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HEAT CONDUCTION AT LOW TEMPERATURE: A NON-LINEAR GENERALIZATION OF THE GUYER-KRUMHANSL EQUATION

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Abstract

A general non-linear and non-local heat transport equation is proposed in view to study heat conduction at low temperature (< 25 K) in non-metallic crystals. It is shown that the proposed relation generalizes the classical laws of Guyer and Krumhansl, Cattaneo and Fourier. The problem is treated within the framework of Extended Irreversible Thermodynamics. Special emphasis is placed on the consistency of the results with the second law of thermodynamics.

Keywords: heat conduction, low temperature, extended irreversible thermodynamics.

1. Introduction

Our purpose is to provide a rather general review of constitutive equations used to describe heat transport in rigid bodies. Of particular interest is the problem of heat conduction at low temperature, say below 25 K in dielectric crystals.

The best model for heat conduction in undeformable solids is undoubtedly Fourier's law which relates linearly the temperature gradient (the cause) to the heat flux (the effect). Despite its success, Fourier's law possesses some deficiencies, pointed out by several people and in particular by L. ONSAGER himself in his celebrated paper of 1931, where he noted that Fourier's model is in contradiction with the principle of microscopic reversibility. Quoting ONSAGER [1], he writes that this contradiction ... *'is removed when we recognize that [the Fourier law] is only an approximate description of the process of conduction, neglecting the time needed for acceleration of the heat flow'.*

In other terms, Fourier's law has the unphysical properties that it lacks inertial effects: if a sudden temperature perturbation is applied at one point in the solid, it will be felt instantaneously and everywhere at distant points. To eliminate this anomaly, CATTANEO [2] proposed a damped version of Fourier's law by introducing a heat-flux relaxation term. After insertion of the Cattaneo relation into the energy balance for a rigid solid, one obtains a hyperbolic differential equation for the temperature. In one dimension, this equation has the form of the well-known telegrapher equation allowing for propagation of waves at finite velocity. However, even with Cattaneo's equation, not all the problems are alleviated. In particular, it does not reproduce experiments on ultrasonic wave propagation in dilute gases and cannot be used to describe heat pulse propagation in non-metallic crystals, like Bi or Na F at very low temperature. This has motivated the search for a further extension of Fourier's law. GUYER and KRUMHANSL [3] solved the linearized Boltzmann equation for a phonon field in dielectric crystals at low temperature and derived an extension of Cattaneo's equation involving nonlocal contributions. However, even Guyer and Krumhansl's model presents some limitation: it is a linearized equation, further, when coupled to the classical energy equation, it predicts infinite speed of propagation at very large frequencies, finally it is unable to describe the non-linear features characterizing second sound propagation at very low temperature.

These observations have motivated the formulation of a non-linear extension of Guyer–Krumhansl's result. In the present work, we propose a derivation of such a generalized equation within the framework of Extended Irreversible Thermodynamics (EIT). Particular attention will be paid on the consequences placed by the second law.

The paper will run as follows. After a historical record of the Fourier, Cattaneo and Guyer and Krumhansl equations, with emphasis on the thermodynamic theories underlying these relations (section 2), we propose a non-linear and non-local extension of Cattaneo's model (section 3). Restrictions placed by the second law of thermodynamics are analyzed in section 4. The results are rewritten in terms of the temperature gradient in section 5 and concluding remarks are made in section 6.

The general hypotheses underlying the present work are isotropy of the material, absence of deformation and no global convection.

2. Historical Record: from Fourier's Model to Guyer–Krumhansl's Model

2.1. Fourier's Model

Fourier's law of heat conduction is one of the most popular laws in continuum physics, as it provides an excellent agreement between theory and experiment for more than 90% of the problems. It relates the heat flux vector $\mathbf{q}$ to the temperature gradient ∇T through

$$\mathbf{q} = -\lambda \nabla T \ , \tag{1}$$

wherein λ is the heat conductivity, depending generally on the temperature. By combining (1) with the energy balance

$$c\partial_t T = -\nabla \cdot \mathbf{q}, \tag{2}$$

where c is the heat capacity (measured per unit volume), one obtains a parabolic differential equation for the temperature given by

$$c\partial_t T = \nabla \cdot (\lambda \nabla T) \ . \tag{3}$$

Such expression suffers from some pathological deficiencies: the most important is that it implies that heat signals propagate with an infinite speed. Moreover, Fourier's model is not adequate for describing heat transport at very high frequencies and short wave lengths.

