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Abstract. Operators $\hat{\sigma}_{\alpha\beta}$ for elastic strain and $\hat{C}_{\alpha\beta}$ for inelastic strain rate are introduced to describe a small volume V in a liquid undergoing steady Couette flow at high shear rate. An information-theoretic distribution $\tilde{\rho}$ is constructed depending on the operators and on $C_{\alpha\beta} \equiv \langle \hat{C}_{\alpha\beta} \rangle$ and $\sigma_{\alpha\beta} \equiv \langle \hat{\sigma}_{\alpha\beta} \rangle$, the ensemble averages which, along with the heat flow components, constitute the measured information. Two components, $\hat{J}_s$ and $\hat{J}_p$, stemming from self-diffusion and phonons, are identified in the heat flux. The distribution $\tilde{\rho}$ is used to calculate $J_s \equiv \langle \hat{J}_s \rangle$ which, unlike $\langle \hat{J}_p \rangle$, depends on $\sigma_{\alpha\beta}$ and $C_{\alpha\beta}$ in such a way as to imply that the thermal conductivity tensor $L_{\alpha\beta}$ exhibits anisotropies $L_{xx} > L_{zz}$ and $0 < L_{xy}$ when the velocity gradient $\partial u_x / \partial y \neq 0$. Such anisotropies can be inferred from computer simulations of self-diffusion under shear.

1. Introduction

An early work (Nettleton 1961) on thermal conduction in liquids identifies two independent components of the heat flux. One of these, which we designate J_s, is carried by self-diffusing molecules. A molecule oscillates in a cage formed by neighbours until a local expansion permits it to diffuse into a neighbouring cage. As it diffuses, it carries a heat h which is an average energy, not enthalpy. The excitations contributing to the thermal motion include longitudinal acoustic modes which propagate in liquids and whose frequency spectrum has been extracted from molecular dynamics and neutron scattering (de Schepper *et al* 1983, Bruin *et al* 1985). These modes, as is the case with phonons in a crystal, can carry heat, and they contribute a component J_p to the heat flux. The model does not contemplate a high density of locally-expanded regions in which diffusive motion is occurring, and the phonons are treated as propagating in an average structure without reference to the 'holes'. For the mutual independence of J_p and J_s we argue at greater length in section 2.

The paper (Nettleton 1961) which originally introduced J_p and J_s postulated time-evolution equations for them which coupled the fluxes to each other and to the temperature gradient. An evolution equation was also postulated for the density gradient, linking its time derivative to the two heat flux components. However, for a system consisting of a macroscopically-small volume immersed in a large, non-uniform fluid, which is also the system used here, the density gradient characterizes the difference between the density of the system and that of its surroundings. Therefore, this gradient is not an internal state variable. Its evolution equation is derived from the hydrodynamic continuity equation and does not obey the equation postulated in the earlier paper (Nettleton 1961). The remaining evolution equations of that paper resemble the ones derived here. We show, however, that many of the coupling coefficients are zero, using statistical methods not in general use when the original paper was written. The molecular picture drawn in that paper has been partially superseded.

Operators used in the present statistical calculation did not appear in the earlier (Nettleton 1961) phenomenology.

The coupling coefficients in the original paper were all isotropic. In the presence of Couette flow, with mass velocity $u_x(R)$ in the x-direction at point $R = (x, y, z)$ and a gradient $\partial u_x/\partial y$, the coefficients become anisotropic. This anisotropy has been demonstrated at high shear rates for self- and binary diffusion by molecular dynamics (Sarman *et al* 1992), and computer simulations have been made for heat conduction (Baranyai *et al* 1992). As we proceed to show in the following sections, the thermal conductivity tensor $L_{\alpha\beta}$ should have $L_{xx} > L_{zz}$ and $L_{xy} < 0$ for the flow geometry described above.

To investigate shear-induced anisotropy in the coupling coefficients, we employ the information-theoretic phase-space distribution $\tilde{\rho}(x)$ where x denotes the phase coordinates of a system of N molecules. The system is contained in a macroscopically-small subvolume V immersed in a much larger non-uniform system in which there is a macroscopic velocity gradient $\partial u_x/\partial y$ and a very small macroscopic temperature gradient ∇T. Because $|\nabla T|$ is small, J_s and J_p are also small, being proportional in a steady state to ∇T, and we can neglect $O(J_k^2)$ ($k = $ s, p). The volume V is in the middle of the molecular dynamics cell at a point R where $u(R) = 0$. If $\hat{J}_s$ and $\hat{J}_p$ are operators whose non-equilibrium ensemble averages are, respectively, J_s and J_p, whilst $\hat{\sigma}_{\alpha\beta}$ and $\hat{C}_{\alpha\beta}$ are operators for the elastic component of strain and the inelastic strain rate, respectively, in V, we have for $\tilde{\rho}$ the expression

$$\tilde{\rho}(x) = Z^{-1} \exp\left[-\beta\left\{ \hat{H} + \sum_{\alpha,\beta}(\Omega_{\alpha\beta}^\dagger\hat{\sigma}_{\alpha\beta} + \Psi_{\alpha\beta}^\dagger\hat{C}_{\alpha\beta}) + \Phi_s \cdot \hat{J}_s + \Phi_p \cdot \hat{J}_p \right\} \right]. \tag{1}$$

Here $\beta \equiv (\kappa T)^{-1}$; $\beta\Omega_{\alpha\beta}^\dagger$, $\beta\Psi_{\alpha\beta}^\dagger$, $\beta\Phi_s$ and $\beta\Phi_p$ are Lagrange multipliers which maximize the information-theoretic entropy subject to specification of the values of J_s, J_p, $\sigma_{\alpha\beta} \equiv \langle\hat{\sigma}_{\alpha\beta}\rangle$ and $C_{\alpha\beta} \equiv \langle\hat{C}_{\alpha\beta}\rangle$ which, along with the temperature and density, constitute the measured information. $\hat{H}$ is the Hamiltonian for the N particles in V. The daggers denote traceless tensors, since the parametrizations of shear and compressional relaxation are distinct. Z normalizes $\tilde{\rho}$ to unity on integration over phase space. Z depends quadratically on the variables to lowest order in this dependence.

