Fluctuation expressions for fast thermal transport processes:
Vortex viscosity

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The vortex viscosity of a model diatomic fluid is calculated using both equilibrium and nonequilibrium molecular dynamics. The two calculations agree within statistical uncertainties. The results show that vortex viscosity does not have a conventional Kubo-Green relation. An argument as to why this is so is presented.

In this report we discuss the calculation of vortex viscosity which is of particular interest because this quantity does not have the usual Green-Kubo expression. This is a consequence of vortex viscosity being associated with the relaxation of internal angular momentum which is not a conserved quantity.

The generalized Langevin equation for a phase variable $A(p,q)$ is

$$\frac{dA}{dt}(t) = -\int_0^t d\tau\, M(\tau) A(t-\tau) + F(t) , \qquad (1)$$

where F is the random force and M is the memory function which can be expressed in terms of the Mori-Zwanzig projection operator.[1] The exact expression for the memory function involves the *modified* propagator[1] e^{QiLt} rather than the usual time propagator e^{iLt}. It is well known that for the transport of conserved quantities, e^{QiLt} may be replaced by e^{iLt} in the zero-wave-vector limit. This is a consequence of the infinite slowness of Navier-Stokes processes at infinite wavelength. In this slow limit, Navier-Stokes transport coefficients are related to equilibrium fluctuations by the Kubo-Green time-correlation functions.

In general, a "fast" variable A, may be defined as any variable which is *not* considered in the limit

$$\lim_{\xi \to 0} \dot{A}(\xi, t) \to 0 , \qquad (2)$$

where ξ is a parameter analogous to wave-vector or Brownian-particle mass.[2] The problem of relating

fast transport coefficients to equilibrium correlation functions was solved by Zwanzig[2] and by Berne, Boon, and Rice[3] (ZBBR). If the equilibrium current correlation function $C(t)$ is defined as

$$C(t) \equiv \langle A(0) A^*(t) \rangle , \qquad (3)$$

and the equilibrium flux correlation function $\phi(t)$ as

$$\phi(t) \equiv -\langle \dot{A}(0) \dot{A}^*(t) \rangle , \qquad (4)$$

then ZBBR[2,3] showed that one could solve the exact Langevin Eq. (1) for $M(t)$ in terms of $C(0)$ and $\phi(t)$. In the Laplace-transform domain the result is

$$\tilde{M}(s) = \frac{\tilde{\phi}(s)}{C(0) - \tilde{\phi}(s)/s} . \qquad (5)$$

We have recently applied the ZBBR result to the calculation of the frequency and wave-vector dependent shear viscosity.[4] As expected, for this Navier-Stokes transport coefficient we obtained the Kubo-Green result at zero wave vector

$$\tilde{M}(s) = \tilde{\phi}(s)/C(0) . \qquad (6)$$

At nonzero wave vector, however, we showed that shear viscosity does *not* have a conventional Kubo-Green relation to equilibrium fluctuations.

In this paper we apply the ZBBR result to vortex viscosity and use a computer simulation to test the validity of the more general Eq. (5). The vortex viscosity η_r describes the exchange of the orbital and intrinsic components of angular-momentum density in a molecular fluid. The defining consti-

tutive relation[5] is

$$\vec{\mathbf{P}}^d = -\eta_r(\vec{\nabla}\times\vec{\mathbf{u}}-2\vec{\omega}) \; , \tag{7}$$

where $\vec{\nabla}\times\vec{\mathbf{u}}$ and $\vec{\omega}$ are the vorticity and local average angular velocity, respectively, and $\vec{\mathbf{P}}^d$ is the pseudovector dual of the antisymmetric part of the pressure tensor $\vec{\mathbf{P}}^d = \frac{1}{2}\epsilon:\overset{\leftrightarrow}{P}$. In terms of molecular angular velocities $\vec{\omega}$, taken about individual molecule centers of mass $\vec{\mathbf{r}}_i$ one has