In view of future comparison, it is interesting to show how Fourier's equation can be derived from nonequilibrium thermodynamics. Fourier's law is well described within the framework of Classical Irreversible Thermodynamics [e.g., [4]]. The main pillar of this formalism is to assume that even outside equilibrium, the entropy s (per unit volume) depends on the same variables as in equilibrium (local equilibrium hypothesis). For heat conduction in rigid bodies, s depends only on the internal energy u per unit volume:

$$s = s(u) \ , \tag{4}$$

or cast in differential form

$$\mathrm{d}s = T^{-1}\mathrm{d}u \qquad \text{(Gibbs equation)} \tag{5}$$

with $T^{-1} = \partial s/\partial u$, the so-called local equilibrium temperature. The entropy obeys a balance equation of the form

$$\rho\dot{s} = -\nabla \cdot \mathbf{J}^s + \sigma^s \ , \qquad (\sigma^s > 0) \ , \tag{6}$$

wherein the entropy flux $\mathbf{J}^s$ and the positive entropy production σ^s are given respectively by

$$\mathbf{J}^s = \frac{1}{T}\mathbf{q} \ , \tag{7}$$

$$\sigma^s = \mathbf{q} \cdot \nabla T^{-1} \geq 0 \ . \tag{8}$$

Assuming a linear relationship between the flux $\mathbf{q}$ and the driving force ∇T^{-1}, one obtains

$$\mathbf{q} = L \nabla T^{-1} \ , \tag{9}$$

which is identical to Fourier's law at the condition to set $L = \lambda T^2$.

2.2. Cattaneo's Model

To circumvent the problems associated with Fourier's law, CATTANEO [2] proposes a time-dependent relaxational model of the form

$$\tau \partial_t \mathbf{q} + \mathbf{q} = -\lambda \nabla T \ , \tag{10}$$

wherein τ is the relaxation time which, in heat conduction, is extremely small ($\tau \approx 10^{-13}$ s) at room temperature; it is the smallness of τ which accounts for the success of Fourier's model. Substituting (10) in the energy balance (1) yields, for constant values of τ and λ,

$$\tau \partial_t^2 T + \partial_t T = \kappa_T \nabla^2 T \ , \tag{11}$$

wherein $\kappa_T \ (= \lambda / c)$ denotes the heat diffusivity. Being of the hyperbolic type, (11) possesses three important properties that the classical parabolic equation, obtained by setting $\tau = 0$, does not. First, it predicts a finite speed of propagation at infinite frequency given by

$$\lim_{\omega \to \infty} V = \sqrt{\frac{\kappa_T}{\tau}} \ . \tag{12}$$

Secondly, unlike the parabolic equation which is irreversible in time, (11) is reversible within periods of time of the order of the thermal relaxation time. Thirdly, expression (11) is of second order in the time derivative, and therefore not only the initial value of the temperature but also its rate of change must be given at $t = 0$, unlike the parabolic equation which permits only the initial value to be specified.

Nevertheless, Cattaneo's equation presents also some shortcomings. Although it leads to a finite value for the wave velocity, the latter differs from the value observed in experiments on ultrasonic propagation in dilute gases. As shown in *Fig. 1*, Cattaneo's approach predicts that V/c_s where c_s is Laplace sound velocity, tends asymptotically to 1.6 instead of the value 2.1 found experimentally. In addition, Cattaneo's model is unable to provide a complete interpretation of heat-pulse experiments at very low temperature in very pure crystals [5].

It is well known that Cattaneo's relation is backwarded by Extended Irreversible Thermodynamics [e.g. [6]]. In this formalism, the entropy $s(u, \mathbf{q})$ is assumed to depend on the heat flux $\mathbf{q}$ besides the energy u; the corresponding generalized Gibbs equation is now written as [6]

$$\mathrm{d}s = T^{-1} \mathrm{d}u - \frac{\tau}{\lambda T^2} \mathbf{q} \cdot \mathrm{d}\, \mathbf{q} \ . \tag{13}$$

