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Influence of the composition gradient on the propagation of heat pulses in functionally graded nanomaterials

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A theoretical model to describe heat transport in functionally graded nanomaterials is developed in the framework of extended thermodynamics. The heat-transport equation used in our theoretical model is of the Maxwell–Cattaneo type. We study the propagation of acceleration waves in functionally graded materials (FGMs). In the special case of functionally graded $\text{Si}_{1-c}\text{Ge}_c$ thin layers, we point out the influence of the composition gradient on the propagation of heat pulses. A possible use of heat pulses as exploring tool to infer the inner composition of FGMs is suggested.

1. Introduction

Functionally graded materials (FGMs) are composite materials with an inhomogeneous micromechanical structure [1–4]. FGMs are generally made of two components and, in contrast to traditional composites, they are characterized by a compositional gradient from one component to the other. In more concrete words, in FGMs the different material functions may change continuously (i.e. the changes in composition and microstructure occur continuously with position), or quasi continuously (i.e. the changes in composition and microstructure occur in a stepwise manner) along a given direction. In many cases, FGMs can be sketched as a composition of several connected thin layers. An usual example is the alloy $\text{Si}_{1-c}\text{Ge}_c$, which has been

much studied in semiconductor physics to engineer heat or current transport, with the stoichiometric variable c ranging in the interval $[0; 1]$ [5]. Depending on the number of directions along which the material functions may change, one can discriminate among one-, two- and three-dimensional FGMs.

In the last decade, beams and plates made of FGMs have been widely applied in micro/nano electromechanical systems (also known as MEMS/NEMS) [6–8]. As MEMS/NEMS display a high sensitivity to external stimulations, a better understanding of their thermomechanical properties will have a great relevance in the design and fabrication of those modern sensors.

The classical Fourier law (FL) of heat conduction is usually employed in studying heat transfer in FGMs [9–13]. However, in nanodimensional systems, as well as in several non-equilibrium situations (as for example, in miniaturized systems submitted to high-frequency perturbations which are comparable to the reciprocal of the internal relaxation times), both numerical simulations, and experimental observations point out that the limit of validity of FL is clearly exceeded [4,14–19]; therefore, current frontiers in nanotechnology and materials' science require heat-transport equations which go both beyond FL, and beyond the local-equilibrium theory [15,19,20]. Those equations can be obtained, for instance, by solving the linearized Boltzmann equation [21–23], considering the time-lag effect [24,25], flux-history effect [26,27] or ballistic phonon transport [28,29], analysing the equivalence principle of energy and mass [14,30,31], or other generalized thermodynamic formalisms [15,19,32].

Among the different generalizations of FL, great consideration deserves the so-called Maxwell–Cattaneo equation [33], namely,

$$\tau \dot{q}_i + q_i + \lambda \theta_{,i} = 0, \quad (1.1)$$

wherein q_i is the local heat flux, and θ is the non-equilibrium temperature [34]. Moreover, in that equation τ means the relaxation time of heat carriers (i.e. the time-lag needed to establish steady-state heat conduction in an element of volume when a temperature gradient is suddenly imposed on that element) and λ is the thermal conductivity. These material functions, which for standard materials only depend on temperature, in the case of FGMs depend on c , too, as previously said.

In the present paper, we aim to study how heat pulses (i.e. high-frequency heat waves) propagate in FGMs. From the theoretical point of view, thermal waves have been an inspiring topic in modern non-equilibrium thermodynamics [15,35]; whereas the classical transport theory based on FL predicts an infinite speed of propagation of heat pulses [33], in fact, the observed speed is finite [15,35]. Thermal waves have fostered researches on generalized transport equations leading to finite speed in this limit, and the theoretical aspects related to them are nowadays reasonably understood; nevertheless, there is still a wide field of research for practical applications of thermal waves which may provide dynamical information that is lacking from usual steady-state measurements. Starting from theoretical models, a very compelling challenge may be the searching of what type of information could be obtained from unsteady-state measurements; in particular, it may be interesting to study the possible exploitation of thermal waves in the analysis of nanomaterial properties.

Our goal will be pursued by starting from a theoretical model which lies on equation (1.1) as the heat-transport equation, and lets the different material functions depend not only on temperature, but also on the stoichiometric variable. The novelty of the results contained in present paper with respect to previous ones is the investigation of the role played by the composition gradient, i.e. $c_{,i}$, in several predicted cases of variation of c . The present analysis, which initially may appear only as an academic motivation, becomes especially acute if it is observed that, in principle, the variation of c can be accurately chosen during the fabrication process in order to tailor the final device for own practical needs [36].

