

Predicting the Newtonian viscosity of complex fluids from high strain rate molecular simulations

Clare McCabe^{a),b)}

Department of Chemical Engineering, University of Tennessee, Knoxville, Tennessee 37996, and Chemical Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831

Charles W. Manke

Department of Chemical Engineering and Materials Science, Wayne State University, Detroit, Michigan 48202

Peter T. Cummings

Departments of Chemical Engineering, Chemistry and Computer Science, University of Tennessee, Knoxville, Tennessee 37996, and Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831

(Received 10 September 2001; accepted 3 December 2001)

The prediction of viscosity by molecular simulation has been a goal of molecular modeling essentially since its inception. With today's computing power, the Newtonian or zero shear viscosity of a low molecular weight fluid can easily be determined using equilibrium and nonequilibrium molecular dynamics simulation methods. However, both methods are constrained to systems with relatively short relaxation times that are accessible on the timescale of a molecular dynamics simulation. Here we demonstrate that using a simple scaling relation enables us to predict the Newtonian viscosity of a molecule at any state point for a small fraction of the time that it takes to obtain the same result through nonequilibrium or equilibrium molecular dynamics simulation.

© 2002 American Institute of Physics. [DOI: 10.1063/1.1446045]

INTRODUCTION

The prediction of viscosity by molecular simulation has long been a goal of molecular modeling essentially since its inception. Molecular simulation methods for calculating viscosity can be broadly classified into equilibrium molecular dynamics (EMD) and nonequilibrium molecular dynamics (NEMD) methods. In an EMD simulation, Newton's equations (or a variant thereof) describing the motion of the atoms in the model system are solved as a function of time. The viscosity η is then given as an integral of the stress–stress autocorrelation functions determined during the simulation, viz.

$$\eta = \frac{V}{k_B T} \lim_{\tau \rightarrow \infty} \int_0^\tau dt \langle P_{xy}(t) P_{xy}(0) \rangle, \quad (1)$$

where V is the volume of the system, k_B is Boltzmann's constant, T is temperature, and t is time. The quantity $P_{xy}(t)$ is the value of the xy component of the traceless symmetric stress tensor at time t , and so $P_{xy}(t)P_{xy}(0)$ is the stress–stress autocorrelation function and $\langle P_{xy}(t)P_{xy}(0) \rangle$ is its ensemble average (indicated by $\langle \dots \rangle$) measured during the course of the simulation. Equation (1), known as the Green–Kubo formula, is easily and efficiently applied to low molecular weight fluids since the relaxation time of the stress–

stress autocorrelation function is very short in such fluids.¹ A more general form of Eq. (1) is that derived by Daivis and Evans²

$$\eta = \frac{V}{10k_B T} \lim_{\tau \rightarrow \infty} \int_0^\tau \sum_{\alpha=1}^3 \sum_{\beta=1}^3 q_{\alpha\beta} \langle P_{\alpha\beta}(t) P_{\alpha\beta}(0) \rangle dt, \quad (2)$$

where $q_{\alpha\beta} = 1 + \delta_{\alpha\beta}/3$. Another variant of the Green–Kubo method is the Einstein formula, obtained by integrating Eq. (2), and given by

$$\eta = \lim_{t \rightarrow \infty} \frac{V}{20k_B T t} \left\langle \sum_{\alpha=1}^3 \sum_{\beta=1}^3 q_{\alpha\beta} [\Delta A_{\alpha\beta}(t)]^2 \right\rangle, \quad (3)$$

where

$$\Delta A_{\alpha\beta}(t) = \int_0^t P_{\alpha\beta}(t') dt'. \quad (4)$$

EMD methods based on the application of one of Eqs. (1) through (3) have been applied routinely and successfully to low molecular weight fluids.^{3,4} The success of these methods for such fluids is at least partly the result of the short relaxation times (of the order of 10 ps or less) for the stress–stress autocorrelation function in such systems. The time over which the stress–stress autocorrelation function needs to be computed in order to obtain high-accuracy results from Eqs. (1)–(3) is at least several relaxation times. As a result, when the relaxation time is of the order of 10 ps or less, the stress–stress autocorrelation function needs to be computed for 10^3 – 10^4 time steps, since the time step in molecular dynamics simulations is typically of the order of 10^{-15} s.

