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Shear-driven heat flow in absence of a temperature gradient

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Abstract. Jaynesian statistical inference is used to predict that steady, non-uniform Couette flow in a simple liquid will generate a heat flux proportional to the gradient of the square of the strain-rate when the temperature gradient is negligible. The heat flux is divided into phonon and self-diffusion components, with the latter coupling to the elastic strain and inelastic strain-rate. Operators for all these are substituted into the information-theoretic phase-space distribution. By taking moments of an exact equation for this distribution derived by Robertson, one obtains an evolution equation for the self-diffusion component of the heat flux which, in a steady state, predicts shear-driven heat flow.

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1 Introduction

Baranyai *et al.* [1] have studied, using molecular dynamics, a liquid undergoing Couette flow in a cell of length L in the y-direction with a steady flow $u_x(y)$ driven by a force

$$F_x(y) = F_{x1}\sin(q_1 y), \quad q_1 = 2\pi/L. \tag{1}$$

These conditions induce a temperature $T(y)$ which could be adjusted so that the first-order term in the Fourier expansion of $T(y)$, proportional to $\cos(2q_1 y)$, is zero. It is found that the first Fourier component, $\mathbf{J}_{\mathrm{Q}1}$, of the heat flow can be explained if $\mathbf{J}_\mathrm{Q}$ has a term $\xi\partial\gamma_1^2/\partial y$, where γ_1 is the leading Fourier component of the velocity gradient. Accordingly, when the temperature gradient can be neglected, a y-dependent shear-rate $\gamma \equiv \partial u_x/\partial y$ will generate a heat flux $J_{\mathrm{Q}y}$.

In this paper, we seek a theoretical prediction of the ξ term in $\mathbf{J}_\mathrm{Q}$ which is postulated in [1] to fit the computer results. Such a prediction can be effected by making a statistical derivation of a generalized Cattaneo-Vernotte equation [2] which, in the absence of a temperature gradient, has the form at a point $\mathbf{R}$ in the fluid:

$$\partial\mathbf{J}_\mathrm{s}(\mathbf{R},t)/\partial t = -(1/\tau_\mathrm{s})\mathbf{J}_\mathrm{s}(\mathbf{R},t) + \mathbf{F}_\mathrm{s}(\mathbf{R},t) \tag{2}$$

where $\mathbf{F}_\mathrm{s}$, in a steady state with negligible ∇T, is $-\xi\,\nabla\gamma^2$. $\mathbf{J}_\mathrm{s}$ is the component of $\mathbf{J}_\mathrm{Q}$ carried by self-diffusing particles. As discussed below, we do not predict an equation resembling (2) for the phonon component, $\mathbf{J}_\mathrm{p}$, with a nonzero driving term when $\nabla T = 0$.

The derivation of equation (2) invokes the exact Robertson approach [3]. This method introduces a Jaynes-type [4] statistical distribution $\tilde\rho(x)$ over phase coordinates x, given the number density $n(\mathbf{R})$, velocity $\mathbf{u}(\mathbf{R})$, elastic strain $\sigma_{\alpha\beta}(\mathbf{R})$, and inelastic strain-rate $C_{\alpha\beta}(\mathbf{R})$ at each point $\mathbf{R}$. $\mathbf{F}_\mathrm{s}$ depends on these variables. The distribution $\tilde\rho$ satisfies the matching conditions:

$$\mathbf{J}_\mathrm{s}(\mathbf{R}) = \int \tilde\rho\hat{\mathbf{J}}_\mathrm{s}(\mathbf{R})\mathrm{d}x \tag{3a}$$

$$\sigma_{\alpha\beta}(\mathbf{R}) = \int \tilde\rho\hat\sigma_{\alpha\beta}(\mathbf{R})\mathrm{d}x \tag{3b}$$

$$C_{\alpha\beta}(\mathbf{R}) = \int \tilde\rho\hat C_{\alpha\beta}(\mathbf{R})\mathrm{d}x \tag{3c}$$

where $\hat{\mathbf{J}}_\mathrm{s}$, $\hat\sigma_{\alpha\beta}$, and $\hat C_{\alpha\beta}$ are operators to be defined in what follows. Robertson derives from the Liouville equation an exact equation for $\partial\tilde\rho/\partial t$. Multiplying this equation by the operators and integrating over phase space, we derive evolution equations for $\partial\mathbf{J}_\mathrm{s}(\mathbf{R},t)/\partial t$ and $\partial C_{\alpha\beta}(\mathbf{R},t)/\partial t$ as illustrated in previous work [5]. The equation for $\partial C_{\alpha\beta}/\partial t$ shows that, in a state where $\partial C_{\alpha\beta}/\partial t$ can be neglected, $\sigma_{\alpha\beta}$ is proportional to $C_{\alpha\beta}$, the total strain-rate in such a state. Substitution of this into equation (2) yields the desired steady-state result, with an explicit expression for $\tilde\rho$ in terms of parameters of the model.

In the following section, we define the model and the operators $\hat{\mathbf{J}}_\mathrm{s}$, $\hat{\mathbf{J}}_\mathrm{p}$, $\hat\sigma_{\alpha\beta}$, and $\hat C_{\alpha\beta}$ and summarize the Robertson formalism. A definition is given of $\tilde\rho$ and an equation written down for $\partial\tilde\rho/\partial t$ from which we can, by taking moments, extract the evolution equations for $\mathbf{J}_\mathrm{s}$ and $C_{\alpha\beta}$. In Section 3, we calculate $\mathbf{F}_\mathrm{s}$ in terms of the Lagrange multipliers introduced to satisfy (3a–c). This is done by deriving the evolution equation for $\partial\mathbf{J}_\mathrm{s}/\partial t$ and specializing to the steady state under conditions $\nabla n = 0 = \nabla T$. We also derive the equation for $\partial C_{\alpha\beta}/\partial t$. In Section 4, we use (3c) to complete the expression

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of the Lagrange multipliers in terms of $C_{\alpha\beta}$, permitting us to express $\mathbf{F}_\mathrm{s}$ in terms of the strain-rate. In Section 5, we find the explicit coefficient relating $\mathbf{F}_\mathrm{s}$ to $\nabla\gamma^2$. In Section 6, there is a summary and discussion.

