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Bulk viscosity via nonequilibrium and equilibrium molecular dynamics

William G. Hoover, Anthony J. C. Ladd, and Richard B. Hickman
Department of Applied Science, University of California at Davis-Livermore, Livermore, California 94550
and Lawrence Livermore Laboratory, Livermore, California 94550

Brad Lee Holian
Los Alamos Scientific Laboratory, Los Alamos, New Mexico 87545

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Two new nonequilibrium methods for determining the bulk viscosity via molecular dynamics are described. These methods are applied to a soft-sphere dense fluid. Viscosities obtained from the equilibrium Green-Kubo-correlation-function method agree with the nonequilibrium results. The viscosities found are considerably smaller than those predicted by the Enskog theory of dense fluids.

I. INTRODUCTION

Two distinct coefficients of viscosity are needed to describe the flow of simple isotropic fluids. Of these coefficients, the shear viscosity η is the more familiar. It describes the resistance of the fluid to changes of shape. The bulk viscosity η_v describes the irreversible resistance, over and above the reversible resistance given by the isentropic bulk modulus, to changes of volume. The effects of bulk viscosity can be ignored for dilute monatomic gases and for incompressible fluids. Accordingly, η_v is often omitted in hydrodynamic problems. In dense fluids undergoing strong compression, the bulk viscosity plays an important role in determining shock-wave structure.[1]

The phenomenological stress tensor (minus the pressure tensor) for a "Newtonian" fluid is

$$\overleftrightarrow{\sigma} = [\sigma_{\mathrm{eq}} + \lambda \vec{\nabla}\cdot\vec{u}]\overleftrightarrow{I} + \eta[\vec{\nabla}\vec{u} + \vec{\nabla}\vec{u}^{t}]\,. \tag{1}$$

The equilibrium stress, as well as the viscosities η and $\eta_v = \lambda + \frac{2}{3}\eta$, is calculated as a function of the local density and energy in a frame moving with the fluid. $\overleftrightarrow{I}$ is the unit tensor and $\vec{u}$ is the local stream velocity. On physical grounds, the stress tensor $\overleftrightarrow{\sigma}$ is known to be symmetric—divergent angular accelerations would result otherwise—so that the symmetric combination of $\vec{\nabla}\vec{u}$ with its transpose $\vec{\nabla}\vec{u}^{t}$ is required.

Experimentally, the bulk viscosity is more difficult to measure than the shear viscosity. So far a laboratory technique providing homogeneous isotropic compression has not been developed. Even with such a hypothetical experiment, a steady-state measurement, possible in the case of shear, is impossible. At best the bulk viscosity can be measured by a cyclic compression and expansion. Bulk viscosity is usually inferred from sound-attenuation experiments.[2] It is assumed to provide the residual attenuation once the effects of heat conduction and shear viscosity have been taken into account.

From the microscopic viewpoint the structure of a fluid can be described by the pair-distribution function. This function changes during isentropic compression and that change requires a characteristic relaxation time. During nonequilibrium compressions which are rapid on the scale of that relaxation time the effective modulus of the fluid is increased. The first structural theories of bulk viscosity were based on this idea.[3] The more fundamental work of M. S. Green and Kubo led to an exact connection between the bulk viscosity and the averaged decay of pressure fluctuations:

$$\eta_v = (V/kT)\int_0^\infty \langle \delta P(0)\,\delta P(t)\rangle dt\,, \tag{2}$$

where V is the volume, k is Boltzmann's constant, T is the temperature, and t is time. This expression for the bulk viscosity has been applied both to the Lennard-Jones fluid at its triple point and to the hard-sphere fluid.[4,5] These results are mixed. The triple-point viscosity lies well below the Enskog prediction while the hard-sphere results agree well with the theory over a wide range of density.

The capacity and speed of modern computers make it quite feasible to simulate nonequilibrium problems involving a few thousand particles. These simulations often reveal details inaccessible to ordinary laboratory experiments. Recently, strong shockwaves in dense fluids have been successfully simulated in computer experiments.[6] In order to understand the microscopic structure found in these simulations[1] both the equilibrium equation of state and the transport coefficients must be known for all the thermodynamic states found within the shockwave.

