Power-law exponents for the shear viscosity of non-Newtonian simple fluids

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Nonequilibrium molecular-dynamics simulations are performed to compute the shear viscosities of a simple Lennard-Jones fluid across a wide range of densities and temperatures that span the liquid phase. It is found that the standard mode-coupling value of $\beta=0.5$ for the exponent of the strain rate power-law dependence ($\eta=\eta_0-\eta_1\dot{\gamma}^\beta$) is only applicable in a very narrow region of the thermodynamic state-space. More generally, the exponent is a remarkably simple linear function of temperature and density, analogous to the linear relationship that exists for the scaling exponents of the pressure and energy found previously by Ge *et al.* [Phys. Rev. E **67**, 061201 (2003)], and ranges between ~0.2 and 1.6. It is also found that the parameters η_0 and η_1 are steep functions of increasing density for any particular temperature and can be represented by a stretched exponential of the density.

The viscoelastic behavior of simple nonequilibrium fluids remains an active field of theoretical and simulation research that has been stimulated recently by some interesting and unexpected results. Theoretical investigations are largely motivated by the drive toward more comprehensive descriptions and predictions of steady-state thermodynamic behavior [1,2] or by the development and/or refinement of liquid state theories based on mode-coupling formalisms [3] and alternative fluctuation-dissipation relationships [4]. Simulation work is invaluable in exploring the implications of theory [5] as well as being a useful guide to theory by providing data that would otherwise be difficult to obtain experimentally. There are few experimental measurements of the viscosities of noble gas liquids, such as those for argon [6] and more recently xenon [7]. To the author's knowledge, there are no published data on shear thinning of such simple fluids.

Recently, nonequilibrium molecular-dynamics (NEMD) results on the pressure and energy of shearing fluids were obtained that are in variance with standard mode-coupling theory predictions [8]. In particular, it was demonstrated that the energy and pressure of a simple Lennard-Jones fluid can be described by simple power-law scaling, and that the power exponents are linear functions of temperature and density [8(c)]. The same relationship was seen to apply to the Barker-Fisher-Watts fluid [9], suggesting it is independent of the specifics of the interaction potential [10]. It was also demonstrated that a useful consequence of this simple scaling behavior is that it can be used to predict the solid-liquid phase coexistence curve at equilibrium [8(d)].

In this Brief Report, the previous work is extended by computing the viscosities for the Lennard-Jones fluid across a range of densities and temperatures that span the liquid state. It will be shown that the exponents of the viscosity versus strain rate curves have a remarkably simple analogous linear dependence on the temperature and density in the liquid phase.

As in previous work [8], the standard sllod equations of

motion [11] coupled to a Gaussian thermostat are used to simulate a three-dimensional system of 500 Lennard-Jones fluid atoms undergoing homogeneous planar shear flow. A truncation cutoff distance of 2.5σ is used and the potential parameters are set to $\sigma=\varepsilon=1.0$. Previous work on the power-law exponents for the pressure and energy of simple fluids [8(c)] showed that the value of the exponent was essentially independent of the cutoff distance. No long-range corrections are used because these do not affect the shape of any of the pressure, energy, or viscosity profiles, and hence do not affect the values of the scaling exponents [8(a)]. All units quoted hereafter are in standard reduced, dimensionless form. The equations of motion were integrated using a fifth-order Gear predictor-corrector algorithm with an integration time step of $\Delta t=0.002$.

