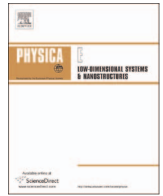Dear Author,

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A thermodynamic model for heat transport and thermal wave propagation in graded systems

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ABSTRACT

We study the effects of a composition gradient and of a non-vanishing heat flux on the phase velocity of thermal waves along a graded system. We take into account non-local and non-linear effects by applying a generalized heat transport equation. We compare the results for high-frequency and low-frequency waves. For low frequency, we discuss the conditions in which thermal waves may propagate in Si_xGe_{1-x} and $(Bi_{1-x}Sb_x)_2Te_3$ systems. For high frequency, we discuss the influence of the relaxation of the flux of the heat flux on the heat wave propagation.

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1. Introduction

Graded materials are inhomogeneous materials, layered or continuous, which are increasingly used in technology, in such a way that the change of a material property with temperature may be compensated by its change with composition, in order to achieve optimization of some process [1–8]. A usual example is the alloy Si_xGe_{1-x}, which has been much studied in semiconductor physics to engineer heat or current transport [9–13]. Other examples arise in thermoelectricity, where the maximization of ZT, with Z being the figure of merit and T being the absolute temperature, is important to optimize the efficiency of energy conversion from heat to electricity [14–18]. The figure of merit is defined as $Z = S^2\sigma/\lambda$, S being the Seebeck coefficient, σ the electrical conductivity and λ the thermal conductivity. Besides the difficulty in finding materials with high enough ZT, an additional difficulty is its variation with temperature, because usually σ increases with T while S decreases, in such a way that ZT has a maximum in a relatively narrow range of temperatures. Thus, the use of graded systems is very natural, namely to optimize ZT not only at one point, but along the whole system.

The thermoelectric materials that are most used for energy conversion are Bi_2Te_3, Sb_2Te_3 and Pb Te and/or their alloys $Bi_{2-2x}Te_{3-2x}Pb_x$ and $(Bi_{1-x}Sb_x)_2$ Te_3 [1,10], with x changing along the longitudinal direction Z. The alloys with x ranging in the interval [0, 1], as, for instance, Bi_2Te_3 for $x=0$, and Pb Te or Sb_2Te_3, for to $x=1$, are of special interest, as Pb Te has a maximum of ZT around $T=400\,°C$, Bi_2Te_3 around $200\,°C$, and Sb_2Te_3 $T=130\,°C$. Consequently, their combination along a system allows us to improve the global efficiency of the energy conversion [19–21].

In this work we consider the practical consequences of the inhomogeneity of the composition on the evolution equation for the heat flux in graded materials, which allows us to obtain the temperature distribution along the system. This information is relevant for the optimization of the thermoelectric energy conversion. Furthermore, we explore the consequences of such evolution equation on thermal wave propagation, in order to infer which information could be obtained on the system by using low-frequency and high-frequency thermal waves as exploration technique [22]. To achieve that task, it is possible to take into account the influence of ∇x and, in the case of systems which are out of equilibrium, also of the heat flux due to a non vanishing superimposed heat flux $\mathbf{q}_0$. The consequences of a non-monotonic dependence of the thermal conductivity on x on the behaviour of slow thermal waves are pointed out in Section 2. In Section 3, a generalized equation for heat transport, incorporating non-local and non-linear terms, is derived. Its consequences on the speed of high-frequency heat waves are considered in Sections 4–6.

2. Heat waves in a graded system: Maxwell–Cattaneo approach

In this preliminary section, we use the Maxwell–Cattaneo equation for the heat flux $\mathbf{q}$ as a model of generalized heat

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transport equation yielding finite wave speed for high-frequency heat waves, and we search the speed of thermal waves, in the presence of a composition gradient ∇x and of an initial heat flux $\mathbf{q}_0$. The Maxwell–Cattaneo equation is [23–25]

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

with τ being the heat flux relaxation time and λ being the thermal conductivity. Combined with the energy balance equation in the absence of external sources, namely

$$\rho \dot{u} = \rho c \dot{T} = -\nabla \cdot \mathbf{q}, \tag{2}$$

with $u = cT$ being specific internal energy, ρ mass density and c specific heat per unit mass, one gets

$$\tau \rho c \frac{\partial^2 T}{\partial t^2} + \rho c \frac{\partial T}{\partial t} = \lambda \nabla^2 T + \frac{\partial \lambda}{\partial x} (\nabla x) \cdot \nabla T + \frac{\partial \lambda}{\partial T} \nabla T \cdot \nabla T. \tag{3}$$

We explore the consequences of this equation on the heat wave propagation, a topic of much interest in non-equilibrium thermodynamics [22–24,26,27,25,28–34].

2.1. Propagation along an equilibrium state ($\mathbf{q}_0 = 0$)

We consider small-amplitude temperature perturbations $\delta T = \delta T_0 \exp[i(\omega t - \kappa z)]$, with T_0 being a constant reference temperature, ω the frequency of the perturbation and κ the component of the wave-vector along Z. First, we neglect the non-linear term in $(\nabla T)^2$, because we consider propagation along an equilibrium state. In such condition it is logical to suppose that (∇T) is very small, in such a way that $(\nabla T)^2$ may be considered negligible. Then, by Eq. (3) one gets for the dispersion relation

$$\chi \kappa^2 - Bi\kappa + (i\omega - \tau \omega^2) = 0, \tag{4}$$

with $\chi = \frac{\lambda}{\rho c}$, $B = \frac{1}{\rho c} \frac{\partial \lambda}{\partial x} \nabla_z x$. From here, one obtains

$$\kappa = \frac{Bi \pm \sqrt{B^2 i^2 - 4\chi(i\omega - \tau \omega^2)}}{2\chi}. \tag{5}$$

Thus, the phase speed

$$v_p \equiv \omega / Re(\kappa), \tag{6}$$

reads

$$v_p = \frac{\sqrt{2\chi\omega}}{\sqrt{\tau\omega - \frac{B^2}{4\chi\omega} + \sqrt{\left(\tau\omega - \frac{B^2}{4\chi\omega}\right)^2 + 1}}}. \tag{7}$$

For $B = 0$, from Eq. (7) we get the classical expression of the phase speed corresponding to Maxwell–Cattaneo equation, well-known in the literature [24–26]. For $B \neq 0$ and low-frequency waves ($4\chi\tau\omega^2 \ll B^2$) we obtain

$$v_p = B\sqrt{1 - \frac{4\chi\tau}{B^2}\omega^2} \approx B. \tag{8}$$

Thus, the presence of a composition gradient yields a propagatory character to low-frequency heat waves, which otherwise, would proceed with speed $v_p = \sqrt{2\chi\omega}$, vanishing for $\omega \to 0$.

