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Argon Shear Viscosity via a Lennard-Jones Potential with Equilibrium and Nonequilibrium Molecular Dynamics*

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Nonequilibrium molecular dynamic simulation of liquid argon yields the strain-rate dependence of shear viscosity. Near the triple point the apparent viscosity *decreases* with increasing strain rate; the extrapolated zero-gradient viscosity is consistent with the equilibrium Green-Kubo viscosity calculated by Levesque, Verlet, and Kurkijarvi. At higher temperatures along the saturated vapor pressure line, our results are insensitive to the strain rate and agree well with experimental data for liquid argon.

We have developed a *nonequilibrium* molecular-dynamic method to simulate directly dense-fluid transport.¹ The shear-viscosity coefficient is determined from a Couette flow where the bounding planar fluid walls have steady relative velocity. Systems of 108 and 216 Lennard-Jones particles have been simulated² for real time durations (for argon) of 10^{-10} sec. The average flow velocity has a linear profile, and when divided into the wall shear stress determines the Newtonian shear-viscosity coefficient $\eta \equiv -P_{xz}/u_{xz}$. In Fig. 1 our results are compared with experimental argon shear viscosity³⁻⁵ along the saturated vapor-pressure line of argon. The overall excellent agreement indicates successful simulation of nonequilibrium Couette flow with few-particle systems.

More extensive calculations have been made in

the triple-point region for comparison with a recent equilibrium molecular-dynamic calculation by Levesque, Verlet, and Kurkijarvi (LVK).⁶ These equilibrium calculations use the Green-Kubo relations to relate the transport coefficients to time correlations of the equilibrium fluctuations. An 864-atom Lennard-Jones system was studied for 10^{-9} sec (for argon) with a shear-viscosity coefficient of $\eta\sigma^2(m\epsilon)^{-1/2} = 4.02 \pm 0.3$ and thermal-conductivity coefficient of $\lambda\sigma^2(m/\epsilon)^{1/2}/k = 14.8$ at $N\sigma^3/V = 0.8442$ and $kT/\epsilon = 0.772$ (for argon, $\sigma = 3.405 \text{ \AA}$ and $\epsilon/k = 119.8^\circ\text{K}$).

Our nonequilibrium results for shear viscosity at the triple-point region depend upon the velocity gradient u_{xz} . See Table I. Thus while the highest velocity-gradient result is below the experimental argon results, the lowest velocity-gradient result approaches the equilibrium molecular-dy-

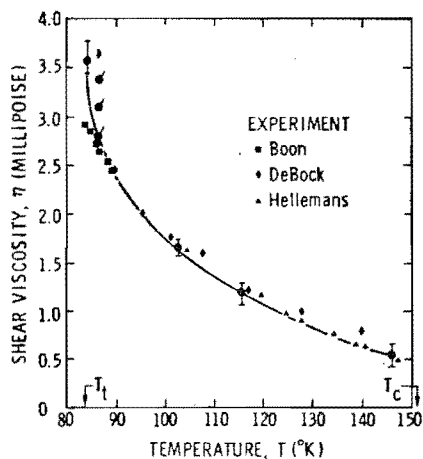


FIG. 1. Experimental argon shear-viscosity coefficient along saturated vapor-pressure line. Boon, Legros, and Thomaes (Ref. 4) used a capillary viscometer with accuracy better than 3%; De Bock, Grevendonk, and Herreman (Ref. 3) used a torsionally vibrating piezoelectric quartz crystal; and Hellemans, Zink, and Van Paemel (Ref. 5) used an oscillating-disk viscometer with accuracy better than 2%. Lennard-Jones shear-viscosity coefficient calculated with molecular dynamics ($\sigma = 3.405 \text{ \AA}$, $\epsilon/k = 119.8^\circ\text{K}$). The nonequilibrium calculation used 108 atoms with a reduced velocity gradient of $u_{xx}L(m/kT)^{1/2} = \frac{1}{2}$; a time step of $\Delta t = 0.002L(m/kT)^{1/2}$ and 8000 time steps constitute one run. Filled circles, four-run viscosity averages with a vertical line connecting extreme viscosity values. The mean viscosities (in millipoise) and temperature values are 3.57 at 84.1°K , 1.65 at 103°K , 1.17 at 116°K , and 0.54 at 146°K for reduced densities $N(\sigma/L)^3$ of 0.85, 0.76, 0.69, and 0.48. Flagged filled circles, six-run viscosity averages at reduced velocity gradients of $u_{xx}L(m/kT)^{1/2} = \frac{3}{4}, \frac{1}{2},$ and $\frac{1}{4}$ (order of increasing viscosity). Half filled circle, the equilibrium molecular-dynamic result of LVK (Ref. 6).

dynamic result of LVK, which is significantly above experimental results. The three calculated points at the higher temperatures do *not* indicate such a large velocity-gradient dependence.

Our apparent viscosity results ($\eta \equiv -P_{xx}/u_{xx}$) can be described by Eyring's theory of non-Newtonian viscous flow:

$$\eta = \eta_0 \sinh^{-1}(\tau u_{xx})/\tau u_{xx}.$$

Fitting our triple-point results with this function indicates a zero-gradient viscosity of $\eta_0 = 3.88(m\epsilon)^{1/2}/\sigma^2$ and a relaxation time of $\tau = 13.5\sigma \times (m/\epsilon)^{1/2}$, with a standard error of 0.0026. Fitting only the lowest three velocity-gradient results produces very little change in the above parameters (3.87, 13.3, and 5×10^{-4} , respectively).

TABLE I. Calculated nonequilibrium shear viscosity as a function of velocity gradient.

$u_{xx}\sigma(m/\epsilon)^{1/2}$	$\eta\sigma^2(m\epsilon)^{-1/2} (\pm 5\%)$	$\eta(\text{Ar})$ (mP)
0.247	2.24	2.02
0.155	2.75	2.48
0.113	3.09	2.79
0.0737	3.43	3.09
0.0371	3.73	3.37

Fitting our results with other functional forms (linear and quadratic in gradient) produces standard errors larger by at least a factor of 10. The relaxation time corresponds to over 10 times the period of an Einstein oscillator in a face-centered Lennard-Jones crystal at this same density, $\tau_E = 0.80\sigma(m/\epsilon)^{1/2}$. The non-Newtonian flow found here in a monatomic fluid at high rates of strain corresponds to that found in laboratory experiments on more complicated molecules.⁷

Our zero-gradient shear-viscosity coefficient at the triple point is consistent with the Green-Kubo value calculated by LVK. The equilibrium molecular-dynamic thermal-conductivity coefficient is about twice the experimental argon value,⁸ whereas the measured quadratic temperature profile in our nonequilibrium results implies a thermal-conductivity coefficient *smaller* than the experimental results (within 15 to 50% for the range of gradients treated here).

Additional equilibrium molecular-dynamic calculations along the saturated vapor-pressure line at higher temperatures would be most welcome.

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