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Second sound speed in a crystal of NaF at low temperature

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WE DERIVE a physically justifiable model of heat conduction for rigid heat conductors based on a recent approach involving the gradient generalization of an internal state variable. The model accounts for observable phenomena in solid dielectric crystals, related to wave-like conduction of heat in certain ranges of low temperatures and a rapid decay of the speed of thermal waves close to a temperature value ϑ_λ, at which the conductivity of the material reaches a peak.

1. Introduction

FINITE SPEED thermal waves, known collectively as second sound, distinguishing them from generally faster propagating mechanical waves, were first detected in ^{3}He, ([1]), and then in high purity dielectric crystals of sodium fluoride, NaF, ([8]), and bismuth, Bi, ([16]). It has been observed that there exists a (material-dependent) temperature value below which second sound begins to be observed. The temperature values of this type have been measured to be close to those at which the conductivity of the material reaches a peak, a useful discussion of which can be found in the review papers [6, 10, 11].

In order to match regimes of different material behaviour, we will adapt the gradient generalization of the internal state variable theory in [14] to qualitative experimental results from the literature, so as to specify admissible forms of constitutive equations and material functions. In particular, our derivation is based on two experimentally observed phenomena not included in existing thermodynamic theories of second sound. The first is related to the propagation of heat pulses in solid specimens. It has been observed, ([8]), that in some range of temperature at which experiments have been performed, the time of arrival of heat pulses sent through a specimen is an approximately linear function of the reference temperature. However near the upper limit of measured temperature values, the time, measured by the leading edge of heat pulses, rises rapidly with increasing temperature. The latter corresponds to a very fast decay (with respect to temperature) of the second sound speed. The second phenomenon concerns the heat conductivity, in that close to a particular temperature the conductivity of the material reaches a peak, ([9]). In our model, motivated by the experimental data, we make the hypothesis that the temperature of maximum heat conductivity coincides with that below which second sound appears. Above this temperature value the heat conduction becomes purely diffusive, obeying a general nonlinear Fourier law. We call this *critical* temperature ϑ_λ. Furthermore, our approach allows us to relate ϑ_λ, the temperature at which heat conductivity reaches a maximum, to ϑ_m, a temperature separating two distinct families of discontinuity waves.

2. General framework

In [12], the material gradient of an internal, scalar, state variable was introduced as a fundamental state variable in the response functions of thermoelastic materials. In the course of obtaining consequences for the laws of thermodynamics, a modified Fourier-type law was found leading to finite speeds of propagation of thermal and thermomechanical waves. This model differed from an earlier one, ([13]), in the form of the evolution and constitutive equations, however essentially the same model as earlier has been used in the investigation of second sound phenomena ([3, 4]).

In the present paper we will begin with the generalized semi-empirical model, developed recently in [14]. The principal assertion is that the thermodynamic temperature ϑ is not by itself sufficient in describing some highly nonequilibrium phenomena, including the observed occurrence of low temperature heat pulses. Thus, besides the temperature and its gradient, a further internal variable, β, and *its* gradient are introduced into the constitutive equations. The variable β is in a certain sense a nonequilibrium temperature, related to the thermodynamic temperature through an initial value problem, and represents a history of the temperature field.

A rather general dependence of the free energy ψ was allowed in [14] on the various variables. However to avoid constraints between ϑ and β, this framework reduces to the following set of constitutive relations,

$$\psi = \psi(\vartheta, \beta, \nabla\beta), \qquad \eta = -\partial_\vartheta \psi(\vartheta, \beta, \nabla\beta), \tag{2.1}$$

$$\mathbf{q} = \mathbf{q}(\vartheta, \nabla\vartheta, \beta, \nabla\beta), \qquad \dot{\beta} = f(\vartheta, \beta), \tag{2.2}$$

in which the symbol ∇ denotes the gradient operator. Here $\mathbf{q}$ is the heat flux vector, η the entropy density, ϑ the thermodynamic temperature measured on the absolute scale, and ψ the free energy per unit volume related to ε, the internal energy per unit volume, by