Of the transport coefficients, the bulk viscosity is the least understood. To reduce this uncertainty we have developed two computer methods for measuring that coefficient. These methods simulate a cyclic process in which a small periodic system is periodically compressed and expanded. In Sec. II we describe both nonequilibrium methods for simulating this flow. We then apply both methods to the inverse 12th power soft-sphere potential, for which the equation of state and other transport coefficients are well known.[1,7] In the final section, we compare the calculated viscosities with the predictions of the Enskog theory.[8] We also include a comparison with the Green-Kubo fluctuation calculation in order to show that the substantial disagreement between our results and the Enskog theory, and its elaborations[9] is not an artifact of our computational model.

II. CYCLIC-COMPRESSION METHODS

The homogeneous periodic compression and expansion of an infinite system can be imitated in a small periodic system by changing the size of the small system as time passes:

$$L/L_0 = 1 + \xi \sin\omega t\,. \tag{3}$$

The strain is homogeneous throughout the system, corresponding to the long-wavelength limit. As the strain amplitude ξ and frequency ω describing the linearized strain rate (we use ϵ and σ in this paper to indicate the strength and range of the interaction potential and we also use these same symbols, sometimes with dots to indicate time derivatives, to represent strain and stress)

$$\dot\epsilon = \xi\omega\cos\omega t \tag{4}$$

approach zero, we expect that the average pressure within the system will deviate from the equilibrium pressure by $-3\xi\omega\eta_v\cos\omega t$. The factor 3 arises from the additive contributions of the x, y, and z strain rates to $\vec\nabla\cdot\vec u$.

If the deformation (3) takes place through the mechanism of external work, then hydrodynamics implies that the "lost" work, or irreversible heating, will be equal to the integrated irreversible part of $\dot E = -3PV\dot\epsilon$, corresponding to an energy increase per cycle (the cycle time is $2\pi/\omega$) of $(2\pi/\omega)9\xi^2\omega^2\eta_v V/2$. Thus the bulk viscosity could be obtained either by analyzing the pressure tensor components proportional to $\cos\omega t$ or alternatively by measuring the system's energy gain due to irreversible heating in the cyclic process (3).

To simulate the cyclic process we modify Hamilton's equations of motion. First we add an extra term to $\dot{\underline{q}}$ to describe the homogeneous straining of the coordinates:

$$\dot{\underline{q}} = (\underline{p}/m) + \dot\epsilon\underline{q}\,. \tag{5}$$

Here, and in the following equations, we use the roman $\underline{q}$, $\underline{p}$, and $\underline{F}$ to indicate sets of coordinates $\underline{q}$, momenta $\underline{p}$, and forces $\underline{F}$.

Hamilton's equations for $\dot{\underline{p}}$ must also be modified. In quasistatic compression, the added term in (5) does external work against the potential energy Φ. In addition to this potential-energy work, quasistatic compression must also do work against the kinetic pressure, $\underline{p}\cdot\underline{p}/3$ mV. If this kinetic-energy work is expended in rescaling the momentum distribution, the result is an effective force varying with the strain rate:

$$\dot{\underline{p}} = \underline{F} - \dot\epsilon\underline{p}. \tag{6}$$

If the time derivative of the internal energy $E(\underline{p},\underline{q}) = \Phi + \underline{p}\cdot\underline{p}/(2\mathrm{m})$, where Φ is the potential energy, is then calculated from (5) and (6) the result,

$$\dot E = -\dot{\underline{q}}\cdot\underline{F} + \dot{\underline{p}}\cdot\underline{p}/\mathrm{m} = -3PV\dot\epsilon\,, \tag{7}$$

obtained by using the instantaneous microscopic representation of the mean pressure,

$$3PV \equiv \underline{p}\cdot\underline{p}/m + \underline{q}\cdot\underline{F}\,, \tag{8}$$

agrees with macroscopic hydrodynamics. An alternative derivation of (5) and (6) can be based on the application of Hamilton's equations of motion,

$$\dot{\underline{q}} = \partial H/\partial\underline{p};\quad \dot{\underline{p}} = -\partial H/\partial\underline{q} \tag{9}$$

to the Hamiltonian $\Phi + (\underline{p}\cdot\underline{p}/2m) + \underline{qp}:\vec\nabla\vec u$. This same Hamiltonian can be used to derive (2) from perturbation theory or linear-response theory.