The Lagrange multipliers in (1) can be evaluated as functions of J_s, J_p, $\sigma_{\alpha\beta}$ and $C_{\alpha\beta}$ via the matching conditions:

$$J_{k\alpha} = \int \tilde{\rho}\hat{J}_{k\alpha}\,\mathrm{d}x \qquad (k = \text{s, p}) \tag{2a}$$

$$\sigma_{\alpha\beta} = \int \tilde{\rho}\hat{\sigma}_{\alpha\beta}\,\mathrm{d}x \tag{2b}$$

$$C_{\alpha\beta} = \int \tilde{\rho}\hat{C}_{\alpha\beta}\,\mathrm{d}x. \tag{2c}$$

To study the anisotropy in $L_{\alpha\beta}$, we expand the exponent in $\tilde{\rho}$ and write (2a) in the form

$$J_{k\alpha} = \sum_{\beta} K_{\alpha\beta}^{(k)}\Phi_{k\beta} \qquad (k = \text{s, p}). \tag{3}$$

The operators defined below in sections 2 and 3 have such a structure that $\hat{J}_p$ is not appreciably correlated with the other operators. To the extent that this is true, the normalization Z^{-1} will cause Φ_p to cancel out of (2a) when $k = $ s and terms in Φ_s to cancel out with $k = $ p. A proportionality between $K_{\alpha\beta}^{(s)}$ and $L_{\alpha\beta}^{(s)}$, the self-diffusion contribution to $L_{\alpha\beta}$, can be inferred if we use the information-theoretic entropy,

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

as a model for thermodynamic entropy. Under this assumption, $\Phi_s = -\partial F/\partial J_s$, where F is the Helmholtz free energy, and similarly for the other multipliers. Nettleton and Freidkin (1989) have demonstrated this by showing that if $\tilde{\rho}$ from equation (1) is substituted into (4), a Gibbs equation is obtained provided we identify Φ_s with a free-energy derivative. To make the contribution to $\dot{S}$ from irreversible processes within the system positive definite, we shall point out in section 4 that an anti-reciprocal relation, implying the above-mentioned proportionality between $K_{\alpha\beta}$ and thermal conductivity, should hold. Such an anti-reciprocity relation has also been derived (Nettleton 1997) to all orders from the evolution equations derived from the equation obtained by Robertson (1966) from the Liouville equation. The shear-induced anisotropy in the conductivity can be predicted from the information-theoretic result (3).

To calculate the right-hand members of (2a)–(2c) as expansions in the Lagrange multipliers, we need explicit analytic expressions for the operators $\hat{J}_s$, $\hat{J}_p$, $\hat{\sigma}_{\alpha\beta}$ and $\hat{C}_{\alpha\beta}$. The heat flux operators will be defined in section 2. From the structure of the operators, we infer that J_s and J_p obey time-evolution equations which are not linearly coupled and that these two flux components make independent contributions to $L_{\alpha\beta}$. The papers of Robertson (1966) and Nettleton (1997) are most relevant in connection with the statistical derivation of the evolution equations.

In section 3, we discuss the operators for $\hat{\sigma}_{\alpha\beta}$ and $\hat{C}_{\alpha\beta}$. The mathematical structure of these operators is such that $K_{\alpha\beta}^{(p)}$ should not depend on shear and so the shear anisotropy in thermal conduction stems from $K_{\alpha\beta}^{(s)}$. Accordingly, the shear anisotropy of $L_{\alpha\beta}$ should relate to that seen in computer simulations of self-diffusion (Sarman *et al* 1992). The reference most relevant to section 3 (Nettleton 1996) discusses the model for the phonon spectrum, inferred from the shape of the dispersion curve obtained by de Schepper *et al* (1983). It also proposes a model for $\hat{\sigma}_{\alpha\beta}$ which is modified here for reasons discussed later. A purely phenomenological treatment (Nettleton 1964) exhibits the usefulness of $\sigma_{\alpha\beta}$ and $C_{\alpha\beta}$ as state variables.

In section 4, we give the detailed expressions for the anisotropic coefficients in the expansion (2a) for J_s. This permits us to derive an explicit expressing for $K_{\alpha\beta}^{(s)}$. In section 5, the shear-induced anisotropies are written down, and a comparison is made with computer studies of self-diffusion. In section 6 a summary and discussion are given of the foregoing results.

2. Structure and coupling of the heat flux operators

The phonon model of heat conduction was originally put forward by Debye (1914) for gases and was subsequently (Nettleton 1960) applied to liquids. This application gave a crude derivation of the heat flux time-evolution equation from a wave model. In the present work, evolution equations are derived instead by multiplying by $\hat{J}_s$ and $\hat{\sigma}_{\alpha\beta}$ the equation derived by Robertson (1966) for $\partial\tilde{\rho}/\partial t$ and then integrating over phase space. The phonon spectrum extracted from molecular dynamics and neutron scattering (de Schepper *et al* 1983, Bruin *et al* 1985) has a typical longitudinal acoustic branch $\omega(k)$ which rises and then bends over, as it does in a solid. We suppose that the phonons with finite group velocity $\partial\omega/\partial k > 0$ carry heat. The top of the phonon branch, where it bends over, is taken to be approximately flat with $\omega(k) = \bar{\omega}$ for all N_p modes in this narrow propagating band.

