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Thermodynamic aspects of continued-fraction expansions in heat conduction

Carlos Pérez-García and David Jou

Departament de Termologia, Facultat de Ciències, Universitat Autònoma de Barcelona, Bellaterra (Barcelona), Catalonia, Spain

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Abstract. A generalisation of the so-called extended irreversible thermodynamics (EIT) is proposed. It leads, in a natural manner, to evolution equations of the Ginzburg-Landau type for the fast non-conserved variables. In this generalised scheme the thermal conductivity can be written as a continued-fraction expansion. This corresponds to a macroscopic analogue of some well accepted microscopic theories.

1. Introduction

Some experimental techniques, such as neutron scattering or molecular dynamics simulations, provide an insight into the region of short wavelength and high frequencies (Boon and Yip 1980). In the thermodynamic limit ($k, \omega \rightarrow 0$), linear irreversible thermodynamics (LIT) has shown to be the suitable thermodynamic framework for the analysis of such phenomena in macroscopic systems. In order to account for the wider region accessible to experimental techniques, the so-called generalised hydrodynamics (GH) has been introduced which uses, instead of dissipative coefficients, suitable memory functions. The latter gather phenomenologically the non-local response both in space and time when a perturbation acts on the system. However, generalised hydrodynamics is compatible with LIT only when memories are delta functions. The local-equilibrium hypothesis is a central assumption in LIT, and this feature limits its validity to a narrow region of very small k and ω . The question that arises is then: what kind of thermodynamics corresponds to the region of non-zero k and ω ? Several macroscopic approaches project some light on this question, especially that known as extended irreversible thermodynamics (EIT) (Casas-Vázquez *et al* 1984). This theory, not restricted to the local-equilibrium hypothesis, includes dissipative fluxes amongst the independent variables and, using a development similar to LIT, it may derive evolution equations for these fluxes, of the form of the Maxwell-Cattaneo equations (Maxwell 1965, Cattaneo 1948). This framework is justified in kinetic theory by Grad's thirteen-moments method (Grad 1958) of solving the Boltzmann equation.

In the present paper, we provide a phenomenological development of Grad's ideas by including higher-order dissipative fluxes into the thermodynamical description of the system. Here, for the sake of simplicity, we restrict ourselves to the case of rigid heat conductors. The physical motivation for such an analysis is evident, since the present results could be applied to generalised hydrodynamics (Jou *et al* 1985), to phonon hydrodynamics and ultrafast thermometry (Jou and Pérez-García 1981, Bampi *et al* 1981), ultrasound attenuation in metals (Jou *et al* 1982), critical phenomena

(Zubarev and Tischenko 1972) and also to physical systems with long relaxation times such as, for instance, polymeric solutions, superfluids and superconductors. The present development is original in that it recovers in purely macroscopic ways some results similar, at least in form, to those obtained by microscopic theories. This brings the limits of irreversible thermodynamics, up to now too restricted to the local equilibrium hypothesis, a step further towards a wider experimental and theoretical domain presently reserved to statistical considerations.

In § 2 we develop the macroscopic formalism and some aspects of its implications in fluctuation theory. In § 3 the general form of the memory functions is analysed by means of EIT and it is shown that this theory leads quite naturally to a continued-fraction expansion for thermal conductivity, analogous to that obtained by Mori (1965a, b) starting from the Liouville equation. Finally, this continued-fraction expansion is compared with Burnett and super-Burnett expansions of the Chapman–Enskog method (Chapman and Cowling 1970).