A particular method for solving Eqs. (5) and (6) is given in the next section. An alternative method can be derived by combining these equations to eliminate $\underline{p}$ and $\dot{\underline{p}}$. The coupled set of Newtonian second-order equations

$$\ddot{\underline{q}} = (\underline{F}/m) + \ddot\epsilon\underline{q}\,, \tag{10}$$

results when a term of order $\dot\epsilon^2$ is dropped. We have used the first-order equations (5) and (6) in most of our calculations but have also used (10) to verify that the results of the two methods agree within the statistical uncertainties of the calculated viscosities. Note that if the particle kinetic energies are defined relative to the local velocity $\dot\epsilon\underline{q}$, then once again the linearized change of the thermodynamic internal energy E with time is given by (7).

III. RESULTS

Because we use periodic boundaries, we hope that the number dependence of our results is small. In addition to this number dependence, our results must also depend on the strain amplitude ξ and frequency ω. Exploratory calculations indicated that strains of order a few percent, and frequencies of order the Einstein frequency, are necessary in order to obtain statistically useful results. The first-order equations were solved in two steps:

(1) Solve $\dot{\underline{q}} = (\underline{p}/m)$ and $\dot{\underline{p}} = \underline{F}$ between t and $t + dt$.

(2) Change $\underline{q}$, $\underline{p}$, and L at time $t+dt$, doing external work.

The first step was carried out by finding approximate coordinates and forces at time $t + (dt/2)$, using these to obtain $\underline{q}$ and $\underline{p}$ at time $t+dt$, and finally rescaling the momenta at time $t+dt$ in such a way as to conserve exactly the energy in that time interval. We took this precaution in order to ensure that external work caused all energy change in the cyclic compression process. At the end of a cycle of time length $2\pi/\omega$ we accumulated the energy change for the cycle and rescaled the momenta so that the next cycle would begin with the proper energy for the desired thermodynamic state.

The second-order differential equations provide an alternative method for simulating the cyclic compression. If these differential equations are replaced by equivalent centered difference equations, we have

$$\begin{aligned}\Delta\underline{q}(t + (dt/2)) &= \Delta\underline{q}(t - (dt/2)) \\ &\quad + (dt)^2(\underline{F}/m + \ddot{\epsilon}\underline{q}).\end{aligned} \qquad (11)$$

In solving this set of equations it is necessary to recompute the old displacement, $\Delta\underline{q}(t - (dt/2))$, for any particle traversing a periodic boundary, in order to account for the velocity component difference, $\dot{\epsilon}L$ across the periodic box. With either scheme, a time step of order $0.001\sigma(m/\epsilon)^{1/2}(\epsilon/kT)^{7/12}$ was sufficiently small so that the viscosity obtained by accumulating $-3PV\dot{\epsilon}\,dt$ was statistically indistinguishable from that obtained directly from the energy change per cycle.

Either scheme appears to be capable of determining bulk viscosities with an uncertainty of a few percent. The efficiency of the calculations is not great. About 100 000 time steps were required for each of our 32-particle calculations. The results are illustrated in Fig. 1. The parameters used are listed in Table I along with the predictions of the Enskog theory. That theory gives for the bulk viscosity

$$\eta_v(\text{Enskog}) = 1.002 b\rho y \eta_0. \qquad (12)$$

For soft spheres interacting with the potential $\phi(r) = \epsilon(\sigma/r)^{12}$ we have

$$\begin{aligned} &b\rho = 2.7222x, \quad x = (N\sigma^3/\sqrt{2}V)(\epsilon/kT)^{1/4}, \\ &y = 2.722x + 3.791x^2 + 2.495x^3 - 1.131x^5, \end{aligned} \qquad (13)$$

and

$$\eta_0 = 0.171(m\epsilon)^{1/2}(kT/\epsilon)^{2/3}/\sigma^2.$$

(We have used here the soft-sphere equation of state suggested by Cape and Woodcock.[10]) "Improvements" of the Enskog theory predict much the same result as Eq. (12).[9]

IV. DISCUSSION

The failure of the Enskog theory to predict correctly the soft-sphere bulk viscosities was unexpected. This failure led us first to solve both the first- and second-order differential equations as a check of our calculation. When these methods agreed, we decided to work out some Green-Kubo viscosities as a further check. These calculations, carried out for 32 and 108 particles at $(N\sigma^3/\sqrt{2}V)(\epsilon/kT)^{1/4} = 0.5$, produced results not very different from the nonequilibrium calculations. The Green-Kubo correlation function is subject to an additional check in that the pressure fluctuation is simply related to the temperature fluctuation:

$$\tfrac{1}{25}(V/N)^2\langle\delta P^2\rangle = k^2\langle\delta T^2\rangle. \qquad (14)$$

