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1995 J. Phys.: Condens. Matter 7 1461

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A non-local thermodynamic analysis of second sound propagation in crystalline dielectrics

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Received 6 May 1994

Abstract. A thermodynamic model of second sound propagation in rigid solids like dielectric crystals is proposed: this is achieved within the framework of extended irreversible thermodynamics. The independent variables are the temperature, the heat flux vector plus a supplementary variable that is identified as the flux of the heat flux; to include non-local effects, the constitutive equations are assumed to depend on the gradients of the temperature and the heat flux vector. After establishing the evolution equations governing the behaviour of the basic variables in the course of space and time, the entropy production is calculated and a generalized Gibbs equation is derived. The present model is shown to be rather general as it encompasses the particular models of Cattaneo and Guyer–Krumhansl. Onsager-like reciprocal relations are also displayed and discussed. Working within the lowest-order approximation, a general wave equation for the temperature is derived. This relation is a third-order hyperbolic differential equation with respect to time, allowing for propagation of waves at finite velocity. A dispersion relation between the wavevector and the frequency is established and the corresponding phase velocity is calculated.

1. Introduction

The study of second sound in crystals has received growing interest during the past few years [1–3]. Moreover, it is known that second sound cannot be interpreted within the scheme of classical irreversible thermodynamics proposed by Onsager [4], Prigogine [5], De Groot and Mazur [6] and Woods [7] among others. Indeed this formalism predicts that heat conduction is governed by the Fourier law relating the heat flux linearly to the temperature gradient, while second sound requires a more involved relation between heat flux and temperature gradient. Several extensions of Fourier's law have been proposed recently (see [1] for a review). In particular it was observed that generalized Fourier laws emerge naturally from a new thermodynamic formalism, referred to as extended irreversible thermodynamics (EIT) [8–10]. Our purpose is to propose a phenomenological description of second sound in dielectric crystals based on EIT. Earlier papers using either EIT [2, 3, 8–10], internal variables theories [11–13] or rational thermodynamics [14, 15] have been proposed. The new feature of the present work is that we incorporate spatial inhomogeneities into the framework of EIT. Only lower-order spatial inhomogeneities (weak non-locality) will be investigated in order to keep the model as simple as possible; by weak locality is meant the property that the governing constitutive equations involve only first-order spatial derivatives of the independent variables, higher-order derivatives not being accounted for.

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In section 2, the relevant evolution and constitutive equations are established. Restrictions on the form of these equations are placed by the second law of thermodynamics and the requirement that entropy is maximum at equilibrium (section 3). Comparison with earlier models [16–18] is made: it is shown that the present model contains as particular cases the Fourier, Cattaneo, and Guyer and Krumhansl relations. Onsager's relations are displayed in section 4. After elimination of the fluxes one is left with a partial differential equation for the temperature only. This equation is hyperbolic, in contrast with Guyer and Krumhansl's analogous expression; comparison with results obtained within the framework of rational thermodynamics [14] is also discussed (section 5). Wave propagation properties in dielectric crystals at low temperature are established in section 6 while final conclusions are drawn in section 7.

The basic hypothesis underlying EIT is to extend the space of the classical variables (like temperature, velocity, pressure, mass, concentration) by including supplementary variables taking the form of fluxes, like the heat flux, the flux diffusion, the flux of momentum and even higher-order fluxes. The main consequence is to replace the classical constitutive steady equations of Fourier, Fick, Newton, . . . by unsteady evolution equations involving the first-order time derivative of the variables. To be explicit the Fourier law of heat conduction:

$$q = -\lambda \nabla T \quad (1)$$

is, in EIT, generalized as

$$\tau \dot{q} + q = -\lambda \nabla T. \quad (2)$$

The latter relation is known as the Cattaneo equation [16]; in (1) and (2), q designates the heat flux vector, λ the heat conductivity, T the absolute temperature, τ the relaxation time, an upper dot means (partial) derivation with respect to time and ∇ is the nabla operator with components $\partial_x, \partial_y, \partial_z$ in Cartesian coordinates. To obtain Cattaneo's relation from EIT, it was shown in earlier publications (e.g. [8, 9]) that it is sufficient to consider the heat flux q as additional variables besides the classical variable T . However, Cattaneo's model is too crude to study some subtle phenomena like propagation of heat waves in dielectric crystals at low temperature (e.g. [2]). Therefore, the common approach consists of complementing the pair variables T and q by an additional one, say Q , representing the flux of the heat flux; since q is a vector, Q represents necessarily a tensor of rank 2. The new variable Q is however of different nature compared to T and q : indeed T and q appear explicitly in the ordinary balance laws (like the energy balance) while Q does not figure in the usual balance equations. Moreover, Q is not directly experimentally measurable. For this reason, Q will be referred to as an internal variable because it is not controllable from the external world [19–21]. The variable Q is comparable to the convolution tensor widely introduced in rheology [22] to describe the geometric configuration of the polymer chains. It is interesting to note that, in their description of heat waves in dielectric crystals at low temperature, Guyer and Krumhansl [17] also use internal variables to describe the deviations from equilibrium of the distribution function of phonons. By comparison with the kinetic theory, it is shown [2, 3] that Q is related to the fourth moment of the non-equilibrium distribution with respect to velocity.