2 Summary of the model and Robertson approach

In Jaynesian statistical inference [4] maximization of

$$S = -\kappa \int \tilde{\rho}(t,x) \ln \tilde{\rho}(t,x) \mathrm{d}x \tag{4}$$

subject to specified energy and (3a–c) yields:

$$\begin{aligned} \tilde{\rho}(x) = Z^{-1} \exp \Big[- \int \mathrm{d}\mathbf{R}\beta(\mathbf{R}) \Big\{ & \hat{H}_\mathrm{d}(\mathbf{R}) \\ & + \sum_\alpha (\lambda^\alpha_\mathrm{qs}(\mathbf{R}) \hat{\mathbf{J}}^\alpha_\mathrm{s}(\mathbf{R}) + \lambda^\alpha_\mathrm{qp}(\mathbf{R}) \hat{\mathbf{J}}_\mathrm{p}(\mathbf{R})) \\ & + \sum_{\alpha\beta} (\lambda_{\sigma,\alpha\beta}(\mathbf{R}) \hat{\sigma}_{\alpha\beta}(\mathbf{R}) + \lambda_{\mathrm{c},\alpha\beta}(\mathbf{R}) \hat{C}_{\alpha\beta}(\mathbf{R})) \Big\} \Big]. \end{aligned} \tag{5}$$

Temperature, heat flow, elastic strain, and inelastic strain-rate in the fluid vary continuously with position $\mathbf{R}$. The $\lambda(\mathbf{R})$ parameters are the aforementioned Lagrange multipliers determined to satisfy (3a–c) identically, $\beta(\mathbf{R}) = \{\kappa T(\mathbf{R})\}^{-1}$. Z is a functional of the Lagrange multipliers which normalizes $\tilde{\rho}(x)$ to unity. $\hat{H}_\mathrm{d}(\mathbf{R})$ is an energy density operator. In the present paper, we deal with the case where $\beta(\mathbf{R})$ does not depend appreciably on $\mathbf{R}$, and so

$$\int \mathrm{d}\mathbf{R}\beta(\mathbf{R}) \hat{H}_\mathrm{d}(\mathbf{R}) = \beta \hat{H}. \tag{6}$$

Particle velocities in $\hat{H}_\mathrm{d}$ are referred to the mass velocity $\mathbf{u}(\mathbf{R})$, and so those in $\hat{H}$ depend on the set $\{\mathbf{u}(\mathbf{r}_i)\}$, where $\{\mathbf{r}_i\}$ are the configuration coordinates, in a way not important for the present calculation.

Robertson [3] has derived from the Liouville equation an evolution equation satisfied exactly by $\tilde{\rho}$ in the form:

$$\begin{aligned} \partial\tilde{\rho}/\partial t = & -\mathrm{i}\hat{p}_\mathrm{R}(t) \hat{L} \tilde{\rho}(t) \\ & - \int_0^t \mathrm{d}t' \hat{p}_\mathrm{R}(t) \hat{L} \hat{T}(t,t') [1 - \hat{p}_\mathrm{R}(t')] \hat{L} \tilde{\rho}(t') \end{aligned} \tag{7}$$

where $\hat{L}$ is the Liouville operator, and $\hat{T}(t,t')$ is the solution of

$$\partial\hat{T}(t,t')/\partial t' = \mathrm{i}\hat{T}(t,t')[1 - \hat{p}_\mathrm{R}(t')]\hat{L} \tag{8}$$

$\hat{p}_\mathrm{R}(t)$ is defined by

$$\hat{p}_\mathrm{R}\chi \equiv \sum_n \int \mathrm{d}\mathbf{R} \{\delta\tilde{\rho}/\delta\langle \hat{F}_\mathrm{n}(\mathbf{R})\rangle\} \mathrm{Tr}\{\hat{F}_\mathrm{n}(\mathbf{R},x)\chi\} \tag{9}$$

where $\chi(x)$ is arbitrary and the $\{\hat{F}_\mathrm{n}(\mathbf{R},x)\}$ are operators such as $\hat{\mathbf{J}}_\mathrm{p}(\mathbf{R})$, $\hat{\mathbf{J}}_\mathrm{s}(\mathbf{R})$, $\hat{\sigma}_{\alpha\beta}(\mathbf{R})$, and $\hat{C}_{\alpha\beta}(\mathbf{R})$ in equation (5).

If we multiply equation (7) by $\hat{J}^\mathrm{r}_\mathrm{s}(\mathbf{R},x)$ or $\hat{C}_{\alpha\beta}(\mathbf{R},x)$ and integrate over phase space, we obtain equations for $\partial\hat{\mathbf{J}}_\mathrm{s}(\mathbf{R},t)/\partial t$ and $\partial C_{\alpha\beta}(\mathbf{R},t)/\partial t$. These will be derived below. From their steady-state limits, we can predict that $\mathbf{J}_\mathrm{s}$ will be driven, when ∇T is negligible, by a term proportional to $\nabla\gamma^2$. To use this formalism, we must first define the operators.

