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1987 J. Phys. A: Math. Gen. 20 4017

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Non-linear heat conduction in dense fluids

R E Nettleton

Department of Physics, University of the Witwatersrand, Johannesburg, South Africa

Received 13 January 1987

Abstract. In a dense fluid with very large heat flow J , the thermal conductivity $\lambda = \lambda_0 + \lambda_2 J^2$. An estimate of λ_2/λ_0 is made for hard spheres with mass and diameter appropriate to Ar and density just below the gas-solid transition. This estimate indicates that Fourier's law will hold in the form appropriate to low J if $J \leq 10^9 \text{ W m}^{-2}$ and that the J dependence of pressure and internal energy is of the same order as that of λ . The calculation utilises an earlier derivation from the classical Liouville equation which expresses λ at high density in terms of the thermodynamic pressure. The latter can be calculated with the aid of reciprocity and integrability conditions of extended non-equilibrium thermodynamics which treats J as a state variable.

1. Introduction

It has been shown (Nettleton 1985a) that if the non-equilibrium state variables include dissipative fluxes of the type $\eta = \langle i \hat{L} A(x) \rangle$, where \hat{L} is the self-adjoint Liouville operator and $A(x)$ a function of the phase point x in Γ space which is even under momentum reversal, then the rate equations for η can be cast in Onsager-Casimir canonical form. The coefficients are, in general, non-linear in the η variables and exhibit reciprocity. In the case to be considered here, the system is a cube of side $l \sim 1 \mu\text{m}$ immersed in a continuous fluid and the state variables are N , the number of particles, $V = l^3$, T , and J , the heat flux density, which is an η type variable. Our aim is to apply the reciprocity and integrability conditions of non-equilibrium thermodynamics to calculate the $O(J^2)$ contributions to the thermal conductivity, pressure and internal energy of a dense fluid in a steady state in which J may be large. Quantitative estimates will be made for hard spheres in the high-density limit of the gas phase to show that the $O(J^2)$ corrections for that case are negligible unless J is extremely large.

The relaxation of J toward the steady state, where it is proportional to ∇T , is governed by the Cattaneo-Vernotte equation (Cattaneo 1958, Vernotte 1958) which has the form

$$\partial J / \partial t = aJ - \gamma \nabla T \quad (1)$$

where $a < 0$ and both a and γ have contributions $O(J^2)$. If those contributions can be evaluated with the aid of expressions from microscopic theory, then we can obtain the $O(J^2)$ contribution to the thermal conductivity, $\lambda = -\gamma/a$. An expression for γ has been derived (Nettleton 1984a) by applying a projection operator to the classical Liouville equation generalised to include interactions with the surroundings. This limits us to high densities since use of the N -particle Liouville equation assumes that N does not vary appreciably during the relaxation of the fast variable, J , so that the relaxation dynamics is approximately that of a closed system. The surrounding fluid

is represented by heat reservoirs whose temperature difference creates the macroscopic ∇T . These reservoirs exert, across the boundaries of the system, forces which can be expressed in terms of the thermodynamic pressure, thus giving an expression for γ which we can calculate.

Once γ is evaluated, we can cast (1) in the Onsager–Casimir form by setting $a\mathbf{J} = L\Phi$ where $\Phi = -\partial F/\partial \mathbf{J}$ is a thermodynamic force and L a phenomenological coefficient. By invoking a reciprocity relation involving γ , we can determine the $O(\mathbf{J}^2)$ and $O(|\mathbf{J}|^4)$ terms in the Helmholtz function F , and from it the leading \mathbf{J} dependence of the pressure and internal energy, U . From U we can estimate the difference $T - \theta$ between the thermodynamic and local equilibrium temperatures. Then invoking an estimate of the $O(|\mathbf{J}|^4)$ terms in F , we can, with the aid of an expression from microscopic theory, evaluate the $O(\mathbf{J}^2)$ contribution to a , which is used in finding the leading \mathbf{J} dependence of λ .