The summary of the paper is the following.

In §2, we show the thermodynamic consistency of a model wherein equation (1.1) is the evolution equation for the heat flux. In §3, we study the propagation of heat pulses, and analyse,

in particular, the influence of the composition gradient on that propagation in the special case of a functionally graded $\text{Si}_{1-c}\text{Ge}_c$ layer. Final considerations can be found in §4.

2. Theoretical thermodynamic considerations

In this section, by means of second law of thermodynamics, we point out the physical validity of a theoretical model based on equation (1.1) as the evolution equation for the heat flux.

To do this, at the very beginning, we have to claim the state-space variables. According with extended irreversible thermodynamics (EIT) [15], here we assume that the state space $\mathcal{Z}$ is

$$\mathcal{Z} = \{\theta, q_i, c\}, \quad (2.1)$$

with each state-space variable displaying its own evolution equation. EIT is a modern thermodynamic theory which upgrades the dissipative fluxes to the rank of independent state-space variables [15], and the evolution of these variables is governed by local balance laws following by Grad's hierarchical system of moments which approximates the Boltzmann equation [15].

As we previously said, we postulate that the evolution equation of q_i is given by equation (1.1).

The evolution equation of θ , instead, can be obtained by coupling the local balance of energy in a rigid body, namely,

$$\rho \dot{e} + q_{i,i} = 0, \quad (2.2)$$

wherein e means the specific (i.e. per unit mass) internal energy and $\rho = \rho(c)$ the mass density, together with the constitutive relation

$$e = c_v \theta, \quad (2.3)$$

with $c_v = c_v(c)$ being the specific heat at constant volume, in order to obtain

$$\rho c_v \dot{\theta} + \rho \theta \left(\frac{\partial c_v}{\partial c} \right) \dot{c} + q_{i,i} = 0. \quad (2.4)$$

Although not properly the main argument of the present paper, the evolution equation of the last state-space variable (that is, c) deserves some comments; in fact, whereas the derivations of previous evolution equations (i.e. equations (1.1) and (2.4)) arise from well-established physical considerations, the derivation (or the postulation) of an evolution equation for c , at the present stage, can only follow from pure theoretical conjectures, since there are no experimental evidences about the time variations of the composition of an FGM. In a first approximation, actually, c should be viewed as an internal variable, in order to constitute an efficient tool when dealing with non-equilibrium processes involving complex thermodynamical systems [37]. In this case, the evolution equation of c might be written:

$$\dot{c} = \mathcal{F}(\theta, q_i, c), \quad (2.5)$$

with $\mathcal{F}$ being a scalar-valued function of the indicated arguments. More refined considerations (or theoretical models) could be surely made; however, equation (2.5) has the great advantage of preserving the essential physics of the problem still retaining a sufficient simplicity since it is well defined on the state space.

On the other hand, it is well known that each thermodynamic process has its *own privileged direction*. Second law of thermodynamics, restricting the form of constitutive equations [38], accounts for the natural evolution of a system in any possible thermodynamic process. In the present case, its local form reads

$$\rho \sigma^{(s)} = \rho \dot{s} + j_{i,i}^{(s)}, \quad (2.6)$$

wherein s is the specific entropy, $j_i^{(s)}$ is its flux, and $\sigma^{(s)}$ is its production which has to be non-negative in any admissible thermodynamic process.

The exploitation of equation (2.6) allows to show the physical compatibility of our model equations. To do this, we firstly observe that both the entropy and the entropy flux have to

be assigned by constitutive equations. Here we do not postulate any particular form for those functions, but we only generically write them as

$$s = s(\theta, q_i, c) \quad (2.7a)$$

and

$$J_i^{(s)} = J_i^{(s)}(\theta, q_i, c), \quad (2.7b)$$

and let the second law give their explicit forms below.

(a) Exploitation of second law

In order to investigate whether our theoretical model based on equations (1.1), (2.4) and (2.5) is compatible with second law of thermodynamics, or not, we have to determine a set of conditions restricting the constitutive equations [38] (in the present case equations (2.7)) which are necessary and sufficient to guarantee that the unilateral differential inequality $\sigma^{(s)} \geq 0$ is satisfied along any arbitrary thermodynamic process.

