Modified equations for heat conduction and entropy production

1973 J. Phys. A: Math. Nucl. Gen. 6 1543

(http://iopscience.iop.org/0301-0015/6/10/013)

J. Phys. A: Math., Nucl. Gen., Vol. 6, October 1973. Printed in Great Britain. © 1973

Modified equations for heat conduction and entropy production

S Simons

Department of Applied Mathematics, Queen Mary College, Mile End Road, London E1, UK

Received 18 May 1973

Abstract. A microscopic derivation is given of the changes required in the classical equations for heat conduction and entropy production due to the existence of a finite mean free path for thermal carriers. The modified equation for heat conduction is in agreement with previous suggestions, but the result for entropy production differs from that suggested in an earlier discussion.

1. Introduction

It has been pointed out on many occasions (Maxwell 1867, Cattaneo 1958, Vernotte 1958, Ulbrich 1961, Chester 1963, Kranys 1966a, b, Luikov 1966, Gurtin and Pipkin 1968, Carrassi and Morro 1972, Lambermont and Lebon 1973) that the phenomenological law of heat conduction

$$\boldsymbol{J} = -K \operatorname{grad} T \tag{1}$$

requires to be modified in the presence of rapid changes of heat flux $\boldsymbol{J}$, since equation (1) coupled with the conservation of energy equation gives rise to the well known conduction equation

$$C\frac{\partial T}{\partial t} = K\nabla^2 T. \tag{2}$$

The latter equation, being parabolic, predicts an infinite velocity of propagation whereas the true velocity cannot exceed that of the thermal carriers. It was therefore suggested by the above authors that the heat conduction equation should be modified to

$$\boldsymbol{J}+\tau\frac{\partial \boldsymbol{J}}{\partial t} = -K \operatorname{grad} T \tag{3}$$

where τ is a characteristic relaxation time for carrier collisions. This equation clearly reduces to the form (1) when $\boldsymbol{J}$ does not change substantially over times of the order of τ, and at the same time it gives rise to a modification of equation (2), which being hyperbolic, corresponds to a finite propagation velocity. However, apart from some rough kinetic theoretical arguments no fundamental basis has been given for the modified equation (3), and it is the purpose of the present paper to remedy this.

A problem of a similar nature arises with the classical relation

$$\frac{\mathrm{d}S}{\mathrm{d}t} = \frac{1}{T}\frac{\mathrm{d}U}{\mathrm{d}t} \tag{4}$$

between the entropy per unit volume S and the internal energy per unit volume U. It is readily shown that equation (4) yields a rate of entropy production per unit volume σ given by $\sigma = -\boldsymbol{J}T^{-2}\,.\,\mathrm{grad}\ T$, and if the relationship (1) holds this leads to $\sigma = J^2/KT^2$, a quantity which is intrinsically positive. If, however, the modified relationship (3) holds, the corresponding modified form for σ is not necessarily positive. It has therefore been suggested by Lambermont and Lebon (1973) that corresponding to the modification (3) in the conduction equation, a modification should be introduced in the entropy equation (4) in order that σ should remain intrinsically positive. The modification they suggest is

$$\frac{\mathrm{d}S}{\mathrm{d}t} = \frac{1}{T}\frac{\mathrm{d}U}{\mathrm{d}t} - \frac{\tau}{T^2}\,\mathrm{grad}\ T\,.\,\frac{\mathrm{d}\boldsymbol{J}}{\mathrm{d}t}$$

since this leads to

$$\sigma = \frac{1}{KT^2}\left(\boldsymbol{J}+\tau\frac{\mathrm{d}\boldsymbol{J}}{\mathrm{d}t}\right)^2. \tag{5}$$

