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# Extended thermodynamics revisited: renormalized flux variables and second sound in rigid solids

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## Abstract

Propagation of heat waves in rigid bodies is investigated. The originality of the approach is that it rests on a revisited version of extended irreversible thermodynamics. In comparison with earlier developments, two innovations are proposed. First, we depart from the linear approach, best illustrated by Cattaneo's relation, to explore the non-linear regime. Second, the extra variables are no longer the usual dissipative fluxes, but renormalized expressions of the fluxes, in order to include the specific material properties of the systems under study. The present model is particularly well suited for studying heat transport at low temperatures in dielectric crystals.

## 1. Introduction

In this work, we propose a non-linear model of heat transport in rigid conductors based on extended irreversible thermodynamics (EIT), a non-equilibrium thermodynamic formalism developed two decades ago among others by Jou, Casas-Vázquez and Lebon [1] and Müller and Ruggeri [2]. The basic idea underlying EIT is to upgrade the physical fluxes of energy, matter and momentum to the status of independent variables at the same level as the classical variables like energy, mass, and momentum. The motivations for this selection is that these fluxes are typically non-equilibrium quantities vanishing at equilibrium. This choice is rather natural because the only accessibility to a system is through its boundaries. Moreover, in high frequencies processes like ultrasound propagation, or systems with large relaxation times like polymers, the fluxes lose their status of fast and negligible variables and must be included in the space of state variables. This choice finds also its roots in the kinetic theory of gases, wherein it is frequent to select the higher moments of the velocity distribution as variables as suggested by Grad's thirteen-moment theory [3]. An important problem is to determine the time evolution

equations of the new flux variables. In the problem of heat conduction in rigid bodies, the extra variable is selected as the heat flux vector  $\mathbf{q}$ . The simplest evolution equation for  $\mathbf{q}$  is given by

$$\tau \partial_t \mathbf{q} = -\lambda \nabla T - \mathbf{q}, \quad (1)$$

which is the celebrated Cattaneo's relaxation relation [4],  $T$  designating the temperature,  $\lambda$  the heat conductivity and  $\tau$  the relaxation time. For negligible values of  $\tau$ , expression (1) reduces to Fourier's law  $\mathbf{q} = -\lambda \nabla T$ . The term in  $\tau$  is responsible for inertial effects and allows to circumvent the paradox associated with Fourier's law, i.e. that heat will be felt instantaneously and everywhere in space after the application of a temperature gradient. Cattaneo's relation is also compatible with experiences in superfluids like He II exhibiting the property that heat propagates as a true wave, called the second sound.

However, the selection of the fluxes is open to some criticisms [5] as they constitute the response to interactions generally expressed in terms of gradients of intensive variables rather than expressing intrinsic non-equilibrium features of the systems. Moreover most applications of EIT concern the linear regime, i.e. linear constitutive relations and evolution equations of the Cattaneo type. It should nevertheless be

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stressed that recently, efforts have been devoted to cover non-linear situations as encountered for instance in radiative heat transfer, dusty plasmas and rapid phase transformations (e.g. [1, 2, 6]).

The aim of the present work is twofold. First, to replace the classical heat flux variable  $\mathbf{q}$  by a normalized expression, taking into account of the constitutive properties of the heat conductor, like the heat conductivity and the relaxation time. The explicit form of this normalized variable will not be arbitrary but imposed by the second principle of thermodynamics. Other reasons to prefer this new variable to the heat flux  $\mathbf{q}$  will be made more explicit in the next section. The second objective of this paper is to generalize the linear Cattaneo's relation by including non-linear contributions.

The procedure may be easily extended to other processes as matter diffusion or electrical conduction, wherein the flux of diffusion and the electrical current will be replaced by new 'weighted' fluxes including the diffusion coefficient and the electrical resistivity respectively. Incorporating the material properties of the system into the definition of the non-equilibrium variables offers an interesting alternative and broadening of the space of state variables. A first step in this direction can be found in a previous paper [8] by two of the authors wherein  $\mathbf{q}/\lambda$  was selected as variable. In the present work, we propose a more general formulation which is shown to be particularly well suited to describe waves and shocks propagations in heat conductors.

In earlier EIT analyses of rigid heat conductors (e.g. [1, 2, 7]), the space of state variables was formed by the union of the classical variable  $u$ , the internal energy per unit volume, and the corresponding energy flux, i.e. the heat flux vector  $\mathbf{q}$ . Here, we depart from this attitude by replacing the set  $(u, \mathbf{q})$  by the set  $(T, \mathbf{c})$  where  $T$  is the temperature and  $\mathbf{c}$  the new flux variable. The laws of transformation are given by

$$u, \mathbf{q} \rightarrow T, \mathbf{c}, \quad (2)$$

with

$$u = u(T, c^2), \quad (3)$$

$$\mathbf{q} = g(T, c^2)\mathbf{c}, \quad (4)$$

wherein  $c^2 = \mathbf{c} \cdot \mathbf{c}$ . Expression (4) provides the definition of the new variable  $\mathbf{c}$  with the factor  $g(T, c^2)$  playing the role of a 'weighting' function whose explicit expression will be determined later on from thermodynamic considerations. It will be shown that  $g$  depends explicitly on the heat conductivity  $\lambda(T)$  and the relaxation time  $\tau(T)$ . The results presented in this work generalize and unify previous analyses [8–11].

The paper will run as follows. In section 2 are formulated the non-linear evolution equations of the basic variables:  $T$  is obeying the well-known energy balance but the time evolution of  $\mathbf{c}$  is *a priori* unknown and will therefore be expressed in a rather general form in terms of the divergence of a flux and a source term. This evolution equation cannot take any possible form but must satisfy the restrictions imposed by the second law of thermodynamics requiring that the rate of entropy production is a positive definite quantity. The constraints placed by the second law are discussed in section 3 and detailed in an appendix by appealing to a particularly elegant technique

due to Liu [12]. Non-linear constitutive relations of the internal energy, the Helmholtz free energy and the entropy flux are formulated. In contrast with earlier analysis, these expressions are not postulated from the outset but are obtained as derived results. Another important result is that, as a bonus, we obtain the explicit expression of the weighting function  $g(T, c^2)$ . Identification of all the phenomenological coefficients, at the exception of a single one, and information about their sign are found in section 4. The remaining undetermined coefficient is obtained from an analysis of propagation of waves (section 5) and shocks (section 6). Experimental data about shock waves in NaF and Bi dielectric crystals at low temperature are presented in section 7. Concluding comments and comparison with earlier works are found in the final section (section 8).

## 2. A non-linear model of heat conduction in rigid bodies

Consider an isotropic rigid heat conductor at rest. In the classical theory of irreversible processes (e.g. [13]), the temperature distribution inside the body is obtained by solving the energy balance

$$\partial_t u = -\nabla \cdot \mathbf{q}, \quad (5)$$

which is also referred to as the first law of thermodynamics, by writing (5) it is understood that heat sources are absent. To close the description, two constitutive equations for  $u(T)$  and  $\mathbf{q}$  are needed, the first one is  $u(T) = \int c_{ve}(T)dT$  with  $c_{ve}$  the positive heat capacity at local equilibrium, the second being usually given by Fourier's law. The corresponding temperature equation

$$c_{ve}\partial_t T = \nabla \cdot (\lambda \nabla T) \quad (6)$$

is a parabolic partial differential equation with the drawbacks of predicting propagation of signals with infinite velocity and to be inapplicable to high frequency processes and short wavelength phenomena [1, 2].