This model was used (Nettleton 1996) to define an operator expression for $\hat{\sigma}_{\alpha\beta}$, assuming that the elastic component of displacement of particle i was a superposition of modes with $\omega > \bar{\omega}$. This expression had mathematical complications, including derivatives of Dirac deltas and the difficulty of obtaining an extensive entropy, which have been eliminated through introduction of the modified expression for $\hat{\sigma}_{\alpha\beta}$ given below in section 3.

In our present model, phonons are assumed to propagate in an average disordered structure which takes no explicit account of the small volume fraction of localized regions in which self-diffusive motion is taking place. In this model, there should be no correlation between phonon operators and the operator $\hat{\boldsymbol{J}}_s$. $\hat{\boldsymbol{J}}_s$ depends on the particle configuration and on the velocities of randomly diffusing molecules.

The velocities of the diffusing molecules are part of the large-amplitude motion induced by superposing the amplitudes of short-wavelength modes with $\omega = \bar{\omega}$ which expand a region of diameter of the order of two intermolecular lengths. In the model, this picture is replaced by an effective Maxwellian distribution of molecular velocities and a barrier-crossing probability which is negligibly small for molecular configurations other than the locally-expanded ones. Averages are taken over the Maxwellian distribution independently of averages computed using the phonon Hamiltonian which refers to an average medium.

The operator $\hat{\boldsymbol{J}}_p$ for the phonon component of the heat flux $\boldsymbol{J} = \boldsymbol{J}_p + \boldsymbol{J}_s$ should have, by analogy with the corresponding expression for a solid, the form

$$\hat{\boldsymbol{J}}_p = V^{-1} \sum_k h\omega_k (\partial\omega_k/\partial k)\hat{n}(k) \tag{5}$$

where the sum on k is taken over the portion of the longitudinal acoustic branch where $\partial\omega_k/\partial k \neq 0$. $\hat{n}$ is a phonon number operator. Equation (5) resembles the expression for heat carried by phonons in an isotropic elastic solid. Equation (5) should be obtained if we quantize the hydrodynamic modes at the long-wavelength end of the spectrum. The dispersion curve in the region where $\partial\omega_k/\partial k \neq 0$ has been found (de Schepper *et al* 1983) to be hydrodynamic throughout most of its length, although the reason for this is not clear at short wavelengths.

To construct the operator $\hat{\boldsymbol{J}}_s$ we suppose that $\Lambda_i(T, \boldsymbol{r}_1, \ldots, \boldsymbol{r}_N)$ is the probability that particle i can cross the potential barrier produced by its near neighbours and diffuse into a new cage, carrying heat h as it diffuses. The symbol h should not be confused with enthalpy. The configuration dependence of Λ_i should involve only positions $\boldsymbol{r}_j$ of near neighbours of particle i appreciably. In general, Λ_i should be expressible as an expansion in Hermite functions of the components of $\boldsymbol{p}_i$. Since there are no data to be fitted for which such a fine-tuned model is needed, Λ_i is taken to be average over an equilibrium momentum distribution to give a function of T. From these considerations, at a point where mass velocity $u(R) = 0$, we take

$$\hat{\boldsymbol{J}}_s = (mV)^{-1} \sum_{i=1}^{N} \boldsymbol{p}_i \Lambda_i h. \tag{6}$$

In a hard-sphere model (Nettleton 1959), Λ_i would be the probability that the cage has expanded sufficiently to permit molecule i to escape. h would then be the average kinetic energy. h is analogous, in the context of self-diffusion, to a heat of transfer. Thus equation (6) implies $\boldsymbol{J}_s = h\phi_s$, where ϕ_s is the flux of particles moving to neighbouring cages. In a model where the particle crosses a barrier of finite height, h can be taken to be the average energy of particles at the top of the barrier. In general, h, like Λ_i, should be an expansion in Hermite functions of the $\{\boldsymbol{p}_i\}$. However, the qualitative conclusions we seek to predict and the accuracy of existing computer algorithms does not require an expansion of h.

Given equations (5) and (6) for the operators, one can construct evolution equations for $\partial\boldsymbol{J}_k/\partial t$ ($k = $ p, s). To do this one can use an exact equation for $\partial\tilde{\rho}/\partial t$ derived by Robertson (1966) from the Liouville equation. Time-evolution equations for $\boldsymbol{J}_p$ and $\boldsymbol{J}_s$ are obtained by multiplying the Robertson equation by the two operators and integrating over phase space. Equations of this kind have been derived for variables which, like $\boldsymbol{J}_p$ and $\boldsymbol{J}_s$, are odd under time reversal (Nettleton 1997). This formalism, in a study to be given in detail elsewhere, expresses the terms in $\partial\boldsymbol{J}_k/\partial t$ linear in $\boldsymbol{J}_s$ and $\boldsymbol{J}_p$ in terms of correlation functions

$C_{ij}(t) = \langle \hat{J}_i \exp(-i\hat{L}t)\hat{J}_j \rangle_0$ calculated in an equilibrium ensemble, with $\hat{L}$ the Liouville operator. If we adopt the model

$$C_{ij}(t) = \langle \hat{J}_i \hat{J}_j \rangle_0 \exp(-\gamma_{ij}t) \tag{7}$$

which is often used for mathematical convenience and which is consistent with the structure of linear non-equilibrium thermodynamics, then there will be no linear coupling of $\hat{J}_s$ and $\hat{J}_p$ in the dissipative terms provided, as we have argued above, we have $\langle \hat{J}_{s\alpha} \hat{J}_{p\beta} \rangle_0 = 0$. We can reach the same conclusion about the coupling of $\hat{J}_s$ and $\hat{J}_p$ without going into the mathematical details by observing that the expansion of a cage of diameter one or two intermolecular lengths is produced by waves of wavelength comparable to the diameter of the cage, which are waves at the top of the phonon spectrum. These modes contribute to the motion of the diffusing molecule and are independent of the longer wavelengths which contribute to J_p. The local expansion involves a superposition at random of the wavelengths of these short-wavelength modes. There is, in this process, no interchange of energy between J_s and J_p. Consequently, there is no coupling between J_s and J_p in the dissipative terms of the evolution equations.