In the following section, we write down the results, obtained by applying reciprocity to (1), which enable us to calculate the \mathbf{J} -dependent terms in F from those in γ . We shall also describe the calculation of the $O(\mathbf{J}^2)$ terms in the other thermodynamic functions and in $T - \theta$. In § 3, we shall express γ in terms of the thermodynamic pressure in the dense fluid limit. In § 4, these results are specialised to the case of the hard sphere model, and numerical estimates made of the coefficients of the leading \mathbf{J} -dependent terms in all the above-mentioned functions. A discussion is given in § 5 where we remark on the limitation of the formalism used here to high densities and near-steady states and calculate λ_0 , the $\mathbf{J} \rightarrow 0$ limit of λ , giving the corresponding limit of a and the relaxation time.

2. Application of reciprocity and integrability conditions

We proceed here to show how we can calculate the \mathbf{J} dependence of the Helmholtz function, $F(N, V, T, \mathbf{J})$ if we can calculate γ . This involves an antireciprocity relation which couples the thermodynamic force $-VT^{-1}\nabla T$ to the force $\Phi = -(\partial F/\partial \mathbf{J})_{N, V, T}$ conjugate to $\dot{\mathbf{J}}$. Since (1) for $\partial \mathbf{J}/\partial t$ depends on the first of these forces, the antireciprocity relation implies that we should be able to write the trivial equation $\mathbf{J} = \mathbf{J}$ in the form

$$\mathbf{J} = -\gamma TV^{-1}\Phi. \quad (2)$$

This relation is a necessary condition that the irreversible entropy production be positive definite. By comparing similar powers of \mathbf{J} on each side of (2), we can express the expansion coefficients of Φ in terms of those in γ .

To this end, assume

$$\gamma = \gamma_0(n, T) + \gamma_2 \mathbf{J}^2 + \dots \quad (3a)$$

$$\Phi = -\mu_2 \mathbf{J} + \mu_4 \mathbf{J}^2 \mathbf{J} + \dots \quad (3b)$$

where $n \equiv (N/V)$. μ_2 should be > 0 and $\gg \mu_4$, since $-\frac{1}{2}\mu_2 \mathbf{J}^2$ is the leading term in the \mathbf{J} dependence of entropy, S , expanded at constant U , and this term is less than 0 to make S a strong maximum in thermal equilibrium. Substituting (3a, b) into the right-hand side of (2), and comparing coefficients of corresponding powers of \mathbf{J} on the right- and left-hand sides, we infer that

$$\mu_2 \gamma_0 V^{-1} T = 1 \quad (4a)$$

$$\mu_2 \gamma_2 = \mu_4 \gamma_0. \quad (4b)$$

This shows that we can determine the coefficients in the \mathbf{J} expansion of Φ , and therefore of F , if we can obtain γ_0, γ_2 and the higher-order coefficients in γ . Calculation of γ will be taken up in § 3.

Once we have μ_2 , we can invoke the integrability conditions to calculate the $O(\mathbf{J}^2)$ contributions in the thermodynamic pressure P and in U :

$$P = P_0(n, T) + P_2\mathbf{J}^2 + \dots \tag{5a}$$

$$U = U_0(N, V, T) + U_2\mathbf{J}^2 + \dots \tag{5b}$$

P_0 and U_0 are equilibrium equations of state, while U_2 and P_2 are calculated with the aid of the Gibbs equation (Nettleton 1961)

$$T dS = dU + P dV + \Phi \cdot d\mathbf{J} \tag{6}$$

which is equivalent to

$$dF = -P dV - S dT - \Phi \cdot d\mathbf{J}. \tag{7}$$

The condition that dF be a perfect differential implies that

$$\partial P / \partial \mathbf{J} = \partial \Phi / \partial V \tag{8a}$$

$$P_2 = -\frac{1}{2} \partial \mu_2 / \partial V. \tag{8b}$$

Similarly, from (6) and the integrability condition $\partial S / \partial \mathbf{J} = \partial \Phi / \partial T$, we obtain