In the present work, the classical approach [13] will therefore be abandoned on behalf of EIT. In this formalism, the heat flux is upgraded to the status of independent variable and obeys an evolution equation which, in the simplest case, is of the Cattaneo type (1). Our purpose in the present work is to go a step further compared to the usual developments of EIT. First, instead of  $\mathbf{q}$ , we select a more general variable  $\mathbf{c}$  defined by

$$\mathbf{q} = g(T, c^2)\mathbf{c}, \quad (7)$$

where  $g(T, c^2)$  is a kind of weighting function. Selecting  $\mathbf{c}$  rather than  $\mathbf{q}$  is equivalent in a certain sense to a renormalization procedure. The choice of  $\mathbf{c}$  is essentially motivated by the objective to concentrate into one single variable, a maximum of non-equilibrium transport properties of the system. Since the factor  $g$  is generally not dimensionless, the new variable  $\mathbf{c}$ , unlike  $\mathbf{q}$ , will not have the dimension of a flux of energy.

In terms of  $\mathbf{c}$  and in Cartesian coordinates, the first law (5) takes the form

$$\partial_t u = -g_{,i}c_i - gc_{i,i}. \quad (8)$$

with  $u$  a function of  $T$  and  $c^2$ . The second advancement with respect to previous developments of EIT is that the evolution of the ‘flux’ variable  $\mathbf{c}$  is no longer governed by a linear Cattaneo type equation, but rather by a non-linear expression of the general form

$$\partial_t c_i = \Phi_{ij,j} + \sigma_i^c, \quad (9)$$

the quantity  $\Phi$ , a second order tensor, stands for the flux of  $\mathbf{c}$ , while the vector  $\sigma^c$  represents the source term, summation convention on repeated indices will be used throughout this work. To summarize, heat transport is assumed to be described by the set of variables  $(T, \mathbf{c})$  whose time evolution is expressed by the balance laws (8) and (9). A complete description requires to close this set of differential equations by constitutive equations for  $u$ ,  $\Phi$  and  $\sigma^c$  in terms of the state variables  $T$  and  $\mathbf{c}$ . Here, we restrict our analysis to the second order of approximation in  $\mathbf{c}$ , meaning that the components  $\Phi$  and  $\sigma^c$  will be given by

$$\Phi_{ij} = D(T)\delta_{ij} + D_0\left(\frac{1}{2}c^2\delta_{ij} + c_i c_j\right), \quad (10)$$

$$\sigma_i^c = -\frac{1}{\tau(T)}c_i, \quad (11)$$

where  $\delta_{ij}$  is the Kronecker’s symbol,  $D(T)$  and  $\tau(T)$  are two scalar functions of  $T$  while the coefficient  $D_0$  is supposed to be independent of  $T$ , we will see in the forthcoming that this assumption can be given up without difficulty. At this stage of the analysis,  $D_0$ ,  $D$  and  $\tau$  are undetermined coefficients. Expressions (10) and (11) provide the simplest non-linear modelling generalizing Cattaneo’s equation. Recalling that  $g$  is a function of  $T$  and  $c^2$ , the energy balance equation (8) will be written as

$$\partial_t u + g_T c_i T_{,i} + 2g^* c_i c_j c_{j,i} + g c_{i,i} = 0, \quad (12)$$

with the following notation:  $\xi_T = \partial\xi/\partial T$ ,  $\xi^* = \partial\xi/\partial c^2$ ,  $\xi(T, c^2)$  being a generic function of both  $T$  and  $c^2$ . After substitution of (10) and (11) in the evolution equation (9) of  $\mathbf{c}$ , one is led to

$$\partial_t c_i - D'T_{,i} - D_0(c_j c_{j,i} + c_j c_{i,j} + c_i c_{j,j}) + \frac{1}{\tau}c_i = 0, \quad (13)$$

where we are using the upper prime to denote the derivative  $d/dT$  of a quantity depending only of the temperature.

Equations (12) and (13) constitute the basic relations of the model, besides the two state variables  $T$  and  $\mathbf{c}$ , they involve four undetermined functions:  $g$ ,  $\tau$ ,  $D$  and  $D_0$  to be expressed in terms of  $T$  and  $\mathbf{c}$  by means of constitutive equations. Interesting information about them will be provided by the second law of thermodynamics and will be examined in the next section.

### 3. Restrictions placed by the second law of thermodynamics

The second law states that the rate of entropy production per unit volume  $\sigma^s$  is a positive definite quantity, it is defined through the entropy balance written as

$$\sigma^s = \partial_t s + J_{i,i}^s \geq 0, \quad (14)$$

wherein  $s$  is the entropy per unit volume and  $\mathbf{J}^s$  the entropy flux vector, both quantities depending on  $T$  and  $c^2$ . Without loss of generality, we may assume that  $\mathbf{J}^s$  is collinear with  $\mathbf{c}$ ,

$$J_i^s = \gamma(T, c^2)c_i, \quad (15)$$

where  $\gamma(T, c^2)$  is an undetermined function of the variables, to be specified later on.

Since the temperature is one of the state variables, it is natural to work with the Helmholtz free energy  $f = u - Ts$ . The entropy inequality reads now as

$$T\sigma^s = \partial_t u - \partial_t f - s\partial_t T + T J_{i,i}^s \geq 0, \quad (16)$$

wherein  $\partial_t u$  is given by the energy balance (12).

The consequences of inequality (16) are established in the appendix. The most relevant results are the following:

- (1) The weighting factor  $g(T, c^2)$  takes the form

$$g(T, c^2) = \frac{\lambda}{\tau} + \alpha(T)c^2, \quad (17)$$

with  $\alpha(T)$  given by

$$\alpha(T) = -D_0 T^2 \left( \frac{\lambda}{T^2 D' \tau} \right)', \quad (18)$$

$\lambda(T)$  is an arbitrary functions of  $T$ , which will be identified later on as the heat conductivity,  $\tau(T)$  is the phenomenological coefficient still introduced in equation (11).

- (2) The constitutive equations of the Helmholtz free energy  $f(T, c^2)$  and internal energy  $u(T, c^2)$  read as

$$f(T, c^2) = f_e(T) - \frac{\lambda}{2T D' \tau} c^2, \quad (19)$$

$$u(T, c^2) = u_e(T) + \frac{1}{2} T^2 \left( \frac{\lambda}{T^2 D' \tau} \right)' c^2, \quad (20)$$

with subscript e referring to the local equilibrium value, defined by  $\mathbf{c} = \mathbf{0}$ .

- (3) The entropy flux and entropy production are given by

$$J_i^s = \frac{1}{T} (g + 2D_0 f^* c^2) c_i, \quad (21)$$

$$\sigma^s = \frac{2}{T\tau} f^* c^2 \geq 0. \quad (22)$$

It is observed that the above expressions depend, among others, on the quantities  $\lambda(T)$ ,  $\tau(T)$  and  $D(T)$  which did not receive a physical interpretation so far. This will be achieved in the next section.

### 4. Identification of the coefficients $\lambda$ , $\tau$ , $D$

Within the linear approximation in the fluxes, i.e.  $D_0 = 0$ , it is clear from (18) that the coefficient  $\alpha(T)$  vanishes so that the weighting factor  $g$  is equal to  $\lambda/\tau$  with the consequence that  $\mathbf{c} = (\tau/\lambda)\mathbf{q}$ . The evolution equation (13) of  $\mathbf{c}$  writes then as

$$\partial_t \left( \frac{\tau}{\lambda} q_i \right) - D'T_{,i} = -\frac{1}{\lambda} q_i. \quad (23)$$

This equation is of the Grioli type [8], and generalizes Cattaneo's relation (1), which is obtained by supposing that the ratio  $\tau/\lambda$  is constant.

