Green-Kubo relations for weak vector processes in strongly shearing fluids

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By extending a recent calculation of self-diffusion in shearing systems [Cummings *et al.*, J. Chem. Phys. **94**, 2149 (1991)] we derive a Green-Kubo formula for the thermal-conductivity tensor in fluids subject to planar Couette flow. These expressions are valid for weak heat flows in strongly shearing fluids.

I. INTRODUCTION

The lubrication of an elastohydrodynamic contact by a fluid involves the combined processes of shear flow and thermal conduction [1]. If both processes are weak, Curie's principle states that there is no effect on the viscosity of the fluid by the presence of the heat flow and conversely, no effect on the thermal conductivity by the shearing process [2]. Industrial lubricants are often subject to much more extreme conditions. Shear rates are often so large that nonlinear shear thinning of the fluid occurs [1]. Under such conditions the assumption of linearity implicit in Curie's principle will lead to errors. The macroscopic equation for heat flow in the presence of a flow field $u(r) = i\gamma y$ is

$$\frac{\partial e}{\partial t} + u \cdot \nabla e \equiv \frac{De}{Dt} = \nabla \cdot \lambda_t \cdot \nabla e - P_{xy}\gamma \tag{1}$$

where $e(r, t)$ is the internal energy per unit volume, P_{xy} is the shear stress, and λ_T is the thermal diffusivity *tensor*, defined by the relation

$$\lambda = \rho c_v \lambda_T . \tag{2}$$

In this equation ρ is the mass density, λ the thermal-conductivity tensor, and c_v the constant volume specific heat per unit mass. In Eq. (2), we define the specific heat in terms of the isochoric derivative of the internal energy of the shearing system with respect to the thermodynamic temperature of an *equilibrium* system with the same internal energy and density as the shearing system.

In this paper we will derive a fluctuation expression for the thermal-conductivity tensor λ valid for strongly shearing fluids subject to weak energy (temperature) gradients. The method we use to derive this expression is also applicable to self-diffusion in shearing fluids and yields results which generalize those we recently derived [3] for self-diffusion using a quite different method.

II. MICROSCOPIC ENERGY CONTINUITY EQUATIONS

The thermostatted equations of motion for a fluid under shear are the Sllod equations (so-named because of their close relationship to the Dolls tensor algorithm) [4]

$$\frac{d r_i}{dt} = \frac{p_i}{m} + i\gamma y_i , \tag{3a}$$

$$\frac{d p_i}{dt} = F_i - i\gamma p_{yi} - \alpha p_i . \tag{3b}$$

In these equations r_i is the laboratory position of particle i, m the particle mass, and F_i the interatomic force on particle i due to the other particles. At low Reynolds number the streaming velocity at the position of particle i, is $i\gamma y_i$. Thus p_i/m is the peculiar velocity of particle i. The αp_i term in (3b) represents the thermostat [4].

At low Reynolds number therefore, the instantaneous internal energy of the system H_0 is [4]

$$H_0(t) = \sum_i \frac{p_i^2}{2m} + \frac{1}{2} \sum_{i(\neq j)} \phi(r_{ij}) \tag{4}$$

where $r_{ij} = |r_{ij}| = |r_j - r_i|$. We define the instantaneous contribution of particle i to the internal energy as

$$e_i(t) = \frac{p_i^2}{2m} + \frac{1}{2} \sum_{j=1}^N \phi(r_{ij}) . \tag{5}$$

As we shall see, it is convenient to define the *Lagrangian* position of a particle as the integral of its peculiar velocity,

$$q_i(t) = r_i(0) + \int_0^t \frac{p_i(s)}{m} ds . \tag{6}$$

Actually the laboratory positions of all the particles move to their convected positions $r_i(t) = r_i(0) + i\gamma t y_i(0)$. If all the particles move at the local streaming velocity, $i\gamma y_i$, all the p_i will be zero for all time and thus $q_i(t) = q_i(0) = r_i(0)$. Therefore the *Lagrangian* energy density is

$$e(q, t) = \sum_i e_i(t)\delta(q_i(t) - q) . \tag{7}$$

The time derivative of (7) will give the streaming hydrodynamic derivative De/Dt. We find it convenient to work with the Fourier transform of the Lagrangian energy density,

$$e(k, t) = \sum_i e_i(t)e^{ik \cdot q_i(t)}$$
$$= \sum_i e_i(t) + i k \cdot \sum_i q_i(t)e_i(t) + O(k^2) . \tag{8}$$

We will choose our thermostat such that, the energy $\sum_i e_i(t)$ is independent of time. We can then ignore the zero wave-vector component in (8).

