where G is the shear relaxation modulus. By taking the infinite time limit for the constant strain-rate case, we see that the integral of the shear relaxation modulus is equal to the steady shear viscosity [3].

In measurements of the extensional viscosity, it is sometimes impossible to reach the steady-state. In such cases, the transient elongational viscosity, which is then a function of time, is calculated [6]. The transient elongational viscosity is defined by Eq. (6) where the strain rate is constant after a step increase from zero, but the stress and the elongational viscosity may be time dependent and, in the more general case, strain rate dependent. Equivalent relationships for shear in the linear limit are well known [7] and take the form

$$\overset{\mathrm{os}}{\mathbf{P}}(t) = -2 \int_0^t G(t-s)(\overset{\mathrm{os}}{\nabla \mathbf{u}})\, ds = -2\eta(t)(\overset{\mathrm{os}}{\nabla \mathbf{u}}) \tag{7}$$

from which we see that the same relationships between the shear and the elongational viscosities hold for the transient quantities as for their steady-state counterparts in the linear limit.

In the case of a sinusoidally varying strain rate, the linear constitutive relation above yields

$$\overset{os}{\mathbf{P}}(t) = -2\eta(\omega)(\overset{os}{\nabla\mathbf{u}}(t)) \tag{8}$$

where $\eta(\omega) = \eta'(\omega) - i\eta''(\omega)$ is now the complex, frequency-dependent shear viscosity [3]. The components of the frequency dependent viscosity have the following properties:

$$\lim_{\omega \to 0} \eta'(\omega) = \eta \tag{9}$$

$$\lim_{\omega \to 0} \eta''(\omega) = 0 \tag{10}$$

For a sinusoidal strain rate in the linear regime, the pressure tensor is periodic but may be out of phase with the strain rate. The tensorial properties of Eq. (8) are the same as those of Eq. (5), so we can immediately deduce that for planar elongational flow,

$$\eta_{\mathrm{EP}}(\omega) = \frac{P_{xx}(t) - P_{yy}(t)}{4\dot{\varepsilon}(t)} \tag{11}$$

The case of periodic uniaxial elongational flow is more interesting. With $\dot{\varepsilon}(t) = \dot{\varepsilon}_0 \cos(\omega t)$ in Eq. (1), we see that the flow is actually uniaxial extensional for the first half of the cycle and biaxial elongation for the second half, because the strain rate changes sign. In the linear limit, this does not pose any difficulties, because in the limit as $\dot{\varepsilon}_0$ approaches zero, the biaxial viscosity, when defined with the appropriate numerical factor also approaches the Newtonian shear viscosity. Thus, calculation of both the uniaxial and biaxial elongational viscosities is possible in a single experiment, both of them related to the Newtonian viscosity in the limit of zero strain rate and frequency.

The more general case of high-amplitude or strain-rate oscillatory elongation requires the full machinery of nonlinear constitutive equations for a complete description. However, we can deduce the limiting behavior in the zero frequency limit by the following argument. As the frequency is decreased to zero, each cycle becomes infinitely long and the extrema of the elements of the pressure tensor approach the values that they would reach in the infinite time limit for constant strain rate elongation. Thus, we have

$$\eta_{\mathrm{EP}}(\dot{\varepsilon}_0) = \lim_{\omega \to 0} \frac{\mathrm{Max}[P_{xx}(t)] - \mathrm{Min}[P_{yy}(t)]}{4\dot{\varepsilon}_0} \tag{12}$$

for planar elongational flow. This relationship applies to the portion of the cycle during which P_{xx} is positive. The complementary part of the cycle also corresponds to planar elongational flow, but with the xx and yy elements of the strain rate and pressure tensors interchanged. In the case of uniaxial elongational flow, a similar relationship holds, but the lack of symmetry on reversal of the sign of $\dot{\varepsilon}$ restricts consideration to only the positive parts of the cycle for uniaxial elongation, because the negative part of the cycle now corresponds to biaxial elongation. This suggests that it is possible to obtain both the biaxial and the uniaxial strain-rate-dependent elongational viscosities from one oscillatory elongation experiment.