$$\psi = \varepsilon - \eta\vartheta\,. \tag{2.3}$$

Balance of energy and the second law of thermodynamics imply

$$\varepsilon_t + \mathrm{div}\mathbf{q} = r, \tag{2.4}$$

$$\eta_t + \mathrm{div}(\mathbf{q}/\vartheta) \geq r/\vartheta\,, \tag{2.5}$$

where r is the body heat supply per unit volume. In this case the second law will take the form of the residual inequality

$$-\partial_{\nabla\beta}\psi\cdot\partial_{\beta}f\nabla\beta - \partial_{\beta}\psi f - (\partial_{\nabla\beta}\psi\partial_{\vartheta}f + \vartheta^{-1}\mathbf{q})\cdot\nabla\vartheta \geq 0. \tag{2.6}$$

In the isotropic case, the dependence of $\mathbf{q}$ on the gradients $\nabla\vartheta$ and $\nabla\beta$ can take the form

$$\mathbf{q} = -k\nabla\vartheta - \alpha\nabla\beta\,, \tag{2.7}$$

where the coefficients k and α may depend on the scalar quantities ϑ, β, $|\nabla\vartheta|$, $|\nabla\beta|$ and $\nabla\vartheta\cdot\nabla\beta$.

However, as discussed in [2], it becomes reasonable to make the following assumptions while remaining consistent with classical thermostatics, at the same time making it straightforward to use experimental results to identify the material functions needed:

- the free energy is independent of β and quadratic in $|\nabla\beta|$,
- the coefficients k and α depend only on ϑ.

Then we have the following representation for the free energy (cf. [2])

$$\psi = \psi_1(\vartheta) + \frac{1}{2}\psi_2(\vartheta)|\nabla\beta|^2 \tag{2.8}$$

and the residual inequality simplifies to the form

$$-\psi_2\partial_{\beta}f|\nabla\beta|^2 + \left(\vartheta^{-1}\alpha - \psi_2\partial_{\vartheta}f\right)\nabla\vartheta\cdot\nabla\beta + \vartheta^{-1}k|\nabla\vartheta|^2 \geq 0. \tag{2.9}$$

We note that the form (2.8) is one of consequences of the second law of thermodynamics in the original semi-empirical theory (i.e. when $k = 0$) under the hypothesis that α depends only on ϑ, as we have assumed above.

It is not hard to show that the last inequality will be satisfied for any choice of $\nabla\vartheta$ and $\nabla\beta$ if and only if

$$\partial_{\beta}f(\vartheta,\beta)\psi_2(\vartheta) \leq 0, \qquad k(\vartheta) \geq 0 \tag{2.10}$$

and

$$\left(\partial_{\vartheta}f(\vartheta,\beta)\psi_2(\vartheta) - \vartheta^{-1}\alpha(\vartheta)\right)^2 \leq -4\partial_{\beta}f(\vartheta,\beta)\psi_2(\vartheta)\vartheta^{-1}k(\vartheta). \tag{2.11}$$

The latter inequality should hold for any choice of $k(\vartheta) \geq 0$, in particular for $k(\vartheta) = 0$. This gives the compatibility condition

$$\alpha(\vartheta) = \vartheta\psi_2(\vartheta)\partial_{\vartheta}f(\vartheta,\beta) \tag{2.12}$$

(cf. [2]). From (2.12), we obtain the consequence $\partial_\beta \partial_\vartheta f(\vartheta, \beta) = 0$, which leads to the existence of two single-variable functions f_1, f_2, and to the splitting

$$f(\vartheta, \beta) = f_1(\vartheta) + f_2(\beta). \tag{2.13}$$

In this way we have the same set of compatibility conditions as in the previous setup, however, now the heat flux vector can satisfy the more general constitutive equation (2.7).