In the presence of a temperature gradient, we have

$$\partial J_{k\alpha}/\partial t = -\gamma_k J_{k\alpha} - \sum_{\beta} \gamma_k L_{\alpha\beta}^{(k)}(\nabla T)_\beta \qquad (k = s, p). \tag{8}$$

$L_{\alpha\beta} = L_{\alpha\beta}^{(s)} + L_{\alpha\beta}^{(p)}$ is the thermal conductivity tensor in a steady state in which the time derivatives vanish. If we substitute for $\tilde{\rho}$ from equation (1) into (4) and take the result to be a model for thermodynamic entropy, we have remarked above that the requirement $(\partial S/\partial t)_{\text{irrev}} \geqslant 0$ leads to the anti-reciprocal relation

$$\gamma_k T L_{\alpha\beta}^{(k)} = K_{\alpha\beta}^{(k)} V \qquad (k = p, s). \tag{9}$$

We shall proceed to explain in section 3 why $K_{\alpha\beta}^{(s)}$, but not $K_{\alpha\beta}^{(p)}$ should exhibit shear-induced anisotropy whose structure can be extracted from equation (3). The γ_k are, phenomenologically, reciprocals of the mean lifetimes of energy carriers. They may depend nonlinearly on J_s, J_p, $\sigma_{\alpha\beta}^\dagger$ and $C_{\alpha\beta}^\dagger$, but they do not contribute to the anisotropy in $L_{\alpha\beta}$ calculated from equation (9).

3. Operators for elastic strain and inelastic strain rate

An expression for $\hat{\sigma}_{\alpha\beta}(\boldsymbol{R})$ (Nettleton 1996) has been proposed on the assumption that the recoverable elastic strain, which disappears at zero stress, can be represented by its value at a specified point $\boldsymbol{R}$ in V. If the information-theoretic entropy (4) is to serve as a model for thermodynamic entropy, the latter should be extensive, and this has been achieved with $\hat{\sigma}_{\alpha\beta}(\boldsymbol{R})$ by artificially inserting a factor $N^{-1/2}$. This artificiality can be removed if we modify the earlier definition by setting

$$\hat{\sigma}_{\alpha\beta}(\boldsymbol{R}) = [\rho(\boldsymbol{R})]^{-1} \sum_{i=1}^{N} m\delta(\boldsymbol{r}_i - \boldsymbol{R})(\partial s_i^\beta/\partial r_i^\alpha + \partial s_i^\alpha/\partial r_i^\beta) \tag{10}$$

where m is the particle mass, $\rho(\boldsymbol{R})$ the mass density at $\boldsymbol{R}$ and s_i the elastic component of the displacement of particle i at $\boldsymbol{r}_i$. We shall neglect $\partial\rho/\partial\boldsymbol{R}$ in a liquid. $\hat{\sigma}_{\alpha\beta}(\boldsymbol{R})$, unlike the previous expression (Nettleton 1996) can be averaged over all points $\boldsymbol{R}$ in V by multiplying by V^{-1} and integrating over $\boldsymbol{R}$ to yield

$$\hat{\sigma}_{\alpha\beta}(x) = N^{-1} \sum_{i=1}^{N} (\partial s_i^\beta/\partial r_i^\alpha + \partial s_i^\alpha/\partial r_i^\beta). \tag{11}$$

We shall see in section 4 that this definition leads to a Φ_s which is O(N) consistent with $\Phi_s = -\partial F/\partial J_s$ where F is the Helmholtz function.

To motivate equation (11) as a natural expression for $\hat{\sigma}_{\alpha\beta}(x)$, consistent with the model, we reflect that s_i is the elastic part of the displacement of particle i, arising from Fourier components of the particle motion with frequencies above the shear relaxation frequency. If we imagine a continuous elastic solid in which the displacement at a point r_i is s_i then the curved bracket in (11) is the elastic strain in this solid at r_i. The expression in (11) is the average of this strain over the set of points $\{r_i\}$. This is then averaged over $\tilde{\rho}$ and the coefficient of the linear term in $\Omega^{\dagger}_{\alpha\beta}$ evaluated to make $\langle \hat{\sigma}_{\alpha\beta} \rangle = \sigma_{\alpha\beta}$. The operator in (11) is the one we substitute into $\tilde{\rho}$ and which we use in the calculations of this paper. A further motivation for (11) is found if we use an appropriate operator (Nettleton 1996) expression $\hat{P}_{\alpha\beta}$ in terms of the displacements $\{s_i\}$. We find $\langle \hat{P}_{\alpha\beta}\hat{\sigma}_{\alpha\beta} \rangle$ to be proportional to $\sigma_{\alpha\beta}$, so that $P_{\alpha\beta}$ ($\alpha \neq \beta$) to a first approximation is linear in the elastic strain, as in a visco-elastic solid. Accordingly, the definition (11) has the physical properties we expect of elastic strain.

