PHYSICAL REVIEW E VOLUME 54, NUMBER 2 AUGUST 1996

Nonlinear heat conduction in gases

R. E. Nettleton
Department of Physics, University of the Witwatersrand, Johannesburg 2050, South Africa

(Received 21 February 1996)

Terms in thermal conductivity λ that are quadratic in heat flux **J** are estimated via Onsager reciprocity and the maximum entropy formalism, which relate them to measurable coefficients. To observe these terms in Ar at 0 °C, 1 atm, one should require a temperature gradient $\gtrsim 10^7$ K/m. If density is reduced by a given factor, the required temperature gradient is reduced by the same factor. Convergence problems arise at very low densities. [S1063-651X(96)06108-9]

PACS number(s): 44.10.+i, 05.70.Ln

I. INTRODUCTION

In linear heat conduction obeying Fourier's law, the thermal conductivity λ in a pure gas depends only on number density n and temperature T. For large heat flux **J** and large temperature gradients, we should expect from the kinetic theory of Grad [1] that

$$\lambda=\lambda_0(n,T)+\lambda_2(n,T)J^2+O(J^4), \tag{1}$$

where $J\equiv|\mathbf{J}|$. Standard kinetic theory will not yield a reliable estimate of λ_2 because it is based on the linearized Boltzmann equation and, in the case of Grad, it assumes an approximate solution to the Boltzmann equation, which neglects terms $O(J^2)$, which we have reason to believe, discussed below, is of significance. Accordingly, we develop here a more phenomenological approach that uses the maximum entropy formalism and Onsager reciprocity to relate the phenomenological coefficients of extended thermodynamics [2] to quantities such as λ_0 that are accessible to experiment.

Such a treatment has been given [3] for liquids, where λ_2 was found to be negligible except for very large J. The system was taken to be a macroscopically small subvolume immersed in a large nonuniform liquid phase, which is also the model we postulate in the present paper, except that here we deal with a gas. A term coupling the system to its surroundings was added to the Liouville equation and it was assumed that, at high density, appreciable numbers of particles would not be exchanged with the surroundings during the time τ required for **J** to approach a steady state. Such an assumption is not applicable to gases, since molecules can freely enter and leave the system, and so we proceed here in a different way.

We suppose that relaxation of **J** to a steady state is given by a general, nonlinear Cattaneo-Vernotte [4,5] equation

$$\partial\mathbf{J}/\partial t=L\boldsymbol{\phi}-\gamma T^{-1}\boldsymbol{\nabla}T, \tag{2a}$$

$$L=L_0+L_2J^2+O(J^4), \tag{2b}$$

$$\gamma=\gamma_0+\gamma_2J^2+O(J^4), \tag{2c}$$

$$\boldsymbol{\phi}=\nu_0\mathbf{J}+\nu_2J^2\mathbf{J}+O(J^4\mathbf{J}). \tag{2d}$$

The linearized form of (2a) has been extensively discussed [2,6] and the possibility of generalization of such equations to the nonlinear case has been derived [7] via a Grad-type treatment of the Liouville equation. $\boldsymbol{\phi}$ is a thermodynamic force appearing in the Gibbs equation

$$TdS=dU+PdV+\boldsymbol{\phi}\cdot d\mathbf{J}. \tag{3}$$

Equations (2a) and (3) assume no mass flow, so that the total particle number N in the system of volume V, with $n\equiv N/V$, is constant.

From the maximum entropy formalism of Jaynes [8], we can evaluate $\boldsymbol{\phi}$ and therefore ν_0 and ν_2 in (2d). This is done in Sec. II. Rewriting (2d) in the form

$$\mathbf{J}=[\nu_0^{-1}-(\nu_2/\nu_0^2)J^2+O(J^4)]\boldsymbol{\phi}, \tag{4}$$

we find [3] that the condition of positive definiteness of the irreversible entropy production calculated from (3) requires the antisymmetric Onsager coupling

$$V\mathbf{J}=V[\nu_0^{-1}+(\nu_2/\nu_0^2)J^2]\boldsymbol{\phi}=-\gamma\boldsymbol{\phi}, \tag{5}$$

where we drop the $O(J^4)$ terms. From (5)

$$-\gamma_0\nu_0=V, \tag{6a}$$

$$-\gamma_0\nu_2-\gamma_2\nu_0=0. \tag{6b}$$

We can thus determine γ_0 and γ_2 from ν_0 and ν_2.