The inequality above, indeed, taking into account equations (2.6) and (2.7), on the state space $\mathcal{Z}$ can be written in the following explicit form:

$$\rho \sigma^{(s)} = \rho \left(\frac{\partial s}{\partial \theta} \dot{\theta} + \frac{\partial s}{\partial q_i} \dot{q}_i + \frac{\partial s}{\partial c} \dot{c} \right) + \frac{\partial J_i^{(s)}}{\partial \theta} \theta_{,i} + \frac{\partial J_i^{(s)}}{\partial q_j} q_{i,j} + \frac{\partial J_i^{(s)}}{\partial c} c_{,i} \geq 0. \quad (2.8)$$

To achieve our task, here we apply the classical Liu procedure [39]. According to it, the thermodynamic restrictions on the constitutive functions can be obtained by checking the positiveness of the linear combination of $\sigma^{(s)}$ (expressed by the right-hand side of equation (2.8)) and of the evolution equations of the state variables for all thermodynamic processes [40]. This linear combination is obtained by means of Lagrange multipliers, which depend on the state variables themselves [40]. Thus, we add to $\sigma^{(s)}$ equations (1.1), (2.4) and (2.5), multiplied by the respective Lagrange multipliers $\Lambda_i^{(q)}$, $\Lambda^{(\theta)}$ and $\Lambda^{(c)}$. That way, after rearrangement, inequality (2.8) takes the form:

$$\begin{aligned} & \rho \left(\frac{\partial s}{\partial \theta} - c_v \Lambda^{(\theta)} \right) \dot{\theta} + \rho \left(\frac{\partial s}{\partial c} - \Lambda^{(\theta)} \theta \frac{\partial c_v}{\partial c} - \frac{\Lambda^{(c)}}{\rho} \right) \dot{c} + \rho \left(\frac{\partial s}{\partial q_i} - \frac{\Lambda_i^{(q)}}{\rho} \right) \dot{q}_i \\ & + \left(\frac{\partial J_i^{(s)}}{\partial \theta} - \Lambda_i^{(q)} \frac{\lambda}{\tau} \right) \theta_{,i} + \left(\frac{\partial J_i^{(s)}}{\partial q_j} - \Lambda^{(\theta)} \delta_{ij} \right) q_{i,j} + \frac{\partial J_i^{(s)}}{\partial c} c_{,i} - \Lambda_i^{(q)} \frac{q_i}{\tau} + \Lambda^{(c)} \mathcal{F} \geq 0. \end{aligned} \quad (2.9)$$

The inequality above is linear both in the time derivatives $\dot{\theta}$, $\dot{q}_i$, $\dot{c}$, and in the spatial derivatives $\theta_{,i}$, $q_{i,j}$ and $c_{,i}$ which can assume completely arbitrary values due to the arbitrariness of the thermodynamic process. As a consequence, the positiveness of the inequality (2.9) demands that:

$$\frac{\partial s}{\partial \theta} = c_v \Lambda^{(\theta)}, \quad (2.10a)$$

$$\frac{\partial s}{\partial c} = \Lambda^{(\theta)} \theta \frac{\partial c_v}{\partial c} + \frac{\Lambda^{(c)}}{\rho}, \quad (2.10b)$$

$$\frac{\partial s}{\partial q_i} = \frac{\Lambda_i^{(q)}}{\rho}, \quad (2.10c)$$

$$\frac{\partial J_i^{(s)}}{\partial \theta} = \Lambda_i^{(q)} \frac{\lambda}{\tau}, \quad (2.10d)$$

$$\frac{\partial J_i^{(s)}}{\partial q_j} = \Lambda^{(\theta)} \delta_{ij}, \quad (2.10e)$$

$$\frac{\partial J_i^{(s)}}{\partial c} = 0 \quad (2.10f)$$

and

$$-\Lambda_i^{(q)} \frac{q_i}{\tau} + \Lambda^{(c)} \mathcal{F} \geq 0. \quad (2.10g)$$

Referring the readers to appendix A at the end of the paper for deeper details, here we only observe that if we assume

$$\Lambda^{(\theta)} = \frac{1}{\theta}, \quad (2.11a)$$

$$\Lambda_i^{(q)} = -\frac{\tau}{\lambda \theta^2} q_i \quad (2.11b)$$

and

$$\Lambda^{(c)} = \frac{\partial s_{\text{eq}}}{\partial c} - \frac{\partial c_v}{\partial c} - \frac{q_i q_i}{2\theta^2} \frac{\partial}{\partial c} \left(\frac{\tau}{\lambda \rho} \right), \quad (2.11c)$$

straightforward calculations show that the thermodynamic restrictions (2.10a–f) are compatible with the following forms of the specific entropy and of the specific-entropy flux, respectively:

$$s = s_{\text{eq}}(\theta, c) - \frac{\tau}{2\rho\lambda\theta^2} q_i q_i \quad (2.12a)$$

and

$$J_i^{(s)} = \frac{q_i}{\theta}. \quad (2.12b)$$

Both the above equations are well known in EIT [15]. From equation (2.10a), in particular, it also follows that our theoretical model suggests that there will be a very strict relation between the relaxation time and the thermal conductivity, i.e. $\tau/\lambda \propto \theta^2$.