$$2U_2 = -T(\partial \mu_2 / \partial T) + \mu_2. \tag{9}$$

The expressions (5a) and (5b) permit us to expand $\tilde{C}_p \equiv N^{-1}(\partial U / \partial T)_p$ and $\alpha_p \equiv V^{-1}(\partial V / \partial T)_p$ in powers of \mathbf{J} . We give the result for use in § 4:

$$\begin{aligned} \tilde{C}_p = \tilde{C}_p^0 - \frac{1}{2} n^{-1} \mathbf{J}^2 \{ T V^{-1} \partial^2 \mu_2 / \partial T^2 - \alpha_p^0 (\partial \mu_2 / \partial V - T \partial^2 \mu_2 / \partial V \partial T) \\ + (B_t)^{-1} (\partial U_0 / \partial V)_T [\partial^2 \mu_2 / \partial V \partial T + (\partial V / \partial T)_p \partial^2 \mu_2 / \partial V^2] \} \end{aligned} \tag{10a}$$

$$\alpha_p = \alpha_p^0 - \frac{1}{2} (B_t)^{-1} \mathbf{J}^2 \{ \partial^2 \mu_2 / \partial V \partial T - [(\partial P_0 / \partial T) / (\partial P_0 / \partial V)] \partial^2 \mu_2 / \partial V^2 \} \tag{10b}$$

where B_t is the equilibrium isothermal bulk modulus.

We can also calculate the difference between the thermodynamic temperature, T , which appears in (1) and (6), and the local equilibrium temperature, θ , defined as a function of U by

$$U \equiv U_0(N, V, \theta). \tag{11}$$

It has been remarked (Casas-Vázquez and Jou 1981) that the inequality of T and θ must be taken into consideration in comparing thermodynamic predictions with experiment. A computer simulation can yield θ and then T must be calculated from

$$T - \theta = -U_2 \mathbf{J}^2 / C_v^0(\theta) + O(|\mathbf{J}|^4) \tag{12}$$

where C_v^0 is the equilibrium specific heat. Equation (12) will be used to make a numerical estimate for hard spheres in § 4.

If $T - \theta$ should be appreciable, which we shall find is not the case for dense hard spheres, then the expression for thermal conductivity will depend on whether T or θ is used in Fourier's law in the steady state. To express the steady-state heat flow in terms of ∇T , we expand

$$a = a_0 + a_2 \mathbf{J}^2 + O(|\mathbf{J}|^4) \tag{13}$$

in (1) and obtain

$$\mathbf{J} = \nabla T \{ (\gamma_0/a_0) + \mathbf{J}^2 [(\gamma_2/a_0) - \gamma_0 a_2 (a_0)^{-2}] + O(|\mathbf{J}|^4) \}. \quad (14)$$

Equation (14) permits us to evaluate the ratio of the $O(\mathbf{J}^2)$ contribution to thermal conductivity, $\lambda_2 \mathbf{J}^2$, to the value λ_0 applicable to the $\nabla T \rightarrow 0$ limit provided we can obtain a_2/a_0 which we proceed to discuss.

A discussion of the derivation of the kinetic equations for the η variables by application of a Zwanzig (1960, 1961) projection operator to the classical Liouville equation has given (Nettleton 1985a, equation (27)) general expressions for coefficients such as a_2 in (1). These can be used to relate a_2 and a_0 if we make an ansatz (Nettleton 1987) for a correlation function appearing therein which is determined to cancel unphysically large contributions which would otherwise figure in a_2 . In doing this, however, we must take into account the fact that in the earlier work (Nettleton 1985a) the system was closed, and expansions were at constant U, N, V , so that we must transform to coefficients at constant T, N, V . Also, the forces here are $T \partial S/\partial \eta$ instead of $\partial S/\partial \eta$ as in the earlier work (Nettleton 1985a). All these considerations give

$$a_2 - (C_v^0)^{-1} U_2 \partial a_0 / \partial T = -a_0 (\mu_2)^{-1} [\mu_4 + (U_2 / C_v^0) (\partial \mu_2 / \partial T - \mu_2 / T)]. \quad (15)$$

