UNIVERSITÀ DEGLI STUDI DI SALERNO

**Dipartimento di Fisica "E.R. Caianiello"**

**Dottorato di Ricerca in Matematica, Fisica ed Applicazioni**

**XXXIII Ciclo - Curriculum Matematica**

Tesi di dottorato in:

# Nonlocal and nonlinear transport theories at nanoscale: Applications to wave propagation

Settore Scientifico-Disciplinare MAT/07 Fisica Matematica

Dottoranda:

**Maria Di Domenico**

Maria Di Domenico

**Tutor:**
**Prof. Antonio Sellitto**

Antonio Sellitto

**Coordinatore:**
**Prof. Carmine Attanasio**

**Anno Accademico 2019-2020**

*Per aspera ad astra*

*A mio padre*

# Introduction

Many books and/or papers have been published on linear generalizations of Fourier's equation in order to introduce relaxational and nonlocal effects for the heat flux [1–9]. Describing a heat-pulse propagation with a finite speed [10–15], in agreement with experimental observations, such works are of much conceptual interest both because they may be applied to small systems (the characteristic size of which is comparable to the mean-free path of heat carriers) [16–23] or to fast processes (as for instance response to short laser pulses) [24–28], and because they have stimulated generalized formulations of non-equilibrium thermodynamics, with generalized expressions of the entropy and of the entropy flux incorporating heat-flux contributions [1–4, 7, 22, 29, 30].

The linear generalizations of Fourier's equation should be only employed to analyze the propagation of small-amplitude waves. When the amplitude of temperature waves (or of heat-flux waves) is not negligible, in fact, nonlinear effects cannot be neglected: this is the case, for example, when short and intense laser pulses are applied to heat a given material. Therefore, there is much interest in generalizing the linear theory of heat waves which has been, up to now, a fruitful stimulus to generalizations of non-equilibrium thermodynamics [1–4, 7, 9, 11, 12, 14, 29, 31–34] to nonlinear situations, namely, for waves with sufficiently high amplitudes [13, 20, 35–39]; indeed, there are many possible nonlinear generalizations and, from a thermodynamic point of view, it is of special interest selecting the forms which fit in a most direct way with the requirements of the second law of thermodynamics.

The present thesis aims at being a contribution to the study of heat waves when nonlinear and/or nonlocal generalizations of the Maxwell-Cattaneo equation in the context of extended thermodynamics [1, 4, 7, 35, 40] are introduced. Whereas nonlocal effects in heat transport have led to fruitful analogies with hydrodynamics, especially in the so-called phonon hydrodynamics, in the present thesis we also show how some particular nonlinear effects lead to fruitful analogies with nonlinear optics. We think that these analogies of heat transport with hydrodynamics and with optics are a nice illustration of the deep unity of physics, where results in some field may also be helpful to other fields, provided that the connection between both fields is found. The present thesis is a contribution in that direction, and the results contained in it may be of interest to current researches aiming to find new ways of control and applications of the heat flux, which is the main goal of the so-called phononics [25, 27]. In particular, the interaction of intense laser pulses with heat-conducting solids has motivated nonlinear phononics [26, 28, 24], requiring a combination of nonlinear optics and nonlinear heat transport.

The plan of this thesis is the following.

In Chapter 1 we recall the basic mathematical definitions and concepts which will be employed in this thesis, and briefly summarize the theoretical thermodynamic background.

In Chapter 2 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 the proposed theoretical model is of the Maxwell-Cattaneo type. We study the propagation of acceleration waves in functionally graded materials. In the special case of functionally graded $Si_{1-c}Ge_c$ 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 functionally graded materials is suggested.

In Chapter 3 we analyze the role played by nonlocal and genuinely nonlinear effects in the wave propagation. The study is performed both in the case of a rigid body (i.e., for heat pulse propagation), and in the case of a non-rigid body (i.e., for thermoelastic pulse propagation). In the framework of Extended Irreversible Thermodynamics the compatibility of our theoretical model with second law is proved.

In Chapter 4, starting from a nonlinear generalization of the Maxwell-Cattaneo equation (derived in a conservation-dissipation formalism in the framework of extended thermodynamics), an analogy with the theory of nonlinear electromagnetic waves is pointed out. This analogy emphasizes several physical aspects of the nonlinear theory and allows a parallelism with nonlinear optics, which may be of interest in nonlinear phononics. The proposed nonlinear equation for heat waves is used to analyze how the amplitude of nonlinear heat wave may influence the speed of propagation.

In Chapter 5 we finally study the influence of nonlocal and nonlinear effects on the heat-wave propagation when a two-temperature model, which allows to describe the different regimes which electrons and phonons can undergo in the heat-transfer phenomenon, is used.

The research presented in this thesis has led to the following published papers:

1. A. Sellitto, M. Di Domenico, "Nonlocal and nonlinear contributions to the thermal and elastic high-frequency wave propagations at nanoscale", *Continuum Mech. Thermodyn.*, vol. 31, pp. 807-821 (2019).

2. B.-Y. Cao, M. Di Domenico, B.-D. Nie, A. Sellitto, "Influence of the composition gradient on the propagation of heat pulses in functionally graded nanomaterials", *Proc. R. Soc. A*, vol. 475, p. 20180499 (15 pages) (2019).

3. M. Di Domenico, D. Jou, A. Sellitto, "Nonlinear heat waves and some analogies with nonlinear optics", *Int. J. Heat Mass Transfer*, vol. 156, pp. 119888 (8 pages) (2020).

4. M. Di Domenico, D. Jou, A. Sellitto, "Heat-flux dependence of the speed of nonlinear heat waves: Analogies with the Kerr effect in nonlinear optics", *Int. J. Therm. Sci.*, vol. 161, pp. 106719 (2021).

5. A. Sellitto, I. Carlomagno, M. Di Domenico, "Nonlocal and nonlinear effects in hyperbolic heat transfer in a two-temperature model", *Z. Angew. Math. Phys.*, vol. 72, pp. 1 (2021).

# Contents

# Chapter 1

# Mathematical and Physical foundations

## 1.1 The mathematical tools

This abstract mathematical part will allow giving more generality and depth to the analysis of the physical equations we will later introduce. Indeed, much of the work in the field of transport theory is very phenomenological, dealing with relatively simple mathematical conditions. This is good for a fast examination of the physical consistency of the proposed equations in some simple situations (plane waves in infinite media, for instance), but it is insufficient to give a general powerful setting allowing the analysis of more complicated kinds of waves and in a wider variety of geometrical situations. This will be necessary, for instance, if one tries to study all the consequences of nonlinear equations leading, for instance, to self-focusing of waves, which makes them depart from an initial plane wave. Since my original graduation is in mathematics, I will try here contributing to the more mathematical aspects of the theory, when possible, in order to complement and enrich the usually narrower range of application of the physical theories.

### 1.1.1 Reciprocal basis

Let $V$ be the vector space associated to the Euclidean three-dimensional space $E^3$. Any set $\{\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3\}$ of three independent vectors (which are not necessarily orthogonal, nor of unit length) is called basis of $V$ if the generic element $\mathbf{a}$ of $V$ can be expressed as

$$\mathbf{a} = a^i \mathbf{e}_i$$

with $a^i$ being the contravariant components of $\mathbf{a}$. The set $\{\mathbf{e}^1, \mathbf{e}^2, \mathbf{e}^3\}$, instead, is called reciprocal (or *dual*) basis of $V$ if

$$\mathbf{e}_i \cdot \mathbf{e}^j = \delta_i^j = \begin{cases} 1 & \text{if } i = j \\ 0 & \text{if } i \neq j \end{cases} \tag{1.1}$$

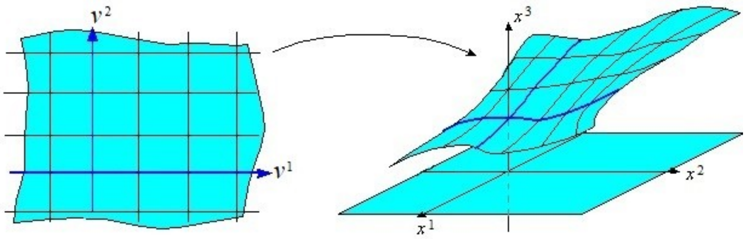
With respect to $\{\mathbf{e}^1, \mathbf{e}^2, \mathbf{e}^3\}$, one instead has

$$\mathbf{a} = a_j \mathbf{e}^j$$

wherein $a_j$ are the covariant components of $\mathbf{a}$.

### 1.1.2 Surfaces

Let $S$ be a regular surface of the Euclidean three-dimensional space $E^3$, and $x^i(v^1, v^2)$ a local parametrization of $S$, with $(v^1, v^2) \in D \subseteq \mathbb{R}^2$.




The regularity hypothesis implies that the scalar functions $x^i = x^i(v^1, v^2) \in C^1(\mathbb{R}^2)$ with $i = 1, 2, 3$, and the rank of their Jacobian matrix $\dfrac{\partial x^i}{\partial v^\alpha}$ is equal to 2. Furthermore, the relations

$$\mathbf{r}_\alpha = \frac{\partial \mathbf{x}}{\partial v^\alpha}, \quad \alpha = 1, 2 \tag{1.2}$$

define two vectors which are tangent to the coordinate curves on $S$. These vectors are also linearly independent at all points of $S$ since previous hypotheses imply that

$$\mathbf{n} = \frac{\mathbf{r}_1 \times \mathbf{r}_2}{|\mathbf{r}_1 \times \mathbf{r}_2|} \neq \mathbf{0} \tag{1.3}$$

As a consequence, the set $\{\mathbf{r}_1, \mathbf{r}_2, \mathbf{n}\}$ represents a basis for the tangent space of $S$.

**Definition 1.1.** The inner product of the tangent vectors defines

$$g_{\alpha\beta} := \mathbf{r}_\alpha \cdot \mathbf{r}_\beta \tag{1.4}$$

the *metric tensor* or *first fundamental form*.

Note that Eq. (1.4) shows that $g_{\alpha\beta}$ is a covariant second-order tensor, but it also let us go from contravariant to covariant components of a vector or a tensor. Indeed, by defining the dual basis $\{\mathbf{r}^1, \mathbf{r}^2\}$, for every tangent vector $\mathbf{w} = \mathbf{r}_\alpha w^\alpha$ one gets

$$w^\alpha \mathbf{r}_\alpha = w_\alpha \mathbf{r}^\alpha$$

with $w_\alpha = g_{\alpha\beta} w^\beta$ and $w^\alpha = g^{\alpha\beta} w_\beta$, where $g^{\alpha\beta}$ is the inverse of $g_{\alpha\beta}$.

### The Gauss-Weingarten equations

According with the aforementioned observations, the derivatives of the basis vectors $\{\mathbf{r}_1, \mathbf{r}_2, \mathbf{n}\}$ with respect to $v^\alpha$ can be expressed as

$$\mathbf{r}_{\alpha,\beta} = \Gamma^\gamma_{\alpha\beta} \mathbf{r}_\gamma + b_{\alpha\beta} \mathbf{n} \tag{1.5a}$$

$$\mathbf{n}_{,\beta} = A^\gamma_\beta \mathbf{r}_\gamma + B_\beta \mathbf{n} \tag{1.5b}$$

wherein $\Gamma^\gamma_{\alpha\beta}$, $b_{\alpha\beta}$, $A^\gamma_\beta$, $B_\beta$, with $\gamma \in \{1, 2\}$, are suitable coefficients [41, 42]. Indeed, since from Eq. (1.3) one has $\mathbf{n} \cdot \mathbf{n} = 1$, then it is easy to obtain

$$\mathbf{n}_{,\beta} \cdot \mathbf{n} = 0 \quad \Rightarrow \quad B_\beta = 0$$

so that Eq. (1.5b) reduces at

$$\mathbf{n}_{,\beta} = A^\gamma_\beta \mathbf{r}_\gamma \tag{1.6}$$

Similarly, by differentiating both side of the relation $\mathbf{n} \cdot \mathbf{r}_\alpha = 0$ with respect to $v^\beta$ one has

$$\mathbf{n}_{,\beta} \cdot \mathbf{r}_\alpha + \mathbf{n} \cdot \mathbf{r}_{\alpha,\beta} = 0$$

for $\alpha = 1, 2$, which, by means of Eqs. (1.5a) and (1.6), yields

$$0 = A^\gamma_\beta \mathbf{r}_\gamma \cdot \mathbf{r}_\alpha + \mathbf{n} \cdot \Gamma^\gamma_{\alpha\beta} \mathbf{r}_\gamma + b_{\alpha\beta} \mathbf{n} = A^\gamma_\beta g_{\gamma\alpha} + b_{\alpha\beta} \Longrightarrow A^\gamma_\beta g_{\gamma\alpha} = -b_{\alpha\beta} \tag{1.7a}$$

$$A^\gamma_\beta g_{\gamma\alpha} g^{\alpha\sigma} = -b_{\alpha\beta} g^{\alpha\sigma} \Longrightarrow A^\gamma_\beta \delta^\sigma_\gamma = -b_{\alpha\beta} g^{\alpha\sigma} \Longrightarrow A^\sigma_\beta = -b^\sigma_\beta \tag{1.7b}$$

By inserting the coupling of Eqs. (1.6) and (1.7) in Eqs. (1.5) one may finally reach the so-called *Gauss-Weingarten equations*:

$$\begin{cases} \mathbf{r}_{\alpha,\beta} = \Gamma^\gamma_{\alpha\beta} \mathbf{r}_\gamma + b_{\alpha\beta} \mathbf{n} \\ \mathbf{n}_{,\beta} = -b^\gamma_\beta \mathbf{r}_\gamma \end{cases} \tag{1.8}$$

The second-order tensor $b_{\alpha\beta}$ is called the *second fundamental form*; instead, the quantity $\Gamma^\gamma_{\alpha\beta}$ denotes the *Christoffel symbols of the second kind*.

The *Christoffel symbols of the first kind* are the corresponding values with a covariant first index:

$$\Gamma_{\gamma\alpha\beta} = g_{\gamma\delta}\Gamma^{\delta}_{\alpha\beta} \Longleftrightarrow \Gamma^{\gamma}_{\alpha\beta} = g^{\gamma\delta}\Gamma_{\delta\alpha\beta}$$

They only depend on the derivatives of the first fundamental form: in fact, one can prove that

$$\Gamma_{\gamma\alpha\beta} = \frac{1}{2}\left(g_{\gamma\alpha,\beta} + g_{\gamma\beta,\alpha} - g_{\alpha\beta,\gamma}\right) \tag{1.9}$$

Note that the Christoffel symbols of the second kind are symmetric with respect to the lower indices, then the Christoffel symbols of the first kind are symmetric with respect to the second and the third index.

*Remark* 1. The Christoffel symbols are **not** tensors.

### 1.1.3 Singular surfaces

Let $R$ be an open region, i.e., an open connected set. Let $S$ be a surface that divides $R$ into two regions $R^-$ and $R^+$. For simplicity, we can suppose that $S$ is limited in $R$.

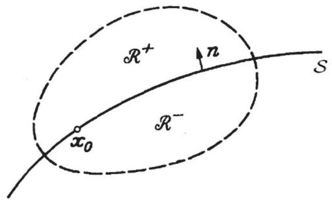



Figure 1.1: A singular surface

Let $\psi$ be a scalar function defined over $R$ which is continuous in the interior of $R^-$ and $R^+$ and let $\psi_{R^-}$ and $\psi_{R^+}$ be the restrictions of $\psi$ over $R^-$ and $R^+$ respectively. Suppose that $\psi$ approaches finite limit values $\psi^-$ and $\psi^+$ as $x$ approaches a point $x_0$ on $S$ while remaining within $R^-$ and $R^+$ respectively:

$$\psi^-(x_0) = \lim_{x\to x_0} \psi_{R^-}(x) \tag{1.10a}$$

$$\psi^+(x_0) = \lim_{x\to x_0} \psi_{R^+}(x) \tag{1.10b}$$

**Definition 1.2.** The *jump* of the function $\psi$ across $S$ is denoted by

$$[\psi] = \psi^- - \psi^+ \tag{1.11}$$

**Definition 1.3.** If $[\psi] \neq 0$, the surface $S$ is said to be *singular* with respect to $\psi$.

**Lemma 1.1.1.** *The jump across $S$ of a product of functions $\alpha$ and $\beta$ is*

$$[\alpha\beta] = \alpha^+[\beta] + \beta^+[\alpha] + [\alpha][\beta] \tag{1.12}$$

If $\psi$ is continuously differentiable in the interior of $R^+$, and $\psi^+$ is differentiable on the smooth curve $x^i = x^i(s)$ upon $S$, then

$$\frac{d}{ds}\psi^+ = \psi^+_{,i}\frac{dx^i}{ds} \tag{1.13}$$

once $\psi$ and $\psi_{,i}$ approach, respectively, the finite limits $\psi^+$ and $\psi^+_{,i}$ as $S$ is approached upon paths interior to $R^+$. In other words, the theorem of the total differential holds for the limiting values as $S$ is approached from one side only. Note that the function $\psi$ doesn't need to be defined upon the other side of $S$. If it is, and if the corresponding limiting values $\psi^-$ and $\psi^-_{,i}$ exist and have the required smoothness, a similar result holds for them:

$$\frac{d}{ds}\psi^- = \psi^-_{,i}\frac{dx^i}{ds} \tag{1.14}$$

By coupling Eqs. (1.13) and (1.14) one get

$$\frac{d}{ds}[\psi] = \frac{d}{ds}\psi^- - \frac{d}{ds}\psi^+ = \psi^-_{,i}\frac{dx_i}{ds} - \psi^+_{,i}\frac{dx_i}{ds} = [\psi_{,i}]\frac{dx_i}{ds} \tag{1.15}$$

where $[\psi_{,i}] = \psi^-_{,i} - \psi^+_{,i}$ means the jump of the gradient of $\psi$. One can also calculate the derivatives of $[\psi]$ with respect to the coordinate system $(u^1, u^2)$ as

$$[\psi]_{;\alpha} = \frac{\partial}{\partial u^\alpha}[\psi] = [\psi_{,i}]\frac{\partial x^i}{\partial u^\alpha} = [\psi_{,i}]\, r^i_\alpha \tag{1.16}$$

where $r^i_\alpha$ means the $i$-th component of the vector $\mathbf{r}_\alpha$.

### Geometric conditions of compatibility

**Lemma 1.1.2** *Let $\{\mathbf{e}_1, ..., \mathbf{e}_n\}$ be a basis of a vectorial space and let $\{\mathbf{e}^1, ..., \mathbf{e}^n\}$ be the dual basis. Then*

$$e^h_i\,(e_h)^j = \delta^j_i \tag{1.17}$$

From Eq. (1.17) one directly has $\delta^j_i = r^\alpha_i r^j_\alpha + n_i n^j$. Since $[\psi_{,i}] = \delta^j_i\,[\psi_{,j}]$, then it follows

$$[\psi_{,i}] = \left(r^\alpha_i r^j_\alpha + n_i n^j\right)[\psi_{,j}] = r^\alpha_i r^j_\alpha\,[\psi_{,j}] + n_i n^j\,[\psi_{,j}] \tag{1.18}$$

which firstly leads to $[\psi_{,i}] = r^\alpha_i\,[\psi]_{;\alpha} + n_i\, n^j[\psi_{,j}]$, and finally to

$$[\psi_{,i}] = r^\alpha_i\,[\psi]_{;\alpha} + Bn_i \tag{1.19}$$

where $B = n^j[\psi_{,j}]$ is the jump of the normal component of the gradient. Equation (1.19) is the *geometric condition of compatibility of first order* (i.e., on the first-order derivatives).

**Theorem 1.1.3.** *Maxwell Theorem*
*In the particular case in which $\psi$ has an equal jump in all points, i.e., $[\psi]$ is constant over S, then $[\psi]_{,\alpha} = 0$. In this case, the geometric condition becomes*

$$[\psi_{,i}] = B n_i \qquad (1.20)$$

*The jump of the gradient is longitudinal, because it has the same direction of $n_i$.*

Let now $c_k$ be a vector field defined over $R$, and let the jump of the field (i.e., the jump of the components $c_k$) be constant over a surface S. The Maxwell theorem 1.1.3 leads to

$$c_{k,i} = B_k n_i \qquad (1.21)$$

where $B_k = c_{k,j} n^j$. Then it is possible to evaluate the jump of the divergence since

$$\delta_{ki} c_{k,i} = \delta_{ki} B_k n_i \Rightarrow c_{k,k} = B_k n_k \Rightarrow [\nabla \cdot \mathbf{c}] = \mathbf{B} \cdot \mathbf{n} \qquad (1.22)$$

and the jump of the curl operator since

$${}_{jik} c_{k,i} = {}_{jik} B_k n_i \Rightarrow {}_{jik} c_{k,i} = {}_{jik} n_i B_k \Rightarrow [\nabla \times \mathbf{c}] = \mathbf{n} \times \mathbf{B} \qquad (1.23)$$

Since every vector can be written in a longitudinal component and a transversal one, i.e., since

$$\mathbf{B} = \mathbf{B}^{k} + \mathbf{B}^{\perp} = (\mathbf{n} \cdot \mathbf{B})\, \mathbf{n} - \mathbf{n} \times (\mathbf{n} \times \mathbf{B})$$

then the use of Eqs. (1.22) and (1.23) yields the following result

$$\mathbf{B} = [\nabla \cdot \mathbf{c}]\, \mathbf{n} - \mathbf{n} \times [\nabla \times \mathbf{c}] \qquad (1.24)$$

which is well-known as the *first Weingarten theorem*.

The geometric condition of compatibility (1.19) can be indeed also applied to $\psi_{,j}$ in order to have

$$\psi_{,ji} = \psi_{,j\ ,\alpha}\, r_i^{\alpha} + \psi_{,jk}\, n^k\, n_i \qquad (1.25)$$

If we suppose that $\psi_{,j}$ is constant, we get $\psi_{,ji} = \psi_{,jk}\, n^k\, n_i$ and, similarly, $\psi_{,ij} = \psi_{,ik}\, n^k\, n_j$. In this last equation, we can multiply times $n^i$ both sides and get

$$\psi_{,ij}\, n^i = \psi_{,ik}\, n^k n^i\, n_j \qquad (1.26)$$

which in its turn yields

$$\psi_{,ij} = \psi_{,ij}\, n^i\, n_i = \psi_{,ik}\, n^k n^i\, n_j\, n_i = \psi_{,ik}\, n^k n^i\, n_j n_i \qquad (1.27)$$

in order to obtain the *geometric condition of compatibility of the second order* (i.e. on the second-order derivatives)

$$\left[\psi_{,ij}\right] = C n_i n_j \tag{1.28}$$

where $C = B_i n^i$ and

$$B_i = \left[\psi_{,ik}\right] n^k \tag{1.29}$$

In general, the condition for the derivative of order $p$, supposing that the derivative of order $(p-1)$ has a constant jump, can be written as

$$\left[\psi_{,i_1 i_2 \ldots i_p}\right] = Z^{(p)} n_{i_1} n_{i_2} \ldots n_{i_p} \tag{1.30}$$

wherein

$$Z^{(p)} = \left[\psi_{,j_1 j_2 \ldots j_p}\right] n^{j_1} n^{j_2} \ldots n^{j_p} \tag{1.31}$$

### Normal Velocity

Consider a family of surfaces given by

$$x^i = x^i(\mathbf{v}, t) \tag{1.32}$$

namely, the place $x^i$ occupied by the surface point $(v^1, v^2)$ as the time $t$ progresses. The motion of a point on the surface is described by the velocity[1]

$$c^i = \partial_t x^i \tag{1.33}$$

Since it depends on the choice of the surface coordinate system, this surface velocity is not intrinsic to the moving surface. Indeed, suppose that $x^i = \xi^i(\mathbf{z}, t)$ is another parametric representation of the same surface and suppose that the relation $v^j = v^j(\mathbf{z}, t)$ holds $\forall j$, which is tantamount to assume that

$$x^i(\mathbf{v}(\mathbf{z}, t), t) = \xi^i(\mathbf{z}, t) \tag{1.34}$$

Deriving Eq.(1.34) with respect to time one firstly has

$$\partial_t x^i + \frac{\partial x^i}{\partial v^\alpha} \partial_t v^\alpha = \partial_t \xi^i \tag{1.35}$$

and finally

$$c^i + \partial_t v^\alpha r^i_\alpha = v^i \tag{1.36}$$

[1] We recall that $\partial_t$ denotes the derivative with respect to time.

$v^i$ being the velocity with respect to the new parametric representation. The latter equation shows that, in general, two distinct parametric representations lead to different velocities at the same point. By multiplying both sides of Eq. (1.36) times the unit normal vector, one gets

$$c^i n_i = v^j n_i = U \tag{1.37}$$

with $U$ being the *normal speed*. In this way, the *normal velocity* $U_i$ of the surface can be defined as

$$U_i = U n_i \tag{1.38}$$

### 1.1.4 Displacement derivative

**Definition 1.4.** A coordinate system for which the velocity is normal to the surface in all points, i.e., $c^i = U^i$, $\forall i \in \{1, 2, 3\}$, is called a *convective coordinate system*.

**Definition 1.5.** Given a *moving surface* $S$ in an open region $R$ and given a scalar function $\psi(\mathbf{x}, t)$ defined over $R$, the *displacement derivative* with respect to the moving surface is

$$\frac{\delta\psi}{\delta t} = \lim_{\Delta t \to 0} \frac{\psi(\mathbf{x} + \mathbf{U}\Delta t, t + \Delta t) - \psi(\mathbf{x}, t)}{\Delta t} \tag{1.39}$$

where $\mathbf{x} + \mathbf{U}\Delta t$ is the point occupied by $\mathbf{x}$ at the time $t + \Delta t$ when it is moving along the normal vector.

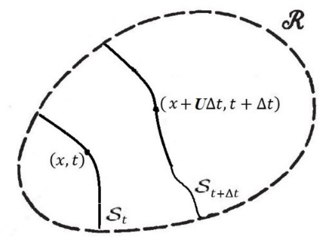



Figure 1.2: Motion of a singular surface

If the following expansion of $\psi$ is considered [43–45]

$$\psi(\mathbf{x} + \mathbf{U}\Delta t, t + \Delta t) = \psi(\mathbf{x}, t) + \psi_{,i} U^i \Delta t + \partial_t \psi \Delta t + o(\Delta t) \tag{1.40}$$

then displacement derivative (1.39) becomes

$$\frac{\delta\psi}{\delta t} = \partial_t \psi + U n^i \psi_{,i} \tag{1.41}$$

which is also called *time derivative at the wave*. Similarly, the definition of the displacement derivative at the wave can be also given for a field $\phi\,(\mathbf{v}, t)$ defined on the surface $S$ as

$$\frac{\delta\phi}{\delta t} = \lim_{\Delta t \to 0} \frac{\phi\,(\mathbf{v} + \Delta\mathbf{v}, t + \Delta t) - \phi\,(\mathbf{v}, t)}{\Delta t} \tag{1.42}$$

If the following expansion of $\phi$ is considered [43–45]

$$\phi\,(\mathbf{v} + \Delta\mathbf{v}, t + \Delta t) = \phi\,(\mathbf{v}, t) + \frac{\partial\phi}{\partial v^\alpha}\Delta v^\alpha + \partial_t\phi\Delta t + o\,(\Delta t) \tag{1.43}$$

then Eq. (1.42) becomes

$$\frac{\delta\phi}{\delta t} = \frac{\partial\phi}{\partial v^\alpha} \lim_{\Delta t \to 0} \frac{\Delta v^\alpha}{\Delta t} + \partial_t\phi \tag{1.44}$$

The velocity $c^i$ and the normal velocity $U^i$ can be written in terms of the basis $\{\mathbf{r}_1, \mathbf{r}_2, \mathbf{n}\}$, namely

$$c^i = Un^i + c^\alpha r^i_\alpha$$
$$U^i = Un^i$$

respectively.

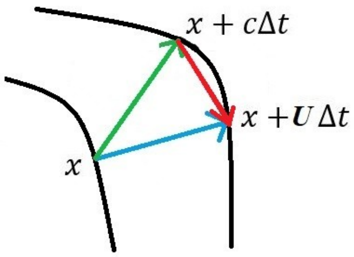



Figure 1.3: In the time laps $\Delta t$ the displacement is $\mathbf{c}\Delta t$ with respect to a generic parametric representation; the displacement is $\mathbf{U}\Delta t$ with respect to a convective representation.

It means that the vector $x^i + U^i\Delta t - (x^i + c^i\Delta t) = (U^i - c^i)\,\Delta t$ (see Fig.1.3) has not normal component since

$$U^i - c^i = -c^\alpha r^i_\alpha \tag{1.45}$$

Then we can compute

$$(U^i - c^i)\,\Delta t = -c^\alpha r^i_\alpha \Delta t = (-c^\alpha \Delta t)\, r^i_\alpha$$

By substituting $\Delta v^\alpha = -c^\alpha \Delta t$ in Eq. (1.44), one gets

$$\frac{\delta \phi}{\delta t} = \partial_t \phi - c^\alpha \phi_{,\alpha} \tag{1.46}$$

*Remark* 2. Choosing a convective coordinate system one gets $\Delta v^\alpha = 0$ and then the displacement derivative and the derivative with respect to time coincide.

### 1.1.5 Kinematic Condition of Compatibility

A surface in cartesian coordinates $\varphi(\mathbf{x}, t) = 0$ can be described as a 3-variety embedded in $\mathbb{R}^4$. Since $\mathbf{x} = \mathbf{x}(\mathbf{v}, t)$, then

$$\varphi(\mathbf{x}(\mathbf{v}, t), t) = 0 \; \forall \mathbf{v}, \forall t \tag{1.47}$$

Then, differentiating both sides of Eq. (1.47) with respect to time one may have

$$(\varphi_{,i}, \partial_t \varphi) \cdot c^i, 1 = \varphi_{,i} c^i + \partial_t \varphi = 0 \tag{1.48}$$

Referring to the inner product $c^i \varphi_{,i}$ and reminding that the gradient $\varphi_{,i}$ is orthogonal to the surface, one gets

$$\varphi_{,i} c^i = \varphi_{,i} U^i \tag{1.49}$$

namely, the vector $(U^i, 1)$ is orthogonal to the gradient $(\varphi_{,i}, \partial_t \varphi)$. For this reason, we can apply Eq(1.13) (also known as the Hadamard lemma) to a curve whose tangent vector is $(U^i, 1)$ and get, for a given function $\psi$,

$$\frac{d}{ds}\psi^+ = \psi^+_{,i} U n^i + \partial_t \psi^+ = \frac{\delta \psi^+}{\delta t} \tag{1.50}$$

once the definition of the displacement derivative (i.e., Eq. (1.41)) for $\psi^+$ has been used. Similarly,

$$\frac{d}{ds}\psi^- = \psi^-_{,i} U n^i + \partial_t \psi^- = \frac{\delta \psi^-}{\delta t} \tag{1.51}$$

The coupling of Eqs. (1.50) and (1.51) leads to the following *kinematic condition of compatibility*

$$\frac{\delta}{\delta t}[\psi] = [\partial_t \psi] + [\psi_{,i}] U n^i \tag{1.52}$$

also known as *Hadamard* (H-) *relation*. When the jump of $\psi$ is constant, Eq. (1.52) turns out

$$[\partial_t \psi] = -UB \tag{1.53}$$

wherein $B = n^j \psi_{,j}$ .