The purpose of the present paper is to consider the required modifications of equations (1) and (4) from a microscopic viewpoint; that is, basing their derivation on the Boltzmann equation which governs the transport of the thermal carriers. For the sake of simplicity we shall assume these carriers to be phonons in order to avoid the additional complications of varying electric and magnetic fields that would occur with electrons. We proceed in § 2 to set up the relevant Boltzmann equation for the situation where the phonon distribution is everywhere close to a local equilibrium distribution, but in which the temperature characterizing this equilibrium is allowed to possess an arbitrary variation in space and time. An infinite power series solution of this equation is then obtained which is valid when the changes in temperature are not too rapid, and in § 3 and § 4 the solution is used to calculate $\boldsymbol{J}$ and $\mathrm{d}S/\mathrm{d}t$. This solution is initially obtained in terms of the inverse of the phonon collision operator and on approximating this operator by a model, the solution is expressed as an infinite power series in the relaxation time τ. It is therefore to be expected that the required modifications of equations (1) and (4) should be obtained as the first few terms of this infinite power series expression. However, since the solution is really an infinite series, these first few terms will only be reliable when they are sufficiently small for the series to converge, and this means that the argument of Lambermont and Lebon, based on the necessarily positive nature of σ for all τ, and leading to equation (5), is in fact invalid. Thus, even if the result (4) were to remain unchanged we would obtain

$$\sigma = \frac{\boldsymbol{J}}{KT^2}\,.\left(\boldsymbol{J}+\tau\frac{\partial\boldsymbol{J}}{\partial t}\right),$$

and it is certainly possible that σ remains positive for all values of τ for which the true infinite series solution converges. In fact, even this is not necessary since it is clearly possible for a finite number of terms of a convergent infinite series representing a necessarily positive function such as σ to be itself negative—consider the first two terms of the expansion of $(1+x)^{-2}$ for $\frac{1}{2} < x < 1$. It follows therefore that the positive nature of σ can offer no guide to the required first-order modification of result (4). In fact, it will be shown in this paper that while equation (3) is correct to first order, the modified equation (4) takes the form

$$\frac{\mathrm{d}S}{\mathrm{d}t} = \frac{1}{T}\frac{\mathrm{d}U}{\mathrm{d}t} + \frac{\tau}{T^2}\,\mathrm{grad}\,T \cdot \frac{\mathrm{d}J}{\mathrm{d}t}$$

in which the correction term is exactly minus that suggested by Lambermont and Lebon. It will also be shown that the corresponding proportional change in σ compared with the classical result is proportional to τ^2, while in the result (5) it would be proportional to τ.

2. Boltzmann equation and solution

Let $f(\boldsymbol{k}, \boldsymbol{r}, t)$ be the distribution function for phonons of wavenumber $\boldsymbol{k}$ at position $\boldsymbol{r}$ and time t. Then the Boltzmann equation for the phonons takes the form

$$\left.\frac{\partial f}{\partial t}\right)_{\mathrm{c}} = v_p \frac{\partial f}{\partial x_p} + \frac{\partial f}{\partial t} \tag{6}$$

where v_p is the phonon velocity (summation convention assumed) and $\partial f/\partial t)_{\mathrm{c}}$ is the rate of change of f due to collisions. We suppose f to be close to a local Bose–Einstein equilibrium distribution $F(E, T)$, where E is the phonon energy and $T \equiv T(\boldsymbol{r}, t)$, and let

$$f = F - T^{-1}\left(\frac{\partial F}{\partial E}\right)\phi(\boldsymbol{k}, \boldsymbol{r}, t). \tag{7}$$

Then

$$\left.\frac{\partial f}{\partial t}\right)_{\mathrm{c}} = L\phi$$

where L is the standard linear collision operator (Ziman 1960), and on defining the linear operator M by

$$M = -T\left(\frac{\partial F}{\partial E}\right)^{-1} L, \tag{8}$$

we obtain equation (6) in the form

$$M\phi - \left(v_p \frac{\partial \phi}{\partial x_p} + \frac{\partial \phi}{\partial t}\right) = E v_p \frac{\partial T}{\partial x_p} + E\frac{\partial T}{\partial t}. \tag{9}$$

We wish to obtain a solution of equation (9) as a series involving inverse powers of the operator M. The difficulty here is that since energy is always conserved in interparticle collisions, $ME = 0$ (Simons 1960), and this means that M does not possess a true inverse. To deal with this we proceed to take the scalar product of both sides of equation (9) with E, where the scalar product of functions $A(\boldsymbol{k})$ and $B(\boldsymbol{k})$ is defined by

$$(A, B) = \int \left(\frac{\partial F}{\partial E}\right) AB\,\mathrm{d}\boldsymbol{k},$$

the integral being taken over all $\boldsymbol{k}$ space. It can be shown that M is self-adjoint, that is, $(A, MB) = (MA, B)$, and thus we obtain