3. The NaF model

We now specialize to one space dimension and make some refinements in the behaviour of constitutive terms, particularly in the light of experimental evidence concerning NaF, ([9]). In the absence of a body heat supply, the balance of energy, Eq. (2.4), reduces to

$$\varepsilon_t + q_x = 0, \tag{3.1}$$

and, using (2.2) and (2.13), the evolution of β is described by

$$\beta_t = f_1(\vartheta) + f_2(\beta). \tag{3.2}$$

The heat flux, (2.7), is given by

$$q = -k(\vartheta)\vartheta_x - \alpha(\vartheta)\beta_x, \tag{3.3}$$

while the second law implies

$$\alpha(\vartheta) = \psi_{20}\vartheta^2 f_1'(\vartheta), \tag{3.4}$$

by (2.12) and the following particular choice

$$\psi = \psi_1(\vartheta) + \frac{1}{2}\psi_{20}\vartheta\beta_x^2 \tag{3.5}$$

for ψ, where $\psi_2(\vartheta) = \psi_{20}\vartheta$, and ψ_{20} is a constant (see (2.8). In this case ε reduces to a function of ϑ alone, by (2.1) and (2.3).

Finally, we define the specific heat c_v by

$$c_v(\vartheta) = \varepsilon'(\vartheta) = c_0\vartheta^3, \tag{3.6}$$

where c_0 denotes Debye's constant.

Combining Eqs. (3.1), (3.3) and (3.6) provides an equation describing the evolution of ϑ, which can be used in conjunction with (3.2) to give a third order system in the pair (ϑ, β),

$$c_v(\vartheta)\vartheta_t - (k(\vartheta)\vartheta_x + \alpha(\vartheta)\beta_x)_x = 0. \tag{3.7}$$

As concrete examples, let us define two C^1-homeomorphisms

$$f_1 : \mathbb{R} \to (-\infty, 0], \qquad \text{and} \qquad f_2 : \mathbb{R} \to \mathbb{R}.$$

For the first, we set

$$f_1(z) = a(|z|^{p-1}z)_- , \qquad 1 < p < 2, \tag{3.8}$$

where a is a positive constant, and the subscript $_-$ means that when $z \geq 0$, f_1 is taken to be zero. For the second, put

$$f_2(z) = -b|z|^{h-1}z, \qquad h \geq \frac{p}{2-p}, \tag{3.9}$$

where b is another positive constant. In both cases, z represents $\vartheta - \vartheta_\lambda$ where ϑ_λ denotes the *critical* temperature at which the heat conductivity of the material reaches a peak.

The basic form of f_1 becomes evident when the characteristic velocity, as a function of temperature, is compared with empirical data (cf. Fig. 1). The form of f_2, however, is taken in order to describe qualitatively the observed phenomenon of the heat conductivity peak; further experimental data for heat conduction obtained under quasi-static conditions would be useful to refine this.

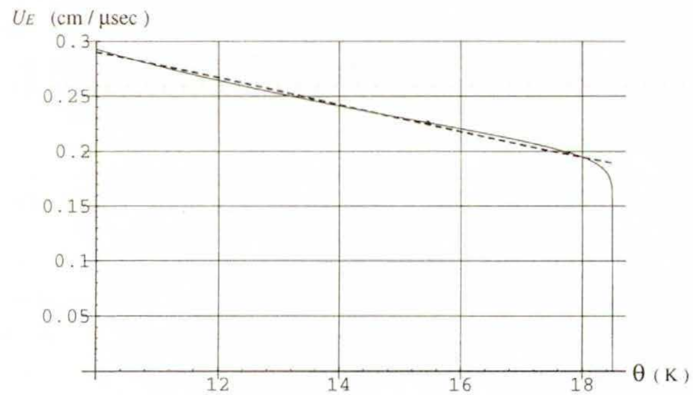

FIG. 1. Characteristic velocity (solid curve), $U_E = 0.85(18.5 - \vartheta)^{0.04}/\vartheta^{0.5}$, ahead of wave for $p = 1.04$, $\vartheta_\lambda = 18.5$, together with empirical data (dotted curve), $U_E = (9.09 + 0.00222\vartheta^{3.1})^{-0.5}$, (COLEMAN and NEWMAN, [4]).

It can be shown that in the *quasi-static* case, for which $f_1(\vartheta) + f_2(\beta) = 0$, (i.e. β is a function of ϑ), the heat flux (3.3) now reduces to

$$q = -(k(\vartheta) + c\psi_{20}\vartheta^2|(\vartheta - \vartheta_\lambda)_-|^{p(1+1/h)-2})\vartheta_x , \tag{3.10}$$

where c depends on a, b, p and h.