In addition, in some physical systems with strong inhomogeneities like interfaces, and processes like light and neutron scattering in liquids and gases, non-local effects play a decisive role. To include these effects, it is necessary to refine the model by introducing non-local integral operators. For the present purpose, it is however sufficient to introduce weak non-locality with respect to the 'external' variables T and q .

By comparison with Cattaneo's description [16], two supplementary ingredients are supplied by the present model.

First, in addition to the 'external' variables T and q , we introduce an extra variable Q , which will be identified as an internal variable whose physical meaning is that of a flux of the heat flux. Within the kinetic theory description of dilute gases, T is interpreted as the kinetic energy moment, q as the flux of energy moment and Q as the next higher-order moment; designating by f the distribution function and by C_i the relative speed of the particles with respect to the barycentric velocity, one has

$$\frac{3}{2}kT = \int C^2 f \, dc \quad q_i = \int C^2 C_i \, dc \quad Q_{ij} = \int C^2 C_i C_j f \, dc \quad (3)$$

where C^2 stands for $C_k C_k$. Einstein summation convention rule and Cartesian coordinates will be used throughout this work. It follows direction from (3c) that Q_{ij} is a symmetric tensor.

The second difference with Cattaneo's approach is non-locality: it is admitted that the constitutive equation may depend on ∇T and ∇q (weak non-locality); higher-order derivatives with respect to the space coordinates are neglected. It should however be kept in mind that ∇T and ∇q are not considered as independent and supplementary variables. The set of independent variables is formed by T , q and Q whose behaviour in the course of time has to be described by means of evolution equations; no evolution equations will be formulated for the quantities ∇T and ∇q in contrast with the approach adopted by some authors [23, 24].

Since Q_{ij} is a symmetric tensor, we may decompose it into a bulk and a deviatoric part according to

$$Q_{ij} = \frac{1}{3} Q_{kk} \delta_{ij} + Q_{(ij)} \quad (4)$$

wherein brackets means a symmetric and traceless tensor:

$$Q_{(ij)} = Q_{ij} - \frac{1}{3} Q_{kk} \delta_{ij}.$$

In the following, for the sake of generality, we shall consider $Q_{(ij)}$ and Q_{kk} as independent variables.

2. The relevant equations

Let us now write down the evolution equations governing heat conduction in non-deformable isotropic bodies. We assume that the 'external' variables T and q have the so-called conservative form

$$\dot{\phi} = -\nabla \cdot \Phi + \sigma^\phi \quad (5)$$

involving the divergence of a flux Φ plus a dissipative contribution σ^ϕ ; ϕ stands for T and q respectively.

The evolution equation for the absolute temperature T is given by the balance of energy

$$\dot{u} = -q_{i,i} \quad (6)$$

wherein u is the internal energy per unit volume, energy sources are assumed to be absent. Energy is conserved because it is well known from phonon hydrodynamics that interactions of phonons with the lattice imperfections and the boundaries conserve energy but not necessarily momentum [25].

The second variable q satisfies the evolution equation

$$\dot{q}_i = -Q_{ij,j} + \sigma_i^q$$

wherein σ_i^q is a dissipative term to be given by a constitutive equation. However, since $Q_{(ij)}$ and Q_{kk} are considered as independent variables, the above relation lacks generality and will therefore be replaced by the more general expression

$$\dot{q}_i = -C^* Q_{(ij),j} - \frac{1}{3} D^* Q_{kk,i} + \sigma_i^q \quad (7)$$

where C^* and D^* are arbitrary dimensionless coefficients, which may depend on the temperature.

The next task is to formulate evolution equations for the bulk Q_{kk} and the deviatoric tensor $Q_{(ij)}$: it is assumed that their structure is no longer conservative but that they satisfy relations of the form

$$\dot{Q}_{(ij)} = \sigma_{(ij)}^Q \quad (8)$$

$$\dot{Q} = \sigma^Q \quad (9)$$

wherein $\sigma_{(ij)}^Q$ and σ^Q are the source terms to be given by constitutive equations. For simplicity we have used the notation

$$Q = \frac{1}{3} Q_{kk}.$$

Equations (8) and (9) do not contain a divergence term because $Q_{(ij)}$ and Q_{kk} have been identified as internal variables that cannot be controlled from the outside through the boundaries of the system. The set of relations (6)–(9) will be closed by appealing to constitutive relations for u , σ_i^q , $\sigma_{(ij)}^Q$ and σ^Q . These quantities will generally depend on the whole set of variables (T , q , Q) and the gradients of T and q , unless in contradiction with the general laws of thermodynamics. In the remainder of this paper, it is assumed that σ_i^q , $\sigma_{(ij)}^Q$ and σ^Q are linear functions of q_i , $Q_{(ij)}$, Q , $T_{,i}$ and $q_{i,j}$. Under this restriction, the most general expressions of σ_i^q , σ_{ij}^Q and σ^Q are given by