$$\left(E, v_p \frac{\partial \phi}{\partial x_p}\right) + \left(E, \frac{\partial \phi}{\partial t}\right) + (E, E)\frac{\partial T}{\partial t} = 0 \tag{10}$$

since $(E, Ev_p) = 0$. Eliminating $\partial T/\partial t$ between equations (9) and (10) then yields

$$M\phi - \left\{\left(v_p\frac{\partial\phi}{\partial x_p} - \frac{E(E, v_p\partial\phi/\partial x_p)}{(E, E)}\right) + \left(\frac{\partial\phi}{\partial t} - \frac{E(E, \partial\phi/\partial t)}{(E, E)}\right)\right\} = Ev_p\frac{\partial T}{\partial x_p}. \tag{11}$$

Further, if we define T to be the *actual* temperature at $\boldsymbol{r}$, t (as would be measured by a minute thermometer placed there), then equating the total energy densities gives

$$\int fE\,\mathrm{d}\boldsymbol{k} = \int FE\,\mathrm{d}\boldsymbol{k},$$

whence it follows from equation (7) that

$$(\phi, E) = 0. \tag{12}$$

Now it follows from equation (12) that ϕ lies in the function subspace $\mathscr{G}$ orthogonal to E, and within $\mathscr{G}$, the operator M *does* possess an inverse since within this subspace $M\Gamma = 0$ has no nonzero solution. Further, for any function $\theta(\boldsymbol{k})$, the function

$$R\theta \equiv \theta - \left(\frac{(\theta, E)E}{(E, E)}\right) \tag{13}$$

will lie in $\mathscr{G}$ since $(R\theta, E) = 0$, and so the two bracketed expressions on the left-hand side of equation (11) both lie in $\mathscr{G}$, as also does the right-hand side. If we therefore restrict the domain of M to $\mathscr{G}$, equation (11) may be expressed in the form

$$\left\{1 - M^{-1}R\left(v_p\frac{\partial}{\partial x_p} + \frac{\partial}{\partial t}\right)\right\}\phi = (M^{-1}Ev_p)\frac{\partial T}{\partial x_p} \tag{14}$$

where the operator R is defined in equation (13). This equation has the formal solution

$$\phi = \left\{1 + M^{-1}\left(Rv_p\frac{\partial}{\partial x_p} + \frac{\partial}{\partial t}\right) + M^{-1}\left(Rv_p\frac{\partial}{\partial x_p} + \frac{\partial}{\partial t}\right)M^{-1}\left(Rv_p\frac{\partial}{\partial x_p} + \frac{\partial}{\partial t}\right) + \dots\right\}$$
$$\times (M^{-1}Ev_p)\frac{\partial T}{\partial x_p} \tag{15}$$

where the R operator has been omitted in front of the $\partial/\partial t$ terms, as the relevant function lies automatically in $\mathscr{G}$. It will be shown presently that within the framework of a relaxation time approximation the error in satisfying equation (14) with the solution (15) curtailed after $n-1$ terms is of the order of τ^n times an nth differential coefficient of T with respect to space or time, and so we would expect the solution (15) to be satisfactory if the change in temperature over a mean free path is not too great.

We proceed to consider further the first three terms of equation (15) as these are required later. On expanding we obtain

$$\phi = (M^{-1}Ev_p)\frac{\partial T}{\partial x_p} + (M^{-2}Ev_p)\frac{\partial^2 T}{\partial x_p\,\partial t} + (M^{-1}Rv_pM^{-1}Ev_q)\frac{\partial^2 T}{\partial x_p\,\partial x_q}$$
$$+ (M^{-3}Ev_p)\frac{\partial^3 T}{\partial x_p\,\partial t^2} + (M^{-1}v_pM^{-1}Rv_qM^{-1}Ev_r)\frac{\partial^3 T}{\partial x_p\,\partial x_q\,\partial x_r}$$
$$+ (M^{-1}Rv_pM^{-2}Ev_q + M^{-2}Rv_pM^{-1}Ev_q)\frac{\partial^3 T}{\partial x_p\,\partial x_q\,\partial t}. \tag{16}$$