Since it is required that our model contains the Cattaneo and Fourier laws as particular cases, it is inferred that  $\lambda(T)$  and  $\tau(T)$  can be identified as the heat conductivity and the relaxation time of the flux respectively and that moreover

$$D' = -1. \quad (24)$$

Integration with respect to the temperature leads directly to the expression of  $D(T) = -T$ . These results are important as they allow us to express the weighting parameter  $g$  as well as the thermodynamic potentials  $f$  and  $u$  in terms of physical quantities as the heat conductivity  $\lambda(T)$  and relaxation time  $\tau(T)$ , the results are:

$$g = \frac{\lambda}{\tau} - 2D_0\beta(T)c^2, \quad (25)$$

$$f = f_e(T) + \frac{1}{2} \frac{\lambda}{T\tau} c^2, \quad (26)$$

$$u = u_e(T) + \beta(T)c^2, \quad (27)$$

with

$$\beta(T) = -\frac{1}{2}T^2 \left( \frac{\lambda}{T^2\tau} \right)'. \quad (28)$$

At this stage, a comment is in form. In the particular case that  $\lambda/(T^2\tau) = \text{constant}$ , it is seen that  $\beta = 0$ , with the consequences that  $g = \lambda/\tau$  while  $u$  reduces to its local equilibrium value. Concomitantly, expression (26) of  $f$  writes as

$$f = f_e(T) + \frac{1}{2} \frac{\tau}{\lambda T} q^2, \quad (29)$$

in agreement with Grad's kinetic theory [3] and earlier developments of EIT [1, 2].

The next point is to obtain the expression of the entropy flux  $\mathbf{J}^s$ . Taking into account of (17) and (19), relation (21) reads as

$$J_i^s = \frac{\lambda}{T\tau} c_i + D_0 \left( \frac{\lambda}{T\tau} \right)' c^2 c_i. \quad (30)$$

In the linear approximation ( $D_0 = 0$ ), expression (30) boils down to the classical relation  $\mathbf{J}^s = \mathbf{q}/T$  [13]. This observation exhibits the strong connection between dynamics (i.e. the evolution equation of  $\mathbf{c}$ ) and thermodynamics (i.e. the expression of the entropy flux). For  $D_0 = 0$ , the evolution equation of  $\mathbf{c}$  is linear, of the Cattaneo type, and the entropy flux is the local equilibrium one, still linear in the flux. In the case  $D_0 \neq 0$ , the evolution equation of  $\mathbf{c}$  is non-linear in the flux and this property is automatically reflected in the expression of the entropy flux.

We will end this section by examining the consequences issued from the positiveness of the entropy production and the stability properties of equilibrium. According to (22) and (26), the entropy production can be written as

$$\sigma^s = \frac{\lambda}{(T\tau)^2} c^2 \geq 0 \quad (31)$$

and positiveness of  $\sigma^s$  requires that the heat conductivity is positive:

$$\lambda > 0. \quad (32)$$

Moreover, stability properties impose that Helmholtz's free energy is minimum in local equilibrium at fixed values of temperature and volume. It follows then from (26) that  $\lambda/\tau > 0$ , which coupled to inequality (32), leads to

$$\tau > 0, \quad (33)$$

indicating that the relaxation time is indeed positive. Up to now, we were not able to provide any information about the last undetermined coefficient  $D_0$ . It is shown in the next two sections that useful enlightenments are provided by an analysis of waves and shocks propagation.

## 5. Waves propagation and hyperbolicity

In this section, we study the propagation of heat waves in rigid solids on the basis of the model described by the evolution equations (12) and (13) for  $T$  and  $\mathbf{c}$  and the constitutive equation (27) for  $u$ . For simplicity, let us assume one-dimensional waves,  $T \equiv T(x, t)$  and  $\mathbf{c} \equiv c(x, t)$ , propagating along the positive  $x$ -direction. Referring to the classical procedure [14], one considers a smooth surface of equation  $\varphi(x, t) = 0$  propagating through the body. It is supposed that across the surface, the state variables  $T$  and  $c$  are continuous but their first order derivatives suffer discontinuities defined by

$$\delta = \left( \frac{\partial}{\partial \varphi} \right)_{\varphi=0^+} - \left( \frac{\partial}{\partial \varphi} \right)_{\varphi=0^-}. \quad (34)$$

Making use of the standard transformations

$$\partial_t \rightarrow -v\delta, \quad \partial_x \rightarrow \delta, \quad (35)$$

with  $v$  the wave speed, one obtains from equations (12) and (13) a system of two homogeneous algebraic relations for the discontinuities  $\delta T$  and  $\delta c$ :

$$(g_T c - v u_T) \delta T + \left[ \frac{\lambda}{\tau} - 2\beta(v + 3D_0 c) c \right] \delta c = 0, \quad (36)$$

$$\delta T - (v + 3D_0 c) \delta c = 0. \quad (37)$$

The linear set (36) and (37) has non-trivial solutions at the condition that the following characteristic polynomial is satisfied:

$$P(v) \doteq u_T v^2 - (g_T - 2\beta - 3D_0 u_T) c v - 3D_0 (g_T - 2\beta) c^2 - \frac{\lambda}{\tau} = 0. \quad (38)$$

In virtue of (38), the system of equations (12) and (13) is hyperbolic if and only if

$$\Delta \doteq [(g_T - 2\beta + 3D_0 u_T) c]^2 + 4 \frac{\lambda}{\tau} u_T > 0, \quad (39)$$

which implies that  $u_T$  is positive; in virtue of (27),  $u_T$  can be expressed as

$$u_T = c_{ve} + \beta' c^2 > 0. \quad (40)$$

Defining  $u_T$  as the heat capacity  $c_v(T, c^2)$  outside equilibrium, one may therefore conclude that positiveness of  $c_v(T, c^2)$  implies hyperbolicity. However, in the case that  $\beta' < 0$ , this property is not guaranteed for any value of the variable  $c$  but only for these values smaller than its upper bound which, according to (40), is equal to

$$|c_{\max}| = \sqrt{\frac{c_{ve}}{|\beta'|}}. \quad (41)$$

The slopes of the characteristic lines, i.e. the characteristic velocities corresponding to (38) are given by

$$v^\pm(T, c) = \frac{(g_T - 2\beta - 3D_0u_T)c \pm \sqrt{\Delta}}{2u_T}. \quad (42)$$

In equilibrium for which  $c = 0$ , the velocities of propagation are simply

$$v_0^\pm = \pm \sqrt{\frac{\lambda}{\tau c_{ve}}}. \quad (43)$$

In principle, measurements of the velocities of propagation (42) will offer a mean to determine the only left undetermined coefficient  $D_0$ . Unfortunately, to our knowledge, no experimental data outside equilibrium are available. Although careful experiments on second sound have been performed in dielectric crystals at low temperature ( $< 20$  K) [15–17], they concern only equilibrium velocities  $v_0$  but these data are of no help for the determination of the quantity  $D_0$  which is absent from expression (43). A way out is proposed in the next section wherein propagation of shock waves in dielectric crystals is investigated.