$$\sigma_i^q = -a^* q_i - b^* T_{,i} \quad (10)$$

$$\sigma_{(ij)}^Q = -A^* Q_{(ij)} - B^* q_{(i,j)} \quad (11)$$

$$\sigma^Q = -\alpha^* Q - \beta^* q_{k,k} \quad (12)$$

wherein all the coefficients with an asterisk may depend on the temperature; the expression of the internal energy need not to be specified at the present stage of the analysis. In a local theory all the terms involving $T_{,i}$ and $q_{i,j}$ should be dropped in (10)–(12). After substitution of the constitutive relations (10)–(12) in the evolution equations (7)–(9), one is led to

$$\dot{q}_i = C^* Q_{(ij),i} - D^* Q_{,i} - a^* q_i - b^* T_{,i} \quad (13)$$

$$\dot{Q}_{(ij)} = -A^* Q_{(ij)} - B^* q_{(i,j)} \quad (14)$$

$$\dot{Q} = -\alpha^* Q - \beta^* q_{k,k}. \quad (15)$$

For convenience, the following notation is introduced

$$\begin{aligned} \frac{1}{a^*} = \tau_1 & & \frac{C^*}{a^*} = c & & \frac{D^*}{a^*} = d & & \frac{b^*}{a^*} = \lambda \\ \frac{1}{A^*} = \tau_2 & & \frac{B^*}{A^*} = \eta & & \frac{1}{\alpha^*} = \tau_3 & & \frac{\beta^*}{\alpha^*} = \zeta \end{aligned} \tag{16}$$

from which it follows that expressions (13)–(15) take the form

$$\tau_1 \dot{q}_i = -c Q_{(ij),j} - d Q_{,i} - q_i - \lambda T_{,i} \tag{17}$$

$$\tau_2 \dot{Q}_{(ij)} = -Q_{(ij)} - \eta q_{(i,j)} \tag{18}$$

$$\tau_3 \dot{Q} = -Q - \zeta q_{k,k}. \tag{19}$$

By setting $c = 0$ and $d = 0$ in (17) one recovers Cattaneo’s equation (2). If in addition in (17) we put $\tau_1 = 0$ but λ finite, one obtains Fourier’s law (1) and this result allows us to identify the coefficient λ with the heat conductivity. It is interesting to observe that equations (18) and (19) have the same structure as the Maxwell equation of rheology if we replace $q_{i,j}$ by the velocity gradient tensor and Q_{ij} by the stress tensor respectively. The quantities τ_1 , τ_2 and τ_3 have the dimensions of time and will be called relaxation times, although at the present stage of the analysis, we have not proven that they are positive. Relations (17)–(19) coupled to the energy balance (6) are the basic relations of our model.

In the particular case of very slow variations of $Q_{(ij)}$ and Q in the course of time ($\tau_2 \dot{Q}_{(ij)} = \tau_3 \dot{Q} = 0$) one obtains by substituting in (17) the expressions of $Q_{(ij)}$ and Q drawn respectively from (18) and (19),

$$\tau_1 \dot{q}_i + q_i + \lambda T_{,i} = \frac{1}{2} c \eta (q_{i,jj} + \gamma q_{j,ji}) \tag{20}$$

with

$$\gamma = 2(d\zeta + c\eta/6)/c\eta.$$

Expression (20) can be identified with Guyer and Krumhansl’s equation [17]

$$\tau_R \dot{q}_i + q_i + \lambda T_{,i} = \frac{1}{3} \tau_R \tau_N c_s^2 (q_{i,jj} + 2q_{j,ji}) \tag{21}$$

where c_s is the velocity of sound under conditions to make the following identification:

$$\tau_1 = \tau_R \quad c\eta = 2\tau_R \tau_N c_s^2 / 5 \quad \gamma = 2. \tag{22}$$

$1/\tau_R$ is a measure of the frequency of the resistive processes while $1/\tau_N$ is related to the frequency of the normal processes where phonon momentum is conserved.

In passing it should be noticed that Guyer and Krumhansl’s equation (20) can directly be derived by utilizing only q_i as extra variable and by introducing non-locality. Indeed the most general evolution equation for q_i can be written as

$$\dot{q}_i = -J_{ij,j} + \sigma_i^q \tag{23}$$

with J_{ij} a flux term and σ_i^q a source term. Assuming that J_{ij} and σ_i^q are linear in q_i , $q_{i,j}$ and $T_{,i}$ one obtains

$$J_{ij} = -C^* q_{i,j} - D^* q_{k,k} \delta_{ij}$$

$$\sigma_i^q = -a^* q_i - b^* T_{,i}$$

wherein all the coefficients may depend on the temperature. Substituting the above expressions in (23), using the same notation as in (16) and omitting non-linear terms in $T_{,i} q_{i,j}$, it is found that

$$\tau \dot{q}_i + q_i + \lambda T_{,i} = \frac{1}{2} c [q_{i,jj} + (2d/c) q_{j,ji}]$$

which is clearly of the Guyer–Krumhansl type.

