

## Nonlinear heat flux dependence of pressure in nonequilibrium gases

R. E. Nettleton

*Department of Physics, University of the Witwatersrand, Johannesburg 2050, South Africa*

(Received 27 June 1995; revised manuscript received 21 August 1995)

Dominguez and Jou [Phys Rev. E **51**, 158 (1995)] have used the information theory to calculate pressure  $\mathbf{P}$  in a dilute gas with steady heat flow  $\vec{J}$ . Their  $\mathbf{P}$  has a  $\vec{J}\vec{J}$  term, found here to be negligible in Ar at 0 K, except at very low density or high  $J$ . The statistical calculation could be modified, in conformity with experiment or phenomenological requirements to reduce or eliminate this term.

PACS number(s): 05.70.Ln

Dominguez and Jou [1] have derived via the maximum entropy formalism of Jaynes expressions exhibiting dependence of pressure tensor  $P_{\alpha\beta}$  and internal energy on heat flow  $\vec{J}$  in a dilute gas for which number density  $n$ , thermodynamic temperature  $T$ , and  $\vec{J}$  characterize a nonequilibrium steady state with zero mass flow. Pressure and thermodynamic potentials have contributions  $O(J^2)$  to which we try here to give a statistical interpretation which goes beyond the discussion offered by these authors.

The statistical method [2] calculates a phase space distribution  $\rho(x)$  which maximizes the entropy functional,

$$S = -\kappa \int \rho(x) \ln \rho(x) dx, \quad (1)$$

where the integration is over phase space, subject to

$$\hat{J} = \int \rho(x) \vec{J}(x) dx, \quad (2)$$

where the heat flux operator is

$$\hat{J}(x) = V^{-1} \sum_{i=1}^N (\vec{p}_i/m) [(p^2/2m) - h], \quad (3a)$$

$$h = (5/2)\kappa T. \quad (3b)$$

$h$  is the enthalpy per particle and  $V$  the system volume. One obtains [1]

$$\rho = Z^{-1} \exp[-\beta \hat{H} - \beta \vec{\Phi} \cdot \hat{J}], \quad (4)$$

where  $Z$  normalizes  $\rho$  to unity. If we set  $\beta = (\kappa T)^{-1}$ , substitution into (1) yields

$$TdS = dU + PdV + \vec{\Phi} \cdot d\vec{J}. \quad (5)$$

This is the extended thermodynamic Gibbs equation provided  $T$  is the empirically defined thermodynamic temperature and  $\vec{\Phi}$  the thermodynamic force associated with  $\vec{J}$ .  $\vec{\Phi}$  is calculated to satisfy (2) identically, giving an asymptotic expansion,

$$\vec{\Phi} = v_0 \vec{J} + O(J^2 \vec{J}), \quad (6a)$$

$$v_0 = -2Nm / \{5(n\kappa T)^2\}. \quad (6b)$$

The pressure tensor is calculated by using  $\rho$  given by (4) to average the operator,

$$\hat{P}_{\alpha\beta} = (mV)^{-1} \sum_{i=1}^N p_i^\alpha p_i^\beta. \quad (7)$$

We obtain to  $O(J^2)$

$$P_{\alpha\beta} = [n\kappa T + \{J^2(v_0 n\kappa T)^2 / (NmV)\}] \delta_{\alpha\beta} + \{9(n\kappa T)^2 / (2NmV)\} v_0^2 J_\alpha J_\beta. \quad (8)$$

The trace of  $\mathbf{P}$  in (8) is  $3n\kappa T_K$ , where  $T_K$  is the kinetic or local equilibrium temperature and  $(3/2)\kappa T_K$  the mean kinetic energy per particle. We have [1]

$$T_K = T [1 + 2mJ^2 / \{5(n\kappa T)^2 \kappa T\}] + O(J^4), \quad (9a)$$

$$(1/3) \text{Tr} P_{\alpha\beta} \equiv \bar{P} = n\kappa T_K, \quad (9b)$$

$$\begin{aligned} P &= -(\partial F / \partial V)_{T, \vec{J}} \\ &= n\kappa T [1 - 2mJ^2 / \{5(n\kappa T)^2 \kappa T\}] + O(J^4) \\ &= n\kappa T_K - 2n\kappa(T_K - T), \end{aligned} \quad (9c)$$

where  $F$  is the Helmholtz free energy.