## 6. Shock waves

A possible mean to determine the undetermined coefficient  $D_0$  can be obtained from a shock waves analysis. To be explicit, consider the propagation of one-dimensional shock waves travelling in a medium initially in equilibrium with  $(T, c) = (T_0, 0)$ . In contrast with the previous section, we now assume a smooth surface propagating through the body across which the functions  $T(x, t)$  and  $c(x, t)$  may suffer jumps. We first establish the Rankine–Hugoniot equations reflecting the compatibility conditions for the existence of shocks. They are obtained by making the following substitutions in the evolution relations (12) and (13):

$$\partial_t \rightarrow -\Sigma[\cdot], \quad \partial_x \rightarrow [\cdot], \quad (44)$$

wherein  $\Sigma$  is the shock wave speed,  $[\xi] = \xi - \xi_0$  denoting the jump between a generic quantity  $\xi$  in the perturbed state ( $\xi$ ) behind the shock wavefront and the unperturbed value ( $\xi_0$ ) ahead of the front. The results of this procedure are

$$-\Sigma [u_e + \beta c^2] + [(\lambda/\tau - 2D_0\beta c^2)c] = 0, \quad (45)$$

$$-\Sigma [c] + [T - (3/2)D_0c^2] = 0. \quad (46)$$

Expressions (45) and (46) constitute an algebraic set of three scalar unknowns  $T$ ,  $c$  and  $\Sigma$  in terms of the assigned

unperturbed field  $(T_0, 0)$ . By taking the perturbed temperature  $T$  as the shock parameter and solving with respect to  $\Sigma$  and  $c$ , one obtains

$$\begin{aligned} & \beta(T)\Sigma^4(T, T_0) - \left\{ \beta(T) \left[ \frac{\lambda(T)}{\tau(T)} - \beta(T)(T - T_0) \right] \right. \\ & \quad \times \frac{(T - T_0)}{u_e(T) - u_e(T_0)} + D_0 \left[ \frac{27D_0 [u_e(T) - u_e(T_0)]}{4} \right. \\ & \quad \left. \left. - 9\beta(T)(T - T_0) + \frac{9\lambda(T)}{2\tau(T)} \right] \right\} \Sigma^2(T, T_0) \\ & \quad + D_0 \left\{ \beta(T)(T - T_0) \left[ 8\beta(T)(T - T_0) \right. \right. \\ & \quad \left. \left. - \frac{12\lambda(T)}{\tau(T)} \right] + \frac{9\lambda^2(T)}{2\tau^2(T)} \right\} \frac{(T - T_0)}{u_e(T) - u_e(T_0)} = 0, \end{aligned} \quad (47)$$

$$c(T, T_0) = \frac{-\Sigma(T, T_0) \pm \sqrt{\Sigma^2(T, T_0) + 6D_0(T - T_0)}}{3D_0}. \quad (48)$$

In (48), one must select the sign plus when  $\Sigma > 0$  and minus when  $\Sigma < 0$  in order to satisfy the condition  $\lim_{T \rightarrow T_0} c(T, T_0) = 0$ .

It is well known that, among the mathematical solutions of the Rankine–Hugoniot equations, only the stable ones are physically admissible. A well accepted stability criterion was proposed by Lax [18]. Accordingly, the admissible shocks are those for which the shock velocity is greater than the unperturbed characteristic velocity  $v_0(T_0)$  ahead of the shock front and less than the perturbed one  $v(T_0, T)$  behind the front. In our case, by choosing  $\Sigma(T_0, T) > 0$ , the Lax conditions read as

$$0 < v_0(T_0) < \Sigma(T_0, T) < v(T_0, T), \quad \lim_{\Sigma \rightarrow v_0(T_0)} T = T_0, \quad (49)$$

where, the unperturbed velocity is given by expression (43) evaluated at  $T = T_0$ , while the expression of the perturbed characteristic velocity  $v(T_0, T)$  is obtained by substitution of the solution (48) in (42). Moreover, as pointed out by Ruggeri *et al* [19], there exists a critical value  $T_0 = T_c$  of the unperturbed temperature at which no shock is admissible. These authors have also demonstrated that the critical value  $T_c$  corresponds to a maximum of the so-called shape function  $\psi(T)$ . These observations are important as they allow us to establish the link between the undetermined coefficient  $D_0$  and the critical temperature  $T_c$ . By following the same procedure as in [19], it is found that the shape function  $\psi(T)$  is here given by

$$\psi(T) = \frac{v_0^3 c_{ve}}{T} e^{-\frac{3}{2} D_0 \int v_0^{-2} dT}, \quad (50)$$

it has stationary points for values of the temperature  $T_c$  which are solution of the following equation:

$$\frac{c_{ve}'(T_c)}{c_{ve}(T_c)} + 3 \frac{v_0'(T_c)}{v_0(T_c)} - \frac{1}{T_c} - \frac{3}{2v_0^2(T_c)} D_0 = 0. \quad (51)$$

Solving (51) with respect to  $D_0$  yields

$$D_0 = \frac{2}{3} \left[ v_0^2 \left( \ln \frac{c_{ve} v_0^3}{T} \right)' \right]_{T=T_c}, \quad (52)$$

wherein all the quantities in the right-hand side are available from experimental data (see next section). Measurements on dielectric crystals at low temperature have also shown that the critical temperature  $T_c$  can be identified with the measured value at which second sound is experimentally detected [15–17].

### 7. Experimental data and shock waves

Accurate measurements on heat pulse propagations [15–17] have been carried out in NaF and Bi dielectric crystals at low temperature ( $<20$  K), under equilibrium conditions with uniform temperature  $T_0$  and  $\mathbf{c} = \mathbf{0}$ . It was found [20] that the temperature dependence of the velocity of propagation  $v_0$  is well fitted by an empirical law of the form

$$v_0^2 = \frac{1}{A + BT^n}, \quad (53)$$

where  $A$ ,  $B$  and  $n$  are constants taking the following values in SI units:

$$\begin{aligned} A &= 9.09 \times 10^{-8}, & B &= 2.22 \times 10^{-11}, \\ n &= 3.1 & \text{for NaF,} \\ A &= 9.07 \times 10^{-7}, & B &= 7.58 \times 10^{-9}, \\ n &= 3.75 & \text{for Bi.} \end{aligned}$$

Referring to Debye’s law, at low temperatures, the heat capacity of dielectric crystals varies with  $T$  according to

$$c_{ve} = \epsilon T^3, \quad (54)$$

where  $\epsilon = 2.3 \text{ J m}^{-3} \text{ K}^{-4}$  for NaF and  $\epsilon = 55 \text{ J m}^{-3} \text{ K}^{-4}$  for Bi. In virtue of (43), (53) and (54), the ratio  $\lambda/\tau$  is a well determined function of the temperature expressed by

$$\frac{\lambda}{\tau} = \frac{\epsilon T^3}{A + BT^n}. \quad (55)$$

This result is interesting as it provides a mean to calculate the value of the relaxation time once the heat conductivity is known.

It should however be stressed that the above data are only valid in the temperature range in which the second sound is observed, i. e.  $10 \text{ K} \leq T \leq 18.5 \text{ K}$  for NaF and  $1.4 \text{ K} \leq T \leq 4 \text{ K}$  for Bi.