Going back to the set (17)–(19), let q_i and Q_{ij} tend to zero. It is then found that the gradient of temperature is zero while the energy balance (6) implies that $\partial T / \partial t = 0$; it is thus clear that $q_i = Q_{ij} = 0$ corresponds to the equilibrium state.

Up to now no restriction has been imposed either on the form of equations (17)–(19), or on the sign of the various coefficients. More information about the properties of these coefficients will be gained from thermodynamics and more particularly from the second law and the general property that the equilibrium state ($q_i = Q_{ij} = 0$) is stable. In order to explore the thermodynamic consequences, we have to introduce a non-equilibrium entropy per unit volume. It is supposed that such a potential function s exists with the following properties:

- (i) s is given by a constitutive relation depending on the whole set of variables,
- (ii) s is a convex function with a maximum value at equilibrium, and
- (iii) s obeys an evolution equation of the form

$$\dot{s} = -J_{i,i}^s + \sigma^s \quad (24)$$

with J_i^s the entropy flux vector and σ^s the entropy production, which according to the second law of thermodynamics is non-negative:

$$\sigma^s \geq 0. \quad (25)$$

3. Restrictions imposed by thermodynamics

We now explore the constraints placed by the property $\sigma^s \geq 0$. Since T is selected as independent variable, it is indicated to work with the Helmholtz free energy $f = u - Ts$ as basic function. In terms of f , the entropy balance (24) can be written as

$$T\sigma^s = \dot{u} - \dot{f} - s\dot{T} + T J_{i,i}^s \geq 0 \quad (26)$$

where f and J_i^s are *a priori* functions of the whole set T , q_i , $Q_{(ij)}$, Q . Concerning the expression of J_i^s we shall assume that it takes the form

$$J_i^s = (1/T) q_i + \beta Q_{(ij)} q_j + \beta' Q q_i \quad (27)$$

wherein β and β' are undetermined coefficients that are allowed to depend on the temperature. For $Q_{(ij)} \equiv Q = 0$, one recovers the classical results q_i/T as one should.

Applying the differentiation rule to calculate \dot{f} and making use of the evolution equations (6) and (17)–(19), relation (26) may be written, up to second-order terms in the fluxes and their derivatives, as

$$T\sigma^s = \left(\frac{\partial f}{\partial T} + s\right)\dot{T} + \frac{1}{\tau_1}\frac{\partial f}{\partial q_i}(q_i + \lambda T_{,i} + cQ_{(ij),j} + dQ_{,i}) + \frac{1}{\tau_2}\frac{\partial f}{\partial Q_{(ij)}}(Q_{(ij)} + \eta q_{(i,j)}) + \frac{1}{\tau_3}\frac{\partial f}{\partial Q}(Q + \zeta q_{k,k}) - \frac{1}{T}q_i T_{,i} + T(\beta Q_{(ij),i}q_j + \beta Q_{(ij)}q_{(j,i)} + \beta' Q_{,i}q_i + \beta' Q q_{i,i}) \geq 0. \tag{28}$$

In (28), third- and higher-order terms involving the products of the fluxes and the gradients of the variables have been omitted. Inequality (28), which is linear in the quantity \dot{T} , could be violated except if

$$\partial f/\partial T + s = 0. \tag{29}$$

With this result in mind, expression (28) takes the form

$$T\sigma^s = T_{,i}\left(\frac{\lambda}{\tau_1}\frac{\partial f}{\partial q_i} - \frac{q_i}{T}\right) + q_{(i,j)}\left(\frac{\eta}{\tau_2}\frac{\partial f}{\partial Q_{(ij)}} + \beta T Q_{(ij)}\right) + q_{k,k}\left(\frac{\zeta}{\tau_3}\frac{\partial f}{\partial Q} + \beta' T Q\right) + Q_{(ij),j}\left(\frac{c}{\tau_1}\frac{\partial f}{\partial q_i} + T\beta q_i\right) + Q_{,i}\left(\frac{d}{\tau_1}\frac{\partial f}{\partial q_i} + T\beta' q_i\right) + \frac{1}{\tau_1}\frac{\partial f}{\partial q_i}q_i + \frac{1}{\tau_2}\frac{\partial f}{\partial Q_{(ij)}} + \frac{1}{\tau_3}\frac{\partial f}{\partial Q}Q \geq 0. \tag{30}$$