2. Extended irreversible thermodynamics (EIT)

A general problem in dealing with systems out of equilibrium is that one has more variables than equations, because the fluxes of the variables remain, in principle, unspecified. In the case of heat conduction, the flux \mathbf{q} appearing in the energy balance equation is indeed unspecified. In LIT this problem is solved by relating \mathbf{q} with ∇T in a linear way, so that \mathbf{q} is completely determined by the spatial distribution of u . This choice leads to some physical inconsistencies, such as, for instance, an infinite velocity of propagation of thermal signals. In EIT one considers that \mathbf{q} is an independent variable, whose time evolution is described by Maxwell–Cattaneo equations. These add a relaxation time to the usual Fourier equation, but ignore non-local effects. In order to consider the latter, the Maxwell–Cattaneo equations should be replaced by a general balance equation for \mathbf{q} . As usual in such equations, the temporal variations of \mathbf{q} will be the sum of a production (volume) term plus a flux (surface) term. This flux, \mathbf{Q} will be a tensor of order two. In accordance with the hypotheses of EIT, we will consider now that both \mathbf{q} and \mathbf{Q} are independent variables. Of course, one could proceed with this argument to higher and higher orders. This would generate a hierarchy of fluxes and balance equations for them, which should be closed at a certain level. The situation would be analogous to Grad's development (Grad 1958) of the Boltzmann equation in term of higher moments of molecular velocity. Therefore, though abstract and unusual, the conceptual meaning of \mathbf{Q} (the flux of the vector \mathbf{q}) is clear and it will be developed further in the following section.

In the present paper we present a thermodynamical formalism allowing us to describe this hierarchical development, up to now restricted to microscopic theories.

While the classical variable u is governed by the balance equation

$$\rho \dot{u} = -\nabla \cdot \mathbf{q} \quad (1)$$

with ρ the mass density, we need evolution equations for \mathbf{q} and \mathbf{Q} in order to have a complete description of the system. We will proceed to obtain it through a generalisation of the usual methods of EIT (Casas-Vázquez *et al* 1984). For the sake of simplicity, we will assume in the following that \mathbf{Q} is symmetric and traceless. Otherwise, some new variables might enter in the description.

The generalised Gibbs equation corresponding to the entropy $s = s(u, \mathbf{q}, \mathbf{Q})$ is

$$ds = T^{-1} du + T^{-1} v \alpha_1 \mathbf{q} \cdot d\mathbf{q} + T^{-1} v \alpha_2 \mathbf{Q} : d\mathbf{Q}. \quad (2)$$

Here, T is the absolute temperature and α_1 and α_2 are coefficients which will be determined later on. The double dot stands for the double contraction of the corresponding tensors. This form has been justified elsewhere (Casas-Vázquez *et al* 1984): it comes from assuming that s is an analytic function of \mathbf{q} and \mathbf{Q} . Since s is a scalar, the simplest dependence on these variables is through q^2 and $\mathbf{Q} : \mathbf{Q}$, i.e. to assume $s(u, \mathbf{q}, \mathbf{Q}) = s(u) + T^{-1} v \alpha_1 q^2 / 2 + T^{-1} v \alpha_2 \mathbf{Q} : \mathbf{Q} / 2$. Furthermore, we will assume for the entropy flux \mathbf{J}_s the following form:

$$\mathbf{J}_s = T^{-1} \mathbf{q} + \beta_1 \mathbf{Q} \cdot \mathbf{q}. \quad (3)$$

This is the more general vector that can be constructed from \mathbf{q} and $\mathbf{Q} \cdot \mathbf{q}$ which reduces to the classical entropy flux when second-order terms are neglected.

The standard form of the balance equation for s

$$\rho \dot{s} + \nabla \cdot \mathbf{J}_s = \sigma \quad (4)$$

leads, together with (1)-(3), to the following expression for the entropy production σ :

$$\sigma = \mathbf{q} \cdot (\nabla T^{-1} + T^{-1} \alpha_1 \dot{\mathbf{q}} + \beta_1 \nabla \cdot \mathbf{Q}) + \mathbf{Q} : (\beta_1 \nabla \mathbf{q} + T^{-1} \alpha_2 \dot{\mathbf{Q}}). \quad (5)$$

Our purpose is to obtain an expression for the evolution of \mathbf{q} and \mathbf{Q} in terms of the basic variables, subject to the restrictions of the second law, which states that entropy production must be positive. Therefore, in view of the bilinear form of (5) and in the linear approximation we will assume, in analogy with LIT, the following equations:

$$\nabla T^{-1} + T^{-1} \alpha_1 \dot{\mathbf{q}} + \beta_1 \nabla \cdot \mathbf{Q} = \mu_1 \mathbf{q} \quad (6)$$

and

$$\beta_1 \nabla \mathbf{q} + T^{-1} \alpha_2 \dot{\mathbf{Q}} = \mu_2 \mathbf{Q}. \quad (7)$$

The positive character of σ is then ensured provided that $\mu_1 \geq 0$ and $\mu_2 \geq 0$.

