Shear Viscosity of the Hard-Sphere Fluid via Nonequilibrium Molecular Dynamics

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The shear viscosity η of the hard-sphere fluid, at volumes of 1.6 and 2 times the close-packed volume, is computed with use of nonequilibrium molecular dynamics. At high shear rate $\dot{\epsilon}$ we observe a phase transition in which the system undergoes two-dimensional ordering in the plane perpendicular to the flow, accompanied by a sharp decrease in η. For small $\dot{\epsilon}$, no evidence is found for the square-root dependence on $\dot{\epsilon}$ reported by previous investigators.

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Nonequilibrium molecular dynamics (NEMD) has been used to study the shear viscosity of simple fluids via a number of different techniques.[1-7] In part, at least, these calculations are regarded as alternatives to the Green-Kubo method in which the viscosity coefficient is obtained from the time-correlation function of the momentum-flux tensor. In contrast to the equilibrium-ensemble Green-Kubo method, the NEMD calculations impose shear boundary conditions on the system which typically (although not always) are expected to drive the system to a steady state. The viscosity coefficient, then, is obtained from the time average of the momentum flux divided by the shear rate.

Interest in NEMD calculations includes both the "nonlinear" regime of shear rates $\dot{\epsilon}$ sufficiently large that the viscosity deviates significantly from its small-$\dot{\epsilon}$ limit, as well as the approach to the $\dot{\epsilon}=0$ limit. For simple intermolecular interactions, the first regime involves rates of shear which are orders of magnitude larger than those accessible experimentally in real fluids (but comparable to those obtained in the experiments of Ackerson and Clark[8] on colloidal suspensions). Nonetheless, it is important in understanding the mechanism whereby the viscosity observed in NEMD calculations for simple fluids decreases with increasing shear rate that we consider the limiting case in which particle motions are dominiated by the shear forces.

In the present Letter, we study the shear-rate dependence of η for a system of hard spheres in the dense-fluid regime using the "isothermal Lees-Edwards" technique which has been described previously.[7] We consider a system of N hard spheres, each a diameter σ, in a cubic volume $V=L^3$, subject to the quasiperiodic boundary conditions of Lees and Edwards.[7] The system is maintained near a fixed temperature by rescaling the peculiar velocity of each particle, $\vec{v}_i(t)-\hat{e}_x v_T(y_i(t))$, in which $\vec{r}_i(t)$ and $\vec{v}_i(t)$ denote the position and velocity of particle i, $y_i(t)$ is the y component of $\vec{r}_i(t)$, and $\hat{e}_x v_T$ is the expected steady, linear profile of the velocity in the x direction, $v_T(y)=(y-L/2)\dot{\epsilon}$. Calculations have been made at two values of the volume $\tau=V/V_0$, given in units of the close-packed volume $V_0=N\sigma^3/2^{1/2}$, in the dense-fluid regime, $\tau=2$ and 1.6, and for two different system sizes, $N=500$ and 4000.

Large-shear-rate behavior.—In Fig. 1 we plot the observed viscosity coefficient relative to the Enskog value η_E for both densities as a function of the shear rate, the latter scaled by the Boltzmann mean free time, t_{00}. The Green-Kubo results[9,10] (for the same finite systems) are also included as the $\dot{\epsilon}=0$ points. The statistical uncertainties associated with results are smaller than the plotting symbols, except at the smallest shear rates. For the $\tau=1.6$ calculations for which 500 and 4000 particle results are