Since $B = (1/\rho c)(\partial \lambda/\partial x)\nabla x$, it turns out that the phase speed is positive (i.e., the speed will propagate to the right-hand side) for positive gradient of λ. Moreover, the higher $\nabla \lambda$, the higher v_p, so that the waves proceed faster in regions with higher inhomogeneity in the thermal conductivity. This result could be also interpreted in terms of the Le Châtelier–Braun principle [35], according to which the system reacts against perturbations; in this case, since heat diffuses faster in regions with high thermal

conductivity, going towards such direction will provide the most efficient way to react against the perturbation. For $\omega \to \infty$, in (7) one has

$$v_p(\omega \to \infty) = \sqrt{\frac{\lambda}{\rho c \tau}}, \tag{9}$$

which is the usual expression of high-frequency wave speed for Maxwell–Cattaneo equation [23–26].

By Eq. (5) we also obtain the attenuation length

$$A = -\frac{1}{\mathrm{Im}(\kappa)}$$

$$= -\frac{1}{\frac{B}{2\chi} - \sqrt{\frac{\omega}{\chi}}\sqrt{\frac{-\tau\omega + \frac{B^2}{4\chi\omega} + \sqrt{\left(\tau\omega - \frac{B^2}{4\chi\omega}\right)^2 + 1}}{2}}}. \tag{10}$$

For $B \neq 0$, and in the limit of low-frequency waves, the expression above reduces to

$$A = \frac{1}{\frac{B}{2\chi} - \omega\sqrt{\frac{1}{B^2 - \tau\omega^2 4\chi}}} \cong \frac{2\chi}{B}. \tag{11}$$

2.2. Propagation along a non-equilibrium steady state ($\mathbf{q}_0 \neq 0$)

In a non-equilibrium steady state, characterized by a non-vanishing heat flux $\mathbf{q}_0$, the term $\frac{\partial \lambda}{\partial T} \nabla T \cdot \nabla T$ is no longer negligible. However, up to the first-order approximation in ∇T, it may be linearized as $-\frac{2}{\lambda} \frac{\partial \lambda}{\partial T} \mathbf{q}_0 \cdot \nabla T$. Then, Eq. (3) becomes

$$\tau \rho c \frac{\partial^2 T}{\partial t^2} + \rho c \frac{\partial T}{\partial t} = \left[\frac{\partial \lambda}{\partial x}(\nabla x) - \frac{2}{\lambda}\frac{\partial \lambda}{\partial T}\mathbf{q}_0\right] \cdot \nabla T + \lambda \nabla^2 T. \tag{12}$$

From this expression one gets the dispersion relation still in the form (4), with

$$B = \frac{1}{\rho c}\left(\frac{\partial \lambda}{\partial x}\nabla_z x - \frac{2}{\lambda}\frac{\partial \lambda}{\partial T}q_0\right), \tag{13}$$

where q_0 denotes the scalar value of $\mathbf{q}_0$. The phase speed v_p is still given by Eq. (7), with B given by this expression above. When $B \neq 0$ and $\omega \to 0$, it reduces to Eq. (8).

It is worth observing that B contains now both the contributions of ∇x and of $\mathbf{q}_0$. When $\mathbf{q}_0 = \mathbf{0}$, one recovers Eq. (7). Finally, in the high-frequency limit, Eq. (9) is recovered.

Thus, we conclude that in this model ∇x and $\mathbf{q}_0$ influence the low-frequency speed but not the high-frequency speed.

2.3. Illustration in $Si_x Ge_{1-x}$, and in $(Bi_{1-x}Sb_x)_2 Te_3$ alloys

Eq. (8) yields $v_p = \frac{1}{\rho c}\frac{\partial \lambda}{\partial x}\nabla_z x$. For many systems $\lambda(T, x)$ is a non-monotonic function of x because crystals with atoms with different atomic masses disperse phonons more intensely than uniform crystals. Thus, the value of $\partial \lambda/\partial x$ may be positive or negative. For instance, at $T = 300$ K, the system $Si_x Ge_{1-x}$, $\lambda(T, x)$ has $\lambda_{Si}(300) = 148$ W/m K, $\lambda_{Ge}(300) = 60$ W/m K and has a minimum near $x = 0.4$ with $\lambda_{Si_{0.4}Ge_{0.6}} = 15$ W/m K [9], and the system $(Bi_{1-x}Sb_x)_2$ Te$_3$, $\lambda(T, x)$ has $\lambda_{Bi_2}Te_3(300) = 1,75$ W/m K, $\lambda_{Sb_2}Te_3(300) = 1.70$ W/m K and has a minimum near $x = 0.5$ with $(Bi_{0.5}Sb_{0.5})_2$ Te$_3 = 0.2$ W/m K [19]. In Fig. 1 we plot a sketch of them. For the alloy $Si_x Ge_{1-x}$, for x between 0 and 0.4, $\partial \lambda/\partial x < 0$, and for x between 0.4 and 1, $\partial \lambda/\partial x > 0$. Then, the low-frequency waves will propagate to the left-hand side (from $Si_{0.4}Ge_{0.6}$ to Ge) in the former case, and to the right-hand side (from $Si_{0.4}Ge_{0.6}$ to Si) in the latter
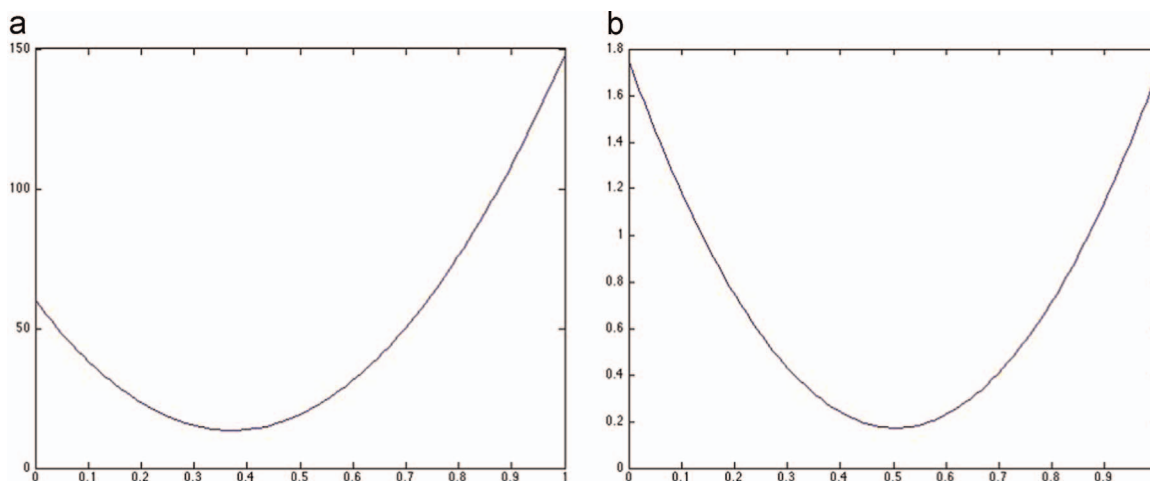
Fig. 1. Sketch of thermal conductivity of the alloys Si_xGe_{1-x} and $(Bi_{1-x}Sb_x)_2$ Te_3 as a function of x, at room temperature ($T=300$ K) according to [9,19].

