

Comparison of Nonequilibrium Molecular Dynamics with Experimental Measurements in the Nonlinear Shear-Thinning Regime

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Nonequilibrium molecular dynamics of a low-molecular-weight fluid (squalane) are compared with experimental measurements in both the linear (Newtonian) and nonlinear (non-Newtonian) regimes. The experimental and simulation data are shown to follow the same time-temperature superposition master curve. This represents the first comparison of the nonlinear rheology predicted by nonequilibrium molecular dynamics with experiment, and is thus the first experimental test of nonequilibrium molecular dynamics simulations in the nonlinear regime.

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Nonequilibrium molecular dynamics (NEMD) is a powerful method for the molecular-based study of transport phenomena [1,2]. The essence of the NEMD method is to create a nonequilibrium steady state in a molecular simulation by application of an appropriate external field F . The applied external field produces a conjugate flux J , and the constitutive relation between the field and the flux, $J = -FX$, defines a transport coefficient X . NEMD methods date to the 1970s [3]; however, it was not until the mid 1980s that the development of linear and nonlinear response theory made it possible to derive rigorously correct homogeneous algorithms consistent with periodic boundary conditions and to prove that in the zero-field (linear regime) limit, a properly defined transport property X reduces to its corresponding equilibrium system value [4]. One caveat in the theory of NEMD is that the existence of a nonlinear steady state is predicated on the ability to thermostat the system (i.e., remove heat generated dissipatively by the application of the external field) in a physically meaningful way.

NEMD is a particularly useful technique for studying rheological properties since the key algorithm (SLLOD) [4], is a direct implementation of the experimental method for measuring viscosity and because 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 SLLOD 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

$$\eta = -\frac{\langle P_{xy}^{0,s} \rangle}{\dot{\gamma}}, \quad (1)$$

where $P_{xy}^{0,s}$ 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 $\dot{\gamma}_c \approx \tau^{-1}$, where τ is the longest relaxation time at equilibrium (i.e., in the absence of shear). This is usually τ_{rot} , the rotational relaxation time. For more than a decade, we have been applying NEMD to the prediction of the Newtonian viscosity in systems ranging in complexity from carbon dioxide and its mixtures [5] to short polymers [6] using atomistically detailed and united atom force fields. We have been specifically interested in characterizing lubricants [7–10], and NEMD has shown particular promise in this area. While we have been predominantly interested in the Newtonian viscosities predicted by these models, our simulations have resulted in predictions for the nonlinear non-Newtonian regime. Questions about the validity of thermostating mechanisms in the nonlinear regime have recently been raised [11,12]. In particular, while it is clear that in principle the method of thermostating atomic velocities using a Nosé thermostat (as used in our simulations) is an approximation to a truly unbiased thermostat, evidence from NEMD simulations [12] suggests that it is effectively correct at reduced strain rates $\dot{\gamma}^* = \dot{\gamma}(m\sigma^2/\varepsilon)^{1/2}$ less than approximately 2. Here m , σ , and ε are characteristic mass, length, and energy quantities for the system under consideration; for alkanes, these are typically the mass, diameter, and Lennard-Jones interaction energy of a methylene (CH₂) group. The absence hitherto of any strain-rate dependent (i.e., non-Newtonian) experimental data on molecules accessible to NEMD simulation has made it impossible to evaluate the nonlinear regime predictions and, in particular, assess the

TABLE I. State points studied by experiment (*E*) and simulation (*S*). The results for simulated states *S1* and *S2* have been reported previously [7,14].

State point	Temperature [°C]	Density [g/cm ³]	Pressure [GPa]	Newtonian viscosity [cP]
<i>E1</i>	20	0.976	0.796	2.6×10^6
<i>E2</i>	20	0.984	0.875	6.0×10^6
<i>E3</i>	20	0.991	0.955	1.45×10^7
<i>E4</i>	8	0.995	0.955	1.50×10^8
<i>S1</i>	38	0.798	1.01×10^{-4}	14.52
<i>S2</i>	60	0.784	1.01×10^{-4}	5.304
<i>S3</i>	99	0.891	0.316	36.95

validity of thermostating mechanisms from a practical point of view.

Recently, one of us (S.B.) has measured the viscosity of squalane (2-, 6-, 10-, 15-, 19-, and 23-hexamethyl-tetracosane) at high pressures (0.636–0.955 GPa) and low temperature (20 °C and 8 °C) resulting in shear-thinning viscosities for this compound. A pressurized Couette rheometer was employed to measure the shear stress for various imposed rates of shear. This instrument is similar to one previously described [13], except that a strain-gauge-based torque sensor has replaced the use of light to transmit shear stress information outside of the high-pressure environment. The liquid sample is sheared between the surfaces of a pair of concentric cylinders fabricated from a high thermal conductivity and high strength metal composite. The radial clearance is 4 μm and the relative rotational velocity is provided by a digitally controlled stepper motor acting through a rotating unsupported area seal. Pressure is generated by an integral intensifier and is measured with a manganin resistance gauge.