We finally also observe that the coupling of the thermodynamic restriction (2.10g) (i.e. the reduced entropy inequality) and the assumption in equation (2.11b) suggests that $\Lambda^{(c)} \mathcal{F}$ should be always positive.

The considerations above are enough to claim the compatibility of our theoretical model with the basic principles of continuum mechanics.

3. Heat-pulse propagation

In this section, we study the propagation of heat pulses (i.e. high-frequency heat waves) in FGMs. In doing this, in order to reduce at the minimum the indetermination level of our model (in such a way that it may be appealing from the practical point of view), here we assume that the state-space variable c can not change in time, namely,

$$\dot{c} = 0. \quad (3.1)$$

Then, consider an acceleration (A-) wave for a solution of equations (1.1) and (2.4), that is, a travelling surface $\mathcal{S}$ across which the time and/or the spatial derivatives of the state-space variables suffer at most finite discontinuities, whereas those variables are continuous everywhere [35,41]. For the sake of simplicity, we assume that $\mathcal{S}$ is moving into an equilibrium region, i.e. the region ahead the A-wave is such that

$$\theta = \theta^+ \quad q_i = q_i^+, \quad (3.2)$$

wherein (as in what follows) the superscript $+$ means the (constant) value of the corresponding quantity at $\mathcal{S}$ approaching from the region which $\mathcal{S}$ is about to enter.

By taking the jumps of equations (1.1) and (2.4) at S , we have

$$\tau^+[\dot{q}_i] + \lambda^+[\theta_{,i}] = 0 \quad (3.3a)$$

and

$$(\rho c_v)^+[\dot{\theta}] + [q_{i,i}] = 0 \quad (3.3b)$$

and the consequent use of the classical Hadamard (H-) relation (see appendix in Ref. [41] for deeper details about the relation we use here) yields

$$\tau^+ U_N Q_i - \lambda^+ n_i \Theta = 0 \quad (3.4a)$$

and

$$n_i Q_i - (\rho c_v)^+ U_N \Theta = 0, \quad (3.4b)$$

wherein U_N is the speed at the point on S with unit normal n_i , and

$$\Theta(t) = [n_i \theta_{,i}] \quad Q_i(t) = [n_j q_{i,j}] \quad (3.5)$$

are the A-wave amplitudes.

Since from equation (3.4a) we have that the A-waves have to be longitudinal, i.e.

$$Q_i = Q n_i, \quad (3.6)$$

with

$$Q(t) = [n_i n_j q_{i,j}], \quad (3.7)$$

then the requirement of non-zero A-wave amplitudes, applied to the homogeneous system of linear equations (3.4), implies that the A-wave speed is

$$U_N = \sqrt{\left(\frac{\lambda}{\tau \rho c_v}\right)^+}. \quad (3.8)$$

The above equation (3.8) points out that in FGMs the speed of propagation of thermal pulses:

- (i) depends on the local value of the non-equilibrium temperature (i.e. on the value of θ at S);
- (ii) depends on the stoichiometric variable c (i.e. on the value of c at S), but not on the concentration gradient (i.e. how fast, or slow c changes along the direction of propagation of S).

Roughly speaking, from the results above we may infer that a heat pulse will travel with a speed which is not constant during the motion, since in any point it depends on the local values of the different material functions (which in turn depend both on θ , and on c for the system at hand). As a consequence, the two boundaries of a propagating pulse will travel with slightly different speeds; this may intuitively yield focusing problem of a heat pulse since the latter may either shrink (when the frontal border is slower than the rear border), or squeeze along the propagation (when the frontal border is faster than the rear border). We explicitly note that such problem, which is well known in literature to arise from the temperature dependence of the different material functions in common materials [42], in FGMs becomes more evident owing to the dependence of them on the stoichiometric variable, too. Whereas the global behaviour of U_N (i.e. whether it is increasing or decreasing) depends on the particular direction of propagation, it is also worth noticing that in a given point the value of the pulse speed will be always the same either the heat pulse is propagating from the zone wherein $c = 0$ to the zone wherein $c = 1$, or it is propagating in the opposite direction.