Taking into account expressions (53) and (54), it is a simple matter to show that there exists only one maximum for the shape function  $\psi$  and, consequently only one single value of the critical temperature  $T_c$  at which no shock is possible. According to (52), the corresponding value of  $D_0$  is

$$D_0 = \frac{4A - (3n - 4)BT_c^n}{3T_c(A + BT_c^n)^2}. \quad (56)$$

The value of  $T_c$  corresponding to the linear approximation [8], i.e.  $D_0 = 0$ , is given by

$$T_c^{\text{lin}} = \left[ \frac{4A}{((3n - 4)B)} \right]^{1/n} \quad (57)$$

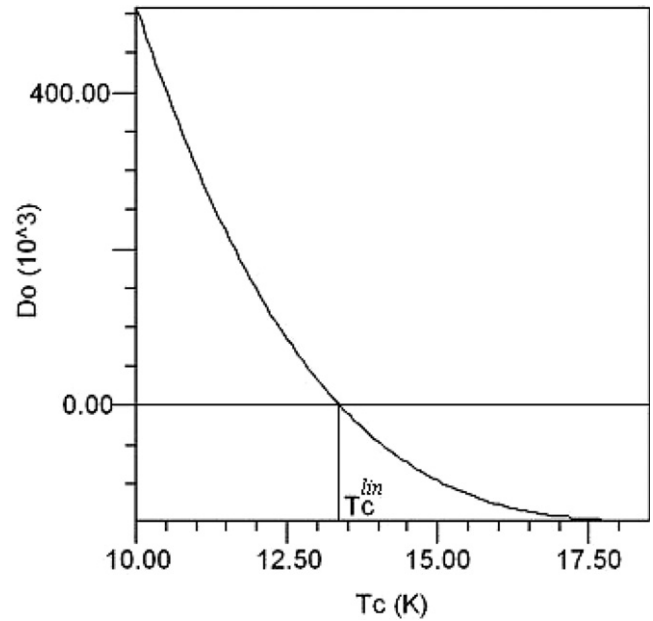
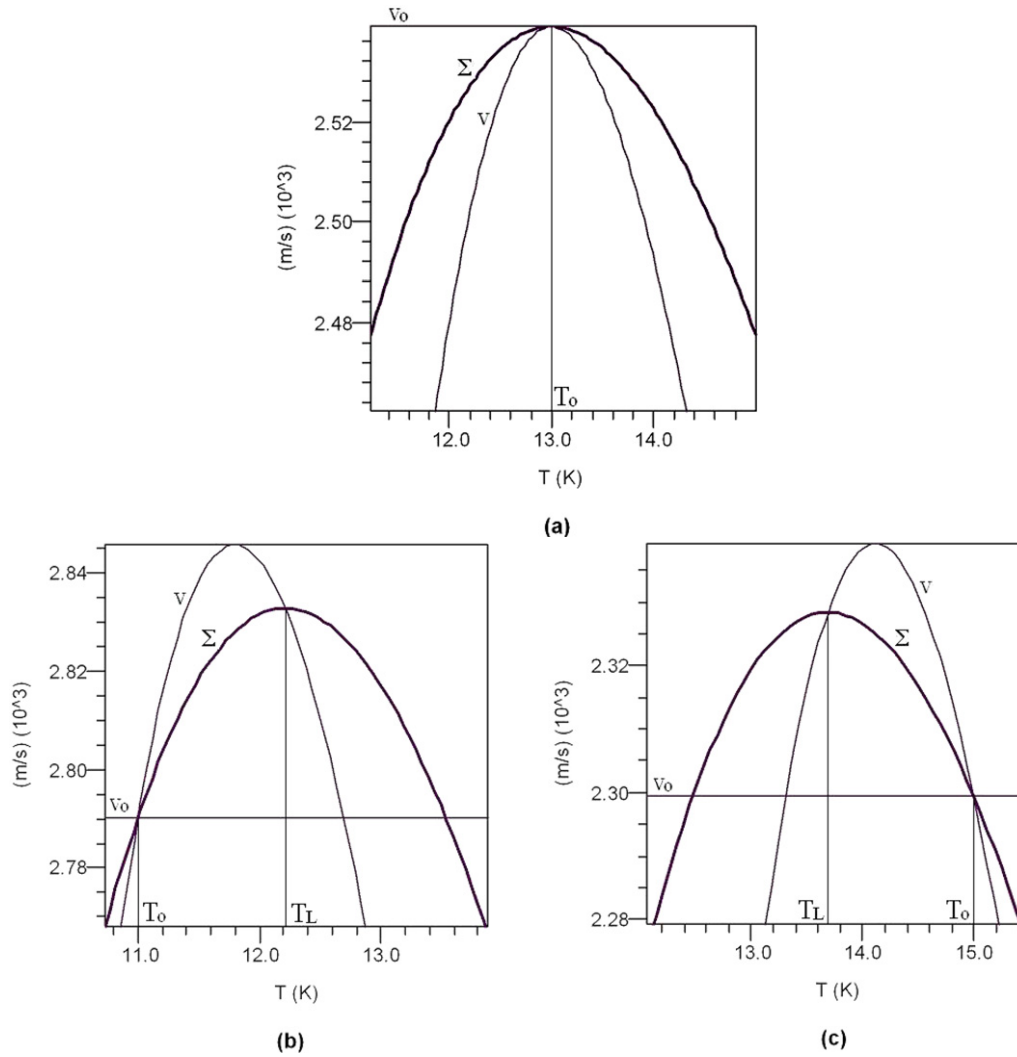


Figure 1.  $D_0$  versus  $T_c$  in NaF.

and, making use of the above values of  $n$ ,  $A$  and  $B$ , it is found that  $T_c^{\text{lin}} = 13.36 \text{ K}$  for NaF and  $T_c^{\text{lin}} = 3.06 \text{ K}$  for Bi. The behaviour of  $D_0$  as a function of  $T_c$  is displayed in figure 1 in the case of NaF: it is observed that  $D_0$  is positive for  $T_c < T_c^{\text{lin}}$  and negative for  $T_c > T_c^{\text{lin}}$ . A similar curve is obtained for Bi and will therefore not be reproduced. Now, taking for  $T_c$  the measured value at which the second sound pulse is appearing, namely  $T_c = 13 \text{ K}$  for NaF [16] and  $T_c = 3 \text{ K}$  for Bi [17], we are in position to determine the values of the velocities  $\Sigma$  and  $v$  for fixed values of  $T_0$  and to determine the domains of temperature  $T$  where shocks are possible. In figures 2(a)–(c) are displayed the results corresponding to NaF when the unperturbed temperatures  $T_0$  ahead of the front are respectively equal, smaller and larger than the critical temperature  $T_c$ . Figure 2(a) shows that the maximum value  $v_c$  of the velocity, at which  $v_0 = v = \Sigma$  and  $T = T_c$  is  $v_c = 2.54 \times 10^3 \text{ m s}^{-1}$ . It is observed that for  $T_0 < T_c$  (figure 2(b)), the allowed temperature range for which the Lax condition is satisfied is  $T_0 < T < T_L$  where the maximum temperature  $T_L$  is a function of  $T_0$ . It follows that the temperature is increased when passing from the front to the back side of the shock, such a behaviour is classical and is referred to as a hot shock. However for  $T_0 > T_c$  (see figure 2(c)), the Lax criterion predicts that shock waves will only propagate when they are produced by a negative temperature jump  $T - T_0 < 0$ . Stable shocks whose temperature behind the shock is lower than ahead of it are called cold shocks because they cool the body. By increasing the equilibrium temperature  $T_0$  in the case of hot shocks, we observe (figure 3(a)) that the range of temperature where shocks are allowed is only slightly diminished. The same remark remains true by decreasing  $T_0$  in the case of cold shocks (figure 3(b)). Curves similar to these of figures 2 and 3 can also be drawn at other values of the critical temperature  $T_c$ . It is shown that the results are not very sensitive to the values of  $T_c$ . When  $T_c$  is increased, the window of admissible



**Figure 2.**  $\Sigma$  and  $v$  versus  $T$  in NaF with  $T_c = 13 \text{ K}$ : (a) no shocks ( $T_0 = 13 \text{ K}$ ); (b) hot shocks ( $T_0 = 11 \text{ K} < T_c$ ); (c) cold shocks ( $T_0 = 15 \text{ K} > T_c$ ).

shocks is slightly decreased (see figures 4(a) and (b) drawn for  $T_c = 14 \text{ K}$ ) while a larger window is displayed by decreasing  $T_c$ . We have also repeated the calculation in the case of Bi crystals; qualitatively, the results and conclusions remain unchanged: for  $T_0 = T_c$ , no shock is admissible, for  $T_0 < T_c$ , only hot shocks are possible while for  $T_0 > T_c$ , cold shocks are predicted.