It is also easily checked that the entropy flux keeps the classical form

$$\mathbf{J} = \frac{1}{T} \mathbf{q} \ , \tag{14}$$

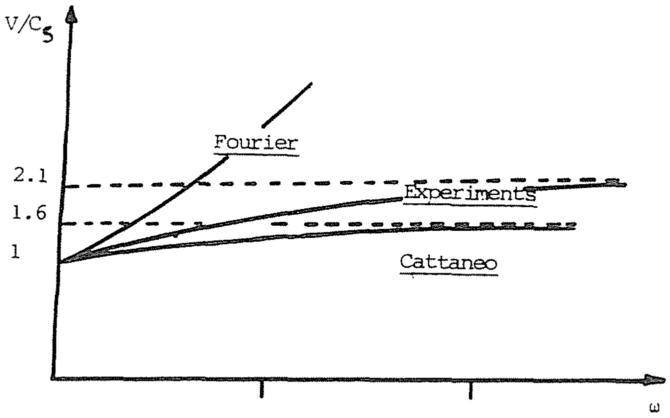

Fig. 1. Ultrasonic wave propagation in dilute gases: comparison between Fourier's and Cattaneo's models with experiments

while the entropy production reads as

$$\sigma^s = \frac{1}{\lambda T^2}\mathbf{q}\cdot\mathbf{q} \ . \tag{15}$$

From the positiveness of σ^s, it is inferred that $\lambda > 0$ while from the convexity property of s, it is shown that $\tau > 0$.

2.3. Guyer–Krumhansl's Model

Guyer–Krumhansl's equation is a non-local generalization of Cattaneo's. It is well adapted to the description of phonon gases where heat transport is not only governed by diffusion (like in Fourier's description) and second sound (like in Cattaneo's model) but in addition by ballistic transport. Guyer–Krumhansl's equation reads as [3]

$$\tau\partial_t\mathbf{q} + \mathbf{q} + \lambda\nabla^2 T = \ell_1^2\left(\nabla^2\mathbf{q} + 2\nabla\nabla\cdot\mathbf{q}\right) \ , \tag{16}$$

the nonlocal corrective terms are collected in the r.h.s. of (16), ℓ_1 is a new phenomenological coefficient with the dimension of a length.

There exist several ways to recover Guyer–Krumhansl's equation from a thermodynamic description. A possible approach is to assume that s depends on an extra 'internal' variable $\mathbf{Q}$, besides u and $\mathbf{q}$ so that

$$s = s(u, \mathbf{q}, \mathbf{Q}) \ . \tag{17}$$

By comparison with the kinetic theory of gases, it is seen that $\mathbf{Q}$, a tensor of rank two, represents the flux of the heat flux vector. The corresponding Gibbs equation is [6]

$$ds = T^{-1}du - \frac{\tau_1}{\lambda T^2}\mathbf{q}\cdot\mathbf{q} - \tau_2\alpha\mathbf{Q}\cdot d\mathbf{Q}\ , \tag{18}$$

wherein τ_1 and τ_2 are the relaxation times of $\mathbf{q}$ and $\mathbf{Q}$ respectively, and α is a phenomenological coefficient. The entropy flux is no longer given by the classical expression $\mathbf{q}/T$ but contains an extra contribution in $\mathbf{Q}\cdot\mathbf{q}$

$$\mathbf{J}^s = \frac{1}{T}\mathbf{q} + \gamma\mathbf{Q}\cdot\mathbf{q}\ , \tag{19}$$

the entropy production takes the form

$$\sigma^s = \frac{1}{\lambda T^2}\mathbf{q}\cdot\mathbf{q} + \alpha\mathbf{Q} : \mathbf{Q} \geq 0 \tag{20}$$

with $\lambda > 0$, $\alpha > 0$ as a consequence of the positiveness of σ^s.

As mentioned in section 1, Guyer and Krumhansl's equation provides only partial answers to the questions raised by energy transport in phonon gases. This has motivated the present work wherein an extension of Guyer–Krumhansl's equation in the non-linear regime is proposed.

3. A Non-linear and Non-local Heat Transport Equation

In a first step, a transport equation of heat generalizing Guyer–Krumhansl's equation will be formulated. Afterwards, some consequences resulting from an analysis of the results within the frame of Extended Irreversible Thermodynamics (EIT) are established and analyzed.

