

and R. Z. Sagdeev for enlightening discussions.

¹F. W. Perkins and J. Flick, Phys. Fluids **14**, 1012 (1971). This paper deals with the decay of an electromagnetic wave into Langmuir and ion-acoustic waves, and thresholds are given for an inhomogeneous unbounded plasma with damping. See M. N. Rosenbluth, Phys. Rev. Lett. **29**, 565 (1972), where thresholds are given for any decay-type parametric instabilities in inhomogeneous dissipationless unbounded plasmas.

²J. S. Clarke, H. N. Fisher, and R. J. Mason, Phys. Rev. Lett. **30**, 89 (1973).

³A. Bers and R. J. Briggs, Quarterly Progress Report No. 71, Research Laboratory of Electronics, Massachusetts Institute of Technology, 1963 (unpublished), p. 122.

⁴K. Nishikawa, J. Phys. Soc. Jap. **24**, 916 (1968).

⁵For SBS, the exact dispersion equation can be obtained without the weak-coupling approximation $a_i^{-1} \times da_i/dt < \omega_i$. It can be checked that when $V_1 V_2 < 0$, the absolute instability growth rate keeps approximately the same value $2\gamma_0(C_s/c)^{1/2}$ provided that $\gamma_0 < \omega_s(c/C_s)^{1/2}$ and the approximate dispersion relation can be used. If $V_1 V_2 > 0$, in the same range $\gamma_0 < \omega_s(c/C_s)^{1/2}$ we find again $\text{Re}(\nu) = \gamma_0/(cC_s)^{1/2}$ which insures $a_i^{-1} da_i/dx < k_i$.

⁶A. A. Galeev *et al.*, Pis'ma Zh. Eksp. Teor. Fiz. **17**, 48 (1973) [JETP Lett. **17**, 35 (1973)]. In this paper, it is pointed out that the inhomogeneity of the blowoff velocity U can be more important than the electron temperature inhomogeneity. In this case L_T should be replaced by $L_U = [d/dx \ln U]^{-1}$.

⁷D. W. Forslund, J. M. Kindel, and E. L. Lindman, Phys. Rev. Lett. **30**, 739 (1973).

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

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(Received 30 May 1973)

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-

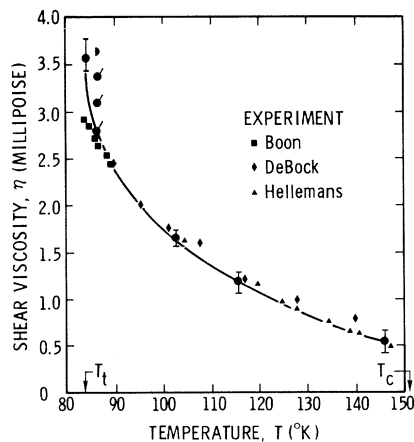


FIG. 1. Experimental argon shear-viscosity coefficient along saturated vapor-pressure line. Boon, Legros, and Thomaes (Ref. 4) used a capillary viscometer with accuracy better than 3%; De Bock, Grevendonk, and Herreman (Ref. 3) used a torsionally vibrating piezoelectric quartz crystal; and Hellemans, 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 ($\sigma = 3.405 \text{ \AA}$, $\epsilon/k = 119.8 \text{ K}$). The nonequilibrium calculation used 108 atoms with a reduced velocity gradient of $u_{xz}L(m/kT)^{1/2} = \frac{1}{2}$; a time step of $\Delta t = 0.002L(m/kT)^{1/2}$ and 8000 times 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 $u_{xz}L(m/kT)^{1/2} = \frac{3}{4}, \frac{1}{2}$, 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 ($\eta \equiv -P_{xz}/u_{xz}$) can be described by Eyring's theory of non-Newtonian viscous flow:

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

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.

$u_{xz}\sigma(m/\epsilon)^{1/2}$	$\eta\sigma^2(m\epsilon)^{-1/2} (\pm 5\%)$	$\eta(\text{Ar})$ (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.

*Work performed under the auspices of the U. S. Atomic Energy Commission.

†Work done in partial fulfillment of the requirements for a Ph. D., University of California at Davis, Department of Applied Science, at Livermore.

¹W. T. Ashurst and W. G. Hoover, *Bull. Amer. Phys. Soc.* **17**, 1196 (1972); W. G. Hoover and W. T. Ashurst, *ibid.*

²W. T. Ashurst and W. G. Hoover, Sandia Laboratories, Livermore, Report No. SCL-DC-720305, 1973 (to be published).

