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Thermal Conductivity of a Shearing Molecular Fluid[1]

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We have investigated the thermal conductivity tensor of strongly sheared atomic and molecular liquids by computer simulation methods. According to linear nonequilibrium thermodynamics, heat and transverse momentum transport are uncoupled in the linear regime. We also expect the thermal conductivity to be independent of the zero-wavevector strain rate in the linear regime. Away from the linear regime, the situation is different. Although even a large zero-wavevector strain rate cannot induce a heat flux, the thermal conductivity can become strain-rate dependent. Furthermore, the thermal conductivity becomes a tensor because a strong velocity profile can destroy the isotropy of a fluid. These effects are only apparent at extremely high strain rates for atomic liquids, but are experimentally observable for polymeric liquids.

KEY WORDS: butane; molecular liquid; shear flow; thermal conductivity.

1. INTRODUCTION

The effect of shear flow on the transport properties of liquids is an interesting subject of study, not only in relation to its possible practical applications in polymer science and lubrication science, but also theoretically. Evans [1] suggested an approach to the calculation of the thermal conductivity of a shearing fluid that was based on a similar approach used earlier to calculate the self-diffusion coefficient of a shearing fluid [2]. The resultant correlation function expression for the thermal conductivity tensor was used by Daivis and Evans [3] to calculate the strain-rate dependence of the thermal conductivity tensor of a simple liquid. In this paper, we present preliminary results of calculations of the thermal conductivity tensor of a shearing molecular fluid—butane.

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2. THEORY

The linear thermal conductivity is defined by the linear consitutive relation for heat flow in a small temperature gradient (Fourier's law)

$$\mathbf{J}_q(\mathbf{r}, t) = -\boldsymbol{\lambda} \cdot \nabla T(\mathbf{r}, t) \tag{1}$$

where $\mathbf{J}_q(\mathbf{r}, t)$ is the heat flux vector expressed as a function of the laboratory position vector $\mathbf{r}$ and the time t. In general, the thermal conductivity is a second-rank tensor. This is important when considering anisotropic materials. The linear thermal conductivity of an isotropic fluid reduces to a scalar, given by the well-known Green–Kubo relation [4, 5]

$$\lambda = \frac{V}{3k_B T^2} \int_0^{\infty} dt \, \langle \mathbf{J}_q(t) \cdot \mathbf{J}_q(0) \rangle_0 \tag{2}$$

where $\mathbf{J}_q(t) V$ is the zero-wavevector limit of the spatial Fourier transform of $\mathbf{J}_q(\mathbf{r}, t)$. The 0 subscript indicates that the average is carried out at equilibrium. The microscopic expression for $\mathbf{J}_q(t) V$ in the case of a simple atomic liquid is

$$\mathbf{J}_q(t) V = \sum_i \frac{\mathbf{p}_i}{m} e_i - \frac{1}{2} \sum_{i, j \neq i} \mathbf{r}_{ij} \mathbf{F}_{ij} \cdot \frac{\mathbf{p}_i}{m} \tag{3}$$

where $\mathbf{p}_i$ is the momentum of particle i, m is the atomic mass, $\mathbf{r}_{ij}$ is equal to $\mathbf{r}_j - \mathbf{r}_i$, $\mathbf{F}_{ij}$ is the force on atom i due to atom j, and V is the volume of the system. Equation (2) is evaluated at equilibrium, so the time-averaged fluid streaming velocity $\mathbf{u}(\mathbf{r})$ is zero. In this case, the internal energy per particle e_i is given by

$$e_i = \frac{p_i^2}{2m} + \frac{1}{2} \sum_{j \neq i} \phi_{ij} \tag{4}$$

where ϕ_{ij} is the potential energy of atom i due to interaction with atom j.

Now consider a fluid undergoing planar shear, with a linear velocity profile given by $\mathbf{u}(\mathbf{r}) = \mathbf{i}\gamma y$, where $\mathbf{i}$ is a unit vector in the x direction and γ is the strain rate. The continuity equation for the internal energy density for such a system is given by

$$\frac{\partial \rho [U(\mathbf{r}, t)]}{\partial t} = -\nabla \cdot \mathbf{J}_q - \nabla \cdot (\rho(\mathbf{r}, t) \, U(\mathbf{r}, t) \, \mathbf{u}(\mathbf{r}, t))$$

$$- \mathbf{P}^{\mathrm{T}}(\mathbf{r}, t) : \nabla \mathbf{u}(\mathbf{r}, t) + W(\mathbf{r}, t) \tag{5}$$

