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Abstract. An extension is developed for an *inhomogeneous* system of a result originally derived for a *homogeneous* system concerning the sign of successive time derivatives of the entropy in the passage to equilibrium. A new microscopic derivation is given of two macroscopic thermodynamic equations used in the treatment.

1. Introduction

Consider a general isolated physical system which is not in equilibrium. Then, apart from possible conservation laws, probably the only general statement concerning the passage to equilibrium which has so far been enunciated is that the entropy S of the system continually increases; that is, for any time t,

$$dS/dt \geqslant 0 \qquad (1)$$

with the equality sign holding only at equilibrium. In view of this important role played by the entropy in characterizing the return to equilibrium it is clearly of interest to consider whether anything further can be stated about the time variation of the entropy. Now, in Simons (1969) it was shown that for a homogeneous gas whose behaviour can be described by the linearized Boltzmann equation, the time variation of Boltzmann's H function is such that $(-)^n d^n H/dt^n \geqslant 0$ for all integral n, and since $S = -kH$ this implies that for such a gas

$$(-)^n \, d^n S/dt^n \leqslant 0 \qquad (1 \leqslant n \leqslant \infty). \qquad (2)$$

The general form of the result (2) suggests that it may be of wider application than the homogeneous gas case for which it was originally proved, and indeed it may be readily shown by a proof similar to that of Simons (1969) that the result holds for the relaxation to equilibrium of a *homogeneous* assembly of electrons or phonons whose behaviour can be described by the usual Boltzmann equation.

The main purpose of the present paper is to consider to what extent the result (2) may be extended to the case of isolated *inhomogeneous* systems, and in the current work we deal with two such systems. The first is one in which general spatial and temporal variations in temperature exist and in which equilibrium is established through thermal conduction, while the second involves similar variations in particle concentration and equilibrium arises through diffusion. In both cases we restrict ourselves to the situation in which the variations in the relevant physical variable (temperature or concentration) are small compared with the equilibrium value of that variable for the system.

Consider $d^n S/dt^n$ for the system. We proceed to show that this may be expressed in the form

$$d^n S/dt^n = S_v^{(n)} + S_b^{(n)} \qquad (3)$$

where $S_v^{(n)}$ (the 'internal' contribution to $d^n S/dt^n$) is a term involving a volume integral throughout the system and $S_b^{(n)}$ (the 'boundary' contribution to $d^n S/dt^n$)

is a term involving a surface integral over the boundary surface of the system.†
We shall give an explicit form for $S_v{}^{(n)}$ and prove that it is such that

$$(-)^n S_v{}^{(n)} \leqslant 0 \qquad (1 \leqslant n \leqslant \infty). \tag{4}$$

In §2 we deal with the thermal conduction problem and in §3 the case of diffusion. A statistical mechanical derivation of the macroscopic equations employed in §2 is given in the Appendix for the case of a system in which the usual Boltzmann equation is valid.

In view of the general form of the result (2) it would seem worthwhile examining whether it may be extended to other physical systems—possibly in a modified form as in the present paper.

2. Thermal conduction

Consider an isolated system with average temperature T_0 and let $\theta(x_p, t)$ be the amount by which the temperature at position $x_p(1 \leqslant p \leqslant 3)$ and time t departs from T_0. Then it is known (e.g. Landau and Lifshitz 1959) that θ satisfies the differential equation

$$C \frac{\partial \theta}{\partial t} = K_{pq} \frac{\partial^2 \theta}{\partial x_p \partial x_q} \tag{5}$$

inside the system. For the rate of entropy production we follow Landau and Lifshitz (1959) who show by a macroscopic approach that

$$\frac{\mathrm{d}S}{\mathrm{d}t} = \int_V \frac{K_{pq}}{T^2} \frac{\partial T}{\partial x_p} \frac{\partial T}{\partial x_q} \mathrm{d}\tau \tag{6}$$

for a general temperature $T(x_p, t)$ where the volume integral is taken throughout the volume V of the system. We are currently considering the case where $|\theta| \ll T_0$, and thus

$$\frac{\mathrm{d}S}{\mathrm{d}t} = \frac{1}{T_0{}^2} \int_V K_{pq} \frac{\partial \theta}{\partial x_p} \frac{\partial \theta}{\partial x_q} \mathrm{d}\tau. \tag{7}$$

We may note at this stage that the macroscopic derivation of both equations (5) and (7) depends on the usual linear relationship between heat flow and temperature gradient applying even when these quantities are time-dependent. For reasons given in Appendix I this assumption cannot be strictly true and we therefore give in this Appendix an alternative statistical mechanical derivation of these equations.