Simulations were conducted at a number of densities for each of three fixed temperatures such that the state-space of the system is in the liquid phase [8(c)]. Temperatures were set at $T=0.722$, 1.00, and 1.25, and densities ranged from 0.7 to 0.95, to replicate the thermodynamic conditions of the
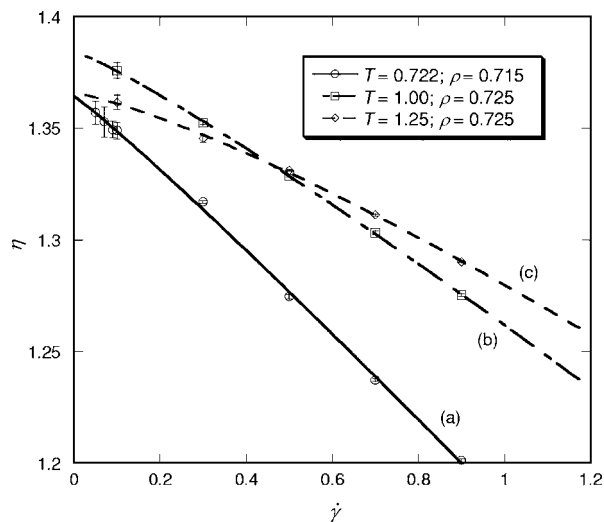

FIG. 1. Typical viscosity curves. (a) $T=0.772$, $\rho=0.715$; (b) $T=1.00$, $\rho=0.725$; (c) $T=1.25$, $\rho=0.725$.
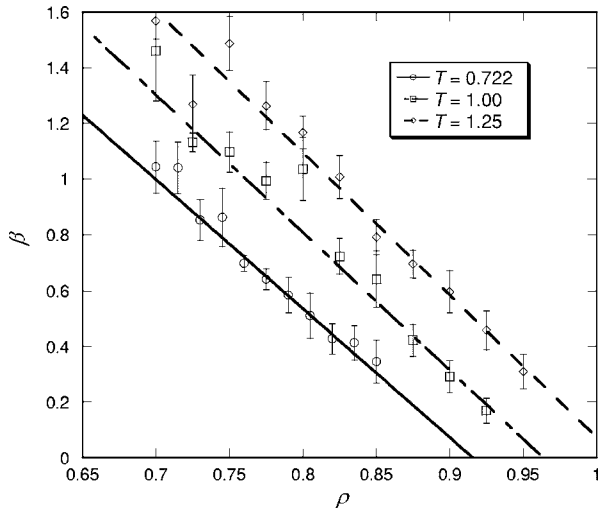
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FIG. 2. Viscosity exponents as a function of density for the three temperatures studied. Symbols represent exponents computed from the simulation data via Eq. (1), whereas lines are linear fits to the data.

systems studied previously [8(c)]. For each temperature (T), density (ρ), and strain rate ($\dot{\gamma}$), the system was first allowed to reach a nonequilibrium steady state, after which accumulation of averages took place. Generally, five independent trajectories of 2 million time steps each were run for each state point ($T, \rho, \dot{\gamma}$) and averages were accumulated over these trajectories. Thus each ($T, \rho, \dot{\gamma}$) data point is an average taken over 10 million time steps, corresponding to 20 000 reduced time units. Strain rates generally varied between 0.1 and 0.9, which are in the non-Newtonian shear-thinning regime [8(c),12] and are safely lower than the notorious and artificially induced "string-phase" region [13]. As this corresponds to very large strain rates of the order of $10^{10} - 10^{12}$ Hz
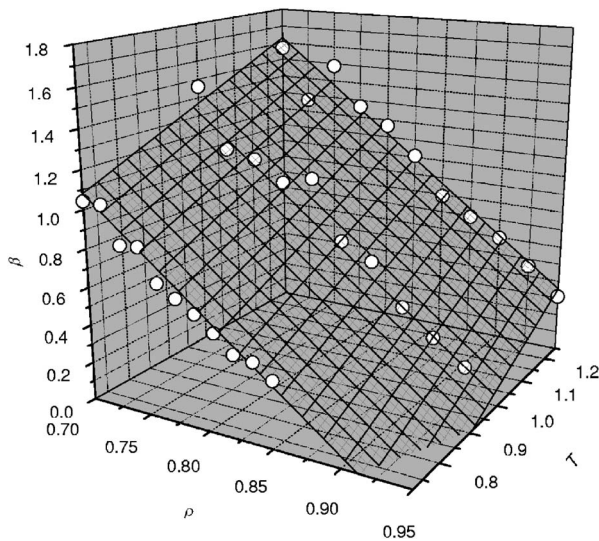

FIG. 3. Viscosity exponents presented in Fig. 2, but represented as a three-dimensional surface. Circles are simulation data as in Fig. 2, while the planar surface is the fit given by Eq. (3), where the coefficients are determined as $a = 3.9 \pm 0.2$, $b = 1.04 \pm 0.06$, and $c = 5.1 \pm 0.2$.