Equation (10) has been included here because, on averaging, it leads to (11). Equation (10), as an operator for strain at R, can be compared with the operator introduced earlier (Nettleton 1996) which was associated with the picture in which the strain $\sigma_{\alpha\beta}(R)$ at one point R in V could characterize the strain for the whole system, for V small. The operator introduced could not be averaged over V to produce a finite result. Operators defined at one point R are needed in the formalism of Robertson (1966) in which the physical state of a large system is characterized by the values of variables taken at all points R within it. In the present picture, variables refer to average properties of the whole system and are not defined to vary over the volume V.

The elastic displacement $s_i(r_i)$ is taken (Nettleton 1996) to be a superposition of a number N_p of high-frequency modes with $\omega = \bar{\omega}$ at the top of the phonon spectrum where the model takes the dispersion curve to be flat. These frequencies are above the relaxation frequency for structural re-arrangement. Following the corresponding expression for phonons in a solid, we take

$$s_i = N^{-1/2} \sum_{\nu} e_{\nu} q_{\nu} \exp[\mathrm{i}k_{\nu} \cdot r_i] \tag{12}$$

where the sum is over the N_p modes of frequency $\bar{\omega}$ and polarizations e_{ν} parallel to k_{ν}. We have

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

To construct an operator $\hat{C}_{\alpha\beta}$, we take

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

The motivation for this definition resides in the observation that a particle oscillates within a cage until it self-diffuses to a new position, and so the non-equilibrium average over momenta, $m^{-1}\langle \Lambda_i p_i \rangle$ represents the rate of inelastic displacement of particle i. Then $(\partial/\partial r^{\alpha}_i)\langle \Lambda_i p^{\beta}_i \rangle + (\alpha \leftrightarrow \beta)$ is the inelastic strain rate multiplied by m. If we sum over all particles and divide by $\rho V = Nm$, we get an average over all particle positions resembling the average taken in equation (11).

The s-dependent term in $\hat{C}_{\alpha\beta}$ arises because the inelastic self-diffusive displacement changes r_i and thus also $s_i(r_i)$. This change of the elastic strain at r_i, produced by the inelastic displacements, gives an additional inelastic contribution to the total strain rate.

Having defined the $\hat{\sigma}_{\alpha\beta}$ and $\hat{C}_{\alpha\beta}$ operators, we have observed that there should be no correlation between these operators and $\hat{J}_p$. The elastic displacements depend on high-frequency modes at the top of the phonon band which should not couple strongly via

multiphonon processes to the energy-carrying modes. To a good approximation, the phonon Hamiltonian can treat the energy-carrying and non-energy-carrying modes as independent. As we have explained above, the phonon operators and diffusing particle momentum operators are averaged separately. Then the factor Z^{-1} in $\tilde{\rho}$ will cause powers of $\sigma_{\alpha\beta}$ and $C_{\alpha\beta}$, as well as powers of J_s, to cancel out of equation (2a) when $k = \mathrm{p}$. It is, accordingly, $K_{\alpha\beta}^{(\mathrm{s})}$ and not $K_{\alpha\beta}^{(\mathrm{p})}$ which will exhibit a dependence on $C_{\alpha\beta}$ and $\sigma_{\alpha\beta}$ and a resultant shear-induced anisotropy. This anisotropy will be obtained explicitly in the following section.

4. Determination of $K_{\alpha\beta}^{(\mathrm{s})}$

To calculate $K_{\alpha\beta}^{(\mathrm{s})}$, we substitute from (1) into (2a) in which $k = \mathrm{s}$ and then expand in powers of ϕ_s, $\Omega_{\alpha\beta}^\dagger$ and $\Psi_{\alpha\beta}^\dagger$. In a steady state with a velocity gradient having $\partial u_x / \partial y$ as the sole non-vanishing component, σ_{xy} and C_{xy} plus $x \leftrightarrow y$ will be the sole non-zero components of the elastic strain and inelastic strain-rate tensors, respectively. From considerations of tensorial invariance, (2a) with $k = \mathrm{s}$ must assume the form

$$J_{\mathrm{s}\alpha} = -\beta \Phi_{\mathrm{s}\alpha}/\Upsilon_s - \beta^3 \phi_\mathrm{a}^{(3)} \sum_{\zeta\chi} \Phi_{\mathrm{s}\zeta} \Psi_{\zeta\chi}^\dagger \Psi_{\chi\alpha}^\dagger - \beta^3 \phi_\mathrm{b}^{(3)} \sum_{\zeta\chi} \Phi_{\mathrm{s}\alpha} \Psi_{\zeta\chi}^\dagger \Psi_{\chi\zeta}^\dagger$$

$$+\beta^4 \phi^{(4)} \sum_{\zeta\chi\varepsilon} \Psi_{\alpha\zeta}^\dagger \Psi_{\zeta\chi}^\dagger \Omega_{\chi\varepsilon}^\dagger \Phi_{\mathrm{s}\varepsilon} + \mathrm{O}(J_\mathrm{s}^2 J_\mathrm{s}) \tag{15}$$

where Υ_s, $\phi_\mathrm{a}^{(3)}$, $\phi_\mathrm{b}^{(3)}$ and $\phi^{(4)}$ are extracted in the course of expanding (2a) in powers of the Lagrange multipliers in (1).