To justify using this result, one must show that \mathbf{J} is an η variable, as assumed in the earlier work (Nettleton 1985a, 1987), i.e. that there is a dynamical function \hat{A}_J such that $\mathbf{J} = \langle i \hat{L} \hat{A}_J \rangle$. A suitable choice is

$$i^3 \hat{A}_J = \sum_i (p_i^2 / 2m) \mathbf{r}_i + \frac{1}{4} \sum_{j \neq i} (\mathbf{r}_i + \mathbf{r}_j) \phi_{ij} - h \sum_i \mathbf{r}_i$$

where ϕ is the pair potential and h the enthalpy per particle.

If we insert (15) into (13), we obtain

$$\mathbf{J} = (\gamma_0/a_0) \nabla T \{ 1 + \mathbf{J}^2 [2(\gamma_2/\gamma_0) - (a_0 C_v^0)^{-1} \partial a_0 / \partial T - 2(T C_v^0 \mu_2)^{-1} U_2^2] \} \quad (16a)$$

$$= (\gamma_0/a_0) \nabla \theta \{ 1 + \mathbf{J}^2 [2(\gamma_2/\gamma_0) - 4(\theta C_v^0 \mu_2)^{-1} U_2^2 + 2(\theta C_v^0)^{-1} U_2 + (\partial^2 U_0 / \partial \theta^2) (C_v^0)^{-2} U_2 - (C_v^0)^{-1} \partial U_2 / \partial \theta] \}. \quad (16b)$$

In a hard sphere fluid θ is proportional to the readily calculated kinetic energy per particle, making it the most natural temperature to use in computer simulation. Therefore, we shall evaluate in § 4 the $O(\mathbf{J}^2)$ term in (16b). We shall also show there that the difference between ∇T and $\nabla \theta$ is negligible for the dense hard sphere model.

3. Evaluation of γ

We have previously derived (1) from the classical Liouville equation (Nettleton 1984a) by including in the latter the forces which act on the particles of the system as a result of pair interactions with atoms of the surrounding fluid. The latter is regarded as a pair of reservoirs at $x = \pm \frac{1}{2}l$ and temperatures T_{\pm} . Since this model presumes N constant, the description should be limited to high density where each particle moves about in a cage formed by its neighbours. Only a fraction of the particles can move out of their cages and the dynamics of the system will not be affected appreciably by self-diffusion across the boundaries with the reservoirs during the short time required for relaxation of \mathbf{J} to the steady-state value, $-\lambda \nabla T$. So long as fluctuations in N are slow in comparison with those in the heat flow, we can generalise the picture to allow for them by replacing $N \rightarrow \bar{N}$, the ensemble average steady-state value, in the theoretical expressions derived here (Nettleton 1984b).

Under these circumstances it has been found (Nettleton 1984a, equation (A2)) that interactions with the surroundings contribute to the Fokker-Planck equation for $g(v)$, the distribution function for values v of the heat flux taken to be along x , a term

$$\gamma(\partial g/\partial v_x)(\partial T/\partial x) = R_+ - R_- \tag{17a}$$

$$R_{\pm} = (\partial/\partial v) \sum_i g(v) \int (\partial A_j^x/\partial p_{ix}) P_{\pm} f_{\pm}(r_i, \mathbf{R}_{N-1}, \mathbf{P}|v) d\mathbf{P} d\sigma d\mathbf{R}_{N-1}. \tag{17b}$$

In R_{\pm} , r_i is on the surface of the system in contact with a reservoir at temperature T_{\pm} and f_{\pm} is the phase space distribution of the N particles in the system with this restriction on r_i together with the specification that the magnitude of the heat flow through the system is v . P_{\pm} is the thermodynamic pressure under heat flow v when the temperature is T_{\pm} . Furthermore, in deriving (17b) we represent the forces acting across the element of area $d\sigma$ on the boundary at $x = \pm \frac{1}{2}l$ by $\mp P_{\pm} d\sigma$. This picture must fail at very low densities, where particles move freely across the boundary without collision with the surrounding fluid.