FIG. 4. η_0 as a function of density for each of the three temperatures studied. Symbols are simulation data determined by Eq. (1), while curves are fits to the data determined via Eq. (4). Values of all fitting parameters are given in Table IV.

[14], comparisons to existing theories that are valid only in the weak-field regime should be treated cautiously. The viscosity was computed as the ratio of the shear stress to the strain rate [11].

For each value of temperature and density, a viscosity profile was computed, as displayed in Fig. 1. For all state points simulated, a simple power law of the form

$$\eta = \eta_0 - \eta_1 \dot{\gamma}^\beta \qquad (1)$$

was found to fit the data very well, where η_0, η_1, and β are all positive constants. In this case, η_0 gives a rough approximation to the zero-shear viscosity and is likely to overestimate its value. For example, comparison of η_0 near the
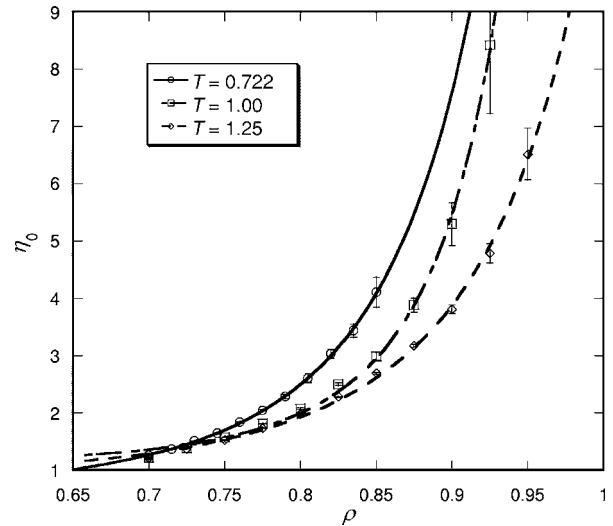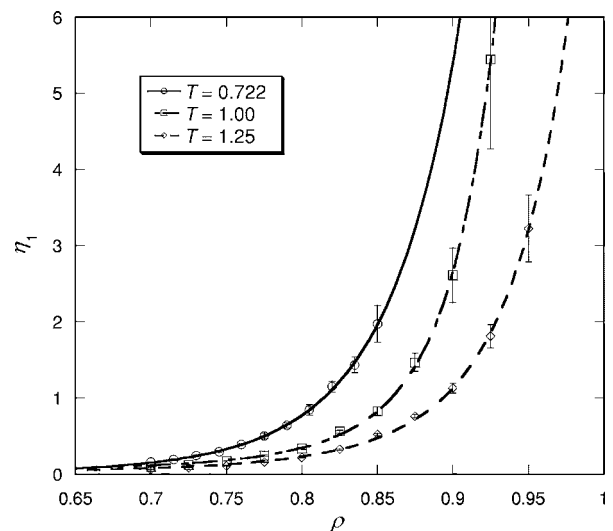

FIG. 5. η_1 as a function of density for each of the three temperatures studied. Symbols are simulation data determined by Eq. (1), while curves are fits to the data determined via Eq. (4). Values of all fitting parameters are given in Table IV.

TABLE I. Viscosity exponents (β) for all temperatures and densities. Values in parens are errors.