In order to further simplify these results we shall now assume that the collision operator M can be satisfactorily approximated by a model of the type considered by Simons (1971). Since M conserves only the energy we take

$$M\phi = \frac{1}{\tau(\boldsymbol{k})}\left(\frac{(E\tau^{-1}, \phi)}{(E\tau^{-1}, E)}E - \phi(\boldsymbol{k})\right) \tag{17}$$

where $\tau(\boldsymbol{k})$ is a relaxation time whose $\boldsymbol{k}$ dependence corresponds to the singular part of the true collision operator. Now

$$M\phi = Z \tag{18}$$

only possesses a solution if Z lies in $\mathscr{G}$; that is, if $(E, Z) = 0$, and if this condition is satisfied and the model (17) is used, it is clear that a solution of equation (18) is given by $\phi(\boldsymbol{k}) = -\tau(\boldsymbol{k})Z(\boldsymbol{k})$. This solution may, however, not lie in $\mathscr{G}$. Under such circumstances we therefore take as the solution of equation (18)

$$\phi = -R\tau Z. \tag{19}$$

Thus with the model (17), the solution (16) reduces to

$$\begin{aligned}\phi = {} & -(\tau E v_p)\frac{\partial T}{\partial x_p} + (\tau^2 E v_p)\frac{\partial^2 T}{\partial x_p\,\partial t} + (R\tau R v_p \tau E v_q)\frac{\partial^2 T}{\partial x_p\,\partial x_q} - (\tau^3 E v_p)\frac{\partial^3 T}{\partial x_p\,\partial t^2} \\ & -(\tau v_p R\tau R v_q \tau E v_r)\frac{\partial^3 T}{\partial x_p\,\partial x_q\,\partial x_r} - (R\tau R v_p \tau^2 E v_q + R\tau R\tau R v_p \tau E v_q)\frac{\partial^3 T}{\partial x_p\,\partial x_q\,\partial t}\end{aligned} \tag{20}$$

since if $Z(-\boldsymbol{k}) = -Z(\boldsymbol{k})$, the R operator on the right-hand side of equation (19) can be omitted. A final simplification occurs if $\tau(\boldsymbol{k})$ can be taken as independent of $\boldsymbol{k}$. This yields

$$\begin{aligned}\phi = {} & -\tau(E v_p)\frac{\partial T}{\partial x_p} + \tau^2(E v_p)\frac{\partial^2 T}{\partial x_p\,\partial t} + \tau^2(R_{pq})\frac{\partial^2 T}{\partial x_p\,\partial x_q} - \tau^3(E v_p)\frac{\partial^3 T}{\partial x_p\,\partial t^2} \\ & -\tau^3(v_p R_{qr})\frac{\partial^3 T}{\partial x_p\,\partial x_q\,\partial x_r} - 2\tau^3(R_{pq})\frac{\partial^3 T}{\partial x_p\,\partial x_q\,\partial t}\end{aligned} \tag{21}$$

where $R_{pq} = R v_p v_q E$.

If the solution (15) with $n-1$ terms on the right-hand side is substituted into equation (14) the magnitude of the error in satisfying the latter is readily seen to be

$$\begin{aligned}Y & = \left\{M^{-1}\left(R v_p \frac{\partial}{\partial x_p} + \frac{\partial}{\partial t}\right)\right\}^{n-1} M^{-1}(E v_p)\frac{\partial T}{\partial x_p} \\ & = \tau^n \left(R v_p \frac{\partial}{\partial x_p} + \frac{\partial}{\partial t}\right)^{n-1} (E v_p)\frac{\partial T}{\partial x_p}\end{aligned} \tag{22}$$

if the model (17) is used with a constant relaxation time. It is clear that all terms in Y are of the form τ^n times an nth differential coefficient of T with respect to space or time—in agreement with the result stated earlier.

3. The heat current

We proceed to calculate the heat current J_s corresponding to the solution (16). By the usual argument

$$J_s = \frac{1}{8\pi^3}\int fEv_s\,\mathrm{d}\boldsymbol{k} = -\frac{1}{8\pi^3 T}(Ev_s, \phi) \tag{23}$$

and therefore

$$-8\pi^3 TJ_s = (Ev_s, \phi) = (v_sE, M^{-1}Ev_p)\frac{\partial T}{\partial x_p} + (v_sE, M^{-2}Ev_p)\frac{\partial^2 T}{\partial x_p\,\partial t}$$