We now modify the treatment given earlier (Nettleton 1984a) of (17a, b) in two ways. Firstly, we no longer assume the fluid to be dilute, and so we use in (17b) the full expression

$$l^3(\partial A_j^x/\partial p_{ix}) = (2m^2)^{-1} p_i^2 + m^{-2} p_{ix}^2 + (2m)^{-1} \sum_{j \neq i} (\phi_{ij} - \phi'_{ij} x_{ij}^2 r_{ij}^{-1}) - m^{-1} h \tag{18}$$

which is obtained by differentiating the general expression (Nettleton 1984a, equation (7)) for A_j , the classical heat flux. Secondly, we are specifically concerned with steady states, and so we impose the condition of mechanical equilibrium,

$$P_+ = P_- = P(n, T, \mathbf{J}) \tag{19}$$

i.e. the thermodynamic pressure is constant across the system as we go from the reservoir at T_+ and $x = \frac{1}{2}l$ to the reservoir at T_- and $x = -\frac{1}{2}l$. If this condition is not imposed, $R_+ - R_-$ could also depend on ∇n , an additional state variable not needed for the description of steady states of the type we consider here. When ∇n is a relaxing state variable, additional complications are required (Nettleton 1961) such as the division of \mathbf{J} into two independent components, of which one component is carried by self-diffusing particles. These components are proportional to one another in a steady state, and so only one variable, \mathbf{J} , is needed.

Substituting (18) into (17b), we find, after carrying out the surface integration, that we can cast R_{\pm} in the form:

$$R_{\pm} = (ml)^{-1} (\partial/\partial v) [g(v)(P_{\pm}/n_{\pm})(n_{\pm} u_{\pm} + P_{\pm} - n_{\pm} h)] \tag{20}$$

where n_{\pm} and u_{\pm} are, respectively, the number density and energy per particle at $x = \pm \frac{1}{2}l$, i.e. in the system boundaries. There is a density gradient across the system imposed by the mechanical equilibrium condition $\nabla P = 0$, so that ∇n is proportional to ∇T . Thus $R_+ - R_-$, which has terms in both ∇n and ∇T , can be expressed in terms of ∇T only. Putting (20) into (17a), and noting that $J_x = \int g(v)v dv$ so that the first moment of the Fokker-Planck equation for g gives the Cattaneo-Vernotte equation, we find (Nettleton 1984a) that

$$-\gamma \partial T/\partial x = \int (R_+ - R_-) v dv \tag{21}$$

where γ has the form

$$\gamma = m^{-1} P(\tilde{C}_p + P_0 n^{-1} \alpha_p). \tag{22}$$

The notation is that of (10a, b).

The dependence of P on J^2 implies that γ , \tilde{C}_p and α_p all have a corresponding J dependence found in (10a, b). Utilising the latter equations in (22), we have

$$\gamma_0 = m^{-1} P_0 [\tilde{C}_p^0 + P_0 n^{-1} \alpha_p^0] \tag{23a}$$

$$\begin{aligned} \gamma_2 = m^{-1} P_2 [\tilde{C}_p^0 + P_0 n^{-1} \alpha_p^0] \\ - (2mn)^{-1} T \{ V^{-1} \partial^2 \mu_2 / \partial T^2 + \alpha_p^0 [\partial^2 \mu_2 / \partial V \partial T + (\partial V / \partial T)_p \partial^2 \mu_2 / \partial V^2] \}. \end{aligned} \tag{23b}$$

Equations (4a) and (23a) imply that

$$\mu_2 = mV [P_0 T (\tilde{C}_p^0 + P_0 n^{-1} \alpha_p^0)]^{-1}. \tag{24}$$

These results can be used to calculate μ_4 from (4b), P_2 from (8b), U_2 from (9) and the $O(J^2)$ term in the thermal conductivity from (16b). This will be done for the hard-sphere model in the following section.