From the steady-state form of (2a),

$$-(L_0+L_2J^2)(\nu_0+\nu_2J^2)\mathbf{J}=-(\gamma_0+\gamma_2J^2)T^{-1}\boldsymbol{\nabla}T. \tag{7}$$

Comparing Eq. (7) with the nonlinear Fourier law $\mathbf{J}=-\lambda\nabla T$, we get

$$\lambda_0=-T^{-1}\gamma_0/L_0\nu_0, \tag{8a}$$

$$\lambda_2=-(T^{-1}\gamma_2/L_0\nu_0)+\{T^{-1}\gamma_0/(L_0\nu_0)^2\}(L_2\nu_0+L_0\nu_2). \tag{8b}$$

From (8a) we can calculate L_0 from the experimental λ_0 and then from (8b) we can find λ_2 if we can estimate L_2.

In Sec. III we discuss the calculation of L_2. This proceeds from the phenomenological condition that $L\boldsymbol{\phi}=-\tau^{-1}\mathbf{J}$, where τ is the collision time and also the response time for

J. We thus assume that a heat flux cannot be produced in response to an imposed temperature gradient in a time $<\tau$. We have

$$\tau = l/v, \tag{9}$$

where l is the mean free path and v the rms speed. We can calculate v in terms of **J** from the maximum entropy formalism, as we do in Sec. III, and l from λ_0. Thus we find L_2.

In Sec. IV we are able to make numerical estimates of λ_2/λ_0. Assuming a large value $J \sim 10^6$ W m^{-2}, we find $\lambda_2 J^2/\lambda_0 \sim 10^{-3}$ in Ar at 0 °C, 1 atm. Under conditions normally found in the laboratory, the nonlinear effects will not be seen and the linear Fourier law, with $\lambda \cong \lambda_0$, will obtain. We shall discuss the statistical significance of these results in Sec. V and possible generalizations of the maximum entropy calculation made in Sec. II. Such generalizations could make λ_2 even smaller than the estimates made here.

II. STATISTICAL PREDICTION VIA MAXIMUM ENTROPY

To calculate $\boldsymbol{\phi}$ and thus ν_0 and ν_2 in (2d), we follow Jaynes [8] in calculating the information-theoretic entropy

$$S = -\kappa \int \rho(x)\ln\rho(x)dx, \tag{10}$$

where the integration is over phase space. The S functional is maximized subject to the conditions

$$\mathbf{J} = \int \rho(x)\hat{\mathbf{J}}dx, \tag{11a}$$

$$\hat{\mathbf{J}}(x) \equiv V^{-1}\sum_{i=1}^{N} (\mathbf{p}_i/m)[(p_i^2/2m) - h], \tag{11b}$$

$$h = \tfrac{5}{2}\kappa T. \tag{11c}$$

m is the atomic mass and h the enthalpy per particle. The solution $\rho(x)$ to this variation problem can be used as a phase-space distribution to predict the value of any operator given the measured value of **J**. One obtains

$$\rho(x) = Z^{-1}\exp[-\beta(\hat{H} + \boldsymbol{\phi}\cdot\hat{\mathbf{J}})], \tag{12a}$$

$$Z = \int \exp(-\beta\hat{H})[1 + \tfrac{1}{2}\beta^2(\boldsymbol{\phi}\cdot\hat{\mathbf{J}})^2 + \cdots]dx, \tag{12b}$$

where $\hat{H}$ is the Hamiltonian operator representing the kinetic energy in a dilute gas.

$\boldsymbol{\phi}$ is a Lagrange multiplier determined to satisfy (11a) identically on substitution of (12) into the latter equation. If (12a) is substituted into (10), the Gibbs equation (3) is satisfied provided $\boldsymbol{\phi}$ in (12a) is identified with the thermodynamic $\boldsymbol{\phi}$ in (3) and provided $\beta = 1/\kappa T$. We can obtain a $\boldsymbol{\phi}$ expansion for **J** from the right-hand member of (11a), which, on inversion, yields the expansion in (2d). ν_0 has previously been calculated [9] and we add here the result for ν_2:

$$\nu_0 = -2V^2 m/\{5N(\kappa T)^2\}, \tag{13a}$$

$$\nu_2 = -203\nu_0^3\kappa T/\{10V^2 m\}. \tag{13b}$$

The expansion in (2d) is asymptotic and may not be useful for very small n, since higher terms in the expansion involve increasingly negative powers of n.