$$+ (v_sE, M^{-3}Ev_p)\frac{\partial^3 T}{\partial x_p\,\partial t^2} + (v_sE, M^{-1}v_pM^{-1}Rv_qM^{-1}Ev_r)\frac{\partial^3 T}{\partial x_p\,\partial x_q\,\partial x_r};$$

the other terms are zero since the integrand in the scalar product is an odd function of $\boldsymbol{k}$. On calculating $(M^{-1}Ev_s, \partial\phi/\partial t)$ with the solution (16) we obtain

$$(Ev_s, \phi) - \left(M^{-1}Ev_s, \frac{\partial\phi}{\partial t}\right)$$

$$= (v_sE, M^{-1}Ev_p)\frac{\partial T}{\partial x_p} + (v_sE, M^{-1}v_pM^{-1}Rv_qM^{-1}Ev_r)\frac{\partial^3 T}{\partial x_p\,\partial x_q\,\partial x_r} \tag{24}$$

retaining terms up to the third differential coefficients of T. If we now employ the model (17) with constant τ on the left-hand side of equation (24), it follows from equation (23) that

$$J_s + \tau\frac{\partial J_s}{\partial t} = -K_{sp}\frac{\partial T}{\partial x_p} - L_{spqr}\frac{\partial^3 T}{\partial x_p\,\partial x_q\,\partial x_r} \tag{25}$$

where

$$K_{sp} = \frac{1}{8\pi^3 T}(v_sE, M^{-1}Ev_p)$$

and

$$L_{spqr} = \frac{1}{8\pi^3 T}(v_sE, M^{-1}v_pM^{-1}Rv_qM^{-1}Ev_r).$$

It is readily shown by a consideration of the Boltzmann equation for the steady state that K_{pq} is the usual conductivity tensor. Equation (25) thus verifies that equation (3) is true if terms up to and including second differential coefficients are included.

The first correction term to equation (3) is the last term in equation (25), and we now proceed to estimate the tensor L_{spqr} contained in it. We employ the model (17) with constant τ and also assume that the phonon speed v is independent of $\boldsymbol{k}$. If α_p is the cosine of the angle between $\boldsymbol{k}$ and the x_p axis it is then readily shown that

$$\frac{L_{spqr}}{K_{sp}} = l^2\left(\frac{\int \alpha_p\alpha_q\alpha_r\alpha_s\,\mathrm{d}\Omega}{\int \alpha_p\alpha_s\,\mathrm{d}\Omega} - \frac{\int \alpha_q\alpha_r\,\mathrm{d}\Omega}{\int \mathrm{d}\Omega}\right) \tag{26}$$

where $l = v\tau$ is the mean free path for phonon interactions and $\int \mathrm{d}\Omega$ is an integral over solid angle. For one-dimensional flow this gives $L = \frac{4}{15}l^2K$ and equation (25) then yields

$$J+\tau\frac{\partial J}{\partial t} = -K\frac{\partial T}{\partial x}-\frac{4}{15}l^2K\frac{\partial^3 T}{\partial x^3}. \tag{27}$$

4. Entropy production

We begin with the statistical-mechanical definition of entropy per unit volume

$$S = -\frac{k}{8\pi^3}\int \{f\ln f-(1+f)\ln(1+f)\}\,\mathrm{d}\boldsymbol{k} \tag{28}$$

where k is Boltzmann's constant (Landau and Lifshitz 1958). It follows that

$$\frac{\mathrm{d}S}{\mathrm{d}t} = -\frac{k}{8\pi^3}\int\frac{\partial f}{\partial t}\ln\left(\frac{f}{1+f}\right)\mathrm{d}\boldsymbol{k}.$$

We substitute for f from equation (7), and retaining only terms linear in ϕ, since f is close to F, we obtain

$$\frac{\partial S}{\partial t} = -\frac{k}{8\pi^3}\int\frac{\partial f}{\partial t}\ln\left(\frac{F}{1+F}\right)\mathrm{d}\boldsymbol{k}-\frac{1}{8\pi^3T^2}\int\frac{\partial f}{\partial t}\phi\,\mathrm{d}\boldsymbol{k}. \tag{29}$$

For a suitable choice of the entropy flux vector $\boldsymbol{H}$, we would expect equation (29) to be capable of being expressed in the form

$$\frac{\mathrm{d}S}{\mathrm{d}t} = -\mathrm{div}\,\boldsymbol{H}+\sigma \tag{30}$$

where σ is the rate of entropy production per unit volume due to phonon interactions, and is necessarily positive. The precise way in which this can be done is shown in the appendix.