NEMD simulations for squalane have been performed in the Cummings group over a wide range of densities (0.759–0.891 g/cm³) and temperature (38–100 °C), corresponding to experimental pressures of 1 bar to 0.32 GPa [7,8,14,15]. The commonly used united atom model of Siepmann, Karaborni, and Smit [16,17] was used to de-

scribe the squalane molecules. Full details of the simulation method can be found in earlier papers on similar systems at ambient and high pressure [7,9]. A complete compilation of the state points studied, and the experimental data and simulation results, is provided in Tables I, II, and III, respectively.

Note that in Tables I–III we do not report experimental and simulational results at the same state conditions, because it is not possible with present-day computers to perform molecular dynamics simulations on the same state conditions as the experiment. The experiments had to be performed at low temperature (~ 20 °C) and very high pressure (~ 1 GPa) in order to obtain shear-thinning data for squalane over the accessible range of experimental shear rates (up to 10^4 s⁻¹) [18]. Under these conditions squalane's relaxation time would be of the order of 10^{-3} – 10^{-2} s. In order to obtain credible NEMD results requires the simulation to equilibrate (in the absence of shear) or reach a steady state (in the presence of shear). Hence we must integrate the equations of motion for a time equal to several relaxation times. Time scales of 10^{-3} – 10^{-2} s are inaccessible to molecular dynamics simulation. However, although the experiments and simulations cannot be directly compared, we can place the results in comparable form using the standard rheological analysis technique of temperature-time superposition [19], a well-established technique in polymer rheology for collapsing experimental data for a given polymer at different temperatures, densities, and strain rates onto a single curve characteristic of that polymer. Its theoretical basis is discussed by Bird *et al.* [19,20], including a derivation based on kinetic theory [20]. In time-temperature superposition, the viscosity(η)–strain rate($\dot{\gamma}$) curve is plotted in reduced form as η/a_η versus $\dot{\gamma}a_\tau$ where a_η and a_τ are given by

$$a_\eta = \frac{\eta_0(T, \rho)}{\eta_0(T_{\text{ref}}, \rho_{\text{ref}})}, \quad (2)$$

$$a_\tau = \frac{\eta_0(T, \rho)}{\eta_0(T_{\text{ref}}, \rho_{\text{ref}})} \frac{T_{\text{ref}} \rho_{\text{ref}}}{T \rho} = a_\eta \frac{T_{\text{ref}} \rho_{\text{ref}}}{T \rho}.$$

TABLE II. Experimental data for squalane at state points *E1*–*E4* as given in Table I.

State <i>E1</i>		State <i>E2</i>		State <i>E3</i>		State <i>E4</i>	
$\dot{\gamma}$ [s ⁻¹]	η [cP]	$\dot{\gamma}$ [s ⁻¹]	η [cP]	$\dot{\gamma}$ [s ⁻¹]	η [cP]	$\dot{\gamma}$ [s ⁻¹]	η [cP]
2.23×10^2	2.65×10^6	4.45×10^1	5.84×10^6	4.45×10^1	1.36×10^7	2.23×10^1	1.45×10^8
4.45×10^2	2.63×10^6	8.90×10^1	5.96×10^6	8.90×10^1	1.47×10^7	3.34×10^1	1.38×10^8
8.90×10^2	2.57×10^6	2.23×10^2	6.10×10^6	2.23×10^2	1.36×10^7	4.45×10^1	1.40×10^8
1.78×10^3	2.39×10^6	4.45×10^2	5.98×10^6	4.45×10^2	1.33×10^7	6.68×10^1	1.19×10^8
3.56×10^3	1.93×10^6	6.68×10^2	5.73×10^6	6.68×10^2	1.11×10^7	8.90×10^1	1.09×10^8
5.34×10^3	1.64×10^6	8.90×10^2	5.31×10^6	8.90×10^2	9.79×10^6	1.34×10^2	9.21×10^7
8.90×10^3	1.28×10^6	1.34×10^3	4.95×10^6	1.34×10^3	8.24×10^6	1.78×10^2	7.53×10^7
1.34×10^4	1.03×10^6	1.78×10^3	4.23×10^6	1.78×10^3	7.08×10^6	2.67×10^2	5.77×10^7
		2.67×10^3	3.80×10^6			3.56×10^2	5.06×10^7
		3.56×10^3	3.23×10^6				
		5.34×10^3	2.60×10^6				

TABLE III. NEMD simulation data for squalane at state points $S1-S3$ as given in Table I.