The basic variables are selected as u and $\mathbf{q}$ in agreement with EIT. Their evolution in the course of time and space is governed by general balance equations taking the form

$$\partial_t u = -\nabla\cdot\mathbf{q} + r\ , \tag{21}$$

$$\partial_t \mathbf{q} = -\nabla\cdot\mathbf{Q} + \sigma^q\ . \tag{22}$$

One recognizes the usual balance law of energy (21) with a source term r; expression (22) is written in strict analogy with (21) wherein $\mathbf{Q}$ designates the flux of the heat flux and σ^q the corresponding source term. At this stage of the analysis, neither $\mathbf{Q}$ nor σ^q are known which means that they must be given by constitutive equations. Since one has in mind to develop a weakly non-local and non-linear formalism, it is reasonable to select as constitutive equations

$$\mathbf{Q} = A\mathbf{I} - L_1(\nabla\mathbf{q}) - L_2(\nabla\cdot\mathbf{q})\mathbf{I} - L_3(\nabla\mathbf{q})^T + B\mathbf{q}\mathbf{q}\ , \tag{23}$$

$$\sigma^q = -a\mathbf{q} - b\nabla u + \mathbf{F}\cdot(\nabla\mathbf{q}) + (\nabla\mathbf{q})\cdot\mathbf{H} + \mathbf{G}\nabla\cdot\mathbf{q}\ , \tag{24}$$

where $\mathbf{I}\,(=\delta_{ij})$ stands for the identity tensor and $(\nabla\mathbf{q})_{ij}$ for $\partial q_i/\partial x_j$, superscript T means transposition. The scalar coefficients a, b, A, L_i ($i = 1, 2, 3$) depend generally on u and $\mathbf{q}\cdot\mathbf{q}$ and the vectors $\mathbf{F}$, $\mathbf{H}$, $\mathbf{G}$ are assumed to be linear functions of the vectors ∇u and $\mathbf{q}$:

$$\begin{aligned} \mathbf{F} &= \alpha_1(u)\mathbf{q} + \alpha_2(u)\nabla u\ , \\ \mathbf{H} &= \tilde{\beta}_1(u)\mathbf{q} + \beta_2\nabla u\ , \\ \mathbf{G} &= \tilde{\gamma}_1(u)\mathbf{q} + \gamma_2(u)\nabla u\ . \end{aligned} \tag{25}$$

For further purposes, one introduces also the following notation

$$a = \frac{1}{\tau}\ , \qquad \frac{\partial A}{\partial u} + b = \kappa\ , \qquad L_i' = \frac{\partial L_i}{\partial u}\ . \tag{26}$$

After substitution of (23) and (24) in (22), one obtains (when third order terms in $q^2\mathbf{q}$, $\mathbf{q}\cdot\nabla\mathbf{q}\cdot\nabla\mathbf{q}$, $\mathbf{q}\,(\nabla u)^2, \ldots$ are omitted) the following evolution equation for $\mathbf{q}$:

$$\begin{aligned} \partial_t\mathbf{q} = & -\kappa\nabla u - \frac{1}{\tau}\mathbf{q} + \alpha_1\mathbf{q}\cdot(\nabla\mathbf{q}) + \beta_1(\nabla\mathbf{q})\cdot\mathbf{q} \\ & + \gamma_1(\nabla\cdot\mathbf{q})\,\mathbf{q} + \alpha_2\nabla u\cdot(\nabla\mathbf{q}) + \beta_2(\nabla\mathbf{q})\cdot\nabla u + \gamma_2(\nabla\cdot\mathbf{q})\,\nabla u \\ & + L_1\nabla^2\mathbf{q} + L_2\nabla(\nabla\cdot\mathbf{q}) + L_3\nabla\cdot(\nabla\mathbf{q}) \\ & + L_1'(\nabla\mathbf{q})\cdot\nabla u + L_2'(\nabla\cdot\mathbf{q})\,\nabla u + L_3'\nabla u\cdot(\nabla\mathbf{q})\ , \end{aligned} \tag{27}$$

wherein β_1 and γ_1 stand for $\tilde{\beta}_1 + B$, $\tilde{\gamma}_1 + B$, respectively. In view of a better apprehension of the above result, let us consider some particular cases.