Consider first the phonon heat flow, $\mathbf{J}_\mathrm{p}(\mathbf{R})$. It is known from Brillouin and neutron scattering [6] that phonon-like modes propagate in simple liquids. We imagine an ideal medium of uniform density and temperature in which such modes propagate, and, by analogy with the corresponding expression for a solid, introduce the operator,

$$\hat{\mathbf{J}}_\mathrm{p}(\mathbf{R}) = \sum_k \hbar\omega_k (\partial\omega_i/\partial\mathbf{k}) \hat{n}(\mathbf{k},\mathbf{R}) \tag{10}$$

for the heat flux carried by phonons, with $\hat{n}(\mathbf{k},\mathbf{R})$ an operator for the density of phonons with wave vector $\mathbf{k}$ at $\mathbf{R}$. The sum is over longitudinal modes. The spectrum $\omega(\mathbf{k})$ bends over [6] at high k, as in a solid, and so an approximate model [7] has been proposed in which heat is carried by hydrodynamic modes with $\omega < \bar{\omega}$, with a flat spectrum for $\omega > \bar{\omega}$. Modes in the latter region exceed the shear relaxation frequency, and so elastic displacements can be regarded as superpositions of modes with $\omega > \bar{\omega}$.

The ideal medium in which the hydrodynamic heat-carrying modes propagate does not provide for an additional heat flux component, $\mathbf{J}_\mathrm{s}$, carried by molecules which diffuse randomly out of their cages as a result of local expansions in regions having diameter of a few intermolecular lengths. In their interaction with phonons, these regions are analogous to lattice defects which scatter phonons in a solid at low temperature. They are caused by a superposition of modes with wavelength of the order of the diameter of the localized expansion, which the model treats as independent of the hydrodynamic modes. Since the phonon model makes no provision for such an interaction, we neglect all correlations between the phonon operators in $\hat{\mathbf{J}}_\mathrm{p}$ and the particle operators in $\hat{\mathbf{J}}_\mathrm{s}$.

As an operator $\hat{\mathbf{J}}_\mathrm{s}$ to represent the self-diffusing heat flux, let us take

$$\hat{\mathbf{J}}_\mathrm{s}(\mathbf{R}) = m^{-1} \sum_{i=1}^N \mathbf{p}_i \Lambda_i h_i \delta(\mathbf{r}_i - \mathbf{R}). \tag{11}$$

Λ_i is the probability that a particle i ($1 \leqq i \leqq N$) of mass m at $\mathbf{r}_i$ can cross the potential barriers formed by its neighbours and diffuse out of its cage. Λ_i depends on the set $\{\mathbf{r}_i - \mathbf{r}_j\}$, where $\{\mathbf{r}_j\}$ are positions of near neighbours. We neglect any dependence on more distant neighbours, since a local expansion occurs, in this picture, in a region whose diameter is of the order of the intermolecular spacing. Λ_i should, in general, have an expansion in Hermite functions of the particle momenta, but there are no experiments requiring this refinement, and so we use for Λ_i a thermal average depending on $n(\mathbf{r}_i)$, $T(\mathbf{r}_i)$ and the relative positions of near neighbours of i. In this paper, the $\mathbf{R}$-dependence of $n(\mathbf{R})$ and $T(\mathbf{R})$ is not important, and so they are treated as constants, as is $h(\mathbf{R})$. The momenta $\{\mathbf{p}_i\}$ are calculated in a frame in which mass velocity, $\mathbf{u}(\mathbf{R})$, vanishes. Particle i carries heat h_i.

For the elastic strain operator, we shall use:

$$\hat{\sigma}_{\alpha\beta}(\mathbf{R})=[\rho(\mathbf{R})]^{-1}\sum_{i=1}^{N} m\delta(\mathbf{r}_i-\mathbf{R})[\{\partial s_i^{\beta}/\partial r_i^{\alpha}+\partial s_i^{\alpha}/\partial r_i^{\beta}\}] \tag{12}$$

where $\mathbf{s}_i$ is the elastic component of displacement at position $\mathbf{r}_i$ of particle i. The displacements $\mathbf{s}_i$ are superpositions of modes, whose total number is N_{p}, having frequency $> \bar{\omega}$. Because of low liquid compressibility, mass density ρ is treated as a constant. For the $\mathbf{s}_i$, by analogy with the corresponding expressions for a solid, we take

$$\mathbf{s}_i = N^{-\frac{1}{2}}\sum_{\nu}\mathbf{e}_{\nu}q_{\nu}\exp(\mathrm{i}\mathbf{k}_{\nu}\cdot\mathbf{r}_i) \tag{13a}$$

$$\langle q_{\nu}q_{\nu'}\rangle = (\kappa T/m\bar{\omega}^2)\delta_{\nu\nu'}. \tag{13b}$$

The self-diffusive motion in regions of local expansion contributes to the inelastic displacement at $\mathbf{r}_i$ and therefore to the inelastic strain-rate. There is an additional inelastic component of the strain-rate at $\mathbf{R}$ arising from self-diffusive motion caused by the fact that the motion of the particle at $\mathbf{r}_i$ displaces it relative to the elastic stain field, since the latter is calculated from an independent model. The inelastic displacements produce an irrecoverable change in the strain $\sigma_{\alpha\beta}$ given by the expression (12). Combining the two inelastic strain-rate contributions, we have:

$$\hat{C}_{\alpha\beta}(\mathbf{R}) = [\rho(\mathbf{R})]^{-1}\sum_{i}(\partial/\partial r_i^{\alpha})[\Lambda_i(p_i^{\beta}+\mathbf{p}_i\cdot\nabla_{\mathbf{r}_i}s_i^{\beta})] \times\delta(\mathbf{r}_i-\mathbf{R})+(\alpha\leftrightarrow\beta). \tag{14}$$

From the way in which the model is set up, the phonon operators in $\hat{\mathbf{J}}_{\mathrm{p}}$ are uncorrelated with the operators in (11), (12), and (14). Therefore, if we calculate statistical averages using $\tilde{\rho}$, $\mathbf{J}_{\mathrm{s}}$ will not depend on $\boldsymbol{\lambda}_{\mathrm{p}}$ nor $\mathbf{J}_{\mathrm{p}}$ on $\boldsymbol{\lambda}_{\mathrm{s}}$. For similar reasons, $\partial\mathbf{J}_{\mathrm{s}}/\partial t$ and $\partial\mathbf{J}_{\mathrm{p}}/\partial t$ are independent when $\nabla T = 0$; it is $\mathbf{J}_{\mathrm{s}}$ and not $\mathbf{J}_{\mathrm{p}}$ which depends on $\nabla(\underset{\approx}{\mathbf{C}} : \underset{\approx}{\mathbf{C}})$. In a steady state, $\underset{\approx}{\mathbf{C}}$ is the total strain-rate, with $C_{xy} = C_{yx} = \gamma$.