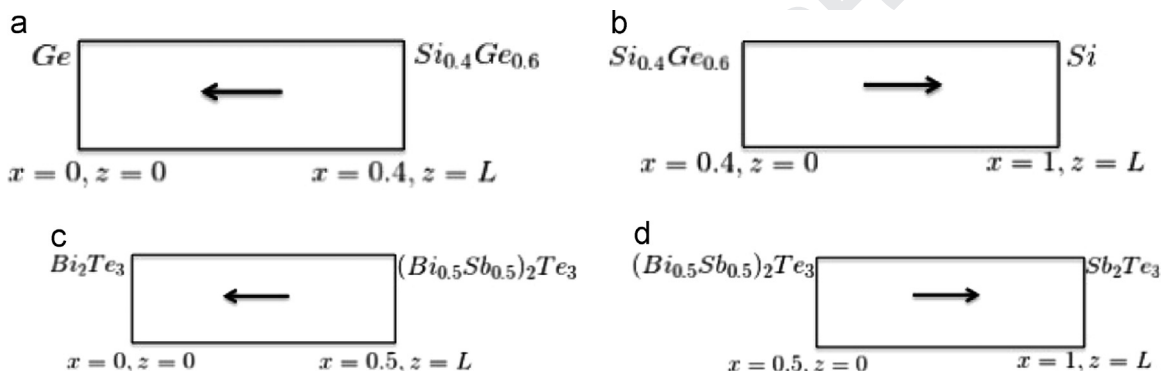**Fig. 2.** Propagation of low-frequency waves in Si_xGe_{1-x} alloys (a and b), and in $(Bi_{1-x}Sb_x)_2Te_3$ alloys (c and d). (a) From Ge to $Si_{0.4}Ge_{0.6}$, (b) from $Si_{0.4}Ge_{0.6}$ to Si, (c) from Bi_2Te_3 to $(Bi_{0.5}Sb_{0.5})_2$ Te_3 and (d) from $(Bi_{0.5}Sb_{0.5})_2Te_3$ to Sb_2Te_3.
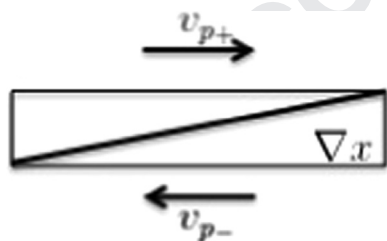
Fig. 3. Sketch of the situation considered in Section 4.

case. These situations are sketched in Fig. 2(a). Analogously, for the system $(Bi_{1-x}Sb_x)_2$ Te_3, for x between 0 and 0.5, $\partial\lambda/\partial x < 0$, and for x between 0.5 and 1, $\partial\lambda/\partial x > 0$. Then, the low-frequency waves will propagate to the left-hand side (from $(Bi_{0.5}Sb_{0.5})_2$ Te_3 to Bi_2Te_3) in the former case, and to the right-hand side (from $(Bi_{0.5}Sb_{0.5})_2$ Te_3 to Sb_2Te_3) in the latter case. These situations are sketched in Fig. 2(b). By the previous observations we conclude that if a low-frequency heat wave is produced in the pure Si or the pure Ge sides, it will be **Q3** not capable to penetrate the system (Figs. 3 and 4).

The situation may change in the presence of a heat flux **q**$_0$. Since both for Si and Ge the thermal conductivity decreases for increasing temperature $(\lambda_{Si}(350) = 119$ W/m K, $\lambda_{Ge}(350) = 49.5$ W/m K $)$, one has $\partial\lambda/\partial T < 0$. According to Eq. (7), a positive value of q_0 (to the right) will reduce the values of the phase speed B. In particular, under the condition

$$q_0 < -2\lambda_{Ge}\left(\frac{\partial\lambda_{Ge}}{\partial x}\right)/\left(\frac{\partial\lambda_{Ge}}{\partial T}\right)\nabla_z x,\qquad(14)$$

heat waves will be able to go from Ge to $Si_{0.4}Ge_{0.6}$, while under the condition

$$q_0 > 2\lambda_{Si}\left(\frac{\partial\lambda_{Si}}{\partial x}\right)/\left(\frac{\partial\lambda_{Si}}{\partial T}\right)\nabla_z x,\qquad(15)$$

heat waves will be able to go from Si to $Si_{0.4}Ge_{0.6}$ (i.e. the sign of B will change at those values of q_0).

Then, the presence of a heat flux may allow heat waves to penetrate into the system also in situations in which, in equilibrium, they would not be able to penetrate it.