T	ρ																		
	0.700	0.715	0.725	0.730	0.745	0.750	0.760	0.775	0.790	0.800	0.805	0.820	0.825	0.835	0.850	0.875	0.900	0.925	0.950
0.722	1.04 (0.09)	1.04 (0.09)		0.85 (0.07)	0.9 (0.1)		0.70 (0.03)	0.64 (0.04)	0.58 (0.06)		0.51 (0.08)	0.43 (0.05)		0.41 (0.06)	0.34 (0.08)				
1.00	1.5 (0.2)		1.13 (0.03)		1.10 (0.07)			0.99 (0.07)		1.0 (0.1)			0.72 (0.06)		0.6 (0.1)	0.42 (0.06)	0.29 (0.06)	0.17 (0.05)	
1.25	1.57 (0.07)		1.3 (0.1)		1.5 (0.1)			1.26 (0.09)		1.17 (0.06)			1.01 (0.08)		0.79 (0.06)	0.69 (0.05)	0.60 (0.08)	0.46 (0.07)	0.31 (0.06)

TABLE II. Values of η_0 for all temperatures and densities. Values in parens are errors.

T	ρ																		
	0.700	0.715	0.725	0.730	0.745	0.750	0.760	0.775	0.790	0.800	0.805	0.820	0.825	0.835	0.850	0.875	0.900	0.925	0.950
0.722	1.261 (0.005)	1.367 (0.006)		1.507 (0.009)	1.64 (0.02)		1.836 (0.007)	2.04 (0.01)	2.29 (0.04)		2.60 (0.08)	3.03 (0.08)		3.4 (0.1)	4.1 (0.3)				
1.00	1.219 (0.004)		1.385 (0.001)		1.577 (0.004)			1.812 (0.006)		2.08 (0.01)			2.50 (0.02)		2.99 (0.06)	3.9 (0.1)	5.3 (0.4)	8 (1)	
1.25	1.2115 (0.0007)		1.366 (0.002)		1.527 (0.002)			1.734 (0.004)		1.975 (0.004)			2.28 (0.01)		2.69 (0.02)	3.18 (0.03)	3.81 (0.08)	4.8 (0.2)	6.5 (0.5)

TABLE III. Values of η_1 for all temperatures and densities. Values in parens are errors.

T	ρ																		
	0.700	0.715	0.725	0.730	0.745	0.750	0.760	0.775	0.790	0.800	0.805	0.820	0.825	0.835	0.850	0.875	0.900	0.925	0.950
0.722	0.154 (0.005)	0.186 (0.005)		0.242 (0.008)	0.29 (0.01)		0.389 (0.006)	0.50 (0.04)	0.64 (0.03)		0.84 (0.07)	1.15 (0.07)		1.4 (0.1)	2.0 (0.2)				
1.00	0.090 (0.004)		0.123 (0.001)		0.171 (0.004)			0.243 (0.006)		0.33 (0.01)			0.55 (0.02)		0.82 (0.06)	1.5 (0.1)	2.6 (0.4)	5 (1)	
1.25	0.0587 (0.0009)		0.086 (0.002)		0.107 (0.002)			0.154 (0.004)		0.218 (0.004)			0.323 (0.008)		0.51 (0.02)	0.76 (0.02)	1.13 (0.07)	1.8 (0.2)	3.2 (0.4)

TABLE IV. Parameters for the fit to Eq. (4). Values in parens are errors in the fit parameters.

	i	$T=0.722$	$T=1.00$	$T=1.25$
k_i	0	0.62 (0.05)	1.14 (0.09)	0.89 (0.09)
	1	0.002 (0.003)	0.05 (0.01)	0.019 (0.009)
m_i	0	4.24 (0.05)	3.94 (0.09)	2.61 (0.07)
	1	10 (1)	7.6 (0.2)	6.4 (0.5)
q_i	0	5.0 (0.3)	8.8 (0.6)	5.5 (0.5)
	1	2.4 (0.6)	5.9 (0.4)	4.2 (0.5)

Lennard-Jones triple point ($\rho=0.835$, $T=0.722$) gives a value of 3.4 ± 0.1, compared with 3.0 ± 0.1 obtained by an independent Green-Kubo calculation. It is well known that even simple fluids have Newtonian and non-Newtonian regions [15]. In order to obtain an accurate estimation of the zero-shear viscosity, more data are required at weak-field strengths, but this is not the goal of this Brief Report. In this paper, no assumption has been made about the value of the exponent β, which is known to be $\sim\frac{1}{2}$ for simple fluids near the Lennard-Jones triple point by NEMD simulation [16]. In this work, the values of all parameters η_0, η_1, and β are found by fitting Eq. (1) to the simulation data.