3. SIMULATIONS

The equations of motion that are usually used [4, 5] to simulate elongational flow in simple liquids are the SLLOD equations of motion (so named because of their close relationship with the DOLLS tensor equations) [1]

$$\dot{\mathbf{r}}_i = \frac{\mathbf{p}_i}{m_i} + \mathbf{r}_i \cdot \nabla\mathbf{u} \tag{13}$$

$$\dot{\mathbf{p}}_i = \mathbf{F}_i - \mathbf{p}_i \cdot \nabla\mathbf{u} - \alpha\mathbf{p}_i \tag{14}$$

The $\alpha\mathbf{p}_i$ term is a thermostat term, which is essentially a spatially homogeneous constraint force that removes exactly the amount of heat required to maintain a constant temperature. The expression for the thermostat multiplier α that is required to do this can be shown to be [1]

$$\alpha = \frac{\sum_i \mathbf{p}_i \cdot [\mathbf{F}_i - (\mathbf{p}_i \cdot \nabla\mathbf{u})]}{\sum_i \mathbf{p}_i^2} \tag{15}$$

These equations of motion for N particles are numerically solved for an infinite periodic system in which the basic simulation box is replicated to infinity in each direction, so as to eliminate surface and wall effects. When $\nabla\mathbf{u}$ is given by the constant strain-rate tensor Eq. (1), the box dimensions change according to the following equation of motion:

$$\dot{\mathbf{L}} = \mathbf{L} \cdot \nabla\mathbf{u} \tag{16}$$

which, when solved, gives

$$L_\alpha = L_{\alpha 0} \exp(\nabla_\alpha u_\alpha) \tag{17}$$

for elongational flows.

The generalization to oscillatory strain rates is straightforward. In this case, we define the time-dependent strain-rate tensor as

$$\nabla \mathbf{u}(t) = \dot{\varepsilon}_0 \cos(\omega t) \tag{18}$$

where $\dot{\varepsilon}_0$ is the strain-rate amplitude tensor. The box dimensions now oscillate according to

$$L_\alpha(t) = L_\alpha(0) \exp(\dot{\varepsilon}_{\alpha\alpha} \omega^{-1} \sin(\omega t)) \tag{19}$$

Note that in the same way as the condition that $L_\alpha \geqslant 2r_c$ imposes a maximum time on a steady-state elongational flow simulation, a minimum frequency is imposed by the same condition when applied to Eq. (19). In a sense, the problem of extrapolating to infinite time from the transient response to a step increase to a steady elongation is replaced by the problem of extrapolating to zero frequency in the oscillatory elongation case. However, the transient elastic response in the steady elongation experiment is replaced by a steady-state phase shift in the oscillatory experiment, which we expect to be far easier to extrapolate in cases where the steady state cannot be reached in the transient experiment.

4. RESULTS AND DISCUSSION

We performed both steady elongation and oscillatory elongational flow simulations on a 108-atom WCA fluid [8] at the state point defined by a reduced density of $\rho = 0.8442$ and a reduced temperature of $T = 0.722$. A more detailed description of the simulation method, together with a discussion of the use of this technique to obtain the zero frequency strain-rate-dependent elongational viscosity, may be found in Ref. 9.

The results obtained by first extrapolating the extrema of the pressure tensor to zero frequency and then calculating the strain-rate-dependent planar elongational viscosity are compared with the results of steady planar elongation simulations in Fig. 1. Figure 1 shows that the results obtained by the two methods are in good agreement, the largest difference between any two calculations of the elongational viscosity at a given elongation rate being about 5%. The zero-shear Newtonian viscosity for this system obtained by evaluating the Green–Kubo integral for an 864-particle system at the same state point is 2.3 ± 0.1 in reduced units [10], which is consistent with the data given in Fig. 1 and the limiting behavior of η_{EP} expected from Eq. (4). Note that the extrapolation of the elongational viscosity to zero strain rate will have similar difficulties to the

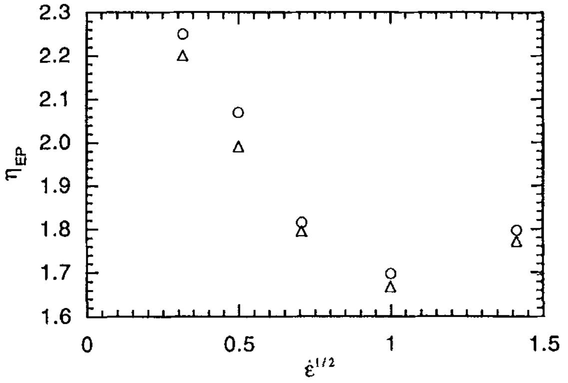

Fig. 1. The planar elongational viscosity for the WCA fluid obtained from steady elongation (triangles) and oscillatory elongation (circles) nonequilibrium molecular dynamics simulations is plotted against the elongational strain rate.

extrapolation of the shear viscosity to zero strain rate. It has been observed by several authors that the shear viscosity goes as the square root of the shear rate at intermediate shear rates, but tends to shear rate independence at small strain rates, as expected in the Newtonian region (see, e.g., Ref. 11). The results shown in Fig. 1 are all outside the Newtonian region.