where $W(\mathbf{r}, t)$ is a term allowing for the effect of external forces on the internal energy of the system. In our case, it represents the work done by the force of constraint (the thermostat) that keeps the peculiar kinetic energy constant. In order to eliminate the effect of the streaming terms in Eq. (5), Evans [1] introduced a microscopic Lagrangian coordinate $\mathbf{q}_i$ defined as

$$\begin{aligned} \mathbf{q}_i(t) &= \mathbf{r}_i(0) + \int_0^t \frac{\mathbf{p}_i(s)}{m}\, ds \\ &= \mathbf{r}_i(t) - \int_0^t \mathbf{u}_i(s)\, ds \end{aligned} \tag{6}$$

The microscopic Lagrangian internal energy density is then given by

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

This leads to the following expression for the zero-wavevector Lagrangian heat flux vector [1]:

$$\mathbf{J}_\mathrm{L}(t)\, V = \sum_i \frac{\mathbf{p}_i}{m} e_i - \frac{1}{2} \sum_{i, j \neq i} \mathbf{q}_{ij} \mathbf{F}_{ij} \cdot \frac{\mathbf{p}_i}{m} \tag{8}$$

This expression differs from Eq. (3) in that the microscopic Lagrangian displacement $\mathbf{q}$ rather than the laboratory displacement $\mathbf{r}$ appears in the potential part. A derivation very similar to that used to obtain the equilibrium thermal conductivity [5] leads to an expression for the thermal conductivity tensor [1]

$$\boldsymbol{\lambda} = \frac{V}{k_\mathrm{B} T_\mathrm{c}^2} \int_0^\infty dt\, \langle \mathbf{J}_\mathrm{L}(t)\, \mathbf{J}_\mathrm{L}(0) \rangle_{\dot{\gamma}} \tag{9}$$

Here, $\langle \cdots \rangle_{\dot{\gamma}}$ denotes an average over an equilibrium canonical ensemble of systems that have been brought into a shearing steady state with constant-energy dynamics. It is assumed that the strain rate was applied at time $t = -\infty$ and that a steady state has been achieved by the time $t = 0$. Note that a canonical ensemble of systems that have been brought into a shearing steady state with constant-energy dynamics has the same energy fluctuations as the equilibrium ensemble from which it was generated. This means that the zero-time value of the correlation function of internal-energy-density fluctuations is the same as it is at equilibrium. This, in turn, is related to the specific heat and the temperature T_c of the generating equilibrium ensemble. Therefore, the temperature appearing in Eq. (9) is the equilibrium temperature, not the kinetic temperature of the nonequilibrium steady state [1]. At equilibrium, Eq. (9) reduces to Eq. (2). An analysis of Eq. (9) reveals that it is only the xx, xy, and xz elements of the thermal conductivity tensor that are affected by the use of the microscopic Lagrangian coordinates $\mathbf{q}_i$. As we have shown previously [3], these elements of the thermal conductivity tensor are much more difficult to calculate than the others, because of the appearance of the $\mathbf{q}_i$. On the other hand, the remaining elements of λ are more interesting in a sense, as they govern the flow of heat transverse to the streaming velocity, which is the interesting quantity in lubrication, for example. Therefore, we have restricted this study to an investigation of the yx, yy, yz, zx, zy, and zz elements of λ.

3. SIMULATION DETAILS

In previous work, we have presented results for the thermal conductivity tensor of a shearing simple liquid [3]. In this paper, we present new results for the thermal conductivity tensor of shearing liquid butane. We have used the anisotropic united atom model [AUA(2)] of butane that was recently proposed by Padilla and Toxvaerd [6]. The nonequilibrium molecular dynamics equations of motion that were used to generate the shearing steady states for this model were

$$\dot{\mathbf{r}}_{i\alpha} = \frac{\mathbf{p}_{i\alpha}}{m_\alpha} + \mathbf{i}\gamma y_i \qquad (10)$$

and

$$\dot{\mathbf{p}}_{i\alpha} = \mathbf{F}^{\phi}_{i\alpha} + \mathbf{F}^{C}_{i\alpha} - \frac{m_\alpha}{M_i}\,\mathbf{i}\gamma p_{yi} - \frac{m_\alpha}{M_i}\,\zeta\,\mathbf{p}_i \qquad (11)$$