Focusing problems, indeed, appear more evident if we investigate how the wave amplitude Θ behaves in time (i.e. during the propagation). To do this, let us firstly observe that from

equation (3.4b), we have

$$Q = (\rho c_v)^+ U_N \Theta. \quad (3.9)$$

Then, let us derive equation (1.1) with respect to space (assuming that $\tau = \tau(\theta, c)$) and equation (2.4) with respect to time, in order to have

$$\left(\frac{\partial \tau}{\partial \theta} \theta_{,i} + \frac{\partial \tau}{\partial c} c_{,i} \right) \dot{q}_i + \tau \dot{q}_{i,i} + q_{i,i} + \left(\frac{\partial \lambda}{\partial \theta} \theta_{,i} + \frac{\partial \lambda}{\partial c} c_{,i} \right) \theta_{,i} + \lambda \theta_{,ii} = 0 \quad (3.10a)$$

and

$$\rho c_v \ddot{\theta} + \dot{q}_{i,i} = 0 \quad (3.10b)$$

once the hypothesis in equation (3.1) has been used. The jumps of equations (3.10) are

$$\begin{aligned} & \left(\frac{\partial \tau}{\partial \theta} [\theta_{,i}] + \frac{\partial \tau}{\partial c} [c_{,i}] \right) [\dot{q}_i] + \tau^+ [\dot{q}_{i,i}] + [q_{i,i}] \\ & + \left(\frac{\partial \lambda}{\partial \theta} [\theta_{,i}] + \frac{\partial \lambda}{\partial c} [c_{,i}] \right) [\theta_{,i}] + \lambda^+ [\theta_{,ii}] = 0 \end{aligned} \quad (3.11a)$$

and

$$(\rho c_v)^+ [\ddot{\theta}] + [\dot{q}_{i,i}] = 0. \quad (3.11b)$$

Recalling equation (3.6) and that we are only considering A-waves moving into equilibrium, by straightforward calculations (which require the recursive use of the H-relation [41], too) from equations (3.11) we obtain

$$\begin{aligned} & \left(\Theta \frac{\partial \tau}{\partial \theta} + c_{,i}^+ n_i \frac{\partial \tau}{\partial c} \right) U_N Q - \tau^+ \frac{\delta Q}{\delta t} + \tau^+ U_N [n_i n_j n_k q_{i,jk}] - Q \\ & - \left(\Theta \frac{\partial \lambda}{\partial \theta} + c_{,i}^+ n_i \frac{\partial \lambda}{\partial c} \right) \Theta - \lambda^+ [n_i n_j \theta_{,ij}] = 0 \end{aligned} \quad (3.12a)$$

and

$$(\rho c_v)^+ \left(-2U_N \frac{\delta \Theta}{\delta t} + U_N^2 [n_i n_j \theta_{,ij}] \right) + \frac{\delta Q}{\delta t} - U_N [n_i n_j n_k q_{i,jk}] = 0. \quad (3.12b)$$

The coupling of equations (3.9) and (3.12) consequently yields the following Bernoulli-type ordinary differential equation

$$\frac{\delta \Theta}{\delta t} = \alpha \Theta^2 - \beta \Theta, \quad (3.13)$$

with

$$\alpha = -\frac{U_N}{2} \frac{\partial}{\partial \theta} \left[\ln \left(\frac{\lambda}{\tau} \right) \right]^+ \quad (3.14a)$$

and

$$\beta = \frac{1}{2} \left\{ \frac{1}{\tau^+} + c_{,i}^+ n_i U_N \frac{\partial}{\partial c} \left[\ln \left(\frac{\lambda}{\tau} \right) \right]^+ \right\} \quad (3.14b)$$

If we suppose that the initial amplitude of the pulse is $\Theta(t=0) \equiv \Theta_0$, then the solution of equation (3.13) is

$$\Theta(t) = \frac{1}{\alpha/\beta + (1/\Theta_0 - \alpha/\beta) e^{\beta t}}. \quad (3.15)$$

Equations (3.14) and (3.15) point out that the thermal-pulse amplitude:

- (i) depends on the local value of the non-equilibrium temperature;
- (ii) depends both on the concentration c , and on the concentration gradient $c_{,i}$;
- (iii) depends on the scalar product $c_{,i} n_i$ (i.e. on the direction of propagation of the pulse).

Figure 1. Schematic diagram of concept of gradation in FGMs.

The observations in the items above better confirm what we previously said about the focusing of a heat pulse, namely, it continuously changes its shape (shrinking and squeezing) during the propagation. These changes arise since the different material functions depend both on θ (the effects of which are accounted by the coefficient α in equation (3.14a)), and on c (the effects of which are accounted by the coefficient β in equation (3.14b)).