- Assume that the coefficients L_i are constant and that α_i, β_i, γ_i ($i = 1, 2, 3$) vanish. Expression (27) then becomes a Guyer–Krumhansl-type equation

$$\partial_t\mathbf{q} = -\kappa\nabla u - \frac{1}{\tau}\mathbf{q} + L_1\nabla^2\mathbf{q} + L_2\nabla\nabla\cdot\mathbf{q} + L_3\nabla\cdot(\nabla\mathbf{q})\ . \tag{28}$$

- If, in addition, it is supposed that $L_1 = L_2 = L_3 = 0$, one finds

$$\tau\partial_t\mathbf{q} = -\tau\kappa\nabla\cdot u - \mathbf{q}\ , \tag{29}$$

  which is reminiscent of Cattaneo's equation.
- Finally by setting $\tau = 0$ (but $\tau\ \kappa$ finite), one recovers a Fourier-like equation

$$\mathbf{q} = -\tau\kappa\nabla u\ . \tag{30}$$

4. Restrictions Placed by the Second Law of Thermodynamics

In EIT, it is assumed that there exists a non-equilibrium entropy $s(u, \mathbf{q})$, which is a convex function of the basic variables and whose rate of production σ^s is non-negative. In other terms, s obeys an evolution equation of the form

$$\partial_t s = -\nabla \cdot \mathbf{J}^s + \sigma^s \ , \tag{31}$$

with

$$\sigma^s \geq 0 \ . \tag{32}$$

Solving (31) with respect to σ^s, one has

$$\sigma_s = \partial_t s + \nabla \cdot \mathbf{J}^s \geq 0 \ , \tag{33}$$

from which it follows that, the determination of σ^s implies the knowledge of the constitutive equation expressing s and $\mathbf{J}^s$ in terms of the variables u, $\mathbf{q}$ and their gradients, these quantities should be a priori present as one has in mind a non-local formalism; therefore

$$s = s(u, \mathbf{q}, \nabla u, \nabla \mathbf{q}) \ , \tag{34}$$

$$\mathbf{J}^s = \mathbf{J}^s(u, \mathbf{q}, \nabla u, \nabla \mathbf{q}) \ . \tag{35}$$

As usually, let us define the non-equilibrium temperature θ through [6]

$$\theta^{-1} = \frac{\partial s}{\partial u} \ , \tag{36}$$

while for simplicity we shall assume that $\partial s / \partial \mathbf{q}$ is a linear function of $\mathbf{q}$:

$$\frac{\partial s}{\partial \mathbf{q}} = f(u)\mathbf{q} \tag{37}$$

with $f(u)$ an undetermined function of u. To explore the consequences resulting from inequality (33), we follow the procedure widely applied in Rational [7] and Extended Thermodynamics [6]. More details about the specific problem treated here can be found in [8], therefore, it is sufficient here to recall the main results.

- s is found to be independent of the gradients ∇u and $\nabla \mathbf{q}$ so that, by virtue of (36) and (37), the relevant Gibbs equation reads as

$$\mathrm{d}s = \theta^{-1}\mathrm{d}u + f\mathbf{q} \cdot \mathrm{d}\ \mathbf{q} \ . \tag{38}$$

- The entropy flux contains non-local and non-linear contribution in $\mathbf{q} \cdot \nabla \mathbf{q}$ and writes as

$$\mathbf{J}^s = \frac{1}{T}\mathbf{q} - L_1 f\mathbf{q} \cdot (\nabla \mathbf{q}) - L_2 \mathbf{q} \nabla \cdot \mathbf{q} - L_3 (\nabla \mathbf{q}) \cdot \mathbf{q} \ . \tag{39}$$

- The entropy production is quadratic in $\mathbf{q}$ and its gradients

$$\sigma^s = -\frac{f}{\tau}\mathbf{q}\cdot\mathbf{q} - L_1 f\left(\nabla\mathbf{q}\right):\left(\nabla\mathbf{q}\right)^T - L_2\left(\nabla\cdot\mathbf{q}\right)^2 - L_3\left(\nabla\mathbf{q}\right):\left(\nabla\mathbf{q}\right) \geq 0\ , \tag{40}$$

where a colon stands for the double scalar product $\mathbf{A}\ :\mathbf{B} = A_{ij}B_{ji}$; as a consequence of $\sigma^s \geq 0$, one has

$$\frac{f}{\tau} < 0\ , \qquad L_2 f < 0\ , \qquad \left(L_1 + L_3\right) f < 0\ , \qquad \left(L_1 - L_3\right) f < 0. \tag{41}$$