3 Evolution equations for heat flux and inelastic shear-rate

To predict that $\mathbf{J}_{\mathrm{s}}$ is proportional to $\nabla\gamma^2$ in a quasi-steady state, under circumstances where $\nabla_{\mathbf{R}}n(\mathbf{R})$ and $\nabla_{\mathbf{R}}T(\mathbf{R})$ and time-derivatives are negligible, we need a derivation of equation (2), yielding an explicit expression for $\mathbf{F}_{\mathrm{s}}$ in terms of $\nabla(\underset{\approx}{\mathbf{C}} : \underset{\approx}{\mathbf{C}})$. Since $\mathbf{F}_{\mathrm{s}}$ depends on $\sigma_{\alpha\beta}$ and on $C_{\alpha\beta}$, we need a similar evolution equation for $C_{\alpha\beta}$ which predicts that, when $\partial C_{\alpha\beta}/\partial t$ is neglected, $\sigma_{\alpha\beta}$ is proportional to $C_{\alpha\beta}$.

In the framework of the Robertson formalism [3], an equation for $\partial\mathbf{J}_{\mathrm{s}}/\partial t$ can be derived by multiplying equation (7) by $\hat{\mathbf{J}}_{\mathrm{s}}$ and integrating over phase space. It has been shown [5] that the driving term comes from

$$F_{\mathrm{s}}^{\mathrm{r}} = -\int \mathrm{d}x\hat{J}_{\mathrm{s}}^{\mathrm{r}}(\mathbf{R},x)i\hat{L}\tilde{\rho}(x,t) \tag{15}$$

from the first term on the right in equation (7). The dissipative terms stem from the term involving $\hat{T}$ in equation (7). We can provide for the fact that $\mathbf{J}_{\mathrm{s}}(\mathbf{R})$ is defined in a frame in which mass velocity vanishes by interpreting momentum $\mathbf{p}_i = \tilde{\mathbf{p}}_i - \mathbf{u}(\mathbf{r}_i)$ in the definitions of all the operators other than $\hat{L}$, where $\tilde{\mathbf{p}}_i$ is the momentum in the laboratory frame. It has been shown [8] that for a dilute gas this interpretation of $\mathbf{p}_i$, when $\beta(\mathbf{R})$ depends on $\mathbf{R}$, will yield linear contributions to the driving term calculated from (15) which agree identically with Grad theory [9]. The distinction between $\mathbf{p}_i$ and $\tilde{\mathbf{p}}_i$ makes no explicit contribution to the term proportional to $\nabla\gamma^2$ in $\mathbf{F}_{\mathrm{s}}$. We shall suppose for convenience that $\mathbf{R}$ is a point in space where $\mathbf{u}(\mathbf{R}) = 0$.

From tensorial invariance, the leading dissipative term in $\partial\mathbf{J}_{\mathrm{s}}(\mathbf{R},t)/\partial t$ should have the form $(-1/\tau_{\mathrm{s}})\mathbf{J}_{\mathrm{s}}$, as in (2). This and non-linear dissipative terms are algebraic combinations of $\mathbf{J}_{\mathrm{s}}$, $\sigma_{\alpha\beta}$, and $C_{\alpha\beta}$ arising from fast irreversible processes in the vicinity of $\mathbf{R}$. Gradients in the driving term $\mathbf{F}_{\mathrm{s}}$ arise from the interaction with the surroundings of the fluid in a volume element centred at $\mathbf{R}$. τ_{s} may depend non-linearly on the shear-rate, but this dependence can be neglected when we multiply the right-hand member of (15) by τ_{s} to calculate the lowest-order contribution to $\mathbf{F}_{\mathrm{s}}$, in a quasi-steady state, proportional to $\nabla\gamma^2$.

Substituting from (5), (11), and (14) into (15), and expanding about the λ-independent term, we find that, among the leading non-zero contributions to $F_{\mathrm{s}}^{\mathrm{r}}$, the one which can involve a gradient of λ_{σ} is

$$\begin{aligned}&-(h\beta^2/\rho^2)\langle\sum_{i=1}^{N}p_i^r\Lambda_i\delta(\mathbf{r}_i-\mathbf{R})\\ &\times\sum_{\alpha\gamma,\chi\varepsilon}\int\mathrm{d}\mathbf{R}'\mathrm{d}\mathbf{R}''\lambda_{\sigma,\alpha\gamma}(\mathbf{R}')\lambda_{\sigma,\chi\varepsilon}(\mathbf{R}'')\\ &\times\sum_{k=1}^{N}\tilde{\mathbf{p}}_k\cdot\nabla_{\mathbf{r}_k}\delta(\mathbf{r}_k-\mathbf{R}')\{(\partial s_k^{\gamma}/\partial r_k^{\alpha})+(\partial s_k^{\alpha}/\partial r_k^{\gamma})\}\\ &\times\sum_{w=1}^{N}\delta(\mathbf{r}_w-\mathbf{R}'')\{(\partial s_w^{\chi}/\partial r_w^{\varepsilon})+(\partial s_w^{\varepsilon}/\partial r_w^{\chi})\}\rangle_0.\end{aligned} \tag{16}$$