Each of the coefficients $\phi_\mathrm{a}^{(3)}$, $\phi_\mathrm{b}^{(3)}$ and $\phi^{(4)}$ is proportional to an average of a sum of products of four momentum operators. One of these comes from $\hat{J}_{\mathrm{s}\alpha}$ in (2a) and the three others from products such as $\hat{J}_{\mathrm{s}\zeta} \hat{C}_{\zeta\chi} \hat{C}_{\chi\alpha}$ which multiply $\hat{J}_{\mathrm{s}\alpha}$. These four momenta can be paired in various ways according to the scheme

$$\langle p_i^\alpha p_k^\gamma p_y^\mu p_z^\zeta \rangle_0 = (m\kappa T)^2 [\delta_{ik}\delta_{\alpha\gamma}\delta_{yz}\delta_{\mu\zeta} + \delta_{iy}\delta_{\alpha\mu}\delta_{kz}\delta_{\gamma\zeta} + \delta_{iz}\delta_{\alpha\zeta}\delta_{ky}\delta_{\gamma\mu}]. \tag{16}$$

The first term on the right-hand side, proportional to $\delta_{\alpha\gamma}$, is cancelled in (2a) by contributions from the normalization factor Z^{-1}. Once the momentum operators have been paired, one picks out of the products of the operators $\hat{\sigma}_{\alpha\beta}$ and $\hat{C}_{\alpha\beta}$ the terms involving an even number of displacements s_i, which are averaged with the aid of equation (13).

To simplify the results, we appeal to the model which assumed that the displacements s_i could be calculated as a superposition of high-frequency acoustic modes which propagate in an average structure. This structure is independent of the particle configuration within the locally-expanded regions where self-diffusion is occurring. Thus we set, for example,

$$\langle \Lambda_i^2 \Lambda_j^2 s_i^\alpha s_j^\beta \rangle_0 \cong \langle \Lambda_i^2 \Lambda_j^2 \rangle_0 \langle s_i^\alpha s_j^\beta \rangle_0. \tag{17a}$$

Here, if $i \neq j$,

$$\langle s_i^\alpha s_j^\beta \rangle_0 = N^{-1} (\kappa T/m\omega^{-2}) \sum_\nu e_\nu^\alpha e_\nu^\beta g(k_\nu) \tag{17b}$$

where $g(k_\nu)$ is the liquid structure factor and the sum is over modes with $\omega_\nu = \bar{\omega}$. The operators $\hat{C}_{\alpha\beta}$ and $\hat{\sigma}_{\alpha\beta}$ involve spatial derivatives of the $\{s_i\}$, and so we encounter the following combinations of products of k_ν factors:

$$\chi_{1\nu} \equiv k_\nu^x k_\nu^y e_\nu^x e_\nu^y \tag{18a}$$

$$\chi_{3\nu} \equiv (k_\nu^x k_\nu^y e_\nu^z)^2. \tag{18b}$$

There are also spatial derivatives of the Λ_i operators in the strain and strain-rate expressions, and so we also encounter

$$\Theta_{ij} \equiv \langle \Lambda_i \Lambda_j (\partial \Lambda_i / \partial r_i^x)(\partial \Lambda_j / \partial r_j^x) \rangle_0 \tag{19a}$$

$$\Pi_{ij} \equiv \langle (\Lambda_i \Lambda_j)^2 \rangle_0. \tag{19b}$$

A further simplification is used which is necessary if we are to neglect in $\phi^{(4)}$ terms of $O(N^{-3})$, which are incompatible with an extensive entropy. We observe that if particle i is diffusing, its near neighbours will, in most cases, not be so doing because this would require a local expansion in a region of several molecular diameters. This is improbable and indeed structural 'holes' do not appear in molecular dynamics simulations. Accordingly, if particle i is diffusing out of its cage, it is improbable that j is also diffusing unless j is not a near neighbour of i. The function Λ_i depends on r_i and on the coordinates of near neighbours, and so the arguments of Λ_i and Λ_j should not overlap in any important way. In the non-overlapping configurations which have an appreciable probability of occurring, Λ_i and Λ_j with $j \neq i$ should be independent, and so we set

$$\Theta_{12} \cong (1/4)\langle \partial \Lambda_1^2 / \partial r_1^x \rangle_0 \langle \partial \Lambda_2^2 / \partial r_2^x \rangle_0 = 0. \tag{20}$$

Λ_i depends on the interactions between i and its neighbours, i.e. on $\{|r_i - r_k|\}$ for k close to i. Then, in equilibrium, the averages of the spatial derivatives in (20) will be zero.

With the foregoing approximations and simplifications, we obtain after lengthy calculations

$$\phi_a^{(3)} = 2(h\kappa T / \rho V^2)^2$$
$$\times \left[2N\Theta_{11} + (\kappa T / m\bar{\omega}^2) \sum_\nu \{ 4\chi_{1\nu}\Theta_{11} + 16\chi_{3\nu}\Pi_{11} + 12\chi_{3\nu}\Pi_{12} ng(k_\nu) \} \right] \tag{21a}$$

$$\phi_b^{(3)} = 2(h\kappa T / \rho V^2)^2 (\kappa T / m^{-2}) \sum_\nu [2\chi_{1\nu}\Theta_{11} + 4\chi_{3\nu}\Pi_{11} + 4\chi_{3\nu}\Pi_{12} ng(\kappa_\nu)] \tag{21b}$$

$$\phi^{(4)} = 16(h\kappa T / \rho V^2)^2 (\kappa T / Nm\bar{\omega}^2)\Theta_{11} \sum_\nu \chi_{1\nu}[ng(k_\nu) + 1]. \tag{21c}$$

If the density of phonon modes in k-space is $O(N)$, which is usually the case, the sums over the N_p modes at the top of the spectrum in (21a)–(21c) will each be proportional to N. This makes $\phi_a^{(3)}$ and $\phi_b^{(3)}$ each $O(N^{-3})$. In equation (14), these coefficients are multiplied by three Lagrange multipliers. These are all $O(N)$, being free-energy derivatives, and so the right and left members of (14) are both of zero order in N, as required for consistency. From (21c), we conclude that $\phi^{(4)}$ is $O(N^{-4})$. Since $\phi^{(4)}$ is multiplied by four Lagrange multipliers in equation (14), again we obtain consistency.