^{a)}Permanent address from 1 January 2002: Department of Chemical Engineering, Colorado School of Mines, Golden, CO 80401.

^{b)}Author to whom correspondence should be addressed; electronic mail: cmccabe@mines.edu

Questions have been raised about the applicability of these EMD formulas to larger molecules, such as the alkanes C_nH_{2n+2} beyond n in the range 10–16. For example, Cui *et al.*³ showed that Eqs. (1) and (2) gave identical results for $n \leq 10$ (i.e., for decane and shorter) but that the numerical results from the two equations were inconsistent for $n = 16$ (hexadecane). They interpreted the failure of the EMD method as resulting from the long relaxation times of the stress–stress autocorrelation function. Two factors appear to be at work: first, shorter relaxation times mean that proportionally more independent samples of the stress–stress correlation function can be accumulated over similar length simulations; and second, the numerical accuracy of the stress–stress correlation function computed to the very long times needed for systems with long relaxation times is at least questionable. The simulations reported by Cui *et al.* for decane covered 5.4 ns (corresponding to 529 relaxation times) and 13.1 ns for hexadecane (corresponding to only 70 relaxation times).³

Whether the EMD methods can be used for long molecules or not, what is clear is that the simulations need to be run for many multiples of the stress–stress autocorrelation relaxation time, and as a result will become prohibitively long computations as the molecular weight of the molecules increases. Hence, EMD simulation as a route to the Newtonian viscosity, appears not to be a viable approach for long molecules (e.g., alkanes beyond around C_{16}) with today's computing power.

While EMD has been used extensively for calculating transport properties, in recent years the NEMD method has become increasingly popular. In particular NEMD is a useful technique for studying rheological properties since it can also be used to probe the non-Newtonian regime, common to polymers and other high molecular weight systems, in which the transport properties are nonlinear in the applied field. The NEMD algorithm for viscosity involves applying a planar Couette flow field at strain rate $\dot{\gamma} = \partial u_x / \partial y$, which characterizes the constant change in streaming velocity u_x in the x direction with vertical position y . The viscosity at strain rate $\dot{\gamma}$ is then computed from

$$\eta = - \frac{\langle P_{xy} \rangle}{\dot{\gamma}}, \quad (5)$$

where again P_{xy} is the traceless symmetrized pressure tensor computed in the course of the simulation. The result is a strain-rate dependent shear-thinning viscosity. The critical strain rate transition $\dot{\gamma}_c$ above which we see shear-thinning and below which we see a Newtonian plateau (η independent of $\dot{\gamma}$) typically occurs at $\dot{\gamma}_c \approx \tau_{rot}^{-1}$, where τ_{rot} is the rotational relaxation time at equilibrium (i.e., in the absence of shear).

As a method for predicting the Newtonian viscosity of a fluid, NEMD also has its limitations. In particular, while the viscosity converges rapidly at high strain rate, the length of the simulation needed to obtain reliable averages for $\langle P_{xy} \rangle$ increases nonlinearly as the strain rate is reduced; in particular, for $\dot{\gamma} < \dot{\gamma}_c$ $\langle P_{xy} \rangle$ must be averaged through at least several, and preferably many, rotational relaxation times. The result is that the total amount of computation required to obtain a reliable enough viscosity-strain rate curve to be able

TABLE I. State points studied.

State point	Temperature/K	Pressure/GPa	Density/g cm ⁻³
A	310.93	1.01E-04	0.791
B	372.04	1.01E-04	0.751
C	372.04	0.682	0.943
D	372.04	0.829	0.964
E	372.04	0.958	0.980

to confidently extrapolate to a Newtonian viscosity well exceeds that of the corresponding EMD Green–Kubo calculation in those cases that the latter is feasible. In the case of long molecules where EMD calculations appear to be infeasible, the NEMD method is the only reliable route to the Newtonian viscosity, albeit computationally expensive. This becomes particularly apparent at high pressures where the rotational relaxation time is of the order of tens of ns and the shear-thinning regime extends down to very low strain rates.⁵