3. Approximate constitutive equation for heat flux in graded materials

In the previous section we have taken the Maxwell–Cattaneo equation as a model for heat transport. Now, we consider a more general equation, including non-local and non-linear effects, which may be especially relevant in nanosystems and may influence the high-frequency wave speed. The formulation of generalized heat transport equations with non-linear and non-local terms has became a relevant area in heat transport in the last decade [36–38,28,29,39,25,40–45].

In a graded material with the composition x depending on the longitudinal position Z, x is an independent parameter, but it
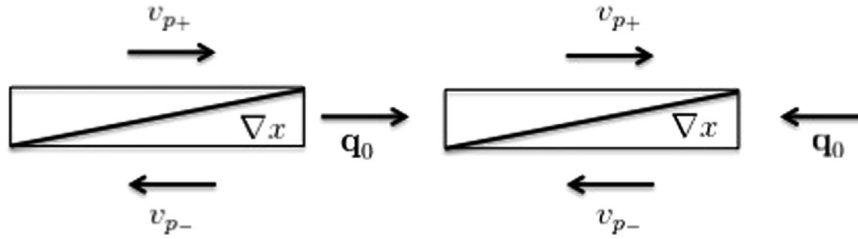
Fig. 4. Sketch of the situation considered in Section 5.

cannot be regarded as a dynamical variable, since it does not change with time. In this paper we consider non-local effects related to $l\nabla x$, with l the phonon mean free path, which had not been considered in above mentioned analyses of non-local theories of heat transport. If the composition changes significantly along l, this modifies the phonon collisions and may influence the heat dynamics. In previous references [28,29,36,37] non-local effects in the heat transport equation were analyzed, with emphasis on nanosystems, but the non-localities considered there were only due to inhomogeneities of the heat flux itself. Here, the presence of ∇x adds a further motivation to non-local analysis.

We deal with this modelization in the thermodynamic framework of extended irreversible thermodynamics [15,24,45–49], in which the entropy and the entropy flux depend not only on the classical variables but also on the fluxes present in the system. Let us assume the entropy S and the entropy flux $\mathbf{J}^{(s)}$ depending on internal energy, on the heat flux, and on the flux of the heat flux Q, so that

$$ds = T^{-1}\,du - \rho^{-1}\alpha_1\mathbf{q}\cdot d\mathbf{q} - \rho^{-1}\alpha_2 Q : dQ, \tag{16}$$

$$\mathbf{J}^{(s)} = T^{-1}\mathbf{q} + \beta Q\cdot\mathbf{q}, \tag{17}$$

with α_1, α_2 and β being material parameters, to be identified below in physical terms [48]. The flux of the heat flux is a second-order tensor usually considered in non-local models of heat transport [24,50–53]. We aim to obtain evolution equations for $\mathbf{q}$ and Q compatible with the second law of thermodynamics, which requires a positive definite character of the entropy production. From Eq. (16) we have for the time derivative of the entropy

$$\rho\dot{s} = T^{-1}\rho\dot{u} - \alpha_1\mathbf{q}\cdot\dot{\mathbf{q}} - \alpha_2 Q : \dot{Q}. \tag{18}$$

The coupling of Eqs. (2) and (18) yields

$$\rho\dot{s} = - T^{-1}\nabla\cdot\mathbf{q} - \alpha_1\mathbf{q}\cdot\dot{\mathbf{q}} - \alpha_2 Q : \dot{Q} = - \nabla\cdot[T^{-1}\mathbf{q}]$$

$$+ \mathbf{q}\cdot\nabla T^{-1} - \alpha_1\mathbf{q}\cdot\dot{\mathbf{q}} - \alpha_2 Q : \dot{Q}. \tag{19}$$

On the other hand, the entropy production (per unit volume and time) can be written as [15,24,48]

$$\sigma = \rho\dot{s} + \nabla\cdot\mathbf{J}^s. \tag{20}$$

Introducing in the previous expressions Eqs. (17) and (19), one has

$$\sigma = - \nabla\cdot[T^{-1}\mathbf{q}] + \mathbf{q}\cdot\nabla T^{-1} - \alpha_1\mathbf{q}\cdot\dot{\mathbf{q}} - \alpha_2 Q : \dot{Q}$$

$$+ \nabla\cdot[T^{-1}\mathbf{q}] + \nabla\cdot[\beta Q\cdot\mathbf{q}] \geq 0. \tag{21}$$

Then

$$\sigma = \mathbf{q}\cdot\nabla T^{-1} - \alpha_1\mathbf{q}\cdot\dot{\mathbf{q}} - \alpha_2 Q : \dot{Q} + \nabla\cdot[\beta Q\cdot\mathbf{q}] \geq 0. \tag{22}$$

Writing explicitly the last term in Eq. (22), the latter may be rewritten as

$$\sigma = \mathbf{q}\cdot[\nabla T^{-1} - \alpha_1\dot{\mathbf{q}} + \nabla\cdot(\beta Q)] + Q : [\beta\nabla\mathbf{q} - \alpha_2\dot{Q}] \geq 0. \tag{23}$$

The left-hand side of the above inequality is a bilinear form in $\mathbf{q}$ and Q times their conjugate thermodynamic forces, which contain the time derivatives of the fluxes $\dot{\mathbf{q}}$ and $\dot{Q}$. We are looking for evolution equations giving $\dot{\mathbf{q}}$ and $\dot{Q}$ in terms of $\mathbf{q}$, Q and ∇x. The simplest way to get these equations, by preserving the positive character of the entropy production, is to express the thermodynamic forces in terms of the fluxes as [15,24,35,48]

$$\nabla T^{-1} - \alpha_1\dot{\mathbf{q}} + \nabla\cdot(\beta Q) = \alpha_1'\mathbf{q} + \alpha_2' Q\cdot\mathbf{q} + \alpha_3' Q\cdot\nabla x + \alpha_4'\nabla x, \tag{24}$$

$$\beta\nabla\mathbf{q} - \alpha_2\dot{Q} = \beta_1 Q + \beta_2\mathbf{qq} + \beta_3(\nabla x)\mathbf{q} + \beta_4\nabla x\nabla x, \tag{25}$$

where α_i', $i = 1\ldots4$, and β_k, $k = 1\ldots3$, are phenomenological coefficients. In usual approaches, only the first terms on the right-hand side are considered. Here, instead, we also include intrinsic non-linear terms (in α_2' and β_2), and additional non-linear terms (in α_3' and β_3) related to inhomogeneities in x. Introducing them in the inequality (23), we obtain

$$\alpha_1'\mathbf{q}\cdot\mathbf{q} + \beta_1 Q : Q + (\alpha_2' + \beta_2)\mathbf{qq} : Q + (\alpha_3' + \beta_3)Q : \mathbf{q}\nabla x$$

$$+ \alpha_4'\mathbf{q}\cdot\nabla x + \beta_4 Q : \nabla x\nabla x \geq 0. \tag{26}$$