A further relation between the temperature fluctuation and the specific heat has been derived by Lebowitz *et al.*[11] The version of this last relation quoted in a recent book is in error by a factor of $\frac{4}{9}$.[12] The Green-Kubo bulk viscosity is relatively sensitive to the sample trajectories used to determine the correlation function (see Fig. 2). We base our Green-Kubo estimate on a section selected to reproduce properly the zero-time value of the correlation function.

The Green-Kubo calculation is also consistent with the frequency dependence of our calculated viscosities. If the correlation function were an exponential $\sim\exp(-t/\tau)$ then the frequency-dependent bulk viscosity, calculated from (2) but with $\cos\omega t$ included in the integrand, would have the form

$$\eta_v(\omega) = \eta_v(0)/(1 + \omega^2\tau^2). \qquad (15)$$

This same frequency dependence (15) follows also from the generalized linear constitutive relation

$$\sigma + \tau(\dot{\sigma} - B\dot{\underline{\epsilon}}) = B\underline{\epsilon} + \eta_v\dot{\underline{\epsilon}}, \qquad (16)$$

which implies a frequency-dependent bulk modulus:

$$B(\omega) = B(0) + [\eta\tau\omega^2/(1 + \omega^2\tau^2)]. \qquad (17)$$

Both the nonequilibrium data in Table I and the Green-Kubo–equilibrium-correlation function shown in Fig. 2 suggest a stress-relaxation time τ of about $0.04\sigma(m/\epsilon)^{1/2}(\epsilon/kT)^{7/12}$. This time is very short compared to the Einstein period at

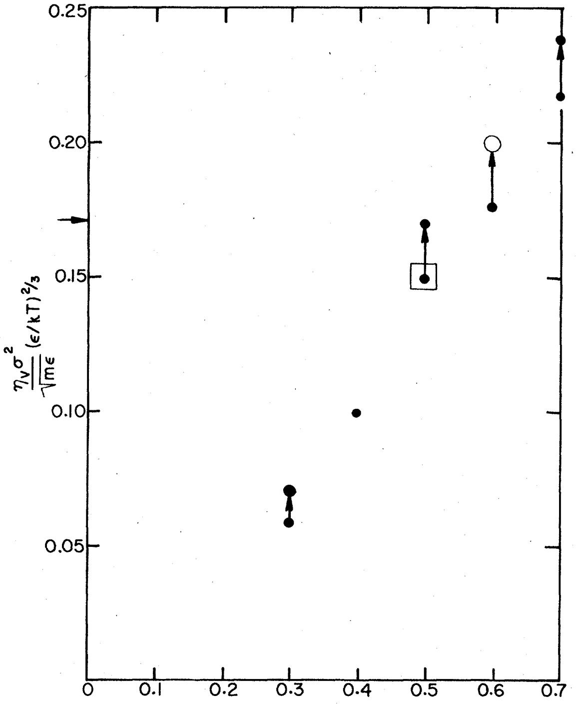

FIG. 1. Soft-sphere bulk viscosities. 32-particle results are indicated by filled circles (the arrows show the increase in viscosity as the reduced frequency decreases from 10 to 5). 108-particle results are indicated by open symbols. The square is the result of a Green-Kubo autocorrelation function calculation. The horizontal arrow indicates the low-density shear-viscosity coefficient for soft spheres.