Recently, we have performed large scale NEMD simulations of several linear and branched alkanes (see, for example, Refs. 5, 6) using simple united atom models.⁷ In particular we have studied 9-octylheptadecane at a range of state points that included state conditions corresponding to very high giga-pascal pressures.⁵ The quantity of strain-rate dependent viscosity results collected in the course of this work makes it possible for the first time to assess whether the results follow the corresponding states behavior typically observed in polymers. The state points studied are summarized in Table I. In Fig. 1, we show a plot of η/Z versus $\dot{\gamma}Z$ for 9-octylheptadecane where Z is the ratio of the Newtonian viscosity at the temperature and density of interest to that of a chosen reference point, $Z = \eta / \eta_{ref}$. As such, this plot is a simple version of time-temperature superposition, an empirical scaling method that is widely applicable to viscoelastic liquids.⁸ Since time-temperature superposition is closely associated with free volume theory, it seems reasonable to suppose that the scaling factor Z used here will depend on density. In the figure, the reference state corresponds to state A in Table I (311 K, atmospheric pressure, and a density of $\rho = 0.790$ g cm⁻³). Details of the set of simulation results used to generate Fig. 1 are given in Table's 5 and 6 of Ref. 5. We

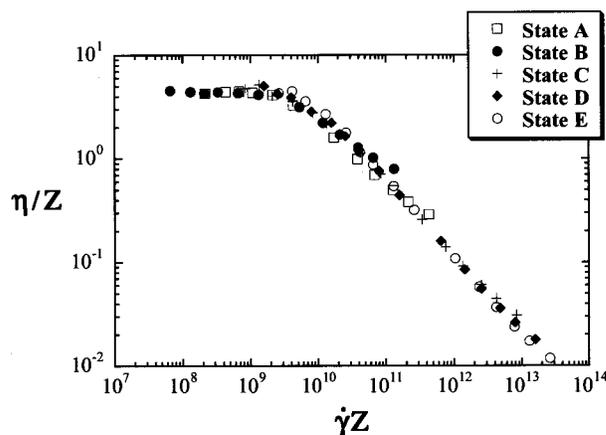


FIG. 1. Reduced strain rate dependent viscosity for 9-octylheptadecane at state points given in Table I.

see from the figure that the simulation results when presented in this reduced form show a remarkable degree of consistency with a single master curve, even when using this simple scaling relation over a wide range of temperatures and pressures, from atmospheric to 1 Gpa.

Having established this master curve, we can now use this curve to predict the Newtonian viscosity of 9-octylheptadecane at an arbitrary temperature and density from just two high-strain-rate simulations, which as noted earlier are very efficient to perform. We shall illustrate this by using only the simulation data for 9-octylheptadecane at atmospheric pressure (state points A and B in Table I) to obtain the master curve and then predict the Newtonian viscosity at each of the high pressure state points (state points C, D, and E in Table I) using simulation results at just two strain rates for each state point. Again, choosing state A as the reference state in the expression for Z, we generate the master curve, though now from states A and B only. In order to predict the Newtonian viscosity at a given state point, say C from Table I, we need to determine Z, the ratio of the Newtonian viscosity of state point C to that of the reference state, A. To determine Z we need to find where the points $(\eta^C/Z, \dot{\gamma}^C Z)$ at two given strain rates lie on the master curve. To aid in the fitting procedure we obtained an analytical expression for the master curve by fitting to the Carreau–Yasuda model,⁹

$$\frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} = [1 + (\lambda \dot{\gamma})^a]^{(n-1/a)}, \quad (6)$$

where η_0 is the Newtonian or zero-shear rate viscosity, η_∞ the infinite-shear rate viscosity, λ a time constant, and n the power law exponent which describes the slope of the viscosity as a function of shear rate in the “shear-thinning” regime, and a a dimensionless parameter that describes the transition region between the zero-shear and the power law region. The parameters of the model of Eq. (4) were optimized to reproduce the master curve obtained from states A and B. We found that we could simplify the above expression by setting η_∞ to 0 and still achieve a good description of the master curve. The parameters obtained were $\eta_0 = 4.42$ cP, $\eta_\infty = 0$ cP, $\lambda = 0.275 \times 10^{-9}$ s, $n = 0.27$, and $a = 1.81$. Now we have an analytical expression for the master curve we can easily determine the value of Z for state point C using the strain rate dependant viscosity data at just two points. (In principal, Z could be determined from only one high-shear-rate viscosity value. However, the use of two high shear rate points, as recommended here, greatly improves the accuracy and also provides an internal check of the applicability of time-temperature superposition at the new state high shear rate point.) We proceed by finding the value of Z that causes the two points to deviate in a least squares fashion from Eq. (6). The results for state point C, along with those obtained for states D and E, are plotted on the master curve in Fig. 2 where we see that the value of Z determined at each state point is such that the data for both strain rates fall on the master curve. Now we have the value of Z for state C, we can calculate the Newtonian viscosity from $\eta_C = \eta_{\text{ref}} Z$. In Table II we compare the predicted Newtonian viscosity from this simple scaling relationship with that obtained from the