### General Kinematic Compatibility Relation

The H-relation applied to the space derivative of the function $\psi$ turns out

$$\frac{\delta}{\delta t}[\psi_{,i}] = [\partial_t \psi_{,i}] + U n^j [\psi_{,ij}] \tag{1.54}$$

and it reduces to

$$[\partial_t \psi_{,i}] = -U n^j [\psi_{,ij}] \tag{1.55}$$

when the jump of the first order derivatives is constant. In this case, by using the geometric condition of the second order (i.e., Eq. (1.28)), from Eq. (1.55) one may have

$$[\partial_t \psi_{,i}] = -U n^j n_i n_j C = -U C n_i \tag{1.56}$$

The H-relation applied to the time derivative of the function $\psi$ turns out, instead,

$$\frac{\delta}{\delta t}[\partial_t \psi] = [\partial_t^2 \psi] + U n^j [\partial_t \psi_{,j}] \tag{1.57}$$

When Eq.(1.56) is used in Eq. (1.57), in the case of a constant jump of the first order derivatives, one gets

$$[\partial_t^2 \psi] = -U n^j [\partial_t \psi_{,j}] = -U n^j (-U n_j C) = U^2 C \tag{1.58}$$

In general, the kinematic condition for the derivatives of order $p+q$ (the order $p$ being with respect to space and order $q$ being with respect to time, by supposing that the derivative of the previous order has constant jump) is

$$\left[\partial_t^q \psi_{,i_1 \ldots i_p}\right] = (-U)^q Z^{(p+q)} n_{i_1} n_{i_2} \ldots n_{i_p} \tag{1.59}$$

where $Z^{(k)} = \left[n^{i_1} n^{i_2} \ldots n^{i_k} \psi_{,i_1 \ldots i_k}\right]$.

At the end of this section, we recall a useful lemma [46] involving the jump of the derivatives of the second order in a general case (i.e., when the jump of the first order derivatives is not constant).

**Lemma 1.1.4.** *Let $\psi$ be a function, the derivatives of which suffer discontinuities across an acceleration wave S moving into equilibrium. Then*

$$[\partial_t \psi_{,i}] = \eta \frac{\delta B}{\delta t} - U [n^j \psi_{,ij}] \tag{1.60a}$$

$$[\partial_t^2 \psi] = -2U \frac{\delta B}{\delta t} + U^2 [n^i n^j \psi_{,ij}] \tag{1.60b}$$

### 1.1.6 Acceleration waves

In the preceding sections we have obtained the conditions of compatibility for a moving surface singular with respect to some field $\psi$. In Ref. [44] all quantities associated with a motion are regarded as functions $\psi(\mathbf{x}, t)$. This leads to the following definition:

**Definition 1.6.** The *order* of a singular surface with respect to $\psi$ is the order of the derivative $\partial_t^q \psi_{,i_1 \ldots i_p}$ of lowest order $p + q$ suffering a non-zero jump upon the surface.

In general, propagating singular surfaces are called *waves*.

**Definition 1.7.** Waves of second order are called *acceleration waves*.

Now we shall apply some results to particular singular surfaces defined in terms of the motion of a deformable body $B$.

Let $S(t)$ be a regular surface in the current configuration $B_t$ characterized by the condition

$$\varphi\left(x^i, t\right) = 0 \tag{1.61}$$

If we rewrite (1.61) as

$$\varphi\left(x^i\left(X^A, t\right), t\right) = \Phi\left(X^A, t\right) \tag{1.62}$$

then, the condition

$$\Phi\left(X^A, t\right) = 0 \tag{1.63}$$

is an equation that for each $t$ identifies a set of material points of the continuous body that form a surface $S_0(t)$ on $B_0$.

*Remark* 3. $\Phi$ and $\varphi$ are $C^1$ functions.

By denoting the unit normals of $S(t)$ and $S_0(t)$ with $n_i$ and $N_A$, respectively, if $\nabla\varphi \neq \mathbf{0}$ on $S(t)$, then it follows

$$n_i = \pm \frac{1}{\|\nabla\varphi\|}\varphi_{,i} \tag{1.64a}$$

$$N_A = \pm \frac{1}{\|\nabla\Phi\|}\Phi_{,A} = \pm \frac{1}{\|\nabla\Phi\|}F^i_A \varphi_{,i} \tag{1.64b}$$

once the differentiation of Eq. (1.62) with respect to space, i.e.,

$$\Phi_{,A} = F^i_A \varphi_{,i} \tag{1.65}$$

is used. It is easy matter to see that merging Eqs. (1.64) one has

$$N_A = \frac{\| \nabla\varphi \|}{\| \nabla\Phi \|} F_A^i n_i \tag{1.66}$$

If the normal speeds $U$ and $U_0$ for $S$ and $S_0$ respectively, are introduced, in view of the representations (1.61) and (1.63) above one has

$$U = \mp \frac{1}{\| \nabla\varphi \|} \partial_t \varphi \tag{1.67a}$$

$$U_0 = \mp \frac{1}{\| \nabla\Phi \|} \partial_t \Phi \tag{1.67b}$$

Then, by using the relation

$$\partial_t \Phi = \partial_t \varphi + c^i \varphi_{,i} \tag{1.68}$$

yielding from the differentiation of Eq. (1.62) with respect to time, direct manipulations of Eqs. (1.67) lead to the following result:

$$\begin{aligned} U_0 &= \mp \frac{1}{\| \nabla\Phi \|} \partial_t \Phi = \mp \frac{1}{\| \nabla\Phi \|} \partial_t \varphi + c^i \varphi_{,i} = \\ &\mp \frac{\| \nabla\varphi \|}{\| \nabla\Phi \|} \frac{1}{\| \nabla\varphi \|} \partial_t \varphi + c^i \frac{1}{\| \nabla\varphi \|} \varphi_{,i} = \\ &U - c^i n_i \frac{\| \nabla\varphi \|}{\| \nabla\Phi \|} \end{aligned} \tag{1.69}$$

The quantity $\bar{u} = U - c^i n_i$ is called the *intrinsic speed* of $S$.

## 1.2 The physical background

The best-known model for heat conduction is Fourier's law (FL)

$$q_i = -\kappa \theta_{,i} \tag{1.70}$$

$q_i$ being the local heat-flux vector (i.e., the amount of energy per unit time and unit area transported by conduction), $\kappa$ the thermal conductivity, and $\theta$ the non-equilibrium temperature [47–49].

*Remark* 4. In the very general case (i.e., in the case of anisotropic systems), one should properly speak about the matrix of thermal conductivity. That matrix can be either symmetric [50, 51], or non-symmetric [52]. Throughout this thesis the thermal conductivity will be represented by a scalar-valued function, since we will always refer to isotropic systems.

Although Eq. (1.70) is well tested for most practical problems, it fails to describe the transient temperature field in situations involving short times, high frequencies and small wavelengths. According to FL, in fact, a sudden application of a temperature difference gives instantaneously rise to a heat flux everywhere in the system, that is, any temperature disturbance will propagate at infinite velocity. From a microscopic point of view, one can also observe that the FL is valid in the collision-dominated regime, where there are many collisions among the particles, but it loses its validity when one approaches the ballistic regime, in which the dominant collisions are those of the particles with the boundaries of the system rather than the collisions among particles themselves [2].

### 1.2.1 The Maxwell-Cattaneo Theory

From the physical point of view, the instantaneous propagation of a temperature disturbance is unacceptable since a change in the temperature gradient should be felt after some time (the so-called *relaxation time*). To eliminate these anomalies, Cattaneo in Ref. [53] proposed a damped version of FL by introducing a heat flux relaxation time, $\tau_1$, namely,

$$\tau_1 \dot{q}_i = -\left(q_i + \kappa \theta_{,i}\right) \tag{1.71}$$

which is well-known as the Maxwell-Cattaneo (MC) equation.[2]

#### Acceleration waves in the MC theory

In the MC theory, the governing equations for the basic fields of a rigid body in $\mathbb{R}^3$ are

$$\rho c_v \dot{\theta} + q_{i,i} = 0 \tag{1.72a}$$

$$\tau_1 \dot{q}_i + q_i + \kappa \theta_{,i} = 0 \tag{1.72b}$$

wherein the former equation directly follows from the coupling of the energy local-balance equation

$$\rho \dot{e} + q_{i,i} = 0 \tag{1.73}$$

with the usual thermodynamic assumption

$$c_v = \frac{\partial e}{\partial \theta} \tag{1.74}$$

[2] Throughout this thesis, a superposed dot also denotes the partial derivative with respect to time of the indicated argument (i.e. $\dot{f} = \partial f/\partial t$)

$c_v$ being the specific heat at constant volume, $\varepsilon$ being the internal energy per unit mass and $\rho$ the mass density.

An acceleration wave for a solution of Eqs. (1.72) is a surface $S$ across which $\dot{\theta}$, $\theta_{,i}$, $\dot{q}_i$, $q_{i,j}$ suffer at most finite discontinuities, with the functions $\theta$, $q_i$ continuous everywhere. If that wave is moving into an equilibrium region for which

$$\theta = \text{const}, q_i = 0 \tag{1.75}$$

then

$$\dot{\theta}^+ = 0,\ \theta^+_{,i} = 0 \tag{1.76}$$

We may take the jump of Eqs. (1.72) to find

$$\rho c_v \left[\!\left[\dot{\theta}\right]\!\right] = -\left[q_{i,i}\right] \tag{1.77a}$$

$$\tau_1 [\dot{q}_i] = -\kappa \left[\theta_{,i}\right] \tag{1.77b}$$

By defining the three-dimensional wave amplitudes as

$$A(t) = n^i \theta_{,i} \ ,\ B_i(t) = n^j q_{i,j} \tag{1.78}$$

and using the H-relations (see Eq. (1.52))

$$0 = \frac{\delta}{\delta t}[q_i] = [\dot{q}_i] + U n^j q_{i,j} \tag{1.79a}$$

$$0 = \frac{\delta}{\delta t}[\theta] = \left[\!\left[\dot{\theta}\right]\!\right] + U n^j \theta_{,j} \tag{1.79b}$$

we get at first

$$[\dot{q}_i] = -UB_i, \quad \left[\!\left[\dot{\theta}\right]\!\right] = -UA \tag{1.80}$$

and, finally we have

$$-\rho c_v UA + n_i B_i = 0 \tag{1.81a}$$

$$-\tau_1 UB_i + \kappa n_i A = 0 \tag{1.81b}$$

From Eq. (1.81b) one can see that the wave has to be longitudinal, i.e., $B_i = Bn_i$, where

$$B = n^i n^j q_{i,j} \tag{1.82}$$

Then, it is easy matter to point out that the system of equations (1.81) does not admit the only-one trivial solution if, and only if,

$$U = \sqrt{\frac{\kappa}{\rho c_v \tau_1}} \tag{1.83}$$

which is the wave speed in the MC theory.

### 1.2.2 Second law of Thermodynamics

From the theoretical point of view, one can derive in several ways a heat-transport equation beyond Eq. (1.70); therefore different theories can be found in literature, some of which being very refined from the mathematical point of view. It seems worth noticing that in developing a new heat-transport theory one should not forget that the model has to be compatible with the basic tenets of Continuum Mechanics. To be sure about this, a very valuable tool is represented by the second law of thermodynamics which states that the rate of entropy production has to be always larger than zero in any admissible irreversible thermodynamic process [54, 55]. The rate of entropy production $\rho\sigma^{(s)}$ is given by the local-balance equation of the specific entropy $s$ as

$$\rho\sigma^{(s)} = \rho\dot{s} + J^{(s)}_{i,i} \tag{1.84}$$

where $J^{(s)}_i$ is the specific-entropy flux

### 1.2.3 Extended Irreversible Thermodynamics

Equilibrium thermodynamics deals with ideal processes taking place at infinitely slow speed, considered as a sequence of equilibrium states. For arbitrary processes, it may only compare the initial and final equilibrium states, but the processes themselves cannot be described. To handle more realistic situations involving finite velocities and inhomogeneous effects, an extension of equilibrium thermodynamics is needed. A first insight is provided by the so-called *classical irreversible thermodynamics*. This borrows most of the concepts and tools from equilibrium thermodynamics but transposed at a local scale because non-equilibrium states are usually inhomogeneous. The goal is to cope with non-equilibrium situations in which basic physical quantities like mass, temperature, pressure, etc. are not only allowed to change from place to place, but also over time. Nevertheless, modern technology points towards miniaturized devices and high-frequency processes, whose length and timescales are comparable to the mean-free path of the particles and to the internal relaxation times of the devices. To describe these phenomena, extensions of the classical transport laws are needed. Indeed, these laws assume an instantaneous response of the fluxes to the imposed thermodynamic forces, whereas, actually, it takes some time for the fluxes to reach the values predicted by the classical laws. As a consequence, when working at short timescales or high frequencies, and correspondingly at short length scales or short wavelengths, the generalized transport laws must include also memory and non-local effects. The analysis of these generalized transport laws is one of the main topics in modern non-equilibrium thermodynamics, statistical mechanics, and engineering. Such transport laws are generally not compatible with the local equilibrium hypothesis and a more general thermodynamic framework must be looked for. A very formally simple theory that meets these needs is the *Extended Irreversible Thermodynamics* (EIT), which provides a macroscopic and causal description of non-equilibrium processes and is based on the introduction of the fluxes as additional non-equilibrium independent variables [2, 4].

### The entropy in EIT

When the state-space variables are the internal energy $e$ per unit mass, the heat flux $q_i$ and the flux of the heat flux $Q_{ij}$, in EIT the entropy has the form $s = s(e, q_i, Q_{ij})$ in such a way that its differential reads [3, 4, 7, 29]

$$ds(e; q_i) = \left(\frac{\partial s}{\partial e}\right)_{q_i, Q_{ij} = \text{const}} de + \left(\frac{\partial s}{\partial q_i}\right)_{e, Q_{ij} = \text{const}} dq_i + \left(\frac{\partial s}{\partial Q_{ij}}\right)_{e, q_i = \text{const}} dQ_{ij} \quad (1.85)$$

wherein

$$\left(\frac{\partial s}{\partial e}\right)_{q_i, Q_{ij} = \text{const}} = \frac{1}{\theta} \quad (1.86a)$$

$$\left(\frac{\partial s}{\partial q_i}\right)_{e, Q_{ij} = \text{const}} = -\frac{\tau_1 q_i}{\kappa\rho\theta^2} \quad (1.86b)$$

$$\left(\frac{\partial s}{\partial Q_{ij}}\right)_{e, q_i = \text{const}} = -\frac{\tau_2 Q_{ij}}{\kappa\rho\theta^2 \ell^2} \quad (1.86c)$$

are the thermodynamic conjugates of the state-space variables $e$, $q_i$ and $Q_{ij}$, respectively. In Eq. (1.86c) $\tau_2$ stands for the relaxation time of $Q_{ij}$, and $\ell$ means the mean-free path of the heat carriers. As a consequence of Eqs. (1.85) and (1.86), in EIT one has [2, 4, 7, 56]

$$s = \frac{e}{T} - \frac{\tau_1}{2\kappa\rho\theta^2} q_i q_i - \frac{\tau_2}{2\kappa\rho\theta^2 \ell^2} Q_{ij} Q_{ij} \quad (1.87)$$

with $T$ being the local-equilibrium temperature.

### The nonequilibrum temperature in EIT

In non-equilibrium situations the correct definition of temperature is a very compelling and interesting task, besides being still an open problem [4]. For linear harmonic chains (where the local-equilibrium temperature is related to the average energy per particle $u$ through the Boltzmann constant $k_B$, i.e., $T = \frac{u}{k_B}$), for example, by using the maximum-entropy formalism one may obtain [4]

$$\frac{1}{\theta}=\frac{1}{T}\frac{1+x_i x_i}{1-x_i x_i}$$

wherein $x_i=\frac{q_i}{v_0 u}$, with $v_0$ being the speed of elastic waves. For thermal radiation, instead, the maximum-entropy formalism yields [4]

$$\frac{1}{\theta}=\frac{1}{T}\left[\frac{(y+2)^{1/2}}{(y-1)^{3/4}}\right] \qquad (1.88)$$

wherein $y$ is given by

$$y=\sqrt{4-3\left(\frac{Vq}{v_l U}\right)^2}$$

wherein $U=aT^4V$ is the internal energy of radiation in the volume $V$, $a$ is the radiation constant, and $v_l$ is the speed of light. Indeed, the coupling of Eqs. (1.86a) and (1.87), leads

$$\frac{1}{\theta}=\frac{1}{T}-\frac{\partial}{\partial e}\left(\frac{\tau_1}{2\kappa\rho\theta^2}\right)q_i q_i-\frac{\partial}{\partial e}\left(\frac{\tau_2}{2\kappa\rho\theta^2}\right)Q_{ij}Q_{ij} \qquad (1.89)$$

which clearly points out how in the framework of EIT $\theta$ is a truly nonequilibrium variable. Indeed, the second and third term in the right-hand side of Eq. (1.89), which represent the corrective terms due to nonequilibrium situations, may be small in some practical applications [4]. In that cases, for the sake of simplicity, one can assume

$$\frac{1}{\theta}\approx\frac{1}{T} \qquad (1.90)$$

In this thesis we always refer to Eq. (1.90) as the *non-equilibrium temperature approximation*.

## The entropy flux in EIT

In developing a theory of heat transport beyond the classical FL, one should look for an appropriate constitutive equation not only for the entropy flux, but also for the specific entropy [55]. In EIT the specific-entropy flux $J_i^{(s)}$ reads [2, 4, 7]

$$J_i^{(s)}=\frac{q_i}{\theta}+K_i \qquad (1.91)$$

with $K_i$ being the specific-entropy extra flux. That vector has to be assigned by a suitable constitutive equation [1, 57, 58], in agreement with second law of thermodynamics.

### 1.2.4 Nonlinear heat-transport equations

In non-metallic solids the heat transport in only due to phonons, i.e., to the collective vibrations of atoms [59–61]. Their transport is diffusive and describable by the classical FL (1.70) in all practical applications which involve systems whose characteristic size is of the order of micrometer, or larger. In modern devices which are widely applied in micro/nano electronics the phonon transport regime, instead, can be also ballistic, or hydrodynamic [16,17,21,23,62–67]. In these transport regimes (which are particularly relevant, for example, in two-dimensional systems as graphene sheets) Eq. (1.70) breaks down [4,7,56,68], as it is confirmed by the experimental observations on heat transfer in nanosystems [69, 70].

Phonon hydrodynamics, in particular, represents a regime of phonon heat transfer in which the role played by memory and nonlocal effects becomes as more releva as the characteristic size of the system decreases [4,7]. In this regime the constitutive equation for the heat flux is usually of the Guyer-Krumhansl type [14,56,71,72], namely,

$$\tau_1 \dot{q}_i + q_i = -\kappa\theta_{,i} + \ell^2 q_{i,jj} \tag{1.92}$$

In principle Eq. (1.92) not only includes memory and nonlocal effects, but also the nonlinear ones since in that equation all thermophysical quantities (i.e., the relaxation time, the mean-free path, and the thermal conductivity) are temperature dependent. Indeed, since in nanosystems small temperature differences could lead to high values of temperature gradient, nonlinear terms accounting for products of the temperature gradient (or the heat flux) should be also taken into consideration. These "genuinely" nonlinear terms may be important in all situations wherein the different thermophysical quantities only displays vanishingly small changes with the temperature, i.e., when the material functions can be practically assumed constant. To this end, in the hypothesis of constant material functions, in Ref. [36] Eq. (1.92) has been generalized as

$$\tau_1 \dot{q}_i + q_i = -\kappa\theta_{,i} + \ell^2 q_{i,jj} + \frac{2\tau_1}{\rho c_v \theta} q_j q_{j,i} \tag{1.93}$$

which reduces to

$$\tau_1 \dot{q}_i + q_i = -\kappa\theta_{,i} + \frac{2\tau_1}{\rho c_v \theta} q_j q_{j,i} \tag{1.94}$$

when the nonlocal effects do not play any relevant role, i.e., when in Eq. (1.93) the term $\ell^2 q_{i,jj}$ can be neglected with respect the other terms [36, 46].

# Chapter 2

# Heat waves in functionally graded nanomaterials

Functionally graded materials (FGMs) are composite materials with an inhomogeneous micromechanical structure [52, 73–75]. 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 $Si_{1-c}Ge_c$, which has been much studied in semiconductor physics to engineer heat or current transport, with the stoichiometric variable $c$ ranging in the interval $[0, 1]$ [76]. Depending on the number of directions along which the material functions change, one can discriminate between 1-dimensional, 2-dimensional, and 3-dimensional FGM.

In the last decade, beams and plates made of FGMs have been widely applied in micro/nano electromechanics systems (also known as MEMS/NEMS) [77–79]. Since MEMS/NEMS display a high sensitivity to external stimulations, a better understanding of their thermomechanical properties will have a very relevance in the design and fabrication of those modern sensors.

In the present chapter we principally investigate how the composition gradient $c_{,i}$ (of the stoichiometric variable) influences the propagation of high-frequency heat waves (i.e., heat pulses) in FGMs. This analysis may be interesting for practical applications because 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 [80].

Our goal will be pursued in the framework of the MC theory, namely, we assume that Eqs.(1.72) are the governing equations for the two basic fields $\theta$ and $q_i$, let us the different material functions depend not only on temperature, but also on the stoichiometric variable. In particular, we assume

$$c_v = c_v(c) \tag{2.1a}$$

$$\tau_1 = \tau_1(\theta, c) \tag{2.1b}$$

$$\kappa = \kappa(\theta, c) \tag{2.1c}$$

## 2.1 Influence of the composition gradient on the heat-pulse propagation

The analysis of heat waves is strictly related to the time variation of the state spaceAccording with the basic tenets of EIT [4, 7], in fact, each state-space variable has to display its own evolution equation. 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,

$$\dot{c} = 0 \tag{2.2}$$

Consider then an acceleration (A-) wave $S$ for a solution of Eqs. (1.72) and, for the sake of simplicity, assume that travelling surface $S$ is moving into an equilibrium region, i.e., the region ahead the A-wave is such that

$$\theta = \theta^+ \qquad q_i = q_i^+ \tag{2.3}$$

wherein (as in what follows) the superscript + means the (constant) value of the corresponding quantity at $S$ approaching from the region which $S$ is about to enter. By taking the jumps of Eqs. (1.72) at $S$ we have

$$\tau_1^+ [\dot{q}_i] + \kappa^+ [\theta_{,i}] = 0 \tag{2.4a}$$

$$(\rho c_v)^+ \left[\dot{\theta}\right] + [q_{i,i}] = 0 \tag{2.4b}$$

which by means of the classical H-relation (1.52) yields

$$\tau_1^+ U_N \hat{q}_i - \kappa^+ n_i \hat{\theta} = 0 \tag{2.5a}$$

$$n_i \hat{q}_i - (\rho c_v)^+ U_N \hat{\theta} = 0 \tag{2.5b}$$

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

$$[q_{,i}] = \eta\hat{q}_i \qquad [\theta_{,i}] = \eta\hat{\theta} \tag{2.6}$$

with

$$\hat{\theta}(t) = [n_i\theta_{,i}] \qquad \hat{q}_i(t) = n_j q_{i,j} \tag{2.7}$$

the 3-dimensional A-wave amplitudes.

Since from Eq. (2.5a) we have that the A-waves have to be longitudinal, i.e.,

$$\hat{q}_i = \hat{q}n_i \tag{2.8}$$

with

$$\hat{q}(t) = n_i n_j q_{i,j} \tag{2.9}$$

then the requirement of non-zero A-wave amplitudes, applied to the homogeneous system of linear equations (2.5), implies that the A-wave speed is

$$U_N = \sqrt{\frac{\kappa}{\tau_1\rho c_v}} \tag{2.10}$$

We note that Eq. (2.10) is formally similar to the wave speed (1.83) obtained in Sec. 1.2.1, but the former fundamentally differs from the latter since the value of $U_N$ predicted by Eq. (2.10) depends on the local value of the different material functions (which depend, in their turn, on the local value of $c$). Equation (2.10) also points out that in FGMs the speed of propagation of thermal pulses:

i. depends on the local value of the nonequilibrium temperature (i.e., on the value of $\theta$ 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 $\theta$, 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 [18], FGMs becomes more evident owing to the dependence of them on the stoichiometric variable, too. Whereas the global behavior 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 $\hat\theta$ behaves in time (i.e., during the propagation). To do this, let us firstly observe that from Eq. (2.5b) the relation

$$\hat q = (\rho c_v)^+ U_N \hat\theta \tag{2.11}$$

between the two A-wave amplitudes arises. Then, let us differentiate Eq. (1.72b) with respect to space and Eq. (1.72a) with respect to time, in order to have

$$\left(\frac{\partial\tau_1}{\partial\theta}\theta_{,i} + \frac{\partial\tau_1}{\partial c}c_{,i}\right)\dot q_i + \tau_1\dot q_{i,i} + q_{i,i} + \left(\frac{\partial\kappa}{\partial\theta}\theta_{,i} + \frac{\partial\kappa}{\partial c}c_{,i}\right)\theta_{,i} + \kappa\theta_{,ii} = 0 \tag{2.12a}$$

$$\rho c_v\ddot\theta + \dot q_{i,i} = 0 \tag{2.12b}$$

once the hypothesis in Eq. (2.2) has been used (which is a tantamount to suppose that the time variation of $c$ can be neglected during the phenomenon at hand). The jumps of Eqs. (2.12) are

$$\begin{aligned}\left(\frac{\partial\tau_1}{\partial\theta}\right)^+[\theta_{,i}] + \left(\frac{\partial\tau_1}{\partial c}\right)^+[c_{,i}]\,[\dot q_i] + \tau_1^+[\dot q_{i,i}] + [q_{i,i}]&\\ + \left(\frac{\partial\kappa}{\partial\theta}\right)^+[\theta_{,i}] + \left(\frac{\partial\kappa}{\partial c}\right)^+[c_{,i}]\,[\theta_{,i}] + \kappa^+[\theta_{,ii}] &= 0\end{aligned} \tag{2.13a}$$

$$(\rho c_v)^+[\ddot\theta] + [\dot q_{i,i}] = 0 \tag{2.13b}$$

Recalling Eqs. (2.7) and (2.8) and that we are only considering A-waves moving into equilibrium, by straightforward calculations (which require the use of lemma 1.1.4) from Eqs. (2.13) we obtain

$$\begin{aligned}\left(\hat\theta\left(\frac{\partial\tau_1}{\partial\theta}\right)^+ + c^+_{,i}n_i\left(\frac{\partial\tau_1}{\partial c}\right)^+\right)\left(U_N\hat q - \tau_1^+\frac{\delta\hat q}{\delta t} + \tau_1^+U_N\, n_in_jn_kq_{i,jk}\right) - \hat q&\\ - \left(\hat\theta\left(\frac{\partial\kappa}{\partial\theta}\right)^+ + c^+_{,i}n_i\left(\frac{\partial\kappa}{\partial c}\right)^+\right)\left(\hat\theta - \kappa^+ n_in_j\theta_{,ij}\right) &= 0\end{aligned} \tag{2.14a}$$

$$(\rho c_v)^+\left(-2U_N\frac{\delta\hat\theta}{\delta t} + U_N^2\, n_in_j\theta_{,ij}\right) + \frac{\delta\hat q}{\delta t} - U_N\, n_in_jn_kq_{i,jk} = 0 \tag{2.14b}$$

where $\frac{\delta}{\delta t}$ means the displacement derivative (see Sec. 1.1.4).

The coupling of Eqs. (2.11) and (2.14) consequently yields the following Bernoulli-type ordinary differential equation

$$\frac{\delta\hat{\theta}}{\delta t} = \alpha\hat{\theta}^2 - \beta\,\hat{\theta} \tag{2.15}$$

with

$$\alpha = -U_N \frac{\partial}{\partial\theta} \ln\left(\frac{\kappa}{\tau_1}\right)^{+} \tag{2.16a}$$

$$\beta = \frac{1}{\tau_1^+} + c_{,i}^+ n_i U_N \frac{\partial}{\partial c} \ln\left(\frac{\kappa}{\tau_1}\right)^{+} \tag{2.16b}$$

If we suppose that the initial amplitude of the pulse is $\hat{\theta}(t=0) \equiv \hat{\theta}_0$, then the solution of Eq. (2.15) is

$$\hat{\theta}\,(t) = \left[\frac{\alpha}{\beta} + \left(\frac{1}{\hat{\theta}_0} - \frac{\alpha}{\beta}\right) e^{\beta t}\right]^{-1} \tag{2.17}$$

Equations (2.16) and (2.17) point out that the thermal-pulse amplitude:

i. depends on the local value of the nonequilibrium 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).

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 $\theta$ (the effects of which are accounted by the coefficient $\alpha$ in Eq. (2.16a)), and on $c$ (the effects of which are accounted by the coefficient $\beta$ in Eq. (2.16b)).

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 $\hat{\theta}$ 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 $\beta$.

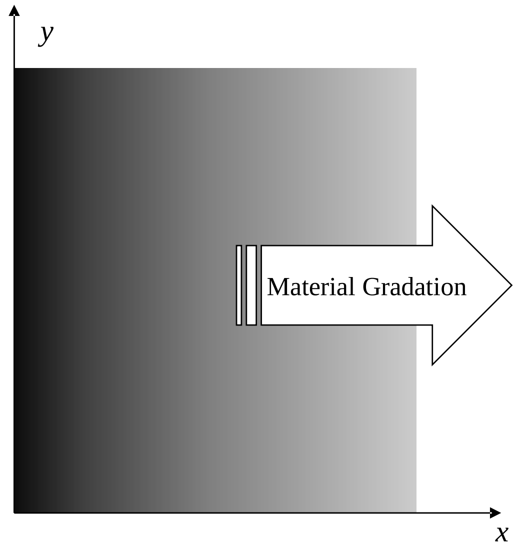



Figure 2.1: Schematic diagram of the concept of gradation in FGMs.

### 2.1.1 Application to functionally graded $Si_{1-c}Ge_c$ layer

In order to make attractive previous theoretical results for practical applications, the autors in Ref. [81] applied them to a functionally graded $Si_{1-c}Ge_c$ layer. $Si_{1-c}Ge_c$ layer, in fact, has 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 [82]. 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 Fig. 2.1 for a qualitative sketch of the system). Recalling that during the fabrication process one can select a variation law for $c$ [80], the particular cases below will be analyzed in what follows:

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

The computations will be performed under the further hypotheses below.

⑧ The material functions $\kappa$ and $\tau_1$ do not depend on temperature, which is tantamount to suppose that those material functions only display vanishingly small variations with the temperature.

⑧ The average temperature of the system is 300 K.

⑧ The size of the layer is $L = 10^{-7}$ m.