These equations may be written in the more suitable form

$$\dot{\mathbf{q}} = T \alpha_1^{-1} (\mu_1 \mathbf{q} - \nabla T^{-1} - \beta_1 \nabla \cdot \mathbf{Q}) \quad (8)$$

and

$$\dot{\mathbf{Q}} = T \alpha_2^{-1} (\mu_2 \mathbf{Q} - \beta_1 \nabla \mathbf{q}). \quad (9)$$

In the stationary limit and when non-local effects are ignored, (8) must reduce to Fourier's law, so that we must identify $\mu_1 = (\lambda T^2)^{-1}$, λ being thermal conductivity. Furthermore, in the local but non-stationary case, one must recover the Maxwell-Cattaneo equation for the heat flux, so that we have $\alpha_1 = -\tau_1 (\lambda T^2)^{-1}$, with τ_1 the corresponding relaxation time. Finally, we denote $\gamma_1 = \beta_1 \lambda T^2$. The physical meaning of the coefficient β_1 will be determined later on. By analogy, we rewrite the coefficients in (9) as $\mu_2 = (\chi T^2)^{-1}$, $\alpha_2 = -\tau_2 (\chi T)^{-1}$, $\gamma_2 = \beta_1 \chi T^2$, where χ is a transport coefficient relating \mathbf{Q} and \mathbf{q} and τ_2 is the relaxation time of \mathbf{Q} . Then (8) and (9) can be written as

$$\tau_1 \dot{\mathbf{q}} = -(\mathbf{q} + \lambda \nabla T - \gamma_1 \nabla \cdot \mathbf{Q}) \quad (10)$$

and

$$\tau_2 \dot{\mathbf{Q}} = -(\mathbf{Q} - \gamma_2 \nabla \mathbf{q}). \quad (11)$$

Therefore, the generalised Gibbs equation (2) takes the explicit form

$$ds = T^{-1} du - (\tau_1 v / \lambda^2) \mathbf{q} \cdot d\mathbf{q} - (\tau_2 v / \chi T^2) \mathbf{Q} \cdot d\mathbf{Q}. \tag{12}$$

Note that, introducing (11) into (10) we may write for the heat flux the following equation:

$$\begin{aligned} \dot{\mathbf{q}} = & - \int_0^t \{ \tau_1^{-1} \delta(t-t') - \gamma_1 \gamma_2 \tau_1^{-1} \tau_2^{-1} \exp[-(t-t')/\tau_2] \nabla^2 \} \mathbf{q}(t') dt' \\ & - \lambda \tau_1^{-1} \nabla T + \gamma_1 \tau_1^{-1} \nabla \cdot \mathbf{Q}(0). \end{aligned} \tag{13}$$

We have written this equation in such a way that a memory function appears explicitly. Such a memory function is the sum of a delta part plus an exponential part. Note that the term in $\mathbf{Q}(0)$, due to the initial value of \mathbf{Q} , gives rise to a fluctuating term in (13), due to the thermodynamic fluctuations of the initial values of \mathbf{Q} . Finally, when $\tau_2 \rightarrow 0$, (13) reduces to

$$\tau_1 \dot{\mathbf{q}} = -(\mathbf{q} + \lambda \nabla T - l^2 \nabla^2 \mathbf{q}) \tag{14}$$

where we have identified l as $l^2 = \gamma_1 \gamma_2$. In this case, \mathbf{Q} loses its independent character and then it disappears from the Gibbs equation (2). We have obtained in a natural way a Ginzburg-Landau type of equation for the heat flux. This scheme may justify the form of these equations for the dissipative fluxes used in previous works (Zubarev and Tischenko 1972, Jou and Pérez-García 1981, Bampi *et al* 1981, Jou *et al* 1982, 1985) for a wide variety of systems.