$$n\,\vec{\omega}(\vec{\mathbf{r}},t) = \sum_i \vec{\omega}_i\delta(\vec{\mathbf{r}}_i-\vec{\mathbf{r}}) \; , \tag{8}$$

where n is the number density. The intrinsic angular-momentum density $\overset{\leftrightarrow}{S}(\vec{\mathbf{r}},t)$ is not conserved but satisfies a balance equation

$$n\frac{\partial\vec{\mathbf{S}}}{\partial t} = -\vec{\nabla}\cdot\overset{\leftrightarrow}{Q}-2\vec{\mathbf{P}}^d \; . \tag{9}$$

In this equation $\overset{\leftrightarrow}{Q}$, the couple tensor, is the angular-momentum analog of the pressure tensor.[6] Microscopically the intrinsic angular-momentum density is given by

$$n\vec{\mathbf{S}}(\vec{\mathbf{r}},t) = \sum_i \overset{\leftrightarrow}{I}_i\vec{\omega}_i\delta(\vec{\mathbf{r}}_i(t)-\vec{\mathbf{r}}) \; , \tag{10}$$

where $\overset{\leftrightarrow}{I}_i$ is the molecular moment of inertia. Because of the tensorial character of the sprain rate $(\vec{\nabla}\times\vec{\mathbf{u}}-2\vec{\omega})$, there is no linear sprain-induced molecular alignment.[7] Consequently, in this linear theory $\langle I_{i\alpha\beta}\rangle = I\delta_{\alpha\beta}/3$.

At zero wave vector, $\vec{\mathbf{q}}=\vec{0}$, Eqs. (7)—(10) imply that

$$\frac{\partial\vec{\mathbf{S}}}{\partial t}(\vec{\mathbf{q}}=\vec{0},t) = -\frac{4\eta_r}{nI}\vec{\mathbf{S}}(\vec{\mathbf{q}}=\vec{0},t) \; , \tag{11}$$

which was first derived microscopically by Ailawadi, Berne, and Forster[8] who pointed out that the relaxation of intrinsic angular momentum is a fast process. The relaxation should not therefore be related to an equilibrium flux correlation function by the Kubo-Green Eq. (6) but rather by the ZBBR Eq. (5). Accordingly, one can derive from Eq. (11)

$$\tilde{\eta}_r(s) = \frac{\tilde{\pi}(s)}{1-\dfrac{4}{nI}\tilde{\pi}(s)/s} \; , \tag{12}$$

where $\tilde{\pi}(s)$ is the Laplace transform of the antisymmetric stress equilibrium time-correlation function

$$\tilde{\pi}(s) = \int_0^\infty dt\, e^{-st}\frac{1}{VkT}$$
$$\times\langle P_z^d(q=0,t)P_z^d(q=0,0)\rangle \; , \tag{13}$$

and V,k,T are the volume, Boltzmann's constant, and the temperature, respectively. The zero-wave-vector pressure tensor $\vec{\mathbf{P}}^d(\vec{\mathbf{q}}=\vec{0})$ is well known,[5]

$$\vec{\mathbf{P}}^d = \frac{1}{4}\sum_{i\neq j}\vec{\mathbf{r}}_{ij}\times\frac{\partial\phi_{ij}}{\partial\vec{\mathbf{r}}_j} \; . \tag{14}$$

In molecular fluids where the intermolecular force $(-\partial\phi_{ij}/\partial\vec{\mathbf{r}}_j)$ is not parallel to the center-of-mass separation vector $(\vec{\mathbf{r}}_{ij})$, the molecular pressure tensor (14), is in general, nonsymmetric. Thus $\vec{\mathbf{P}}^d$ is nonzero. The first person to realize that the antisymmetric part of the pressure tensor governs the collective relaxation of angular velocities was Max Born in 1920.[9] The theory was later developed more fully by Grad.[10] The formal connection between "atomic" and "molecular" hydrodynamics of a *molecular* fluid where the atomic theory uses a symmetric pressure tensor and the molecular theory employs a nonsymmetric tensor, has been discussed in detail by Olmsted and Snider.[11]