Each term must have a product of two $\mathbf{s}$-operators in order not to vanish. We have $i\hat{L} = \sum_k \mathbf{p}_k\cdot(\partial/\partial\mathbf{r}_k)+\ldots$ The gradient $\partial/\partial\mathbf{r}_k$, after a partial integration over $\mathbf{R}'$, will yield a factor $\partial\lambda_{\sigma,\alpha\gamma}/\partial\mathbf{R}'$. This will be proportional to $\partial\gamma(\mathbf{R})/\partial\mathbf{R}$ once we show below that $\lambda_{\sigma,\alpha\beta}$, in a steady state, is proportional to $C_{\alpha\beta}$. The average indicated by angular brackets is over an equilibrium ensemble. As explained above, we average the products of phonon operators using (13a, b) and then average the resulting expression over an equilibrium canonical distribution, since phonon and self diffusion models are defined independently of one another.

Neglecting second-order spatial derivatives of $\lambda_{\sigma,\alpha\beta}$, we get for the contribution to $\mathbf{F}_{\mathrm{s}}$ calculated from (16) the result:

$$F^{\mathrm{r}}_{\mathrm{s},\sigma} = -\{2n^2 h\Gamma_1/N(\bar{\omega}\rho)^2\}(\partial/\partial R_{\mathrm{r}})\{\sum_{\alpha\beta}\lambda^2_{\sigma,\alpha\beta}\} \quad (17a)$$

$$\Gamma_1 \equiv \sum_{\nu} g(k_\nu)k_\nu^2(e^x_\nu e^y_\nu)^2 \quad (17b)$$

where $g(k_\nu)$ is the liquid structure factor and the index ν runs over all modes with $\omega_\nu > \bar{\omega}$. The structure factor appears, from the factors $\exp(\mathrm{i}\mathbf{k}_\nu\cdot\mathbf{r}_i)$, if we take a canonical average of $\langle s^\alpha_1 s^\alpha_2\rangle$ in (13a), after taking the phonon average, with $\mathbf{r}_1$ fixed.

Instead of the two $\hat{\sigma}_{\alpha\beta}$-operators appearing in (16), we can have another contribution, $F^{\mathrm{r}}_{\mathrm{s,c}}$, calculated from (15), involving two $\hat{C}_{\alpha\beta}$ operators. This contribution will depend on $\nabla\lambda_{\mathrm{c}}$. Terms of this type will be non-zero if they have no $\mathbf{s}$-operators or two of these. We get from the terms with no $\mathbf{s}$-operators:

$$\begin{aligned}F^{\mathrm{r}(1)}_{\mathrm{s,c}} = &-(h\beta^2/\rho^2 m)\Big\langle\sum_{i=1}^{N} p_i^2 \Lambda_i(\mathbf{R})\delta(\mathbf{r}_i-\mathbf{R})\\ &\times\int \mathrm{d}\mathbf{R}'\mathrm{d}\mathbf{R}''\sum_q \tilde{\mathbf{p}}_q\cdot(\partial/\partial\mathbf{R}')\sum_{\alpha\gamma,\chi\varepsilon}\lambda_{\mathrm{c},\alpha\gamma}(\mathbf{R}')\lambda_{\mathrm{c},\chi\varepsilon}(\mathbf{R}'')\\ &\times\sum_w(\partial/\partial r^\alpha_q)(\Lambda_q p^\gamma_q)\delta(\mathbf{r}_q-\mathbf{R}')(\partial/\partial r^\chi_w)(\Lambda_w p^\varepsilon_w)\\ &\times\delta(\mathbf{r}_w-\mathbf{R}'')\Big\rangle_0 + (\alpha\leftrightarrow\gamma)+(\chi\leftrightarrow\varepsilon)+(\alpha\leftrightarrow\gamma,\chi\leftrightarrow\varepsilon).\end{aligned} \quad (18)$$

Again, a partial integration over $\mathbf{R}'$ will yield a factor $\partial\lambda_{\mathrm{c},\alpha\gamma}(\mathbf{R}')/\partial\mathbf{R}'$. Integration over a product of four momenta gives:

$$\begin{aligned}\langle p^\sigma_k p^\gamma_q p^{\mathrm{r}}_i p^\varepsilon_w\rangle = (m\kappa T)^2[&\delta_{\sigma\gamma}\delta_{kq}\delta_{r\varepsilon}\delta_{iw}\\ &+\delta_{\sigma r}\delta_{ki}\delta_{qw}\delta_{\gamma\varepsilon}+\delta_{\sigma\varepsilon}\delta_{kw}\delta_{\gamma r}\delta_{qi}].\end{aligned} \quad (19)$$

Putting (19) back into (18), we consider the contribution to $F^{\mathrm{r}(1)}_{\mathrm{s,c}}$ from the first product of Kronecker deltas in the square bracket. This is:

$$\begin{aligned}&-(2hm/\rho^2)\sum_{\alpha\gamma,\chi\varepsilon}\int \mathrm{d}\mathbf{R}' n^2 g(\mathbf{R}-\mathbf{R}')\\ &\times\langle(\partial/\partial\mathbf{R}_\chi)\Lambda_1^2(\mathbf{R})(\partial/\partial\mathbf{R}'_\alpha)\Lambda_2(\mathbf{R}')\rangle_{\mathbf{R},\mathbf{R}'}\\ &\times\lambda_{\mathrm{c},\chi\mathrm{r}}(\mathbf{R})(\partial/\partial\mathbf{R}'_\gamma)\lambda_{\mathrm{c},\alpha\gamma}(\mathbf{R}')\end{aligned} \quad (20)$$