Positiveness of expression (30) requires that all the terms in parentheses must vanish. It follows that

$$\frac{\partial f}{\partial q_i} = \frac{\tau_1 q_i}{\lambda T} \quad \frac{\partial f}{\partial Q_{(ij)}} = -T\frac{\beta}{\eta}\tau_2 Q_{(ij)} \quad \frac{\partial f}{\partial Q} = -\frac{T\beta'\tau_3 Q}{\zeta} \tag{31}$$

while β and β' are related to the quantities c , d and λ by

$$\beta = -c/\lambda T^2 \quad \beta' = -d/\lambda T^2. \tag{32}$$

Making use of the results (29), (31) and (32), the differential form of f is given by

$$df = -s dT + \frac{\tau_1}{\lambda T}q_i dq_i + \frac{c}{\lambda\eta T}\tau_2 Q_{(ij)} dQ_{(ij)} + \frac{\tau_3 d}{\lambda\zeta T}Q dQ. \tag{33}$$

This relation is usually called the generalized Gibbs equation. In the particular case that c and d are zero, the entropy flux and the Gibbs relation are simply

$$J_i^s = \frac{1}{T}q_i \quad df = -s dT + \frac{\tau_1}{\lambda T}q_i dq_i$$

in agreement with earlier developments of extended irreversible thermodynamics [8].

Making use of the results (31) and (32), expression (30) of $T\sigma^s$ simplifies as

$$T\sigma^s = \frac{q_i q_i}{\lambda T} + \frac{c}{\lambda \eta T} Q_{(ij)} Q_{(ij)} + \frac{d}{\lambda \zeta T} Q^2 \geq 0 \quad (34)$$

from which it follows that

$$\lambda > 0 \quad c/\eta > 0 \quad d/\zeta > 0. \quad (35)$$

After expanding f around its equilibrium value $f_{eq}(T)$ and taking into account that f_{eq} is extremum at equilibrium ($q_i = Q_{(ij)} = Q = 0$), it is found from (31) that

$$f = f_{eq} + \frac{1}{2} \frac{\tau_1}{\lambda T} q_i q_i + \frac{1}{2} \frac{c \tau_2}{\lambda \eta T} Q_{(ij)} Q_{(ij)} + \frac{1}{2} \frac{\tau_3 d}{\lambda \zeta T} Q^2. \quad (36)$$

Since f is minimum at equilibrium, one has

$$\frac{\tau_1}{\lambda} > 0 \quad \frac{c}{\eta} \frac{\tau_2}{\lambda} > 0 \quad \frac{d}{\zeta} \frac{\tau_3}{\lambda} > 0. \quad (37)$$

In virtue of the results (35), it can be concluded from (37) that the three relaxation times are positive, namely

$$\tau_1 > 0 \quad \tau_2 > 0 \quad \tau_3 > 0. \quad (38)$$

4. Onsager relations

In classical irreversible thermodynamics [4–7], the evolution equations of the state variables a^α can be given the general form

$$\dot{a}^\alpha = - \sum_{\beta} L^{\alpha\beta} \frac{\partial f}{\partial a^\beta} \quad (39)$$

where \dot{a}^α is the thermodynamic flux, $\partial f / \partial a^\beta$ the thermodynamic force, and $L^{\alpha\beta}$ the phenomenological coefficient. The latter obeys the relation

$$L^{\alpha\beta} = \pm L^{\beta\alpha} \quad (40)$$

wherein the sign + (respectively –) refers to state variables a^α and a^β with the same (respectively different) parity under time reversal. Expressions (40) are the celebrated Onsager–Casimir reciprocal relations.

It may be asked whether the Onsager–Casimir relations remain satisfied when the classical evolution equations (39) are replaced by more complicated equations like (17)–(19). Making use of the results (31) and (33), we can reformulate the evolution equations (17)–(19) as

$$\dot{q}_i = - \frac{\lambda \eta T}{\tau_1 \tau_2} \frac{\partial}{\partial x_j} \left(\frac{\partial f}{\partial Q_{(ij)}} \right) - \frac{\lambda \zeta T}{\tau_1 \tau_3} \frac{\partial}{\partial x_i} \left(\frac{\partial f}{\partial Q} \right) - \frac{\lambda T}{\tau_1^2} \frac{\partial f}{\partial q_i} - \frac{\lambda}{\tau_1} T_{,i} \quad (41)$$

$$\dot{Q}_{(ij)} = - \frac{\lambda \eta T}{c} \frac{\partial f}{\partial Q_{(ij)}} - \frac{\lambda \eta T}{\tau_1 \tau_2} \frac{\partial}{\partial x_{ij}} \left(\frac{\partial f}{\partial q_{ij}} \right) \quad (42)$$

$$\dot{Q} = - \frac{\lambda \zeta T}{\tau_1 \tau_3} \frac{\partial}{\partial x_k} \left(\frac{\partial f}{\partial q_k} \right) - \frac{\lambda \rho T}{d \tau_3^2} \frac{\partial f}{\partial Q}. \quad (43)$$