The question which now arises concerns the physical and statistical meaning of Eq. (8). Assume that we perform experiment 1 from which the data yield values of  $n$ ,  $T$ , and  $\vec{J}$ . We can proceed via information theory to make a statistical prediction (8) concerning the outcome of experiment 2 which measures  $P_{\alpha\beta}$ , provided precautions are taken to keep  $n$ ,  $T$ , and  $\vec{J}$  constant and equal to the values measured in experiment 1. In an experiment in which both traceless pressure  $\mathbf{P}$  and  $\vec{J}$  are measured, they are independent variables and are not related by an expression such as Eq. (8).

There is reason to believe that the  $O(J^2)$  terms in (8) and (9a) are of the order of the uncertainty in the statistical prediction. If the traceless pressure  $\mathbf{P}$  was measured in experiment 1, we should add to (9a) a term in  $\hat{\mathbf{P}} \cdot \hat{\mathbf{P}}$ . Similarly, additional terms, quadratic in the forces, will appear in  $T_K - T$  for every additional independent variable included [3]. Velasco and García-Colín [4] have shown that if we could measure in one experiment an infinite number of moments of the single-particle distribution, corresponding to an exact solution of the linearized Boltzmann equation, we should predict  $T = T_K$ .

We can estimate the magnitude of  $T - T_K$  for Ar. At 0 K, 1 atm,  $m = 6.63 \times 10^{-26}$  kg;  $n = 2.69 \times 10^{25}/\text{m}^3$ . If the  $O(J^2)$  contribution to thermal conductivity does not materially change its order of magnitude, as will be demonstrated in a later communication, we should need a

temperature gradient  $J/\lambda = 7.32 \times 10^7$  K/m to make  $|(T - T_K)/T| = 0.001$ , which we could not easily achieve in the laboratory. Since  $(T - T_K)/T$  is proportional to  $(J/n)^2$ , if  $n$  were two orders of magnitude smaller at the same  $T$ , the required heat flux and temperature gradient would be reduced by the same factor 0.01, but they would still be very large. If  $n$  becomes so small that the predicted  $(T_K - T)/T$  becomes appreciable, then higher terms in the asymptotic expansion become significant. At the same time, the prediction becomes more uncertain, and thus less useful.

Aside from usefulness of the prediction, the thermodynamic question raised by the result (8) is whether it is a constitutive equation which we should substitute into, e.g., the hydrodynamic equations in making an analysis of experiment 1. In a fluid where the velocity gradient is  $\nabla \vec{u} \neq 0$ , nonequilibrium thermodynamics has asserted that  $P_{\alpha\beta} - P\delta_{\alpha\beta}$  is proportional to the traceless symmetrized velocity gradient tensor, or, where viscoelasticity is observed, to a force or forces associated with shear relaxation. These forces can be associated with an independent state variable such as  $\mathbf{P}$  in a gas or with the elastic strain in a dense fluid. However, such variables are not measured in experiment 1, and so the corresponding forces are absent from the description. Similarly,  $\bar{P} - P$  should be a sum of scalar forces associated with compressional relaxation provided the rate equations for these depend on  $\nabla \cdot \vec{u}$ . Such variables are also not measured in experiment 1, implying, as  $\nabla \vec{u} \rightarrow 0$ ,  $\bar{P} = P$  and  $P_{\alpha\beta} = P\delta_{\alpha\beta}$ . If  $\nabla \vec{u}$  vanishes identically, this conclusion is not necessary, but then the limit  $\nabla \vec{u} \rightarrow 0$  differs from the case of strictly zero velocity gradient. We wish to inquire whether information theory compels us to introduce such a complication.