⑧ The form of the relaxation time (s) is

$$\frac{1}{\tau_1} = \frac{1-c}{\tau_{Si}} + \frac{c}{\tau_{Ge}}$$

according to the Matthiessen rule, wherein $\tau_{Si}$ and $\tau_{Ge}$ mean, respectively, the relaxation time of silicon and germanium. For the sake of simplicity, in the computations, those quantities were estimated as $\tau_{Si} = \frac{\ell_{Si}}{v_{Si}}$ and $\tau_{Ge} = \frac{\ell_{Ge}}{v_{Ge}}$ with $\ell_{Si}$ and $\ell_{Ge}$ 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 $\ell_{Si} = 8,05 \cdot 10^{-8}$ m, $v_{Si} = 2894,96$ m s$^{-1}$, $\ell_{Ge} = 5,83 \cdot 10^{-8}$ m, $v_{Ge} = 1757,7$ m s$^{-1}$. These values have been taken from Ref. [7] (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 $\kappa = \frac{\rho c_v v \ell}{3}$ of the kinetic theory's relaxation-time approximation [61, 83]; 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 [83, 84].

⑧ The form of the thermal conductivity (W m$^{-1}$ K$^{-1}$) is [76]:

$$\kappa(c) = \kappa_{Ge} c + \kappa_{Si}(1-c) - \sqrt{\kappa_{Ge}\kappa_{Si}} \left[ \sum_{k=1}^{8} A_k (1-c)^k \right]$$

At the room temperature $\kappa_{Si} = 149,95$ and $\kappa_{Ge} = 77,95$ [7]. The values of the eight constants $A_k$ are quoted in Table 2 in Ref. [76]. 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 nonlocal effects [7], in such a way that one should properly use an effective thermal conductivity [83, 84], 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 $c$.

⑧ The form of the mass density (g cm$^{-3}$) is [85]:

$$\rho(c) = 2,329 + 3,493c - 0,499c^2$$

⑧ The form of the specific heat at constant volume (J mol$^{-1}$K$^{-1}$) is [85]:

$$c_v(c) = 19,6 + 2,9c$$

In the several cases above and for a heat pulse traveling along the $x$ direction, the predicted results for the speeds of propagation are plotted in Fig. 2.2. 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 traveling 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 Fig. 2.2 suggest to use, for example, heat pulses as exploring tool for the inner structure of a 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.

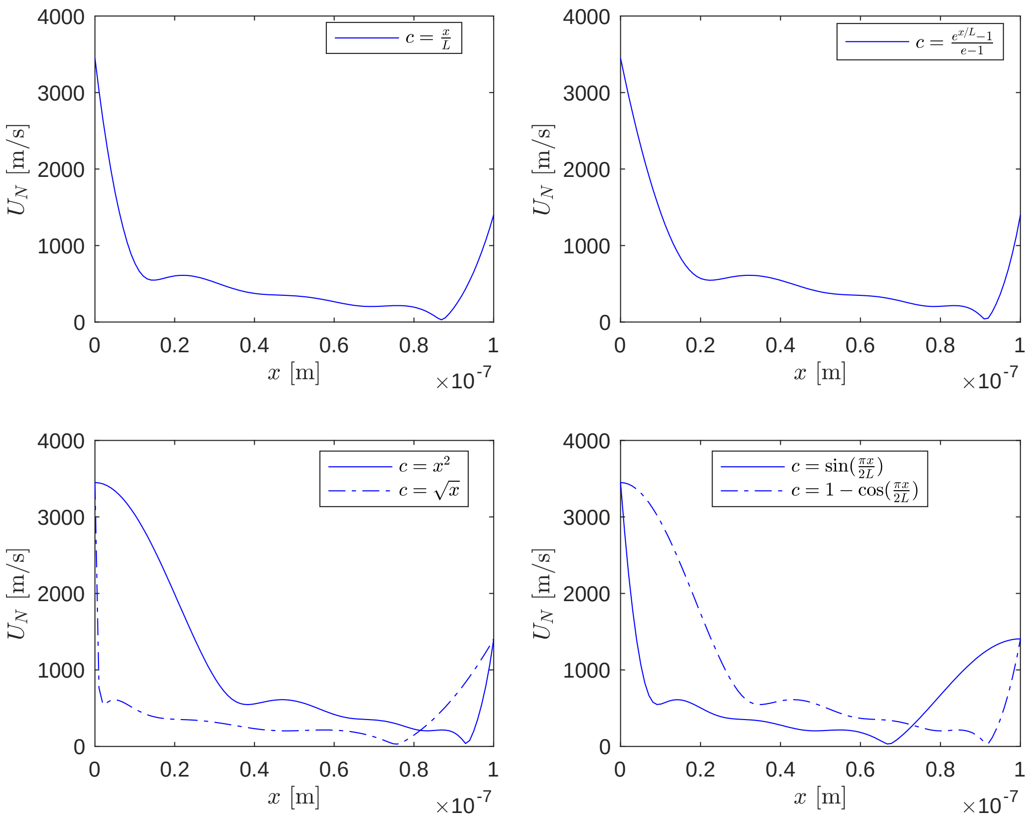



Figure 2.2: Heat-pulse speed versus the distance at 300 K: theoretical results arising from Eq. (2.10).

In the several cases above the predicted results for the pulse amplitude, instead, are plotted in Fig. 2.3 when the heat pulse travels along the $x$ direction from 0 to $L$ (i.e., when $c$ varies from 0 to 1), and in Fig. 2.4 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, $\hat{\theta}$ 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 behavior is only due to the role played by the concentration gradient, since if $c_{,r} = 0$ then from Eq. (2.17) we would have

$$\frac{\hat{\theta}\,(t)}{\hat{\theta}_0} = e^{-\frac{t}{2\tau_1}}$$

and the expected monotonically decreasing behavior of $\hat{\theta}$ is recovered.

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.

## 2.2 Theoretical thermodynamic considerations

In this section, by means of second law of thermodynamics, we point out the physical validity of a model based on the MC theory to describe the thermomechanical behavior of FGMs. To do this, at the very beginning, we have to claim the state-space variables; therefore, according with the basic basic tenets of EIT [4, 7], here we assume that the state space $Z$ is

$$Z = \{\theta, q_i, c\} \tag{2.18}$$

with each state-space variable displaying its own evolution equation. We postulate that the evolution equation of $q_i$ is given by MC equation (1.71). The evolution equation of $\theta$, instead, can be obtained by coupling the local balance of energy in a rigid body (1.73) with mass density $\rho = \rho\,(c)$ together with the constitutive relation

$$e = c_v\theta \tag{2.19}$$

with $c_v = c_v\,(c)$, in order to obtain

$$\rho c_v\dot{\theta} + \rho\theta\,\frac{\partial c_v}{\partial c}\,\dot{c} + q_{i,i} = 0 \tag{2.20}$$

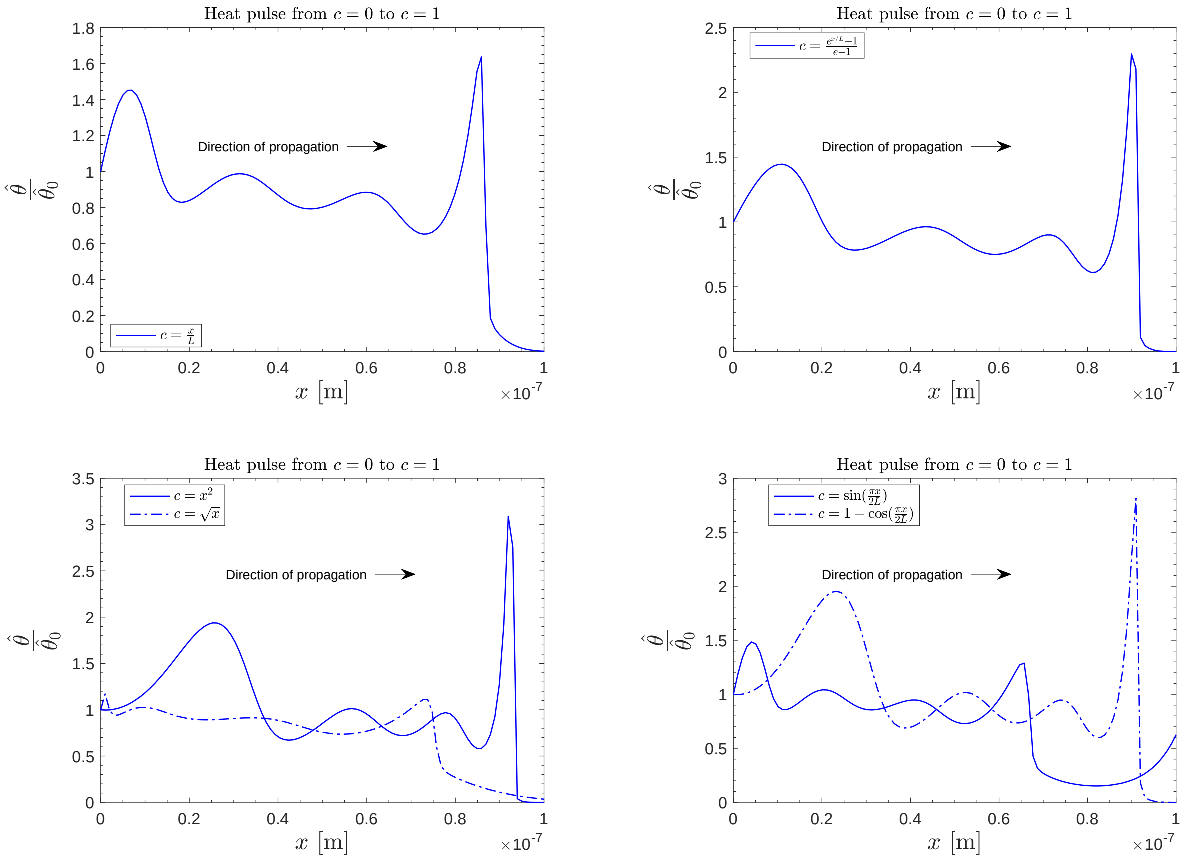



Figure 2.3: Heat-pulse amplitude versus the distance at 300 K: theoretical results arising from Eq(2.17) when the pulse is moving from $c = 0$ to $c = 1$. In the subfigures the direction of propagation of the heat pulse is also indicated.

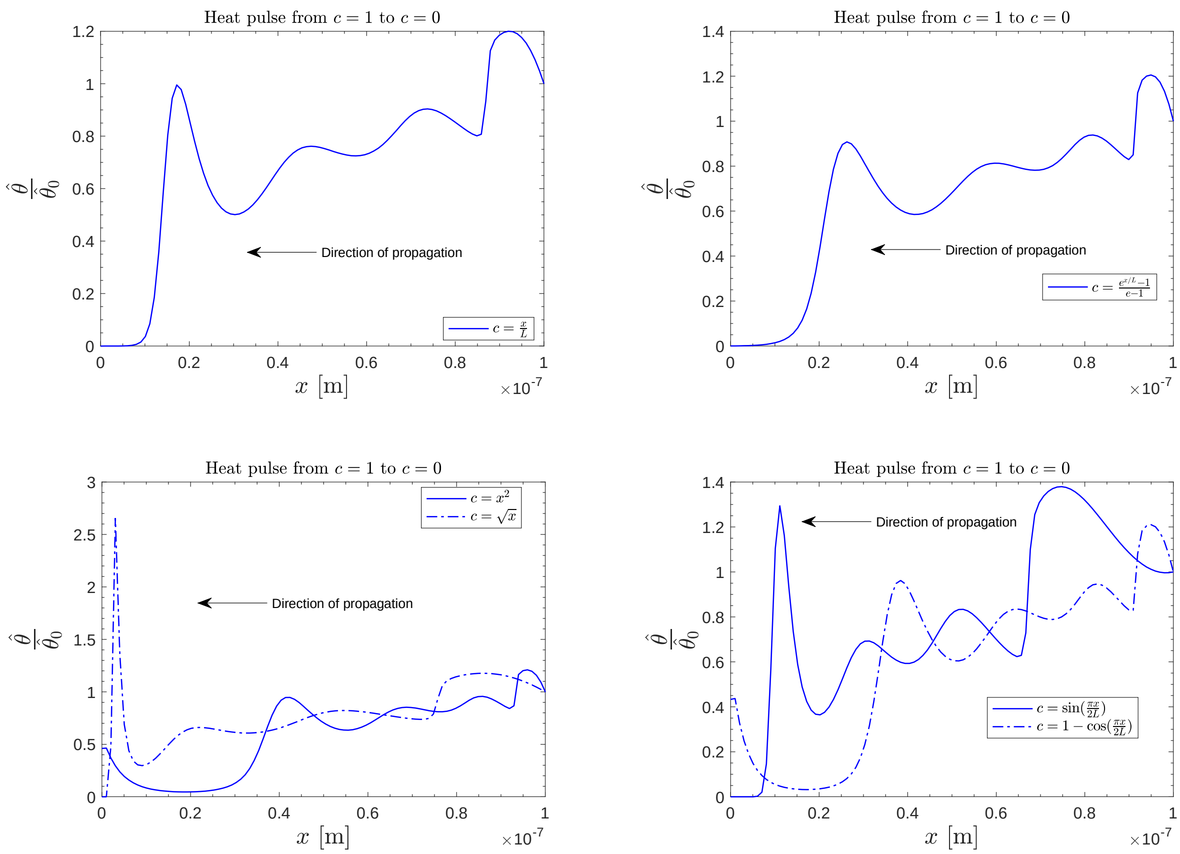



Figure 2.4: Heat-pulse amplitude versus the distance at 300 K: theoretical results arising from Eq(2.17) when the pulse is moving from $c = 1$ to $c = 0$. In the subfigures the direction of propagation of the heat pulse is also indicated.

which reduces to Eq. (1.72a) when Eq. (2.2) holds. 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., MC equation and Eq. (2.20)) 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 a FGM. In a first approximation, actually, $c$ should be viewed as an internal variables, in order to constitute an efficient tool when dealing with nonequilibrium processes involving complex thermodynamical systems [86]. In this case, the evolution equation of $c$ might be written in the following form

$$\dot{c} = F\left(\theta, q_i, c\right) \tag{2.21}$$

with $F$ being a scalar-valued function of the indicated argument. More refined considerations (or theoretical models) could be surely made; however, Eq. (2.21) 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.

## 2.2.1 Exploitation of second law

In order to exploit the second law of thermodynamics, we may assume the following very general constitutive equations for the specific entropy and for the entropy flux

$$s = s\left(\theta, q_i, c\right) \tag{2.22a}$$

$$J_i^{(s)} = J_i^{(s)}\left(\theta, q_i, c\right) \tag{2.22b}$$

and let the thermodynamic restrictions to give their explicit forms. We have to determine, in fact, a set of conditions restricting the constitutive equations which are necessary and sufficient to guarantee that thermodynamic constrain

$$\sigma^{(s)} \geq 0$$

is satisfied along any arbitrary thermodynamic process [55]. The inequality above, indeed, taking into account Eqs. (1.84) and (2.22), on the state space $Z$ can be written in the following explicit form:

$$\rho\sigma^{(s)} = \rho\left(\frac{\partial s}{\partial \theta}\dot{\theta} + \frac{\partial s}{\partial q_i}\dot{q}_i + \frac{\partial s}{\partial c}\dot{c}\right) + \frac{\partial J_i^{(s)}}{\partial \theta}\theta_{,i} + \frac{\partial J_i^{(s)}}{\partial q_j}q_{j,i} + \frac{\partial J_i^{(s)}}{\partial c}c_{,i} \geq 0 \tag{2.23}$$

To achieve our task, here we apply the classical Liu procedure [87]. According to it, the thermodynamic restrictions on the constitutive functions can be obtained by checking the positiveness of the linear combination of $\rho\sigma^{(s)}$ (expressed by the right-hand side of Eq. (2.23)) and of the evolution equations of the state variables for all thermodynamic processes [88]. This linear combination is obtained by means of Lagrange multipliers, which depend on the state variables themselves [88]. Thus, we add to $\sigma^{(s)}$ each constitutive equation multiplied by the respective Lagrange multipliers $\Lambda_i^{(q)}$, $\Lambda^{(\theta)}$ and $\Lambda^{(c)}$. That way, after rearrangement, inequality (2.23) takes the form:

$$
\begin{aligned}
&\rho\left(\frac{\partial s}{\partial \theta} - c_v\Lambda^{(\theta)}\right)\dot{\theta} + \rho\left(\frac{\partial s}{\partial c} - \Lambda^{(\theta)}\theta\frac{\partial c_v}{\partial c} - \frac{\Lambda^{(c)}}{\rho}\right)\dot{c} + \rho\left(\frac{\partial s}{\partial q_i} - \frac{\Lambda_i^{(q)}}{\rho}\right)\dot{q}_i \\
&+\left(\frac{\partial J_i^{(s)}}{\partial \theta} - \Lambda_i^{(q)}\frac{\kappa}{\tau_1}\right)\theta_{,i} + \left(\frac{\partial J_i^{(s)}}{\partial q_j} - \Lambda^{(\theta)}\delta_{ij}\right)q_{j,i} + \frac{\partial J_i^{(s)}}{\partial c}c_{,i} - \Lambda_i^{(q)}\frac{q_i}{\tau_1} + \Lambda^{(c)}F \geq 0
\end{aligned}
\tag{2.24}
$$

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 (2.24) demands that:

$$\frac{\partial s}{\partial \theta} = c_v\Lambda^{(\theta)} \tag{2.25a}$$

$$\frac{\partial s}{\partial c} = \Lambda^{(\theta)}\theta\frac{\partial c_v}{\partial c} + \frac{\Lambda^{(c)}}{\rho} \tag{2.25b}$$

$$\frac{\partial s}{\partial q_i} = \frac{\Lambda_i^{(q)}}{\rho} \tag{2.25c}$$

$$\frac{\partial J_i^{(s)}}{\partial \theta} = \Lambda_i^{(q)}\frac{\kappa}{\tau_1} \tag{2.25d}$$

$$\frac{\partial J_i^{(s)}}{\partial q_j} = \Lambda^{(\theta)}\delta_{ij} \tag{2.25e}$$

$$\frac{\partial J_i^{(s)}}{\partial c} = 0 \tag{2.25f}$$

$$-\Lambda_i^{(q)}\frac{q_i}{\tau_1} + \Lambda^{(c)}F \geq 0 \tag{2.25g}$$

Referring the readers to the Appendix to the second law of thermodynamics at the end of this subsection for deeper details, here we only observe that if we assume

$$\Lambda^{(\theta)} = \frac{1}{\theta} \tag{2.26a}$$
$$\Lambda_i^{(q)} = -\frac{\tau_1}{\kappa\theta^2} q_i \tag{2.26b}$$
$$\Lambda^{(c)} = \frac{\partial s_{\mathrm{eq}}}{\partial c} - \frac{\partial c_v}{\partial c} - \frac{q_i q_i}{2\theta^2} \frac{\partial}{\partial c} \frac{\tau_1}{\kappa\rho} \tag{2.26c}$$

straightforward calculations show that the thermodynamic restrictions (2.25a)-(2.25f) are compatible with the following forms of the specific entropy and of the specific-entropy flux, respectively:

$$s = s_{\mathrm{eq}}(\theta, c) - \frac{\tau_1}{2\rho\kappa\theta^2} q_i q_i \tag{2.27a}$$
$$J_i^{(s)} = \frac{q_i}{\theta} \tag{2.27b}$$

which are well-known in EIT [4, 7], as it is has been observed in Chap. 1 (see therein Sec. 1.2.3). From Eq. (2.25a), 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., $\frac{\tau}{\kappa} \propto \theta^2$.

We finally also observe that the coupling of the thermodynamic restriction (2.25g) (i.e., the reduced entropy inequality) and the assumption in Eq. (2.26b) suggests that $\Lambda^{(c)} F$ should be always positive.

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

## Appendix to the second-law exploitation

The Liu procedure [87] allows to obtain necessary and sufficient conditions which, restricting the constitutive relations, yield a theoretical model which is finally compatible with second law [88]. 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 Eqs. (2.25b)-(2.25f). By succeeding integrations, in fact, from those relations we have

$$\frac{\partial J_i^{(s)}}{\partial c} = 0 \Leftrightarrow J_i^{(s)} = J_i^{(s)}(\theta, q_i)$$

$$\Downarrow$$

$$\frac{\partial J_i^{(s)}}{\partial q_j} = \Lambda^{(\theta)}\delta_{ij} \Leftrightarrow J_i^{(s)} = \int \Lambda^{(\theta)} dq_i + K_i(\theta)$$

$$\Downarrow$$

$$\frac{\partial J_i^{(s)}}{\partial \theta} = \Lambda_i^{(q)} \frac{\kappa}{\tau_1} \Leftrightarrow J_i^{(s)} = \int \Lambda_i^{(q)} \frac{\kappa}{\tau_1} d\theta \qquad (2.28)$$

Equation (2.28) 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 [4, 7] is that $J_i^{(s)}$ is proportional to the heat flux, namely, Eq. (2.27b), a simple comparison between Eqs. (2.27b) and (2.28) yields Eq. (2.26b).

Then, the coupling of Eqs. (2.25e) and (2.27b) leads to Eq. (2.26a).

The form of $\Lambda^{(c)}$, instead, can be inferred if we obtain the form of $s$ in our model; it arises from Eqs. (2.25a)-(2.25c) by succeeding integrations as below:

$$\frac{\partial s}{\partial \theta} = c_v \Lambda^{(\theta)} \Leftrightarrow s = \int c_v \Lambda^{(\theta)} d\theta + H_1(q_i, c)$$

$$\Downarrow$$

$$\frac{\partial s}{\partial q_i} = \frac{\Lambda_i^{(q)}}{\rho} \Leftrightarrow s = \int \frac{\Lambda_i^{(q)}}{\rho} dq_i + H_2(c)$$

$$\Downarrow$$

$$\frac{\partial s}{\partial c} = \Lambda^{(\theta)}\theta \frac{\partial c_v}{\partial c} + \frac{\Lambda^{(c)}}{\rho} \Leftrightarrow s = \int \left( \Lambda^{(\theta)}\theta \frac{\partial c_v}{\partial c} + \frac{\Lambda^{(c)}}{\rho} \right) dc \qquad (2.29)$$

Since in EIT the form of $s$ is given by Eq. (2.27a) when $q_i$ is the only thermodynamic flux appearing in the state space [4] (refer to Eq. (1.87) in Sec. 1.2.3 to this end), a simple comparison between Eqs. (2.27a) and (2.29) yields Eq. (2.26c), once Eq. (2.26a) has been taken into account.

# Chapter 3

# Thermal and elastic nonlinear wave propagations

The analysis of heat waves is of great interest in solid-state physics, because it may provide useful and relevant information on phonon scattering process [19, 89, 90]. Indeed, a great part of the works dealing with heat-wave propagation principally focuses its own attention on the analysis of the consequences of the dynamical behavior of the particular generalized heat-transport equation which has been considered. This is a natural consequence of the very important role played by relaxational terms in high-frequencies nonequilibrium situations [19, 89, 90]. However, the same attention should be also put on nonlinear terms. As a consequence, from the theoretical point of view, in the present chapter we investigate how the joint consideration of nonlocal and nonlinear terms in the heat-transport equation can influence the speed of propagation of thermal pulses both in the case of a rigid body, and in the case of a deformable body. Since here we are particularly interested in the consequences of accounting for genuinely nonlinear terms, throughout the present chapter we assume that all material functions are constant which, from the practical point of view, means that the proposed results only hold in temperature ranges wherein those material functions display vanishingly small variations with the temperature.

In this chapter we also combine thermal effects with elastic effects. This is relevant from the practical point of view because, usually, a local change of temperature involves a dilatation or contraction of the system, and this deformation implies elastic stresses. In fact, thermal dilatation coefficient, as well as a finite value of thermal conductivity, is related to non-linear microscopic effects in the material lattice of the system. When such effects are neglected, thermal conductivity is infinite and thermal dilatation coefficient is zero. Thus, in principle, for usual systems with finite thermal conductivity, it should be expected a coupling between thermal effects and elastic effects, which is often neglected. Detailed rigorous comparison with experiments thus requires taking account of such couplings, as we theoretically do in Section 3.2. Nonlinear effects arising from the dependence of the different material functions on the state-space variables will be then analyzed in Chapter 4.

## 3.1 Heat waves in rigid nanosystems

Equation (1.93) has been obtained in Ref. [36] by introducing the concept of a dynamical nonequilibrium temperature [37, 48]. In more general terms, indeed, the compatibility of Eq. (1.93) with the basic tenets of continuum mechanics can be also proven in the framework of EIT [2, 4] wherein the diffusive thermodynamic fluxes have their own evolution equations given by

$$\dot{q}_i = -\frac{q_i}{\tau_1} - \frac{\kappa\theta_{,i}}{\tau_1} + \frac{2q_{i,j}\,q_j}{\rho c_v\theta} + \frac{Q_{ij,j}}{\tau_1} \tag{3.1a}$$

$$\dot{Q}_{ij} = -\frac{Q_{ij}}{\tau_2} + \frac{\ell^2 q_{i,j}}{\tau_2} \tag{3.1b}$$

In particular, in EIT Eq. (1.93) can be recovered whenever the time variations of $Q_{ij}$ are negligibly small with respect to other terms in Eq. (3.1a), or when the non-dimensional ratio $\frac{\tau_2}{\tau_1} \to 0$ [91].

Since in principle the speed of propagation of high-frequency thermal disturbances can be related to the clock speed of a device, it should be interesting to investigate the role of nonlinear effects in modern nanoelectronics. Observing that the specific heat at constant volume per unit mass $c_v$, given by Eq. (1.74), is always larger than zero, then it is possible to switch from the specific internal energy $e$ to the nonequilibrium temperature $\theta$ as state-space variable; therefore, assuming that the evolution equations of the state-space variables $\theta$, $q_i$ and $Q_{ij}$ are given by Eqs. (1.72a) and (3.1), in order to investigate the propagation of heat wave in rigid nanosystems, we can consider an acceleration wave $S$ across which the state-space variables $\theta(x_k; t)$, $q_i(x_k; t)$ and $Q_{ij}(x_k; t)$ are continuous, but their first- and higher-order derivatives suffer at most finite discontinuities. In practical applications, an acceleration wave $S$ can be generated by allowing the temperature in a point of the body to vary periodically in time with respect to its steady-state reference level. Moreover, for the sake of simplicity, we can suppose that the acceleration wave is moving into equilibrium, namely, the region ahead $S$ is such that

$$\theta(x_k,t)=T \qquad q_i(x_k,t)=q_i^0 \qquad Q_{ij}(x_k,t)=Q_{ij}^0 \tag{3.2}$$

$\forall t>0$, with $q_i^0$ and $Q_{ij}^0$ being stationary reference levels. As a consequence, from Eqs. (1.72a) and (3.1) we have

$$\begin{cases} \rho c_v \left[\!\left[\dot\theta\right]\!\right] + \left[\!\left[q_{i,i}\right]\!\right] = 0 \\ \tau_1 \left[\!\left[\dot q_i\right]\!\right] + \kappa \left[\!\left[\theta_{,i}\right]\!\right] - \dfrac{2\tau_1 q_j^0}{\rho c_v T} \left[\!\left[q_{i,j}\right]\!\right] - \left[\!\left[Q_{ij,j}\right]\!\right] = 0 \\ \tau_2 \left[\!\left[\dot Q_{ij}\right]\!\right] - \ell^2 \left[\!\left[q_{i,j}\right]\!\right] = 0 \end{cases} \tag{3.3}$$

once the *non-equilibrium temperature approximation* is used, namely, if Eq. (1.90) holds. Since the classical H-relations (1.52) allows us to write

$$\begin{cases} \left[\!\left[\dot\theta\right]\!\right] = -U_N \hat\theta \\ \left[\!\left[\dot q_i\right]\!\right] = -U_N \hat q_i \\ \left[\!\left[\dot Q_{ij}\right]\!\right] = -U_N \hat Q_{ij} \end{cases} \tag{3.4}$$

wherein $\hat\theta(t)=\left[\!\left[n^i\theta_{,i}\right]\!\right]$, $\hat q_i(t)=\left[\!\left[n^j q_{i,j}\right]\!\right]$ and $\hat Q_{ij}(t)=\left[\!\left[n^k Q_{ij,k}\right]\!\right]$ are the wave amplitudes, with $n_i$ being the positive unit normal to $S$, then the coupling of Eqs. (3.3) and (3.4) leads to the following system of homogenous algebraic equations

$$\begin{cases} \rho c_v U_N \hat\theta - n_i \hat q_i = 0 \\ \kappa n_i \hat\theta - \tau_1 \hat q_i \left(U_N + \dfrac{2q_j^0 n_j}{\rho c_v T}\right) - n_j \hat Q_{ij} = 0 \\ \ell^2 n_j \hat q_i + \tau_2 U_N \hat Q_{ij} = 0 \end{cases} \tag{3.5}$$

once the following relations hold

$$\left[\!\left[q_{i,i}\right]\!\right] = n_i \hat q_i, \quad \left[\!\left[\theta_{,i}\right]\!\right] = n_i\hat\theta, \quad \left[\!\left[q_{i,j}\right]\!\right] = n_j \hat q_i, \quad \left[\!\left[Q_{ij,j}\right]\!\right] = n_j \hat Q_{ij}. \tag{3.6}$$

From Eqs. (3.5), we firstly recover that only longitudinal waves can be obtained, namely $\hat q_i = \hat q n_i$, and $\hat Q_{ij} = \hat Q n_i n_j$. Then, in order to avoid that Eqs. (3.5) display the only trivial solution for the wave amplitudes, the following relation has to be fulfilled

$$U_N^2 + \left(\frac{2q_j^0 n_j}{\rho c_v T}\right) U_N - \frac{\ell^2}{\tau_1\tau_2} - U_0^2 = 0 \tag{3.7}$$

wherein $U_0$ is given by Eq. (1.83). Since $U_N$ stands for the modulus of the wave speed, the only admissible solution (i.e., the positive one) for $U_N$ arising from Eq. (3.7) is

$$U_N = U_0 \left( \sqrt{\Phi^2 + \Phi_1 + 1} - \Phi \right) \tag{3.8}$$

wherein

$$\Phi = \frac{q_j^0 n_j}{T} \sqrt{\frac{\tau_1}{\kappa \rho c_v}} \tag{3.9a}$$

$$\Phi_1 = \frac{\ell^2 \rho c_v}{\kappa \tau_2} \tag{3.9b}$$

Keeping in mind that the non-dimensional parameter $\Phi$ is only related to nonlinear terms in Eq. (3.1a), whereas the non-dimensional parameter $\Phi_1$ is related to the nonlocal ones in that equation, below we list some considerations about the above result for the speed of propagation of heat waves.

i. If both $\Phi \to 0$, and $\Phi_1 \to 0$, then Eq. (3.8) turns out the usual result of the MC theory [53], namely, Eq. (1.83).

ii. If $\Phi \neq 0$ and $\Phi_1 \to 0$, Eq. (3.8) reduces to

$$U_N = U_0 \left( \sqrt{\Phi^2 + 1} - \Phi \right) \tag{3.10}$$

and clearly points out the role played by nonlinear effects: they yields a heat-wave speed which depends on the direction of propagation. In particular, if the heat wave is moving towards the average heat flux $q_j^0$ (i.e., if $q_j^0 n_j > 0$), from Eq. (3.10) it directly follows that the propagation speed is smaller than that of a heat waves moving against $q_j^0$ (i.e., if $q_j^0 n_j < 0$). The absolute value of the difference in the wave speeds, i.e., $\Delta U_N = 2|\Phi|U_0$ represents a thermodynamic prediction of a relation between the speeds of thermal pulses in equilibrium (which give information on the relaxation time) and the speeds of thermal pulses under a heat flux.

iii. If $\Phi \to 0$ and $\Phi_1 \neq 0$, then Eq. (3.8) reduces to the high-frequency pulse speed obtained in EIT [4, 7], i.e.,

$$U_N = \sqrt{U_0^2 + U_1^2} \tag{3.11}$$

with

$$U_1 = \frac{\ell}{\sqrt{\tau_1 \tau_2}} \tag{3.12}$$

which predicts an infinite speed of propagation for heat pulses whenever $\tau_1 = 0$ and/or $\tau_2 = 0$. This means that each thermodynamic fluxes have to display its own relaxation time, in order to have a hyperbolic heat-propagation theory [4]. Nonlocal terms, therefore, have the same influence on the magnitude of the predicted speed both when the heat pulse is moving along the average heat flux, and when it is moving against it.