These equations may formally be cast in the form

$$\dot{a}^\alpha = -L^{\alpha\alpha} \frac{\partial f}{\partial a^\alpha} - \sum_\beta M^{\alpha\beta} \nabla \cdot \left(\frac{\partial f}{\partial a^\beta} \right) + \dots \quad (44)$$

where a^α stands for q_i , $Q_{(ij)}$ and Q respectively. It is directly checked from (41)–(43) that

$$M^{qQ} = M^{Qq} \equiv \lambda\eta T / \tau_1 \tau_2 \quad (45)$$

$$M^{qQ} = M^{Qq} \equiv \lambda\zeta T / \tau_1 \tau_3 \quad (46)$$

or more generally

$$M^{\alpha\beta} = M^{\beta\alpha} \quad (47)$$

The reciprocity relations (47) may be considered as generalizations of the Onsager–Casimir relations. The main difference is that the results (47) are derived on purely macroscopic grounds while Onsager–Casimir’s original relations could only be obtained by invoking supplementary hypotheses like time-reversal symmetry of equilibrium correlation functions and linear regression of fluctuations.

It is worth noticing that the argument leading to the symmetry of the coefficients $M^{\alpha\beta}$ parallels the demonstration given by Onsager himself, who postulated that the fluxes are the time derivatives of the state variables while the forces are the derivatives of a thermodynamic potential with respect to the state variables. These precepts are observed in (41)–(43) wherein the ‘fluxes’ are the time derivatives of the basic variables q , Q and Q while the forces are the gradients of the derivatives of f with respect to q , Q and Q respectively; it is rather natural that the gradients appear in our analysis as we are dealing with a non-local theory.

There is however one important difference with Onsager–Casimir’s results: it concerns the change of sign. Indeed the quantities q and Q have opposite parities under time reversal as Q arises from a higher-order moment with respect to molecular velocity than q . Therefore, one should expect skew symmetry according to Onsager–Casimir’s rules. But instead it is seen that relations (41)–(43) exhibit symmetry properties. The above observations seem to indicate that, under time reversal, microscopic reversibility requires not only that the sign of the time be reversed but also that of operator nabla: $\nabla \rightarrow -\nabla$. This result was justified among others by Vasconcellos *et al* [26] on the basis of microscopic arguments.

5. The temperature equation

From a practical point of view, equations (17)–(19) coupled to the energy balance (6) are not easily tractable as they involve quantities like Q and $Q_{(ij)}$, which are not directly accessible by experimental devices. In the present section, we shall eliminate these higher-order fluxes as well as the heat flux vector by combining (6) and (17)–(19): the outcoming result will be a partial differential equation for the temperature. The present analysis will be restricted to a first-order approximation with all the coefficients appearing in the evolution equations assumed to be constant. Under this hypothesis, the energy balance law can be written as

$$c_v \dot{T} = -q_{i,i} \quad (48)$$

wherein c_v is the heat capacity per unit volume. For simplicity, it is also supposed that the variable Q_{ij} is traceless ($Q = 0$) and the coefficient ζ of equation (19) is zero.

We first eliminate Q_{ij} between expressions (17) and (18). This operation leads to the following expression for the heat flux vector:

$$\tau_1 \tau_2 \ddot{q}_i = -\tau_1 \dot{q}_i - q_i - \lambda T_{,i} + \eta c_v q_{i,jj} - \tau_2 (\dot{q}_i + \lambda \dot{T}_{,i}). \tag{49}$$

The next step consists of eliminating q_i between (48) and (49): the final result is

$$\tau_1 \tau_2 \ddot{T} + (\tau_1 + \tau_2) \dot{T} + T - (\ell^2 + \tau_2 \chi) \dot{T}_{,ii} = \chi T_{,ii} \tag{50}$$

wherein $\ell^2 (= c_v \eta)$ measures the effects of the spatial inhomogeneities while $\chi (= \lambda/c_v)$ stands for the heat diffusivity. Expression (50) is similar to the temperature equation obtained by Gurtin and Pipkin [27] who worked in the framework of rational thermodynamics [15] with an internal energy u and a heat flux vector given by

$$u = u_0 + c_v T + \int_0^\infty F(s) T(t-s) ds \tag{51}$$

$$q_i = \int_0^\infty Q(s) T_{,i}(t-s) ds. \tag{52}$$

Here u_0 is a constant and $F(s)$ and $Q(s)$ are exponential memory kernels:

$$F(s) = F(0) \exp(-s/\tau_1) \quad Q(s) = Q(0) \exp(-s/\tau_2) \tag{53}$$

where τ_1 and τ_2 are relaxation times. It was proved [1, 26] that the differential equation (50) is hyperbolic, thus allowing for propagation of signals at finite speed.

