Fluctuation Expressions for Nonequilibrium Distribution Functions in Adiabatic Flows

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A "nonequilibrium Hamiltonian" that describes adiabatic deformation has recently been used to obtain the bulk and shear viscosities of simple fluids. This Hamiltonian is used to derive *equilibrium* fluctuation experessions for the *nonequilibrium* distribution functions, studying in detail the most important of these, the pair distribution function for simple fluids in the linear-response regime.

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It was recently demonstrated[1,2] that a Hamiltonian of the form

$$H = \sum p^2/2m + \sum \varphi + \sum \vec{q}\vec{p}:\nabla\vec{u}, \tag{1}$$

where $\nabla\vec{u}$ is the macroscopic strain-rate tensor, can be used to simulate adiabatic flows, with nonequilibrium molecular dynamics. The simulations provide numerical estimates for the shear and bulk viscosities. In laboratory deformations, adiabatic flows are driven by external boundary conditions. In systems described by the Hamiltonian (1), the flow is driven instead by the coupling[3] between Doll's tensor ($\sum\vec{q}\vec{p}$) and the macroscopic strain rate. By use of appropriate forms of the strain-rate tensor, cyclic dilation[1,2] and steady planar couette[2] flows have been studied. If $\nabla\vec{u}$ is spatially varying, inhomogeneous flows can be set up.

The nonequilibrium Hamiltonian has two important properties: The energy dissipation agrees with macroscopic hydrodynamics and the perturbing strain rate gives linear-response viscosity coefficients agreeing with Green-Kubo fluctuation theory. In addition, it has the useful feature of making possible the derivation of equilibrium expressions for the nonequilibrium distribution functions in adiabatically deforming systems. The derivation of these expressions is described here.

By considering the double-dot product in (1) as a perturbation, we can use the results of linear-response theory[4,5] to obtain an expression for the N-particle distribution function. For steady planar couette flow, we have, to linear order in the strain rate, $\dot{\epsilon} = \nabla_y u_x$,

$$f_{\text{noneq}}(t) = f_{\text{eq}}\{1 - \beta V \int_0^\infty P_{xy}(s)\dot{\epsilon}(t-s)\,ds\}, \tag{2}$$

where $P_{xy} = (1/V)(d/dt)\sum q_y p_x$ is the xy component of the pressure tensor and the N-particle distribution is normalized, $\int f\, d^N q\, d^N p \equiv 1$. In the case of steady dilation, the time-averaged pressure must be subtracted from the mean pressure, $(P_{xx} + P_{yy} + P_{zz})/3$, at time s.[2] Any required distribution function can be obtained, as an equilibrium conditional average, by integrating over the redundant variables in (2). In particular, for the two-body spatial distribution function, by integrating over all momenta and all but three $\{(x_{12},$

$y_{12}, z_{12}) \equiv \vec{q}_{12}\}$ particle coordinates, we find that

$$\delta g \equiv g_{\text{noneq}} - g_{\text{eq}} = -V^2 \beta \dot{\epsilon} \int_0^\infty \langle P_{xy}(s) \rangle_{\vec{q}_{12}} ds, \qquad (3)$$

where, for simplicity, we have specialized to the case of constant strain rate and where $\int g dr \equiv V$. The ensemble average at time s is a conditional one such that at time 0 the vector $\vec{q}_{12} \equiv \vec{q}_1 - \vec{q}_2$ has the specified value. The analogous expression for the nonequilibrium momentum distribution is

$$\delta f(\vec{p}_1) = -V\beta\dot{\epsilon} \int_0^\infty \langle P_{xy}(s) \rangle_{\vec{p}_1} ds. \qquad (4)$$

These expressions, (3) and (4), can be simplified by following Green,[6] writing the angle dependence explicitly:

$$\delta f(p) = \mu(p) \dot{\epsilon} p_x p_y / p^2; \qquad (5)$$

$$\delta g(q) = \nu(q) \dot{\epsilon} q_x q_y / q^2. \qquad (6)$$

Thus the functions μ and ν, with scalar arguments p and q, can be obtained by working out the angular averages of $15 \delta f p_x p_y / p^2 \dot{\epsilon}$ and $15 \delta g q_x q_y / q^2 \dot{\epsilon}$. These results can easily be generalized to oscillating strains $\dot{\epsilon} \equiv \dot{\epsilon}_0 \exp(i\omega t)$. The usual Green-Kubo expression for the shear viscosity coefficient can be obtained from a nonequilibrium average of the xy pressure-tensor component. The kinetic and potential contributions to the shear viscosity are

$$\eta^k = -\langle P_{xy}{}^k | \delta f \rangle / \dot{\epsilon} = \beta V \int_0^\infty \langle P_{xy}{}^k(t) P_{xy}(0) \rangle dt; \quad (7)$$

$$\eta^\varphi = -\langle P_{xy}{}^\varphi | \delta g \rangle / \dot{\epsilon} = \beta V \int_0^\infty \langle P_{xy}{}^\varphi(t) P_{xy}(0) \rangle dt. \quad (8)$$

Thus the cross term in the equilibrium fluctuation expression contributes equally to the kinetic and potential parts of the nonequilibrium pressure. This result has also been derived directly from linear-response theory, with use of the kinetic and potential parts of the pressure as response functions,[2] and from equivalent projection-operator techniques.[7]

The nonequilibrium pair distribution function has been obtained by nonequilibrium molecular dynamics,[8-10] by a "van der Waals theory,"[11] and from experiments on suspensions of spheres.[12] The results presented here give a new method for obtaining the *nonequilibrium* distribution functions from *equilibrium* molecular dynamics. They should also help in constructing theoretical models for shear flow in fluids.

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