Expression (12) for the generalised entropy may be used to obtain the probability of the fluctuations of fluxes around equilibrium states. With this aim we make the further hypothesis that, in analogy with the classical entropy, the generalised entropy is related to the probability of e equilibrium fluctuations by means of the Einstein relation

$$\text{Pr} \sim \exp(\delta^2 s / 2k_B) \tag{15}$$

where k_B is the Boltzmann constant. One obtains from (12) and (15) the following second moments for the fluctuations of \mathbf{q} and \mathbf{Q} :

$$\begin{aligned} \langle \delta q_i \delta q_j \rangle &= k_B \lambda T^2 (\tau_1 v)^{-1} \delta_{ij} \\ \langle \delta Q_{ij} \delta Q_{kl} \rangle &= k_B \chi T^2 (\tau_2 v)^{-1} \Delta_{ijkl} \end{aligned} \tag{16}$$

with $\Delta_{ijkl} = (\delta_{il} \delta_{kj} + \delta_{ik} \delta_{jl})$. These equations may be seen as particular cases of the fluctuation-dissipation theorem for an exponential regression of fluctuations of \mathbf{q} and \mathbf{Q} , and they allow us to compute λ and χ from equilibrium statistical models. Such fluctuations of \mathbf{q} and \mathbf{Q} , of thermodynamic origin, contribute as a noise in the evolution equations (1) and (10) respectively. In contrast with usual theories, these fluctuations are not introduced as mathematical artefacts, but have an explicit thermodynamic origin.

3. Correlation functions

After the developments of Kubo and Green in the 1950s, the time-correlation function formalism has acquired an increasing importance in calculating transport coefficients. At present, correlation functions play a role similar to that of the partition function

in equilibrium in non-equilibrium statistical mechanics. Moreover, the behaviour of some correlation functions is accessible to experimental techniques or by molecular dynamics simulations (MacQuarrie 1975). Generalised hydrodynamics (Boon and Yip 1980) tries to interpret these experimental results using suitable memory functions instead of the classical transport coefficients. The exact calculation of these memory functions is an extremely difficult task and, in general, phenomenological models are used for them. The memory functions are linked to correlation functions by means of the fluctuation-dissipation theorem (MacQuarrie 1976, Forster 1975, Copley and Lovesey 1975).

Classical correlation functions are defined as equilibrium averages of unequal time products of dynamical variables. We are here especially interested in autocorrelation functions of the form $C_a = \langle a(0)a^*(t) \rangle$ where the brackets mean an equilibrium average and a represents the deviation of a dynamical variable from its equilibrium value $a = \delta A = A - \langle A \rangle$. The asterisk stands for complex conjugation.

In the particular case dealt with in the present paper, the fluctuation-dissipation theorem states that $\lambda(k, \omega) = (kT^2)^{-1} \langle \delta q \delta q \rangle_{k, \omega}$ where the right-hand side is the Fourier transform of the heat correlation function. The Fourier transforms of equations (10) and (11) are

$$i\omega\tau_1\tilde{q}_{\parallel} = -\tilde{q}_{\parallel} - i\gamma_1 k\tilde{Q}_{\parallel} + i\lambda_0 kT \quad (17a)$$

$$i\omega\tau_2\tilde{Q}_{\parallel} = -\tilde{Q}_{\parallel} - i\gamma_2 k\tilde{q}_{\parallel} \quad (17b)$$

where \parallel stands for the longitudinal part of the corresponding variable and the upper tilde for the Fourier transform. When the expression for \tilde{Q}_{\parallel} obtained from (17b) is introduced into (17a), and identifying the expression for \tilde{q}_{\parallel} obtained in this way with a generalised Fourier law $\tilde{q} = ik\tilde{\lambda}(k, \omega)\tilde{T}$, we obtain for the generalised thermal conductivity

$$\tilde{\lambda}(k, \omega) = \frac{\lambda_0\tau_1^{-1}}{i\omega + \tau_1^{-1} + \frac{\gamma_1\gamma_2\tau_1^{-1}\tau_2^{-1}k^2}{i\omega + \tau_2^{-1}} \dots} \quad (18)$$

This equation has the form of the first terms in the development of a continued-fraction expansion for $\tilde{\lambda}(k, \omega)$. Here, according to (16), $\lambda_0\tau_1^{-1} = (kT^2)^{-1} \langle \delta q \delta q \rangle$. The denominator in (18) corresponds to the memory function presented in (13): the delta term gives the τ_1^{-1} in (18) while the exponential term in (13) corresponds to the $\gamma_1\gamma_2\tau_1^{-1}\tau_2^{-1}k^2(i\omega + \tau_2^{-1})^{-1}$ term in the denominator of (18).