where $g(\mathbf{R}-\mathbf{R}')$ is the radial distribution function. This multiplies a canonical average, denoted by angular brackets, taking $\mathbf{r}_1=\mathbf{R}, \mathbf{r}_2=\mathbf{R}'$ to be fixed points. If $\Lambda_1(\mathbf{r}_1)$ is appreciable, so that component 1 is diffusing, we shall suppose that $\Lambda_2(\mathbf{r}_2)$ is very small, since diffusing particles are unlikely to be near neighbours. Otherwise, the locally-expanded region would have a size of several intermolecular lengths, which is improbable. For this reason, the arguments of Λ_1 and Λ_2 should not overlap appreciably in configurations likely to occur. The angular bracket should factor. If $\Lambda_2(\mathbf{R}')$ depends on a set of relative positions $\{|\mathbf{r}_j-\mathbf{R}'|\}$, where $\mathbf{r}_j$ is a neighbour of $\mathbf{R}'$, then $\langle\Lambda_2\rangle_{\mathbf{R}'}$ will not depend appreciably on $\mathbf{R}'$, since the average is an integral over the relative position, and so, to a good approximation,

$$(\partial/\partial\mathbf{R}')\langle\Lambda_2(\mathbf{R}')\rangle_{\mathbf{R}'} = 0. \quad (21)$$

Thus (20) should give a negligible contribution to $F^{\mathrm{r}(1)}_{\mathrm{s,c}}$. The contributions from the remaining two terms in (19) will not, in general, vanish. They will be included in the final result, given below.

By analogy with (18), we can set up $F^{\mathrm{r}(2)}_{\mathrm{s,c}}$, the part of $F^{\mathrm{r}}_{\mathrm{s,c}}$ depending on $\mathbf{s}$-dependent terms in $\hat{C}_{\alpha\beta}$. We have:

$$\begin{aligned}F^{\mathrm{r}(2)}_{\mathrm{s,c}} = &-h\beta^2(\rho m)^{-2}\langle\sum_{i=1}^{N}p^{\mathrm{r}}_i\Lambda_i(\mathbf{R})\delta(\mathbf{r}_i-\mathbf{R})\\ &\times\sum_k\int\mathrm{d}\mathbf{R}'\mathrm{d}\mathbf{R}''\tilde{\mathbf{p}}_k\cdot(\partial/\partial\mathbf{R}')\\ &\times\sum_{\alpha\gamma,\chi\varepsilon}\lambda_{\mathrm{c},\alpha\gamma}(\mathbf{R}')\lambda_{\mathrm{c},\chi\varepsilon}(\mathbf{R}'')\\ &\times\sum_{q,w}(\partial/\partial r^\alpha_q)\{\Lambda_q\sum_y p^y_q(\partial/\partial r^y_q)s^\gamma_q\}\\ &\times\delta(\mathbf{r}_q-\mathbf{R}')\delta_{kq}(\partial/\partial r^\chi_w)\\ &\times\{\Lambda_w\sum_z p^z_w(\partial/\partial r^z_w)s^\varepsilon_w\}\delta(\mathbf{r}_w-\mathbf{R}'')\rangle_0\\ &+(\alpha\leftrightarrow\gamma)+(\chi\leftrightarrow\varepsilon)+(\alpha\leftrightarrow\gamma,\chi\leftrightarrow\varepsilon).\end{aligned} \quad (22)$$

The averages $\langle s^\alpha_q s^\beta_j\rangle_0$ are calculated from (13b) and the products of four momenta from (19). Since the Greek indices are dummy indices, the index interchanges multiply the term shown by 4.

After lengthy computations, we finally determine:

$$\begin{aligned}F^{\mathrm{r}}_{\mathrm{s}} = &-\{(\partial/\partial R_{\mathrm{r}})(\sum_{\alpha,\beta}\lambda_{\mathrm{c},\alpha\beta}\lambda_{\mathrm{c},\beta\alpha})\}\\ &\times[(h/\rho^2 V)\langle(\partial/\partial R_x)\Lambda_1^2(\mathbf{R})(\partial/\partial R_x)\Lambda_1(\mathbf{R})\rangle_{\mathbf{R}}\\ &\times(N+\kappa T\tilde{\Gamma}_1/m\bar{\omega}^2)\\ &+\{8h\kappa Tn^2\Gamma_2/(m\rho^2 N\bar{\omega}^2)\}\langle\Lambda_1^2\rangle_{\mathbf{R}}\langle\Lambda_1\rangle_{\mathbf{R}}\\ &+\{4h\kappa T/\rho^2 m\bar{\omega}^2 V\}\tilde{\Gamma}_2\langle\Lambda_1^3(\mathbf{R})\rangle_{\mathbf{R}}]\\ &-\sum_{\alpha,\beta}\{(\partial/\partial R_\alpha)\lambda_{\mathrm{c},\alpha\beta}\}\lambda_{\mathrm{c},\beta\mathrm{r}}\\ &\times\{32h\kappa Tn^2\Gamma_2/\rho^2 m\bar{\omega}^2 N\}\langle\Lambda_1^2\rangle_{\mathbf{R}}\langle\Lambda_1\rangle_{\mathbf{R}}\\ &-\sum_{\alpha,\beta}\lambda_{\mathrm{c},\alpha\beta}(\partial/\partial R_\beta)\lambda_{\mathrm{c},\alpha\mathrm{r}}\\ &\times[\{3h\kappa Tn^2\Gamma_2/(\rho^2 m\bar{\omega}^2 N)\}\langle\Lambda_1^2\rangle_{\mathbf{R}}\langle\Lambda_1\rangle_{\mathbf{R}}\\ &+\{2hN/(\rho^2 V)\}\langle(\partial/\partial R_x)\Lambda_1^2(\mathbf{R})(\partial/\partial R_x)\Lambda_1(\mathbf{R})\rangle_{\mathbf{R}}]\\ &-(\partial/\partial R_{\mathrm{r}})\sum_{\alpha,\beta}\lambda_{\sigma,\alpha\beta}\lambda_{\sigma,\beta\alpha}n^2 h\Gamma_1/N(\bar{\omega}\rho)^2)\end{aligned} \quad (23a)$$