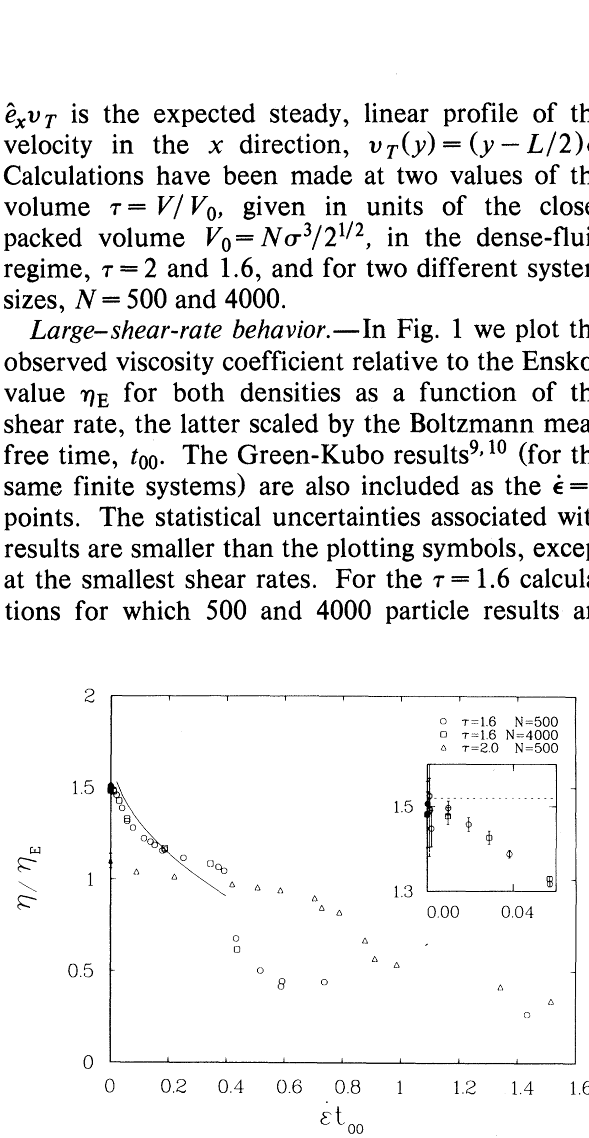

FIG. 1. Shear viscosity coefficient η of hard-sphere systems relative to the Enskog value as a function of shear rate $\dot{\epsilon}$ in units of the inverse Boltzmann mean free time t_{00}, from nonequilibrium (open symbols) and, at $\dot{\epsilon}=0$, equilibrium, Green-Kubo (filled symbols) molecular dynamics. The inset shows the small-$\dot{\epsilon}$ data on an expanded scale. The dashed line shows the prediction of mode-coupling theory, using $\eta(0)=1.52\eta_E$.

given, we note that the shear viscosity coefficient appears to be insensitive to system size. The smooth decrease of η with increasing $\dot{\epsilon}$ appears qualitatively similar to that reported by Evans[11] for the Lennard-Jones (LJ) fluid at the triple point. The curve shown in Fig. 1 is the $\dot{e}^{1/2}$ fit reported by Evans and plotted over the range of his calculations. In rescaling the Evans results to our units,[7] we have taken the LJ parameter σ as the equivalent hard-sphere diameter. This identification yields a reduced volume of $\tau = 1.68$ for the LJ calculation, a value quite close to our high-density value.

At larger shear rates we observe a decrease in the viscosity coefficient, which is particularly dramatic for the $\tau = 1.6$ system. To understand the origin of the dramatic decrease in η, we plot a snapshot of the 500-particle system at $\tau = 1.6$, $\dot{\epsilon}_{00} = 0.593$ in Fig. 1, at the final time of the trajectory. The figure shows the projection of the center of each sphere onto the y-z plane, i.e., normal to the flow. From the remarkable alignment of the particles, it seems clear that the configuration of the system has undergone a two-dimensional ordering whereby individual particles remain localized within a cylinder parallel to the direction of flow. The cylinders are arranged in a triangular lattice which is somewhat distorted by virtue of the fact that the y-z projection of the system is a square and thus incommensurate with the unit cell for the lattice.