Moreover, an expression for the second sound speed, U_E, (the speed of small amplitude waves for the case $k(\vartheta) = 0$) is given by

$$U_E^2 = \frac{\psi_{20}}{c_0 \vartheta} a^2 p^2 (\vartheta - \vartheta_\lambda)_-^{2(p-1)}. \tag{3.11}$$

We note that (3.10) predicts a peak in heat conductivity as ϑ tends to ϑ_λ from below, followed by a sharp drop. At the same time, in particular if p is close to 1, (3.11) delivers a sudden drop to zero of the wave speed U_E. Both phenomena are to be expected on leaving the second sound regime and entering one of purely diffusive heat conductivity.

Raw data for $U_E(\vartheta)$ has been given for crystals of NaF of varying purity in [8], with an empirical relation, $U_E = (9.09 + 0.00222\vartheta^{3.1})^{-0.5}$ cm/μsec provided in [4]. The dependence of conductivity on temperature and purity is also described in [9], temperature of peak conductivity increasing with purity. The purest sample had a peak in conductivity at around 18.5 K which we take here to be ϑ_λ, below which second sound waves began to appear. In the figure above, we observe qualitatively and quantitatively similar behaviour (over the region of data availability) to the empirical form of $U_E(\vartheta)$ in [4, 7]. In the present approach we have obtained this behaviour using the example for f_1 above, when $p = 26/25$. The rapid drop at 18.5 K reflects our assumption that U_E vanishes at ϑ_λ. On reaching this temperature the pulse disappeares into the diffusive signal.

The choices we have made for f_1 and f_2 in this special case lead to a finite conductivity peak as $\vartheta \to 18.5$K if $h = 13/12$, and to infinite conductivity in the same limit if $h > 13/12$. The definition of $f_1(\vartheta - \vartheta_\lambda)$, (3.8), then makes the conductivity drop to $k(\vartheta)$ for $\vartheta > \vartheta_\lambda$.

It is possible to investigate the behaviour of shock waves for the system (3.1) and (3.2), for which the temperature ϑ has a discontinuity when $k(\vartheta) = 0$. These shocks, propagating to the right into an unperturbed state ϑ^+, satisfy Lax's admissibility condition, ([5]), if $s_r \le \sigma \le s_l$, where $\sigma = \sigma(\vartheta^+, \vartheta^-)$ is the shock speed, and $s_l = s_l(\vartheta^+, \vartheta^-)$, $s_r = s_r(\vartheta^+)$ denote the characteristic speeds, respectively in front of and behind the shock. Note that $s_r = U_E$, evaluated at ϑ^+. The choice of the functions f_1, f_2, predicts a temperature state $\vartheta^+ = \vartheta_m < \vartheta_\lambda$ into which shocks do not propagate. This temperature is found to be related to ϑ_λ according to

$$\vartheta_m = \frac{1}{3p-2} \vartheta_\lambda . \tag{3.12}$$

If $\vartheta^+ < \vartheta_m$, then for admissible shocks, the temperature, ϑ^-, behind the wave lies between ϑ^+ and ϑ_{**} ($\vartheta_{**} < \vartheta_m$ is a temperature depending on ϑ^+) and is greater than ϑ^+. If $\vartheta^+ > \vartheta_m$, the temperature behind the wave lies between ϑ^+ and ϑ_{**} (now $\vartheta_{**} > \vartheta_m$), which is here less than ϑ^+. These two cases correspond to "hot" and "cold" shocks, respectively. A similar result was obtained in [17], however the current model manages to connect the observed transition to diffusive behaviour at ϑ_λ with the change in wave propagation at ϑ_m.

This model appears to have some additional flexibility as compared to other theories where second sound persists to certain degrees at all temperatures, ([8, 15]). The presence of two regimes, hyperbolic and parabolic, provides the possibility of describing further phenomena related to ballistic phonons and second sound as discussed in [6], including broadening of smooth heat pulses, ([8, 9]), and diffusive heat conduction related to the parabolic regime.

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