To illustrate use of the distribution $\rho(x)$, we predict the outcome of a measurement of internal energy U, given that **J** is known. We have

$$\begin{aligned} U &= \int \rho(x)\hat{H}(x)dx \equiv \tfrac{3}{2}N\kappa T_K \\ &= \tfrac{3}{2}N\kappa T[1 + 2mJ^2/\{5n^2(\kappa T)^3\}] + O(J^4). \end{aligned} \tag{14}$$

This result defines the kinetic temperature T_K, which differs from the operationally defined thermodynamic temperature T obtained via thermometry. It has been argued [10] that if we could measure simultaneously an infinite number of moments of the single-particle momentum-space distribution, we should predict $T_K = T$. This implies that the $O(J^2)$ term in (14) is of the order of the uncertainty in the statistical prediction. All the $O(J^2)$ contributions we calculate here are small and of the same order.

III. ESTIMATE OF L_2

Since we can estimate L_0 from λ_0, using (8a), we have only to obtain L_2 to calculate λ_2 from (8b). As stated above, we impose the phenomenological condition that $\lambda(\omega) \to 0$ if $\omega \gg \tau^{-1}$, which is achieved by setting $L\boldsymbol{\phi} = -\tau^{-1}\mathbf{J}$. τ is the collision time given by (9). We postulate an expansion

$$\tau^{-1} = a_0 + a_2 J^2 + O(J^4), \tag{15a}$$

$$L_0\nu_0 = -a_0, \tag{15b}$$

$$L_2\nu_0 + L_0\nu_2 = -a_2. \tag{15c}$$

The mean free path l should be the average of an operator that depends on the atomic configuration and not appreciably on particle momenta. If $\rho(x)$ is used to calculate the average, l will not depend on **J**. On the other hand,

$$\tfrac{3}{2}\kappa T_K = \tfrac{1}{2}mv^2. \tag{16}$$

From (14) we have

$$\begin{aligned} v &= (3\kappa T/m)^{1/2}[1 + mJ^2/\{5n^2(\kappa T)^3\}] + O(J^4) \\ &= v_0 + v_2 J^2 + O(J^4). \end{aligned} \tag{17}$$

Now, from (15b),

$$L_0\nu_0 = -v_0/l, \tag{18a}$$

$$l^{-1} = -L_0\nu_0/(3\kappa T/m)^{1/2}, \tag{18b}$$

$$a_2 = v_2/l = -mL_0\nu_0/\{5n^2(\kappa T)^3\}. \tag{18c}$$

From (15c) and (18c),

$$L_2\nu_0 + L_0\nu_2 = mL_0\nu_0/\{5n^2(\kappa T)^3\}, \tag{19}$$

where, from (8a),

$$L_0\nu_0 = -T^{-1}\gamma_0/\lambda_0. \tag{20}$$

After some algebra, (8b) predicts that

$$\lambda_2 = \lambda_0 m \tfrac{381}{25}/\{5n^2(\kappa T)^3\}. \tag{21}$$

IV. NUMERICAL ESTIMATE OF $\boldsymbol{\lambda_2}$

Consider Ar at 0 °C, 1 atm. If this is not highly dilute, it will provide an order-of-magnitude estimate that we can readily extend to lower densities where λ_2 is proportional to the estimate we make here. We take $m = 6.6336\times 10^{-26}$ kg and $n = 2.689\times 10^{25}$ m^{-3}. If $|T_K - T|/T = 0.001$, we find $|\mathbf{J}| = 1.209\times 10^6$ J/m^2 s. This large value is of the order required to render barely observable all the $O(J^2)$ terms we calculate from the distribution (12a).

For this value of J, we estimate from (21)

$$\lambda_2 J^2/\lambda_0 = 7.62\times 10^{-3}, \tag{22}$$

so that the $O(J^2)$ term does not affect the order of magnitude of λ. Then the temperature gradient $|J/\lambda| \sim |J/\lambda_0| = 7.3\times 10^7$ K/m, which we cannot readily realize in the laboratory. Steady states under such circumstances might be simulated on a computer, but such simulations are normally made at high density. From (21), we see that $\lambda_2 J^2/\lambda_0$ is proportional to $(J/n)^2$. If n were two orders of magnitude smaller, we should obtain (22) unchanged with a temperature gradient $\sim 10^5$–10^6 K/m, which is still very large. The nonlinear contributions to Fourier's law will prove very difficult to observe in steady heat conduction measurements in both simple liquids and gases.