where $\mathbf{F}^{\phi}$ represents the force due to Lennard-Jones, dihedral, and bond-angle-bending potential interactions, and $\mathbf{F}^{C}$ represents the intramolecular bond-length constraint forces. In these equations, m_α is the mass of a site, M_i is the mass of the molecule, $\mathbf{i}$ is a unit vector in the x direction, γ is the strain rate, ζ is the thermostatting multiplier, and p_{yi} is the y component of the momentum of molecule i. The thermostat keeps the translational (or center-of-mass) kinetic temperature fixed, and the multiplier is obtained from Gauss' principle of least constraint as

$$\zeta = \frac{\sum_{i=1}^{N} (1/M_i)\{\mathbf{F}^{\phi}_i \cdot \mathbf{p}_i - \gamma p_{xi} p_{yi}\}}{\sum_{i=1}^{N} (1/M_i)\,\mathbf{p}_i^2} \qquad (12)$$

These equations of motion, and techniques for implementing them, are fully described in other publications [7]. Note that although the previous calculations of the strain-rate-dependent thermal conductivity tensor were for constant energy (i.e., keeping the energy fixed while increasing the strain rate), these simulations are for constant kinetic temperature. We expect averages obtained by the two different methods at a given state point to agree, although plots of properties against strain rate will traverse different energies at constant temperature, and different temperatures at constant energy.

The AUA(2) model differs from other united atom models of alkanes in that the center of the Lennard-Jones force between two functional groups representing CH_2 or CH_3 groups is located at the geometrical center of the corresponding functional group rather than at the position of the corresponding backbone carbon atom [6]. The exact position of the center of interaction may depend on the positions of as many as three different mass-site positions, giving rise to as many as six forces resulting from the interaction of two united atom interaction sites. In addition to the anisotropic site–site interactions, the AUA(2) model includes a bond-angle-bending potential and a torsional potential. The masses of the sites representing CH_2 and CH_3 functional groups differ, unlike in the Ryckaert–Bellemans model, as do the Lennard-Jones energy and distance parameters. The reader is referred to the literature for further details [6]. The peculiarities of the AUA(2) potential lead to a somewhat unusual form for the molecular heat flux vector, i.e.,

$$\mathbf{J}_q(t)\,V = \sum_i \frac{\mathbf{p}_i}{M_i} e_i + \frac{1}{2} \sum_i \sum_\alpha \sum_{j \neq i} \sum_\beta \mathbf{r}_{ij} \frac{\mathbf{p}_{i\alpha}}{m_{i\alpha}} \cdot \left(\frac{\partial \phi_{i\alpha j\beta}}{\partial \mathbf{r}_{i\alpha}} + \frac{\partial \phi_{i\alpha-1 j\beta}}{\partial \mathbf{r}_{i\alpha}} + \frac{\partial \phi_{i\alpha+1 j\beta}}{\partial \mathbf{r}_{i\alpha}} \right) \tag{13}$$

4. RESULTS

The state point that we have chosen to simulate has a reduced temperature of 2.2720 and a reduced density of 1.05880. These correspond to a temperature and density, in real units, of 272.635 K and 601.1 $\text{kg} \cdot \text{m}^{-3}$, which is the boiling point of liquid butane at atmospheric pressure. In this work, we focus on the elements of the thermal conductivity tensor governing the flow of heat transverse to the streaming velocity. Therefore, we only consider the yx, yy, yz, zx, zy, and zz elements of λ. Furthermore, we can immediately say that the xz, yz, zx, and zy elements are equal to zero due to symmetry. This leaves the yy, yx, and zz elements.

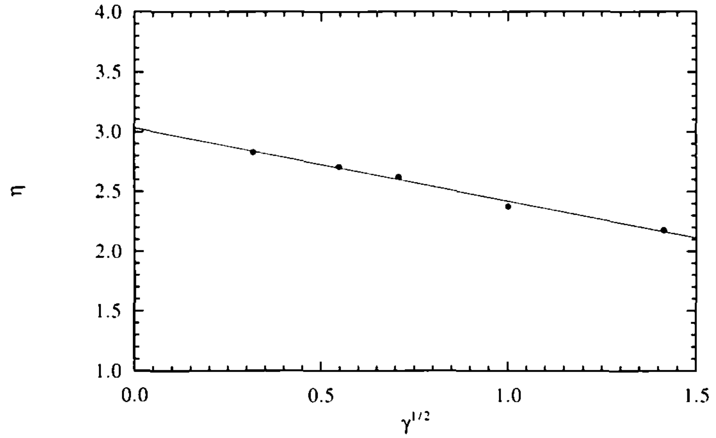

Fig. 1. Strain-rate dependence of the viscosity of AUA(2) model butane at temperature $T = 272.635$ K and density $\rho = 601.1\ \mathrm{kg \cdot m^{-3}}$.