- Since s is assumed to be a convex function of the variables u and $\mathbf{q}$ [6], it follows directly from $\partial^2 s/\partial\mathbf{q}\cdot\partial\mathbf{q} < 0$ that

$$f < 0 \tag{42}$$

and, by virtue of (41),

$$\tau > 0\ , \qquad L_1 > 0\ , \qquad L_2 > 0\ , \qquad L_1 > L_3 > 0\ . \tag{43}$$

- The coefficients L_1, α_2, β_2, γ_2, f are not independent but linked by

$$L_1 f' = \beta_2 f\ , \qquad L_2 f' = \gamma_2 f\ , \qquad L_3 f' = \alpha_2 f\ , \qquad 2\gamma_1 = f'\ ,$$
$$\left(f' = \frac{\partial f}{\partial u}\right)\ . \tag{44}$$

- An expression of the non-equilibrium temperature is easily derived: from the equality of the mixed derivatives of s (see (38)), it is found that

$$\frac{\partial\theta^{-1}}{\partial\mathbf{q}} = f'\mathbf{q}\ , \tag{45}$$

and, after integration,

$$\theta^{-1}\left(u, q^2\right) = \frac{1}{2}f' q^2 + T^{-1}(u)\ , \tag{46}$$

wherein $T(u)$ is the temperature corresponding to zero heat flux, i.e., the local equilibrium temperature.

5. Results in Terms of the Temperature Gradient

For practical use, it is convenient to reformulate the transport equation (27) in terms of the temperature gradient $\nabla\theta$ rather than in terms of ∇u. Since θ, like s depends only on u and $\mathbf{q}$, one has

$$\nabla\theta^{-1} = \frac{\partial\theta^{-1}}{\partial u}\nabla\theta + \frac{\partial\theta^{-1}}{\partial\mathbf{q}}\cdot\nabla\mathbf{q}\ . \tag{47}$$

Solving with respect to ∇u and making use of the results of the previous section, it is found that

$$\kappa \nabla u = \frac{\lambda}{\tau} \nabla \theta + \frac{f'}{f} \mathbf{q} \cdot \nabla \mathbf{q} \ , \tag{48}$$

wherein λ is defined by

$$\lambda = -\frac{\tau}{f \theta^2} \ . \tag{49}$$

As $\tau > 0$ and $f < 0$, it is clear that λ is a positive quantity which will be identified as the heat conductivity. In view of (48) and the results of section 4, the heat transport equation (27) will be written as

$$\begin{aligned} \partial_t \mathbf{q} &= -\frac{1}{\tau} \mathbf{q} - \frac{\lambda}{\tau} \nabla \theta + L_1 \nabla^2 \mathbf{q} + L_2 \nabla \nabla \cdot \mathbf{q} + L_3 \nabla \cdot (\nabla \mathbf{q})^T \\ &+ \alpha_1 (\mathbf{q} \cdot \nabla \mathbf{q} - \nabla \mathbf{q} \cdot \mathbf{q}) + \gamma_1 (2\mathbf{q} \cdot \nabla \mathbf{q} + \mathbf{q} \nabla \cdot \mathbf{q}) \\ &+ (L_3' + 2\gamma_1 L_3) \nabla u \cdot \nabla \mathbf{q} + (L_2' + 2\gamma_1 L_2) \nabla u \nabla \cdot \mathbf{q} \\ &+ (L_1' + 2\gamma_1 L_1) \nabla \mathbf{q} \cdot \nabla u \ . \end{aligned} \tag{50}$$

This expression contains seven unknown parameters, namely $\lambda > 0$ (heat conductivity), $\tau > 0$ (relaxation time), L_1, L_2, L_3 (all three quantities are positive and describe non-locality), α_1 and γ_1 (whose sign is not determined and which are related to non-linearities).

