Frequency dependent elongational viscosity by non-equilibrium molecular dynamics[1]

P. J. Daivis[2,4] and B. D. Todd[3]

[1] Paper presented at the Thirteenth Symposium on Thermophysical Properties, June 22-27, 1997, Boulder, Colorado, U.S.A.

[2] Department of Applied Physics, Royal Melbourne Institute of Technology, GPO Box 2476V, Melbourne, Victoria 3001, Australia

[3] Cooperative Research Centre for Polymers, c/o CSIRO Division of Chemicals and Polymers, Private Bag 10, Rosebank MDC, Clayton, Victoria 3169, Australia

[4] To whom correspondence should be addressed.

ABSTRACT

The elongational viscosity of a liquid describes the response of the liquid to simultaneous symmetric stretching and compression in various directions, subject to the restriction that the trace of the rate of strain tensor is zero. Despite the growing popularity and usefulness of non-equilibrium 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 elonational 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 taken for this to occur 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 elongation elongational viscosity. We have used this method to compute the elongational viscosity of a simple atomic liquid, and will discuss its possible application to a model polymeric liquid.

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

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 non-equilibrium 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

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

For constant volume to be maintained, we must have $\mathrm{Tr}(\mathbf{u}) = 0$. 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 will only consider planar and uniaxial elongational flow.

In all of the non-equilibrium 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 cut off 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. The purpose of this paper is to elaborate on this technique and discuss the results that are obtained when it is applied.

2. THEORY

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

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

while for steady uniaxial elongational flow, we define

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

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.

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

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.

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

and since eqn (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 (4). Equation (5) can be generalized to arbitrary time-dependent strain rates in the small strain rate, small deformation limit as

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

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 eqn (6) where the strain rate is constant after a step increase from zero, but the stress and the elongational viscosity may be time 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

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

from which we see that the same relationships between the shear and 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

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

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;

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

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

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 eqn (8) are the same as those of eqn (5), so we can immediately deduce that for planar elongational flow,

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

The case of periodic uniaxial elongational flow is more interesting. With $\dot{\varepsilon}(t) = \dot{\varepsilon}_0 \cos(\omega t)$ in eqn (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 large amplitude or strain rate oscillatory elongation requires the full machinery of non-linear constitutive equations for a complete description. However, we can deduce the limiting behaviour 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

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

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 swapped. 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 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]

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

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

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]

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

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 $\mathbf{u}$ is given by the constant strain rate tensor eq (1), the box dimensions change according to the following equation of motion:

$$\dot{\mathbf{L}} = \mathbf{L} \quad \mathbf{u} \tag{16}$$

which when solved, gives

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

for elongational flows.

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

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

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

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

Note that in the same way as the condition that $L_\alpha \geq 2r_c$ imposes a maximum time on a steady state elongational flow simulation, a minimum frequency is imposed by the same condition when applied to eqn (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 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 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. Fig. 1 shows that the results obtained by the two methods are in good agreement. 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 behaviour of η_{EP} expected from eq (4).

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 part of the effective fequency dependent viscosity as

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

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 peak in the pressure. It is important to recall that in the non-linear region, the response may contain higher frequency components, thus the definition of δ becomes ambiguous. Only in the zero strain rate limit is the response given by eqn (21) expected.

To check the relationship (21) we have plotted the result of eqn (21) against frequency in Fig. 2 for the three 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. Fig. 2 shows that the results for $\dot{\varepsilon}_0$ = 0.1 and 0.25 are in good agreement with the linear limit, but at $\dot{\varepsilon}_0$= 0.5, there is a dramatic departure from the linear limit.

In conclusion, we have shown that non-equilibrium 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 behaviour. In the zero frequency, non-zero strain rate case, we recover the steady elongation results, and in the zero strain rate, non-zero frequency case, we recover linear viscoelastic behaviour. Our challenge now is to develop a detailed understanding of the non-zero frequency, non-zero strain rate behaviour.

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. We are currently investigating the application of these techniques to polymeric systems and hope to report more fully on this work in the oral presentation.

REFERENCES

1. D.J. Evans and G.P. Morriss, *Statistical Mechanics of Nonequilibrium Liquids*, Academic Press, London (1990).
2. P. T. Cummings and D, J. Evans, *Ind. Eng. Chem. Res.* **31**, 1237 (1992).
3. H. A. Barnes, J. F. Hutton and K. Walters, *An Introduction to Rheology*, Elsevier, Amsterdam (1989).
4. M.N. Hounkonnou, C. Pierleoni, and J.-P. Ryckaert, *J. Chem. Phys.* **97**, 9335 (1992).
5. A. Baranyai and P.T. Cummings, *J. Chem. Phys.* **103**, 10217 (1995).
6. G. Astarita and G. Marrucci, *Principles of Non-Newtonian Fluid Mechanics*, McGraw-Hill, London (1974).
7. J. D. Ferry, *Viscoelastic Properties of Polymers*, Wiley, New York (1980).
8. J.D. Weeks, D. Chandler, and H.C. Andersen, J. Chem. Phys. 54, 5237 (1971).
9. B. D. Todd and P. J. Daivis, accepted for publication in J. Chem. Phys. (1997).
10. P. J. Daivis and D. J. Evans, in preparation.

FIGURE CAPTIONS

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

Fig. 2. The real part of the elongational viscosity defined by eqn (21) is plotted against frequency for three different elongational strain rates. The $\dot{\varepsilon}_0 = 0.25$ data are represented by squares, $\dot{\varepsilon}_0 = 0.50$ by empty circles and $\dot{\varepsilon}_0 = 1.0$ by filled circles. Also shown is the real part of the linear shear viscosity obtained from the Green-Kubo formula (crosses). The convergence as $\dot{\varepsilon}_0$ falls shows that the linear limit is approached.

Fig. 1

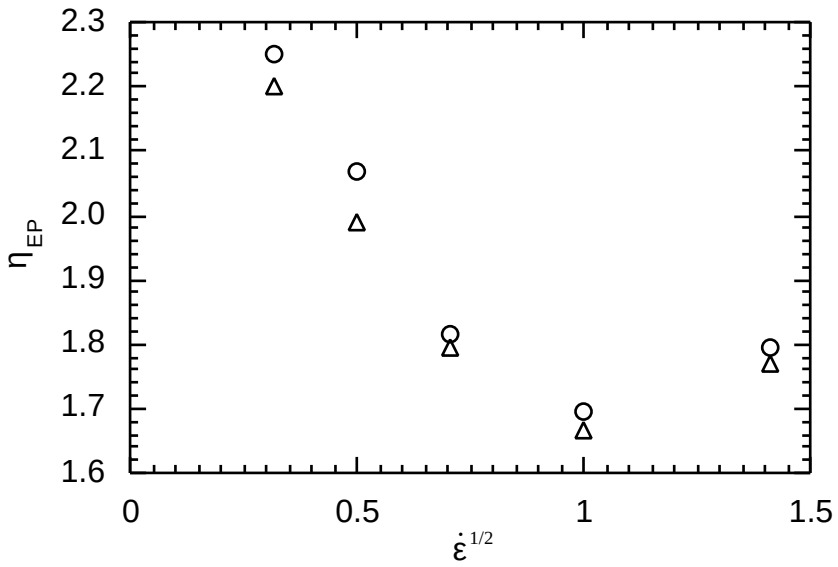

Fig. 2