The scheme presented in this paper is easy to generalise to a greater number of variables $a_1, a_2, a_3 \dots a_n \dots$ of increasing tensorial order n . (In our particular case $a_0 = T, a_1 = q, a_2 = Q$). An example of this situation is provided by the successive moments of the velocity distribution function in the kinetic theory of gases. In this case, and in a bilinear approximation, one has

$$s = s_{\text{eq}} - \frac{1}{2}v \sum_n \alpha_n a_n^{(n)} a_n \quad (19)$$

where $^{(n)}$ denotes the total contraction of a_n with a_n and $\alpha_n \geq 0$. For the entropy flux we assume, in such a bilinear approximation

$$J_s = \sum_n \beta_n a_{n+1}^{(n)} a_n.$$

From (19), (20) and (4) one obtains the following expression for the entropy production:

$$\sigma = \sum_n a_n \cdot^n (-\alpha_n \dot{a}_n + \beta_n \nabla \cdot a_{n+1} + \beta_{n-1} \nabla a_{n-1}). \tag{20}$$

Always in the bilinear approximation studied here, we will assume

$$-\alpha_n \dot{a}_n + \beta_n \nabla \cdot a_{n+1} + \beta_{n-1} \nabla a_{n-1} = \mu_n a_n \tag{21}$$

with $\mu_n \geq 0$ because of the positive character of σ . Then, the evolution equations for the a_n are

$$\alpha_n \dot{a}_n = -\mu_n a_n + \beta_n \nabla \cdot a_{n+1} + \beta_{n-1} \nabla a_{n-1} \tag{22}$$

where, obviously, α_n/μ_n define the corresponding relaxation time τ_n of a_n . This set of equations is precisely of the form predicted by kinetic theory (MacQuarrie 1975, Roldughin 1984) in a linear approximation, but here it follows from macroscopic arguments. Expression (22) is more specific than those which could be obtained simply by dimensional geometrical arguments, because it provides restrictions on the coefficients appearing in them. Furthermore, the fluctuation theory leads to

$$\langle \delta a_n \delta a_n \rangle = k/\alpha_n v \tag{23}$$

which constitutes a generalisation of the fluctuation-dissipation theorem linking dissipative coefficients to equilibrium fluctuations of dissipative fluxes. Note that, from (22) one may get a continued-fraction expansion for the correlation function $C_{a_1}(k, \omega)$ (Hess 1977)

$$\langle \widetilde{\delta a_1 \delta a_1} \rangle_{k,\omega} = \frac{\langle \delta a_1(0) \delta a_1(0) \rangle}{i\omega\alpha_1 + \mu_1 + \frac{\beta_1^2 k^2}{i\omega\alpha_2 + \mu_2 + \frac{\beta_2^2 k^2}{i\omega\alpha_3 + \mu_3 + \dots}}}. \tag{24}$$

For the special choice $a_0 = T, a_1 = q, a_2 = Q$, etc, this continued-fraction expansion can be rewritten, following the notation in (17), as

$$\tilde{\lambda}(k, \omega) = \frac{\lambda_0 \tau_1^{-1}}{i\omega + \tau_1^{-1} + \frac{K'_1(k, 0)}{i\omega + \tau_2^{-1} + \frac{K'_2(k, 0)}{i\omega + \tau_3^{-1} + \frac{K'_3(k, 0)}{i\omega + \dots}}}} \tag{25}$$

with $K'_n(k, 0) = \gamma_n \gamma_{n+1} \tau_n^{-1} \tau_{n+1}^{-1} k^2$.