4. Numerical estimates for rigid spheres

To use the theoretical expressions for P_2 , γ_2 , μ_2 and the $O(J^2)$ term in $T - \theta$ developed in preceding sections, we require equilibrium equations of state for $P_0(n, \theta)$ and $U_0(N, V, \theta)$. In the hard-sphere model, P_0 is proportional to θ and $U_0 = \frac{3}{2} N \kappa \theta$, leading to simplifications in the expressions to be evaluated. Furthermore, θ is proportional to the kinetic energy per particle which facilitates computer simulations to determine the coefficient of $\nabla \theta$ in (16b). Therefore, with a view to prediction of possible computer results we shall evaluate the $O(J^2)$ term in (16b) for hard spheres of diameter σ at a local equilibrium temperature θ . The density is chosen below but close to the hard-sphere gas-solid transition to validate the assumption that most particles move about in cages in which they are imprisoned by their neighbours.

If we define $b_0 \equiv \frac{2}{3} \pi \sigma^3$ and $x \equiv b_0 n$, the gas phase hard-sphere equation of state, obtained by fitting a Padé approximant to computer results (Ree and Hoover 1964), assumes the form

$$P_0 = (x \kappa T / b_0) (1 + x \Phi_1 / \Phi_2) \tag{25a}$$

$$\Phi_1(x) \equiv 1 + 0.063\,507x + 0.017\,329x^2 \tag{25b}$$

$$\Phi_2(x) \equiv 1 - 0.561\,493x + 0.081\,313x^2. \tag{25c}$$

Thus $\partial P_0 / \partial T = P_0 / T$ depends only on x and μ_2 is proportional to T^{-2} from (24), which simplifies some of the expressions we have to evaluate. In particular, with μ_2 from (24),

$$U_2 = \frac{3}{2} \mu_2 \tag{26a}$$

$$T - \theta = -(\mu_2 / N \kappa) J^2 \tag{26b}$$

$$P_2 = -\frac{1}{2} (\mu_2 / V) [1 + (B_i / P_0) + x (\tilde{C}_p^0 + P_0 \alpha_p^0 / n)^{-1} (\partial / \partial x) P_0 \alpha_p^0 / n] \tag{26c}$$

$$\gamma_2 = m^{-1} P_2 [\tilde{C}_p^0 - (3 P_0 / n) \alpha_p^0] - P_0 (mN)^{-1} [3 \mu_2 \theta^{-1} + \frac{1}{2} \theta (V \alpha_p^0)^2 \partial^2 \mu_2 / \partial V^2] \tag{26d}$$

$$J = (\gamma_0 / a_0) \nabla \theta \{ 1 + J^2 [(2 \gamma_2 / \gamma_0) - 3 \mu_2 / (\theta C_v^0)] \}. \tag{26e}$$

For the numerical evaluation of the constants in (26a)-(26e), we shall take $x = 1.7$, which is just below the value $x = 1.866$ corresponding to the gas-solid transition. We shall set atomic mass $m = 6.633 \times 10^{-26}$ kg appropriate to Ar and $\sigma = 3.64 \times 10^{-10}$ m

corresponding to an effective hard-sphere diameter for Ar (Hirschfelder *et al* 1954, p 545), giving $b_0 = 1.01 \times 10^{-28} \text{ m}^3$. The value $\theta = 87 \text{ K}$ is near the gas-liquid transition for Ar and we shall use this value to which the qualitative conclusions about the smallness of the coefficients in (26a)–(26e) are not highly sensitive. The numerical values calculated from the data and (25a) and (26a)–(26e) are listed in table 1. We include there the value of

$$\lambda_2 a_0 / \gamma_0 = (2\gamma_2 / \gamma_0) - 3\mu_2 / (\theta C_v^0) \tag{27}$$

which is the square bracket in (26c). This determines the non-linear effects, if any, in heat conduction.