On using the result $F = \{\exp(E/kT)-1\}^{-1}$ it follows that the first term on the right-hand side of equation (29) takes the form

$$\frac{1}{8\pi^3T}\frac{\partial}{\partial t}\int Ef\,\mathrm{d}\boldsymbol{k} = \frac{1}{T}\frac{\mathrm{d}U}{\mathrm{d}t} \tag{31}$$

where U is the internal energy per unit volume. Equation (29) becomes

$$\frac{\mathrm{d}S}{\mathrm{d}t} = \frac{1}{T}\frac{\mathrm{d}U}{\mathrm{d}t}-\frac{1}{8\pi^3T^2}\int\frac{\partial f}{\partial t}\phi\,\mathrm{d}\boldsymbol{k}, \tag{32}$$

and the second term on the right-hand side thus corresponds to the departure from the classical equilibrium result $\mathrm{d}S/\mathrm{d}t = T^{-1}\,\mathrm{d}U/\mathrm{d}t$. We investigate this departure by substituting for ϕ from equation (16), retaining the first three terms of the latter equation corresponding to the first two terms of the expansion (15). It follows that

$$\int\frac{\partial f}{\partial t}\phi\,\mathrm{d}\boldsymbol{k} = \frac{\partial T}{\partial x_p}\int\frac{\partial f}{\partial t}(M^{-1}Ev_p)\,\mathrm{d}\boldsymbol{k}+\frac{\partial^2 T}{\partial x_p\,\partial t}\int\frac{\partial f}{\partial t}(M^{-2}Ev_p)\,\mathrm{d}\boldsymbol{k}$$
$$+\frac{\partial^2 T}{\partial x_p\,\partial x_q}\int\frac{\partial f}{\partial t}(M^{-1}Rv_pM^{-1}Ev_q)\,\mathrm{d}\boldsymbol{k}. \tag{33}$$

We proceed to develop the right-hand side of equation (33), consistently retaining terms up to and including those involving M^{-3}. Now it follows from equation (7) that

$$\frac{\partial f}{\partial t} = -\frac{1}{T}\frac{\partial F}{\partial E}\left(E\frac{\partial T}{\partial t}+\frac{\partial \phi}{\partial t}\right). \tag{34}$$

The integral in the last term of equation (33) thus becomes

$$-\frac{1}{T}\frac{\partial T}{\partial t}(E, M^{-1}Rv_pM^{-1}Ev_q)-\frac{1}{T}\left(\frac{\partial \phi}{\partial t}, M^{-1}Rv_pM^{-1}Ev_q\right). \tag{35}$$

The first term in expression (35) is zero since E is orthogonal to $M^{-1}Rv_pM^{-1}Ev_q$ which lies in $\mathscr{G}$. The second term involves M^{-4}, as may be seen by substituting for $\partial\phi/\partial t$ from equation (16), and can therefore be neglected. As far as the first two terms on the right-hand side of equation (33) are concerned, we employ the model (17) with constant τ and thus obtain

$$\int \frac{\partial f}{\partial t}\phi \,\mathrm{d}\boldsymbol{k} = -\tau\frac{\partial T}{\partial x_p}\frac{\partial}{\partial t}\int fEv_p\,\mathrm{d}\boldsymbol{k}+\tau^2\frac{\partial^2 T}{\partial x_p\,\partial t}\frac{\partial}{\partial t}\int fEv_p\,\mathrm{d}\boldsymbol{k}. \tag{36}$$

On substituting into equation (32) and using result (23) it is found that

$$\frac{\mathrm{d}S}{\mathrm{d}t} = \frac{1}{T}\frac{\mathrm{d}U}{\mathrm{d}t}+\frac{\tau}{T^2}\frac{\partial T}{\partial x_p}\frac{\partial J_p}{\partial t}-\frac{\tau^2}{T^2}\frac{\partial^2 T}{\partial x_p\,\partial t}\frac{\partial J_p}{\partial t}. \tag{37}$$

The first two terms here correspond to those suggested by Lambermont and Lebon (1973) but it is seen that the correction to the classical result is now *minus* that given by these authors. The last term in equation (37) is the next correction term in what is of course really an infinite series.

