Heat pulse propagation by second sound in dielectric crystals

A Valenti†, M Torrisi† and G Lebon‡

† Department of Mathematics, University of Catania, Viale A Doria, 6, 95125 Catania, Italy
‡ Institut de Physique, Université de Liège B5, Sart Tilman, 4000 Liège 1, Belgium

Abstract. A non-linear thermodynamic model describing heat pulse propagation in dielectric crystals at low temperature is proposed. This work is a generalization of those of Cattaneo and of Guyer and Krumhansl, and is complementary to an earlier paper (Lebon G, Torrisi M and Valenti A 1995 *J. Phys.: Condens. Matter* **7** 1461), which was mainly devoted to a linear approach. The model is based on extended irreversible thermodynamics, and uses as field variables the temperature, the heat flux, and the flux of the heat flux. Unlike the simple phonon gas model, the present formalism is compatible with the experimental observation that second sound is temperature dependent. In this paper, explicit expressions for the internal energy and velocity of propagation of weak discontinuities are determined. By making use of experimental data for NaF and Bi, the values of the relevant parameters have been evaluated.

1. Introduction

In phonon hydrodynamics, there is a well known model due to Guyer and Krumhansl [1] which allows a successful description of heat pulse propagation in crystals at low temperature. Most of the recent experimental observations on second sound in dielectric crystals like NaF and Bi were based on this model. However, the Guyer–Krumhansl description predicts that within the limit of high frequencies the phase velocity is infinite; in other words, it implies that after application of a disturbance the latter will be felt instantaneously everywhere in space. In that respect, the Guyer–Krumhansl equation presents the same drawback as the classical Fourier law relating the heat flux to the temperature gradient. Indeed when the Fourier equation is replaced in the energy balance law, one finds that the partial differential equation governing the behaviour of the temperature is a parabolic one; the same observation remains true for the Guyer–Krumhansl equation as observed by many authors in the past [2, 3].

 Our objective in the present paper is to propose an extension of the Guyer–Krumhansl equation which circumvents the problem of propagation of signals with an infinite velocity. This task will be achieved by working in the framework of extended irreversible thermodynamics [4]. In this theory the space of variables is enlarged by including the dissipative fluxes (like heat flux, the flux of momentum, and the flux of mass) as independent variables in addition to the classical variables (like energy or temperature, mass, and momentum). EIT has proved particularly useful for describing high-frequency and short-wavelength phenomena; it is also well adapted for studying the behaviour of viscoelastic fluids and polymers. A notable domain of application of EIT is that of relativity. In this article, heat propagation in samples at rest is considered, so that the only relevant variables

are temperature and heat flux. However, it is well known from the early work on EIT that the choice of these two variables only allows one to recover Cattaneo's equation, which is, in Cartesian coordinates,

$$\tau \, \partial_t q_i + q_i = -\lambda T_{,i}. \tag{1}$$

The notation is classical: τ is a relaxation time, q_i the ith component of the heat flux vector, λ the heat conductivity, T the temperature, and the comma stands for differentiation with respect to space variables. Cattaneo's relation is the simplest non-steady extension of Fourier's law $q_i = -\lambda T_{,i}$. However, to recover the Guyer–Krumhansl relation, one needed to introduce either extra non-local terms [3, 5] or a supplementary variable [4]—for instance, the flux of the heat flux, Q_{ij}, which is a second-order symmetric tensor. From the kinetic theory point of view, the internal energy u and the heat flux q_i are identified as

$$u = \frac{1}{2} \int m f C^2 \, dc \qquad q_i = \int m C^2 C_i \, dc \tag{2}$$

where C_i is the relative velocity of molecules with respect to their barycentric velocity, f is the distribution function and m is the mass of the molecules.

The extra variable, namely the flux of the heat flux Q_{ij}, is defined by

$$Q_{ij} = \int m C^2 C_i C_j \, dc \qquad (Q_{ij} = Q_{ji}). \tag{3}$$

From now on, we leave the microscopical description, and will focus solely on macroscopic aspects. The present paper is an extension of work presented in [3]; it will be organized as follows. In section 2 we establish the basic evolution and constitutive equations governing the behaviour of the three basic variables, namely the temperature, heat flux, and flux of the heat flux. These equations are not free to take any possible form, as they have to comply with the laws of continuum thermodynamics. Restrictions imposed by the second law of thermodynamics are derived. In particular, an explicit expression for the internal energy as a function of the various variables T, q_i, and Q_{ij} is established. In section 3 the characteristic velocities of propagation are determined, with special emphasis on media whose unperturbed temperature is uniform. Comparisons with experimental data are presented in section 4, while final comments are made in section 5.