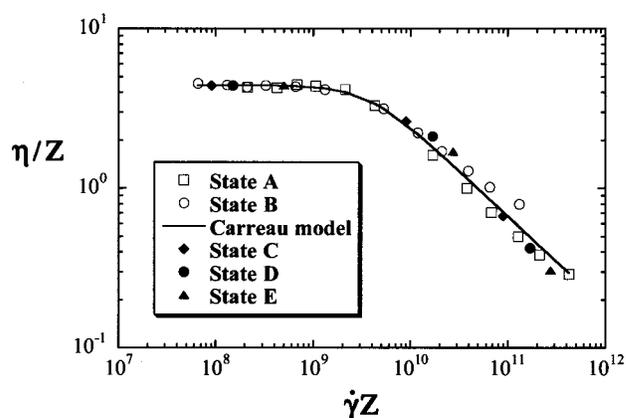


FIG. 2. Reduced strain rate dependant viscosity for 9-octylheptadecane at state points A and B (open symbols). The Carreau fit to the reduced curve is shown by the solid line and the predicted data at state points C, D, and E by the filled symbols.

lengthy NEMD simulations.⁵ Using this simple scaling relation and the master curve we are able to accurately predict the Newtonian viscosity at these high pressure state points for a fraction of the time that it took to obtain the same result through NEMD simulation alone. The reader should note that the points used to obtain Z were in no way chosen in order to optimize the agreement obtained with the predicted Newtonian plateau. Since we had a body of simulation data with which to test the predictive power of this relationship we studied the variance of the predicted values. We recommend the two strain rates simulated in order to fit Z be approximately an order of magnitude apart and that the largest resulting $\dot{\gamma}Z$ should lie in the range of values to which the master curve is fitted. This meant that since the atmospheric pressure simulations used as the reference were not performed over as wide a range of strain rate as those at high pressures, the highest strain rate we could use in the fitting of Z was 0.01 in reduced units. Had we chosen states C and D to determine the master curve, we could have chosen much higher strain rates at which to perform the simulations required for fitting Z. In this latter case using a reduced strain rate of 1.0 and 0.1 we can predict the Newtonian viscosity of state A and B to be 1.56 cP and 4.68 cP, respectively, which compares very well with the reported values of 1.36 cP and 4.40 cP from the results of NEMD simulations alone.

As in the example presented here, the master curve can be determined by performing NEMD simulations at state conditions at which the relaxation times are relatively short and then be used to accurately predict the Newtonian viscosity at high pressures where the simulations take considerably longer to perform. In Table III the simulation time used to

TABLE II. Viscosity vs strain rate data for 9-octylheptadecane at state points C, D, and E used to predict the Newtonian viscosity (Ref. 5).

Strain rate/s ⁻¹	Viscosity/cP		
	State point C	State point D	State point E
4.24×10^9	14.23	16.79	19.85
4.24×10^8	55.46	83.93	110.1

TABLE III. Comparison of the Newtonian viscosity obtained from NEMD simulations given in Ref. 5 and this work at state points *C*, *D*, and *E* from Table I.