In addition to the N-dependence, we can establish the signs of $\phi_k^{(j)}$ in (21a)–(21c). All quantities therein are greater than zero save $g(k_\nu)$. A calculation of the structure factor for a hard-sphere model (Verlet 1968) gives $-1 < ng(k) < 0$ for $k_\nu \bar{\sigma} \lesssim 6$, where $\bar{\sigma}$ is the hard-sphere diameter. The shortest wavelength which can propagate should be $\sim 2\bar{\sigma}$ which should make $k_\nu \bar{\sigma} \lesssim \pi$. The factor $ng(k_\nu) + 1$ should be greater than zero in (21c). A similar conclusion holds for (21a) and (21b) if $\Pi_{12} < \Pi_{11}$. Now by the reasoning leading up to equation (20)

$$\Pi_{12} \cong \langle \Lambda_1^2 \rangle_0 \langle \Lambda_2^2 \rangle_0 = (\langle \Lambda_1^2 \rangle_0)^2. \tag{22}$$

In a hard-sphere model, if the amplitudes of the modes with $\omega = \bar{\omega}$ superpose to produce a relative displacement of neighbouring molecules $\sim \bar{\sigma}$, a molecule can diffuse, and otherwise it cannot. Thus, either $\Lambda_i \sim 1$ or Λ_i is very small. If $\tilde{q}_1$ is the fraction of states in which

$\Lambda_i \sim 1$, then $\Pi_{11} \sim \tilde{q}_1$ and $\Pi_{12} \sim \tilde{q}_1^2$. Thus, we can set $\Pi_{12} \leqq \Pi_{11}$ which assures that $\phi_a^{(3)} > 0 > \phi_b^{(3)}$.

All the coefficients in equation (15) have been determined save Υ_s. This is given by

$$\Upsilon_s = mV^2/(Nh^2\langle\Lambda_1^2\rangle_0). \tag{23}$$

Similarly, the lowest approximations to equations (2b) and (2c) yield (no sum on repeated indices)

$$\Omega_{\alpha\beta}^\dagger = -\Upsilon_1 \sigma_{\alpha\beta}^\dagger \tag{24a}$$

$$\Psi_{\alpha\beta_1}^\dagger = -\upsilon_1 C_{\alpha\beta}^\dagger \tag{24b}$$

$$\upsilon_1 = 2\beta\langle\hat{C}_{\alpha\beta}\hat{C}_{\beta\alpha}\rangle_0 \tag{24c}$$

$$\Upsilon_1^{-1} = 8\beta N^{-2}(\kappa T/m\bar{\omega}^2)\sum_\nu\{1 + ng(k_\nu)\}. \tag{24d}$$

The average in (24c) is a lengthy expression which is $O(N^{-1})$, like Υ_1^{-1}. We se that Υ_s, Υ_1 and υ_1 are greater than zero.

Rearranging equation (15) and introducing (24a) and (24b), we obtain an expression in the form of (13), with

$$K_{\alpha\beta}^{(s)} = (\beta/\Upsilon_s)\delta_{\alpha\beta} + \beta^2 J_s^2\phi^{(2)}\Upsilon_s^2\delta_{\alpha\beta} + \beta^3\phi_a^{(3)}\upsilon_1^2\sum_\gamma C_{\alpha\gamma}^\dagger C_{\gamma\beta}^\dagger + \beta^3\phi_b^{(3)}\upsilon_1^2\mathbf{C}^\dagger : \mathbf{C}^\dagger$$

$$+ \beta^4\phi^{(4)}\Upsilon_1\upsilon_1^2\sum_{\gamma\omega}\sigma_{\alpha\gamma}^\dagger C_{\gamma\omega}^\dagger C_{\omega\beta}^\dagger \tag{25}$$

where $\delta_{\alpha\beta}$ is the Kronecker delta. This result can be used in equation (9) to determine $L_{\alpha\beta}^{(s)}$, the self-diffusion contribution to the thermal conductivity. This contribution accounts for the entire shear anisotropy, which we discuss in the following section.

5. Shear-induced anisotropy in $L_{\alpha\beta}$

We consider the case of Couette flow, with

$$C_{xy}^\dagger = C_{yx}^\dagger = C \qquad \sigma_{xy}^\dagger = \sigma_{yx}^\dagger = \sigma. \tag{26}$$

In a computer simulation, C may be large. In a steady state, from the kinetic evolution equations for $\dot{C}_{\alpha\beta}^\dagger$ and $\dot{\sigma}_{\alpha\beta}^\dagger$ (Nettleton 1987), we have

$$\sigma = -\eta_s V\Upsilon_1^{-1}C \tag{27}$$

where η_s is the shear viscosity. Then we obtain

$$K_{xy}^{(s)} = -\phi^{(4)}\upsilon_1^2 V\eta_s C^3 \tag{28a}$$

$$K_{xx}^{(s)} = (\beta/\Upsilon_s) + \beta^2\Upsilon_s^2\phi^{(2)}J_s^2 + \beta^{(3)}\upsilon_1^2(\phi_a^{(3)} + 2\phi_b^{(3)})C^2 \tag{28b}$$

$$K_{zz}^{(s)} = (\beta/\Upsilon_s) + \beta^2\Upsilon_s^2\phi^{(2)}J_s^2. \tag{28c}$$

We consider $|\nabla T|$ to be very small, so that the $O(J_3^2)$ terms can be neglected.