2. The governing model

Although most of the contents of this section can be found in [3], we recall them briefly for the sake of completeness. The basic variables are u (the internal energy per unit volume) or—preferably—the temperature T which is directly accessible to experiments, q_i (the flux of the heat), and Q_{ij} (the flux of the heat flux). Moreover, the symmetric tensor Q_{ij} will be separated into a deviatoric $Q_{\langle ij \rangle}$ and a bulk part Q:

$$Q_{ij} = Q_{\langle ij \rangle} + Q \delta_{ij} \qquad \left(Q = \frac{1}{3} Q_{kk} \right).$$

For the sake of generality, and in analogy with fluid mechanics where the deviatoric and bulk parts of the stress tensor are considered as independent variables, we shall from now on also take $Q_{\langle ij \rangle}$ and Q as independent variables.

The set of basic variables u, q_i, $Q_{\langle ij \rangle}$, Q is assumed to satisfy the following evolution equations:

$$\partial_t u = -q_{i,i} \tag{4}$$

$$\partial_t q_i = -LQ_{\langle ij\rangle,j} - MQ_{,i} + \sigma_i^q \tag{5}$$

$$\partial_t Q_{\langle ij\rangle} = \sigma_{\langle ij\rangle}^Q \tag{6}$$

$$\partial_t Q = \sigma^Q \tag{7}$$

where the convention of summation over repeated indices has been used. The quantities σ_i^q, σ_{ij}^Q, and σ^Q are the source terms in the evolution equations for q_i, $Q_{\langle ij\rangle}$, and Q respectively; it is assumed that there is no source of energy in (4). It is clear from (5) that $Q_{\langle ij\rangle}$ and Q are indeed related to the flux of the heat flux, the coefficients L and M being introduced for the sake of generality. There is no flux term present in (6) and (7), as $Q_{\langle ij\rangle}$ and Q are considered as internal variables whose behaviour is only influenced by internal sources and not by effects exerted through the boundary. This explains why (6) and (7) do not contain a divergence term expressing the flux through the surface of the body. To close the set of equations, one needs constitutive relations expressing u, σ_i^q, $\sigma_{\langle ij\rangle}^Q$, and σ^Q in terms of the basic variables T, q_i, $Q_{\langle ij\rangle}$, and Q; to take into account non-locality in space, it is in addition supposed that the unknown functions may also depend on the gradients of T, q_i, $Q_{\langle ij\rangle}$, and Q. At the lowest order of approximation in q_i, $Q_{\langle ij\rangle}$, Q, $T_{,i}$, and the gradients of the fluxes, the source terms σ_i^q, σ_{ij}^Q, and σ^Q take the forms

$$\sigma_i^q = -a_1 q_i - a_2 T_{,i} \tag{8}$$

$$\sigma_{\langle ij\rangle}^Q = -A_1 Q_{\langle ij\rangle} - A_2 q_{\langle ij\rangle}^{sym} \tag{9}$$

$$\sigma^Q = -B_1 Q - B_2 q_{k,k} \tag{10}$$

wherein all of the coefficients are allowed to depend on the temperature; $q_{\langle ij\rangle}^{sym}$ stands for the symmetric part of the deviator of $q_{i,j}$. An explicit expression for the constitutive equation for u will be specified later on. After substitution of (8)–(10) in the evolution equations (5)–(7), one is led to

$$\tau_1 \partial_t q_i = \beta\lambda T^2 Q_{\langle ij\rangle,j} + \beta'\lambda T^2 Q_{,i} - q_i - \lambda T_{,i} \tag{11}$$

$$\tau_2 \partial_t Q_{\langle ij\rangle} = -Q_{\langle ij\rangle} - \eta q_{\langle ij\rangle}^{sym} \tag{12}$$

$$\tau_3 \partial_t Q = -Q - \zeta q_{i,i} \tag{13}$$

wherein we have put

$$\frac{1}{a_1} = \tau_1 \qquad \frac{a_2}{a_1} = \lambda \qquad -\frac{L}{a_1} = \beta\lambda T^2 \qquad -\frac{M}{a_1} = \beta'\lambda T^2 \tag{14}$$

$$\frac{1}{A_1} = \tau_2 \qquad \frac{A_2}{A_1} = \eta \qquad \frac{1}{B_1} = \tau_1 \qquad \frac{B_2}{B_1} = \zeta. \tag{15}$$

It is instructive to examine the particular case where $\tau_2 = \tau_3 = 0$. After substitution of $Q_{\langle ij\rangle}$ and Q derived from (12) and (13) in (11), one obtains

$$\tau_1 \partial_t q_i + \lambda T_{,i} + q_i = -\lambda T^2 \left[\frac{1}{2}\beta\eta q_{i,jj} + \left(\frac{1}{6}\beta\eta + \beta'\zeta\right)q_{j,ji}\right] \tag{16}$$

when it is assumed that η and ζ are constant.