The occurrence of cold shocks was still noticed by Müller and Ruggeri [2] in their analysis of shock waves in heat conducting monatomic gases, by Ruggeri *et al* [9, 17] and Cimmelli and Frishmuth [21] in their study of second sound in high-purity crystals and also in liquid helium [23, 24] as commented in the next section. Such a feature is clearly linked to the introduction of the fluxes as state variables, with the consequence that temperature loses its privilege to be the single relevant physical parameter. It may seem paradoxical that temperature jumps down after the passage of the shock but this is not an unusual process. Indeed, it is true that for compressive shocks in ordinary gases at room temperature, the latter is increased when the gas particles flow across the shock,

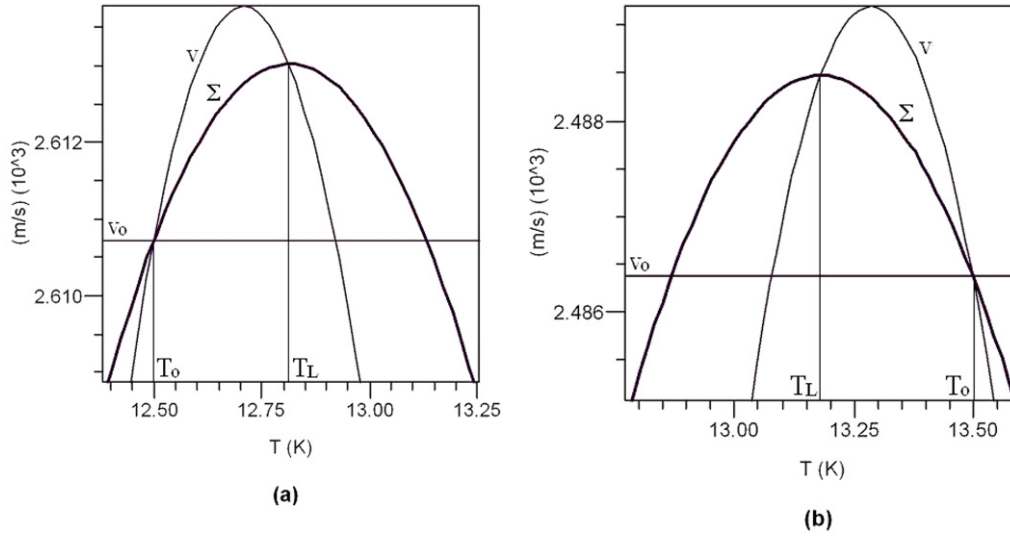
but this is no longer verified for rarefaction flows characterized by a negative jump of temperatures. This is interesting because it allows us to compare the cold shock with a kind of thermal rarefaction. Moreover, it is noted that, in the case  $T_0 > T_c$ , entropy is decreased when passing from the front to the back side of the cold shock. If it is admitted that entropy is a measure of disorder, we may understand that occurrence of cold shocks is accompanied by less disorder, whence a lowering of temperature.

## 8. Concluding comments

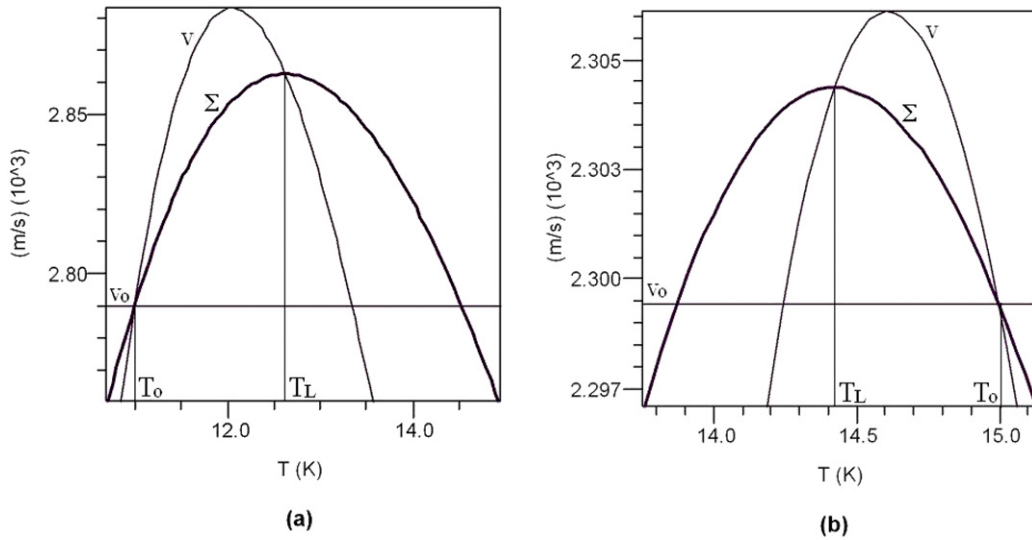
The objectives of this work were twofold: first, to revisit extended irreversible thermodynamics (EIT); second, to generalize the linear classical Cattaneo equation. The most important results are embodied in equations (13), (25) and (27).

In the previous versions of EIT (e.g. [1, 2, 7]), the non-equilibrium state variables are identified with the dissipative parts of the physical fluxes of mass, momentum and energy. In the present paper, we show that the space of the extra state





**Figure 3.**  $\Sigma$  and  $v$  versus  $T$  in NaF with  $T_c = 13$  K: (a) hot shocks ( $T_0 = 12.5$  K  $< T_c$ ); (b) cold shocks ( $T_0 = 13.5$  K  $> T_c$ ). 0



**Figure 4.**  $\Sigma$  and  $v$  versus  $T$  in NaF with  $T_c = 14$  K: (a) hot shocks ( $T_0 = 11$  K  $< T_c$ ); (b) cold shocks ( $T_0 = 15$  K  $> T_c$ ).