## 3.2 Heat waves in non-rigid nanosystems

Thermoelastic analysis at nanoscale is becoming important along with the miniaturization of the device and the wide application of ultrafast lasers, even the novel laser burst technology, where size effect on heat conduction and elastic deformation increase in such a way that the classical theory of thermoelastic coupling does not hold any more [92].

A possible way to go beyond the classical thermoelasticity is to introduce the following theoretical model:

$$E_{ij} = \frac{u_{i,j} + u_{j,i}}{2} \tag{3.13a}$$

$$\rho \ddot{u}_i = T_{ij,j} \tag{3.13b}$$

$$\rho \dot{e} = T_{ij} \dot{E}_{ij} - q_{i,i} \tag{3.13c}$$

$$\tau_1 \dot{q}_i + q = -\kappa \theta_{,i} + \frac{2\tau_1}{\rho c_v \theta} q_{i,j} q_j + Q_{ij,j} \tag{3.13d}$$

$$\tau_2 \dot{Q}_{ij} + Q_{ij} = \ell^2 q_{i,j} \tag{3.13e}$$

wherein $u_i$ is the displacement vector, $E_{ij}$ is the so-called strain tensor, and

$$T_{ij} = (\lambda E_{kk} - b\theta)\, \delta_{ij} + 2\mu E_{ij} \tag{3.14}$$

is the Cauchy stress tensor in the case of isotropic materials with elastic and thermoelastic contributions. In Eq. (3.14) $\lambda$ and $\mu$ are the isothermal Lamé constants, and

$$b = (3\lambda + 2\mu)\, \alpha \tag{3.15}$$

where $\alpha$ is the coefficient of linear thermal expansion. That theoretical model has to be meant in the framework of linear thermoelasticity, the nonlinear terms only appearing in the heat-transport equation. In fact, in the case of nanosystems (at least in a first approximation) one can assume that the deformations induced by the temperature variations are small enough and can be modelled within the frame of linear elasticity. As far as the thermal effects are concerned, instead, second-order terms in the heat flux (or in the temperature gradient) cannot be neglected, since at nanoscale even small differences of temperature, or heat flux, may give rise to high gradients. According with this observation, in Eqs. (3.13) only the evolution equation for the heat flux is nonlinear, while the basic equations of thermoelasticity are linear; as a consequence, in the following it will not be made distinction either between actual and reference configuration, or between Eulerian and Lagrangian quantities.

Equations (3.13) can be used to investigate how nonlocal and nonlinear terms in the heat-transport equations contribute to the propagation of thermoelastic pulses. In doing this, one should observe that the different material functions involved therein depend on temperature (at least), as experimental observations point out. To reduce to a simpler level that analysis, however, in the next we assume that all the material functions are constant, and put ourself in the 1-dimensional case, i.e., we assume that $x$ is the only Cartesian coordinate. In this case, when the constitutive assumption (3.14) is used in Eqs. (3.13), one has

$$\ddot{u}_x - U_e^2 u_{x,xx} + \frac{b}{\rho}\theta_{,x} = 0 \tag{3.16a}$$

$$\dot{\theta} - \left(U_e^2 \frac{u_{x,x}}{c_v} - U_2\sqrt{\frac{\theta}{c_v}}\right)\dot{u}_{x,x} + \frac{q_{x,x}}{\rho c_v} = 0 \tag{3.16b}$$

$$\dot{q}_x + \left(\frac{1}{\tau_1} - \frac{2}{\rho c_v \theta} q_{x,x}\right) q_x + U_0^2 \rho c_v \theta_{,x} - \frac{Q_{xx,x}}{\tau_1} = 0 \tag{3.16c}$$

$$\dot{Q}_{xx} + \frac{Q_{xx}}{\tau_2} - U_1^2 \tau_1 q_{x,x} = 0 \tag{3.16d}$$

wherein $U_1$ is given by Eq. (3.12), we have set

$$U_e = \sqrt{\frac{\lambda + 2\mu}{\rho}} \tag{3.17}$$

as the usual speed of propagation of elastic longitudinal waves in deformable bodies in the limit of high frequencies, and

$$U_2 = \frac{b}{\rho}\sqrt{\frac{\theta}{c_v}} \equiv \frac{(3\lambda + 2\mu)\,\alpha}{\rho}\sqrt{\frac{\theta}{c_v}} \tag{3.18}$$

as a speed arising from the coupling parameter $b$, which connects the equations of elasticity to those for heat transport in thermoelasticity, and vanishes only whenever the coefficient of linear thermal expansion $\alpha \to 0$ (i.e., when the system at hand behaves as a rigid body).

In a linearized approach around the (constant) local-equilibrium temperature $T$ (i.e., in the *non-equilibrium temperature approximation*), if we consider now an acceleration wave $S$ across which the state-space variables $\theta(x,t)$, $u_{x,x}(x,t)$, $q_x(x,t)$ and $Q_{xx}(x_k,t)$ are continuous, but their first- and higher-order derivatives suffer at most finite discontinuities, from Eqs. (3.16) we have

$$\begin{cases} \dfrac{b}{\rho}[\theta_{,x}] + \left(U_N^2 - U_e^2\right)[u_{x,xx}] = 0 \\ U_N[\theta_{,x}] - \dfrac{1}{\rho c_v}[q_{x,x}] + U_N\left(U_2\dfrac{\sqrt{\theta}}{c_v} - U_e^2\dfrac{u^0_{x,x}}{c_v}\right)[u_{x,xx}] = 0 \\ U_0^2\rho c_v[\theta_{,x}] - (U_N + U_3)[q_{x,x}] - \dfrac{1}{\tau_1}[Q_{xx,x}] = 0 \\ U_1^2\tau_1[q_{x,x}] + U_N[Q_{xx,x}] = 0 \end{cases} \tag{3.19}$$

once the classical H-relations (1.52) have been employed. In Eqs. (3.19) it has been set

$$U_3 = \frac{2q_x^0}{\rho c_v T} \tag{3.20}$$

as a speed only arising from the nonlinear term in the heat-transport equation (3.13c): since it is proportional to $q_x^0$, the sign of $U_3$ depends upon the heat pulse is propagating in the same direction as the heat flux (in this case one has $U_3 > 0$), or it is propagating in the opposite direction (in this case one has $U_3 < 0$). In deriving Eqs. (3.19) it has been assumed that the acceleration wave is moving into equilibrium, namely, the region ahead $S$ is such that

$$\theta(x,t) = T \qquad q_x(x,t) = q_x^0 \qquad Q_{xx}(x,t) = Q_{xx}^0 \qquad u_{x,x}(x,t) = u_{x,x}^0 \tag{3.21}$$

$\forall t > 0$, with $q_x^0$, $Q_{xx}^0$ and $u_{x,x}^0$ being stationary reference levels.

The homogeneous system of algebraic equations (3.19) does not admit the only trivial solution if, and only if, the following relation holds

$$\begin{aligned} &U_N^4 + U_3U_N^3 - \left(U_0^2 + U_e^2\xi + U_1^2 + U_2^2\right)U_N^2 - U_3\left(U_e^2\xi + U_2^2\right)U_N \\ &+ U_0^2U_e^2 + U_1^2\left(U_e^2\xi + U_2^2\right) = 0 \end{aligned} \tag{3.22}$$

wherein we introduced the non-dimensional parameter

$$\xi = 1 - \frac{bu_{x,x}^0}{\rho c_v} \tag{3.23}$$

for the sake of having a compact notation.

### 3.2.1 Propagation in equilibrium states

Around equilibrium states one can assume that the reference levels of the thermodynamic diffusive fluxes $q_x$ and $Q_{xx}$ are vanishingly small, and from Eq. (3.20) one has $U_3 = 0$. In these situations, indeed, one may distinguish between two different cases:

1. $\alpha = 0$

2. $\alpha \neq 0$

In the first case (i.e., if the linear thermal-expansion coefficient is vanishingly small), since $b \to 0$ then $U_2 \to 0$ and $\xi \to 1$ as a consequence Eq. (3.22) reduces to

$$\left(U_N^2 - U_0^2 - U_1^2\right)\left(U_N^2 - U_e^2\right) = 0 \tag{3.24}$$

which leads to the following speeds of propagation of thermoelastic pulses:

$$U_{NT,\mathrm{eq}} = \sqrt{U_0 + U_1} \tag{3.25a}$$

$$U_{NE,\mathrm{eq}} = U_e \tag{3.25b}$$

with $U_{NT,\mathrm{eq}}$ and $U_{NE,\mathrm{eq}}$ being the speed of the thermal pulse and of the elastic pulse respectively. Around equilibrium, and when the linear thermal-expansion coefficient is vanishingly small, therefore one can only have a pure thermal pulse propagating with a speed given by Eq. (3.25a), and a pure elastic pulse propagating with a speed given by Eq. (3.25b). In other words, in this case a local thermal gradient can not influence the local elastic stresses, and vice-versa.

In the second case (i.e., if the thermoelastic coupling can not be neglected), instead, Eq. (3.22) becomes a bi-quadratic algebraic equation, the solutions of which are:

$$U_{NTE,\mathrm{eq}}^2 = \frac{U_0^2 + U_1^2}{2}\left(1 + \sqrt{1 + m}\right) + \frac{\xi U_e^2 + U_2^2}{2}\left(1 - \sqrt{1 + m}\right) \tag{3.26a}$$

$$U_{NET,\mathrm{eq}}^2 = \frac{U_0^2 + U_1^2}{2}\left(1 - \sqrt{1 + m}\right) + \frac{\xi U_e^2 + U_2^2}{2}\left(1 + \sqrt{1 + m}\right) \tag{3.26b}$$

wherein

$$m = \frac{4\,(1-\xi)\,(\Phi_1\Phi_{2e} - \Phi_1 - 1)}{(1 + \Phi_1 - \xi\Phi_{e0} - \Phi_{20})\,(\Phi_{0e} + \Phi_{1e} - \xi - \Phi_{2e})} \tag{3.27a}$$

$$\Phi_{e0} = \frac{1}{\Phi_{0e}} = \frac{U_e^2}{U_0^2} \tag{3.27b}$$

$$\Phi_{1e} = \frac{U_1^2}{U_e^2} \tag{3.27c}$$

$$\Phi_{20} = \frac{U_2^2}{U_0^2} \tag{3.27d}$$

$$\Phi_{2e} = \frac{U_2^2}{U_e^2} \tag{3.27e}$$

and $\Phi_1$ is given by Eq. (3.9b). Around equilibrium, when the thermoelastic coupling can not be neglected, one has two thermoelastic pulses travelling with two different speeds. Although in this case there is no a net difference between thermal and elastic pulses, we may see that the speed $U_{NTE,\text{eq}}$, given by Eq. (3.26a), takes its origin by a thermal pulse, whereas the speed $U_{NET,\text{eq}}$, given by Eq. (3.26b), takes its origin by an elastic pulse. Therefore we may call the former *predominantly thermal* (it reduces to Eq. (3.25a) if $\alpha \to 0$), and the latter *predominantly elastic* (it reduces to Eq. (3.25b) if $\alpha \to 0$).

### 3.2.2 Propagation in nonequilibrium states

In nonequilibrium states, the reference levels $q_x^0$ and $Q_{xx}^0$ are no longer vanishing, and in Eq. (3.22) no terms can be neglected in principle. The exact solution of that algebraic equation is rather cumbersome, although easy to be calculated. However, interesting information can be pointed out when the value of $q_x^0$ is small enough in such a way that from Eq. (3.20) one has $U_3 \ll 1$. In this case, up to the first-order approximation in $U_3$, the solution of Eq. (3.22) can be put in the form

$$U_{NTE,\text{neq}} = U_{NTE,\text{eq}} + dU_{NTE} \tag{3.28a}$$

$$U_{NET,\text{neq}} = U_{NET,\text{eq}} + dU_{NET} \tag{3.28b}$$

wherein $U_{NTE,\text{eq}}$ and $U_{NET,\text{eq}}$ are given by Eqs. (3.26), and $dU_{NTE}$ and $dU_{NET}$ mean the perturbations to the speeds $U_{NTE,\text{eq}}$ and $U_{NET,\text{eq}}$, respectively, only due to $U_3$.

When Eqs. (3.28) are inserted into Eq. (3.22), one has

$$
\begin{aligned}
&U^4_{NTE,\mathrm{eq}} + 4U^3_{NTE,\mathrm{eq}}\, dU_{NTE} + U_3\left(U^3_{NTE,\mathrm{eq}} + 3U^2_{NTE,\mathrm{eq}}\, dU_{NTE}\right)\\
&\quad - \left(U_0^2 + U_e^2\xi + U_1^2 + U_2^2\right)\left(U^2_{NTE,\mathrm{eq}} + 2U_{NTE,\mathrm{eq}}\, dU_{NTE}\right)\\
&\quad - U_3\left(U_e^2\xi + U_2^2\right)\left(U_{NTE,\mathrm{eq}} + U_{NTE,\mathrm{eq}}\, dU_{NTE}\right) + U_0^2\left(U_e^2 + U_1^2\right)\left(U_e^2\xi + U_2^2\right) = 0
\end{aligned}
\tag{3.29a}
$$

$$
\begin{aligned}
&U^4_{NET,\mathrm{eq}} + 4U^3_{NET,\mathrm{eq}}\, dU_{NET} + U_3\left(U^3_{NET,\mathrm{eq}} + 3U^2_{NET,\mathrm{eq}}\, dU_{NET}\right)\\
&\quad - \left(U_0^2 + U_e^2\xi + U_1^2 + U_2^2\right)\left(U^2_{NET,\mathrm{eq}} + 2U_{NET,\mathrm{eq}}\, dU_{NET}\right)\\
&\quad - U_3\left(U_e^2\xi + U_2^2\right)\left(U_{NET,\mathrm{eq}} + U_{NET,\mathrm{eq}}\, dU_{NET}\right) + U_0^2\left(U_e^2 + U_1^2\right)\left(U_e^2\xi + U_2^2\right) = 0
\end{aligned}
\tag{3.29b}
$$

By straightforward calculations, the coupling of the results of Eqs. (3.26) with the equations above allows to obtain the following expressions for the perturbations $dU_{NET}$ and $dU_{NTE}$.

$$dU_{NTE} = -\frac{U_3}{4}\left(1 + \frac{\sqrt{1+m}}{1+m}\right) \tag{3.30a}$$

$$dU_{NET} = -\frac{U_3}{4}\left(1 - \frac{\sqrt{1+m}}{1+m}\right) \tag{3.30b}$$

with $m$ being given by Eq. (3.27a). From the physical point of view, below we list some comments about the results above.

i. When the thermoelastic coupling can not be neglected, one still has two thermoelastic pulses travelling with two different speeds. Although in this case there is still no difference between thermal and elastic pulses, we call the speed $U_{NTE,\mathrm{neq}}$, which takes its origin by a thermal pulse, as *predominantly thermal*, whereas we call the speed $U_{NET,\mathrm{neq}}$, which takes its origin by an elastic pulse, *predominantly elastic*.

ii. From Eqs. (3.30) we have that the signs of the perturbations $dU_{NET}$ and $dU_{NTE}$ depend on whether the heat pulse is propagating in the same direction of the average value of the local heat flux (in this case $dU_{NET} < 0$ and $dU_{NTE} < 0$), or the heat pulse is propagating in the opposite direction (in this case $dU_{NET} > 0$ and $dU_{NTE} > 0$). In particular, from Eqs. (3.28) it follows that $U_{NTE,\mathrm{neq}} < U_{NET,\mathrm{neq}}$ when the heat pulse is travelling in the same direction of the local heat flux, and $U_{NTE,\mathrm{neq}} > U_{NET,\mathrm{neq}}$ when the heat pulse is travelling in the opposite direction of the local heat flux.

iii. When the thermoelastic coefficient $\alpha$ is vanishing, from Eqs. (3.27) and (3.30) one has $dU_{NE} = -U_3/2$ (i.e., the speed of propagation of the predominantly thermal pulse still depends on the direction of propagation) and $dU_{NET} = 0$ (i.e., the speed of propagation of the predominantly elastic pulse does not depend on the direction of propagation).

## 3.3 The compatibility with second law

In order to be sure that the results obtained above are physically consistent, one may prove that the theoretical model in Eqs. (3.13) agrees with the second law of thermodynamics. To do this, let the state space $Z$ be given by

$$Z \equiv \{\theta, q_i, Q_{ij}, E_{ij}\} \tag{3.31}$$

By inserting the expression of the specific-entropy flux (1.91) into the local balance of the entropy (1.84), in terms of the Helmholtz free energy $\psi = e - \theta s$, we have the following Clausius-Duhem type inequality

$$\rho\left(\dot{\psi} + \dot{\theta} s\right) - T_{ij}\dot{E}_{ij} + \frac{q_i}{\theta}\left(\theta_{,i} - \theta K_{i,i}\right) \leq 0 \tag{3.32}$$

once the energy balance (3.13c) has been also taken into account. By the chain rule, merging inequality (3.32) with Eqs. (3.13d) and (3.13e) we are led to

$$\begin{aligned}
&\rho\left(\frac{\partial\psi}{\partial\theta} + s\right)\dot{\theta} + \left(\rho\frac{\partial\psi}{\partial E_{ij}} - T_{ij}\right)\dot{E}_{ij} + \left[\frac{q_i}{\theta} - \frac{\rho\kappa}{\tau_1}\left(\frac{\partial\psi}{\partial q_i} - \theta\frac{\partial K_i}{\partial\theta}\right)\right]\theta_{,i} \\
&+ \left[\frac{2q_j}{c_v\theta}\frac{\partial\psi}{\partial q_i} + \frac{\rho\ell^2}{\tau_2}\left(\frac{\partial\psi}{\partial Q_{ij}} - \theta\frac{\partial K_j}{\partial q_i}\right)\right]q_{i,j} + \left[\frac{\rho\delta_k}{\tau_1}\left(\frac{\partial\psi}{\partial q_i} - \theta\frac{\partial K_k}{\partial Q_{ij}}\right)\right]Q_{ij,k} \\
&- \left[\frac{\rho q}{\tau_1}\frac{\partial\psi}{\partial q_i} - \frac{\rho Q_{ij}}{\tau_2}\left(\frac{\partial\psi}{\partial Q_{ij}} - \theta\frac{\partial K_i}{\partial E_{hk}}\right)\right]E_{hk,i} \leq 0
\end{aligned} \tag{3.33}$$

which is never violated if, and only if, the following thermodynamic restrictions hold:

$$\rho\left(\frac{\partial\psi}{\partial\theta}+s\right)\dot{\theta}=0\Rightarrow s=-\frac{\partial\psi}{\partial\theta} \tag{3.34a}$$

$$\left(\rho\frac{\partial\psi}{\partial E_{ij}}-T_{ij}\right)\dot{E}_{ij}=0\Rightarrow T_{ij}=\rho\frac{\partial\psi}{\partial E_{ij}} \tag{3.34b}$$

$$\left(\frac{q_i}{\theta}-\frac{\rho\kappa}{\tau_1}\frac{\partial\psi}{\partial q_i}-\theta\frac{\partial K_i}{\partial\theta}\right)\theta_{,i}=0\Rightarrow\frac{\partial K_i}{\partial\theta}=\frac{q_i}{\theta^2}-\frac{\rho\kappa}{\theta\tau_1}\frac{\partial\psi}{\partial q_i} \tag{3.34c}$$

$$\left(\frac{2q_j}{c_v\theta}\frac{\partial\psi}{\partial q_i}+\frac{\rho\grave{}^2}{\tau_2}\frac{\partial\psi}{\partial Q_{ij}}-\theta\frac{\partial K_j}{\partial q_i}\right)q_{i,j}=0\Rightarrow$$

$$\frac{\partial K_j}{\partial q_i}=\frac{2q_j}{c_v\theta^2}\frac{\partial\psi}{\partial q_i}+\frac{\rho\grave{}^2}{\theta\tau_2}\frac{\partial\psi}{\partial Q_{ij}} \tag{3.34d}$$

$$\left(\frac{\rho\delta_{jk}}{\tau_1}\frac{\partial\psi}{\partial q_i}-\theta\frac{\partial K_k}{\partial Q_{ij}}\right)Q_{ij,k}=0\Rightarrow\frac{\partial K_k}{\partial Q_{ij}}=\frac{\rho\delta_{jk}}{\theta\tau_1}\frac{\partial\psi}{\partial q_i} \tag{3.34e}$$

$$\theta\frac{\partial K_i}{\partial E_{hk}}E_{hk,i}=0\Rightarrow\frac{\partial K_i}{\partial E_{hk}}=0 \tag{3.34f}$$

$$\frac{\rho q_i}{\tau_1}\frac{\partial\psi}{\partial q_i}+\frac{\rho Q_{ij}}{\tau_2}\frac{\partial\psi}{\partial Q_{ij}}\geq 0 \tag{3.34g}$$

The relations above do not prevent $\psi$ depending on the whole set of state space variables. As a consequence, a possible form of the Helmholtz free energy is

$$\psi=\psi_0(\theta)+\frac{\psi_q(\theta)}{2}q_iq_i+\frac{\psi_Q(\theta)}{2}Q_{ij}Q_{ij}+\left(\frac{\lambda E_{kk}}{2}-b\theta\right)\frac{E_{kk}}{\rho}+\frac{\mu}{\rho}E_{ij}E_{ij} \tag{3.35}$$

wherein $\psi_0$, $\psi_q$ and $\psi_Q$ are regular scalar-valued functions of the indicated argument. Then, the coupling of Eqs. (3.34a) and (3.35) allows to obtain the following form of the specific entropy $s$:

$$s=s_0-\frac{s_q}{2}q_iq_i-\frac{s_Q}{2}Q_{ij}Q_{ij}+\frac{b}{\%}E_{kk} \tag{3.36}$$

wherein we set

$$s_0=-\frac{\partial\psi_0}{\partial\theta} \tag{3.37a}$$

$$s_q=\frac{\partial\psi_q}{\partial\theta} \tag{3.37b}$$

$$s_Q=\frac{\partial\psi_Q}{\partial\theta} \tag{3.37c}$$

From Eq. (3.34f) one can also have

$$K_i=K_i(\theta;q_j;Q_{jk}) \tag{3.38}$$

Along with this result, by a simple integration merging Eqs. (3.34c) and (3.35), for the specific-entropy extra flux one firstly has

$$K_i=-\frac{q_i}{\theta}-\frac{\rho\kappa q_i}{\tau_1}\int\frac{\psi_q}{\theta}d\theta+C_i(q_j;Q_{jk}) \tag{3.39}$$

When Eq. (3.39) is inserted in Eq. (3.34d) one then has

$$C_i = \frac{q_i}{\theta} + \frac{\rho\kappa q_i}{\tau_1}\int \frac{\psi_q}{\theta} d\theta + \frac{\psi_q q^2}{c_v \theta^2} q_i + \frac{\rho \ell^2 \psi_Q}{\theta \tau_2} Q_{ij} q_j + \tilde{C}_i (Q_{jk}) \tag{3.40}$$

To reduce to a simpler level the calculations, one can indeed assume $\tilde{C}_i (Q_{jk}) = 0$. In this way, the combination of Eqs. (1.91), (3.39) and (3.40) yields

$$J_i^{(s)} = \frac{q_i}{\theta} + A(\theta; q^2) q_i + B(\theta) Q_{ij} q_j \tag{3.41}$$

with $A$ and $B$ regular scalar-valued functions of the indicated arguments, defined as

$$A = \frac{\psi_q q^2}{c_v \theta^2} \tag{3.42a}$$

$$B = \frac{\rho \ell^2 \psi_Q}{\theta \tau_2} \tag{3.42b}$$

It is also possible to observe that the combination of Eq. (3.34e) with Eqs. (3.39)-(3.42) leads to

$$\psi_Q = \frac{\tau_2}{\tau_1} \frac{\psi_q}{\ell^2} \tag{3.43}$$

which states a strict relation between $\psi_q$ and $\psi_Q$.

At the very end, let us observe that if we put ourself in the framework of EIT [2, 4], the constitutive equations (3.36) and (3.41), respectively, can be specialized in

$$s = s_0 - \frac{\tau_1}{2\rho\kappa\theta^2} q_i q_i - \frac{\tau_2}{2\rho\kappa\theta^2 \ell^2} Q_{ij} Q_{ij} + \frac{b}{\rho} E_{kk} \tag{3.44a}$$

$$J_i^{(s)} = \frac{q_i}{\theta}\left(1 - \frac{\tau_1 q^2}{\rho\kappa c_v \theta^2}\right) - \frac{1}{\kappa\theta^2} Q_{ij} q_j \tag{3.44b}$$

We also observe that if we set

$$s_0 = \frac{c_v \theta}{T} \tag{3.45}$$

then Eq. (3.44a) generalizes the result obtained in Ref. [93] to the situation in which the state space is given by Eq. (3.31). Furthermore, in this case, the Helmholtz free energy (3.35) becomes

$$\psi = -\frac{c_v \theta^2}{2T} - \frac{\tau_1}{2\rho\kappa\theta} q_i q_i - \frac{\tau_2}{2\rho\kappa\theta \ell^2} Q_{ij} Q_{ij} + \left(\frac{\lambda E_{kk}}{2} - b\theta\right) \frac{E_{kk}}{\rho} + \frac{\mu}{\rho} E_{ij} E_{ij} \tag{3.46}$$

# Chapter 4

# Nonlinear heat transfer and some analogies with nonlinear optics

In nanosystems, indeed, nonlinear effects may strongly influence the electronic and optical properties: it could be, therefore, important to examine more deeply those effects by introducing generalized nonlinear heat-transport equations. Nonlinear effects may be understood in two different ways:

*a*. as the presence of nonlinear products of the temperature gradient (or the heat flux) in the transport equation [36, 94–100];

*b*. as a state-space variables' dependence in the material functions [101].

Whereas in Chapter 3 the consequences of accounting for the *a*.-type of nonlinear effects have been investigated, in this chapter the attention especially on the *b*.-type of nonlinear effects. To this end we observe that in principle the relaxation time of the heat carriers $\tau_1$ and the thermal conductivity $\kappa$ may depend both on the internal energy density per unit volume $u$, and on the local heat flux. Generic nonlinear expressions for $\tau_1$ and $\kappa$ as functions of $u$ and $q$, for example, have been derived from maximum-entropy formalism for harmonic chains, electromagnetic radiation, and classical and relativistic ideal gases (see, for example, Chap. 6 in Ref. [4], or see Ref. [102]).

Although in systems wherein the phonons are the main heat carriers the two material functions $\tau_1$ and $\kappa$ are more temperature dependent, rather than heat-flux dependent, here we consider the particular (but conceptually relevant) situation in which

$$\tau_1 = \tau_0 \left(1 + a_{1i} q_i + a_2 q^2\right) \tag{4.1a}$$

$$\kappa = \kappa_0 \left(1 + b_{1i} q_i + b_2 q^2\right) \tag{4.1b}$$

with $\tau_0$ and $\kappa_0$ being the values of the relaxation time and of the thermal conductivity at the local-equilibrium temperature $T$, respectively. $a_{1i}$ and $b_{1i}$ are two vectorial quantities, $a_2$ and $b_2$ are two scalar coefficients, and $q^2$ is the square of the modulus $\|q_i\|$ of the heat-flux vector. Those equations will be coupled with the following nonlinear heat-transport equation

$$\partial_t \left(\frac{\tau_1}{\Lambda} q_i\right) + \frac{q_i}{\Lambda} - \left(\frac{1}{\theta}\right)_{,i} = 0 \tag{4.2}$$

wherein

$$\Lambda = \kappa\theta^2 \tag{4.3}$$

in such a way that MC equation (1.71) and Eq. (4.2) coincide whenever the ratio $\frac{\tau_1}{\Lambda}$ is constant (i.e., when it displays only vanishingly small variations with respect to time).

## 4.1 The theoretical motivation

Before to analyze the consequences of accounting for Eqs. (4.1), some comments about the nonlinear heat-transport equation (4.2) are needed. Indeed, in the framework of EIT if one replaces the heat flux $q_i$ with the following renormalized flux variable

$$w_i = -\frac{\tau_1}{\Lambda} q_i \tag{4.4}$$

then for a rigid body the differential of the generalized-entropy $s$ reads

$$ds\,(e; w_i) = \left(\frac{\partial s}{\partial e}\right)_{w_i = \mathrm{const}} de + \left(\frac{\partial s}{\partial w_i}\right)_{e = \mathrm{const}} dw_i \tag{4.5}$$

wherein

$$\left(\frac{\partial s}{\partial e}\right)_{w_i = \mathrm{const}} = \frac{1}{\theta} \tag{4.6a}$$

$$\left(\frac{\partial s}{\partial w_i}\right)_{e = \mathrm{const}} = q \tag{4.6b}$$

are the thermodynamic conjugates of the state-space variables $e$ and $w_i$, respectively. The combination of Eqs. (4.5) and (4.6) with the local balance of energy per unit volume (in the absence of heat source, for the sake of a formal simplicity), namely, with Eq. (1.72a), furnishes

$$q_i \left[ \left( \frac{1}{\theta} \right)_{,i} + \partial_t w_i \right] = \partial_t s + \left( \frac{q_i}{\theta} \right)_{,i} \tag{4.7}$$

which is just the local balance equation of the generalized entropy per unit volume, namely Eq. (1.84). Therefore, in Eq. (4.7) the following quantities

$$\sigma^{(s)} = q \left[ \left( \frac{1}{\theta} \right)_{,i} + \partial_t w_i \right] \equiv -\frac{\Lambda}{\tau_1} \left[ \left( \frac{1}{\theta} \right)_{,i} + \partial_t w_i \right] w_i \tag{4.8a}$$

$$J_i^{(s)} = \frac{q_i}{\theta} \tag{4.8b}$$

stand for the generalized-entropy production and the generalized-entropy flux, respectively. In particular, if in Eq. (4.8a) we regard the quantity

$$X_i = -\frac{\Lambda}{\tau_1} \left[ \left( \frac{1}{\theta} \right)_{,i} + \partial_t w_i \right] \tag{4.9}$$

as the conjugated thermodynamic force of the thermodynamic flux $w_i$, then it is easy matter to recognize that the second law (i.e., the thermodynamic constraint $\sigma^{(s)} \geq 0$) is always fulfilled if the following condition

$$w_i = \frac{\tau_1^2}{\Lambda} X_i \tag{4.10}$$

which agrees with the classical transport theory stating that the thermodynamic fluxes and their conjugated thermodynamic forces have to be related by linear transport laws (see Ref. [7] – Chap. 1.1, Eq. (1.1), for example), holds.