In order to have this inequality satisfied for arbitrary values of Q, $\mathbf{q}$ and ∇x, we must require

$$\alpha_1' \geq 0; \quad \beta_1 \geq 0; \quad \alpha_4' = \beta_4 = 0;$$

$$\left(\frac{\alpha_2' + \beta_2}{2}\right)^2 \leq \alpha_1'\beta_1; \quad \alpha_3' + \beta_3 = 0. \tag{27}$$

Taking into account the third of the constraints above, and neglecting the relaxation term $\alpha_2\dot{Q}$ (which will be considered in detail in Section 6), Eq. (25) yields

$$Q = \frac{\beta}{\beta_1}\nabla\mathbf{q} - \frac{\beta_2}{\beta_1}\mathbf{qq} - \frac{\beta_3}{\beta_1}(\nabla x)\mathbf{q} \equiv \beta_1'\nabla\mathbf{q} - \beta_2'\mathbf{qq} - \beta_3'(\nabla x)\mathbf{q}. \tag{28}$$

After introducing Eq. (28) into Eq. (24), the evolution equation for $\mathbf{q}$ takes the form

$$\nabla T^{-1} - \alpha_1\dot{\mathbf{q}} + \nabla\cdot[\beta\beta_1'\nabla\mathbf{q} - \beta\beta_2'\mathbf{qq} - \beta\beta_3'(\nabla x)\mathbf{q}]$$

$$= \alpha_1'\mathbf{q} + \alpha_2'[\beta_1'\nabla\mathbf{q} - \beta_2'\mathbf{qq} - \beta_3'(\nabla x)\mathbf{q}]\cdot\mathbf{q}$$

$$+ \alpha_3'[\beta_1'\nabla\mathbf{q} - \beta_2'\mathbf{qq} - \beta_3'(\nabla x)\mathbf{q}]\cdot\nabla x. \tag{29}$$

The relation above represents the heat transport equation when the relaxation time of $\dot{Q}$ is supposed to be much shorter than that of $\mathbf{q}$. Note that $\frac{\alpha_1}{\alpha_1'} \equiv \tau_1$ can be regarded as the relaxation time of the heat flux and $\frac{\alpha_2}{\beta_1} \equiv \tau_2$ as the relaxation time of Q. Then, when τ_1 and τ_2 are null, the second and the third term of Eq. (16) vanish, and one recovers the classical entropy. The new terms with respect to previous non-local and non-linear analyses are those containing ∇x. In the next two sections we explore the consequences of this equation on thermal wave propagation.

4. Heat waves in an equilibrium graded system: generalized

approach

In this section we apply Eq. (28) to the analysis of heat wave propagation in graded systems. Our aim is to study which information may be obtained on the composition changes along the system by means of this technique, and to explore the influence of ∇x on the speed of propagation. First, we will consider heat waves propagating into an equilibrium reference state, with vanishing average $\mathbf{q}$. The linearization of Eq. (29) around $\mathbf{q} = \mathbf{0}$ turns out

$$\nabla T^{-1} - \alpha_1 \dot{\mathbf{q}} + \beta \beta_1' \nabla^2 \mathbf{q} - \beta \beta_3' (\nabla^2 x) \mathbf{q}$$
$$= \alpha_1' \mathbf{q} + [\beta \beta_3' + \alpha_3' \beta_1'](\nabla \mathbf{q}) \cdot \nabla x - \alpha_3' \beta_3' (\nabla x)^2 \mathbf{q}, \tag{30}$$

and then

$$\nabla T^{-1} - \alpha_1 \dot{\mathbf{q}} = A \mathbf{q} + B \nabla^2 \mathbf{q} + C (\nabla \mathbf{q}) \cdot \nabla x, \tag{31}$$

with

$$A = \alpha_1' + \beta \beta_3' \nabla^2 x - \alpha_3' \beta_3' (\nabla x)^2, \quad B = -\beta \beta_1', \quad C = \beta \beta_3' + \alpha_3' \beta_1'. \tag{32}$$

The terms in α_1, α_1', and $\beta \beta_1'$ may be identified by comparing Eq. (31) to

$$\tau \dot{\mathbf{q}} + \mathbf{q} = -\lambda \nabla T + l^2 \nabla^2 \mathbf{q}, \tag{33}$$

used in [28,36,54], which is the Guyer–Krumhansl equation [55] (namely, the Maxwell-Cattaneo equation plus the non-local contribution of the last term, with l being the phonon mean free path), when the temperature of the system is kept constant in time. We conclude that

$$\alpha_1 = \frac{\tau}{\lambda T^2}, \quad \alpha_1' = \frac{1}{\lambda T^2}, \quad \beta \beta_1' = \frac{\beta^2}{\beta_1} = \frac{l^2}{\lambda T^2}, \tag{34}$$

and suppose that the previous identifications remain true also when the temperature is varying in time. We consider for the perturbation a plane wave of the form

$$\delta q(z, t) = \delta q_0 \exp[i(\omega t \mp \kappa z)], \tag{35}$$

and we also assume for the temperature distribution

$$T(z, t) = T_0 + \delta T = T_0 + \delta T_0 \exp[i(\omega t \mp \kappa z)]. \tag{36}$$

The $-$ sign corresponds to waves propagating to the right along the longitudinal direction Z, and the sign $+$ to waves propagating to the left along the same direction. Introducing Eqs. (35) and (36) into Eq. (31), one gets

$$\pm \frac{i\kappa}{T^2} \delta T - \alpha_1 i \omega \delta q = A \delta q + B \kappa^2 \delta q \mp C i \kappa \nabla_z x \delta q. \tag{37}$$