The estimates in table 1 show that we should have to have $J \sim 10^9 \text{ W m}^{-2}$ before non-linear effects become appreciable in heat conduction in the dense rigid-sphere gas. For example $P_2 / P_0 \sim 10^{-18} \text{ m}^4 \text{ W}^{-2}$. The fact that the smallness of the $O(J^2)$ contribution is the same for all the functions considered resides in the circumstance that they are all proportional to $U_2 / U_0 = \mu_2 / N\kappa\theta$. Thus $P_2 / P_0 = -0.339\mu_2 / N\kappa\theta$. This factor does not depend on x , and so the conclusion of negligibility of non-linear effects should continue to hold so long as the gas can be categorised as highly dense.

An estimate is made in table 1 of $\lambda_0 = -\gamma_0 / a_0$, the thermal conductivity in the limit $|\nabla T| \rightarrow 0$. This can be obtained from the computer simulation of Alder *et al* (1970) which indicates that $\lambda_0 / \lambda_e \sim 1.01$, where λ_e is the Enskog dense gas approximation. The latter has been estimated to be $\lambda_e = 1.025 \cdot 13 \times (75/64\sigma^2)(\kappa^3\theta/\pi m)^{1/2} = 9.50 \times 10^{-3} \text{ J s}^{-1} \text{ m}^{-1} \text{ K}^{-1}$ (Chapman and Cowling 1939, p 169). Thus $\lambda_0 = 9.60 \times 10^{-3} \text{ J s}^{-1} \text{ m}^{-1} \text{ K}^{-1}$. This permits us to evaluate a_0 for which no method of estimation is given above. Once a_0 is known, we can calculate the coefficients in

$$L = \lambda_0 + \lambda_2 J^2 + O(|J|^4) \tag{28a}$$

$$a_0 = -\lambda_0 \mu_2 \tag{28b}$$

$$a_2 = -\lambda_2 \mu_2 + \lambda_0 \mu_4. \tag{28c}$$

These are of lesser interest, since they are not determined directly in simulations.

Table 1. Numerical values calculated for a hard-sphere fluid at $\theta = 87 \text{ K}$, $x = 1.7$, with particle mass and diameter appropriate to Ar. Sub- or superscript '0' denotes an equilibrium thermodynamic function and subscript '2' the coefficient of the square of the heat flux in the pressure, internal energy or the coefficient γ of ∇T in (1). $-\gamma_0 / a_0 = \lambda_0$, the thermal conductivity at low heat flow. $\frac{1}{2}\mu_2$ is the coefficient of the quadratic heat flow dependence of the Helmholtz free energy.

P_0	1.62×10^8	Pa
P_2	-2.46×10^{-13}	$\text{kg m}^3 \text{ J}^{-2}$
$(T - \theta) / J^2$	3.90×10^{-19}	$\text{kg m}^6 \text{ K J}^{-3}$
a_p^0	3.24×10^{-2}	K^{-1}
γ_0	1.27×10^{11}	$\text{J}^2 \text{ m}^{-3} \text{ kg}^{-1} \text{ K}^{-1}$
γ_2	-1.26×10^{-9}	$\text{m}^3 \text{ J}^{-1} \text{ K}^{-1}$
U_2 / U_0	4.48×10^{-21}	$\text{kg m}^6 \text{ J}^{-3}$
μ_4 / μ_2	-0.996×10^{-20}	$\text{m}^6 \text{ kg J}^{-3}$
μ_2 / V	9.05×10^{-14}	$\text{kg m}^3 \text{ J}^{-2}$
$-\gamma_0 / a_0$	9.60×10^{-3}	$\text{J s}^{-1} \text{ m}^{-1} \text{ K}^{-1}$
$\lambda_2 a_0 / \gamma_0$	-3.44×10^{-18}	$\text{kg m}^6 \text{ J}^{-3}$

From the foregoing estimate of λ_0 , we obtain the relaxation time $-1/a_0 = \lambda_0/\gamma_0 = 6.08 \times 10^{-11}$ s for J . The probability per unit time for appearance of a 'hole' in which self-diffusion can occur locally in liquid Ar at 87 K is 3.99×10^9 s $^{-1}$ (Nettleton 1985b), and so the fraction of particles on the surface of the cube of side l which can self-diffuse out of their cages in one relaxation time is ~ 0.242 . Of these about $\frac{1}{6}$ or 0.0403 will be moving in the right direction to diffuse across the boundary, and a substantial fraction of these will immediately experience a hard collision, sending them back inside the system from which they have just escaped. Thus it should be a reasonable approximation at high density to imagine the system to be contained in V by the surrounding fluid during the time $-a_0^{-1}$, so that forces across the boundary can be represented by P .