This form is similar to that obtained by Mori (1965a, b) with a very different method. The projection-operator technique developed by Mori and Zwanzig (McQuarrie 1976) shows that, starting from the Liouville equation, the evolution equations for a dynamical variable a may be written in the form

$$\dot{a}(t) - i\Omega a(t) + \int_0^t K(t-t') a(t') dt' = f(t) \tag{26}$$

which is known as the generalised Langevin equation. The random force $f(t)$ introduced in (26) is in fact a dynamical variable resulting from the projection of the dynamics of a into a subspace of the fast variables of the system. It has not a properly stochastic character, but this is assigned to it by analogy with the Langevin

equation of Brownian motion. Then, the stochastic character of $f(t)$ is not a consequence of an exact equation but just a choice to have a Markovian equation in (26). From (26) it may be seen that $K(t-t') = \langle f(t)f^*(t') \rangle$. This relation is a form of the fluctuation-dissipation theorem (Forster 1975) and may be deduced from the projection-operator technique. Furthermore, if $f(t)$ is a white noise, $K(t)$ turns out to be a delta function in time, but if this is not the case, (26) is a non-Markovian stochastic equation. It is known that such an equation may be written as a system of Markovian equations if one adds some variables to the description. Mori (1965a, b) has shown that $f(t)$ obeys in turn an exact generalised equation. Therefore, we have a hierarchy of equations

$$\dot{f}_n = i\Omega_n f_n(t) - \int_0^t K_n(t-t') f_n(t') dt' + f_{n+1}(t) \quad (27)$$

where $f_n(t)$ is the corresponding noise of the f_{n-1} variable and Ω_n and K_n the corresponding frequency and memory functions. Then, one has an infinite set of equations that gives a more and more detailed description of the system. This is equivalent to adding more and more variables in the description. It may be truncated in some step assuming the Markovianity of the last equation, which closes the hierarchy. If this closure is made at the n th equation, the description of the system is based on the independent variables (a, f_1, \dots, f_n) with a white noise f_{n+1} . This Markovian assumption on $f_{n+1}(t)$ is equivalent to giving up the possibility of knowing more details on the system: when we cannot keep up the description, we close the hierarchy of evolution equations assuming the Markovian character for the latter 'random force'.

Such an idea is reflected in the continued-fraction expansion due to Mori (1965a, b). From the Fourier transform of (26) and (27), one may obtain for the spectral distribution function the following expansion:

$$C_a(\omega) = \frac{\langle a(0)a^*(0) \rangle}{i - i\Omega_0 + \frac{K_0(0)}{i\omega - i\Omega_1 + \frac{K_1(0)}{i\omega - i\Omega_2 + \dots}}} \quad (28)$$

where $K_i(0)$ are the memory functions at $\omega = 0$, which can be expressed by means of equilibrium correlation functions at equal times. Of course, a similar expansion is valid for each memory function $K_j(t)$, because, as we have said, K_j is in turn a time correlation function, that of f_{j+1} . Note that when the property in question has a well defined time-reversal parity, the frequency terms Ω_i vanish in equilibrium. If we assume that f_{n+1} is a white noise, $K_n(t) = \lambda_n \delta(t)$ and the continued-fraction expansion truncates at the n th level.

However, although some similarities exist, the two approaches to (25) and (28) differ on fundamental grounds. The first is macroscopic and no hypothesis is made about the random nature of the variables, though a particular hydrodynamical form is assumed. The second is fully general, but it is a formidable task to calculate the coefficients from first principles. Moreover, though we can take $i\Omega_0 = -\tau_1^{-1}$ to make expressions (25) and (28) more similar, this identification is inconsistent from the microscopic point of view, due to the time-reversal parity of q : the term $i\Omega_0$ in (28) has a reversible meaning, while the relaxation terms in (25) are clearly irreversible. In fact the Mori expansion is more general because it does not specify the dependence of the K_n in terms of k , although it seems very difficult to determine this dependence from first principles.

The similarity of these two approaches, however, is far from casual: it is based on an extension of the description of the system. In EIT we add more and more dissipative fluxes, whereas in Mori theory one adds more and more random noises.