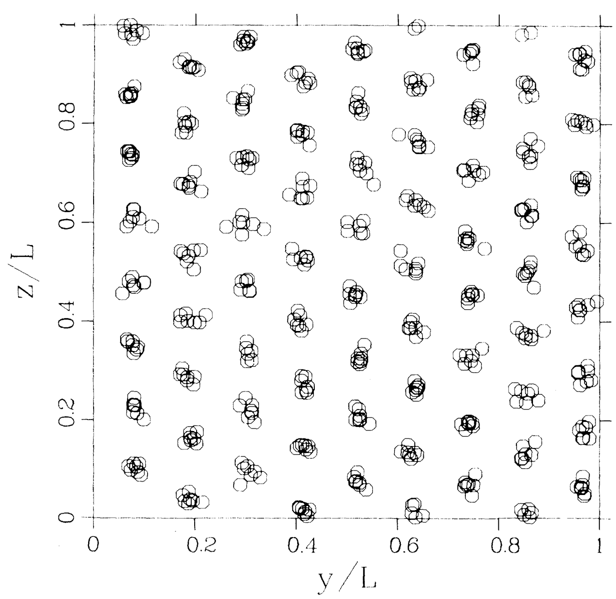

FIG. 2. Snapshot of a 500-particle hard-sphere system at a volume of $1.6V_0$ and at a shear rate of $0.593/t_{00}$, projected onto the plane normal to the flow. The circles are drawn at the center of each particle; the hard-sphere diameter is $0.12L$.

Similar snapshots for other large values of the shear rate show that for both densities the sudden decrease in η with $\dot{\epsilon}$ (at roughly $0.4/t_{00}$ for $\tau = 1.6$ and $0.8/t_{00}$ for $\tau = 2$) signals the onset of the phase transition, with the systems consisting of coexisting (low-density) fluid and (high-density) two-dimensionally ordered phases, separated by an "interface" lying more or less normal to the z axis. With increasing shear rate, the system appears to become a homogeneous, two-dimensionally ordered phase. The $\dot{\epsilon}$ interval over which two phases coexist is much broader for the lower density. We note that the viscosity coefficient reported in Fig. 1 for the two-phase region represents an effective value for the entire system.

To confirm this structural picture, we have also studied the position of individual particles with time for a number of the systems whose late-time snapshots appear ordered. After a short initial interval during which the particle motion appears chaotic, the particle becomes localized, either within a y-z layer (if in the fluid region) or very near a particular y-z lattice position.

The nonisotropic ordering (observed through the pair-correlation function) reported by Heyes *et al.*[6] in their study of the LJ triple-point fluid at shear rates up to $\dot{\epsilon}t_{00} = 0.13$ (as well as higher densities at similar rates of shear) appears to be a precursor to the phase transition observed here. The fact that the directional self-diffusion coefficients observed for the LJ systems were of similar magnitude in all three coordinate directions would seem to indicate that these systems remain fluidlike.

Finally we have looked for evidence of hydrodynamic instability or other nonlaminar structure in the high-$\dot{\epsilon}$ regime by computing the Fourier components of the x component of velocity,

$$a_k(t) = 2N^{-1}\sum_{j=1}^{N}\exp[2\pi iky_j(t)/L] \times [v_{jx}(t) - v_T(y_j(t))], \quad (1)$$

as suggested by Evans.[12] For both $k = 1$ and 2, we find that the time average, $\langle|\alpha_k|^2\rangle$, deviates only slightly from the equilibrium expectation value,[12] irrespective of $\dot{\epsilon}$. This contrasts with the observation by Evans[12] of a large increase of $\langle|\alpha_k|^2\rangle$ with shear rate, above $\dot{\epsilon}t_{00} = 1.8$, for the 32-particle soft-sphere fluid at a reduced volume $\tau = 2.02$. It seems clear that the sharp decrease in η associated with the phase transition is not related to the effect observed by Evans. Indeed, we find $\langle|\alpha_k|^2\rangle$ to decrease slightly with increasing $\dot{\epsilon}$ (above $0.8/t_{00}$) for $\tau=2$, for $\dot{\epsilon}$ as large as $2.0/t_{00}$, suggesting that the Evans effect may occur only at lower densities, or perhaps for small system sizes.

Small–shear-rate results.—In the small–shear-rate regime, the behavior of the viscosity has been the subject of conflicting theoretical studies. The semiphenomenological theory of Ree, Ree, and Eyring[13] yields a $\sinh^{-1}(\dot{\epsilon})/\dot{\epsilon}$ dependence for η. A result of similar mathematical form has been obtained by Eu.[14] On the other hand, the theories of Kawasaki, Gunton, and Yamada[15] and of Ernst *et al.*[16] predict an $\dot{\epsilon}^{1/2}$ dependence, with coefficients which differ in detail but are of similar magnitude. The latter authors, however, conclude that their theory should apply for shear rates much smaller than those typical of the NEMD calculations. While early NEMD evidence seemed to support the $\sinh^{-1}(\dot{\epsilon})/\dot{\epsilon}$ form,[2] more recent calculations have been interpreted in favor of the $\dot{\epsilon}^{1/2}$ dependence,[3,5,11] but with a coefficient which is two orders of magnitude larger than predicted by the theories.