It is of interest to obtain from the result (37) an expression for σ, the collision rate of entropy production. Using the result $\mathrm{d}U/\mathrm{d}t = -\mathrm{div}\,\boldsymbol{J}$ and retaining the first two terms on the right-hand side of equation (37) it is readily shown that

$$\sigma = -\frac{1}{T^2}\frac{\partial T}{\partial x_p}\left(J_p-\tau\frac{\partial J_p}{\partial t}\right),$$

and on substituting for $\partial T/\partial x_p$ from equation (25) we obtain

$$\sigma = \frac{r_{ps}J_pJ_s}{T^2}+\frac{r_{sp}}{T^2}\left(L_{stqr}\frac{\partial^3 T}{\partial x_t\,\partial x_q\,\partial x_r}J_p-\tau^2\frac{\partial J_p}{\partial t}\frac{\partial J_s}{\partial t}\right) \tag{38}$$

where $\boldsymbol{r} = \boldsymbol{K}^{-1}$. The first term is positive and proportional to τ; it is the result given by classical conduction theory. The second term is proportional to τ^3 and is the first correction to the classical result, which is thus seen to remain unchanged to terms of order τ^2. This is in contradistinction to the result suggested by Lambermont and Lebon (1973), where correction terms proportional to τ^2 were given.

Appendix

We consider here how equation (29) may be expressed in the form (30), obtaining explicit expressions for $\boldsymbol{H}$ and σ. Using the form (32) for $\mathrm{d}S/\mathrm{d}t$, we substitute for $\partial f/\partial t$ from equation (34) and obtain

$$\frac{\partial S}{\partial t} = \frac{1}{T}\frac{\partial U}{\partial t} + \frac{1}{8\pi^3 T^3}\left(\phi, \frac{\partial \phi}{\partial t}\right) + \frac{1}{8\pi^3 T^3}\frac{\partial T}{\partial t}(E, \phi) \tag{A.1}$$

of which the last term is zero from equation (12). We substitute for $\partial\phi/\partial t$ from equation (9) and this gives, in view of equation (12),

$$\frac{\mathrm{d}S}{\mathrm{d}t} = \frac{1}{T}\frac{\mathrm{d}U}{\mathrm{d}t} - \frac{1}{8\pi^3 T^3}\left(\frac{\partial T}{\partial x_p}(\phi, Ev_p) + \frac{1}{2}\frac{\partial}{\partial x_p}(v_p, \phi^2) - (\phi, M\phi)\right). \tag{A.2}$$

Now $\mathrm{d}U/\mathrm{d}t = -\mathrm{div}\, \boldsymbol{J}$, and using this together with equation (23) allows (A.2) to be expressed in the form (30) where

$$\boldsymbol{H} = \frac{\boldsymbol{J}}{T} + \frac{1}{16\pi^3 T^3}(\boldsymbol{v}, \phi^2)$$

and

$$\sigma = \frac{1}{8\pi^3 T^3}(\phi, M\phi).$$

M can be shown to be a positive definite operator and thus σ is positive.

References

Carrassi M and Morro A 1972 *Nuovo Cim.* **9** 321–43
Cattaneo C 1958 *C.R. Acad. Sci., Paris* **247** 431–3
Chester P 1963 *Phys. Rev.* **131** 2013–5
Gurtin M E and Pipkin A C 1968 *Archs ration. Mech. Analysis* **31** 113–26
Kranys M 1966a *Nuovo Cim.* B **42** 51–70
—— 1966b *Phys. Lett.* **22** 285–6
Lambermont J and Lebon G 1973 *Phys. Lett.* **42A** 499–500
Landau L D and Lifshitz E M 1958 *Statistical Physics* (London: Pergamon) p 155
Luikov A V 1966 *Int. J. Heat Mass Transf.* **9** 139–52
Maxwell J C 1867 *Phil. Trans. R. Soc.* **157** 49–88
Simons S 1960 *Phil. Trans. R. Soc.* **253** 137–84
—— 1971 *J. Phys.* C: *Solid St. Phys.* **4** 2785–91
Ulbrich C W 1961 *Phys. Rev.* **123** 2001–2
Vernotte P 1958 *C.R. Acad. Sci., Paris* **247** 2103–5
Ziman J M 1960 *Electrons and Phonons* (Oxford: Clarendon) chap 7