With the following identifications:

$$\tau_1 = \tau_R \qquad \frac{1}{2}\lambda\beta\eta T^2 = -\frac{1}{5}\tau_R\tau_N C_s^2 \qquad \lambda\beta'\zeta T^2 = -\frac{1}{3}\tau_R\tau_N C_s^2 \tag{17}$$

where C_s is the Debye phonon velocity, i.e. the sound velocity, and τ_N and τ_R are the relaxation times for phonon collisions which are respectively momentum-preserving (τ_N) and resistive (τ_R), i.e. non-momentum-conserving, expression (16) can be written as

$$\tau_R \,\partial_t q_i + \lambda T_{,i} + q_i = \frac{C_s^2}{5} \tau_R \tau_N (q_{i,jj} + 2q_{j,ji}). \tag{18}$$

This is simply the Guyer–Krumhansl relation [1] which is often employed to describe heat transport at low temperature in non-metallic solids. It should however be observed that like Fourier's law, the Guyer–Krumhansl equation predicts that temperature signals will propagate at infinite velocity, owing to the vanishing of the relaxation times τ_2 and τ_3 (see [2–4]).

Let us now go back to our model whose basic relations are (4) and (11)–(13). They involve eight parameters, namely $\lambda, \beta, \beta', \eta, \zeta, \tau_1, \tau_2, \tau_3$ which are generally temperature dependent. Interesting information about the sign of these coefficients and relations between them is provided by the second law of thermodynamics, stating that the entropy production σ^s is a positive-definite quantity; the latter quantity is defined through the balance equation for the entropy, written in the form

$$\sigma^s = \partial_t s + J_{i,i}^s \geqslant 0 \tag{19}$$

wherein s is the entropy per unit volume and J_i^s the flux of the entropy.

Equations (4) and (11)–(13) coincide formally with (6) and (17)–(19) of [3]; as a consequence, the thermodynamical restrictions imposed by (19) follow directly from those obtained in [3], and will therefore only be stated without proof.

However, at this point one remark is in order. In our previous work [3], we have neglected third-order terms in the expression for the entropy production σ^s. This was justified as the main objective of [3] was to study linear wave propagation. In a more general non-linear analysis, one should include in relation (28) of [3] the sum of two additional (third-order) terms, namely

$$\frac{\mathrm{d}\beta}{\mathrm{d}T} Q_{\langle ij\rangle} q_j T_{,i} + \frac{\mathrm{d}\beta'}{\mathrm{d}T} Q q_i T_{,i}. \tag{20}$$

The coefficients β and β' are those appearing in the expression for the generalized entropy flux J_i^s given by

$$J_i^s = T^{-1} q_i + \beta Q_{\langle ij\rangle} q_j + \beta' Q q_i. \tag{21}$$

It is easily checked that positiveness of the entropy production σ^s requires that the above additional terms (20) must vanish identically, from which it follows that β and β' should be taken as constants. It is then verified that by taking into account the above evolution equations (4) and (11)–(13), the entropy production can be written as

$$\sigma^s = \frac{1}{\lambda} q_i q_i - \frac{\beta}{\eta} T Q_{\langle ij\rangle} Q_{\langle ij\rangle} - \frac{\beta}{\zeta} T Q^2 \geqslant 0 \tag{22}$$

and, from the positiveness of σ^s, it follows that

$$\lambda > 0 \qquad \beta/\eta < 0 \qquad \beta'/\zeta < 0. \tag{23}$$

In view of [3], the corresponding Gibbs equation takes the form

$$\mathrm{d}f = -s \,\mathrm{d}T + \frac{\tau_1}{\lambda T^2} q_i \,\mathrm{d}q_i - \frac{\beta}{\eta} T \tau_2 Q_{\langle ij\rangle} \,\mathrm{d}Q_{\langle ij\rangle} - \frac{\beta'}{\zeta} T \tau_3 Q \,\mathrm{d}Q \tag{24}$$

where f is the Helmholtz free energy.