By straightforward calculations it is possible to derive Eq. (4.2) from Eqs. (4.9) and (4.10) once Eq. (4.4) is taken into account.

### 4.1.1 The renormalized heat flux $w_i$

The quantity $w_i$ above represents a renormalized flux variable [4, 103]. As a consequence, Eq. (4.2) can be also viewed as the evolution equation of the renormalized flux variable $w_i$, which is indeed related to $q_i$ as stated by Eq. (4.4).

On pure thermodynamic grounds, the replacement of $q_i$ with $w_i$ in the state space may have interest, because the former is the thermodynamic conjugate of the latter and therefore it could provide a natural basis for a Legendre transform between a formalism based on $q_i$ and another based on $w_i$.

Though being very similar to $q_i$, the new state-space variable $w_i$ displays qualitative differences with respect to the local heat flux and, therefore, it should deserve a comparative analysis with the formalism based on $q_i$, in an analogous way as Legendre transforms are studied in classical thermodynamics [103, 104]. From the physical point of view, $w_i$ is related to 14-moments theory of Grad [60, 105], wherein the heat flux $q_i$ is related in turn to the first moment $p_i$ by the constitutive equation $q_i = \bar{v}^2 p_i$, with $\bar{v}$ being the mean speed of the phonons [60]. In fact, from the relation $\bar{v} = \sqrt{\frac{3\kappa}{c_v\tau}}$, the identification $w_i = -\frac{3p_i}{c_v\theta^2}$ directly follows [60].

## 4.2 Second-order nonlinear effects

Although the importance of accounting for nonlinear effects in the heat-transport equation at nanoscale is well-known [36, 94], dealing with them in studying heat-wave propagation may not be a simple task; therefore some simplifying assumptions are needed, at least in a first rough approach. For this reason, in order to study high-frequency heat waves, we will consider the situation in which both $\tau_1 \to \infty$ and $\kappa \to \infty$, but the ratio $\frac{\tau_1}{\Lambda}$ remains finite; in this particular case, in the left-hand side of Eq. (4.2) the second term can be neglected with respect to the other two terms, and the combination of the balance equation of energy (1.73) and[1] (4.2) yields

$$\partial_t^2\left(\frac{\tau_1}{\Lambda} q_i\right) - \frac{q_{j,ji}}{c_v T^2} = 0 \qquad (4.11)$$

if the *non-equilibrium temperature approximation* is used, namely, if Eq. (1.90) hods [4]. From the physical point of view, the simplifying hypothesis above means that we are neglecting the dissipation effects since the attenuation distance of heat waves becomes infinite when the linear term in Eq. (4.2) is not taken into account. Without loss of physical consistency, one may indeed neglect the dissipation effects at the very initial times of the heat-wave propagation. According with this observation, all the results that will be obtained in this chapter has to be meant holding only when dissipation effects can be neglected.

On the other hand, according with the constitutive assumptions in Eqs. (4.1), up to the second order in the heat flux, one has

$$\frac{\tau_1}{\Lambda} = \frac{\tau_0}{\Lambda_0}\left[1 + (a_{1j} - b_{1j})\, q + (a_2 - b_2 - a_{1j}b_{1j})\, q^2\right] \qquad (4.12)$$

[1] In this chapter we set $\rho = 1$ only for the sake of simplicity.

wherein $\Lambda_0 = \kappa_0 T^2$. When Eq. (4.12) is inserted into Eq. (4.11) one is finally led to

$$-\partial_t^2 q_i + U_0^2 q_{j,ji} = \frac{\Lambda_0}{\tau_0}\partial_t^2 (f\, q_i) \tag{4.13}$$

wherein $U_0$ still means the speed of heat pulses at the equilibrium (namely, it is given by Eq. (1.83) obtained in Sec. 1.2.1), and the scalar-valued function $f$ is defined as

$$f = \frac{\tau_0}{\Lambda_0}\left[(a_{1i} - b_{1i})\, q + (a_2 - b_2 - a_{1i} b_{1i})\, q^2\right] \tag{4.14}$$

## 4.2.1 Analogy with nonlinear optics

It is possible to point out some formal mathematical analogies between Eq. (4.13) and the nonlinear electric-field equation of nonlinear optics. Such formal analogy will suggest new situations to be considered, and it will allow us to apply mathematical results and experiments on nonlinear electromagnetic waves to nonlinear heat waves. Of course, in general this will be neither automatic nor immediate, because of some significative differences between those kinds of waves; however, it will be a useful guide for exploration. For instance, when heating materials with strong heat pulses, both nonlinear electromagnetic waves and nonlinear heat waves have to be considered, in principle.

The Maxwell equations for electromagnetic fields, in the absence of electric-charge sources, are [106]

$$D_{i,i} = 0 \tag{4.15a}$$

$$B_{i,i} = 0 \tag{4.15b}$$

$$\varepsilon_{ijk} E_{k,j} = -\partial_t B_i \tag{4.15c}$$

$$\varepsilon_{ijk} H_{k,j} = \partial_t D_i \tag{4.15d}$$

where $D_i$ is the displacement vector, $B_i$ the magnetic induction, $E_i$ the electric field and $H_i$ the magnetic field, and $\varepsilon_{ijk}$ is the completely antisymmetric tensor with unitary non-zero components. In the linear approximation and in the vacuum, $D_i$ and $B_i$ are related to $E_i$ and $H_i$, respectively, as $D_i = \epsilon_0 E_i$ and $B_i = \mu_0 H_i$, with $\epsilon_0$ and $\mu_0$ being, respectively, the electrical permittivity and the magnetic permeability of free space [106]. Moreover, in a material medium, the displacement vector $D_i$ is given by

$$D_i = \epsilon_0 E_i + P_i \tag{4.16}$$

with $P_i$ being the electrical polarization of the material.

Applying the curl operation to both sides of Eq. (4.15c), differentiating Eq. (4.15d) and then combining the equations so obtained, one has

$$\frac{\partial_t^2 E_i}{v_l^2} + \varepsilon_{ijk}\,\varepsilon_{klm}\,E_{m,lj} = -\frac{\partial_t^2 P_i}{\epsilon_0 v_l^2} \tag{4.17}$$

with $v_l = \sqrt{\frac{1}{\epsilon_0 \mu_0}}$ being the speed of light in vacuum. Since

$$\varepsilon_{ijk}\,\varepsilon_{klm}\,E_{m,lj} = E_{j,ji} - E_{i,jj}$$

then Eq. (4.17) becomes

$$-\partial_t^2 E_i + v_l^2 E_{i,jj} = \frac{\partial_t^2 P_i}{\epsilon_0} \tag{4.18}$$

In nonlinear optics one takes for the electrical-polarization vector $P_i$ [107, 108]

$$P_i = \epsilon_0 \chi^{(1)} E_i + \epsilon_0 \chi_i^{(2)} E^2 + \epsilon_0 \chi^{(3)} E^2 E_i + \ldots \tag{4.19}$$

wherein $E^2$ means the square of modulus of $E_k$, and $\chi^{(1)}$, $\chi_i^{(2)}$ and $\chi^{(3)}$ are suitable coefficients. In the constitutive equation (4.19) the first term is linear and may be added to the linear free-space contribution in such a way that the following expression for the displacement vector may be used

$$D_i = \epsilon_0 \left(1 + \chi^{(1)}\right) E_i \tag{4.20}$$

instead of Eq. (4.16). Equation (4.20) implies a change in the speed of light in the medium with respect to the speed of light in vacuum, namely,

$$\tilde{v}_l = \sqrt{\frac{1}{\epsilon_0 \mu_0 \left(1 + \chi^{(1)}\right)}} \tag{4.21}$$

which points out that the coefficient $\chi^{(1)}$ (i.e., the linear contribution) is related to the refraction index of the material. The terms in $\chi^{(2)}$ and $\chi^{(3)}$ are non linear contributions, instead. The vector $\chi^{(2)}$, which depends on the material properties, is related to second-harmonic generation. For purely isotropic materials one has $\chi_i^{(2)} = 0$. The scalar coefficient $\chi^{(3)}$ instead, leads to an intensity dependence of the refraction index, with consequences in self-focusing of optical pulses, and many other interesting phenomena [107, 108].

In the 1-dimensional case, Eq. (4.13) for the heat flux is analogous to Eq. (4.18), with $q_i$ instead of $E_i$, $U_0$ instead of $v_l$ (or $\tilde{v}_l$), $\frac{\Lambda_0}{\tau_0}$ instead of $\frac{1}{\epsilon_0}$ and $f\,q$ instead of $P_i$. From a physical point of view, the parallelism between $q_i$ and the electric polarization vector $P_i$ means that the presence of a relevant value of $q_i$ partially organizes the internal motion of the particles of the system along the direction of the heat flux as, in analogy, an electric field $E_i$ organizes the molecular orientation of the material. In such a way, the increasing orientation of the particle motion may influence the collision time $\tau_1$ and the thermal conductivity $\kappa$. Thus, in contrast to the structural polarization in electric system, here the polarization is a dynamical one, namely, the organization of the motion takes the role of the orientation of electric dipoles in polarized systems.

The analogy between Eqs. (4.13) and (4.18) suggests considering for nonlinear heat waves the possibility of the rich variety of phenomena considered in nonlinear optics, though with some relevant differences due to attenuation of thermal waves.

### 4.2.2 Second-harmonic generation of thermal waves in a graded material

As an interesting illustration of the possible applications of the analogy between the nonlinear generalization of the MC equation (4.2) with the nonlinear optics equation (4.18), in this section we deal with second-harmonic generation of thermal waves. To do this, here our attention will be restricted to first-order approximation of the ratio $\frac{\tau_1}{\Lambda}$ in $q_i$ which, from the practical point of view, requires to have an anisotropic system, for example, allowing to a characteristic privileged direction along which the vectors $a_{1i}$ and $b_{1i}$ in Eqs. (4.1) will lay.

A simple possibility of that case is to have a graded material wherein the stoichiometric variable $c$, describing the composition of the system, varies with the position: in this case, in fact, the composition gradient $c_{,i}$ gives the direction of anisotropy, and the vectors $a_{1i}$ and $b_{1i}$ in Eqs. (4.1) will have the form $a_{1i} = a_1 c_{,i}$ and $b_{1i} = b_1 c_{,i}$, namely, Eq. (4.14) becomes

$$f = \frac{\tau_0}{\Lambda_0}\left(a_1 - b_1\right) c_{,i}\, q_i \tag{4.22}$$

In particular, just for the sake of application, we consider a system made of homogeneous Si at left and homogeneous Ge at right, whereas in between a graded layer of thickness $L$ has been intercalated (see Fig. 4.1 for a qualitative sketch of the aforementioned system), i.e., from $z = 0$ to $z = L$ the composition is $Si_c Ge_{1-c}$, where $c = 1$ at $z = 0$ (pure Silicon) and $c = 0$ at $z = L$ (pure Germanium).

In the graded region, in the 1-dimensional case, Eq. (4.13) therefore becomes

$$\partial_t^2 q_z + \partial_t^2 \, \gamma q_z^2 - U_0^2 \partial_z^2 q_z = 0 \tag{4.23}$$

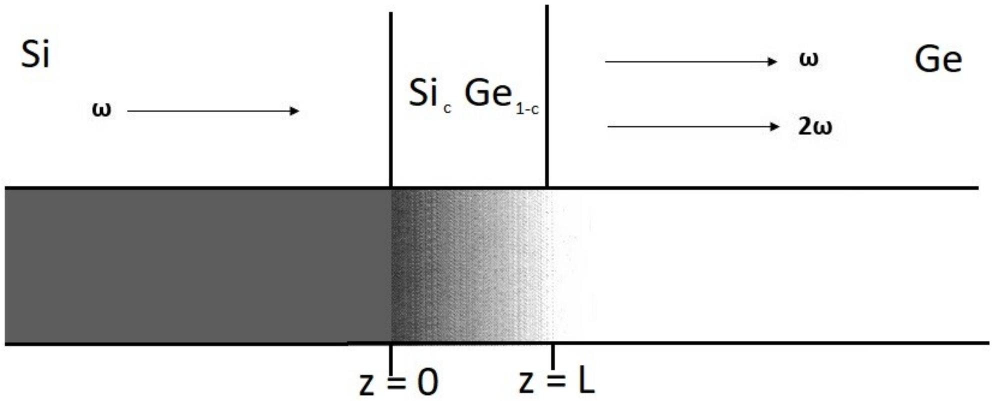



Figure 4.1: A graded layer of $Si_c Ge_{1-c}$ intercalated between homogeneous Si and homogeneous Ge

wherein $q_z$ means the only component of the heat flux, and

$$\gamma = (a_1 - b_1)\, \| c_{,i} \| \operatorname{sign}(c_{,i} q_i) \tag{4.24}$$

with $\| c_{,i} \|$ being the modulus of composition gradient along the $z$ axis in the graded system. We explicitly note that in dealing with graded materials, the values of the different material functions (e.g., the thermal conductivity, the relaxation time and the specific heat per unit volume) depend on the stoichiometric variable $c$ which, in the present case, varies when $z \in [0; L]$. As a consequence, in what follows $U_0 = U_0(z)$.

To obtain the second-harmonic generation of heat waves, we write the local heat flux $q_z$ as

$$q_z(t; z) = q_1(t; z) + q_2(t; z) \tag{4.25}$$

wherein

$$q_1(t; z) = A_1(z)\, e^{i(\omega t - k_1 z)} + \overline{A_1(z)\, e^{i(\omega t - k_1 z)}} = 2Re\left[A_1 e^{i(\omega t - k_1 z)}\right] \tag{4.26a}$$

$$q_2(t; z) = A_2(z)\, e^{i(2\omega t - k_2 z)} + \overline{A_2(z)\, e^{i(2\omega t - k_2 z)}} = 2Re\left[A_2 e^{i(2\omega t - k_2 z)}\right] \tag{4.26b}$$

wherein $k_1$ and $k_2$ are two wave numbers, and $\omega$ is the angular frequency; moreover the syntax $\overline{f}$ indicates the conjugate of the complex number $f$, and $Re[f]$ means its real part. By substituting Eqs. (4.25) and (4.26) into Eq. (4.23), one obtains

$$\begin{aligned}
&Re\left\{\left(k_1^2 U_0^2 - \omega^2\right) A_1 e^{i(\omega t - k_1 z)} + 2iU_0^2 k_1 (\partial_z A_1)\, e^{i(\omega t - k_1 z)} - \left(\partial_z^2 A_1\right) e^{i(\omega t - k_1 z)}\right\} + \\
&Re\left\{\left(k_2^2 U_0^2 - 4\omega^2\right) A_2 e^{i(2\omega t - k_2 z)} + 2iU_0^2 k_2 (\partial_z A_2)\, e^{i(2\omega t - k_2 z)} - \left(\partial_z^2 A_2\right) e^{i(2\omega t - k_2 z)}\right\} = \\
&Re\left[2\gamma\omega^2 \overline{A_1} A_2 e^{i(\omega t + k_1 z - k_2 z)}\right] + Re\left[4\gamma\omega^2 A_1^2 e^{2i(\omega t - k_1 z)}\right]
\end{aligned} \tag{4.27}$$

once terms with angular frequency equal to $3\omega$ or $4\omega$ have been neglected, and we have assumed that the parameter $\gamma$ does not depend on the position.

Whenever the values $\partial_z^2 A_1$ and $\partial_z^2 A_2$ vanish, in order that Eq. (4.27) may hold it is sufficient to require

$$k_1^2 U_0^2 - \omega^2 \; A_1 + 2ik_1 U_0^2 (\partial_z A_1) \; e^{i(\omega t - k_1 z)} = 2\gamma\omega^2 \overline{A_1} A_2 e^{i(\omega t + k_1 z - k_2 z)} \tag{4.28a}$$

$$k_2^2 U_0^2 - 4\omega^2 \; A_2 + 2ik_2 U_0^2 (\partial_z A_2) \; e^{i(2\omega t - k_2 z)} = 4\gamma\omega^2 A_1^2 e^{i(2\omega t - 2k_1 z)} \tag{4.28b}$$

Whenever [109–111]

$$\omega = k_1 U_0 \tag{4.29a}$$

$$k_2 = 2k_1 \tag{4.29b}$$

from Eqs. (4.28) we have:

$$\partial_z A_1 = -i \;\; \gamma k_1 \overline{A_1} A_2 \tag{4.30a}$$

$$\partial_z A_2 = -i \;\; \gamma k_1 A_1^2 \tag{4.30b}$$

### The low-depletion case

For low values of the conversion of the $\omega$-component to the $2\omega$-component (i.e., low depletion values of the $\omega$-component) one will have $\partial_z A_1 \to 0 \Leftrightarrow A_1 \approx$ const. As a consequence, in this case from Eq. (4.30b) we may have

$$A_2(z) = -i \;\; \gamma k_1 A_1^2 \;\; z \tag{4.31}$$

once the condition $A_2(z = 0) = 0$ holds.

The intensity $I_{2\omega}$ of the $2\omega$-wave, given by the square of the modulus of $A_2$, as a function of the position $z$ in the graded layer, will be

$$I_{2\omega} = I_\omega^2 \;\; k_1^2 \gamma^2 \;\; z^2 \tag{4.32}$$

with $I_\omega$ being the square modulus of $A_1$, i.e., of the heat wave arriving to the left boundary of the layer. The amplitude $A_2$ of the $2\omega$-wave at the right-hand boundary $z = L$ is directly obtained from (4.31) with $z = L$. Thus, for a graded medium of thickness $L$ and for an incident heat wave of frequency $\omega$ and amplitude $A_1$, the intensity of the second harmonic going out from the graded layer (at $z = L$) will be

$$I_{2\omega} = \frac{1}{2} \;\; (a_1 - b_1)\; (k_1 L\theta) \quad \frac{dc}{dz} \quad ^2 \tag{4.33}$$

in terms of $T_0$, $\kappa_0$, $a_1$, $b_1$.

### The high-depletion case

When the conversion of $\omega$-mode to $2\omega$-mode is relevant, the amplitude $A_1$ is not homogeneous, but decreases for increasing $z$; in this case one has also to take into account Eq. (4.30a). After some calculations, in this case one will get

$$A_1 = A \sec (A\gamma k_1 z) \tag{4.34a}$$

$$A_2 = -iA \tan (A\gamma k_1 z) \tag{4.34b}$$

wherein we set $A = A_1(z = 0)$. Whenever $A\gamma k_1$ is vanishingly small, $A_1$ remains almost constant and $A_2$ increases linearly as in Eq. (4.31); furthermore, Eqs. (4.34) lead to the following intensity of the $\omega$ and $2\omega$ contributions as a function of the position in the graded layer:

$$I_\omega = A^2 \sec^2 (A\gamma k_1 z) \tag{4.35a}$$

$$I_{2\omega} = A^4 \tan^2 (A\gamma k_1 z) \tag{4.35b}$$

Replacing $z = L$, one also gets the value of $I_\omega$ and $I_{2\omega}$ at the final boundary of the layer. In principle, this proposal could be experimentally checked and it could be useful to achieve higher frequencies, which are of special interest for the MC equation. Note that the intermediate layer of $Si_cGe_{1-c}$ could have values of $c$ different than those we have assumed at $z = 0$ and $z = L$. If $c$ was different from $c = 1$ at $z = 0$ and $c = 0$ at $z = L$, one should consider the thermal resistance of the discontinuity layers at $z = 0$ and $z = L$ between Si and $Si_{c_0}Ge_{1-c_0}$ and between $Si_{c_1}Ge_{1-c_1}$ and Ge, being $c_0$ and $c_1$ the values of $c$ at $z = 0$ and $z = L$.

## 4.3 Heat-flux dependence of the speed of nonlinear heat waves

When nonlinear effects are taken into account, the speed of heat waves may also depend on the wave amplitude. In oder to investigate how speed and amplitude of heat waves are related, in this section we use the following particular version of Eq. (4.2)

$$\partial_t \frac{\tau_0 (1 + \gamma_1 q^2)\, q}{\Lambda_0} + \frac{q_i}{\Lambda_0 (1 - \alpha_1^2 q^2)} - \frac{1}{\theta}_{,i} = 0 \tag{4.36}$$

wherein $\alpha_1$ and $\gamma_1$ are two suitable scalar-valued functions, according with the physical motivations considered below.

### 4.3.1 The physical motivation

In nonlinear heat-conduction theories, constitutive equations leading to the phenomenon of "flux limiters" have been sometimes investigated [4, 112]. Flux limiters are a direct consequence of the finite speed of the thermal perturbation: in fact, for a given energy density, the heat flux has to be bounded by a maximum saturation value in such a way that it should not attain arbitrarily high values [102, 113, 114]. In Ref. [98], for example, the authors pointed out as a heat-flux dependence of the thermal conductivity of the type

$$q_i = -\kappa \left(1 - \alpha_1^2 q^2\right) \theta_{,i} \tag{4.37}$$

characterizes different flux-limited nonlinear heat-transport equations. In Eq. (4.37) $\alpha_1$ stands for a scalar-valued function depending on the particular nonlinear heat-conduction theory [98]. From Eq.(4.37) it is easy to see that the modulus $\|q\|$ of the heat flux cannot indefinitely increase for increasing temperature gradient, but it tends to a saturation value, that is,

$$\|q_i\| \longrightarrow q_{\max} \propto \frac{1}{\alpha_1} \tag{4.38}$$

whenever $\|\theta_{,i}\| \longrightarrow \infty$. This may be the case, for example, of a longitudinal nanowire characterized by a length sufficiently larger than the mean-free path $\ell$ of the heat carriers (in such a way that its thermal conductivity is independent on $\ell$ and, therefore, it can be kept constant[2]), wherein the temperature difference between the two wire's ends continuously increases (for instance, by increasing the higher temperature from the outside). From the physical point of view, the saturation value $q_{\max}$ should be of the order of $q_{\max} \sim uU_{\max}$ with $U_{\max}$ being (the modulus of) the maximum speed of heat pulses. This may be relevant, for instance, in nanosystems, where a small temperature difference may lead to a very high temperature gradient [112].

The FL (1.70) (obtained, for example, from Eq. (4.37) by setting $\alpha_1 = 0$ therein) yields that $U_{\max}$ diverges: consequently, $q_{\max}$ diverges, too, according with Eqs. (4.38). The Fourier's theory is not, therefore, a flux-limited heat-conduction theory. If the MC equation (1.71) is used, instead, one has that $U_{\max}$ is always finite, according with Eq. (1.83), and then $q_{\max}$ no longer diverges: therefore, to be fully self-consistent,

[2] In a nanosystem with a the characteristic size smaller than the mean-free path of the heat carriers, the thermal conductivity is $\ell$-dependent, and a transition from the diffusive heat-transport regime to the ballistic one occurs. In this situation, another kind of flux-limited expressions – not necessarily dependent on the heat flux – can be obtained.

the MC theory should lead to a flux-limited heat-conduction theory. However, in a strict sense, we may note that it is not self-consistent, because in the steady state it reduces to FL, which is not a flux-limited heat-conduction theory, as previously observed.

To overcome this impasse, we may also specialize Eqs. (4.1) as

$$\tau_1 = \tau_0\left(1-\beta_1^2 q^2\right) \tag{4.39a}$$

$$\kappa = \kappa_0\left(1-\alpha_1^2 q^2\right) \tag{4.39b}$$

with $\beta_1$ as a suitable scalar-valued function (which, from the physical point of view, is similar to $\alpha_1$), in such a way, up to a second-order approximation in the local heat flux, Eq. (4.12) becomes

$$\frac{\tau_1}{\Lambda} = \frac{\tau_0}{\Lambda_0}\left(1+\gamma_1 q^2\right) \tag{4.40}$$

wherein we set

$$\gamma_1 = \operatorname{sign}\left(\alpha_1^2-\beta_1^2\right)\left|\alpha_1^2-\beta_1^2\right| \tag{4.41}$$

In this way the use of Eqs. (4.39)-(4.41) straightforwardly yields Eq. (4.36) from Eq. (4.2).

### 4.3.2 Third-order nonlinear effects

If we deal with high-frequency heat waves, and we disregard the dissipation effects (which may indeed also play an important role in heat-wave propagation [90, 115, 116]) the term $\frac{q_i}{\Lambda_0(1-\alpha_1^2 q^2)}$ in Eq. (4.36) can be neglected, in such a way that its combination with the local energy balance (1.72a) leads to

$$\partial_t^2\left[\left(1+\gamma_1 q^2\right) q_i\right] - U_0^2 q_{i,jj} = 0 \tag{4.42}$$

in the *non-equilibrium temperature approximation*.

In the 1-dimensional case, Eq. (4.42) is analogous to

$$\partial_t^2\left[\left(1+\frac{\chi^{(3)}E^2}{1+\chi^{(1)}}\right)E_i\right] - \frac{v_l^2}{1+\chi^{(1)}}E_{i,jj} = 0 \tag{4.43}$$

which follows from Eq. (4.18) when the following special case of constitutive equation (4.19) for the electrical-polarization vector is used:

$$P_i = \left(\chi^{(1)} + \chi^{(3)}E^2\right)\epsilon_0 E_i \tag{4.44}$$

As a consequence, the following formal analogies

$$q_i \leftarrow\rightarrow E_i \tag{4.45a}$$

$$U_0 \leftarrow\rightarrow \mathrm{p}\,\frac{v_l}{1+\chi^{(1)}} \tag{4.45b}$$

$$|\gamma_1| \leftarrow\rightarrow \frac{\chi^{(3)}}{1+\chi^{(1)}} \tag{4.45c}$$

$$\frac{\Lambda_0}{\tau_0} \leftarrow\rightarrow {}_0 \tag{4.45d}$$

cab be set, again. By exploiting this analogy much mathematical efforts may be saved to directly arrive to physical consequences of Eq. (4.42).

### 4.3.3 The Kerr effect in nonlinear optics

Here we firstly recall some well-known results about the speed of propagation of nonlinear electromagnetic waves, and later on we extend those results to the velocity of heat waves. We do so, instead of a direct solution arising from Eq. (4.42), in order to emphasize the formal analogies between nonlinear optics and nonlinear heat transfer, which suggest aspects of nonlinear heat waves not explored up to now.

In the 1-dimensional case ($z$ being the propagation direction of the wave), here we consider a net electric field $E_z$ (produced by a light wave of an angular frequency $\omega$ and a wave number $k$) given by

$$E_z(t;z) = \frac{A_e(z)}{2}\quad e^{i(\omega t-kz)} + e^{-i(\omega t-kz)} \tag{4.46}$$

wherein $A_e(z)$ is the net electric-field amplitude. Recalling the constitutive relation in Eq. (4.44), in this case the use of Eq. (4.46) yields that the electric polarization vector is

$$P_z(t;z) = P_z^{\omega}(t;z) + P_z^{3\omega}(t;z) \tag{4.47}$$

with $P_z^{\omega}$ and $P_z^{3\omega}$ given by

$$P_z^{\omega}(t;z) = \frac{A_e(z)}{2}\quad e^{i(\omega t-kz)} + e^{-i(\omega t-kz)} \quad \chi_{\mathrm{eff}}\ {}_0 \tag{4.48a}$$

$$P_z^{3\omega}(t;z) = \frac{A_e^3(z)}{8}\quad e^{i(3\omega t-3kz)} + e^{-i(3\omega t-3kz)} \quad \chi_2\ {}_0 \tag{4.48b}$$

with

$$\chi_{\mathrm{eff}} = \chi^{(1)} + \frac{3\chi^{(3)}A_e^2(z)}{4} \tag{4.49}$$

Note that in the linear situation, that is, if third-order terms in $E_z$ are neglected in Eq. (4.44), $\chi_{\mathrm{eff}} = \chi^{(1)}$. In Eq. (4.47) the term $P_z^{\omega}$ is related to the so-called Kerr effect, whereas the term $P^{3\omega}$ is related to the third-harmonic generation. Below we focus our analysis on the former effect.

The Kerr effect, also called the quadratic electro-optic (QEO) effect, is a change in the refractive index of a material in response to an applied electric field [117–119]. The following two special cases of the Kerr effect are normally considered:

- The electro-optic Kerr effect (or DC Kerr effect). This is the special case in which a slowly varying external electric field is applied by, for instance, a voltage on electrodes across the material.

- The optical Kerr effect (or AC Kerr effect). This is the special case in which the electric field is due to the light itself. This causes a variation in index of refraction which is proportional to the local irradiance of the light. This refractive index variation is responsible for many nonlinear optical effects, such as self-focusing.

To analyze the Kerr effect, here we neglect $P^{3\omega}(t;z)$ in Eq. (4.47) which, therefore, becomes

$$P_z(t;z) = P_z^{\omega}(t;z) \equiv E_z(t;z)\,\chi_{\mathrm{eff}}\,\epsilon_0 \tag{4.50}$$

When it is introduced in the one-dimensional version of Eq. (4.18), one has

$$\partial_t^2 E_z - \frac{v_l^2}{1+\chi_{\mathrm{eff}}}\partial_z^2 E_z = 0 \tag{4.51}$$

which directly points out that the speed of propagation of electromagnetic waves in the nonlinear case is

$$V_e = \frac{v_l}{\sqrt{1+\chi_{\mathrm{eff}}}} \tag{4.52}$$

wherein the non-dimensional quantity

$$n_{e,\mathrm{eff}} = \sqrt{1+\chi_{\mathrm{eff}}} \tag{4.53}$$

stands for the optical-wave effective refraction index of the material, and yields information about the reduction in the wave speed. In the linear situation (namely, if in Eq. (4.44) only first-order terms in $E_z$ would be accounted), instead, the optical-wave effective refraction index of the material is

$$n_{e,0} = \sqrt{1+\chi^{(1)}} \tag{4.54}$$

Recalling Eq. (4.49), then by direct calculations from Eqs. (4.53) and (4.54) we have

$$n_{e,\mathrm{eff}} = n_{e,0}\sqrt{1+\frac{3\chi^{(3)}A_e^2}{4n_{e,0}^2}} \approx n_{e,0} + \frac{3\chi^{(3)}A_e^2}{8n_{e,0}^2} = n_{e,0} + n_{e,\mathrm{nl}} I_e \tag{4.55}$$

since usually $\chi^{(3)} \ll n^2_{e,0}$; in Eq. (4.55) the quantity

$$I_e = \frac{A_e^2 v_l \epsilon_0 n_{e,0}}{2} \tag{4.56}$$

means the local intensity of the optical wave, and

$$n_{e,\mathrm{nl}} = \frac{3\chi^{(3)}}{4 v_l \epsilon_0 n_{e,0}^2} \tag{4.57}$$

is the nonlinear refractive index per unit of intensity for the optical wave.