We proceed to differentiate equation (7) with respect to time and obtain

$$\frac{\mathrm{d}^2 S}{\mathrm{d}t^2} = \frac{2}{T_0{}^2} \int_V K_{pq} \frac{\partial \theta}{\partial x_p} \frac{\partial(\partial \theta/\partial t)}{\partial x_q} \mathrm{d}\tau$$

since K_{pq} is symmetric, and making use of equation (5) this gives

$$\frac{\mathrm{d}^2 S}{\mathrm{d}t^2} = \frac{2}{T_0{}^2 C} \int_V K_{pq} K_{rs} \frac{\partial \theta}{\partial x_p} \frac{\partial^3 \theta}{\partial x_q \partial x_r \partial x_s} \mathrm{d}\tau. \tag{8}$$

† It should perhaps be emphasized that $S_b{}^{(n)}$ is completely unrelated to the quantity occuring in the theory of non-equilibrium thermodynamics which is conventionally denoted by $\mathrm{d}_e S$ (see for example De Groot and Mazur 1962).

Now it follows from the divergence theorem that if A and B are any spatial derivatives of θ,

$$\int_V A \frac{\partial B}{\partial x_q} \, d\tau = - \int_V B \frac{\partial A}{\partial x_q} \, d\tau + \int_\sigma AB \, dS_q \qquad (9)$$

where σ is the boundary surface of the system. Hence on identifying A with $\partial\theta/\partial x_p$ and B with $\partial^2\theta/\partial x_r \partial x_s$, we obtain from equations (8) and (9)

$$\frac{d^2 S}{dt^2} = - \frac{2}{T_0^2 C} \int_V \left(K_{pq} \frac{\partial^2\theta}{\partial x_p \partial x_q} \right)^2 d\tau + \frac{2}{T_0^2 C} \int_\sigma K_{pq} K_{rs} \frac{\partial\theta}{\partial x_p} \frac{\partial^2\theta}{\partial x_r \partial x_s} \, dS_q. \qquad (10)$$

On comparing this result with equation (3) it is clear that

$$S_v^{(2)} = - \frac{2}{T_0^2 C} \int_V \left(K_{pq} \frac{\partial^2\theta}{\partial x_p \partial x_q} \right)^2 d\tau \qquad (11)$$

and that $S_v^{(2)} \leqslant 0$. A further differentiation with respect to time of equation (11), together with utilization of equations (5), (9) and (3) readily yields

$$S_v^{(3)} = \frac{4}{T_0^2 C^2} \int_V K_{rs} \left(K_{pq} \frac{\partial^3\theta}{\partial x_p \partial x_q \partial x_r} \right) \left(K_{tu} \frac{\partial^3\theta}{\partial x_t \partial x_u \partial x_s} \right) d\tau \qquad (12)$$

and since K_{rs} is a positive definite matrix it follows that $S_v^{(3)} \geqslant 0$. On repeating this procedure we obtain for even values of n

$$S_v^{(n)} = - \frac{2^{n-1}}{T_0^2 C^{n-1}} \int_V \left(K_{pq} \ldots K_{vw} \frac{\partial^n\theta}{\partial x_p \ldots \partial x_w} \right)^2 d\tau \qquad (13)$$

while for odd values of n

$$S_v^n = \frac{2^{n-1}}{T_0^2 C^{n-1}} \int_V K_{\alpha\beta} \left(K_{pq} \ldots K_{vw} \frac{\partial^n\theta}{\partial x_p \ldots \partial x_w \partial x_\alpha} \right) \cdot \left(K_{ab} \ldots K_{lm} \frac{\partial^n\theta}{\partial x_a \ldots \partial x_m \partial x_\beta} \right) d\tau. \qquad (14)$$

The result (4) follows immediately.

3. Particle diffusion

In the case of particle diffusion, the particle concentration $F(x_p, t)$ satisfies the equation

$$\frac{\partial F}{\partial t} = D \nabla^2 F \qquad (15)$$

where D is the diffusion coefficient. It is shown in Landau and Lifshitz (1959) that the rate of entropy production is given by

$$\frac{dS}{dt} = \beta \int \frac{|\text{grad } F|^2}{T_0} \, d\tau \qquad (16)$$

where β is a positive constant. On comparing equations (15) and (16) respectively with equations (5) and (7) it is seen that these are equivalent if we identify θ with F, $C^{-1} K_{pq}$ with $D\delta_{pq}$ and $T_0^{-1} K_{pq}$ with $\beta\delta_{pq}$. The previous argument may therefore be used to show that result (4) holds for particle diffusion.