By expanding f around the local equilibrium, one obtains [3]

$$f = f_{eq}(T) + \frac{1}{2}\frac{\tau_1}{\lambda T^2}q_i q_i - \frac{1}{2}\beta\frac{\tau_2 T}{\eta}Q_{\langle ij\rangle}Q_{\langle ij\rangle} - \frac{1}{2}\beta'\frac{\tau_3 T}{\zeta}Q^2. \tag{25}$$

Imposing the constraint that f is a minimum at (the local) equilibrium, and making use of (23), one recovers the classical result of extended thermodynamics [4]: that the relaxation times are positive, i.e.

$$\tau_1 > 0 \qquad \tau_2 > 0 \qquad \tau_3 > 0. \tag{26}$$

In view of likely future developments, it is important to derive the expressions for the entropy and internal energy. The integrability condition for (24) leads to

$$s = s_{eq} - \frac{1}{2}\frac{\mathrm{d}}{\mathrm{d}T}\left(\frac{\tau_1}{\lambda T}\right)q_i q_i + \frac{1}{2}\beta\frac{\mathrm{d}}{\mathrm{d}T}\left(\frac{\tau_2 T}{\eta}\right)Q_{\langle ij\rangle}Q_{\langle ij\rangle} + \frac{1}{2}\beta'\frac{\mathrm{d}}{\mathrm{d}T}\left(\frac{\tau_3 T}{\zeta}\right)Q^2 \tag{27}$$

$$u = u_{eq} - \frac{1}{2}T^2\frac{\mathrm{d}}{\mathrm{d}T}\left(\frac{\tau_1}{\lambda T^2}\right)q_i q_i + \frac{1}{2}T^2\beta\frac{\mathrm{d}}{\mathrm{d}T}\left(\frac{\tau_2}{\eta}\right)Q_{\langle ij\rangle}Q_{\langle ij\rangle} + \frac{1}{2}T^2\beta'\frac{\mathrm{d}}{\mathrm{d}T}\left(\frac{\tau_3}{\zeta}\right)Q^2 \tag{28}$$

where s_{eq} and u_{eq} are respectively the entropy and the internal energy at equilibrium, which satisfy the Gibbs relation

$$T\frac{\mathrm{d}}{\mathrm{d}T}(s_{eq}) = \frac{\mathrm{d}}{\mathrm{d}T}(u_{eq}) = c_{eq} > 0 \tag{29}$$

where c_{eq} denotes the heat capacity at equilibrium.

At this stage of the analysis, it is convenient to introduce some simplifying hypotheses. It is assumed that the quantities τ_2, η, τ_3, and ζ appearing in the evolution equations (12) and (13) for $Q_{\langle ij\rangle}$ and Q remain constant. This can be justified on the basis of the property that $Q_{\langle ij\rangle}$ and Q are of higher order than the other variables u and q_i, as is evident from the kinetic definitions (2) and (3). As a direct consequence, u will only depend on T and q_i and, according to (28), one has

$$u = u_{eq} + a(T)q_i q_i \tag{30}$$

with

$$a(T) = -\frac{1}{2}T^2\frac{\mathrm{d}}{\mathrm{d}T}\left(\frac{\tau_1}{\lambda T^2}\right). \tag{31}$$

To summarize, we have proposed a model for heat transport in undeformable solids whose state variables are T, q_i, $Q_{\langle ij\rangle}$, and Q. The evolution equations for T and q_i are given by (4) and (11) respectively, and these relations contain several coefficients like a, τ_1, and λ which are temperature dependent. In contrast, the quantities τ_2, η, τ_3, and ζ appearing in the evolution equations (12) and (13) for $Q_{\langle ij\rangle}$ and Q are assumed to remain constant.

3. Heat propagation velocity

We now determine the speed of propagation of heat waves in a rigid crystal on the basis of the model described by (4) and (11)–(13). Let us consider a smooth surface Σ whose equation is $\varphi(x_i, t) = 0$, propagating through the body; it is assumed that across Σ the quantities T, q_i, $Q_{\langle ij\rangle}$, and Q are continuous, but discontinuities between their first derivatives are permitted. As is usual [6], we introduce the normal wave speed v and the unit normal vector n_i to Σ by the following formulae:

$$v := \frac{\partial_t \varphi}{|\varphi_{,i}|} \qquad n_i := \frac{\varphi_{,i}}{|\varphi_{,i}|} \tag{32}$$

and define the jump of the first derivatives across Σ by

$$\delta := \left(\frac{\partial}{\partial\varphi}\right)_{\varphi=0^+} - \left(\frac{\partial}{\partial\varphi}\right)_{\varphi=0^-}. \tag{33}$$