In Fig. 2, the viscosity exponents are plotted for the three temperatures and various densities investigated. For each temperature, a simple linear relationship is found for the exponent

$$\beta(T,\rho) = \beta_0(T,\rho) - \beta_1(T,\rho)\rho, \qquad (2)$$

where $\beta_0(T,\rho)$ and $\beta_1(T,\rho)$ are positive constants. As with the case for the exponents of pressure and energy reported earlier [8(c)], we find that the viscosity exponent can also be expressed as a linear function of both temperature and density,

$$\beta(T,\rho) = a + bT - c\rho. \qquad (3)$$

The values of the constants a, b, and c are determined by multiple regression and have the values $a=3.9\pm0.2$, $b=1.04\pm0.06$, and $c=5.1\pm0.2$. The exponents can therefore be represented as a planar surface in thermodynamic state-space, as depicted in Fig. 3. As can be seen from Figs. 2 and 3, the exponent can have any value between ~0.2 and 1.6 in the liquid phase. The mode-coupling theory value of 0.5 [17] is found in only a narrow region of thermodynamic state space between approximately $0.8\leq\rho\leq0.92$, depending on

the temperature. Values of exponents for each temperature and density are given in Table I. Recently, Santamaría-Holek et al. [2] have derived expressions for the shear viscosity of a gas of Brownian particles that, to leading order, are functions of strain rate raised to some power, δ_γ. They plot flow curves for $\delta_\gamma=\frac{1}{3}$ corresponding to a density of 0.46, but not for a wide range of densities and temperatures.

The values of η_0 and η_1 can also be determined by plotting each value for each temperature and density. These are displayed in Figs. 4 and 5, respectively, and are given in Tables II and III. Note that for each temperature, the values of η_0 and η_1 increase rapidly as density increases. This increase is so rapid that a simple power-law fit to the data results in large power exponents ranging between ~8 and 25. Similarly, a high-order polynomial series provides a reasonable fit, but this is somewhat artificial. For each temperature, η_0 and η_1 can be simply and accurately expressed by a stretched exponential of the form

$$\eta_i = k_i \exp(m_i\rho^{q_i}), \qquad (4)$$

where $i=0$ or 1 labels the parameter η_0 or η_1, respectively, and k_i, m_i, and q_i are constants for each particular temperature. Equation (4) gives a better fit to the data than the simple power-law expression $\eta_i=\hat{c}_i+\hat{k}_i\rho^{\hat{q}_i}$, where $\hat{c}_i$, $\hat{k}_i$, and $\hat{q}_i$ are constants. A further advantage of this relationship is that the exponents q_i are not excessively high. Values of all fitting parameters k_i, m_i, and q_i for each of the three temperatures are given in Table IV.

That η_0 and η_1 are well represented by a stretched exponential (or by a high simple power-law exponent) reflects the rapidity at which η_0 and η_1 diverge as functions of density. This divergence is rapid as the fluid approaches the liquid-solid phase transition, but its actual behavior in this coexistence phase is as yet unknown. There is evidence [18] that the simple linear scaling of the pressure and energy exponents as functions of temperature and density no longer applies in the liquid-solid or vapor-liquid coexistence phase regions, so care must be taken in not extrapolating beyond the data set that spans only the pure liquid phase.

We hope that the new simulation results presented in this Brief Report, along with the complete set of data provided, will be of assistance in the development of more general liquid state theories for the viscoelastic and rheological properties of fluids.

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