Taking into account the energy balance (2) with $\rho \dot{u} = \rho c \dot{T}$, we have

$$i \omega \rho c \delta T = \pm i \kappa \delta q, \tag{38}$$

Introducing this last relation in Eq. (37), one has the following dispersion relation of the perturbations δq:

$$-\frac{\kappa^2}{\rho \omega c T^2} + \alpha_1 \omega = i[A + B\kappa^2] \pm C \kappa \nabla_z x. \tag{39}$$

Let us ignore for a while the term $iB\kappa^2$ in Eq. (39) (this term, which makes the equation parabolic, will be discussed in detail in Section 6, in combination with the term in $\alpha_2 \dot{Q}$ of Eq. (25), which we have also neglected in Eq. (28)). Ignoring also A, which contributes to the wave attenuation, Eq. (39) reduces to**

$$-\kappa^2 + \alpha_1 \rho c \omega^2 T^2 = \pm C T^2 \rho \omega \kappa \nabla_z x. \tag{40}$$

By substituting in Eq. (40) the expression of ω obtained by Eq. (6), we get**

$$-(Re(\kappa))^2 + \alpha_1 \rho c v_p^2 T^2 (Re(\kappa))^2 = \pm C \rho v_p T^2 (Re\kappa)^2 \nabla_z x. \tag{41}$$

Thus, the equation giving the phase speed v_p reads

$$\alpha_1 \rho c T^2 v_p^2 \mp C T^2 \rho c v_p \nabla_z x - 1 = 0. \tag{42}$$

This equation leads to the results

$$v_{p+} = v_{p0} (\sqrt{\phi^2 + 1} + \phi), \tag{43}$$

for the speed of the pulses propagating in the same direction as the heat flux, and

$$v_{p-} = v_{p0} (\sqrt{\phi^2 + 1} - \phi), \tag{44}$$

for the speed of the pulses propagating in the opposite direction. In the equation above

$$v_{p0} = \sqrt{\frac{1}{\alpha_1 \rho c T^2}} = \sqrt{\frac{\lambda}{\rho c \tau}}, \tag{45}$$

which is the usual value of high-frequency thermal wave propagation, while the contribution from the inhomogeneity ϕ is

$$\phi = \frac{(\beta \beta_3' + \alpha_3' \beta_1') T}{2} \sqrt{\frac{\rho c \lambda T^2}{\tau}} \nabla_z x. \tag{46}$$

For $\nabla_z x = 0$, one recovers the usual result (45). Since $\nabla_z x$ has been considered positive, it follows from Eq. (43) that the velocities v_{p+} and v_{p-} will be higher or lower than v_{p0} according to the relative sign of $\beta \beta_3' + \alpha_3' \beta_1'$. However $\beta \beta_3' + \alpha_3' \beta_1' = (\beta/\beta_1)(\beta_3 + \alpha_3) = 0$, because of the constraint (27). Thus, as a consequence of the second law, we have that ∇x does not influence the phase speed in the high-frequency limit. At low-frequency, instead, it does influence the wave speed, as seen in Eq. (8).

5. Heat waves in a non equilibrium graded system: generalized approach

In this section, we consider thermal waves along a non-equilibrium reference state characterized by a non vanishing average heat flux $\mathbf{q}_0$ imposed on the system. We linearize Eq. (29) by considering $\mathbf{q} = \mathbf{q}_0 + \delta \mathbf{q}$ and keeping only first-order terms in $\mathbf{q}_0$. We obtain in this way

$$\nabla T^{-1} - \alpha_1 \dot{\mathbf{q}} + \beta \beta_1' \nabla^2 \mathbf{q} - 2 \beta \beta_2' \mathbf{q}_0 \cdot \nabla \mathbf{q} - \beta \beta_3' (\nabla^2 x) \mathbf{q} - \beta \beta_3' \nabla x \cdot \nabla \mathbf{q}$$
$$= \alpha_1' \mathbf{q} + \alpha_2' \beta_1' \nabla \mathbf{q} \cdot \mathbf{q}_0 - 2 \alpha_2' \beta_3' (\nabla x) \cdot \mathbf{q} \mathbf{q}_0$$
$$+ \alpha_3' \beta_1' (\nabla \mathbf{q}) \nabla x - 2 \alpha_3' \beta_2' \mathbf{q} (\nabla x) \mathbf{q}_0 - \alpha_3' \beta_3' (\nabla x)^2 \mathbf{q}. \tag{47}$$

Here, we have written $\mathbf{q}$ instead of $\delta \mathbf{q}$ for the sake of simplicity of notation. Eq. (47) may be rewritten as

$$\nabla T^{-1} - \alpha_1 \dot{\mathbf{q}} = A' \mathbf{q} + B \nabla^2 \mathbf{q} + (C \nabla x + D \mathbf{q}_0) \cdot \nabla \mathbf{q}, \tag{48}$$

with $A' = A + E$, where A is given just below Eq. (31) and E and D are given by

$$E = -2(\alpha_2' \beta_3' + \alpha_3' \beta_2'), \quad D = (2\beta \beta_2' + \alpha_2' \beta_1'). \tag{49}$$

For the sake of generality, on purely mathematical grounds, we still take into account the term in C, although in Section 4 it has been shown to be null in this particular case, because of second-law restrictions.

The last two terms are new as compared to Eq. (31) used in the previous section. When $\nabla x = \mathbf{0}$, we recover the equation used in [28], except for the term in $\nabla^2 \mathbf{q}$, which was not considered there. Neglecting the term in $\nabla \mathbf{q}$, the equation giving v_p is now

$$\alpha_1 \rho c T^2 v_p^2 \mp (C\nabla x + Dq_0)T^2\rho c v_p - 1 = 0, \tag{49}$$

which leads to results analogous to Eqs. (43) and (44) with

$$\phi = \frac{[(\beta\beta_3' + \alpha_3'\beta_1')\nabla x + (2\beta\beta_2' + \alpha_2'\beta_1')q_0]T}{2}\sqrt{\frac{\rho c \lambda T^2}{\tau}}. \tag{50}$$

When $q_0 = 0$, Eq. (50) reduces to (46). However $2\beta\beta_2' + \alpha_2'\beta_1' = (\beta/\beta_1)(2\alpha_2' + \beta_2)$, which may be different from zero, according to Eq. (27). We observe that none of the relations (27) constraints the sign of the term $(\beta/\beta_1)(2\alpha_2' + \beta_2)$, so that it may be positive or negative.