Equation (4.55) clearly points out that the refraction index of the material depends on the intensity of the incoming optical wave; in particular, since in common materials $n_{e,\mathrm{nl}} > 0$, then it follows that $n_{e,\mathrm{eff}}$ increases in the areas wherein the intensity $I_e$ is higher (usually at the centre of a beam) creating a focusing density profile, since a medium whose refractive index increases with the electric field intensity acts like a focusing lens. In the electro-optical Kerr effect, the refraction index is modified by an externally imposed electric field $E$, instead of the electric field of the own wave.

From the considerations above, it is easy matter to see that in the nonlinear situations the speed of propagation of electromagnetic waves in Eq. (4.52) can be also written as

$$V_e \approx \frac{v_l}{n_{e,0}}\left(1 - \frac{n_{e,\mathrm{nl}}}{n_{e,0}} I_e\right) \tag{4.58}$$

### 4.3.4 The Kerr effect in the nonlinear heat conduction

In analogy with what happens in optics, in the case of heat conduction a thermal wave (of angular frequency $\omega$ and wave number $k$) may produce a heat flux behaving as

$$q_z(t; z) = \frac{A_q(z)}{2}\left(e^{i(\omega t - kz)} + e^{-i(\omega t - kz)}\right) \tag{4.59}$$

with $A_q(z)$ being the heat-flux amplitude. Starting from Eq. (4.42) and according with Eqs. (4.45), the results in Eqs. (4.55)-(4.58) allow us to claim that in the nonlinear case for thermal waves the propagation speed should be

$$U \approx U_0\left(1 - \frac{n_{q,\mathrm{nl}}}{n_{q,0}} I_q\right) \tag{4.60}$$

once the heat flux is given by Eq. (4.59), wherein the quantity

$$I_q = \frac{A_q^2 v_l^2 \Lambda_0}{2 U_0 \tau_0} \tag{4.61}$$

is the local intensity of the heat wave; moreover, if we introduce the quantity

$$n_{q,\mathrm{nl}} = \frac{3\,|\gamma_1|\,\tau_0}{4v_l\Lambda_0} \tag{4.62}$$

to denote the nonlinear refractive index per unit of intensity for the heat wave, and we set

$$n_{q,0} = \frac{v_l}{U_0} \tag{4.63}$$

from Eq. (4.60) we can also obtain the following expression for the speed of propagation of thermal waves in the nonlinear case:

$$U \approx U_0 \left(1 - \frac{3}{8}|\gamma_1|A_q^2\right) \tag{4.64}$$

From Eqs. (4.60) and (4.64) it can be clearly seen that in the nonlinear case the heat-wave speed $U$ depends on the heat-wave local intensity, namely, on the (non-negligible) heat-wave amplitude. In particular, from those expressions it can be inferred that in the very general case in nonlinear situations the heat waves should become slower than the heat haves in the linear situations.

This also happens in nonlinear optics, wherein the maximum speed is that obtained in the linear case. Note, furthermore, that in Eq. (4.64) we have used the maximum amplitude of the heat wave. This is valid with high-frequency thermal waves (which is the case we are considering), but if the frequency is not sufficiently high, the instantaneous amplitude of the wave should be used in the derivation of the wave speed.

It has to be observed, however, that whenever the quantity $\gamma \longrightarrow 0$, then $U \longrightarrow U_0$. The parameter $\gamma_1$, indeed, vanishes not only in the linear situation, but also when the two coefficients $\alpha_1$ and $\beta_1$, appearing in Eqs. (4.39), are such that $\alpha_1 \approx \beta_1$, according with Eq. (4.41). Although interesting studies on the constitutive assumptions in Eqs. (4.39) can be found in literature, we are currently not aware of clear experimental/theoretical expressions for $\alpha_1$ and $\beta_1$. In any cases, those coefficients should be related to the particular material at hand, as well as to the particular working conditions. This means that nonlinear effects may have a subtle role, i.e., they may influence the speed of heat waves in some cases, and have no relevance in other situations.

The present analysis, however, points out that a deeper investigation of the constitutive relations in Eqs. (4.39) may have a great importance for a satisfactory treatment of heat transfer in nonlinear situations.

In closing this part, we note that in the case of heat waves, the speed $v_l$ appearing in Eqs. (4.61)-(4.63) can be also meant as the phonon speed.

## 4.4 Externally controllable lenses for heat waves

In Ref. [120] the authors theoretically studied how curved interfaces in a material medium can be used to concentrate the energy carried by parallel thermal rays into a given focal point. This can be done, for example, by intercalating a piece of a biconvex material *B* into a ribbon of material *A* (see Fig.4.2 for a qualitative sketch): the curved element *B* acts as a lens for the heat waves, and focuses the heat waves into the point *F* (i.e., the focus of the heat lens).

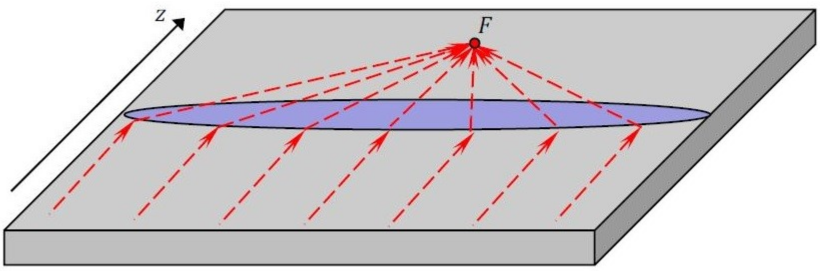



Figure 4.2: Curved interfaces (a piece of a biconvex material *B* in figure) intercalated in a material (a ribbon of material *A*). *B* acts as a heat lens: it concentrates the parallel heat waves (dashed lines in figure) into the point *F* (the heat-lens focal point). In figure *z* indicates the original direction of the heat-wave propagation, namely, that before the curved interface, as well as the direction of propagation of the local heat flux.

In Ref. [120] it has been argued that the above simple device, considered in analogy with linear optics for electromagnetic waves, could be useful to enhance the sensitivity of measurement of heat waves, by concentrating in a point the intensity crossing the total transversal area of the heat lens. In particular those authors obtained (see Eqs. (9) and (10) in Ref. [120]) that the focal distance $f^d$ is

$$\frac{1}{f_b^d} = \frac{2}{R}\left(\frac{U_B}{U_A} - 1\right) \tag{4.65a}$$

$$\frac{1}{f_s^d} = \frac{2}{R}\left(\frac{U_B}{U_A} - 1\right)\frac{U_A}{U_B} \tag{4.65b}$$

in the case of a biconvex (b) thin lens, and in the case of a spherical (s) thin lens, respectively. In Eqs. (4.65) $R$ means the curvature radius of the heat lenses, whereas

$U_A$ and $U_B$ are the speed of heat waves in the medium $A$ and in the medium $B$, respectively. According to Eq. (4.64), the heat-wave speed in a medium may depend on the heat flux in it.

Indeed, instead of intercalating a material $B$ into a material $A$, one may also have an externally controllable heat lens for plane heat waves propagating through a thin curved homogeneous layer, by applying a steady heat flux $q_0$ in the orthogonal direction of the layer to a region of it which is limited by the two lines of curvature radii $R_1$ and $R_2$ (see Fig. 4.3 for a qualitative sketch).

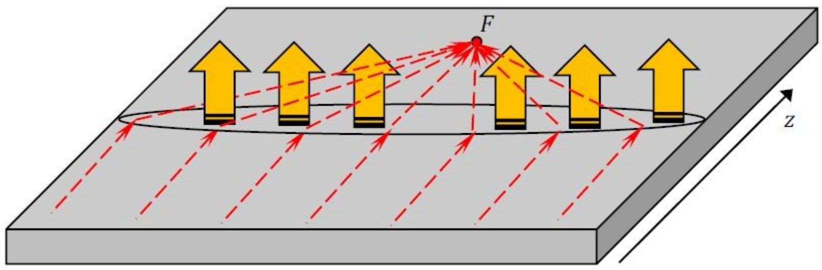



Figure 4.3: Thin layer crossed by small-amplitude heat waves (dashed lines in figure). The steady heat flux $q_0$ (large arrows in figure), in the orthogonal direction of the layer, allows to focalize parallel heat waves into the point $F$. In figure $z$ indicates the original direction of the heat-wave propagation, namely, that before the zone crossed by $q_0$.

The wave speed in curved region of $A$ will be different with respect to that in $A$ without the external heat flux, and it depends on the value of $q_0$ (which may be controlled from the outside). Thus, this situation has two advantages with respect to that considered in Ref. [120]: it does not require intercalating a different material $B$ in $A$, and the refraction index may be externally controlled. This last feature has some analogies with electrically tunable lenses in nonlinear optics (see for instance Refs.[121–123]) based on the electro-optic Kerr effect. As a limit to that analogy, indeed, we note that the heat is easiest to diffract than the electric field. This means that the boundary of the region of the system (atop which the external heat flux $q_0$ will be imposed) should not be sharp, as in the case of electric field in electrically-induced lenses, but blurred. Thus, a more realistic analysis of the proposed heat-induced lens should take this fact into account.

In more general situations, we may consider, as in usual lenses, a curved region of material $B$ intercalated in material $A$, but with the speed of heat waves in material $B$ being especially sensitive to the value of the externally applied heat flux through it; also in this case one will be able to tune the focal distance of the lens from the outside by modifying the value of the applied heat flux.

In the case of a curved region in the material $A$, from Eqs. (4.65) we have

$$f_{\mathrm{b}}^{d} = \frac{R(1-\xi)}{2\xi} \tag{4.66a}$$

$$f_{\mathrm{s}}^{d} = \frac{R}{2\xi} \tag{4.66b}$$

wherein $\xi = \frac{3}{8}|\gamma_1|q_0^2$, with $q_0$ being the steady heat flux applied orthogonally to the layer, in analogy with the applied electric field in the electro-optic Kerr effect. In practical applications, for a given material and operating temperature $T$, the quantity $\gamma$ is fixed (according with previous observations); as a consequence from Eqs. (4.66) it follows that the focal distance can be varied by varying the applied orthogonal heat flux (analogous to the externally applied electric field in electro-optic Kerr effect): this situation has the obvious advantage of allowing a relatively easy external control of the value of the focal distance. Note that though the orthogonal heat flux $q_0$ is assumed to be high in order that the nonlinear effects on the speed of the waves are perceptible, we consider that the heat wave propagating along the plane has a small amplitude.

In Fig. 4.4 the behaviors of the non-dimensional ratios $\frac{f^{d}}{R}$ as functions of the non-dimensional ratio $\xi$, arising from Eqs. (4.66), are plotted. As it can be seen from that figure, for a given value of $q_A$, the use of a spherical heat lens leads to a heat-wave focal distance larger than that arising from the use of a biconvex heat lens.

In closing this part, let us observe that here we are considering an isotropic material, but an anisotropic geometry (i.e., a plane layer) and an anisotropic physical situation (i.e., a small-amplitude linear heat wave in a direction along the layer joined with a strong constant applied heat flux $q_0$ orthogonal to the layer). The focal distances given by Eqs. (4.65) (which directly allowed us to derive Eqs. (4.66) above) were derived for linear waves along the layer. But the focal distances depend on the propagation speed of the waves (namely, on refraction index), which depends on the total heat flux.

In information theory (see, for instance, Chap. 6 in Ref. [4]), it turns out that the quantity $\frac{\tau_1}{\Lambda} q_i$ has the form $\frac{\tau_1}{\Lambda_0} h(q^2)\, q$ in isotropic systems, with $h(q^2)$ being a scalar-valued function of the indicated argument. In our proposed heat-induced lens, the anisotropy of the physical situation is reflected in the fact that $q_i$ along the plate (let us say, along the $i = 1$ direction) is small and oscillating, whereas the

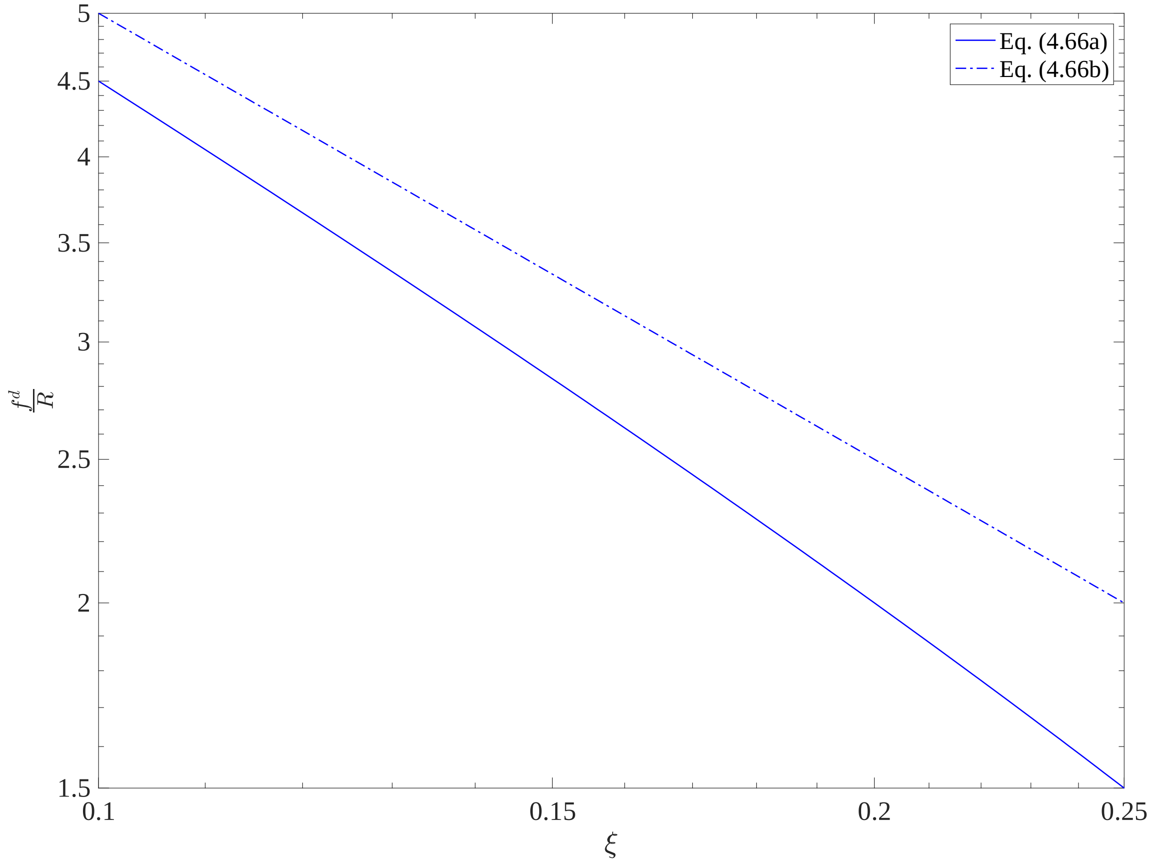



Figure 4.4: Heat-lens focal distances with $\frac{3}{8}\xi/\gamma_{11} = q_0^2$, with $q_0$ the heat flux flowing across the region of the lens, orthogonally to the layer: theoretical results arising from Eqs. (4.66). Logarithmic length scales have been used in figure.

squared heat-flux modulus in ($q^2$) may be well approximated by the (constant) squared modulus $q_0^2$, since the orthogonal applied heat flux $q_0$ (let us say, along the $i = 3$ direction) is assumed much higher than the amplitude of the heat wave along the layer.

In the case of an anisotropic system, the mathematical treatment would be more complex since the different spatial direction may affect in a different way the final results. Extension to anisotropic systems is obviously of interest and physically well motivated.

# Chapter 5

# Nonlocal and nonlinear effects in hyperbolic heat transfer with phonons and electrons

Although with a different importance, in common materials used at nanoscale both the electrons, and the lattice vibrations (i.e., the phonons) are the heat carriers [124–127]. In practical applications, micro/nano electronic devices can be assembled by using different materials as, for instance, pure metals (in which the electrons are the sole heat carriers), nonmetals (in which the phonons are the sole heat carriers) and semimetals (in which heat conduction is due both to phonons and electrons) [128, 129]. Good examples of semimetals are the classical semiconductors such as Germanium, Silicon, and Tellurium. The thermal and electric conductivities of these elements are not so good as those of the metals, but better than those of nonmetals, so that semimetals are also known as semiconductors.

A very compelling task in modeling heat transport at micro/nanoscale is the right understanding of the physics which rules the behavior of the different heat carriers, such as their propagation, scattering, relaxation, and so on [130, 131]. In principle, a correct analysis of these properties should be based on microscopic approaches [132 either from several versions of kinetic theory or fluctuation-dissipation theorems, or from detailed computer simulations. These approaches allow for a detailed understanding and description. However, this should not make us forget the practical usefulness and the conceptual challenge of mesoscopic approaches starting from the macroscopic perspective and deepening into more detailed and accurate description of physical systems.

Although both approaches have their own qualities and flaws, no one is completely preferred with respect the other one, in this chapter we pursue the second type of strategy to investigate heat conduction in semimetals. In particular, by regarding the electrons and the phonons as a mixture of two heat carriers flowing through the crystal lattice, and assuming that they are endowed with their own temperatures [133, 134], here we propose a theoretical model based on the following equations and which allows to take into account memory, nonlocal and nonlinear effects:

$$\dot{\theta}^e + \frac{q^e_{i,i}}{c^e_v} = 0 \tag{5.1a}$$

$$\dot{q}^e_i + \frac{q^e_i}{\tau_{1e}} + \frac{\kappa_e \theta^e_{,i}}{\tau_{1e}} - \frac{2 q^e_j q^e_{j,i}}{c^e_v \theta^e} - \frac{Q^e_{ij,j}}{\tau_{1e}} = 0 \tag{5.1b}$$

$$\dot{Q}^e_{ij} + \frac{Q^e_{ij}}{\tau_{2e}} - \frac{\ell^2_e q^e_{i,j}}{\tau_{2e}} = 0 \tag{5.1c}$$

$$\dot{\theta}^p + \frac{q^p_{i,i}}{c^p_v} = 0 \tag{5.1d}$$

$$\dot{q}^p_i + \frac{q^p_i}{\tau_{1p}} + \frac{\kappa_p \theta^p_{,i}}{\tau_{1p}} - \frac{2 q^p_j q^p_{j,i}}{c^p_v \theta^p} - \frac{Q^p_{ij,j}}{\tau_{1p}} = 0 \tag{5.1e}$$

$$\dot{Q}^p_{ij} + \frac{Q^p_{ij}}{\tau_{2p}} - \frac{\ell^2_p q^p_{i,j}}{\tau_{2p}} = 0 \tag{5.1f}$$

In Eqs. (5.1):

- $\theta^e$ and $\theta^p$ are, respectively, the electron temperature and the phonon temperature. They are related to the internal energy of electrons $u^e$ and that of phonons $u^p$, respectively, by the constitutive assumptions

  $$u^e = c^e_v \theta^e \tag{5.2a}$$

  $$u^p = c^p_v \theta^p \tag{5.2b}$$

  with $c^e_v$ and $c^p_v$ being, respectively, the specific heat of electrons and of phonons [133, 134]. The two above contributions to the internal energy (per unit volume) $u$ of the whole system are such that

  $$u = u^e + u^p \tag{5.3}$$

  whereas the total specific heat is $c_v = c^e_v + c^p_v$.

- $q^e_i$ and $q^p_i$ are, respectively, the electron contribution and the phonon contribution to the local heat flux $q_i$ [133, 134]. These two different contributions are such that

  $$q_i = q^e_i + q^p_i \tag{5.4}$$

- $Q_{ij}^e$ and $Q_{ij}^p$ are the electron contribution and the phonon contribution to the flux of $q_i$ [2, 91, 135]. These two different contributions are such that the flux of heat flux $Q_{ij}$ of the whole system is

$$Q_{ij} = Q_{ij}^e + Q_{ij}^p \tag{5.5}$$

- $\tau_{1e}$ and $\tau_{1p}$ are, respectively, the relaxation time of $q_i^e$ and of $q_i^p$.
- $\tau_{2e}$ and $\tau_{2p}$ are, respectively, the relaxation time of $Q_{ij}^e$ and of $Q_{ij}^p$.
- $\kappa_e$ and $\kappa_p$ are, respectively, the thermal conductivity of electrons and of phonons.
- $\ell_e$ and $\ell_p$ are, respectively, the mean-free path of electrons and of phonons.

## 5.1 Heat-Wave Propagation

Advanced materials could experience very low temperature, or extremely high temperature gradients, for which a precise heat-transport model should be considered to capture temperature rise from thermal wave propagation. Therefore, starting from Eqs. (5.1), in this section we study the propagation of heat ($H$-) waves. From the practical point of view, $H$-waves can be generated by periodically varying in time the temperature in a point of the medium at hand with respect to its steady-state reference levels. A solitary $H$-wave, instead, comes into being and travels along the medium when the latter is heated with a heat pulse.

Here we use the tool of the acceleration ($A$-) waves: in particular we suppose that the region ahead the travelling surface $S$ is such that

$$\theta^e(x_k, t) \equiv \theta^p(x_k, t) = \theta_0 \qquad q_i^e(x_k, t) \equiv q_i^p(x_k, t) = q_i^0 \tag{5.6}$$

$\forall t \in \mathbb{R}^+$, with $\theta_0$ and $q_i^0$ being stationary constant reference levels.

### 5.1.1 Heat-Wave Speeds

By taking the jump of each of Eqs. (5.1) we firstly have

$$\left[\dot{\theta}^e\right] + \frac{\left[q^e_{i,i}\right]}{c^e_v} = 0 \tag{5.7a}$$

$$\left[\dot{q}^e_i\right] + \frac{\kappa_e \left[\theta^e_{,i}\right]}{\tau_{1e}} - \frac{2q^0_j \left[q^e_{j,i}\right]}{c^e_v \theta_0} - \frac{\left[Q^e_{ij,j}\right]}{\tau_{1e}} = 0 \tag{5.7b}$$

$$\left[\dot{Q}^e_{ij}\right] - \frac{\ell_e^2 \left[q^e_{i,j}\right]}{\tau_{2e}} = 0 \tag{5.7c}$$

$$\left[\dot{\theta}^p\right] + \frac{\left[q^p_{i,i}\right]}{c^p_v} = 0 \tag{5.7d}$$

$$\left[\dot{q}^p_i\right] + \frac{\kappa_p \left[\theta^p_{,i}\right]}{\tau_{1p}} - \frac{2q^0_j \left[q^p_{j,i}\right]}{c^p_v \theta_0} - \frac{\left[Q^p_{ij,j}\right]}{\tau_{1p}} = 0 \tag{5.7e}$$

$$\left[\dot{Q}^p_{ij}\right] - \frac{\ell_p^2 \left[q^p_{i,j}\right]}{\tau_{2p}} = 0 \tag{5.7f}$$

and then

$$U\hat{\theta}^e - \frac{\hat{q}^e_i n_i}{c^e_v} = 0 \tag{5.8a}$$

$$\left(U + \frac{2q^0_j n_j}{c^e_v \theta_0}\right)\hat{q}^e_i - \frac{\kappa_e \hat{\theta}^e n_i}{\tau_{1e}} + \frac{\hat{Q}^e_{ij} n_j}{\tau_{1e}} = 0 \tag{5.8b}$$

$$U\hat{Q}^e_{ij} + \frac{\ell_e^2 \hat{q}^e_i n_j}{\tau_{2e}} = 0 \tag{5.8c}$$

$$U\hat{\theta}^p - \frac{\hat{q}^p_i n_i}{c^p_v} = 0 \tag{5.8d}$$

$$\left(U + \frac{2q^0_j n_j}{c^p_v \theta_0}\right)\hat{q}^p_i - \frac{\kappa_p \hat{\theta}^p n_i}{\tau_{1p}} + \frac{\hat{Q}^p_{ij} n_j}{\tau_{1p}} = 0 \tag{5.8e}$$

$$U\hat{Q}^p_{ij} + \frac{\ell_p^2 \hat{q}^p_i n_j}{\tau_{2p}} = 0 \tag{5.8f}$$

once the use of the classical Hadamard relations in Eq. (1.52) has been made. In Eqs. (5.8) the functions $\hat{\theta}^e(t) = [\theta_{,i} n_i]$, $\hat{q}^e_i(t) = \left[q^e_{i,j}\right] n_j$, $\hat{Q}^e_{ij}(t) = \left[Q^e_{ij,k}\right] n_k$, $\hat{\theta}^p(t) = [\theta_{,i} n_i]$, $\hat{q}^p_i(t) = \left[q^p_{i,j}\right] n_j$ and $\hat{Q}^p_{ij}(t) = \left[Q^p_{ij,k}\right] n_k$ are the $A$-wave amplitudes. Moreover, therein V means the $A$-wave speed (or, equivalently, the $H$-wave speed), and $\eta$ means the normal unit to the $A$-wave front.

By straightforward calculations, it is possible to obtain that Eqs. (5.8) do not only admit the trivial solution if, and only if, the following relation holds:

$$\left(U^2 + \frac{2q^0_j n_j U}{c^e_v \theta_0} - \frac{\ell_e^2}{\tau_{1e}\tau_{2e}} - \frac{\kappa_e}{\tau_{1e} c^e_v}\right)\left(U^2 + \frac{2q^0_j n_j U}{c^p_v \theta_0} - \frac{\ell_p^2}{\tau_{1p}\tau_{2p}} - \frac{\kappa_p}{\tau_{1p} c^p_v}\right) = 0 \tag{5.9}$$

Equation (5.9) allows us to claim the following result: the two-temperature theoretical model, introduced by Eqs. (5.1), predicts that a periodical variation of the local temperature in a point of the system generates two different *A*-waves which propagate with different speeds. Those speeds are

$$U^e = U_0^e \sqrt{\varphi_e^2 + 1 + \psi_e} - \varphi_e \tag{5.10a}$$

$$U^p = U_0^p \sqrt{\varphi_p^2 + 1 + \psi_p} - \varphi_p \tag{5.10b}$$

wherein we have introduced the following speeds

$$U_0^e = \sqrt{\frac{\kappa_e}{c_v^e \tau_{1e}}} \tag{5.11a}$$

$$U_0^p = \sqrt{\frac{\kappa_p}{c_v^p \tau_{1p}}} \tag{5.11b}$$

and the following non-dimensional scalar-valued functions

$$\varphi_e = \frac{q_j^0 n_j}{c_v^e \theta_0 U_0^e} \qquad \varphi_p = \frac{q_j^0 n_j}{c_v^p \theta_0 U_0^p}$$
$$\psi_e = \frac{\ell_e^2 c_v^e}{\tau_{2e} \kappa_e} \qquad \psi_p = \frac{\ell_p^2 c_v^p}{\tau_{2p} \kappa_p} \tag{5.12}$$

It seems important to note that throughout the present chapter we use the appellation *electronic heat (EH-) wave* for the *A*-wave whose speed is given by Eq. (5.10a), and the appellation *phononic heat (PH-) wave* for the *A*-wave whose speed is given by Eq. (5.10b).

As it is clearly showed by Eqs. (5.10), the *EH*-wave speed diverges either when $\tau_{1e} \to 0$, or when $\tau_{2e} \to 0$. Similarly, the *PH*-wave speed diverges either when $\tau_{1p} \to 0$, or when $\tau_{2p} \to 0$.

### Nonlocal Effects and Heat-Wave Speeds

Nonlocal effects influence both the *EH*-wave speed, and the *PH*-wave speed. According to Eqs. (5.10), those effects, in fact, are introduced by $\psi_e$ in $U^e$, and by $\psi_p$ in $U^p$. Since those functions are always positive, it is possible to claim that nonlocal effects enhance the speeds of propagation. In fact, when nonlocal effects are negligible, i.e., if we may set $\psi_e = 0$ and $\psi_p = 0$ in Eqs. (5.10), those speeds become

$$U^e = U_0^e \sqrt{\varphi_e^2 + 1} - \varphi_e \tag{5.13a}$$

$$U^p = U_0^p \sqrt{\varphi_p^2 + 1} - \varphi_p \tag{5.13b}$$

### Nonlinear Effects and Heat-Wave Speeds

Throughout the present chapter we use the appellation *positive* (+) for the $H$-wave which is propagating in the same direction of the average heat flux $q_j^0$, and the appellation *negative* (−) for the $H$-wave which is propagating in the opposite direction of the average heat flux $q_j^0$.

Nonlinear effects influence both the $EH$-wave speed, and the $P$ $H$-wave speed. According to Eqs. (5.10), those effects, in fact, are introduced by $\varphi_e$ in $U^e$ and by $\varphi_p$ in $U^p$. Since the sign of the scalar product $q_j^0 n_j$ depends on the direction of propagation, from Eqs. (5.12) it follows that

- $\varphi_e > 0$ and $\varphi_p > 0$ for positive $A$-waves

- $\varphi_e < 0$ and $\varphi_p < 0$ for negative $A$-waves

As a consequence, from Eqs. (5.10) it follows that both $U^e$ and $U^p$ depend on the direction of propagation of the $H$-waves. In particular, from the results above we have $U_+^e \le U_-^e$ and $U_+^p \le U_-^p$.

When nonlinear effects are negligible, i.e., when $\varphi_e = 0$ and $\varphi_p = 0$, Eqs. (5.10) become

$$U^e = U_0^e \sqrt{1 + \psi_e} \tag{5.14a}$$

$$U^p = U_0^p \sqrt{1 + \psi_p} \tag{5.14b}$$

and both those speeds no longer depend on the direction of propagation.

## 5.1.2 Heat-Wave Amplitudes

When the $A$-wave amplitude becomes infinite we may claim that the $A$-wave becomes a shock wave.