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Appendix 1

We consider here the derivation of equations (5) and (7) based on a statistical mechanical formulation, and to simplify the discussion we confine ourselves to the case where the energy is transported by phonons so that the only quantity conserved in interparticle collisions is the energy. This treatment is of interest since the usual macroscopic discussion leading to equations (5) and (6) depends on the assumption that the macroscopic relationship—heat flow equals conductivity tensor times temperature gradient—remains true even when the quantities involved are time-dependent. Now, when these quantities are independent of time the above macroscopic relationship can be readily shown to follow from the linearized time-independent Boltzmann equation. But when the latter takes its time-dependent form, the presence of an additional time-derivative in the equation (see the third term in equation (A3)) means that the above relation between heat flow and temperature gradient must require modification to some extent, and *a priori* it is not clear to what degree this will affect equations (5) and (6). The present treatment shows that when the distribution function at any point is close to an equilibrium distribution characterized by some particular temperature, equations (5) and (6) remain true.

If $f(\mathbf{k}, \mathbf{r}, t)$ is the occupation number at position $\mathbf{r}$ at time t for phonons of wavenumber $\mathbf{k}$, the Boltzmann equation for the phonon assembly takes the form

$$\frac{\partial f}{\partial t} = \frac{\partial f}{\partial t}\bigg)_c - \mathbf{v} \cdot \operatorname{grad} f \qquad (A1)$$

where $\partial f/\partial t)_c$ is the rate of change of f due to phonon collisions and $\mathbf{v}$ is the phonon velocity. We deal with the situation where f is close to the Bose–Einstein distribution $F(\mathbf{k}, T_0)$ characterized by the temperature T_0 of the equilibrium region of the medium, and let

$$f = F - T_0^{-1}\left(\frac{\partial F}{\partial E}\right)\phi \qquad (A2)$$

where $E(\mathbf{k})$ is the phonon energy and $\phi(\mathbf{k}, \mathbf{r}, t)$ measures the deviation from equilibrium. For the present situation of small deviations from the equilibrium distribution, $\partial f/\partial t)_c$ may be represented by its linearized form $L\phi$ where L is a linear integral operator (Ziman 1960) and thus we obtain the Boltzmann equation (A1) in the form

$$M\phi + \mathbf{v} \cdot \operatorname{grad} \phi + \frac{\partial \phi}{\partial t} = 0 \qquad (A3)$$

where

$$M = T_0\left(\frac{\partial F}{\partial E}\right)^{-1} L. \qquad (A4)$$

In order to develop a systematic solution to this equation of the required form, we introduce into the equation a parameter ϵ, and then look for a solution in the form of a power series in ϵ. In order for the solution to be dominated by an equilibrium

distribution which can vary in both space and time we express equation (A3) as

$$M\phi + \epsilon v \cdot \operatorname{grad} \phi + \epsilon^2\left(\frac{\partial \phi}{\partial t}\right) = 0 \tag{A5}$$

and the solution in the form

$$\phi = \sum_{n=0}^{\infty} \epsilon^n \phi_n. \tag{A6}$$

On substituting from equation (A6) into (A5) and equating coefficients of ϵ^n to zero for $n = 0, 1, 2$ we obtain

$$M\phi_0 = 0 \tag{A7}$$

$$M\phi_1 = -v_p\left(\frac{\partial \phi_0}{\partial x_p}\right) \tag{A8}$$

$$M\phi_2 = -v_p\left(\frac{\partial \phi_1}{\partial x_p}\right) - \left(\frac{\partial \phi_0}{\partial t}\right). \tag{A9}$$

Now since energy is the only quantity conserved in phonon collisions, the general solution of equation (A7) is that ϕ_0 is equal to a multiple of E (Simons 1960) and by comparison with equation (A2) it is readily shown that this multiple is the excess temperature $\theta(r, t)$ introduced in § 2. Thus

$$\phi_0 = \theta E. \tag{A10}$$

Substituting into equation (A8) we obtain

$$M\phi_1 = -E v_p\left(\frac{\partial \theta}{\partial x_p}\right) \tag{A11}$$

and for this to possess a solution the right hand side must be orthogonal to the solution Γ of the adjoint homogeneous equation (Friedmann 1956). From equation (A4) it may be shown that the solution of this adjoint equation is

$$\Gamma = \left(\frac{E}{T_0}\right)\left(\frac{\partial F}{\partial E}\right) \tag{A12}$$

and the orthogonality condition is then satisfied since $E(-k) = E(k)$ while $v(-k) = -v(k)$.† The solution of equation (A11) is

$$\phi_1 = -\left(\frac{\partial \theta}{\partial x_p}\right) M^{-1}(E v_p) \tag{A13}$$

and substituting this into equation (A9) gives

$$M\phi_2 = \left(\frac{\partial^2 \theta}{\partial x_p \partial x_q}\right) v_p M^{-1}(E v_q) - E\left(\frac{\partial \theta}{\partial t}\right).$$