³A. De Bock, W. Grevendonk, and W. Herreman, *Physica (Utrecht)* **37**, 227 (1967).

⁴J. P. Boon, J. C. Legros, and G. Thomaes, *Physica (Utrecht)* **33**, 547 (1967).

⁵J. Hellemans, H. Zink, and O. Van Paemel, *Physica (Utrecht)* **46**, 395 (1970).

⁶D. Levesque, L. Verlet, and J. Kurkijarvi, Phys. Rev. A 7, 1690 (1973).

⁷We thank F. Ree for calling Eyring's work to our attention. See for instance, F. H. Ree, T. Ree, and H. Eyring, Ind. Eng. Chem. 50, 1036 (1958). H. Eyring,

D. Henderson, B. J. Stover, and E. M. Eyring, *Statistical Mechanics and Dynamics* (Wiley, New York, 1964), p. 462.

⁸B. J. Bailey and K. Kellner, Physica (Utrecht) 39, 444 (1968).

Long-Time Behavior of the Velocity Autocorrelation: A Measurement*

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(Received 19 March 1973)

The persistent velocity autocorrelation, first discovered by Alder and Wainwright through molecular dynamic computations, is confirmed experimentally in gaseous air and argon for the first time. Analysis is based on hydrodynamic considerations.

The long-time behavior of the velocity autocorrelation function has in the past few years been a center of considerable interest. A slowly decaying tail with a $t^{-3/2}$ dependence (where t denotes time) was initially discovered by Alder and Wainwright¹ in the course of molecular dynamic computations. Many investigators²⁻⁹ have subsequently shown by a number of methods that such a behavior of the velocity autocorrelation for large times is consistent with both kinetic and hydrodynamic theory. The persistent autocorrelation is thought to be related ultimately to the collective effects of the surrounding fluid, specifically, in the form of vorticity.^{10,11} Such a long-time behavior has been deduced for the

Brownian as well as molecular motion in fluids. We wish to report in this Letter on the first laboratory confirmation of the Alder-Wainwright effect.

The design of the experiment is based on the following analysis: Along the line of reasoning first suggested by Alder and Wainwright,^{10,11} Zwanzig and Bixon,³ and Widom⁷ (see also Ref. 8 for a general treatment), we have obtained the $t^{-3/2}$ dependence by making a provision for the time-dependent nature of the fluctuations. The motion of a small sphere of mass m and radius R moving with a small velocity in a fluid at rest in the absence of external force satisfies the modified Langevin equation^{12,13}

$$m d\vec{V}/dt = -6\pi\eta R\vec{V}(t) - \frac{2}{3}\pi R^3\rho d\vec{V}/dt - 6R^2(\pi\eta\rho)^{1/2} \int_{-\infty}^t (t-s)^{-1/2} [d\vec{V}(s)/ds] ds + \vec{f}(t), \quad (1)$$

where η and ρ are the shear viscosity and density of the fluid, respectively. The third term on the right-hand side of Eq. (1) is called the Basset term. The last is the fluctuating force in the fluid.

For a particle of 2.02 μm diam moving in gaseous air or argon with an initial velocity of the order of 10^3 cm/sec, it can be shown that $\vec{f}(t)$ is negligible. Along the direction of the particle motion, Eq. (1) can then be written as

$$dV/dt = -\alpha V(t)/\tau - \beta(\pi\tau)^{-1/2} \int_{-\infty}^t (t-s)^{-1/2} [dV(s)/ds] ds, \quad (2)$$

where $\alpha = (1 + m_f/2m)^{-1}$, $\tau = m/6\pi\eta R$, $m_f = \frac{4}{3}\pi\rho R^3$, and $\beta = 3[\alpha(1-\alpha)]^{1/2}$. It can also be shown that the velocity autocorrelation function satisfies a differential equation which is exactly identical in its physical origin and structure to Eq. (2). The only difference between the two is that the fluctuating force in Eq. (1) becomes exactly zero upon taking an ensemble average in constructing the velocity autocorrelation function, whereas in obtaining Eq. (2) $\vec{f}(t)$ has been neglected.

The initial condition for $V(t)$ is $V(t=0) = V_0$, but Eq. (2) must be supplemented by a boundary condition determining $V(t)$ for $t < 0$. The two extreme cases are (i) $V(t) = 0$ for $t < 0$, (ii) $V(t) = V_0$ for $t < 0$. Case (i) corresponds to the situation in which the sphere gains a finite velocity instantaneously at $t = 0$ through a spontaneous fluctuation. The computation by Alder and Wainwright satisfies this boundary