State point	This work		NEMD taken from Ref. 2	
	Viscosity/cP	Run time/ns	Viscosity/cP	Run time/ns
<i>C</i>	93	34	87(± 12)	330
<i>D</i>	174	35	165(± 18)	325
<i>E</i>	285	27	270(± 7)	340

obtain the Newtonian viscosity for each method is reported. On average to obtain the Newtonian viscosity at these high strain rates takes ~ 300 ns whereas to perform a single high-strain-rate NEMD calculation to obtain the strain rate dependant viscosity takes ~ 15 ns. Once the master curve has been determined, which in the work here took ~ 200 ns, the incremental cost in determining the Newtonian viscosity for the same molecule at any number of additional state points is therefore very small. We have confirmed that other alkanes follow the same master curve formalism described here. In particular, we have extensive NEMD simulation results on the highly branched C_{30} alkane squalane, and we have confirmed that it also follows a master curve that fits the Carreau–Yassuda equation.¹⁰

The implication of this result is rather remarkable. Using a simple scaling relation we are able to accurately predict the Newtonian viscosity for state points in the giga-pascal range from simulations performed at atmospheric pressure. Hence, this simple scaling relation represents a significant saving in computational time, as once the master curve has been determined, only two short runs need to be performed at a different state point in order to predict the zero-shear viscosity at that state point.

We expect that the scaling approach outlined in this paper will be applicable to any fluid that exhibits power law behavior ($\eta \sim \dot{\gamma}^{-\alpha}$) in the shear-thinning regime, such as alkanes of sufficiently high molecular weight and polymers. As a consequence, we note that this suggests that the tech-

nique may not be applicable to low-molecular-weight fluids, including simple fluids, where the shear-thinning behavior often appears to follow the mode coupling theory result $\eta \sim \eta_0 - A \dot{\gamma}^{0.5}$ or related functional forms (for a recent discussion, see Ref. 11). Since the Newtonian viscosity of shorter alkanes and simple fluids is readily calculated using equilibrium Green–Kubo methods,^{1–3} the possible nonapplicability of this approach for such systems is not likely to represent an important limitation.

ACKNOWLEDGMENTS

This work was supported in part by the National Science Foundation under Contract No. CTS-9871919 at the University of Tennessee and by the Division of Materials Sciences of the U.S. Department of Energy at Oak Ridge National Laboratory. The Oak Ridge National Laboratory is managed by UT-Battelle, LLC, for the Department of Energy under Contract No. DE-AC05-00OR22725. Additional funding was provided by ExxonMobil Research and Engineering.

¹M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Oxford University Press, Oxford, 1987).

²P. J. Daivis and D. J. Evans, *J. Chem. Phys.* **100**, 541 (1994).

³S. T. Cui, P. T. Cummings, and H. D. Cochran, *Mol. Phys.* **93**, 117 (1998).

⁴J. M. Haile, *Molecular Dynamics Simulation* (Wiley, New York, 1992); M. Mondello and G. S. Grest, *J. Chem. Phys.* **103**, 7156 (1995).

⁵C. McCabe, S. T. Cui, P. T. Cummings, P. A. Gordon, and R. B. Saeger, *J. Chem. Phys.* **114**, 1887 (2001).

⁶S. T. Cui, S. A. Gupta, P. T. Cummings, and H. D. Cochran, *J. Chem. Phys.* **105**, 1214 (1996); S. T. Cui, P. T. Cummings, H. D. Cochran, J. D. Moore, and S. A. Gupta, *Int. J. Thermophys.* **19**, 449 (1998); J. D. Moore, S. T. Cui, H. D. Cochran, and P. T. Cummings, *J. Chem. Phys.* **113**, 8833 (2000).

⁷J. I. Siepmann, S. Karaborni, and B. Smit, *Nature (London)* **365**, 330 (1993); B. Smit, S. Karaborni, and J. I. Siepmann, *J. Chem. Phys.* **102**, 2126 (1995).

⁸J. D. Ferry, *Viscoelastic Properties of Polymers* (Wiley, New York, 1980).

⁹R. B. Bird, R. C. Armstrong, and O. Hassager, *Dynamics of Polymeric Liquids*, 2nd ed. (Wiley, New York, 1987).

¹⁰S. Bair, C. McCabe, and P. T. Cummings, *Phys. Rev. Lett.* (in press); C. McCabe, P. T. Cummings, P. A. Gordon, and R. B. Saeger, *J. Chem. Phys.* (in preparation).

¹¹K. P. Travis, D. J. Searles, and D. J. Evans, *Mol. Phys.* **97**, 415 (1999).