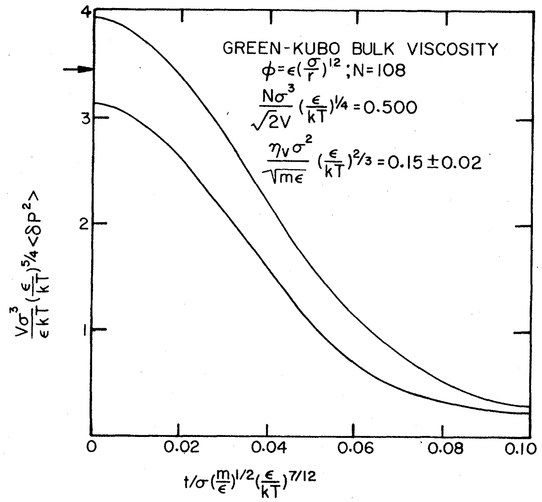

FIG. 2. Pressure correlation function for 108 soft spheres at a reduced density of $(N\sigma^3/\sqrt{2}V)(\epsilon/kT)^{1/4}=0.50$. The two curves shown correspond to different sections, each 5000 time steps long from a solution of Newton's equilibrium equations of motion. If the correlation function is chosen to coincide with the known intercept (indicated by an arrow) then the bulk viscosity integral is 0.15 in reduced units, agreeing with our nonequilibrium calculations. If the integrand is multiplied by $\cos(\omega t)$ the frequency shift observed between reduced frequencies of 5 and 10 is reproduced.

TABLE I. Bulk viscosities for the soft-sphere potential from nonequilibrium molecular dynamics. The reduced viscosity is tabulated in units of $(m\epsilon)^{1/2}(kT/\epsilon)^{2/3}/\sigma^2$. The unit of time in terms of which the reduced frequency and time step are expressed is $(\epsilon/kT)^{7/12}\sigma(m/\epsilon)^{1/2}$.

N	$(N\sigma^3/\sqrt{2}V)(\epsilon/kT)^{1/4}$	ω	ξ	$2\pi/dt$	cycles	η_v	η_v (Enskog)
32	0.30	2	0.03	4000	400	0.04 ± 0.01	0.17
		5	0.02	4000	200	0.07 ± 0.01	
		10	0.02	4000	400	0.06 ± 0.01	
32	0.40	5	0.02	4000	400	0.10 ± 0.01	0.34
		10	0.02	4000	400	0.10 ± 0.01	
32	0.50	5	0.02	4000	400	0.17 ± 0.01	0.60
		10	0.02	4000	400	0.15 ± 0.01	
		10	0.02	4000	480	0.15 ± 0.01 [a]	
32	0.60	5	0.03	1000	200	0.18 ± 0.03 [b]	0.97
		10	0.01	1000	400	0.21 ± 0.01 [b]	
		10	0.03	3000	500	0.18 ± 0.01	
		10	0.03	6000	400	0.17 ± 0.01	
32	0.70	5	0.02	4000	400	0.24 ± 0.03	1.45
		10	0.02	4000	800	0.22 ± 0.02	
108	0.60	5	0.02	2000	200	0.20 ± 0.01	0.97
108	0.70	10	0.02	5000	500	0.22 ± 0.01	1.45

[a] Calculated using the Newtonian second-order equations of motion. The other calculations use the first-order Hamilton equations.

[b] The time step used in these calculations is probably large enough to cause systematic errors in the results.

the same density, $1/\nu_E = 1.37\sigma(m/\epsilon)^{1/2}(\epsilon/kT)^{7/12}$. This consistency of the nonequilibrium and equilibrium calculations of the bulk viscosity is gratifying in view of the considerable discrepancy with the Enskog-theory predictions.

Why does the Enskog theory overestimate the soft-sphere dense-fluid bulk viscosity? A semiquantitative explanation can be based on thermodynamic estimates of pressure-tensor fluctuations.[13] In the dense hard-sphere fluid, upon which the Enskog theory is based, the variances of P_{xy} and $(P_{xx}+P_{yy}+P_{zz})/3$ are approximately equal, leading, through the Green-Kubo relations,[5] to nearly equal values of η and η_v. A corresponding near equality does not hold for soft-sphere systems. In these systems the shear fluctuations not only exceed the bulk fluctuations but also decay more slowly. Both effects increase η relative to η_v. The trend of η/η_v with density predicted from fluctuation theory is consistent with our results from molecular dynamics, and also predicts much larger values of the viscosity ratio for the softer inverse-power potentials.

In view of the demonstrated shortcomings of the Enskog theory for the bulk viscosity, direct measurements of η_v are essential to the reliable interpretation of results from computer experiments involving rapid compression. We are in the process of carrying out dense-fluid determinations of the Lennard-Jones bulk viscosity in order to interpret a recent calculation: Holian *et al.*[14] have simulated the shock compression of liquid argon from the triple point to a temperature of nearly 12 000 K. This shock-wave calculation provides valuable data for the testing of nonequilibrium theories of dense fluids.

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