variables is not restricted of the physical fluxes, we propose another choice by using as state variables the dissipative fluxes balanced by a weighting coefficient instead of the fluxes themselves. This is motivated by the fact that the question has been raised whether or not the fluxes can be regarded as the most appropriate state variables in non-equilibrium situations. Indeed, the fluxes represent essentially the response of a system to external solicitations through the boundaries. To award a quantity the status of state variables requires that it be expressed in terms of intrinsic macroscopic properties of the material. This is precisely what is achieved in the present paper wherein the non-equilibrium variable takes the form of a heat flux with a factor depending explicitly on the specific properties of the material, like heat conductivity  $\lambda$  and relaxation time  $\tau$ . It is important to stress that this ‘weighting’ function is not arbitrary but is determined *a posteriori*, as a consequence of the constraints placed by the second law

of thermodynamics. More explicitly, in the problem of heat conduction in rigid bodies, we have selected as state variables the temperature  $T$ , which is rather natural and an extra variable  $\mathbf{c}$  related to the heat flux vector  $\mathbf{q}$  by

$$\mathbf{q} = g(T, c^2)\mathbf{c}, \quad (58)$$

with the ‘weighting’ factor given by

$$g = \frac{\lambda}{\tau} + D_0 T^2 \left( \frac{\lambda}{T^2 \tau} \right)' c^2. \quad (59)$$

$D_0$  is a constant but the ratio  $\lambda$  and  $\tau$  are allowed to be temperature dependent. In equilibrium situations for which  $\mathbf{q} = 0$ , one has similarly  $\mathbf{c} = 0$ . For constant values of  $\lambda/(T^2\tau)$  or in the linear approximation  $D_0 = 0$ , the quantity  $\mathbf{c}$  reduces simply to  $(\tau/\lambda)\mathbf{q}$ . Since  $\tau$  is generally very small, of the order of  $10^{-12}$ – $10^{-8}$  s, the new variable  $\mathbf{c}$  is a small

parameter in terms of which higher order expansions can be made. This is useful because it provides a hierarchy in the evolution and constitutive equations with the possibility to cut the developments according to a fixed degree of accurateness.

A further comment about the solution of the differential equation (A.12), namely  $\partial^2 g / \partial (c^2)^2 = 0$  is in form. Its solution (A.13) is written in terms of a ‘constant’ of integration given here by  $\lambda / \tau$ . The expression of this ‘constant’ is dictated by the physics of the problem and remains to a certain point arbitrary. For instance, in the present problem, one could as well have selected the heat conductivity  $\lambda$  itself or the ratio  $\lambda / (T^n \tau)$  ( $n = \pm 1$  or  $\pm 2$ ) or  $k / \tau$ , with  $k$  the heat diffusivity. In other problems, like matter diffusion, electrical conduction or in presence of a viscous stress tensor, good candidates will be the diffusion coefficient, the electrical resistivity, or the dynamic viscosity respectively.

Another attempt to prefer state variables different from the physical fluxes can be found in a work by Velasco and Garcia-Colin [22], wherein the moments of the Grad distribution function [3] were assigned this role. Restricting their analysis to linear evolution equations, Velasco and Garcia-Colin found that in the case of dilute monatomic gases, the relevant flux variable takes the form  $5(\frac{k_B}{mT})^{1/2} \frac{\tau}{\lambda} \mathbf{q}$ , which is clearly similar to the quantity  $\mathbf{c}$  introduced in the present approach,  $m$  designates the mass of the particles and  $k_B$  the Boltzmann constant.

In short, the reasons to prefer  $\mathbf{c}$  rather than  $\mathbf{q}$  as variable are the following:

- (i) Because it depends explicitly on the material properties  $\lambda$  and  $\tau$ , the quantity  $\mathbf{c}$  is reflecting the material properties of the system, which would not have been the case by selecting simply the variable  $\mathbf{q}$ .
- (ii) The new variable  $\mathbf{c}$  being proportional to the relaxation time  $\tau$ , it is a small parameter and therefore it may be very helpful in the determination of the closure of non-linear series expansions.
- (iii) Its expression is related to the second moments of the distribution function as introduced by Grad [3].
- (iv) The final form of the expression of  $g$  is not arbitrary but is obtained by referring to the second law of thermodynamics.
- (v) The price to be paid by selecting  $\mathbf{c}$  as variable is the lack of clear physical meaning compared to  $\mathbf{q}$ . However, it is worth to stress that each of the individual factors, namely  $\lambda$ ,  $\tau$  and  $\mathbf{q}$ , defining  $\mathbf{c}$  has per se a clear significance. The same situation occurs in other branches of physics, like in rheology and solid mechanics, where the basic variables are sometimes also selected as combinations of well-defined physical quantities.

The second purpose of this work was to go beyond Cattaneo’s linear law. Instead, it is assumed that propagation of second sound is governed by the more general non-linear time evolution equation (13). Such a relation, when coupled to the energy balance, is well suited for modelling high frequency phenomena, like waves and shocks propagations occurring at low temperatures in dielectric crystals for which Cattaneo’s approach fails. Equation (13) involves two undetermined coefficients  $D(T)$ , assumed to be temperature dependent and

$D_0$ , a constant. The quantity  $D(T)$  is shown to be equal to  $-T$  while  $D_0$  is given by (52).

As illustrative example, propagation of shocks in NaF and Bi dielectric crystals at low temperature is investigated. It should also be noted that letting  $D_0$  to depend on the temperature will not raise fundamental difficulties. It will only result in a supplementary term of the form  $D'_0(\frac{1}{2}c^2\delta_{ij}+c_i c_j)T_{,i}$  in (13) with the consequence that, relation (A.18) of  $\alpha(T)$  will contain an extra contribution in  $D'_0 T f^*$ . Derivation of the corresponding expressions of the thermodynamic potentials  $f$ ,  $u$  and the weighting factor  $g$  is rather straightforward.

Extension to rigid bodies in motion with a velocity  $\mathbf{v}$  will not raise fundamental problems. Now the space of state variables will contain, besides  $T$  and  $\mathbf{c}$ , the velocity  $\mathbf{v}$  obeying the momentum balance equation. The consequences are that the partial time derivative in the evolution equations (5) and (9) will be replaced by the material time derivative and that an extra Lagrange multiplier must be introduced in the entropy inequality (A.2) to account for the constraints placed by the momentum equation. Most of the conclusions drawn from the entropy inequality in appendix remain valid as the new variable  $\mathbf{v}$  is essentially a kinematical one.

Similarities and differences with the propagation of second sound in superfluid helium He II are also worth to be underlined. In Landau’s two-fluid model [23–26], He II is viewed as a mixture of two coexisting fluids: the normal fluid with a non-zero viscosity and the superfluid with zero viscosity and zero entropy. In the thermodynamic description of He II [23, 24], the space of state functions is not restricted to the classical total mass density  $\rho$  and temperature  $T$ , but contains in addition a flux variable related to the relative velocity  $\mathbf{v}_n - \mathbf{v}_s$  between the normal and super fluids. This shows that thermodynamics underlying the two-fluid model is based on a generalized space concept which is closer to EIT than classical non-equilibrium thermodynamics [13]. More striking similarities between our approach and Landau’s model are observed in the study of shock waves. Indeed, it was shown [23, 24] that the formation of shock waves in He II is strongly influenced by the coefficient  $(\ln \frac{c_{ve} v_n^2}{T})'$  in the expression of the velocity of propagation of temperature discontinuity. Now going back to the definition (52) of our corresponding coefficient  $D_0$ , one notices a strong similarity. Like  $D_0$ , the above coefficient of Landau’s theory changes sign with temperature and likewise, the formation of rarefaction (or cold) shocks occurs for negative values of this coefficient. Although the foundations underlying Landau’s model are rather different from ours, it is interesting to note that both descriptions lead to similar conclusions.