In principle, there are two independent ways of calculating the zero-frequency vortex viscosity: either via a *nonequilibrium* simulation and the defining constitutive relation (7), or via an *equilibrium* simulation and Eq. (12) to relate the equilibrium fluctuations to $\tilde{\eta}_r(s=0)$. The purpose of this report is to relate the results of both types of calculation. The degree of agreement of the two different calculations then provides a test of the validity of the ZBBR equation and of the nonequilibrium simulation technique.

The system simulated was a 108-molecule diatomic Lennard-Jones potential fluid, i.e., with

$$\phi_{ij} = \sum_{iA}\sum_{jB}4\epsilon[(\sigma/r_{iA,jB})^{12}-(\sigma/r_{iA,jB})^6] \; , \tag{15}$$

where ϕ_{ij} is the potential energy of molecule i and j and $r_{iA,jB}$ is the separation of atom A in molecule i from atom B in molecule j. The two atoms of each molecule are located a fixed distance apart $r_{iA,iB}=0.3292\sigma$. (By appropriate scaling of ϵ,σ and the molecule mass m, this potential forms a good representation of the bulk properties of nitrogen.[12] The state point studied was the same as that studied by Evans and Streett[5]: $\rho\sigma^3=0.622$, $kT/\epsilon=2.10$.

The equilibrium simulation was reported in Ref. 5 by Evans and Streett who used Kubo-Green relations to calculate a wide variety of transport coefficients for this fluid. However, as we have seen, vortex viscosity, which was one of the coefficients they calculated, is not expected to have a conven-

tional Kubo-Green relation.

The points on Fig. 1 show the Laplace transform of the antisymmetric stress correlation function $\pi(t)$, as calculated by Evans and Streett.[5] Because the ZBBR result, Eq. (12), gives a singular relation between vortex viscosity and $\pi(t)$, it is very difficult to use (12) to determine $\tilde{\eta}_r(s)$ numerically. We decided instead to assume a parametric functional form for $\tilde{\eta}_r(s)$ and fit the parameters using the $\tilde{\pi}(s)$ data. In fact, we found that the $\tilde{\pi}(s)$ data could be represented if the vortex viscosity was assumed a Lorentzian[7]:

$$\tilde{\eta}_r(s) = \frac{\eta_r}{1 + s\tau} . \tag{16}$$

The curve through the data is Eq. (16) and corresponding values of $\tilde{\eta}_r(s)$ are shown as the dashed curve. The relaxation time τ and the zero-frequency vortex viscosity η_r were obtained by fitting the location and magnitude of the observed maximum in $\tilde{\pi}(s)$ to give $\tau\sigma^{-1}\sqrt{\epsilon/m} = 0.027$ and
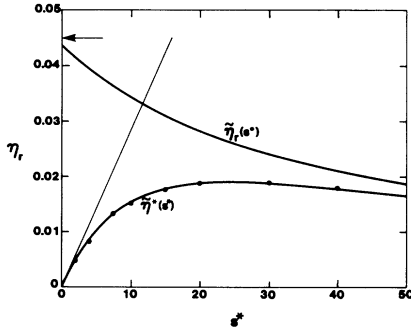

FIG. 1. The points show the reduced quantity $\tilde{\pi}^*(s^*)$ obtained by numerically transforming the Evans and Streett[5] data. The smooth curve through these points was obtained from the Lorentzian (16) for $\tilde{\eta}_r(s)$ with constants

$$\eta_r\sigma^2/\sqrt{m\epsilon} = 0.044$$

and

$$\tau\sigma^{-1}\sqrt{\epsilon/m} = 0.027 .$$

The corresponding plot for $\tilde{\eta}_r^*(s^*)$ is also shown. The variables have been appropriately reduced by m, σ, and ϵ and represented by asterisks. A direct calculation by nonequilibrium molecular dynamics gives

$$\eta_r\sigma^2/\sqrt{m\epsilon} = 0.045 \pm 0.01$$

as shown by the arrow. The straight line gives the theoretical estimate for $d\tilde{\pi}/ds$ as $s \rightarrow 0$ according to Eq. (17).