By setting the relaxation time τ_2 equal to zero in (50), one obtains

$$\tau_1 \ddot{T} + \dot{T} - \ell^2 \dot{T}_{,ii} = \chi T_{,ii} \tag{54}$$

which is an equation of the Jeffreys type [1]. Equation (54) is parabolic and does not permit transmission of waves except if ℓ^2 vanishes. But setting $\ell^2 = 0$ amounts to smoothing out non-local effects in expression (54), which reduces to the well known telegraphist equation

$$\tau_1 \ddot{T} + \dot{T} = \chi T_{,ii}. \tag{55}$$

6. Wave propagation

For simplicity, we consider a one-dimensional problem with heat propagating along the x axis; the viscometric coefficients κ , ℓ and the relaxation times are assumed constants. We seek solutions of the form

$$\begin{pmatrix} T \\ q_x \\ Q_{xx} \end{pmatrix} = \begin{pmatrix} T_0 \\ q_0 \\ Q_0 \end{pmatrix} \exp[i(kx + \omega t)] \tag{56}$$

with $k = k' + ik''$ the complex wavenumber and ω the frequency. After substitution of (56) in the evolution equations (17), (18) and (48), one obtains the following dispersion relation between ω and k :

$$-i\omega = \frac{\kappa k^2}{1 + i\omega\tau_1 + [\ell^2/(1 + i\omega\tau_2)]k^2} \tag{57}$$

wherein as above $\ell^2 = c\eta$.

For $\ell = 0$ and within the limit $\tau_1 = \tau_2 = 0$, relation (57) can be written simply as

$$-i\omega = \kappa k^2. \tag{58}$$

The phase velocity v_{ph} is easily derived and given by

$$v_{ph} = k'/\omega = \sqrt{2\kappa\omega}. \tag{59}$$

As expected, v_{ph} tends to infinity for $\omega = \infty$ as (58) describes a pure diffusion process.

Assuming at present that $\ell \neq 0$, $\tau_1 \neq 0$ but τ_2 is negligibly small. As shown in section 2, these assumptions correspond to Guyer-Krumhansl's model. The phase velocity is now expressed by

$$v_{ph}^2 = 2\chi\omega / \left\{ \omega \left(\tau_1 - \frac{\ell^2 B}{\chi A} \right) + \left[\tau_1^2 \omega^2 + \frac{B^2}{A^2} + \frac{\ell^2 \omega^2 B}{\chi A} \left(\frac{\ell^2 B}{\chi A} - 2\tau_1 \right) \right]^{1/2} \right\} \tag{60}$$

wherein A and B stand respectively for $A = 1 + \omega^2 \ell^4 / \chi^2$, $B = 1 + \tau_1 \omega^2 \ell^2 / \chi$. In the limit of high frequencies, one has $B/A \simeq \tau_1 \kappa / \ell^2$ and it is checked that expression (60) reduces to

$$v_{ph} = \ell(2\omega/\tau_1)^{1/2} \tag{61}$$

which exhibits the property that v_{ph} grows indefinitely as ω is increased. This is not surprising because, as mentioned earlier, Guyer-Krumhansl's formalism leads to a diffusion equation of the Jeffreys type.

If in expression (57), we set $\tau_2 = 0$ and $\ell = 0$, which amounts to ignoring non-local effects, it is found that

$$v_{ph} = \left(\frac{2\chi\omega}{\tau_1\omega + \sqrt{1 + \tau_1^2\omega^2}} \right)^{1/2} \tag{62}$$

which is the result that one would have obtained directly from Cattaneo's equation (20). At high values of $\tau_1\omega$, expression (62) becomes

$$v_{ph} = (\chi/\tau_1)^{1/2} \tag{63}$$

and this regime is usually referred to as the second sound. It thus describes heat propagation in crystals for which $\tau_1\omega$ is large and $\ell \rightarrow 0$; according to (21) this corresponds to a regime where the frequencies $1/\tau_1$ of the resistive phonon interactions, i.e. non-preserving momentum collisions, is low. These conditions are met in crystals like NaF, Bi, LiF, ...

whose temperature is sufficiently high (larger than 12 K) [28, 29] to favour phonon-phonon interactions but at the same time the crystals must be pure enough to reduce the resistance.

Since in dielectric crystals at low temperature heat diffusivity is related to the relaxation time τ_R by [2, 17, 25]

$$\kappa = \frac{1}{3} c_s^2 \tau_1 \quad (64)$$

where c_s is sound velocity, it is inferred from (63) that the second sound waves have a velocity given by

$$v_{\text{ph}} = c_s / \sqrt{3} \quad (65)$$

which is in satisfactory agreement with experimental results [28, 29].