On making the standard transformation [6]

$$\partial_t \to -v\delta \qquad \partial_{x_i} \to n_i\delta \tag{34}$$

the system of equations (4), (11)–(13) provides the following homogeneous algebraic system for the discontinuities, after use is made of (30):

$$vu_T \, \delta T + 2vaq_i \, \delta q_i - n_i \, \delta q_i = 0 \tag{35}$$

$$v\tau_1 \, \delta q_i = -\beta\lambda T^2 n_j \, \delta Q_{\langle ij\rangle} - \beta'\lambda T^2 n_i \, \delta Q + \lambda n_i \, \delta T \tag{36}$$

$$v\tau_2 \, \delta Q_{\langle ij\rangle} = \eta\left[\frac{1}{2}(n_j \, \delta q_i + n_i \, \delta q_j) - \frac{1}{3}n_k \, \delta q_k \, \delta_{ij}\right] \tag{37}$$

$$v\tau_3 \, \delta Q = \zeta n_i \, \delta q_i. \tag{38}$$

When v is different from zero, the linear set (35)–(38) has non-trivial solutions on condition that the following characteristic polynomial is satisfied:

$$P(v) := u_T v^2 + 2\frac{\lambda}{\tau_1}aq_n v - \frac{\lambda}{\tau_1}[1 + \gamma T^2 u_T] = 0. \tag{39}$$

q_n stands for $q_i n_i$ while γ is a positive constant given by

$$\gamma = -\left(\frac{2}{3}\frac{\beta\eta}{\tau_2} + \frac{\beta'\zeta}{\tau_3}\right) > 0. \tag{40}$$

Equation (39) admits real solutions if and only if

$$\left(\frac{\lambda}{\tau_1}aq_n\right)^2 + \frac{\lambda}{\tau_1}(1 + \gamma T^2 u_T)u_T > 0$$

i.e. for

$$u_T > 0. \tag{41}$$

Using expression (30), inequality (41) can be written as

$$c_{eq} + \frac{\mathrm{d}a}{\mathrm{d}T}q^2 > 0. \tag{42}$$

This means that in the case where $(\mathrm{d}a/\mathrm{d}T) < 0$ there exists an upper bound on $|q|$ given by

$$|q| < q_{crit} = \sqrt{-\frac{c_{eq}}{\mathrm{d}a/\mathrm{d}T}}. \tag{43}$$

The slopes of the characteristic lines, i.e. the characteristic velocities obtained from (39), will be denoted as $v_+(T, q)$ and $v_-(T, q)$. At equilibrium, for which T is uniform and equal to T_{eq} and where in addition $q_i = Q_{\langle ij\rangle} = Q = 0$, the velocity of the propagation is simply given by

$$v_{eq}^2 = \frac{\lambda}{\tau_1 c_{eq}}[1 + \gamma T^2 c_{eq}]. \tag{44}$$

By using the identification given as (17), it is possible to express (44) in terms of the relaxation times τ_R and τ_N of the resistive and normal phonon–phonon collisions; it is found that

$$v_{eq}^2 = \frac{\lambda}{c_{eq}\tau_R} + \frac{1}{3}\tau_N\left(\frac{4}{5\tau_2} + \frac{1}{\tau_3}\right)c_s^2. \tag{45}$$

At temperatures sufficiently low to make the frequency of the resistive collisions very small ($1/\tau_R \to 0$), the wave propagation remains finite, and is given by

$$v_{eq}^2 = \frac{1}{3} \tau_N \left(\frac{4}{5\tau_2} + \frac{1}{\tau_3} \right) C_s^2. \tag{46}$$

It is interesting to observe that for the same range of application ($1/\tau_R \to 0$), the Coleman–Newman model [7] would predict a vanishing velocity of propagation, in contradiction with experiments.

For the limit of a high frequency of phonon–phonon collisions with momentum conservation ($1/\tau_N \to \infty$), equation (45) simplifies to

$$v_{eq}^2 = \frac{\lambda}{c_{eq}\tau_R}. \tag{47}$$

Expressing the heat conductivity as

$$\lambda = \frac{1}{3} C_s^2 c_{eq} \tau_R \tag{48}$$

which is a relation widely used in phonon hydrodynamics, one recovers the well known expression for the second sound velocity

$$v_{eq}^2 = C_s^2/3. \tag{49}$$

Although most of the experiments on second sound in solids at low temperature were performed on samples in equilibrium states, interesting features would arise on considering heat pulses or high-frequency thermal waves in non-equilibrium states.