We finally observe that, in contrast with what previously observed for the speed U_N , the aforementioned results point out that in a given point of the system at hand the value of the pulse amplitude Θ also depends on the particular direction of propagation, owing to the presence of the scalar product $c_i n_i$ in the definition of the coefficient β .

(a) Application to functionally graded $\text{Si}_{1-c}\text{Ge}_c$ layer

In order to make attractive previous theoretical results for practical applications, here we apply them to a functionally graded $\text{Si}_{1-c}\text{Ge}_c$ layer. $\text{Si}_{1-c}\text{Ge}_c$ layers, in fact, have many attractive characteristics which can be exploited for numerous applications including wavelength-sensitive photonic devices, high mobility complementary metal oxide semiconductor devices and lattice matching for epitaxial III–V growth [43]. The analysis of pulse propagation will be done by sketching the system above as a quadratic L -size layer with the stoichiometric variable only changing along the x -direction, whereas c will be kept constant along the y -direction (see figure 1 for a qualitative sketch of the system). Recalling that during the fabrication process one can select a variation law for c [36], the particular cases below will be analysed in what follows:

- (1) $c(x) = x/L$
- (2) $c(x) = (e^{x/L} - 1)/(e - 1)$
- (3) $c(x) = (x/L)^2$ and $c(x) = \sqrt{x/L}$
- (4) $c(x) = \sin(\pi x/2L)$ and $c(x) = 1 - \cos(\pi x/2L)$.

The computations will be performed under the further hypotheses below.

- The material functions λ and τ do not depend on temperature, which is tantamount to suppose that those material functions only display vanishingly small variations with the temperature.
- The average temperature of the system is 300 K.
- The size of the layer is $L = 10^{-7}$ m.

- The form of the relaxation time (s) is

$$\frac{1}{\tau} = \frac{1-c}{\tau_{\text{Si}}} + \frac{c}{\tau_{\text{Ge}}}$$

according to the Matthiessen rule, wherein τ_{Si} and τ_{Ge} mean, respectively, the relaxation time of silicon and germanium. For the sake of simplicity, in our computations, we estimate those quantities as $\tau_{\text{Si}} = \ell_{\text{Si}}/v_{\text{Si}}$ and $\tau_{\text{Ge}} = \ell_{\text{Ge}}/v_{\text{Ge}}$ with ℓ_{Si} and ℓ_{Ge} being the phonon mean-free path (mfp) in silicon and germanium, respectively, whereas v_{Si} and v_{Ge} are the phonon speeds in silicon and germanium. At the room temperature $\ell_{\text{Si}} = 8.05 \times 10^{-8} \text{ m}$, $v_{\text{Si}} = 2894.96 \text{ ms}^{-1}$, $\ell_{\text{Ge}} = 5.83 \times 10^{-8} \text{ m}$, $v_{\text{Ge}} = 1757.7 \text{ ms}^{-1}$. These values have been taken from [19] (see tables 1.1 and 1.2 therein). In that reference, in particular, the Si- and Ge-mfp values have been inferred by using the relation $\lambda = \rho c_v v \ell / 3$ of the kinetic theory's relaxation-time approximation [44,45]; in fact, the phonon mfp depends both on phonon frequency, and on the kind of collisions in such a way that several different relevant averages may be used to estimate it [45,46].

- The form of the thermal conductivity ($\text{W m}^{-1} \text{ K}^{-1}$) is [5]

$$\lambda(c) = \lambda_{\text{Ge}}c + \lambda_{\text{Si}}(1-c) - \sqrt{\lambda_{\text{Ge}}\lambda_{\text{Si}}} \left[\sum_{k=1}^8 A_k (1-c)^k \right].$$

At the room temperature $\lambda_{\text{Si}} = 149.95$ and $\lambda_{\text{Ge}} = 77.95$ [19]. The values of the eight constants A_k are quoted in table 2 in [5]. It seems worth noticing that, at nanoscale, the thermal conductivity of a material also depends on the characteristic size of the system, i.e. on non-local effects [19], in such a way that one should properly use an effective thermal conductivity [45,46], and not its bulk value. In the present paper, however, this dependence has been omitted in order to put the attention only on the role played by c_{ii} .

- The form of the mass density (g cm^{-3}) is [47]:

$$\rho(c) = 2.329 + 3.493c - 0.499c^2.$$

- The form of the specific heat at constant volume ($\text{J mol}^{-1} \text{ K}^{-1}$) is [47]

$$c_v(c) = 19.6 + 2.9c.$$

In the several cases above and for a heat pulse travelling along the x -direction, the predicted results for the speeds of propagation are plotted in figure 2. As it can be inferred from that figure, during the propagation U_N globally tends to decrease if the pulse is moving from $x=0$ (i.e. the zone wherein $c=0$) to $x=L$ (i.e. the zone wherein $c=1$), or to increase if the pulse is travelling in the opposite direction. In all cases, however, it reaches a minimum when $x \in]0.6L; L[$, i.e. when $c \in]0.8; 0.9[$.