Of particular interest is the case corresponding to f, L_1, L_2 and L_3 constant. The evolution equation (50) then simplifies as

$$\partial_t \mathbf{q} = -\frac{\lambda}{\tau} \nabla T - \frac{1}{\tau} \mathbf{q} + L_1 \nabla^2 \mathbf{q} + L_2 \nabla \nabla \cdot \mathbf{q} + L_3 \nabla \cdot (\nabla \mathbf{q})^T + \alpha_1 (\mathbf{q} \cdot \nabla \mathbf{q} - \nabla \mathbf{q} \cdot \mathbf{q}) \ . \tag{51}$$

If, in addition, $\alpha_1 = 0$ and $L_1 = L_2 = L_3$, one obtains

$$\partial_t \mathbf{q} = -\frac{\lambda}{\tau} \nabla T - \frac{1}{\tau} \mathbf{q} + L_1 \left(\nabla^2 \mathbf{q} + 2 \nabla \nabla \cdot \mathbf{q} \right) \ . \tag{52}$$

This is nothing but Guyer–Krumhansl's equation at the condition to identify τ and L_1 as

$$\tau = \tau_R \ , \qquad L_1 = \frac{1}{\tau} \tau_N L_1^2 \ . \tag{53}$$

τ_R and τ_N are the relaxation times associated to the resistive and the normal phonon–phonon collisions, respectively. At this point, two remarks are in form. First, it is remarkable to observe that our purely macroscopic approach is able to reproduce the coefficient 2 of the term $\nabla \nabla \cdot \mathbf{q}$ in the r.h.s. of (52). Secondly, it is easily checked that the entropy flux corresponding to

Guyer–Krumhansl's equation is no longer given by the classical result $\mathbf{q}/T$ but rather by

$$\mathbf{J}^s = \frac{1}{T}\mathbf{q} + \frac{L_1 \tau}{\lambda T^2}\left[2\mathbf{q} \cdot (\nabla \mathbf{q})^{sym} + \mathbf{q}\nabla \cdot \mathbf{q}\right] , \tag{54}$$

exhibiting the presence of non-linear terms in $\mathbf{q} \cdot \nabla \mathbf{q}$ and $\mathbf{q}\,(\nabla \cdot \mathbf{q})$.

6. Concluding Remarks

A rather general transport equation (50) has been proposed to describe non-steady, non-local and non-linear effects of heat conduction in rigid solids. *Eq.* (50) contains seven undetermined parameters. Compatibility with the second law of thermodynamics indicates that five of these seven quantities are positive. More information about these parameters should be derived either from experimental observations or from theoretical models based on the kinetic theory statistical mechanics.

Transport equation (50) generalizes Fourier's, Cattaneo's and Guyer–Krumhansl's laws.

To provide an overview of the domain of application of these various laws, we have drawn a three-dimensional reference system (see *Fig. 2*): along the y-axis, we have represented the wave number k, along the x-axis is given the frequency ω, while non-linearities are quantified by the z-axis. Since Fourier's law is valid for small k and w values, its range of application is restricted to a small cube centered at the origin of the reference system. Now by moving along the x-axis, one covers the domain of applicability of Cattaneo's equation while the range of the linearized Guyer–Krumhansl equation is represented by the horizontal $x - y$ plane. Finally, the volume of the large box describes the range of expression (50), which incorporates non-linear effects.

Another important result is that the previous analysis displays the strong correlation existing between dynamics, i.e., the transport equation, and thermodynamics (through the entropy flux). Clearly, one cannot select the transport equation and the entropy flux independently of each other. For instance, while the classical expression $\mathbf{J}^s = \mathbf{q}/T$ is compatible with the Fourier and Cattaneo laws, it is NOT compatible with the Guyer–Krumhansl equation.

Finally, it should be mentioned that an explicit expression of the non-equilibrium temperature in terms of the heat flux has been derived. The result is

$$\theta^{-1}\left(u, q^2\right) = T^{-1}(u) + f' q^2 , \tag{55}$$

from which it follows clearly that θ can be identified as the local equilibrium temperature T either under the conditions that corrective terms in q^2 are

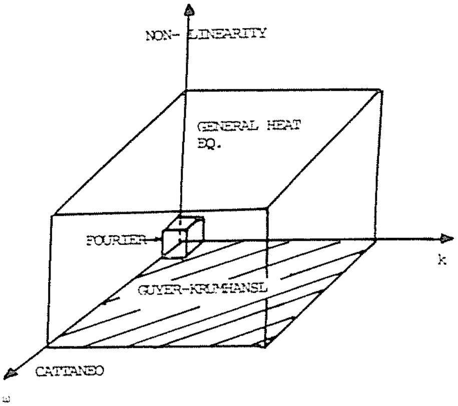

Fig. 2. Domains of application of Fourier's, Cattaneo's, Guyer–Krumhansl's and the generalized heat transport equations

omitted (linear approximation) or in the case of a constant value of the coefficient f.

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