For simplicity, we assume that the heat propagation is properly one dimensional. In the 1-D problem the real roots v_+ and v_- of the characteristic polynomial (39) are given by

$$v_\pm = -\frac{a\lambda}{u_T \tau_1} q \pm \frac{\sqrt{\Delta}}{u_T} \tag{50}$$

where Δ stands for

$$\Delta = \left(\frac{\lambda}{\tau_1} aq \right)^2 + \frac{\lambda u_T}{\tau_1} (1 + \gamma T^2 u_T). \tag{51}$$

Let us introduce the following notation:

$$v_c = \sqrt{\frac{\lambda}{u_T \tau_1}} \qquad \phi = v_c aq. \tag{52}$$

The velocity v_c is generally a function of T and q and should not be confused with v_{eq}, the velocity of propagation in an equilibrium state given by (44).

The solutions $v_\pm$ now take the form

$$v_+ = v_c \left[-\phi + \sqrt{1 + \phi^2 + \gamma T^2 u_T} \right] \tag{53}$$

$$v_- = v_c \left[-\phi - \sqrt{1 + \phi^2 + \gamma T^2 u_T} \right]. \tag{54}$$

It is worth noticing that if $q > 0$, v_+ is the velocity of propagation in the direction of q, while v_- is the velocity of propagation in the opposite direction. When $q < 0$ we are faced with the opposite situation.

It is a simple matter to check that the difference Δv between the velocity of propagation in the direction of the heat flux and the velocity in the opposite direction can be written as

$$\Delta v = -2v_c\phi = -2\frac{\lambda}{u_T \tau_1} a|q|. \tag{55}$$

From (55) it is clear that the sign of Δv depends only of the sign of a. Provided that a is positive, the difference Δv is smaller than zero, indicating that a signal travelling in the direction of the heat flux will move more slowly than in the opposite direction. The property $a > 0$ has been confirmed by Coleman and Newman [7], who based their analysis on a non-linear version of the Cattaneo equation, and by phonon hydrodynamics [8] where it is a proved that for a phonon gas in d dimensions, one finds that a is proportional to $(d + 2)(\tau_R/2\rho\lambda u_T T^3)$ where ρ is the mass density. For all of these reasons, it is henceforth admitted that a is a non-negative quantity. As far as we are aware, experimental measurements of Δv have not been performed yet.

The same result (55) was still obtained by Coleman and Newman; this is not surprising because the difference of speeds (55) depends only on a and not on γ, which is typical of the non-locality introduced in our model.

4. Comparison with experimental results

Experiments on second-sound propagation in high-purity crystals at low temperature have been performed by perturbing systems at uniform temperature. In that respect, to compare our theoretical results with experimental observations, we need only the simplified mathematical expressions derived in the particular case of equilibrium. Nevertheless, these results provide interesting information about the values of the coefficients $a(T)$ and γ. Measurements have been carried out on NaF and Bi samples [9, 10]. It is found that the measured speed of propagation as a function of temperature is well fitted by an empirical law of the form

$$v_{eq}^{-2} = A + BT^n \tag{56}$$

where A, B, and n are constants. For NaF, some values of A, B, and n giving a good fit are

$$A = 9.09 \times 10^{-12} \qquad B = 2.22 \times 10^{-15} \qquad n = 3.1 \tag{57}$$

when the velocities are measured in centimetres per second and the temperature in degrees Kelvin; for Bi, the following values have been obtained:

$$A = 9.07 \times 10^{-11} \qquad B = 7.58 \times 10^{-13} \qquad n = 3.75. \tag{58}$$

The temperature ranges in which the heat pulse propagations have been observed are $10 \text{ K} < T_{eq} < 18.5 \text{ K}$ (for NaF) and $1.4 \text{ K} < T_{eq} < 4 \text{ K}$ (for Bi).

An important relevant quantity is the heat capacity c_{eq} which varies with T according to

$$c_{eq} = \varepsilon T^3. \tag{59}$$

The constant ε depends on the nature of the crystal: for NaF, $\varepsilon = 23 \text{ erg cm}^{-3} \text{ K}^{-4}$ [11], and for Bi, $\varepsilon = 550 \text{ erg cm}^{-3} \text{ K}^{-4}$ [12].