Diagrams like those plotted in figure 2 suggest to use, for example, heat pulses as exploring tool for the inner structure of an FGM: by using some sensors, in fact, which can detect the speed in different points, it should be in principle possible to infer the inner composition by comparing the detected speed with that predicted in those diagrams.

In the several cases above, the predicted results for the pulse amplitude, instead, are plotted in figure 3 when the heat pulse travels along the x -direction from 0 to L (i.e. when c varies from 0 to 1), and in figure 4 when the heat pulse travels along the x -direction from L to 0 (i.e. when c varies from 1 to 0). As it can be inferred from those figures, Θ always (i.e. whatever the direction of propagation is) tends to decrease, but not monotonically; in other words, our theoretical model suggests that the pulse continuously shrinks and enlarges, although it is always globally squeezing during its crossing through the system. This unexpected behaviour is only due to the role played by the concentration gradient, since if $c_{ii} = 0$ then from equation (3.15) we would have

$$\frac{\Theta(t)}{\Theta_0} = e^{-t/2\tau}$$

and the expected monotonically decreasing behaviour of Θ is recovered.

Figure 2. Heat-pulse speed versus the distance at 300 K: theoretical results arising from equation (3.8). (Online version in colour.)

Since in practical applications heat pulses can be used to send information, the results above suggest that, in principle, one should pay attention on the role played by the concentration gradient since it may lead to noise and/or distortion in signals.

4. Final comments

FGMs represent a new generation of engineered materials that are gaining interest in recent years. They are two(or more)-component composites characterized by the gradual variation in their composition and structure over the volume, resulting in corresponding changes in their properties. FGMs show good characteristics in avoiding fierce interface interaction and eliminating reflection, because the properties of the material continuously change. The basic idea is to build a composite material by varying the microstructure from one material to another material with a specific gradient, in order to have a final material which displays the best features of both constituents. Since those materials can be designed for specific functions and applications, in the present paper we have investigated the influence of the composition gradient on the propagation of heat pulses when FGMs are used at nanoscale. In this area, most of the researchers use the FL to simulate the process of heat conduction. But in nanoscale materials, non-Fourier effects [14,18] are significant and influence how heat propagates. As a consequence, at this level, heat equations beyond FL are needed; therefore, in the present paper we use a theoretical model which lays on equation (1.1) as the heat equation.

In the special case of a functionally graded $\text{Si}_{1-c}\text{Ge}_c$ thin layer, our theoretical model pointed out that the composition gradient does not have any influence on the speed of propagation, which however will be not constant during the propagation, as it has been showed in figure 2. As we

Figure 3. Heat-pulse amplitude versus the distance at 300 K: theoretical results arising from equation (3.15) when the pulse is moving from $c = 0$ to $c = 1$. In the subfigures, the direction of propagation of the heat pulse is also indicated. (Online version in colour.)

discussed above, the analysis of the heat-pulse speed may turn out useful information about the inner structure of an FGM.

The composition gradient, instead, seems to play a relevant role on the pulse amplitude, as shown in figures 3 and 4. The pulse amplitude always displays a behaviour which is globally decreasing, but its final value fundamentally depends on c_{μ} , as well as on the direction of propagation. This may be interesting for practical applications. For example, imagine that a component on a chip made of an FGM is perturbing the surrounding system since it is the source of thermal disturbances with an initial temperature-amplitude Θ_0 . Then one may face with the following two problems.

- (i) *Data transfer.* If thermal pulses are used to send data from a component to another one, observing that the temperature of a heat pulse can be related to the amount of energy that it is carrying, then one should pay attention on the way of how c_{μ} changes between them if no information loss is required.
- (ii) *Thermal isolation.* If one aims to isolate a component from another one (that is, if a component has not to be influenced by thermal pulses produced by another component), then one should pay attention on the way of how c_{μ} changes in space between them in order to have a good isolation.

Figure 4. Heat-pulse amplitude versus the distance at 300 K: theoretical results arising from equation (3.15) when the pulse is moving from $c = 1$ to $c = 0$. In the subfigures, the direction of propagation of the heat pulse is also indicated. (Online version in colour.)