5. Discussion

The foregoing theory predicts that in a hard-sphere system, close to the gas-solid transition density, a very large heat flow $\sim 10^9$ W m $^{-2}$ is required before appreciable non-linear effects will be observed. To make this estimate, we had to evaluate γ in (1) in terms of the thermodynamic pressure P which can be calculated from (4a) and (8b). The arguments for this in § 3 rely on the picture according to which most particles are imprisoned in cages formed by their neighbours while those free to self-diffuse are likely to be turned back by collision immediately after crossing the system boundary. Thus, during the very short time of relaxation of J to the steady state the system is contained by the surrounding fluid, so that N is nearly constant and forces across the boundary can be expressed in terms of the pressure.

As x decreases, this picture becomes progressively poorer and non-linear effects are likely to become more important. At very low density, most of the atoms can diffuse across the boundary without collision, and so the model described in preceding sections has no obvious relevance at all. The Boltzmann equation appropriate to dilute gases has predicted appreciable non-linear effects in heat conduction in plasmas (Eu 1985a, b, c), and the Boltzmann equation approach is indicated, rather than the approach used here, at very low density.

At high density, even if approximations made here reduce the quantitative accuracy, we can make a qualitative prediction for hard spheres that Fourier's law will hold if $|\nabla T|$ is not extremely large. To compare such a prediction with a computer or experimental result, we need to be able to calculate or measure T , the thermodynamic temperature. In the laboratory, we can seek to measure T by inserting a gas thermometer into the wall of the tube through which J is flowing. If no appreciable part of J flows through the thermometer, heat should flow into it until it reads T . In a computer simulation, it is easier to calculate the local equilibrium temperature θ . The results in table 1 show that for dense hard spheres $T - \theta$ is $O(J^2)$ and of the order of the non-linear terms in λ , so that Fourier's law will hold whichever definition we use for temperature unless $|J| \sim 10^9$ W m $^{-2}$.

The estimates on which these conclusions have been drawn depend on γ_2 , which, when inserted into (4b), gives a value for μ_4/μ_2 . Table 1 shows that this value is very small, so that the $O(J^2)$ term gives the dominant J dependence of F . The order found here for the ratio of $O(\eta^4)$ to $O(\eta^2)$ terms is similar to the magnitude found for a scalar structural parameter (Nettleton 1987) where η is the time rate of change of the volume fraction of 'holes'. These estimates agree with the conclusion (Nettleton 1984a) that the Einstein approximation $\exp \delta^2 S/\kappa$, with the fourth-order terms neglected,

should give the correlation function for fluctuations in A_j in a closed system and that appreciable deviations from predictions of the Einstein approximation arise from terms in $g(v)$ which depend explicitly on ∇T and arise from the coupling to the surroundings.

All these calculations are based on a non-equilibrium thermodynamic theory, described in § 2, which chooses N , V , T and J as state variables. This should be appropriate to the neighbourhood of steady states far from equilibrium. However, for an arbitrary non-equilibrium state in a system subject to a large temperature gradient, the mechanical equilibrium condition $\nabla P = 0$ no longer holds, and there can be an additional independent state variable which is a linear combination of ∇n and ∇T (Nettleton 1961). Consistency then requires that J be divided into two components, of which one may be associated with self-diffusion and the other with the motion of particles in their cages. These components become mutually proportional in a steady heat flow, in which time derivatives of ∇n and ∇T can be neglected, rendering these complications unnecessary. An exception is a gas-liquid phase boundary, where ∇n is the significant variable (Nettleton 1961).

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