Our objective is to determine the values of the parameters $a(T)$ and γ for the crystals of both NaF and Bi from the experimental values of A, B, n, and ε. After identification of (44) and (56) for v_{eq}, one obtains

$$\frac{\tau_1}{\lambda T^2} = \frac{A + BT^n}{\varepsilon T^5} + \gamma(A + BT^n). \tag{60}$$

From the definition (31) of a, it is easily checked that

$$a = \frac{5 - n}{2\varepsilon} BT^{n-4} + \frac{5A}{2\varepsilon} T^{-4} - \frac{1}{2}n\gamma BT^{n+1}. \tag{61}$$

By setting $\gamma = 0$, one recovers the result of Coleman and Newman [7]. A further differentiation of (61) with respect to temperature yields

$$\frac{da}{dT} = -\frac{20A + (n-5)(n-4)BT^n}{2\varepsilon T^5} - \frac{1}{2}n(n+1)\gamma BT^n. \tag{62}$$
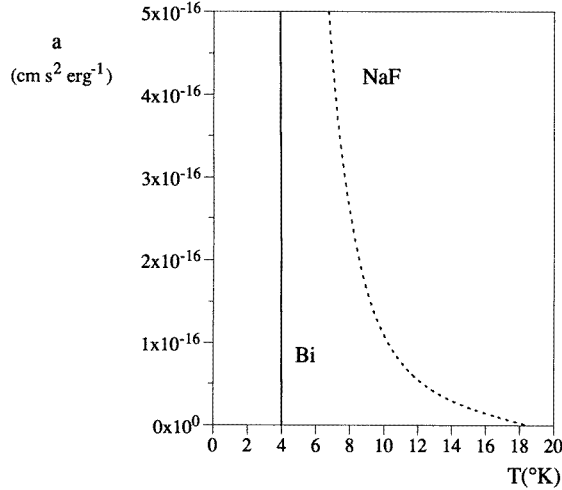

Figure 1. $a(T)$ versus temperature. Solid line: Bi; dotted line: NaF.

Since A, B, and γ are positive, and since the data for NaF and Bi yield $n < 4$, it follows from (62) that $(da/dT) < 0$, which demonstrates the property that a is a decreasing function of T. But since—as was argued in the previous section—a is a non-negative quantity, there exists a maximum temperature T_* (see figure 1) beyond which second sound will not be observed.

This property has indeed received experimental confirmation: for NaF, $T_* = 18.5$ K, and for Bi, $T_* = 4$ K.

Substituting these maximum values for T in (61) leads to the following expression for the constant γ:

$$\gamma = \frac{(5-n)BT_*^n + 5A}{n\varepsilon BT_*^{n+5}} \tag{63}$$

and it is found that

$$\gamma = 2.7928 \times 10^{-8} \text{ (NaF)} \qquad \gamma = 2.615\,67 \times 10^{-6} \text{ (Bi)}. \tag{64}$$

The result $da/dT < 0$ is also of interest because it allows one to determine the critical value q_{crit} above which the model is not applicable. Indeed from (43), (59), and (62), one has

$$q_{crit} = \sqrt{2}\varepsilon T^4 / \sqrt{20A + (n-5)(n-4)BT^n + n(n+1)\varepsilon\gamma BT^{n+5}}. \tag{65}$$

In figure 2 and figure 3 we have plotted the critical values q_{crit} for NaF and Bi respectively. One observes that the presence of non-local effects ($\gamma \neq 0$) reduces the value of the critical bound with respect to that for local theory ($\gamma = 0$). This shift is the price paid for the improvement of the model.
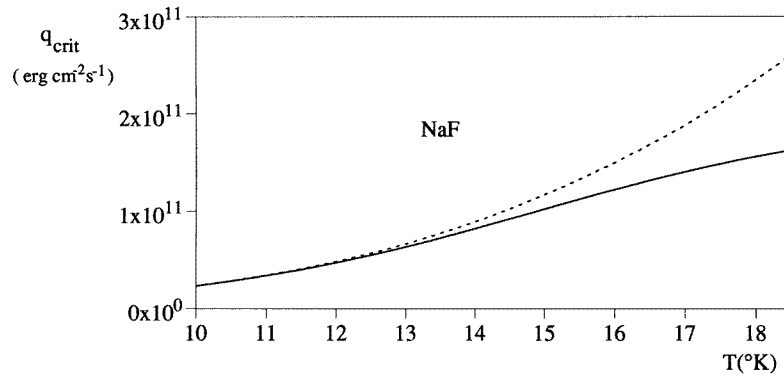
Figure 2. The critical heat flux (q_{crit}) versus temperature for NaF. Solid line: $\gamma \neq 0$ (non-local theory); dotted line: $\gamma = 0$ (local theory).
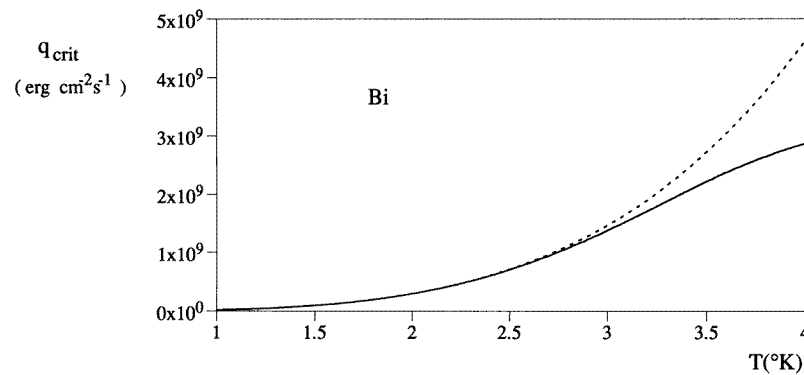
Figure 3. The critical heat flux (q_{crit}) versus temperature for Bi. Solid line: $\gamma \neq 0$ (non-local theory); dotted line: $\gamma = 0$ (local theory).