The condition for this to possess a solution for ϕ_2 is that the right hand side should

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† The reason for the ϵ^2 multiple of $\partial\phi/\partial t$ in equation (A5) should now be apparent, since if an ϵ multiple had been introduced, equation (A11) would have been supplemented by a $-E(\partial\theta/\partial t)$ term on the right hand side, and the orthogonality condition would then only have been met if $\partial\theta/\partial t = 0$, which would have precluded any time variation of θ.

be orthogonal to Γ, and applying this condition gives

$$\frac{\partial^2 \theta}{\partial x_p \partial x_q} \int - \frac{Ev_p}{8\pi^3 T_0} \frac{\partial F}{\partial E} M^{-1}(Ev_q) \, \mathrm{d}\boldsymbol{k} = \frac{\partial \theta}{\partial t} \int - \frac{E^2}{8\pi^3 T_0} \frac{\partial F}{\partial E} \, \mathrm{d}\boldsymbol{k}. \qquad \text{(A14)}$$

By a consideration of the time-independent Boltzmann equation it may be shown that the integral on the left hand side is the conductivity tensor K_{pq}, and since $-(E/T_0)(\partial F/\partial E) = (\partial F/\partial T)$, the integral on the right hand side is the specific heat C. Equation (A14) thus reduces to equation (5).

To evaluate $\mathrm{d}S/\mathrm{d}t$ we begin with the statistical mechanical definition of entropy for the phonon system

$$S = -\left(\frac{k}{8\pi^3}\right) \int \int \{f \ln f - (1+f) \ln(1+f)\} \, \mathrm{d}\boldsymbol{k} \, \mathrm{d}\tau \qquad \text{(A15)}$$

where k is Boltzmann's constant (Landau and Lifshitz 1958). On differentiating this with respect to time and making use of equation (A2) with $|f-F| \ll F$, it is found that since the total energy of the phonons is conserved

$$\frac{\mathrm{d}S}{\mathrm{d}t} = \frac{1}{8\pi^3 T_0{}^3} \int \frac{\partial F}{\partial E} \phi \frac{\partial \phi}{\partial t} \, \mathrm{d}\boldsymbol{k} \, \mathrm{d}\tau.$$

With the help of equation (A3) to eliminate $\partial \phi / \partial t$, we obtain

$$\frac{\mathrm{d}S}{\mathrm{d}t} = -\frac{1}{8\pi^3 T_0{}^3} \int \frac{\partial F}{\partial E} \phi M \phi \, \mathrm{d}\boldsymbol{k} \, \mathrm{d}\tau \qquad \text{(A16)}$$

since the volume integral in the other term ($\int (\partial F / \partial E) \boldsymbol{v} \cdot \nabla \phi^2 \, \mathrm{d}\tau$) transforms into a surface integral over σ which can be shown to be zero to terms of order ϵ^2. We substitute for $\phi M \phi$ in the integrand of equation (A16) from equations (A6), (A7), (A8) to give

$$\phi M \phi = \epsilon \phi_0 M \phi_1 + \epsilon^2 \left\{ \phi_0 M \phi_2 - \phi_1 v_p \left(\frac{\partial \phi_0}{\partial x_p} \right) \right\} + \mathrm{O}(\epsilon^3). \qquad \text{(A17)}$$

The contributions of the terms $\phi_0 M \phi_1$ and $\phi_0 M \phi_2$ to $\mathrm{d}S/\mathrm{d}t$ are zero since $M \phi_0 = 0$ and thus, making use of equations (A10) and (A13) we obtain to terms of order ϵ^2

$$\frac{\mathrm{d}S}{\mathrm{d}t} = \frac{\epsilon^2}{T_0{}^2} \int_V \left(-\frac{1}{8\pi^3 T_0} \int \frac{\partial F}{\partial E} Ev_p M^{-1}(Ev_q) \, \mathrm{d}\boldsymbol{k} \right) \frac{\partial \theta}{\partial x_p} \frac{\partial \theta}{\partial x_q} \, \mathrm{d}\tau.$$

On identifying the large quantity in parentheses with K_{pq} and letting $\epsilon = 1$, equation (5) is obtained.

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