It is now straightforward to show from our equations of motion (3) that

$$\frac{d}{dt}\sum_i \mathbf{q}_i e_i = \mathbf{J}_q V - \gamma \sum_i \mathbf{q}_i P_{xy}(i) - \alpha \sum_i \frac{p_i^2}{m} \mathbf{q}_i \quad (9)$$

where $P_{xy}(i)$ is the instantaneous contribution of particle i to the shear stress, $P_{xy}(t) = \sum_{x,y} P_{xy}(i)/V$,

$$P_{xy}(i) = \frac{p_{ix} p_{yi}}{m} - \tfrac{1}{2}\sum_j y_{ij} F_{xij} \quad (10)$$

and where F_{xij} is the x component of the force on i due to particle j. $\mathbf{J}_q(t)$ is the instantaneous heat flux vector,

$$\mathbf{J}_q(t)V = \sum_i \left[\frac{\mathbf{p}_i e_i}{m} + \tfrac{1}{2}\mathbf{q}_i \sum_j \frac{\mathbf{p}_i + \mathbf{p}_j}{m}\cdot \mathbf{F}_{ij}(\mathbf{r}_{ij}) \right] . \quad (11)$$

We note that this involves the peculiar velocity $\mathbf{p}_i/m$, the Lagrangian coordinate $\mathbf{q}_i$, and in both e_i and $\mathbf{F}_{ij}$, the laboratory coordinates of the particles, $\mathbf{r}_i, \mathbf{r}_j$.

If we choose α as

$$\alpha(t) = \frac{-\gamma P_{xy}(t)V}{\sum_i p_i^2/m} \quad (12)$$

we see that the internal energy is a constant of the motion. Furthermore, since

$$\frac{d}{dt}\sum_i \mathbf{q}_i e_i = \mathbf{J}_q(t)V - \mathbf{Q}(t)\gamma P_{xy}(t)V$$

$$- \mathbf{Q}(t)\alpha(t)\sum_i \frac{p_i^2}{m} + O(N^{1/2}) \quad (13)$$

where $\mathbf{Q}(t) = \sum_i m\mathbf{q}_i/\sum m$, the thermostat will, in the thermodynamic limit, cancel the term involving $\mathbf{Q}(t)\gamma P_{xy}(t)V$. This is because in the thermodynamic limit $\mathbf{Q}(t) = \sum_i m\mathbf{q}_i/\sum_i m = \sum_i \mathbf{q}_i P_{xy}(i)/\sum_i P_{xy}(i) = \sum_i \mathbf{q}_i p_i^2/\sum_i p_i^2$. We therefore obtain, to leading order in $\mathbf{k}$,

$$\dot{e}(\mathbf{k},t) = i\mathbf{k}\cdot\mathbf{J}_q(t)V + O(\mathbf{k}^3) . \quad (14)$$

We assume that the frequency ω and wave vector $\mathbf{k}$, dependent macroscopic constitutive relation

$$\hat{\mathbf{J}}_q(\mathbf{k},\omega) = -\hat{\lambda}_T(\mathbf{k},\omega)\cdot i\mathbf{k}\hat{e}(\mathbf{k},\omega) \quad (15)$$

can be applied to the average relaxation of steady-state fluctuations in the microscopic heat flux and energy density. We are therefore assuming that the thermal fluctuations are *weak* and a linear constitutive relation such as (15) can be applied. We note that by symmetry, even large strain rates cannot generate a flow of heat although they do modify the thermal conductivity. Substituting (15) into (14) gives to leading order in $\mathbf{k}$,

$$i\omega\hat{e}(\mathbf{k},\omega) - e(\mathbf{k},0) = -\mathbf{k}\cdot\hat{\lambda}_T(\mathbf{k},\omega)\cdot\mathbf{k}\hat{e}(\mathbf{k},\omega) . \quad (16)$$

The derivation of a Green-Kubo-like formula for the thermal diffusivity now proceeds in a very similar way to the equilibrium case [4].