Differentiating with respect to time each of Eqs. (5.1) and then evaluating their jumps through $S$ we have

$$[\![\ddot\theta^e]\!] + \frac{\dot q^e_{i,i}}{c^e_v} = 0 \tag{5.15a}$$

$$[\ddot q^e_i] + \frac{[\dot q^e_i]}{\tau_{1e}} + \frac{\kappa_e\,[\![\dot\theta^e_{,i}]\!]}{\tau_{1e}} - \frac{2q^0_j}{c^e_v\theta_0}\left(\dot q^e_{j,i} - \frac{q^e_{j,i}\,[\![\dot\theta^e]\!]}{\theta_0}\right) - \frac{[\![\dot Q^e_{ij,j}]\!]}{\tau_{1e}} = 0 \tag{5.15b}$$

$$[\![\ddot Q^e_{ij}]\!] + \frac{[\![\dot Q^e_{ij}]\!]}{\tau_{2e}} - \frac{\ell_e^2\,[\![\dot q^e_{i,j}]\!]}{\tau_{2e}} = 0 \tag{5.15c}$$

$$[\![\ddot\theta^p]\!] + \frac{\dot q^p_{i,i}}{c^p_v} = 0 \tag{5.15d}$$

$$[\ddot q^p_i] + \frac{[\dot q^p_i]}{\tau_{1p}} + \frac{\kappa_p\,[\![\dot\theta^p_{,i}]\!]}{\tau_{1p}} - \frac{2q^0_j}{c^p_v\theta_0}\left(\dot q^p_{j,i} - \frac{q^p_{j,i}\,[\![\dot\theta^p]\!]}{\theta_0}\right) - \frac{[\![\dot Q^p_{ij,j}]\!]}{\tau_{1p}} = 0 \tag{5.15e}$$

$$[\![\ddot Q^p_{ij}]\!] + \frac{[\![\dot Q^p_{ij}]\!]}{\tau_{2p}} - \frac{\ell_p^2\,[\![\dot q^p_{i,j}]\!]}{\tau_{2p}} = 0 \tag{5.15f}$$

which leads to

$$\frac{\delta\hat\theta^e}{\delta t} - \frac{U\,[\![n_in_j\theta^e_{,ij}]\!]}{2} - \frac{n_i}{2c^e_vU}\frac{\delta\hat q^e_i}{\delta t} + \frac{[\![n_in_jn_kq^e_{i,jk}]\!]}{2c^e_v} = 0 \tag{5.16a}$$

$$\frac{\delta\hat q^e_i}{\delta t} - \frac{U\,[\![n_jn_kq^e_{i,jk}]\!]}{2} + \frac{\hat q^e_i}{2\tau_{1e}} - \frac{\kappa_e}{2\tau_{1e}}\left(\frac{n_i}{U}\frac{\delta\hat\theta^e}{\delta t} - [\![n_j\theta^e_{,ij}]\!]\right) + \frac{q^0_jn_j}{c^e_v\theta_0}\left(\frac{1}{U}\frac{\delta\hat q^e_i}{\delta t} - [\![n_jn_kq^e_{i,jk}]\!] + \frac{\hat q^e_i\hat\theta^e}{\theta_0}\right)$$
$$+ \frac{n_j}{2U\tau_{1e}}\frac{\delta\hat Q^e_{ij}}{\delta t} - \frac{n_jn_kn_sQ^e_{ij,ks}}{2\tau_{1e}} = 0 \tag{5.16b}$$

$$\frac{\delta\hat Q^e_{ij}}{\delta t} - \frac{U\,n_kn_sQ^e_{ij,ks}}{2} + \frac{\hat Q^e_{ij}}{2\tau_{2e}} + \frac{\ell_e^2}{2\tau_{2e}}\left(\frac{n_j}{U}\frac{\delta\hat q^e_i}{\delta t} - [\![n_kq^e_{i,jk}]\!]\right) = 0 \tag{5.16c}$$

$$\frac{\delta\hat\theta^p}{\delta t} - \frac{U\,[\![n_in_j\theta^p_{,ij}]\!]}{2} - \frac{n_i}{2c^p_vU}\frac{\delta\hat q^p_i}{\delta t} + \frac{[\![n_in_jn_kq^p_{i,jk}]\!]}{2c^p_v} = 0 \tag{5.16d}$$

$$\frac{\delta\hat q^p_i}{\delta t} - \frac{U\,[\![n_jn_kq^p_{i,jk}]\!]}{2} + \frac{\hat q^p_i}{2\tau_{1p}} - \frac{\kappa_p}{2\tau_{1p}}\left(\frac{n_i}{U}\frac{\delta\hat\theta^p}{\delta t} - [\![n_j\theta^p_{,ij}]\!]\right) + \frac{q^0_jn_j}{c^p_v\theta_0}\left(\frac{1}{U}\frac{\delta\hat q^p_i}{\delta t} - [\![n_jn_kq^p_{i,jk}]\!] + \frac{\hat q^p_i\hat\theta^p}{\theta_0}\right)$$
$$+ \frac{n_j}{2U\tau_{1p}}\frac{\delta\hat Q^p_{ij}}{\delta t} - \frac{n_jn_kn_sQ^p_{ij,ks}}{2\tau_{1p}} = 0 \tag{5.16e}$$

$$\frac{\delta\hat Q^p_{ij}}{\delta t} - \frac{U\,n_kn_sQ^p_{ij,ks}}{2} + \frac{\hat Q^p_{ij}}{2\tau_{2p}} + \frac{\ell_p^2}{2\tau_{2p}}\left(\frac{n_j}{U}\frac{\delta\hat q^p_i}{\delta t} - [\![n_kq^p_{i,jk}]\!]\right) = 0 \tag{5.16f}$$

when the Hadamard relations (1.52) are employed in a recursive way. Observing that from Eqs. (5.8a), (5.8c), (5.8d) and (5.8f) one respectively has

$$U\hat{\theta}^e c_v^e = \hat{q}_i^e n_i \tag{5.17a}$$

$$\hat{Q}_{ij}^e = -\frac{\ell_e^2 \hat{\theta}^e c_v^e n_i n_j}{\tau_{2e}} \tag{5.17b}$$

$$U\hat{\theta}^p c_v^p = \hat{q}_i^p n_i \tag{5.17c}$$

$$\hat{Q}_{ij}^p = -\frac{\ell_p^2 \hat{\theta}^p c_v^p n_i n_j}{\tau_{2p}} \tag{5.17d}$$

by coupling Eqs. (5.16a)-(5.16c) and Eqs. (5.16d)-(5.16f), respectively, the following Bernoully-type ODEs arise:

$$\frac{\delta \overline{\Theta}_e}{\delta t^\star} + \alpha_e \overline{\Theta}_e + \beta_e \overline{\Theta}_e^2 = 0 \tag{5.18a}$$

$$\frac{\delta \overline{\Theta}_p}{\delta t^\star} + \alpha_p \overline{\Theta}_p + \beta_p \overline{\Theta}_p^2 = 0 \tag{5.18b}$$

For the sake of computational convenience, in writing ODEs (5.18) we introduced the following non-dimensional variable

$$t^\star = t\left(\frac{1}{\tau_{1e}} + \frac{1}{\tau_{1p}}\right) \tag{5.19}$$

as well as the following non-dimensional functions

$$
\begin{aligned}
\overline{\Theta}_e &= \frac{\hat{\theta}^e \ell_e}{\theta_0} & \overline{\Theta}_p &= \frac{\hat{\theta}^p \ell_p}{\theta_0}\\
\alpha_e &= \frac{\left(\gamma_e^2 + \tau_e^\star \psi_e\right)\tau_{1p}}{2\left(\gamma_e + \varphi_e\right)\left(\gamma_e - 4\varphi_e\right)\left(\tau_{1e} + \tau_{1p}\right)} & \alpha_p &= \frac{\left(\gamma_p^2 + \tau_p^\star \psi_p\right)\tau_{1e}}{2\left(\gamma_p + \varphi_p\right)\left(\gamma_p - 4\varphi_p\right)\left(\tau_{1e} + \tau_{1p}\right)}\\
\beta_e &= \frac{\varphi_e \gamma_e^2 \tau_{1p}}{\left(\gamma_e + \varphi_e\right)\left(\gamma_e - 4\varphi_e\right)\left(\tau_{1e} + \tau_{1p}\right)}\sqrt{\frac{\tau_e^\star}{\psi_e}} & \beta_p &= \frac{\varphi_p \gamma_p^2 \tau_{1e}}{\left(\gamma_p + \varphi_p\right)\left(\gamma_p - 4\varphi_p\right)\left(\tau_{1e} + \tau_{1p}\right)}\sqrt{\frac{\tau_p^\star}{\psi_p}}\\
\gamma_e &= \frac{U^e}{U_0^e} & \gamma_p &= \frac{U^p}{U_0^p}\\
\tau_e^\star &= \frac{\tau_{1e}}{\tau_{2e}} & \tau_p^\star &= \frac{\tau_{1p}}{\tau_{2p}}
\end{aligned}
\tag{5.20}
$$

once Eqs(5.10)–(5.12) have been taken into account. If $\gamma_e \neq 4\varphi_e$ and $\gamma_p \neq 4\varphi_p$ then ODEs (5.18) can be solved to find

$$\overline{\Theta}_e(t^\star) = \frac{\overline{\Theta}_0}{e^{\alpha_e t^\star} + \overline{\Theta}_0 \,{}_e \left(e^{\alpha_e t^\star} - 1\right)} \tag{5.21a}$$

$$\overline{\Theta}_p(t^\star) = \frac{\overline{\Theta}_0}{e^{\alpha_p t^\star} + \overline{\Theta}_0 \,{}_p \left(e^{\alpha_p t^\star} - 1\right)} \tag{5.21b}$$

wherein $\overline{\Theta}_0 = \overline{\Theta}_e\,(t^? \equiv 0) = \overline{\Theta}_p\,(t^? \equiv 0)$ are the initial conditions, and

$$ {}_e = \frac{2\varphi_e \gamma_e^2}{\gamma_e^2 + \tau_e^? \psi_e} \sqrt{\frac{\tau_e^?}{\psi_e}} \tag{5.22a} $$

$$ {}_p = \frac{2\varphi_p \gamma_p^2}{\gamma_p^2 + \tau_p^? \psi_p} \sqrt{\frac{\tau_p^?}{\psi_p}} \tag{5.22b} $$

When $\gamma_e = 4\varphi_e$ one simply has $\overline{\Theta}_e(t^?) = 0$, $\forall t^? \in \mathbb{R}^+$, as well as when $\gamma_p = 4\varphi_p$ one simply has $\overline{\Theta}_p(t^?) = 0$, $\forall t^? \in \mathbb{R}^+$.

Although in the very general case the initial condition on the temperature-wave amplitude $\overline{\Theta}_0$ may be either positive, or negative, here we assume $\overline{\Theta}_0 \in \mathbb{R}^+$. Under this assumption, below we comment more in detail some results arising from Eqs. (5.21).

## Positive Heat Waves

According with the observations made in Sec. 5.1.1, we start to observe that from Eqs. (5.20) one may have that

⑧ $\gamma_e > 4\varphi_e \Rightarrow \alpha_e > 0$, and $\gamma_p > 4\varphi_p \Rightarrow \alpha_p > 0$

⑧ $\gamma_e < 4\varphi_e \Rightarrow \alpha_e < 0$, and $\gamma_p < 4\varphi_p \Rightarrow \alpha_p < 0$

whereas from Eqs. (5.22) it follows that ${}_e > 0$ and ${}_p > 0$, when positive $H$-waves are propagating through the medium. In this situation the main cases below may occur.

1. If $\gamma_e > 4\varphi_e$ and $\gamma_p > 4\varphi_p$, then both $\overline{\Theta}_e$, and $\overline{\Theta}_p$ will decay to zero. We may claim, therefore, that in this case both the *EH*-waves, and the *P H*-waves will be damped.

2. If $\gamma_e < 4\varphi_e$ and $\gamma_p < 4\varphi_p$, then both $\overline{\Theta}_e$, and $\overline{\Theta}_p$ will blow-up, respectively, at the following finite values

$$ t_e^? = -\alpha_e^{-1} \ln\left(1 + \frac{1}{\overline{\Theta}_0\ {}_e}\right) \tag{5.23a} $$

$$ t_p^? = -\alpha_p^{-1} \ln\left(1 + \frac{1}{\overline{\Theta}_0\ {}_p}\right) \tag{5.23b} $$

We may claim, therefore, that in this case both the *EH*-waves, and the *P H*-waves will become shock waves.

### Negative Heat Waves

According with the observations made in Sec. 5.1.1, we start to observe that in the case of negative $H$-waves from Eqs. (5.20) one has $\alpha_e > 0$ and $\alpha_p > 0$, whereas from Eqs. (5.22) one has $\alpha_e < 0$ and $\alpha_p < 0$. By indicating with $\alpha_m = \min(|\alpha_e| ; |\alpha_p|)$, and with $\alpha_M = \max(|\alpha_e| ; |\alpha_p|)$, in this situation the cases below may occur.

1. If $\overline{\Theta}_0 \in \; 0; \alpha_M^{-1}$, then both $\overline{\Theta}_e$, and $\overline{\Theta}_p$ will decay to zero. We may claim, therefore, that in this case both the $EH$-waves, and the $PH$-waves will be damped.

2. If $\overline{\Theta}_0 = \alpha_M^{-1}$, then

   (a) $\overline{\Theta}_e$ will decay to zero, and $\overline{\Theta}_p$ will always remain constant (i.e., $\overline{\Theta}_p = -\alpha_p$, $\forall \hat{t} \in \mathbb{R}^+$), when $\alpha_p < \alpha_e$. We may claim, therefore, that in this case the $EH$-waves will be damped, and the $PH$-waves will not change their shapes.

   (b) $\overline{\Theta}_e$ will always remain constant (i.e., $\overline{\Theta}_e = -\alpha_e$, $\forall \hat{t} \in \mathbb{R}^+$), and $\overline{\Theta}_p$ will decay to zero, when $\alpha_e < \alpha_p$. We may claim, therefore, that in this case the $EH$-waves will not change their shapes, and the $PH$-waves will be damped.

3. If $\overline{\Theta}_0 \in \; \alpha_M^{-1}; \alpha_m^{-1}$, then

   (a) $\overline{\Theta}_e$ will decay to zero, and $\overline{\Theta}_p$ will blow-up at the finite value $\hat{t}_p$ given by Eq. (5.23b), when $\alpha_p < \alpha_e$. We may claim, therefore, that in this case the $EH$-waves will be damped, and the $PH$-waves will become shock waves.

   (b) $\overline{\Theta}_e$ will blow-up at the finite value $\hat{t}_e$ given by Eq. (5.23a), and $\overline{\Theta}_p$ will decay to zero, when $\alpha_e < \alpha_p$. We may claim, therefore, that in this case the $EH$-waves will become shock waves, and the $PH$-waves will be damped.

4. If $\overline{\Theta}_0 = \alpha_m^{-1}$, then

   (a) $\overline{\Theta}_e$ will always remain constant (i.e., $\overline{\Theta}_e = -\alpha_e$, $\forall \hat{t} \in \mathbb{R}^+$), and $\overline{\Theta}_p$ will blow-up at the finite value $\hat{t}_p$ given by Eq. (5.23b), when $\alpha_p < \alpha_e$. We may claim, therefore, that in this case the $EH$-waves will not change their shapes, and the $PH$-waves will become shock waves.

   (b) $\overline{\Theta}_e$ will blow-up at the finite value $\hat{t}_e$ given by Eq. (5.23a), and $\overline{\Theta}_p$ will always remain constant (i.e., $\overline{\Theta}_p = -\alpha_p$, $\forall \hat{t} \in \mathbb{R}^+$), when $\alpha_e < \alpha_p$. We may claim, therefore, that in this case the *EH*-waves will become shock waves, and the *P H*-waves will not change their shapes.

5. If $\overline{\Theta}_0 > {}_m^{-1}$, then $\overline{\Theta}_e$ will blow-up at the finite value $\hat{t}_e$ given by Eq. (5.23a), and $\overline{\Theta}_p$ will blow-up at the finite value $\hat{t}_p$ given by Eq. (5.23b). We may claim, therefore, that in this case both the *EH*-waves, and the *P H*-waves will become shock waves.

## 5.2 Thermodynamic considerations

In this section we prove the thermodynamic compatibility of the theoretical model expressed by Eqs. (5.1). To this aim, we put ourself in the context of EIT [4, 7, 34, 135, 136] and assume the following state space:

$$\Sigma = \left\{ \theta^e, q_i^e, Q_{ij}^e, \theta^p, q_i^p, Q_{ij}^p \right\}$$

Then we start from the local balance of the specific entropy, i.e., Eq. (1.84). According with the classical Liu procedure for the exploitation of the second law of thermodynamics [87], a linear combination of the specific-entropy production and of Eqs. (5.1) (which represent the constraints introduced by the state-space variables) has to be always non-negative along any admissible thermodynamic process. As a consequence, from the coupling of Eqs. (5.1) and the balance of the specific entropy, we have that the following extended entropy inequality

$$\begin{aligned}
&\dot{s} + J^s_{i,i} - \Lambda^e \left( \dot{\theta}^e + \frac{q^e_{i,i}}{c^e_v} \right) - \Lambda^p \left( \dot{\theta}^p + \frac{q^p_{i,i}}{c^p_v} \right) - \Lambda^e_i \left( \dot{q}^e_i + \frac{q^e_i}{\tau_{1e}} + \frac{\kappa_e \theta^e_{,i}}{\tau_{1e}} - \frac{2 q^e_j q^e_{j,i}}{c^e_v \theta^e} - \frac{Q^e_{ij,j}}{\tau_{1e}} \right) \\
&- \Lambda^p_i \left( \dot{q}^p_i + \frac{q^p_i}{\tau_{1p}} + \frac{\kappa_p \theta^p_{,i}}{\tau_{1p}} - \frac{2 q^p_j q^p_{j,i}}{c^p_v \theta^p} - \frac{Q^p_{ij,j}}{\tau_{1p}} \right) - \Lambda^e_{ij} \left( \dot{Q}^e_{ij} + \frac{Q^e_{ij}}{\tau_{2e}} - \frac{\ell^2_e q^e_{i,j}}{\tau_{2e}} \right) \\
&- \Lambda^p_{ij} \left( \dot{Q}^p_{ij} + \frac{Q^p_{ij}}{\tau_{2p}} - \frac{\ell^2_p q^p_{i,j}}{\tau_{2p}} \right) \geq 0
\end{aligned} \qquad (5.24)$$

has to be always fulfilled, whatever the thermodynamic process is. In the extended entropy inequality above the functions $\Lambda^e$, $\Lambda^e_i$, $\Lambda^e_{ij}$, $\Lambda^p$, $\Lambda^p_i$ and $\Lambda^p_{ij}$ are the so-called Lagrange multipliers; they may depend on the whole set of state-space variables, in principle.

The agreement of Eqs. (5.1) with second law of thermodynamics cannot be checked until constitutive assumptions on $s$ and $J^s_i$ have been given, since the latter functions do not belong to the state space. In order to remain on a very general level and let the second law give information about them, here we assume

$$s = s \; \theta^e, q_i^e, Q_{ij}^e, \theta^p, q_i^p, Q_{ij}^p \tag{5.25a}$$

$$J_i^s = J_i^s \; \theta^e, q_i^e, Q_{ij}^e, \theta^p, q_i^p, Q_{ij}^p \tag{5.25b}$$

The insertion of Eqs. (5.25) into inequality (5.24) leads (by straightforward calculations) to the following sets of necessary and sufficient conditions which guarantee that second law of thermodynamics is always fulfilled

$$\frac{\partial s}{\partial \theta^e} - \Lambda^e = 0 \tag{5.26a}$$

$$\frac{\partial s}{\partial q_i^e} - \Lambda_i^e = 0 \tag{5.26b}$$

$$\frac{\partial s}{\partial Q_{ij}^e} - \Lambda_{ij}^e = 0 \tag{5.26c}$$

$$\frac{\partial s}{\partial \theta^p} - \Lambda^p = 0 \tag{5.26d}$$

$$\frac{\partial s}{\partial q_i^p} - \Lambda_i^p = 0 \tag{5.26e}$$

$$\frac{\partial s}{\partial Q_{ij}^p} - \Lambda_{ij}^p = 0 \tag{5.26f}$$

and

$$\frac{\partial J_i^s}{\partial \theta^e} - \frac{\Lambda_i^e \kappa^e}{\tau_{1e}} = 0 \tag{5.27a}$$

$$\frac{\partial J_i^s}{\partial q_j^e} - \frac{\Lambda^e \delta_{ij}}{c_v^e} + \frac{2q_j^e \Lambda_i^e}{c_v^e \theta^e} + \frac{\Lambda_{ji}^e \ell_e^2}{\tau_{2e}} = 0 \tag{5.27b}$$

$$\frac{\partial J_i^s}{\partial Q_{jk}^e} + \frac{\Lambda_j^e \delta_{ik}}{\tau_{1e}} = 0 \tag{5.27c}$$

$$\frac{\partial J_i^s}{\partial \theta^p} - \frac{\Lambda_i^p \kappa^p}{\tau_{1p}} = 0 \tag{5.27d}$$

$$\frac{\partial J_i^s}{\partial q_j^p} - \frac{\Lambda^p \delta_{ij}}{c_v^p} + \frac{2q_j^p \Lambda_i^p}{c_v^p \theta^p} + \frac{\Lambda_{ji}^p \ell_p^2}{\tau_{2p}} = 0 \tag{5.27e}$$

$$\frac{\partial J_i^s}{\partial Q_{jk}^p} + \frac{\Lambda_j^p \delta_{ik}}{\tau_{1p}} = 0 \tag{5.27f}$$

together with the following reduced entropy inequality:

$$\frac{q_i^e}{\tau_{1e}} \frac{\partial s}{\partial q_i^e} + \frac{Q_{ij}^e}{\tau_{2e}} \frac{\partial s}{\partial Q_{ij}^e} + \frac{q_i^p}{\tau_{1p}} \frac{\partial s}{\partial q_i^p} + \frac{Q_{ij}^p}{\tau_{2p}} \frac{\partial s}{\partial Q_{ij}^p} \leq 0 \tag{5.28}$$

According with the thermodynamic restrictions in Eqs. (5.25)-(5.27), by direct calculations it is indeed possible to verify that the two-temperature model based on

Eqs. (5.1) always agrees with second law if, for example, the following generalized forms of the specific entropy and specific-entropy flux are used, respectively,

$$
\begin{aligned}
s = s_0\left(\theta^e, \theta^p\right) &- \frac{\tau_{1e}}{2\kappa_e \theta^{e2}} q_i^e q_i^e - \alpha_i^e Q_{ij}^e q_j^e - \frac{\tau_{2e}}{2\kappa_e \theta^{e2} \ell_e^2} Q_{ij}^e Q_{ij}^e \\
&- \frac{\tau_{1p}}{2\kappa_p \theta^{p2}} q_i^p q_i^p - \alpha_i^p Q_{ij}^p q_j^p - \frac{\tau_{2p}}{2\kappa_p \theta^{p2} \ell_p^2} Q_{ij}^p Q_{ij}^p
\end{aligned}
\qquad (5.29a)
$$

$$
J_i^s = \frac{q_i^e}{\theta^e} + \frac{q_i^p}{\theta^p} - \frac{\kappa_e Q_{ij}^e}{\tau_{1e}} \int \alpha_i^e d\theta^e - \frac{\kappa_p Q_{ij}^p}{\tau_{1p}} \int \alpha_i^p d\theta^p \qquad (5.29b)
$$

wherein $s_0(\theta^e, \theta^p)$ is the local-equilibrium entropy, and

$$
\alpha_i^e = \alpha^e\left(\theta^e\right) \frac{q_i^e}{\| q_i^e \|} \qquad (5.30a)
$$

$$
\alpha_i^p = \alpha^p\left(\theta^p\right) \frac{q_i^p}{\| q_i^p \|} \qquad (5.30b)
$$

are suitable vector-valued functions, with $\alpha^e = \alpha^e(\theta^e)$ and $\alpha^p = \alpha^p(\theta^p)$ being suitable scalar-valued functions of the indicated arguments, and $\| q_i^e \|$ and $\| q_i^p \|$ being the moduli of the indicated vectors.

The above considerations allow us to claim that the two-temperature model introduced by Eqs. (5.1) has well-posed theoretical basis.

# Chapter 6

# Conclusions and perspectives

Thermal waves have been an inspiring topic in modern nonequilibrium thermodynamics. Indeed, whereas the classical transport theory based on FL predicts an infinite speed for very high frequency, the observed speed is finite. Thermal waves have fostered research on generalized transport equations leading to finite speed in this limit. In their turn, these generalized transport equations have provided a fruitful challenge to nonequilibrium thermodynamics, because they are not compatible with the positive-definite character of the local-equilibrium entropy and, therefore, new constitutive equations for the entropy have been searched in order to achieve compatibility of these transport laws with the second law of thermodynamics. These theoretical aspects are nowadays reasonably understood, but there is still a wide field of research for practical applications of thermal waves. For instance, in gases they have been useful to explore ultrasound and hypersound velocities, and to check different higher-order approximations to the solutions of Boltzmann equation. From the other hand, in superfluids the thermal waves represent a very useful tool to explore the length density of quantized vortex lines. Moreover, thermal waves may also provide dynamical information that is lacking from usual steady-state measurements. A very compelling challenge is to search from suitable thermal models what information could be obtained from these kinds of measurements. Therefore, starting from the formulation of heat-transport model beyond the classical FL, this thesis is principally devoted to the exploitation of heat waves, the analysis of which may be interesting for the possible analysis of nanomaterial properties.

In more details, after that a brief summary of the main mathematical tools and of the theoretical physical background is made in Chapter 1, in Chapter 2 a theoretical model based on the MC equation has been used to point out the role played by the composition gradient on the speed and the amplitude of heat waves. The obtained results may be interesting for practical applications. For example, imagine that a component on a chip made of a FGM is perturbing the surrounding system since it is the source of thermal disturbances with an initial temperature-amplitude. Then one may face with the following two problems:

- *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 $c_{,i}$ changes between them if no information loss are required.

- *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 $c_{,i}$ changes in space between them in order to have a good isolation.

It has to be noted that in the above analysis the different material functions have been supposed to depend both on the temperature, and on the stoichiometric variable. In the very general case, indeed, material functions as for example $c_v$ and $\kappa$ should depend on the whole set of the state-space variables, i.e., in developing that theoretical model we should had supposed both $c_v = c_v(\theta, q_i, c)$, and $\kappa = \kappa(\theta, q_i, c)$. Although still possible, those assumptions would have lead to several complications in the calculations in view of other nonlinear terms. From the practical point of view, the simplifying assumptions mean that the proposed 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) nonlocal effects, too. To do this, an interesting way is to replace MC equation with the following evolution equation for the heat flux

$$\tau_1 \dot{q}_i + q_i + \kappa \theta_{,i} = \sum_{k=1}^{N} \ell^2 \tau_1^{k-1} \frac{\partial^{k-1}}{\partial t^{k-1}} q_{i,jj} - \tau_1^{k+1} \frac{\partial^{k+1}}{\partial t^{k+1}} q_i \qquad (6.1)$$

which has been derived in Ref. [137] in the framework of EIT [4] by letting $N$ higher-order thermodynamic fluxes belong to the state space. Observing that the thermal conductivity may be frequency dependent [138], we note that Eq. (6.1), which reduces to MC equation 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 [137].

Since in the last decades 1-dimensional nanostructures (such as wires, rods, belts and tubes) have drawn significant attention owing to their potential application in photonics and energy conversion devices, the continuous reduction of their sizes brings up new questions concerning the analysis of heat transport. Several experiments or simulations on heat transport along these devices demonstrated that they exhibit a strong size dependence of their electronic and optical properties. Indeed, due to the small sizes of the systems, the gradients of the heat flux will be important as well as temperature gradients, and their nonlinear effects will be no longer negligible. It is, therefore, important to examine more deeply the influence of nonlocal and nonlinear effects, and generalized heat transport equations must be looked for.

As a consequence, in Chapter 3 we focused our attention especially on nonlocal and pure nonlinear model equations since one of the current hot topics in heat transport is the so-called phononics (wherein classical nonlinear effects are explored for the development of heat rectifiers and heat amplifiers analogous to those used so successfully in electronics), in fact, the analysis of new kinds of nonlocal and nonlinear effects seems especially appropriate. In the special case of pulse propagations, the role played by nonlocal and nonlinear effects has been investigated both in the case of a rigid body, and in the case of a deformable body. In the study of thermoelastic waves, in fact, the role of nonlinear effects may be especially important in miniaturized systems, in structured solids, or disordered solids with local stress: for instance, in the last two decades the study of nonlinear thermoelastic coupling in nanosystems became important due to its application in the analysis of ultrafast-laser pulses, or in the manufacturing of devices with high-frequency switching.

A point for the future research in this field would be considering how elastic stresses may modify the value of the thermal conductivity, and how a heat flux may modify the values of the elastic coefficients. These couplings would allow a practically useful method to control phonon propagation (namely, the heat transfer along the system) by applying suitable external mechanical stresses on it. In particular, these applied stress could be inhomogeneous, in such a way that though the system was homogeneous from the compositional point of view, it would become a graded system (namely, a system where the value of the parameters depends in a controlled way on the position along the system). Such future explorations would then combine results of Chapter 2 in this thesis on wave propagation in graded systems with results in Chapter 3, with non-linear thermal and elastic effects.

The great interest in generalizing the linear theory of heat waves has been, up to now, a fruitful stimulus to generalizations of non-equilibrium to nonlinear situations, namely, for waves with sufficiently high amplitudes. In nanosystems, indeed, nonlinear effects may be understood not only as the presence of nonlinear products of the temperature gradient (or the heat flux) in the transport equation, but also a state-space variable dependence in the material functions. Along with the latter point of view, in Chapter 4 a nonlinear evolution equation for the heat flux has been derived in a conservation-dissipation formalism in the framework of extended thermodynamics. In the case of high-frequency heat waves, that theoretical proposal leads to an equation which is analogous to the equation for electromagnetic wave in nonlinear optics, in such a way that some well-known problems of nonlinear optics (e.g., the second-harmonic generation, the so-called Kerr effect) can be investigated also in the case of heat transfer. To this end we observe that considering nonlinear electromagnetic waves and thermal waves is necessary in practical situations using intense and swept laser pulses to heat a solid. In particular, the results obtained in this chapter follows from the dependence of the relaxation time $\tau_1$ and the thermal conductivity $\kappa$ on the local value of heat flux $q_i$. These features could be exploited for new applications of heat transport: for instance, the aforementioned dependence of $\tau_1$ and $\kappa$ on $q$ could be used to externally control the speed of propagation of heat waves by imposing on a thin nanolayer a steady heat flux $q_0$ perpendicular to the layer. In this case, in fact, if the region wherein the transversal heat flux has been imposed displays curved boundaries, suitable heat lenses could be produced to focalize the heat waves in a priori chosen focal point, the position of which depending on the local intensity of the heat waves. This would be especially interesting, for instance, for the measurement of the intensity and the frequency of heat waves. The use of the external heat flux $q_0$ has the advantages of producing the heat lenses for some interval of time, and eliminating them when they are no longer necessary. In Ref. [120] heat lenses for thermal pulses have been also proposed by inserting in a material $A$ a small region of a material $B$ having curved boundaries. However, this kind of heat lenses is static since they cannot be easily changed, in contrast with imposing a perpendicular external heat flux over a given region of the system.

It is worth to be noted that a deeper comparison of the nonlinear equation for phonons and the equation of nonlinear optics seems promising, because of the very extensive work which has been done in the latter field. This may suggest new physical effects, new applications, and new mathematical techniques in the domain of nonlinear heat transport. Higher harmonic generation, or externally induced focalization, self-focusing of intense signals, or the existence of solitonic solutions may find some applications in the future. In particular, soliton transport may play an interesting role for the transmission of information by means of heat signals. Recently, Sciacca *et al.* [139] have explored some kinds of heat solitons in nanowires with nonlinear heat exchange with the environment, and they have computed the energy associated to the transport of a single bit of information, which depends on the kind of soliton being used to transport it. This may be the subject of future research, too.