The behavior of the shear viscosity for small shear rates is shown in the inset of Fig. 1 in which only the data for small $\dot{\epsilon}$ are shown. Evidently our hard-sphere data show no evidence of the $\dot{\epsilon}^{1/2}$ cusp reported by Naitoh and Ono,[3] Evans,[11] and Hoover *et al.*[5] The present calculations, which are considerably more extensive than previous results, extend to somewhat smaller values of $\dot{\epsilon}$. The figure also shows the square-root dependence given by the theory of Ernst *et al.*,[16] as the dashed curve, drawn through the intercept $\eta_0=1.52$. Because the theoretical coefficient is so small, the curve appears as a straight line. Evidently our data do little to support the theory.

Much attention[11,17-19] has been given to the difference between the predictions of mode-coupling theory and molecular-dynamics results both for the time-correlation function $\rho_\eta(t)$ for shear viscosity and for the shear-rate dependence of η. The present calculations tend to minimize the latter disagreement. With respect to $\rho_\eta(t)$, moreover, the evidence for actual disagreement, at least for hard spheres,[9] is not particularly compelling. Nonetheless, it seems true that the theories both for $\rho_\eta(t)$ and for $\eta(\dot{\epsilon})$ fail to account for the principal effects found in the molecular-dynamics results. The predictions of mode-coupling theory appear to be overshadowed by quite different effects in both the Green-Kubo and the NEMD calculations.

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[1]A. W. Lees and S. F. Edwards, J. Phys. C **5**, 1921 (1972).

[2]W. T. Ashurst and W. G. Hoover, Phys. Rev. Lett. **31**, 206 (1973), and Phys. Rev. A **11**, 658 (175).

[3]T. Naitoh and S. Ono, Phys. Lett. **57A**, 448 (1976), and **69**, 125 (1978), and J. Chem. Phys. **70**, 4515 (1979).

[4]D. J. Evans, Mol. Phys. **37**, 1745 (1979), and J. Stat. Phys. **22**, 81 (1980).

[5]W. G. Hoover, D. J. Evans, R. B. Hickman, A. J. C. Ladd, W. T. Ashurst, and B. Moran, Phys. Rev. A **22**, 1690 (1980).

[6]D. M. Heyes, J. J. Kim, C. J. Montrose, and T. A. Litovitz, J. Chem. Phys. **73**, 3987 (1980); D. M. Heyes, C. J. Montrose, and T. A. Litovitz, J. Chem. Soc. Faraday Trans. 2, **79**, 611 (1983).

[7]J. J. Erpenbeck, Physica (Utrecht) **118A**, 144 (1983).

[8]B. J. Ackerson and N. A. Clark, Physica (Utrecht) **118A**, 221 (1983).

[9]J. J. Erpenbeck and W. W. Wood, J. Stat. Phys. **24**, 455 (1981).

[10]B. J. Alder, D. M. Gass, and T. E. Wainwright, J. Chem. Phys. **53**, 3813 (1970).

[11]D. J. Evans, Phys. Lett. **75A**, 229 (1979), and Phys. Rev. A **23**, 1988 (1981).

[12]D. J. Evans, Physica (Utrecht) **118A**, 51 (1983).

[13]F. H. Ree, T. Ree, and H. Eyring, Ind. Eng. Chem. **50**, 1036 (1958).

[14]B. C. Eu, Phys. Lett. **96A**, 29 (1983).

[15]K. Kawasaki and J. D. Gunton, Phys. Rev. A **8**, 2058 (1973); T. Yamada and K. Kawasaki, Prog. Theor. Phys. **52**, 111 (1975).

[16]M. H. Ernst, B. Cichocki, J. R. Dorfman, J. Sharma, and H. van Beijeren, J. Stat. Phys. **18**, 237 (1978).

[17]E. G. D. Cohen, Physica (Utrecht) **118A**, 17 (1983).

[18]B. J. Alder, Physica (Utrecht) **118A**, 413 (1983).

[19]R. Zwanzig, Physica (Utrecht) **118A**, 427 (1983).