The strain-rate dependence of the viscosity of butane obtained from these experiments is plotted in Fig. 1. The experimental value of the zero strain-rate viscosity of butane at this state point is 0.203 mPa · s (3.93 in reduced units) and the thermal conductivity is $0.117\ \mathrm{W \cdot m^{-1} \cdot K^{-1}}$ (4.09 in reduced units) [8]. Figure 1 shows that the zero-strain-rate viscosity is probably underestimated by this model of butane, but Fig. 2 shows that the

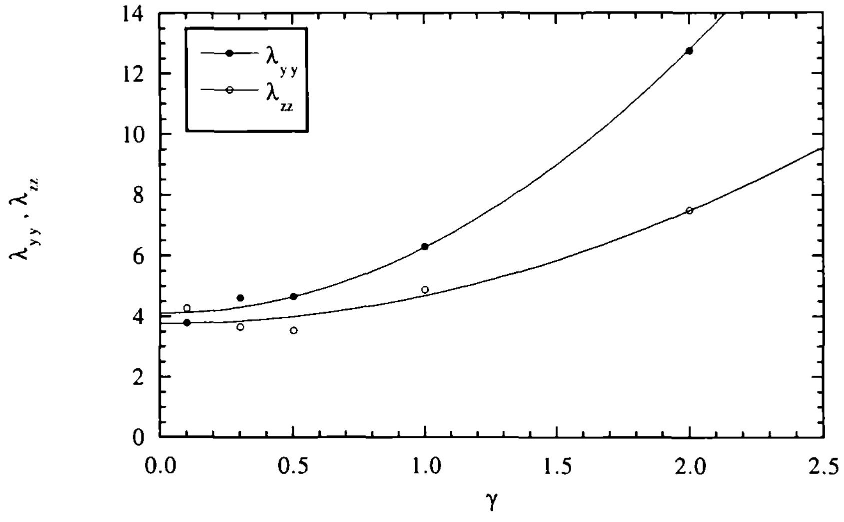

Fig. 2. Strain-rate dependence of the diagonal elements λ_{yy} and λ_{zz} of the thermal conductivity tensor corresponding to heat flow normal to the streaming velocity.

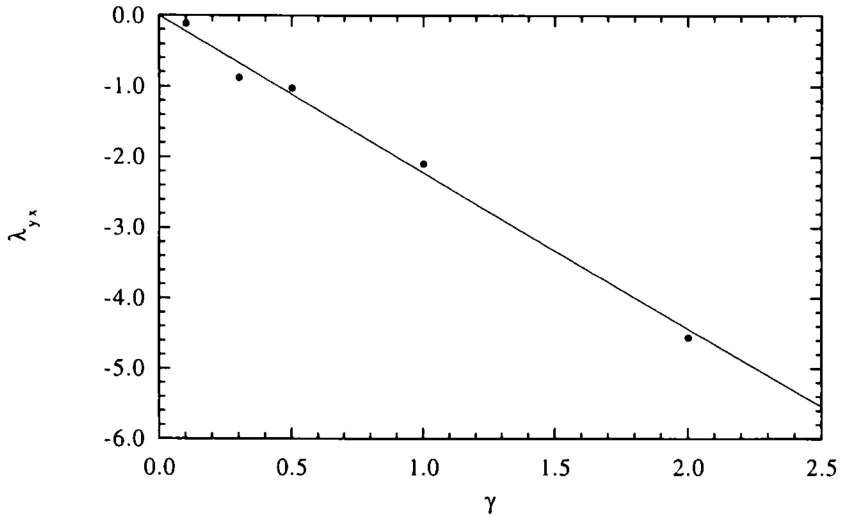

Fig. 3. Strain-rate dependence of the off-diagonal element λ_{yx} of the thermal conductivity tensor corresponding to heat flow normal to the streaming velocity.

linear thermal conductivity is accurately calculated, as both the yy and zz elements of the thermal conductivity tensor seem to be converging to the literature value within the estimated errors of ± 0.2 reduced units. The strain-rate dependence of the diagonal elements of the thermal conductivity tensor is quadratic, and the yx component of the thermal conductivity tensor decreases linearly with increasing strain rate (Fig. 3), as expected from our previous results for a simple atomic fluid. Using the fact that λ_{yx} must be zero at zero strain rate, we find that the errors are consistent with our estimate of ± 0.2 reduced units.

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