Thus, the intensity q_0 of the applied heat flux does influence the wave speed either at high frequency, as seen in Eq. (50), as at low frequency, as seen in Eq. (8). This is in contrast to what happens for ∇x which, according to second-law restriction (27), does not influence the high-frequency speed.

6. Dynamical contribution of the higher-order flux to heat wave propagation

In Sections 4 and 5 we have dropped from the evolution equation for **q** the contribution of the term $\nabla^2 \mathbf{q}$. Of course, this is not admissible in the limit of very short-wavelengths, in which case this term would lead to an infinite speed of propagation. We have also neglected the relaxation of the flux of the heat flux, when we have assumed Eq. (28), neglecting the term in $\alpha_2 \dot{Q}$ present in Eq. (25). In this section we take into account both $\alpha_2 \dot{Q}$ and $\nabla^2 \mathbf{q}$, and prove that we still obtain a hyperbolic system leading to finite speed of propagation.

Besides Eqs. (33) and (35), we consider a perturbation of Q which has been assumed as a dynamical variable in Section 3, of the type

$$\delta Q = \delta Q_0 \exp[i(\omega t \mp \kappa z)], \tag{51}$$

i.e. we consider for it a propagation wave, analogous to those for δq and δT in Eqs. (33) and (36). Eqs. (2), (24) and (25) become, respectively

$$i\omega\rho c\delta T = \pm i\kappa\delta q, \tag{52}$$

$$\pm\frac{i\kappa}{T^2}\delta T - i\omega\alpha_1\delta q \mp i\kappa\cdot\beta\delta Q = \alpha_1'\delta q + \alpha_2'q_0\cdot\delta Q + \alpha_3'\nabla_z x\cdot\delta Q, \tag{53}$$

$$\pm i\beta\kappa\delta q - \alpha_2 i\omega\delta Q = \beta_1\delta Q + 2\beta_2 q_0\delta q + \beta_3(\nabla_z x)\cdot\delta q. \tag{54}$$

We have so an homogeneous system of three equations for δT, δq and δQ, of the form

$$\begin{pmatrix} i\omega\rho c & \mp i\kappa & 0 \\ \pm\frac{i\kappa}{T^2} & -i\omega\alpha_1 - \alpha_1' & \mp i\kappa\beta - \alpha_2'q_0 - \alpha_3'\nabla_z x \\ 0 & \pm i\beta\kappa - 2\beta_2 q_0 - \beta_3\nabla_z x & -\alpha_2 i\omega - \beta_1 \end{pmatrix}\begin{pmatrix} \delta T \\ \delta q \\ \delta Q \end{pmatrix} = 0,$$

which allows for non-trivial solutions if and only if determinant of the matrix of the coefficients vanishes. By putting equal to 0 this determinant, we obtain the following dispersion relation

$$-\alpha_1\alpha_2 i\omega^3\rho c - \alpha_1\beta_1\omega^2\rho c - \alpha_1'\alpha_2\omega^2\rho c + \alpha_1'\beta_1 i\omega\rho c + \beta^2\kappa^2 i\omega\rho c$$

$$\pm 2\beta\beta_2 q_0\kappa\omega\rho c \pm \beta\beta_3\nabla_z x\kappa\omega\rho c \mp \beta\alpha_2'q_0\kappa\omega\rho c$$

$$- 2\beta_2\alpha_2'q_0^2 i\omega\rho c - \beta_3\alpha_2'q_0\nabla_z xi\omega\rho c$$

$$\mp \beta\alpha_3'\nabla_z x\kappa\omega\rho c - 2\beta_2\alpha_3'q_0\nabla_z xi\omega\rho c - \beta_3\alpha_3'(\nabla_z x)^2 i\omega\rho c$$

$$+ \alpha_2\frac{i\kappa^2}{T^2}\omega + \beta_1\frac{\kappa^2}{T^2} = 0. \tag{55}$$

We first consider $q_0 = 0$ and $\nabla_z x = 0$, so that Eq. (55) becomes

$$-\alpha_1\alpha_2 i\rho c\omega^3 - (\alpha_1\beta_1\rho c + \alpha_1'\alpha_2\rho c)\omega^2 + (\alpha_1'\beta_1\rho c + \beta^2\kappa^2\rho c + \alpha_2\frac{\kappa^2}{T^2})$$

$$i\omega + \beta_1\frac{\kappa^2}{T^2} = 0. \tag{56}$$

This equation may be rewritten as

$$-A''i\omega^3 - B''\omega^2 + C''i\omega + D''i\omega\kappa^2 = E''\kappa^2, \tag{57}$$

with

$$A'' = \alpha_1\alpha_2\rho c, \quad B'' = \alpha_1\beta_1\rho c + \alpha_1'\alpha_2\rho c, \tag{58}$$

$$C'' = \alpha_1'\beta_1\rho c, \quad D'' = \beta^2\rho c + \alpha_2\frac{1}{T^2}, \quad E'' = -\beta_1\frac{1}{T^2}. \tag{59}$$

If we write

$$\kappa = \mathrm{Re}(\kappa) + i\,\mathrm{Im}(\kappa) = \kappa_1 + i\kappa_2, \tag{60}$$

Eq. (57) becomes

$$-A''i\omega^3 - B''\omega^2 + C''i\omega + D''i\omega(\kappa_1^2 - \kappa_2^2 + 2i\kappa_1\kappa_2)$$

$$= E''(\kappa_1^2 - \kappa_2^2 + 2i\kappa_1\kappa_2), \tag{61}$$

which leads to

$$-B''\omega^2 - 2D''\omega\kappa_1\kappa_2 = E''(\kappa_1^2 - \kappa_2^2), \tag{62}$$

for the real part, and to

$$-A''\omega^3 + C''\omega + D''\omega(\kappa_1^2 - \kappa_2^2) = 2E''\kappa_1\kappa_2, \tag{63}$$

for the imaginary one.