$$\tilde{\Gamma}_1 \equiv (1/3)\sum_\nu k_\nu^2 (e_\nu^x e_\nu^y)^2 \quad (23b)$$

$$\tilde{\Gamma}_2 \equiv \sum_\nu k_\nu^4 (e_\nu^x e_\nu^y)^2 \quad (23c)$$

$$\Gamma_2 \equiv \sum_\nu g(k_\nu) k_\nu^4 (e_\nu^x e_\nu^y e_\nu^z)^2. \quad (23d)$$

To show that $F_{\mathrm{s}}^{\mathrm{r}}$ is proportional to $(\partial/\partial R_{\mathrm{r}})\{\gamma(\mathbf{R})\}^2$, we must demonstrate that, in a steady state, $\gamma_{\mathrm{c},\alpha\beta}$ and $\chi_{\sigma,\alpha\beta}$ are proportional to $C_{\alpha\beta}$, the inelastic strain-rate which is the total strain-rate in a steady state. To show that $\gamma_{\sigma,\alpha\beta}$ in such a state is proportional to $C_{\alpha\beta}$, we need the evolution equation for $\partial C_{\alpha\beta}/\partial t$. This is calculated by multiplying equation (7) by $\hat{C}_{\alpha\beta}$ and integrating over phase space. The linear terms are easily shown to be:

$$\partial C_{\alpha\beta}/\partial t = (-1/\tau_{\mathrm{c}})C_{\alpha\beta} + (8\kappa T\tilde{\Gamma}_2/\rho\bar{\omega}^2 V)\langle \Lambda_1(\mathbf{R})\rangle_{\mathbf{R}}\lambda_{\sigma,\alpha\beta}. \quad (24)$$

In the quasi-steady-state, where the time-derivative can be neglected:

$$\lambda_{\sigma,\alpha\beta} = \{\rho^2\bar{\omega}^2 V/(8\kappa T\tilde{\Gamma}_2\tau_{\mathrm{c}}\langle\Lambda_1(\mathbf{R})\rangle_{\mathbf{R}})\} \equiv \nu_\sigma C_{\alpha\beta}. \quad (25)$$

4 Evaluation of Lagrange multipliers

$\lambda_{\sigma,\alpha\beta}$ and $\lambda_{\mathrm{c},\alpha\beta}$ can be expressed as sums of products of the variables $\hat{\mathbf{J}}_{\mathrm{s}}$, $\sigma_{\alpha\beta}$, and $C_{\alpha\beta}$ by applying the matching conditions (3a–c). We have already found an expression for $\lambda_{\sigma,\alpha\beta}$ appropriate to the conditions of the present problem, in equation (25), and so we need here to use the matching condition (3c) to find the lowest-order term in $\lambda_{\mathrm{c},\alpha\beta}$. Once it is established that both $\lambda_{\sigma,\alpha\beta}$ and $\lambda_{\mathrm{c},\alpha\beta}$ are proportional to $C_{\alpha\beta}$ under the given conditions, then since $C_{xy} = C_{yx} = \gamma$ are the only non-zero components of $C_{\alpha\beta}$, we see that all the terms in (23a) are proportional to $\nabla\gamma^2$.

Expanding $\tilde{\rho}$ in (3c) about the equilibrium canonical distribution, ρ_{c}, we have:

$$\begin{aligned} C_{\alpha\beta}(\mathbf{R}) &= -\beta\int \rho_{\mathrm{c}}\mathrm{d}x\hat{C}_{\alpha\beta}(\mathbf{R})\sum_{\gamma,\zeta}\int \mathrm{d}\mathbf{R}'\hat{C}_{\gamma\zeta}(\mathbf{R}')\lambda_{\mathrm{c},\gamma\zeta}(\mathbf{R}') \\ &= -\nu_{\mathrm{c}}^{-1}\lambda_{\mathrm{c},\alpha\beta}(\mathbf{R}) \quad (26a) \end{aligned}$$

$$\begin{aligned} \nu_{\mathrm{c}}^{-1} \equiv\ & (4/\rho)[\langle(\partial\Lambda_1/\partial R_x)^2\rangle_{\mathbf{R}} \\ & + (\kappa T/Nm\bar{\omega}^2)\{\Gamma_0\langle(\partial\Lambda_1/\partial R_x)^2\rangle_{\mathbf{R}} \\ & + 2\tilde{\Gamma}_2\langle(\Lambda_1(\mathbf{R}))^2\rangle_{\mathbf{R}}\}] \quad (26b) \end{aligned}$$

$$\Gamma_0 \equiv \sum_\nu k_\nu^2 (e_\nu^x)^2. \quad (26c)$$

5 Prediction of shear-driven heat flow

Equation (23a) predicts that $\mathbf{F}_{\mathrm{s}}$ is proportional to $\nabla\gamma^2$ if we substitute into (23a) our results from (25) and (26a) and simplify. We can use:

$$(\partial/\partial R_y)\sum_{\alpha,\beta}\lambda_{v,\alpha\beta}\lambda_{v,\beta\alpha} = 2\nu_v^2\partial\gamma^2/\partial R_y\ (v=\sigma,\mathrm{c}) \quad (27a)$$

$$\sum_{\alpha,\beta}\{(\partial/\partial R_\alpha)\lambda_{\mathrm{c},\alpha\beta}\}\lambda_{\mathrm{c},\beta y} = \frac{1}{2}\nu_{\mathrm{c}}^2\partial\gamma^2/\partial R_y \quad (27b)$$

$$\sum_{\alpha,\beta}\lambda_{\mathrm{c},\alpha\beta}(\partial/\partial R_\beta)\lambda_{\mathrm{c},\alpha y} = \frac{1}{2}\nu_{\mathrm{c}}^2\partial\gamma^2/\partial R_y. \quad (27c)$$