$\eta_r\sigma^2/\sqrt{m\epsilon} = 0.044$, respectively.

The calculation procedure for vortex viscosity using nonequilibrium molecular dynamics has been described in detail before.[13] We just report here the result for our system; namely, after 4000 time steps we found

$$\eta_r\sigma^2/\sqrt{m\epsilon} = 0.045 \pm 0.01 .$$

We note the agreement within statistical uncertainties of this nonequilibrium result calculated directly, with the equilibrium ZBBR value.

Other consistency checks can be carried out; Eq. (12) shows that $\tilde{\pi}(s=0)=0$. This is precisely what is observed in Fig. 1. Further, we can use use the ZBBR equations to calculate the asymptotic rate at which this Kubo function $\tilde{\pi}(s)$ goes to zero. If $\tilde{\eta}_r(s)$ is *continuous* near $s=0$ then

$$\lim_{s\rightarrow 0} \frac{d\tilde{\pi}(s)}{ds} = \frac{nI}{4} . \tag{17}$$

Thus the limiting slope of $\tilde{\pi}(s)$ near $s=0$, should be independent of transport coefficients. In Fig. 1 the straight line is drawn with the slope given by Eq. (17) and is consistent with the data.

At this point one may ask whether the Kubo transform of the antisymmetric stress autocorrelation function $\tilde{\pi}(s)$ has any physical meaning. The ZBBR equation and the simulation results show that $\tilde{\pi}(s) \neq \tilde{\eta}_r(s)$ but presumably some physical meaning can be attached to $\tilde{\pi}(s)$.

Consider a system at equilibrium $t \leq 0$, suddenly subject to a step increase in the vorticity $\vec{\nabla} \times \vec{u} = \vec{k}$ constant for $t > 0$. It is then simple matter to calculate the linear response of $P_z^d(t)$ using the Doll's tensor Hamiltonian[14]

$$H = H_0 + \sum_i \vec{q}_i \vec{p}_i : \vec{\nabla}\vec{u}, \quad t > 0 . \tag{18}$$

A trivial application of linear-response theory[11] then shows that the susceptibility for this process is the Kubo function $\pi(t)$. At long time the antisymmetric stress $\vec{P}^d$ must be proportional to $\tilde{\pi}(s=0)$. However, since the angular velocity is free to attain its steady-state value $\vec{\omega} = \frac{1}{2}\vec{\nabla} \times \vec{u}$, we know that at long time the sprain rate, and therefore the antisymmetric stress, are zero.

This proves that the Kubo transform of the antisymmetric stress autocorrelation function is zero at zero frequency. This agrees with the ZBBR prediction. It also shows that the Kubo function $\tilde{\pi}(s)$ is the susceptibility of the vortex-induced processes where the intrinsic angular velocity is "free."

We have shown that computer simulation sup-

ports the correctness of the ZBBR equation at least as it pertains to vortex viscosity. (These results do show that the Markovian analysis used by Evans and Streett[5] is incorrect in its prediction that vortex viscosity has a conventional Kubo-Green relation). Although these calculations are specific to vortex viscosity their implications have consider-

able generality. This is the first time a test has been made of the validity of the ZBBR equation for any fast transport coefficient.

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[1]The derivation of Eq. (1) is now standard. Our notation is that of B. J. Berne, *Statistical Mechanics, Part B: Time Dependent Processes* (Plenum, New York, 1977), Chap. 5.

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