The analysis of coupled processes is another outstanding feature of nonequilibrium thermodynamics, and represents an active challenge in practical applications in materials sciences, high-power lasers, and optimization of energy generation. Much emphasis is put nowadays, for example, on the application of the coupling of heat and electricity. From the point of view of heat transport, the most important consequence of such a coupling is that the family of heat carriers is no longer constituted by the phonons only, as it happens in dielectric crystals at low temperature, since electrons and/or holes may contribute to the heat transport. For this reason, finally in Chapter 5 the Extended-Thermodynamic approach has been used to model heat transport due to phonons and electrons, under the hypothesis that the energy and entropy productions due to the presence of an electromagnetic field are negligible. Therein particular emphasis has been given both to nonlocal and to nonlinear effects which are evident in situations wherein the mean-free path of the heat carriers is higher than the characteristic length of the system. Since the phonon mean-free path and the electron mean-free path may be considerably different from each other, the size of the system may have different effects on both constituents and, therefore, it may allow a high degree of control of the transport properties of systems, at spatial scales comparable to the mean-free path of some of the species.

Note that a model considering nonlocal effects in phonons and in electrons could be extrapolated to superconductors. There, instead of having an electron flow, one has a flow of Cooper electron pairs. Due to the macroscopic coherence of the collective wavefunction of the system, there is a relatively long correlation length which, in contrast to what we have been examined in Chapter 5, would be due to quantum effects rather than to the mean free path. In the future, it would be interesting to explore this perspective. Indeed, superfluidity has been the subject of much work in extended thermodynamics, but not yet superconductivity. Thus, one open way to the future is the extrapolation of some of the hydrodynamic behaviour of electrons studied here to the field of superconductivity.

# Acknowledgements

I acknowledge the Italian ”Gruppo Nazionale per la Fisica Matematica” (GNFM-INdAM) and the University of Salerno for supporting me in my stay at the Department of Physics of the Autonomous University of Barcelona in January and September 2019.

Throughout my Ph.D program I have received a great deal of support and assistance.

I would first like to thank my supervisor, Professor Antonio Sellitto, whose expertise was invaluable in formulating the research questions and methodology.

I would also like to thank Professor David Jou, for his excellent suggestions, constructive encouragement and openness to implement new ideas along my work.

Alla mia famiglia, senza la quale tutto questo non sarebbe stato possibile.
Agli amici veri, perché la distanza fisica non è distanza tra i cuori.
All’amore, che fa sorridere il cuore. *R&S*.

# Bibliography


[1] I. Müller and T. Ruggeri, *Rational Extended Thermodynamics*. New York: Springer, second ed., 1998.

[2] G. Lebon, D. Jou, and J. Casas-V´azquez, *Understanding non-equilibrium thermodynamics*. Berlin: Springer, 2008.

[3] V. A. Cimmelli, "Different thermodynamic theories and different heat conduction laws," *J. Non-Equilib. Thermodyn.*, vol. 34, pp. 299–333, 2009.

[4] D. Jou, J. Casas-V´azquez, and G. Lebon, *Extended Irreversible Thermodynamics*. Berlin: Springer, fourth revised ed., 2010.

[5] M. Wang, B.-Y. Cao, and Z.-Y. Guo, "General heat conduction equations based on the thermomass theory," *Front. Heat Mass Transf.*, vol. 1, p. 013005, 2010.

[6] D. Y. Tzou, *Macro- to Microscale Heat Transfer: The Lagging Behaviour*. United Kingdom: Wiley, second ed., 2014.

[7] A. Sellitto, V. A. Cimmelli, and D. Jou, *Mesoscopic Theories of Heat Transport in Nanosystems*, vol. 6 of *SEMA-SIMAI Springer Series*. Springer International Publishing, 2016.

[8] M. Mongiov´ı, D. Jou, and M. Sciacca, "Non-equilibrium thermodynamics, heat transport and thermal waves in laminar and turbulent superfluid helium," *Physics Reports*, vol. 726, pp. 1–72, 2018.

[9] P. Rogolino, R. Kovács, P. Ván, and V. A. Cimmelli, "Generalized heat-transport equations: parabolic and hyperbolic models," *Contin. Mech. Thermodyn.*, vol. 30, pp. 1245–1258, 2018.

[10] F. Vázquez, J. del Río, and A. Aguirre, "Nonlinear heat waves in extended irreversible thermodynamics," *J. Non-Equilib. Thermodyn.*, vol. 20, pp. 252–262, 1995.

[11] B. Straughan, *Heat waves*. Berlin: Springer, 2011.

[12] P. Ván and T. Fülöp, "Universality in heat conduction theory: weakly nonlocal thermodynamics," *Ann. Phys.*, vol. 524, pp. 470–478, 2012.

[13] A. H. Akbarzadeh, Y. Cuib, and Z. T. Chen, "Thermal wave: from nonlocal continuum to molecular dynamics," *RSC Adv.*, vol. 7, pp. 13623–13636, 2017.

[14] R. Kovács and P. Ván, "Generalized heat conduction in heat pulse experiments," *Int. J. Heat Mass Transfer*, vol. 83, pp. 613–620, 2015.

[15] L. Zhang, X. Zhang, and S. Peng, "Wave propagation model of heat conduction and group speed," *Continuum Mech. Thermodyn.*, vol. 30, pp. 879–887, 2018.

[16] D. Jou and J. Casas-Vázquez, "Nonequilibrium absolute temperature, thermal waves and phonon hydrodynamics," *Physica A*, vol. 163, pp. 47–58, 1990.

[17] J. Shiomi and S. Maruyama, "Non-Fourier heat conduction in a single-walled carbon nanotube: Classical molecular dynamics simulations," *Phys. Rev. B*, vol. 73, p. 205420 (7 pages), 2006.

[18] D. Jou and A. Sellitto, "Focusing of heat pulses along nonequilibrium nanowires," *Phys. Lett. A*, vol. 374, pp. 313–318, 2009.

[19] D. Jou, A. Sellitto, and F. X. Álvarez, "Heat waves and phonon-wall collisions in nanowires," *Proc. R. Soc. A*, vol. 467, pp. 2520–2533, 2011.

[20] D.-S. Tang, Y.-C. Hua, and B.-Y. Cao, "Thermal wave propagation through nanofilms in ballistic-diffusive regime by Monte Carlo simulations," *Int. J. Therm. Sci.*, vol. 109, pp. 81–89, 2016.

[21] F. Vázquez, A. Figueroa, and I. Rodríguez-Vargas, "Nonlocal and memory effects in nanoscaled thermoelectric layers," *J. Appl. Phys.*, vol. 121, p. 014311 (4 pages), 2017.

[22] A. Sellitto and M. Di Domenico, "Nonlocal and nonlinear contributions to the thermal and elastic high-frequency wave propagations at nanoscale," *Continuum Mech. Thermodyn.*, vol. 31, pp. 807–821, 2019.

[23] F. Vázquez, P. Ván, and R. Kovács, “Ballistic-diffusive model for heat transport in superlattices and the minimum effective heat conductivity,” *Entropy*, vol. 22, p. 167 (15 pages), 2020.

[24] M. Först, C. Manzoni, S. Kaiser, Y. Tomioka, Y. Tokura, R. Merlin, and A. Cavalleri, “Nonlinear phononics as an ultrafast route to lattice control,” *Nature Phys.*, vol. 7, pp. 854–856, 2011.

[25] N. Li, J. Ren, L. Wang, G. Zhang, P. Hänggi, and B. Li, “Colloquium: Phononics: Manipulating heat flow with electronic analogs and beyond,” *Rev. Mod. Phys.*, vol. 84, pp. 1045–1066, 2012.

[26] A. Subedi, A. Cavalleri, and A. Georges, “Theory of nonlinear phononics for coherent light-control of solids,” *Phys. Rev. B*, vol. 89, p. 220301, 2013.

[27] G. Wehmeyer, T. Yabuki, C. Monachon, J. Wu, and C. Dames, “Thermal diodes, regulators, and switches: Physical mechanisms and potential applications,” *Appl. Phys. Rev.*, vol. 4, p. 041304, 2017.

[28] A. von Hoegen, R. Mankowsky, M. Fechner, M. Först, and A. Cavalleri, “Probing the interatomic potential of solids with strong-field nonlinear phononics,” *Nature*, vol. 555, no. 7694, pp. 79–82, 2018.

[29] D. Jou and L. Restuccia, “Mesoscopic transport equations and contemporary thermodynamics: an introduction,” *Contemp. Phys.*, vol. 52, pp. 465–474, 2011.

[30] V. A. Cimmelli, D. Jou, T. Ruggeri, and P. Van, “Entropy principle and recent results in non-equilibrium theories,” *Electronic Open Journal Entropy*, vol. 16, no. 3, pp. 1756–1807, 2014.

[31] D. D. Joseph and L. Preziosi, “Heat waves,” *Rev. Mod. Phys.*, vol. 61, pp. 41–73, 1989.

[32] M. Honner, “Heat waves simulation,” *Comput. Math. Appl.*, vol. 38, pp. 233–243, 1999.

[33] Y. Dong, B.-Y. Cao, and Z.-Y. Guo, “Generalized heat conduction laws based on thermomass theory and phonon hydrodynamics,” *J. Appl. Phys.*, vol. 110, p. 063504 (6 pages), 2011.

[34] T. Ruggeri and M. Sugiyama, *Rational Extended Thermodynamics beyond the Monatomic Gas*. Berlin: Springer, 2018.

[35] F. X. Álvarez, J. Casas-Vázquez, and D. Jou, "Robustness of the nonequilibrium entropy related to the maxwell-cattaneo heat equation," *Rev. E*, *Phys.* vol. 77, p. 031110, 2008.

[36] V. A. Cimmelli, A. Sellitto, and D. Jou, "Nonequilibrium temperatures, heat waves, and nonlinear heat transport equations," *Phys. Rev. B*, vol. 81, p. 054301 (9 pages), 2010.

[37] A. Sellitto, V. A. Cimmelli, and D. Jou, "Analysis of three nonlinear effects in a continuum approach to heat transport in nanosystems," *Physica D*, vol. 241, pp. 1344–1350, 2012.

[38] C. de Tomas, A. Cantarero, A. F. Lopeandia, and F. X. Álvarez, "Form kinetic to collective behavior in thermal transport on semiconductors and semiconductor nanostructures," *J. Appl. Phys.*, vol. 115, p. 164314, 2014.

[39] D.-S. Tang, Y.-C. Hua, B.-D. Nie, and B.-Y. Cao, "Phonon wave propagation in ballistic-diffusive regime," *J. Appl. Phys.*, vol. 119, p. 124301, 2016.

[40] P. Ván, "Weakly nonlocal irreversible thermodynamics," *Ann. Phys.*, vol. 12, pp. 146–173, 2003.

[41] C. Wang and C. Truesdell, *Introduction to Rational Elasticity*. Netherlands: Springer, 1973.

[42] A. Romano, *Thermomechanics of phase transitions in classical field theory*. Singapore: World Scientific, 1993.

[43] T. Thomas, *Plastic Flow and Fracture in Solids*. New York: Academic Press, 1961.

[44] C. Truesdell and R. A. Toupin, *The classical field theories, Hand. of Phys., Vol. III/1*. Berlin: Springer Verlag, first ed., 1960.

[45] P. J. Chen, *Growth and decay of waves in solids. In Flügge, S. and Truesdell, C., editors, Handbuch der Physik, volume VIa/3, pages 303-402*. Berlin: Springer, 1973.

[46] A. Sellitto, V. Tibullo, and Y. Dong, "Nonlinear heat-transport equation beyond fourier law: Application to heat-wave propagation in isotropic thin layers," *Continuum Mech. Thermodyn.*, vol. 29, pp. 411–428, 2017.

[47] R. Luzzi, A. R. Vasconcellos, J. Casas-Vázquez, and D. Jou, "Characterization and measurement of a nonequilibrium temperature-like variable in irreversible thermodynamics," *Physica A*, vol. 234, pp. 699–714, 1997.

[48] D. Jou, V. A. Cimmelli, and A. Sellitto, "Nonequilibrium temperatures and second-sound propagation along nanowires and thin layers," *Phys. Lett. A*, vol. 373, pp. 4386–4392, 2009.

[49] D. Jou and L. Restuccia, "Caloric and entropic temperatures in non-equilibrium steady states," *Physica A*, vol. 460, pp. 246–253, 2016.

[50] L. Marin, "Numerical solution of the Cauchy problem for steady-state heat transfer in two-dimensional functionally graded materials," *Int. J. Solids Struct.*, vol. 42, pp. 4338–4351, 2005.

[51] V. N. Burlayenko, H. Altenbach, T. Sadowski, S. D. Dimitrova, and A. Bhaskar, "Modelling functionally graded materials in heat transfer and thermal stress analysis by means of graded finite elements," *Appl. Math. Modell.*, vol. 45, pp. 422–438, 2017.

[52] M. Ciarletta, A. Sellitto, and V. Tibullo, "Heat-pulse propagation in functionally graded thin layers," *Int. J. Engng. Sci.*, vol. 119, pp. 78–92, 2017.

[53] C. Cattaneo, "Sulla conduzione del calore," *Atti Sem. Mat. Fis. Univ. Modena*, vol. 3, pp. 83–101, 1948.

[54] B. D. Coleman and W. Noll, "The thermodynamics of elastic materials with heat conduction and viscosity," *Arch. Ration. Mech. Anal.*, vol. 13, pp. 167–178, 1963.

[55] W. Muschik and H. Ehrentraut, "An amendment to the Second Law," *J. Non-Equilib. Thermodyn.*, vol. 21, pp. 175–192, 1996.

[56] G. Lebon, "Heat conduction at micro and nanoscales: A review through the prism of Extended Irreversible Thermodynamics," *J. Non-Equilib. Thermodyn.*, vol. 39, pp. 35–59, 2014.

[57] J. Verhás, "On the entropy current," *J. Non-Equilib. Thermodyn.*, vol. 8, pp. 201–206, 1983.

[58] A. Sellitto, V. A. Cimmelli, and D. Jou, "Entropy flux and anomalous axial heat transport at the nanoscale," *Phys. Rev. B*, vol. 87, p. 054302 (7 pages), 2013.

[59] J. A. Reissland, *The physics of phonons*. London: John Wiley and Sons, 1973.

[60] R. L. Liboff, *Kinetic theory (classical, quantum and relativistic description)*. Englewood Cliffs, New Jersey: Prentice Hall, 1990.

[61] J. M. Ziman, *Electrons and Phonons*. Oxford: Oxford University Press, 2001.

[62] S. Lee, D. Broido, K. Esfarjani, and G. Chen, "Hydrodynamic phonon transport in suspended graphene," *Nature Comm.*, vol. 6, p. 6290 (9 pages), 2015.

[63] M. J. Fryer and H. Struchtrup, "Moment model and boundary conditions for energy transport in the phonon gas," *Cont. Mech. Thermodyn.*, vol. 26, pp. 593–618, 2014.

[64] A. Sellitto, I. Carlomagno, and D. Jou, "Two-dimensional phonon hydrodynamics in narrow strips," *Proc. R. Soc. A*, vol. 471, p. 20150376 (13 pages), 2015.

[65] G.-X. Wang and V. Prasad, "Microscale heat and mass transfer and non-equilibrium phase change in rapid solidification," *Mater. Sci. Eng. A*, vol. 292, pp. 142–148, 2000.

[66] I. H. Chowdhury and X. Xu, "Heat transfer in femtosecond laser processing of metal," *Numer. Heat Transfer, Part A*, vol. 44, pp. 219–232, 2003.

[67] G. Chen, *Nanoscale Energy Transport and Conversion - A Parallel Treatment of Electrons, Molecules, Phonons, and Photons*. Oxford: Oxford University Press, 2005.

[68] Z. M. Zhang, *Nano/Microscale Heat Transfer*. New York: McGraw-Hill, 2007.

[69] D. C. Cahill, W. K. Ford, K. E. Goodson, G. D. Mahan, A. Majumdar, H. J. Maris, R. Merlin, and S. R. Phillpot, "Nanoscale thermal transport," *J. Appl. Phys.*, vol. 93, no. 2, pp. 793–818, 2003.

[70] D. G. Cahill, P. V. Braun, G. Chen, D. R. Clarke, S. Fan, K. E. Goodson, P. Keblinski, W. P. King, G. D. Mahan, A. Majumdar, H. J. Maris, S. R. Phillpot, E. Pop, and L. Shi, "Nanoscale thermal transport. II. 2003-2012," *Appl. Phys. Rev.*, vol. 1, no. 1, p. 011305 (45 pages), 2014.

[71] R. A. Guyer and J. A. Krumhansl, "Solution of the linearized phonon Boltzmann equation," *Phys. Rev.*, vol. 148, pp. 766–778, 1966.

[72] P. Ván, "Weakly nonlocal irreversible thermodynamics – the Guyer-Krumhansl and the Cahn-Hilliard equations," *Phys. Lett. A*, vol. 290, pp. 88–92, 2001.

[73] S. Suresh and A. Mortensen, *Fundamentals of Functionally Graded Materials*. London: IOM Communications Limited, 1998.

[74] Y. Miyamoto, W. A. Kaysser, B. H. Rabin, A. Kawasaki, and R. G. Ford, *Functionally Graded Materials: Design, Processing and Applications*. Dordrecht: Kluwer Academic, 1999.

[75] V. Birman and L.W. Byrd, "Modeling and analysis of functionally graded materials and structures," *Appl. Mech. Rev.*, vol. 60, pp. 195–216, 2007.

[76] D. Jou, I. Carlomagno, and V. A. Cimmelli, "Rectification of low-frequency thermal waves in graded $Si_cGe_{1-c}$," *Phys. Lett. A*, vol. 380, pp. 1824–1829, 2016.

[77] A. Witvrouw and A. Mehta, "The Use of Functionally Graded Poly-SiGe Layers for MEMS Applications," in *Functionally Graded Materials VIII*, vol. 492 of *Materials Science Forum*, pp. 255–260, Trans Tech Publications, 2005.

[78] Z. Lee, C. Ophus, L. M. Fischer, N. Nelson-Fitzpatrick, K. L. Westra, S. Evoy, V. Radmilovic, U. Dahmen, and D. Mitlin, "Metallic NEMS components fabricated from nanocomposite Al-Mo films," *Nanotechnology*, vol. 17, pp. 3063–3070, 2006.

[79] F. Ebrahimi and E. Salari, "Nonlocal thermo-mechanical vibration analysis of functionally graded nanobeams in thermal environment," *Acta Astronaut.*, vol. 113, pp. 29–50, 2015.

[80] Gururaja Udupa, S. Shrikantha Rao, and K. Gangadharan, "Functionally graded composite materials: An overview," *Procedia Materials Science*, vol. 5, pp. 1291 – 1299, 2014.

[81] B.-Y. Cao, M. Di Domenico, B.-D. Nie, and A. Sellitto, "Influence of the composition gradient on the propagation of heat pulses in functionally graded nanomaterials," *Proc. Math. Phys. Eng. Sci.*, vol. 475, p. 20180499 (15 pages), 2019.

[82] C. G. Littlejohns, M. Nedeljkovic, C. F. Mallinson, J. F. Watts, G. Z. Mashanovich, G. T. Reed, and F. Y. Gardes, "Next Generation Device Grade Silicon-Germanium on Insulator," *Scientific Reports*, vol. 5, p. 8882 (6 pages), 2015.

[83] H. Machrafi and G. Lebon, "Effective Thermal Conductivity of Spherical Particulate Nanocomposites: Comparison with Theoretical Models, Monte Carlo Simulations and Experiments," *Int. J. Nanosci.*, vol. 13, p. 1450022 (7 pages), 2014.

[84] F. Hao, D. Fang, and Z. Xu, "Thermal transport in crystalline Si/Ge nanocomposites: Atomistic simulations and microscopic models," *Appl. Phys. Lett.*, vol. 100, p. 091903 (4 pages), 2012.

[85] F. Shäffler, *Properties of Advanced Semiconductor Materials - GaN, AlN, InN, BN, SiC, SiGe*, ch. 6, pp. 149–188. John Wiley and Sons, Inc., New York: Eds. M. H. Levinshtein and S. L. Rumyantsev and M. S. Shur, 2001. Chapter Title: Silicon-Germanium ($Si_{1-x}Ge_x$).

[86] V. A. Cimmelli, "Boundary conditions in the presence of internal variables," *J. Non-Equilib. Thermodyn.*, vol. 27, pp. 327–334, 2002.

[87] I.-S. Liu, "Method of Lagrange multipliers for exploitation of entropy principle," *Arch. Ration. Mat. Anal.*, vol. 46, pp. 131–138, 1972.

[88] V. A. Cimmelli, A. Sellitto, and V. Triani, "A new thermodynamic framework for second-grade Korteweg-type viscous fluids," *J. Math. Phys.*, vol. 50, p. 053101 (15 pages), 2009.

[89] F. Vázquez and J. A. del Río, "Thermodynamic characterization of the diffusive transport to wave propagation transition in heat conducting thin films," *J. Appl. Phys.*, vol. 112, p. 123707 (8 pages), 2012.

[90] D.-S. Tang and B.-Y. Cao, "Ballistic thermal wave propagation along nanowires modeled using phonon Monte Carlo simulations," *Appl. Therm. Eng.*, vol. 117, pp. 609–616, 2017.

[91] A. Sellitto, "Crossed nonlocal effects and breakdown of the Onsager symmetry relation in a thermodynamic description of thermoelectricity," *Physica D*, vol. 243, pp. 53–61, 2014.

[92] Y. J. Yu, X.-G. Tian, and Q.-L. Xiong, "Nonlocal thermoelasticity based on nonlocal heat conduction and nonlocal elasticity," *Eur. J. Mech. A Solid*, vol. 60, pp. 238–253, 2016.

[93] D. S. Chandrasekharaiah, "Thermoelasticity with second sound: A review," *Appl. Mech. Rev.*, vol. 39, pp. 355–376, 1986.

[94] V. A. Cimmelli, A. Sellitto, and D. Jou, "Nonlinear evolution and stability of the heat flow in nanosystems: Beyond linear phonon hydrodynamics," *Phys. Rev. B*, vol. 82, p. 184302 (9 pages), 2010.

[95] M. Wang and Z.-Y. Guo, "Understanding of temperature and size dependences of effective thermal conductivity of nanotubes," *Phys. Lett. A*, vol. 374, pp. 4312–4315, 2010.

[96] M. Wang, X. Shan, and N. Yang, "Understanding length dependences of effective thermal conductivity of nanowires," *Phys. Lett. A*, vol. 376, pp. 3514–3517, 2012.

[97] P. M. Jordan, "Second-sound propagation in rigid, nonlinear conductors," *Mech. Res. Commun.*, vol. 68, pp. 52–79, 2015.

[98] Y. Guo, D. Jou, and M. Wang, "Understanding of flux-limited behaviors of heat transport in nonlinear regime," *Phys. Lett. A*, vol. 380, no. 3, pp. 452–457, 2015.

[99] R. Kovács and P. Rogolino, "Numerical treatment of nonlinear Fourier and Maxwell-Cattaneo-Vernotte heat transport equations," *Int. J. Heat Mass Transf.*, vol. 150, p. 119281 (7 pages), 2020.

[100] S. Carrilo and P. M. Jordan, "On the propagation of temperature-rate waves and traveling waves in rigid conductors of the Graffi-Franchi-Straughan type," *Math. Comput. Simulat.*, vol. 16, pp. 120–133, 2020.

[101] M. Di Domenico, D. Jou, and A. Sellitto, "Nonlinear heat waves and some analogies with nonlinear optics," *Int. J. Heat Mass Transfer*, vol. 156, p. 119888 (8 pages), 2020.

[102] C. D. Levermore, "Relating Eddington factors to flux limiters," *J. Quant. Spec. Rad. Transfer.*, vol. 31, pp. 149–160, 1984.

[103] G. Lebon, M. Ruggieri, and A. Valenti, "Extended thermodynamics revisited: renormalized flux variables and second sound in rigid solids," *J. Phys.: Condens. Matter*, vol. 20, p. 025223 (11 pages), 2008.

[104] D. Jou, V. A. Cimmelli, and A. Sellitto, "Dynamical temperature and renormalized flux variable in extended thermodynamics of rigid heat conductors," *J. Non-Equilib. Thermodyn.*, vol. 36, pp. 373–392, 2011.

[105] H. Grad, "On the kinetic theory of rarefied gases," *Comm. Pure Appl. Math.*, vol. 2, pp. 331–407, 1949.

[106] J. D. Jackson, *Classical Electrodynamics*. New York: Wiley, 1999.

[107] G. New, *Introduction to nonlinear optics*. Cambridge: Cambridge University Press, 2011.

[108] R. Boyd, *Nonlinear optics*. New York: Academic Press, 2008.

[109] D. A. Kleinman, "Theory of second harmonic generation of light," *Phys. Rev.*, vol. 128, pp. 1761–1775, 1962.

[110] J. Ducuing, *Quantum Optics*, pp. 421–472. Ac. Press N.Y.: R.J. Glauber, 1969.

[111] R. L. Byer, *Parametric oscillators and nonlinear materials, Nonlinear Optics*. Ac. Press N.Y.: P.G. Harper and B.S. Wherrett, 1977.

[112] A. Sellitto and VA. Cimmelli, "Flux Limiters in Radial Heat Transport in Silicon Nanolyers," *J. Heat Trans. - T. ASME*, vol. 136, p. 071301 (6 pages), 2014.

[113] A. M. Anile, S. Pennisi, and M. Sammartino, "A thermodynamical approach to Eddington factors," *J. Math. Phys.*, vol. 32, pp. 544–550, 1991.

[114] A. M. Anile and V. Romano, "Covariant flux-limited diffusion theories," *Astrophys. J.*, vol. 386, pp. 325–329, 1992.

[115] M.-K. Zhang, B.-Y. Cao, and Y.-C. Guo, “Numerical studies on dispersion of thermal waves,” *Int. J. Heat Mass Transfer*, vol. 67, pp. 1072–1082, 2013.

[116] B.-D. Nie and B.-Y. Cao, “Thermal wave in phonon hydrodynamic regime by phonon Monte Carlo simulations,” *Nanosc. Microsc. Therm.*, vol. 24, pp. 94–122, 2020.

[117] P. Weinberger, “John Kerr and his effects found in 1877 and 1878,” *Philos. Mag. Lett.*, vol. 88, pp. 897–907, 2008.

[118] J. Kerr, “XL. A new relation between electricity and light: Dielectrified media birefringent,” *London Edinburgh Philos. Mag. J. Sci.*, vol. 50, pp. 337–348, 1875.

[119] J. Kerr, “LIV. A new relation between electricity and light: Dielectrified media birefringent (Second paper),” *London Edinburgh Philos. Mag. J. Sci.*, vol. 50, pp. 446–458, 1875.

[120] A. Sellitto, A. Amendola, and D. Jou, “Focalization of heat waves in an inhomogeneous system,” *J. Non-Equilib. Thermodyn.*, vol. 44, pp. 303–313, 2019.

[121] H. Ren and S.-T. Wu, *Introduction to adaptive lenses*. Hoboken, NJ: John Wiley & Sons, Inc., 2012.

[122] M. Blum, M. Büeler, C. Grätzel, and M. Aschwanden, “Compact optical design solutions using focus tunable lenses,” *Proc. SPIE, Optical Design and Engineering IV*, vol. 8167, p. 81670W, 2011.

[123] H.-C. Lin, M.-S. Chen, and Y.-H-Lin, “A review of electrically tunable focusing liquid crystal lenses,” *Trans. Electr. Electron. Mater.*, vol. 12, pp. 234–240, 2011.

[124] M. L. Roukes, M. R. Freeman, R. S. Germain, R. C. Richardson, and M. B. Ketchen, “Hot electrons and energy transport in metals at millikelvin temperatures,” *Phys. Rev. Lett.*, vol. 55, pp. 422–425, 1985.

[125] A. V. Sergeev, “Electronic Kapitza conductance due to inelastic electron-boundary scattering,” *Phys. Rev. B*, vol. 58, pp. R10199–R10202, 1998.

[126] A. Majumdar and P. Reddy, “Role of electron-phonon coupling in thermal conductance of metal-nonmetal interfaces,” *J. Appl. Phys.*, vol. 84, pp. 4768–4770, 2004.

[127] S. L. Sobolev, "Nonlocal two-temperature model: Application to heat transport in metals irradiated by ultrashort laser pulses," *Int. J. Heat Mass Transfer*, vol. 94, pp. 138–144, 2016.

[128] E. Maciá, "Theoretical prospective of quasicrystals as thermoelectric materials," *Phys. Rev. B*, vol. 64, p. 094206 (8 pages), 2001.

[129] V. Karthik, S. Sahoo, S. K. Pabi, and S. Ghosh, "On the phononic and electronic contribution to the enhanced thermal conductivity of water-based silver nanofluids," *Int. J. Therm. Sci.*, vol. 64, pp. 53–61, 2013.

[130] A. Mogulkoc, M. Modarresi, B. Kandemir, M. Roknabadi, N. Shahtahmasebi, and M. Behdani, "The role of electron-phonon interaction on the transport properties of graphene based nano-devices," *Physica B*, vol. 446, pp. 85–91, 2014.

[131] D. Y. Tzou and Z.-Y. Guo, "Nonlocal behavior in thermal lagging," *Int. J. Thermal Sci.*, vol. 49, pp. 1133–1137, 2010.

[132] B. Y. Huang and S. Bin Mansoor, "Phonon and electron transport in aluminum thin film: Influence of film thickness on electron and lattice temperatures," *Physica B*, vol. 407, pp. 4643–4648, 2012.

[133] D. Jou, A. Sellitto, and V. A. Cimmelli, "Phonon temperature and electron temperature in thermoelectric coupling," *J. Non-Equilib. Thermodyn.*, vol. 38, pp. 335–361, 2013.

[134] D. Jou, A. Sellitto, and V. A. Cimmelli, "Multi-temperature mixture of phonons and electrons and nonlocal thermoelectric transport in thin layers," *Int. J. Heat Mass Transfer*, vol. 71, pp. 459–468, 2014.

[135] R. Luzzi, A. R. Vasconcellos, and J. Galvão-Ramos, *Predictive Statistical Mechanics: A Nonequilibrium Ensemble Formalism (Fundamental Theories of Physics)*. Dordrecht: Kluwer Academic Publishers, 2002.

[136] D. Jou, "Relationships between rational extended thermodynamics and extended irreversible thermodynamics," *Phil. Trans. R. Soc. A*, vol. 378, p. 20190172 (14 pages), 2020.

[137] H. Machrafi and G. Lebon, “General constitutive equations of heat transport at small length scales and high frequencies with extension to mass and electrical charge transport,” *Appl. Math. Lett.*, vol. 52, pp. 30–37, 2015.

[138] Y. K. Koh and D. G. Cahill, “Frequency dependence of the thermal conductivity of semiconductor alloys,” *Phys. Rev. B*, vol. 76, p. 075207 (5 pages), 2007.

[139] M. Sciacca, F. X. Álvarez, D. Jou, and J. Bafaluy, “Heat solitons and thermal transfer of information along thin wires,” *Int. J. Heat Mass Transfer*, vol. 115, p. 119809 (7 pages), 2020.