The final expression for J_{s}^y in the quasi-steady state takes the form:

$$\begin{aligned} J_{\mathrm{s}}^y = & -\tau_{\mathrm{s}}(\partial\gamma^2/\partial R_y)[\nu_{\mathrm{c}}^2\{(h/\rho^2)(3n + 2\kappa T\tilde{\Gamma}_1/m\bar{\omega}^2 V) \\ & \times\langle(\partial\Lambda_1^2/\partial R_x)(\partial\Lambda_1/\partial R_x)\rangle_{\mathbf{R}} \\ & + (48h\kappa Tn^2\Gamma_2/\rho^2 m\bar{\omega}^2 V)\langle\Lambda_1^2\rangle_{\mathbf{R}}\langle\Lambda_1\rangle_{\mathbf{R}} \\ & + (8h\kappa T/\rho^2 m\bar{\omega}^2 V)\tilde{\Gamma}_2\langle\Lambda_1^3\rangle_{\mathbf{R}} \\ & + \nu_\sigma^2\{2n^2 h\Gamma_1/N(\rho\bar{\omega}^2)^2\}]. \end{aligned} \quad (28)$$

The square bracket in equation (28) is > 0. $\nu_\sigma, \nu_{\mathrm{c}}$, and the square bracket in (28) are all intensive, if we suppose that $\tilde{\Gamma}_1, \Gamma_1, \tilde{\Gamma}_2$, and Γ_2 are all sums of a number N_{p} of frequencies ω_ν, and that N_{p} is $O(N)$. One must assume that the density of phonon states in $\mathbf{k}$-space is $O(N)$ at high frequencies as it is in the low-frequency limit.

6 Discussion

The computer simulation for a simple liquid [1] which inspired the present work calculated the leading non-vanishing Fourier component of heat flux and strain-rate under a sinusoidal transverse force $F_x(y)$. The results were consistent with the existence of a term in the heat flux proportional to $\nabla(\nabla\mathbf{u} : (\nabla\mathbf{u})^{\mathrm{T}})$. The present paper sets out to predict such a term in the quasi-steady state, where time-dependence of heat flow can be neglected over the period of measurement, by calculating $\mathbf{F}_{\mathrm{s}}$ in equation (2). Attention is concentrated on $\mathbf{J}_{\mathrm{s}}$, since, according to the model, $\mathbf{J}_{\mathrm{p}}$ should not correlate appreciably with $\hat{C}_{\alpha\beta}$. With the aid of the formalism of Robertson [3,5], we express $\mathbf{F}_{\mathrm{s}}$ in the form (15), and so we have to evaluate the right-hand member of that equation, using equation (5) for $\tilde{\rho}$.

On substituting for $\tilde{\rho}$ from (5) into (15), we expand the exponent in $\tilde{\rho}$ and pick out terms involving an even number of particle momenta $\{\mathbf{p}_i\}$ and an even number of elastic displacement operators $\{\mathbf{s}_i\}$. Such products are evaluated with the aid of equations (13a,b) and (19), with phonon and particle operators averaged independently. The only terms in $i\hat{L}$ which have been found to contribute to the dependence in (15) on $\nabla\gamma$ come from $m^{-1}\sum_k \tilde{\mathbf{p}}_k\cdot(\partial/\partial\mathbf{r}_k)$. If this operates on $\delta(\mathbf{r}_k - \mathbf{R}')$ in (16), we get $-\sum_k \tilde{\mathbf{p}}_k\cdot(\partial/\partial\mathbf{R}')\delta(\mathbf{r}_k - \mathbf{R}')$, giving a factor $\partial\lambda_{\sigma,\alpha\gamma}(\mathbf{R}')/\partial\mathbf{R}'$ on partial integration with respect to $\mathbf{R}'$. λ_σ is shown in Section 3 to be proportional to $C_{\alpha\beta}$, and we obtain $\nabla C_{\alpha\beta} = \partial\gamma/\partial y$ if $C_{\alpha\beta} = C_{xy} = \gamma$. Similar reasoning applies to equation (22). The proportionality coefficient, ξ, calculated here is > 0, as found in the computer simulation. It has not been practicable to estimate ξ quantitatively because we do not have a tractable expression for the average probability $\Lambda_1(\mathbf{R}, x)$ that a particle at $\mathbf{R}$ can cross the potential barriers blocking escape from its cage.

To make the statistical prediction (28), we introduce the operators $\hat{\sigma}_{\alpha\beta}(\mathbf{R})$ given by equation (12) for elastic strain at $\mathbf{R}$ and $\hat{C}_{\alpha\beta}(\mathbf{R})$, equation (14) for inelastic strain-rate. Use of these operators, never proposed by other authors, has been inspired by the use of their statistical averages, $\sigma_{\alpha\beta}$ and $C_{\alpha\beta}$, in a non-equilibrium thermodynamics of visco-elasticity in liquids [10]. All other authors [11] have used the inelastic component of strain rather than the elastic component in setting up a thermodynamics of viscoelasticity. The inelastic component is difficult to define uniquely and therefore does not lend itself to an informational statistical calculation. The present work serves to illustrate the utility of the operators used here. This and an earlier paper [8] which determined the ∇T term in the Cattaneo-Vernotte equation [2] for a dilute gas are the only existing applications to specific problems of Robertson's general theory [3] which supposed a non-uniform system in which the variables and Lagrange multipliers vary continuously with position $\mathbf{R}$ in space.

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