We multiply both sides of (15) by $e(-\mathbf{k},0)$ and take a canonical average over the initial equilibrium state used at $t = -\infty$, to generate the shearing nonequilibrium steady state at $t \geq 0$. Defining the steady-state energy autocorrelation function as

$$c(\mathbf{k},t) \equiv \langle e(\mathbf{k},t)e(-\mathbf{k},0)\rangle_\gamma \quad (17)$$

where $< >_\gamma$ indicates an average over the thermostatted, shearing steady state, we find, as at equilibrium [4]

$$\hat{c}(\mathbf{k},\omega) = \frac{c(\mathbf{k},0)}{i\omega + \mathbf{k}\cdot\hat{\lambda}_T(\mathbf{k},\omega)\cdot\mathbf{k}} . \quad (18)$$

Defining

$$\phi(\mathbf{k},t) \equiv -\frac{d^2}{dt^2}c(\mathbf{k},t) \quad (19)$$

and using the stationarity of nonequilibrium steady-state averages together with (16), one obtains [4] to leading order in k,

$$\phi(\mathbf{k},t) = \mathbf{k}\mathbf{k}:\langle \mathbf{J}_q(\mathbf{k},t)\mathbf{J}_q(-\mathbf{k},0)\rangle_\gamma . \quad (20)$$

Substituting (19) and (20) into (18) and eliminating $c(\mathbf{k},t)$,

$$\mathbf{k}\cdot\hat{\lambda}_T(\mathbf{k},\omega)\cdot\mathbf{k} = \frac{\hat{\phi}(\mathbf{k},\omega)}{c(\mathbf{k},0) - \hat{\phi}(\mathbf{k},\omega)/i\omega} . \quad (21)$$

The term $\hat{\phi}(\mathbf{k},\omega)$ is proportional to k^2. Since we are using a canonical average over initial states, together with constant energy dynamics,

$$c(\mathbf{k},0) = \frac{\rho k_B T^2}{V}c_V . \quad (22)$$

Substituting (22) into (21) we find, using (2), that in the zero wave-vector limit,

$$\lim_{\omega\to 0}\lim_{k\to 0}\hat{\lambda}(\mathbf{k},\omega) = \lambda = \frac{V}{k_B T^2}\int_0^\infty dt\langle \mathbf{J}_q(t)\mathbf{J}_q(0)\rangle_\gamma . \quad (23)$$

Thus the thermal conductivity of a thermostatted, shearing steady state is related to fluctuations in steady-state heat flux.

III. DISCUSSION

Exactly the same arguments can be used to describe an expression for the self-diffusion tensor $\mathbf{D}$ in fluids subject to shear. The self-diffusion tensor is defined by

$$\frac{\partial G}{\partial t} + \mathbf{u}\cdot\nabla G \equiv \frac{DG}{Dt}$$

$$= \nabla\cdot\mathbf{D}\cdot\nabla G , \quad (24)$$

where $G(\mathbf{r},t)$ is the number density of a tracer particle at a point $\mathbf{r}$ and time t.

The Fourier transform of the Lagrangian tracer density $G(\mathbf{k},t)$

$$G(\mathbf{k},t) - \sum_i e^{i\mathbf{k}\cdot\mathbf{q}_i(t)} \quad (25)$$

is analogous to (8). Following the same steps, it is straightforward to derive a Green-Kubo formula for D of the form

$$D = \int_0^\infty dt \left\langle \frac{\mathbf{p}_i(t)}{m} \frac{\mathbf{p}_i(0)}{m} \right\rangle_\gamma . \tag{26}$$

This expression was first derived by Cummings et al. [3] using quite different methods. In fact our previous derivation [3] was limited, for technical reasons, to the case where D is diagonal. We conjectured the above generalization for the case where the diffusion tensor is of arbitrary symmetry. Our present derivation is therefore more general than our earlier work.

ACKNOWLEDGMENTS

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