State $S1$		State $S2$		State $S3$	
γ [s^{-1}]	η [cP]	γ [s^{-1}]	η [cP]	γ [s^{-1}]	η [cP]
4.25×10^{11}	0.35	4.25×10^{11}	0.32	4.25×10^{11}	0.55
2.72×10^{11}	0.45	2.72×10^{11}	0.38	2.13×10^{11}	0.78
1.53×10^{11}	0.59	1.53×10^{11}	0.49	1.28×10^{11}	1.05
1.06×10^{11}	0.72	1.06×10^{11}	0.59	6.80×10^{10}	1.57
6.80×10^{10}	0.93	6.80×10^{10}	0.75	3.83×10^{10}	2.30
3.83×10^{10}	1.31	3.83×10^{10}	1.04	1.70×10^{10}	4.08
1.70×10^{10}	2.24	1.70×10^{10}	1.62	1.06×10^{10}	5.73
4.25×10^9	5.30	4.25×10^9	2.94	4.25×10^9	10.56
2.13×10^9	8.06	2.13×10^9	3.90	2.13×10^9	16.19
1.06×10^9	11.25	1.06×10^9	4.94	1.06×10^9	23.54
4.25×10^8	14.60	4.25×10^8	5.16	6.80×10^8	27.94
2.13×10^8	14.44	2.13×10^8	5.66	4.25×10^8	36.93
				2.13×10^8	38.26
				1.06×10^8	41.83
				6.80×10^7	40.60
				4.25×10^7	36.27
				2.13×10^7	36.85

Here the subscript 0 indicates a Newtonian regime quantity and the ‘ref’ subscript refers to a single reference state chosen to reduce the data. By choosing the simulation results at ambient pressure and 311 K as our reference, we have placed all of the simulation and experimental results on a single plot, shown in Fig. 1. In addition, we have fitted the combined experimental and simulation results to a single Carreau equation,

$$\frac{\eta}{a_\eta} = \eta_0 [1 + (\lambda \dot{\gamma} a_T)^2]^{(n-1)/2}. \quad (3)$$

Least squares fitting of Eq. (3) to the combined experimental and simulation results yields parameters $\eta_0 = 15.69$ cP, $\lambda = 2.26 \times 10^{-9}$ s, and $n = 0.463$. As $n \approx 1/2$, the Carreau equation captures both low-strain-rate analytic behavior and the familiar high-strain-rate power law behavior, viz.,

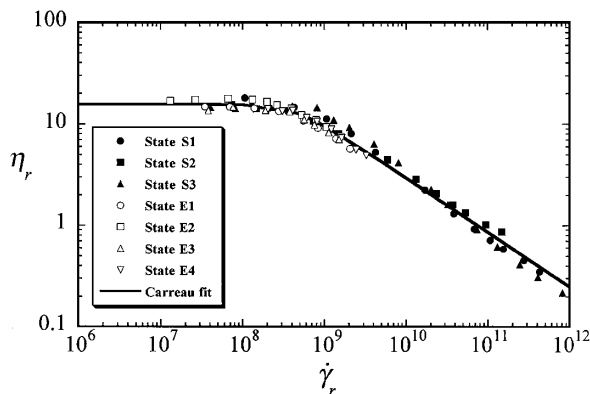


FIG. 1. Plot of reduced viscosity versus reduced strain rate for the experimental and simulation data given in Table I. Details of the reduced units are given in the text. The Carreau fit is to the combined experimental and NEMD results.

$$\begin{aligned} \eta &\sim A - B\dot{\gamma}^2 + \dots && \text{for } \dot{\gamma} \rightarrow 0; \\ \eta &\sim C\dot{\gamma}^{-1/2}, && \text{for } \dot{\gamma} \text{ large.} \end{aligned} \quad (4)$$

The first point to note is that the experimental results include strain-rate dependent viscosities, so we are presenting here, for the first time, a comparison between experiment and the nonlinear non-Newtonian regime of a real fluid. The second point to note is the remarkable fact that the simulation and experimental data follow the same master curve, leading to the conclusion that the behavior of squalane predicted by NEMD in the non-Newtonian region is in good agreement with experiment. Finally, the good agreement between experiment and simulation suggests that the thermostating mechanism used in these simulations provides an adequate approximation of more rigorously correct thermostating techniques [12].

In summary, we have shown here that the availability of shear thinning rheological data for low molecular weight liquids at low temperature and high pressure, such as the squalane data presented here, make it possible for the first time to compare NEMD predictions in the non-Newtonian regime with experiment. The way in which this comparison is achieved is through the theoretically based and experimentally well established method of time-temperature superposition. Specifically, we have shown that the experimental data follow time-temperature superposition, that the simulation data follow time-temperature superposition, and that they follow the same master curve (as one would expect for the same material) with consistency for the onset of non-Newtonian behavior.

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