A systematic difference between the elongational viscosities obtained by oscillatory and steady elongation is discernible in Fig. 1. This difference may be due to the inability of our fitting function to fit the maxima in $P_{xx}(t)$, which are more rapidly varying than the minima in $P_{yy}(t)$. This would easily be remedied by adding another sinusoidal term to the fitting function. On the other hand, the systematic difference may also be due to finite system size effects, since the maximum value of $P_{xx}(t)$ corresponds to the simulation box having its smallest dimension possible without violating the minimum image convention in the x direction. Further investigation is needed to distinguish between these possibilities, but recent transient time correlation function computations of oscillatory elongation imply that the latter explanation may be better [12].

Equations (8)–(11) imply that it should be possible to obtain the zero shear, frequency-dependent complex viscosity from our elongational viscosities by taking the limit as the elongational strain rate approaches zero. Indeed, if we write the pressure tensor elements as

$$\mathbf{P}(t) = \mathbf{P} \exp[i(\omega t + \delta)] \tag{20}$$

where δ is the phase shift between the strain rate and the pressure tensors in the linear limit, we can define the real and imaginary parts of the effective fequency-dependent viscosity as

$$\eta'_{\mathrm{EP}}(\omega, \dot{\varepsilon}_0) = \frac{P_{xx} - P_{yy}}{4\dot{\varepsilon}_0}\cos(\delta), \qquad \eta''_{\mathrm{EP}}(\omega, \dot{\varepsilon}_0) = \frac{-(P_{xx} - P_{yy})}{4\dot{\varepsilon}_0}\sin(\delta) \qquad (21)$$

where P_{xx} and P_{yy} are the amplitudes of the corresponding elements of the pressure tensor and δ is the phase shift of the oscillatory pressure. It is important to recall that in the nonlinear region, the response contains higher-frequency components, thus the definition of δ becomes ambiguous. Only in the zero-strain-rate limit is the response given by Eq. (21) expected.

To check the relationships [Eq. (21)] we have plotted the results of Eq. (21) against frequency in Fig. 2 for the four lowest strain rates investigated. Also plotted are results for the frequency-dependent shear viscosity obtained from the Green–Kubo relation—which gives the zero strain-rate limit precisely [10]. Figure 2 shows that the results for $\dot{\varepsilon}_0 = 0.1$ and 0.25 are in good agreement with the linear limit, and above $\dot{\varepsilon}_0 = 0.5$, there is a gradual departure from the linear limit. It is also worth noting that the agreement improves at higher frequencies for a given elongational strain rate. An explanation for this is that elasticity becomes important at

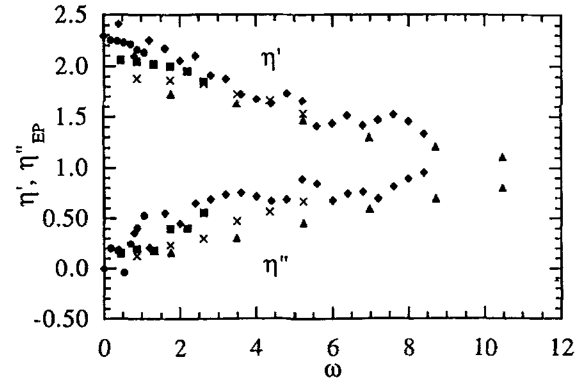

Fig. 2. The real part η' (upper curve) and the imaginary part η'' (lower curve) of the elongational viscosity defined by Eq. (21) are plotted against frequency for four different elongational strain rates. The $\dot{\varepsilon}_0 = 0.1$ data are represented by circles, $\dot{\varepsilon}_0 = 0.25$ by squares, $\dot{\varepsilon}_0 = 0.50$ by crosses, and $\dot{\varepsilon}_0 = 1.0$ by triangles. Also shown is the real part of the linear shear viscosity obtained from the Green–Kubo formula (diamonds). The convergence as $\dot{\varepsilon}_0$ decreases shows that the linear limit is approached.

nonzero frequencies, and the important parameter for the onset of nonlinear elasticity is the strain rather than the strain rate. At a given strain rate, the strain amplitude decreases with increasing frequency, so the linear limit for elasticity is approached as the frequency increases at a given strain-rate amplitude. Similarly, the disparity between results for different strain rates at a given frequency grows as the frequency decreases, as shown in Fig. 2.

In conclusion, we have shown that nonequilibrium molecular dynamics simulations of oscillatory elongational flow provide us with a very rich set of data. We have demonstated that in various limiting cases we obtain the expected behavior. In the zero-frequency, nonzero-strain-rate case, we recover the steady elongation results, and in the zero-strain rate, nonzero-frequency case, we recover linear viscoelastic behavior. Our challenge now is to develop a detailed understanding of the nonzero-frequency, nonzero-strain-rate behavior.

We have already seen for atomic systems that oscillatory elongational flow simulations are competitive with steady elongation simulations in terms of convenience and precision. It is also clear that they provide more information that can easily be extracted from the steady elongation simulations. In the case of molecular and polymeric systems, we expect the advantages of the oscillatory simulations to become more apparent.

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