From equation (9), we see that γ_s does not affect the anisotropy of $L_{\alpha\beta}^{(s)}$. Equations (28a)–(28c) imply the relations

$$L_{xx} > L_{zz} \tag{29}$$

$$L_{xy} = L_{yx} < 0. \tag{30}$$

This corresponds to what is observed (Sarman *et al* 1992) in self-diffusion and we expect it to hold for the self-diffusion component of thermal conduction. Computer simulations do not predict $L_{xy} = L_{yx}$, probably as an artifact of the thermostatting.

6. Summary and discussion

Following an early model (Nettleton 1961), the heat flux J in a liquid is resolved into two components, J_p and J_s. J_p is carried by propagating longitudinal acoustic phonons for which the dispersion curve can be extracted from molecular dynamics and neutron scattering (de Schepper *et al* 1983, Bruin *et al* 1985). At the top of the spectrum, it bends over and is approximated as flat (Nettleton 1996). Since $\partial\omega/\partial k = 0$, these high-frequency modes with $\omega = \bar{\omega}$ carry no heat, but they contribute to the elastic component of strain.

The modes in the flat region of the dispersion curve have a wavelength of a few intermolecular distances. In the present model, their amplitudes superpose randomly to create localized expansions which move the neighbours of a given molecule apart, permitting the molecule to diffuse into a neighbouring cage (Nettleton 1959). The self-diffusing molecules transport heat, creating the self-diffusion heat flow, J_s. The relaxation frequency γ_s is the probability per unit time for such an expansion to occur.

Equation (8) does not provide for appreciable energy exchange between J_p and J_s. The dissipative terms for either flux do not depend on the other save possibly in γ_s and γ_p, which do not affect the anisotropy. The local expansions can scatter phonons as do point defects in a crystal, but the model assumes that the concentration of these defects is small and we are not considering low temperatures. Therefore γ_p, the relaxation frequency for J_p, should be associated with multi-phonon processes. Since the local expansion involves random superpositions of the amplitudes of modes at the top of the band, the expansions can occur without drawing energy from J_p, and the large-amplitude motion in the expanded regions comes from the short-wavelength modes and is independent of J_p. Thus, there is no correlation between the two fluxes and $\langle \hat{J}_{p\alpha} \hat{J}_{s\beta} \rangle_0 = 0$. This observation, plus the model in equation (7), provides an additional reason based on the Robertson (1966) formalism for concluding that the modes have no linear coupling in the dissipative terms of (8). The latter terms should be represented by two relaxation frequencies as we have done.

The shear-induced anisotropy in thermal conductivity $L_{\alpha\beta}$ has been found on the basis of these model assumptions, to arise entirely from J_s. The high-frequency modes which contribute to elastic displacement $s_i(r_i)$ are not correlated appreciably with those which contribute to J_p, as is also the case with Λ_i which depends on these modes and with the random diffusive motions which occur in places where Λ_i is appreciable. Accordingly, the normalization factor Z^{-1} causes any dependence on $\sigma_{\alpha\beta}^{\dagger}$ or $C_{\alpha\beta}^{\dagger}$ to cancel out of equation ($2a$) when $k = p$ and from $K_{\alpha\beta}^{(p)}$ which is proportional to $L_{\alpha\beta}^{(p)}$. The dependence on $\sigma_{\alpha\beta}^{\dagger}$ and $C_{\alpha\beta}^{\dagger}$ appears only in $K_{\alpha\beta}^{(s)}$ and $L_{\alpha\beta}^{(s)}$.

To express the integrals in ($2a$) in a form which can be rearranged into equation (3), we have had to introduce operators $\hat{\sigma}_{\alpha\beta}$ and $\hat{C}_{\alpha\beta}$ for the elastic strain tensor and inelastic, i.e. self-diffusion, component $\hat{C}_{\alpha\beta}$ of the strain rate. These operators are introduced into equation (1) for the Jaynesian distribution $\tilde{\rho}(x)$. The operator $\hat{\sigma}_{\alpha\beta}$ has been proposed previously (Nettleton 1996) and is modified here so that $\hat{\sigma}_{\alpha\beta}$ can be an average over the small volume V rather than the elastic strain at a point. This leads less artificially to an extensive entropy S given by equation (4). The parametrization of viscoelasticity based on $\sigma_{\alpha\beta}^{\dagger}$ and $C_{\alpha\beta}^{\dagger}$ follows an early phenomenological treatment (Nettleton 1964) which has not been followed by others who have invariably used the inelastic strain rather than $\sigma_{\alpha\beta}$. The operators and parametrization used here are designed to conform to the earlier phenomenology (Nettleton 1964, 1987).

The anisotropy in $L_{\alpha\beta}$ given by ($29a$) and ($29b$) is of a type which appears in self-diffusion and also in binary diffusion (Sarman *et al* 1992) where the $\hat{\sigma}_{\alpha\beta}$ and $\hat{C}_{\alpha\beta}$ operators can be given a mathematical structure similar to the one used here. We are not in a position

to make quantitative comparisons with computer simulations since the computer algorithms in the anisotropy studies were in a developmental stage whilst an accurate calculation of Λ_i is a complicated problem. The model operators introduced here should not be used to study the non-analyticity seen (Hanley and Evans 1982) in thermodynamic pressure and viscosity at high shear rate. For that, instead of choosing a small volume V with a limited number of variables, one needs to characterize a large, non-uniform system by specifying $\sigma_{\alpha\beta}^{\dagger}(\boldsymbol{R})$, $C_{\alpha\beta}^{\dagger}(\boldsymbol{R})$, $\rho(\boldsymbol{R})$, and $\boldsymbol{u}(\boldsymbol{R})$ at all points $\boldsymbol{R}$. One uses a generalization of equation (1) in which the exponent contains an integral over $\boldsymbol{R}$ (Robertson 1966). To date, the non-analyticities in such a picture have been predicted via hydrodynamic mode coupling.

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