In the high-frequency limit, namely for $\kappa \to \infty$, $\omega \to \infty$, we obtain

$$v_{p0}^2 = \frac{D''}{A''} = \frac{\beta^2}{\alpha_1\alpha_2} + \frac{1}{\alpha_1\rho c T^2} = \frac{\lambda}{\tau\rho c} + \frac{l^2}{\tau\tau_2}. \tag{64}$$

For $l^2 = 0$, this expression reduces to the well-known expression (45) from the Maxwell–Cattaneo law. Note that when $\alpha_2 \to 0$ or $\tau_2 \to 0$, as we assumed in Sections 4 and 5, the phase velocity would be divergent, because the corresponding approximate equation is parabolic. A finite speed is recovered if the term in β related to $\nabla^2 \mathbf{q}$ in (31) is negligible. Neglecting it, the coupling of Eqs. (37) and (2) yields a hyperbolic equation for temperature perturbations, with finite wave speed in the high-frequency limit, as in Sections 4 and 5.

Now, we consider $q_0 \neq 0$ and $\nabla_z x \neq 0$. From Eq. (55) one may obtain the phase speed and the attenuation factor in full generality. However, in order to avoid cumbersome expressions, we focus our attention on the high-frequency and short-wavelength perturbations (i.e. for ω and κ very high), whose phase speed yields the propagation speed of heat pulses [16,29,43,44]. Thus, keeping only the highest order terms (those in ω^2, κ^2 and $\omega\kappa$) in (55), we arrive to

$$-\beta_1\frac{1}{T^2\rho c}\kappa^2 - (\alpha_1\beta_1 + \alpha_1'\alpha_2)\omega^2 \pm (2\beta\beta_2 - \beta\alpha_2')q_0\kappa\omega$$

$$\pm (\beta\beta_3 - \beta\alpha_3')\kappa\omega\nabla_z x = 0. \tag{65}$$

From here, the corresponding equation for the phase speed v_p may be written in a compact form as

$$F\rho c T^2 v_p^2 \mp (Gq_0 + H\nabla_z x)T^2\rho c v_p + 1 = 0, \tag{66}$$

with

$$F = \frac{\alpha_1\beta_1 + \alpha_1'\alpha_2}{\beta_1}, \quad G = \frac{2\beta\beta_2 - \beta\alpha_2'}{\beta_1}, \quad H = \frac{\beta\beta_3 + \beta\alpha_3'}{\beta_1}.$$

It leads to results analogous to those in Eqs. (43) and (44), but with v_{p0} given by Eq. (64) and

$$\phi = [H\nabla_z x + Gq_0]\frac{T}{2}\sqrt{\frac{\rho c}{F}}. \tag{67}$$

7. Conclusions

In this paper we have generalized previous analyses on non-local and non-linear effects in heat transfer, by including not only non-local effects due to inhomogeneities in the heat flux (the last term in Eq. (33), for instance), but also due to inhomogeneities in the system composition. The motivation for this extension has been the analysis of graded systems, increasingly used in thermoelectric energy conversion. If the systems are small, for instance of nanometric scale, the composition gradient may be high, because the composition changes over a small length. It has been seen that for low-frequency waves, both the composition gradient ∇x and the external heat flux $\mathbf{q}_0$ influence the wave speed in the Maxwell–Cattaneo model (1), while none of them influences the high-frequency speed.

Since the low-frequency wave speed depends on $(\partial\lambda/\partial x)\nabla x$, and since $\lambda(T, x)$ has a minimum as a function of x for systems as Si_xGe_{1-x}, or $(Bi_{1-x}Sb_x)_2Te_3$, it turns out that low-frequency heat waves will not penetrate into the system neither from the $x=0$ [Ge, Bi_2Te_3] nor from the $x=1$ [Si, Sb_2Te_3] sides, but they penetrate into the system from x_{min} to $x=0$ and from x_{min} to $x=1$, being x_{min} the composition for which $\lambda(T, x)$ has the minimum value (see Fig. 2). This situation may be changed under the presence of a non-vanishing average heat flux $\mathbf{q}_0$. In fact, if the flux is sufficiently high and it points in the suitable direction, waves will be able to penetrate both from the $x=0$ side and from the $x=1$ side.

When the Maxwell–Cattaneo equation is generalized in Eq. (29), in order to incorporate non-local and non-linear effects, both ∇x and $\mathbf{q}_0$, in principle, can influence the high-frequency speed.

We have considered different situations with increasing complexity: heat waves along an equilibrium state with $\nabla x \neq \mathbf{0}$ (Section 4), heat waves along a non-equilibrium state, with $\nabla x \neq \mathbf{0}$ and $\mathbf{q}_0 \neq \mathbf{0}$, (Section 5); and we have seen the relevant role of a finite non-vanishing relaxation time for Q (in the analysis of heat pulses in high-frequency thermal waves) with non-local effects (Section 6). If such relaxation time is assumed to vanish, the wave speed in the high-frequency limit diverges. It has been noted that the restrictions (27) from second-law impose that the contribution of ∇x in the high-frequency limit should be zero, but not that of $\mathbf{q}_0$. Finally, we have underlined the role of the relaxation time of the flux of the heat flux Q in the high-frequency wave speed. For a vanishing relaxation time of Q, the non-local contribution $\nabla^2\mathbf{q}$ to Eq. (29) would imply a divergent speed, but the consideration of the a non-vanishing relaxation time of Q gives to it a finite value.

As a final remark, we observe that it is logical to expect that the inhomogeneities in the composition influence also the efficiency of the energy conversion in thermoelectric graded materials. In fact, in thermoelectric devices the conversion efficiency, which strongly depends on the concentration of the heat and current carriers, can be substantially improved by adjusting the carriers' concentration along the material's length. This can be achieved by employing a functionally graded thermoelectric material (FGTM), with the carriers' concentration optimized for operating over a specific temperature gradient [12,13].

Thus, the implications of a non-vanishing composition gradient on the efficiency of functionally graded thermoelectric systems deserve consideration, and will be investigated in future researches.

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