Now we comment on some additional interesting features in (25). When frequencies of relaxation times go to zero the continued-fraction expansion for $\lambda(k)$ reduces to

$$\lambda(k) = \frac{\lambda_0}{1 + \frac{\gamma_1 \gamma_2 k^2}{1 + \frac{\gamma_2 \gamma_3 k^2}{1 + \dots}}} \quad (29)$$

which in the first approximation ($\gamma_i = 0$ for $i \geq 3$) has the form obtained by Alley and Adler (1983) in molecular dynamics simulations. This form differs considerably from the standard power expansion in the Chapman-Enskog method (Chapman and Cowling 1970)

$$\lambda(k) = \lambda_0(1 + \Lambda_1 k^2 + \Lambda_2 k^4 + \Lambda_3 k^6 + \dots) \quad (30)$$

where the Λ_i are higher-order Burnett coefficients. The convergence of this series for transport coefficients presents some difficulties (Dorfmann 1980), whereas (21) is well defined for all values of k .

Starting from a method due to Waldmann (1963), which is a modification of Grad's, a similar expression for the diffusion coefficients has been obtained by Hess (1977). This author shows that in this particular case the continued-fraction expansion has a fast convergence towards the known solutions, whereas a power expansion as (29) for the diffusion coefficients does not show this feature.

The practical applications of this formalism can be found in the domain of ultrafast thermometry, in experiments on temperature waves (second sound) and in phonon hydrodynamic theories in solids (Chester 1966, Guyer and Krumhansl 1966, Roger 1971, Beck *et al* 1974, Fekete 1981). The theory of phonon hydrodynamics leads to the following equation for the temperature (Beck *et al* 1974):

$$-\tau_R \omega^2 \tilde{T} + i\omega \tilde{T} + \tau_R c_{\parallel}^2 k^2 \tilde{T} + 2c_{\parallel}^2 \tau_{\parallel} \tau_R i\omega k^2 \tilde{T} = 0 \quad (31)$$

where c_{\parallel} is the speed of the second sound, τ_R the relaxation time for the resistive scattering of phonon under umklapp processes and τ_{\parallel} the relaxation time of momentum-conserving normal processes.

The present formulation leads to the following equation for the temperature:

$$-(\tau_1 + \tau_2)\omega^2 \tilde{T} - i\tau_1 \tau_2 \omega^3 \tilde{T} + i\omega \tilde{T} + i\omega k^2 \left(\gamma_1 \gamma_2 + \frac{\tau_2 \lambda_0}{\rho c_v} \right) \tilde{T} + \frac{k^2 \lambda_0 \tilde{T}}{\rho c_v} = 0. \quad (32)$$

This equation is of higher order in ω than the previous one, to which it reduces when one assumes that $\tau_2 = 0$. In this case one finds, by identifying both equations, that $\tau_1 = \tau_R$, $\lambda_0 = 2c_{\parallel}^2 \tau_R$. Moreover, if one assumes that τ_2 does not vanish, but the ω^3 term can be neglected in (32), one finds that τ_2 has an influence on the terms of order ω^2 and ωk^2 . A careful analysis of the experimental data could decide which of both models is more suitable for the description of the physical situation. The present experimental data, however, are not yet significant to clarify this point.

4. Concluding remarks

The main results of the present work are the following. First of all, the extension suggested by Grad and Waldmann methods, which amounts to a description of the system in terms of more and faster dissipative variables, may be treated phenomenologically in a thermodynamic framework which shows how to generalise the usual developments of extended irreversible thermodynamics and gives a new and sounder physical insight into some previous generalisations.

Secondly, our phenomenological development leads to a continued-fraction expansion of the thermal conductivity which is the macroscopic analogue of the corresponding microscopic expansion in Mori's formalism. Therefore, the present macroscopic theory is much closer to present microscopic developments than previous thermodynamic theories, based on a local equilibrium hypothesis (LIT) or including as supplementary variables only the usual dissipative fluxes (EIT). When the relaxation times go to zero, the corresponding continued-fraction expansion of the dissipative coefficients in k^2 is more useful than the series expansion in k^2 obtained in the Chapman-Enskog method.

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