A final comment deserves the thermodynamic considerations made in §2a. In the very general case, material functions as for example c_v and λ should depend on the whole set of the state-space variables, namely, in developing our theoretical model we should have supposed both $c_v = c_v(\theta, q_i, c)$, and $\lambda = \lambda(\theta, q_i, c)$. Although still possible, those assumptions would have led to several complications in the calculations of §3 in view of other nonlinear terms. From the practical point of view, the simplifying assumptions above mean that the present analysis has to be meant only as a special case of a very general theoretical model. In this sense, we note that a more refined analysis of heat-pulse propagation in FGMs should take into account (as we previously observed) non-local effects, too. To do this, an interesting way is to replace equation (1.1) with the following evolution equation for the heat flux:

$$\tau \dot{q}_i + q_i + \lambda \theta_{,i} = \sum_{k=1}^N \left(\ell^2 \tau^{k-1} \frac{\partial^{k-1}}{\partial t^{k-1}} q_{i,jj} - \tau^{k+1} \frac{\partial^{k+1}}{\partial t^{k+1}} q_i \right), \quad (4.1)$$

which has been derived in [32] in the framework of EIT [15] by letting N higher-order thermodynamic fluxes belong to the state space. Observing that the thermal conductivity may be frequency dependent [48], we note that equation (4.1), which reduces to equation (1.1) when no higher-order thermodynamic fluxes appear in the state space (i.e. when $N = 0$), is suitable to describe heat transfer in high-frequency processes [32].

Data accessibility. This work does not have any experimental data. All the data we used for the several computations in this paper have been taken from the indicated references.

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Appendix A

The Liu procedure [39] allows to obtain necessary and sufficient conditions which, restricting the constitutive relations, yield a theoretical model which is finally compatible with second law [40]. A thorny topic in that technique, however, is the determination of the form of the different Lagrange multipliers. In our case, this goal can be achieved starting, for example, from equations (2.10d–f). By succeeding integrations, in fact, from those relations we have

$$\begin{aligned} \frac{\partial J_i^{(s)}}{\partial c} = 0 &\Leftrightarrow J_i^{(s)} = J_i^{(s)}(\theta, q_i), \\ &\Downarrow \\ \frac{\partial J_i^{(s)}}{\partial q_j} = \Lambda^{(\theta)} \delta_{ij} &\Leftrightarrow J_i^{(s)} = \int \Lambda^{(\theta)} dq_i + K_i(\theta) \\ &\Downarrow \\ \text{and} \quad \frac{\partial J_i^{(s)}}{\partial \theta} = \Lambda_i^{(q)} \frac{\lambda}{\tau} &\Leftrightarrow J_i^{(s)} = \int \Lambda_i^{(q)} \frac{\lambda}{\tau} d\theta. \end{aligned} \quad (\text{A } 1)$$

The above equation gives the form of the specific-entropy flux in our model, provided that the Lagrange multiplier $\Lambda_i^{(q)}$ is identified on physical ground. Recalling that one of the basic postulates of EIT [15] is that $J_i^{(s)}$ is proportional to the heat flux, namely, equation (2.12b), a simple comparison between equations (2.12b) and (A 1) yields equation (2.11b).

Then, the coupling of equations (2.10e) and (2.12b) leads to equation (2.11a).

The form of $\Lambda^{(c)}$, instead, can be inferred if we obtain the form of s in our model; it arises from equations (2.10a–c) by succeeding integrations as below:

$$\begin{aligned} \frac{\partial s}{\partial \theta} = c_v \Lambda^{(\theta)} &\Leftrightarrow s = \int c_v \Lambda^{(\theta)} d\theta + H_1(q_i, c), \\ &\Downarrow \\ \frac{\partial s}{\partial q_i} = \frac{\Lambda_i^{(q)}}{\rho} &\Leftrightarrow s = \int \frac{\Lambda_i^{(q)}}{\rho} dq_i + H_2(c) \\ &\Downarrow \\ \text{and} \quad \frac{\partial s}{\partial c} = \Lambda^{(\theta)} \theta \frac{\partial c_v}{\partial c} + \frac{\Lambda^{(c)}}{\rho} &\Leftrightarrow s = \int \left(\Lambda^{(\theta)} \theta \frac{\partial c_v}{\partial c} + \frac{\Lambda^{(c)}}{\rho} \right) dc. \end{aligned} \quad (\text{A } 2)$$

Since in EIT the form of s is given by equation (2.12a) when q_i is the only thermodynamic flux appearing in the state space, a simple comparison between equations (2.12a) and (A 2) yields equation (2.11c), once equation (2.11a) has been taken into account.

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