V. DISCUSSION

In the foregoing sections we have extended work of earlier authors [9] by calculating the coefficient ν_2 of the $O(J^2\mathbf{J})$ term in $\boldsymbol{\phi}$ and estimating the $O(J^2)$ term in L. All the $O(J^2)$ contributions to $T_K - T$ and to λ are of the same order and very small except under circumstances where the number density n is very small and higher-order terms in $\mathbf{J}$ are needed to approximate the $\mathbf{J}$ dependence of $\boldsymbol{\phi}$ and λ. To observe the $\mathbf{J}$ dependence of λ, one must have very large temperature gradients and heat flows, which could not readily be achieved in the laboratory.

To calculate $\boldsymbol{\phi}$ and $T_K - T$ we have used the maximum entropy formalism, which provides a statistical distribution $\rho(x)$ in phase space, assuming that values of $n, T, \mathbf{J}$ constitute all the information we have about the system. If we had more information, the $O(J^2)$ terms would be altered. These terms appear to be of the order of the small uncertainty in the statistical prediction, which [10] has been found to give $T_K = T$ when maximum information is available. It is thus not surprising that $\lambda \cong \lambda_0$ in both gases and liquids. In the approaches of Grad [1] and Chapman and Enskog [11], one takes $T_K = T$ by definition and neglects terms of the order of the nonlinear corrections we have been calculating here. To the extent that kinetic theory is successful in any domain of n and T that is being studied, we could say that there is experimental evidence for the neglect of such terms and impose $T_K = T$ as an additional condition on the maximization of the S functional in (10). This would modify the predicted $\mathbf{J}$ dependence of λ.

The most drastic assumption made here is embodied in Eq. (9). One might try to improve on this by substituting $\rho(x)$ in (12a) into the Liouville equation, multiplying the latter by $\hat{\mathbf{J}}(x)$, and integrating over phase space. This is equivalent to Grad's approach to the Boltzmann equation. Such a procedure leads to (2a) with an explicit expression for L. However, this result for L yields a λ_2 that is not intensive. Therefore, the corrections that must be added to a Grad-type ansatz to make it a solution to the Liouville equation must affect the higher-order contributions to transport coefficients. As observed above, we cannot expect to be able to estimate these contributions from Grad-type theories.

The foregoing arguments all apply to simple gases obeying classical statistics. We attempt here to counter the notion that, because second-order effects in gaseous transport are proportional to n^{-2}, they should be large enough to observe in gases if not in liquids. From the calculations made here, it appears that possible observability requires changes in some parameter other than density, e.g., in the mean free path l. In a Bloch model for electrons in a metal, the Pauli exclusion principle makes the mean free path much longer than the interionic distance. Accordingly, electrical conductivity is a possible area in which to look for second-order transport effects. In that case, the remaining constants must be evaluated quantum statistically and so they may have significantly different relative magnitudes from those of the simple raregas model.

---

[1] H. Grad, Commun. Pure Appl. Math. **2**, 331 (1949).

[2] D. Jou, J. Casas-Vázquez, and G. Lebon, Rep. Prog. Phys. **51**, 1105 (1988).

[3] R. E. Nettleton, J. Phys. A **20**, 4017 (1987).

[4] C. Cattaneo, Atti Sem. Mat. Fis. Univ. Modena **3**, 3 (1948).

[5] P. Vernotte, C. R. Acad. Sci. Paris **246**, 3154 (1958).

[6] M. Ferrer and D. Jou, Int. J. Heat Mass Transfer **34**, 3055 (1991).

[7] R. E. Nettleton and E. S. Freidkin, Physica A **158**, 672 (1989).

[8] E. T. Jaynes, Phys. Rev. **106**, 620 (1957).

[9] R. Dominguez and D. Jou, Phys. Rev. E **51**, 158 (1995).

[10] R. M. Velasco and L. S. García-Colín, J. Nonequilib. Thermodyn. **18**, 157 (1993).

[11] S. Chapman and T. G. Cowling, *The Mathematical Theory of Nonuniform Gases* (Cambridge University Press, London, 1952).