To answer this question, we observe that, in maximizing the entropy functional (1), we should include all "information" pertinent to the calculation we seek to make. The Grad [5] and Chapman-Enskog [6] approaches to transport in dilute gases successfully fit experiment by neglecting  $T - T_K$ . In the relevant density-temperature domain, there is experimental evidence that we can set  $T = T_K$ . Since the usual phenomenology has set  $\bar{P} = P$ , we can introduce this as additional "information" in maximizing the entropy functional. It has been pointed out [7] that it is just as reasonable to modify Grad theory to make it agree with the phenomenology as to require that extended thermodynamics include all terms predict-

ed by Grad.

The requirement  $\bar{P} = P$  can be incorporated into the maximum entropy formalism by replacing (4) with

$$\rho = Z'^{-1} \exp[-\beta \hat{H} - \beta \hat{\Phi} \cdot \hat{\vec{J}} - \beta \mathbf{Q} \cdot \hat{\mathbf{P}}'] , \quad (10a)$$

$$\hat{P}'_{\alpha\beta} = \sum_{i=1}^N [p_i^\alpha p_i^\beta (m\kappa T)^{-1} - \delta_{\alpha\beta}] . \quad (10b)$$

This adds a second-order tensor Hermite function to the contracted third-order function  $\hat{\vec{J}}$  in the exponent. We can use  $\hat{\mathbf{P}}'$  because  $\mathbf{P}$  is not measured in the experiment we are analyzing. If we set

$$\mathbf{Q} = \omega \vec{J}\vec{J} , \quad (11)$$

we can determine  $\omega$  to make  $\bar{P} = P$ . We get

$$\omega = 12(2\pi)^{1/2} m / \{25(n\kappa T)^2\} . \quad (12)$$

This modification of  $\rho$  adds a term  $-2n\omega(2\pi)^{-1/2}\vec{J}\vec{J}$  to  $\mathbf{P}$ , but it does not change  $P$ , as a result of the orthogonality of  $\hat{\mathbf{P}}'$  and  $\hat{\vec{J}}$ . To make  $T_K = T$ , we could add another term to the exponent in (10a) involving a contracted fourth-order tensor Hermite function and determine the function which multiplies it, along with  $\omega$ , to make both  $T_K = T$  and  $P = \bar{P}$ .

The  $\vec{J}\vec{J}$  term in (8) appears to correspond to a similar term previously derived via extended thermodynamics for the pressure in a radiation field. The thermodynamic derivations [8,9] introduce the Clausius-Duhem equation as an entropy principle, viewing entropy as locally produced at a point in the field. This picture has been discussed by Essex [10], who points out that the entropy production arises from surface absorption and emission processes. It is highly nonlocal, e.g., in a model where we have two parallel planar surfaces at different temperatures which exchange energy through the radiation field between them. In [1] a local temperature is introduced which is not related to the physical processes of radiation transfer and has no obvious operational definition. As pointed out by Essex [10], such a picture is appropriate to heat transfer in matter, but it seems to have no relevance to a radiation field in the absence of matter. These considerations make it doubtful that the usual nonequilibrium thermodynamics can provide reasons for the presence of a  $\vec{J}\vec{J}$  term in the radiation pressure. Such a term may be justifiable empirically.

- [1] R. Dominguez and D. Jou, *Phys. Rev. E* **51**, 158 (1995).  
 [2] E. T. Jaynes, *Phys. Rev.* **106**, 620 (1957).  
 [3] R. E. Nettleton, *Can. J. Phys.* **72**, 106 (1994).  
 [4] R. M. Velasco and L. S. García-Colín, *J. Nonequilib. Thermodyn.* **18**, 157 (1993).  
 [5] H. Grad, *Commun. Pure Appl. Math.* **2**, 331 (1949).  
 [6] S. Chapman and R. G. Cowling, *The Mathematical Theory of Non-Uniform Gases* (Cambridge University Press, Lon-

- don, 1952).  
 [7] R. E. Nettleton, *Ann. Phys.* **2**, 490 (1993).  
 [8] G. M. Kremer and I. Müller, *J. Math. Phys.* **33**, 2265 (1992).  
 [9] A. M. Anile, S. Pennisi, and M. Sammartino, *J. Math. Phys.* **32**, 544 (1991).  
 [10] G. C. Essex, in *Advances in Thermodynamics* (Taylor and Francis, New York, 1990), Vol. 3, p. 435.