A last case of interest is that for which τ_1 and τ_2 are very large ($\omega\tau_1 \gg 1$, $\omega\tau_2 \gg 1$). The dispersion relation (57) reduces to

$$-i\omega = \frac{\chi k^2 (1 + i\omega\tau_2)}{i\omega(\tau_1 + \tau_2) + \ell^2 k^2 - \omega^2 \tau_1 \tau_2} \quad (66)$$

from which it follows that

$$v_{\text{ph}} = \left(\frac{\chi}{\tau_1} + \frac{\ell^2}{\tau_1 \tau_2} \right)^{1/2}. \quad (67)$$

This situation is more typical of ballistic phonons, i.e. phonons that travel through the crystal without interaction. Ballistic phonons are observed in pure crystals at sufficiently low temperature (below 15 K in NaF) and are characterized by vanishing frequencies of both resistive and conserving momentum collisions. Using the result (64) and the experimental evidence that ballistic phonons travel with the sound velocity, it is inferred from equation (67) that $v_{\text{ph}} = c_s$ is satisfied under the condition

$$\ell^2 = \frac{2}{3} \tau_1 \tau_2 c_s^2 (\omega\tau_1 \rightarrow \infty, \omega\tau_2 \rightarrow \infty). \quad (68)$$

Such a result is interesting as it provides an asymptotic relation between the phenomenological coefficients ℓ , τ_1 and τ_2 .

7. Summary and final comments

Propagation of second sound in dielectric crystals can be described in the framework of extended irreversible thermodynamics. This is achieved in the present work by selecting as basic variables the temperature T , the heat flux vector q and the flux of the heat flux Q . To include (weak) non-local effects, the constitutive equations have been assumed to depend in addition on the gradients of the temperature and the heat flux; the gradient of the flux of the heat flux has not been taken into account because it would correspond to higher-order non-local effects.

The main results that have been obtained can be summarized as follows.

(i) Evolution equations for the fluxes q and Q are proposed: the equation for the heat flux vector q generalizes Cattaneo's relation while the evolution equations for the deviatoric (Q) and bulk parts of Q are of the Maxwell type. The corresponding relaxation times are proved to be positive as a consequence of the minimum property of the Helmholtz free energy at equilibrium.

For very slow variations of $\langle Q \rangle$ in the course of time, one recovers the celebrated equation of Guyer and Krumhansl. However, these authors established their results on a completely different approach based on an analysis of Boltzmann's equation for a phonon gas.

(ii) The entropy flux J^s is no longer given by its classical expression q/T but contains supplementary contributions arising from the coupling of the variables Q and q , namely

$$J^s = (1/T)q + \beta \langle Q \rangle \cdot q + \beta' Qq. \quad (69)$$

Restrictions derived from the positiveness of the entropy production allows us to express the coefficients β and β' in terms of the other coefficients appearing in the evolution equations: in particular, it was shown (see equation (32)) that β and β' are proportional to the coefficients c and d respectively, which means that the presence of extra terms in (69) results essentially from non-locality.

(iii) As expected, Gibbs equation contains extra terms compared to the classical expression proposed in the frame of classical irreversible thermodynamics. It is worth stressing that the coefficients of the supplementary terms are not arbitrary but have been expressed in terms of known quantities like the relaxation times and the heat conductivity.

(iv) Onsager-Casimir's reciprocal relations are displayed. There is however a difference with the reciprocity relations of classical irreversible thermodynamics: indeed, the phenomenological coefficients are symmetric when they connect two processes with the same parity under time reversal and skew symmetric for processes of different parities. Here it was found that the coefficients are symmetric for processes with different parities. However, these results are not in contradiction with Onsager-Casimir's because we are working in a different context. Indeed in Onsager-Casimir's approach, the phenomenological coefficients relate fluxes \dot{a}^α with forces of the form $\partial f / \partial a^\alpha$ while in the present analysis the forces are expressed in terms of the gradient of $\partial f / \partial a^\alpha$.

(v) In the linear approximation, it is an easy task to eliminate the variables q and Q and to obtain a single equation involving only the temperature as variable. The relevant equation is a partial differential hyperbolic equation allowing for the propagation of waves with finite speed and containing the telegraph equation as a particular case.

(vi) Finally one has calculated the phase velocities corresponding to different transports of energy in a phonon gas. These are useful as they relate accessible experimental data, like phase velocities, to the various parameters appearing in the phenomenological description.

Of course, it must be realized that the model presented here provides only partial information as it contains a limited number of variables, 10 in total. Formally, there would be no difficulty to introduce more variables like higher-order fluxes but this would unduly complicate the formalism and generate more and more unknown coefficients whose physical meaning would be difficult to interpret.

Acknowledgments

This paper was initiated during the stay of one of the authors (GL) at the Department of Mathematics of the University of Catania thanks to a grant of the Consiglio Nazionale

delle Recherche (CNR). This work is also partially supported by an EC Human Capital and Mobility Program, under contract CHRX-CT-92-0007, MURST (fondi 40% and 60%) and Progetto Strategico 'Applicazioni della Matematica per la Tecnologia e la Societa' (1994) of GNFM (CNR). Fruitful discussions with Professors D Jou and J Casas-Vazquez (Universitat Autònoma de Barcelona) are acknowledged.

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