The present model contains as particular cases the laws of Fourier and Cattaneo. Indeed, evolution equation (13) boils down to Cattaneo’s law in the linear approximation (no quadratic terms in the fluxes) and for a constant heat conductivity and relaxation time. Our approach goes also beyond previous contributions by Ruggeri *et al* [10, 11, 19] and Coleman and Newman [20]. In this latter work, the authors generalize Cattaneo’s formulation by allowing the heat conductivity and the relaxation time to be temperature dependent but they assume a linear evolution equation for

the heat flux. In our notation, this means that Coleman and Newmann's formalism corresponds to  $\beta \neq 0$  but  $D_0 = 0$ . In Ruggeri *et al* [10, 11, 19], the internal energy is forced to be only temperature dependent while the evolution of the flux of heat is governed by an equation of the form

$$\partial_t(\varepsilon \mathbf{q}) + \nabla v = \frac{v'}{\lambda} \mathbf{q}, \quad (60)$$

wherein the factors  $\varepsilon(T)$  and  $v(T)$  are unspecified quantities to be given by constitutive relations. In our description, the equivalent expression is equation (9) with the main difference that the scalar  $v(T)$  is replaced by a tensor of rank two  $\Phi(T, \mathbf{c})$  allowed to depend on both  $T$  and  $\mathbf{c}$ . To summarize, Ruggeri *et al* approach amounts to set  $\beta = 0$  and  $D_0 = 0$  in the present analysis.

Let us finally briefly comment about the expression of the entropy flux: the latter is no longer given by  $\mathbf{q}/T$  but is more general as exhibited by relation (21). Since this result is compatible with the positive definite entropy production (22), it appears that the second law (14), referred to as the Clausius–Duhem inequality in the rational thermodynamics terminology [27], can be satisfied for non-classical expressions of the entropy flux, in contradiction with one of the statements of rational thermodynamics.

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## Appendix. Consequences of the entropy inequality

Inequality (16) expressing the positiveness of the entropy production can be rewritten in the more explicit form

$$T\sigma^s = -g_T c_i T_{,i} - 2g^* c_i c_j c_{j,i} - g c_{i,i} - \partial_t f - s \partial_t T + T (\gamma_T c_i T_{,i} + 2\gamma^* c_i c_j c_{j,i} + \gamma c_{i,i}) \geq 0, \quad (\text{A.1})$$

after use is made of the energy balance (12) and expression (15) of  $\mathbf{J}^s$ . Note however that inequality (A.1) does not hold for any value of the variables  $T$  and  $\mathbf{c}$  but only for those values which are solutions of the balance equation (13), the energy balance being automatically satisfied. This means that we can consider relation (13) as a constraint for the entropy inequality to hold. A way to take this constraint into account was proposed by Liu [12]: he demonstrated that the entropy inequality becomes completely arbitrary at the condition to complement it by the evolution equation of  $\mathbf{c}$  affected by a multiplying factor  $\Lambda$ , generally a function of  $T$  and  $c^2$ . This factor is called a Lagrange multiplier in analogy with the extremization problem of mathematics in presence of constraints. After

introducing the Lagrange's multiplier, the compatibility of entropy inequality with (13) yields the following inequality which holds for any value of the field variables:

$$T\sigma^s + \Lambda_i \left[ \frac{1}{\tau} c_i + \partial_t c_i - D' T_{,i} - D_0 (c_j c_{j,i} + c_j c_{i,j} + c_i c_{j,j}) \right] \geq 0. \quad (\text{A.2})$$

Substituting  $T\sigma^s$  by expression (A.1) and regrouping the terms in  $\partial_t T$ ,  $\partial_t c_i$ ,  $T_{,i}$  and  $c_{j,i}$ , results in

$$\begin{aligned} & \frac{1}{\tau} \Lambda_i c_i - (f_T + s) \partial_t T + (\Lambda_i - 2f^* c_i) \partial_t c_i \\ & - (\Lambda_i D' + g_T c_i - T \gamma_T c_i) T_{,i} \\ & + [(T \gamma - g - D_0 \Lambda_i c_i) \delta_{ij} \\ & + 2(T \gamma^* c_i - g^* c_i - D_0 \Lambda_i) c_j] c_{j,i} \geq 0, \end{aligned} \quad (\text{A.3})$$

which must be satisfied for all fields  $T$ ,  $c_i$  and, in particular for arbitrary values of their derivatives. Since inequality (A.3) is linear in these derivatives, it will be violated unless the factors of  $\partial_t T$ ,  $\partial_t c_i$ ,  $T_{,i}$  and  $c_{j,i}$  are set equal to zero. It follows that the next relations must be fulfilled:

$$s = -f_T, \quad (\text{A.4})$$

$$\Lambda_i = 2f^* c_i, \quad (\text{A.5})$$

$$\gamma = \frac{1}{T} g + \frac{2D_0}{T} f^* c^2, \quad (\text{A.6})$$

$$\gamma_T = \frac{1}{T} g_T + \frac{2D'}{T} f^*, \quad (\text{A.7})$$

$$\gamma^* = \frac{1}{T} g^* + \frac{2D_0}{T} f^* \quad (\text{A.8})$$

while the entropy production reduces to

$$T\sigma^s = \frac{2}{\tau} f^* c^2 \geq 0. \quad (\text{A.9})$$

Differentiating (A.6) with respect to  $c^2$  and comparing with (A.8) yields the important result

$$f^{**} = 0, \quad (\text{A.10})$$

which means that the Helmholtz's free energy is linear in  $c^2$ . Moreover by identifying the derivative of (A.6) with respect to  $T$  with expression (A.7), it is found that

$$2T D' f^* = 2D_0 (T f_T^* - f^*) c^2 - g, \quad (\text{A.11})$$

and, after differentiation twice with respect of  $c^2$ , one obtains

$$g^{**} = 0. \quad (\text{A.12})$$

This result allows us to cast  $g(T, c^2)$  in the general form

$$g = \frac{\lambda(T)}{\tau(T)} + \alpha(T)c^2, \quad (\text{A.13})$$

wherein  $\lambda(T)$  and  $\alpha(T)$  are arbitrary functions of  $T$ ,  $\tau(T)$  is the relaxation time introduced in equation (11). The next step consists in taking advantage of the invertibility condition  $(\gamma_T)^* = (\gamma^*)_T$  and the result  $\alpha(T) = g^*$ , these operations lead to

$$\alpha = 2D_0 (Tf_T^* - f^*). \quad (\text{A.14})$$

Let us finally establish the constitutive equations of the Helmholtz's free energy  $f(T, c^2)$  and internal energy  $u(T, c^2)$ . After substitution of (A.13) and (A.14) in (A.11), it is easily checked that

$$f^* = -\frac{\lambda}{2TD'\tau}, \quad (\text{A.15})$$

and, after integration with respect to  $c^2$ ,

$$f = f_e(T) - \frac{\lambda}{2TD'\tau}c^2, \quad (\text{A.16})$$

where  $f_e(T)$  designates Helmholtz's energy at local equilibrium which, as it should, corresponds to  $\mathbf{c} = \mathbf{0}$ . Determination of the expression of the internal energy is straightforward. Having in mind the definition  $u = f - Tf_T$ , it is directly found from (A.16) that

$$u(T, c^2) = u_e(T) + \frac{1}{2}T^2 \left( \frac{\lambda}{T^2D'\tau} \right)' c^2, \quad (\text{A.17})$$

with  $u_e(T)$  the local equilibrium internal energy. Similarly, after substitution of (A.16) in (A.14), one obtains the functional dependence of  $\alpha(T)$ , namely

$$\alpha = -D_0T^2 \left( \frac{\lambda}{T^2D'\tau} \right)'. \quad (\text{A.18})$$

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