5. Final remarks

Our purpose was to propose a rather general thermodynamic model of propagation of heat pulses in non-metallic solids at low temperature. The model is non-linear, as the relevant parameters like heat capacity, heat conductivity, and relaxation times are allowed to be temperature dependent. It complements earlier work [3] by the same authors wherein only the linear aspects of the problem were investigated and where no comparison with experimental data was achieved. Our work also generalizes a paper by Coleman and Newman [7], who based their analysis on a non-linear Cattaneo relation. However, it is well known (see, e.g., [13]) that Cattaneo's equation is too simple to describe the complexity of energy transport in dielectric crystals. A better modelling is provided by the Guyer and Krumhansl formalism [1], but the latter has the inconvenience of not being compatible with hyperbolicity. In other words, it predicts that temperature signals propagate with an infinite velocity at high frequencies.

The model developed in this paper presents two improvements with respect to that of Guyer and Krumhansl. Firstly, it allows for temperature-dependent thermal coefficients;

secondly, it is compatible with the hyperbolicity requirement. The price to be paid is a more complicated description with an additional variable Q_{ij}, which is identified as the flux of the heat flux q_i. A direct consequence is that the internal energy will depend on q_i and the components of Q_{ij} in addition to the temperature. Under some simplifying assumptions, the internal energy is found to be quadratic in the heat flux:

$$u = u_{eq}(T) + a(T)q^2. \tag{66}$$

Heat pulse experiments on high-purity dielectric crystals such as NaF and Bi at very low temperature have allowed us to determine the dependence of a on temperature. Another interesting result from the present analysis is that it provides an expression for the velocity of propagation of weak discontinuities. In media in which the unperturbed temperature field was uniform, it was found that

$$v_{eq}^2 = \frac{\lambda}{\tau_R c_{eq}}[1 + \gamma T^2 c_{eq}] \tag{67}$$

wherein τ_R was identified as the relaxation time of the resistive phonon–phonon collisions. In comparison with Coleman and Newman's model [7], equation (67) contains an extra contribution proportional to γ; the latter is given by expression (40), and in the present model it is a constant quantity related to the various coefficients appearing in the evolution equations for the fluxes; the value of γ has been determined from experimental measurements.

It is worth stressing that the extra term $\gamma T^2 c_{eq}$ in expression (67) is certainly not negligible, as it is of the order of 0.3 for both NaF and Bi, in the temperature range of interest.

Acknowledgments

References

[1] Guyer R and Krumhansl J 1964 *Phys. Rev.* **133** 1411
   Guyer R and Krumhansl J 1966 *Phys. Rev.* **148** 778
[2] Joseph D D and Preziozi L 1989 *Rev. Mod. Phys.* **61** 41
[3] Lebon G, Torrisi M and Valenti A 1995 *J. Phys.: Condens. Matter* **7** 1461
[4] Jou D, Casas-Vazquez J and Lebon G 1996 *Extended Irreversible Thermodynamics* 2nd edn (Berlin: Springer)
[5] Lebon G, Jou D, Casas-Vazquez J and Muschik W 1996 submitted
[6] Jeffrey A and Taniuti T 1964 *Nonlinear Wave Propagation* (New York: Academic)
[7] Coleman B and Newman D 1988 *Phys. Rev.* B **37** 1492
[8] Jou D, Llebot J and Casas-Vazquez J 1982 *Phys. Rev.* A **25** 508
[9] Jackson H, Walker C and McNelly T 1976 *Phys. Rev. Lett.* **25** 26
[10] Narayanamurti V and Dynes R 1972 *Phys. Rev. Lett.* **28** 1461
[11] Hardy J and Jaswal S 1971 *Phys. Rev.* B **3** 4385
[12] Kopylov V and Mezhov-Deglin L 1971 *JETP Lett.* **14** 21
[13] Dreyer W and Struchtrup H 1993 *Continuum Mech. Thermodyn.* **5** 3