

Phonon temperature and electron temperature in thermoelectric coupling

David Jou, Antonio Sellitto and Vito A. Cimmelli

Communicated by Wolfgang Muschik

Keywords. Multi-temperature model, second law of thermodynamics, temperature in non-equilibrium states, thermoelectric coefficient.

Abstract

We develop a mesoscopic model of thermoelectric coupling in nanosystems, allowing for different phonon and electron temperatures, and mutual energy exchange. Its compatibility with the second law of thermodynamics is proved. By comparisons with other theoretical proposals, the different coefficients involved in the model are identified. We consider two illustrations: (a) for systems where the electron mean-free path is considerably shorter than the phonon mean-free path, the non-equilibrium phonon temperature may be different with respect to the local-equilibrium temperature of electrons; (b) for systems with large electron mean-free path, one may have the so-called “hot electrons,” namely, electrons having a higher temperature than that of the phonons.

1 Introduction

In the past decades the need for more efficient materials for electronic refrigeration and power generation has driven a heightening interest in the field of thermoelectricity [1]. The cooling of the processors sets a fundamental limit to the electronic-system performances, and the thermoelectric refrigeration is actually viewed as an environmentally “green” method of small-scale localized cooling in computers, infrared detectors, electronics, and optoelectronics, as well as many other applications. An increasing number of the electronic and optoelectronic technologies typically requires only small-scale, or localized spot, cooling of small components that do

not impose a large heat load. Furthermore, high-efficiency thermoelectric materials are important for power-generation devices to convert waste heat into electrical energy, which may play an important role in developing alternative energy technologies.

Novel applications of thermoelectric materials include biothermal batteries to power heart pacemakers, or power generation for deep-space probes via radioisotope thermoelectric generators. Different thermoelectric materials are currently under investigation by many research groups. Some of them are focusing their efforts on minimizing the lattice thermal conductivity, and others on getting large power factors.

Usually, the analysis is especially focused on computer simulations, or statistical mechanical computations [2], while scant attention is paid to continuous models which may give strong physical grounds to practical research and investigate new frontiers.

In the present paper we develop a mesoscopic model leading to a system of enhanced thermoelectric equations, accounting for different phonon and electron temperatures, and mutual energy exchanges. In particular, following the way drawn in recent papers [3, 4], we assume that the overall heat flux \mathbf{q} has two different contributions: the phonon heat flux $\mathbf{q}^{(p)}$ and the electron heat flux $\mathbf{q}^{(e)}$, such that $\mathbf{q} = \mathbf{q}^{(p)} + \mathbf{q}^{(e)}$. We omit the hole contribution to the heat and electric current only for the sake of formal simplicity, as the corresponding equations would be formally analogous to those of the electrons, but would make the analysis more cumbersome.

We regard the phonons and the electrons as a mixture of gases flowing through the crystal lattice [3–8], each of which is endowed with its own temperature. Accounting for two different temperatures may be important, for instance, in:

- (a) *Time-dependent situations: fast laser pulses.* When a laser pulse hits the surface of a system, initially the electrons capture the main amount of the incoming energy with respect to the phonons. Subsequently, through the electron–phonon collisions, they give a part of it to the phonons. This may be of interest, for example, in the Raman thermometry (which is often utilized to measure the temperature in small electronic devices) or in information recording on optical discs (CD, DVD, Blu-Ray).
- (b) *Steady-state situations: non-equilibrium temperatures.* As the electron mean-free path ℓ_e is usually shorter than the phonon mean-free path ℓ_p , in heat propagation and when the longitudinal distance z is such that $\ell_e < z < \ell_p$, a very high number of electron collisions, and only

scant phonon collisions, are expected. Thus the electron temperature may reach its local-equilibrium value, whereas the phonon temperature is still far from its own local-equilibrium value.

- (c) *Hot electrons.* When the electron mean-free path corresponding to electron–phonon collisions is long, one may have the so-called “hot electrons,” namely, a population of electrons whose average kinetic energy (i.e., the kinetic temperature) is considerably higher than that of the phonons.

Therefore, it seems interesting to allow the electron temperature to be different from the phonon temperature. To this end, we take advantage of the theory of mixtures of fluids with different temperatures proposed by Ruggeri et al. [9–11]. In that theory the mixture is supposed to be composed of different media, co-existing in the physical space. Each constituent obeys the same balance laws as a single fluid, and it is supposed to have its own temperature. The average temperature of the mixture is introduced by the consideration that the internal energy of the mixture is the same as in the case of a single-temperature mixture [10].

Our goal will be pursued in the framework of Extended Irreversible Thermodynamics (EIT) [12–14], i.e., a thermodynamic theory regarding the dissipative fluxes as independent thermodynamic variables. Therefore, we suppose that the state space Σ is spanned by the phonon temperature $T^{(p)}$, the electron temperature $T^{(e)}$, the phonon heat flux $\mathbf{q}^{(p)}$, the electron heat flux $\mathbf{q}^{(e)}$, the electric-current density \mathbf{I} , and their first-order gradients in view of a weakly nonlocal description [3, 15], i.e.,

$$\Sigma = \{T^{(p)}; \nabla T^{(p)}; T^{(e)}; \nabla T^{(e)}; \mathbf{q}^{(p)}; \nabla \mathbf{q}^{(p)}; \mathbf{q}^{(e)}; \nabla \mathbf{q}^{(e)}; \mathbf{I}; \nabla \mathbf{I}\}. \quad (1)$$

Indeed, our belief is that weakly nonlocal constitutive equations are necessary in systems whose physical dimension is comparable to the mean-free path of the heat carriers.

Going a bit deeper into the contents of the present paper, let us briefly outline its layout. In Section 2 we set up a mesoscopic theoretical model describing thermoelectric effects and accounting for the different temperatures of the different heat carriers. The physical admissibility of that model is proved by the exploitation of the second law of thermodynamics, the main results of which are only sketched in Section 2.1, whereas readers are referred to the Appendix for the detailed thermodynamic analysis of the constitutive equations. Then we give a more manageable form to our model equations by the identification of the different model’s coefficients in Section 2.2 by comparisons with other theoretical proposals.

In Section 3, we analyze two situations in which accounting for different temperatures may lead to interesting results. In particular, in Section 3.1 we provide an explicit expression for the non-equilibrium phonon temperature, which depends on the value of the heat flux [16–19], in systems with ℓ_e considerably shorter than ℓ_p , in order to give an estimation of the difference between the phonon temperature and the electron one in a practical application. In Section 3.2, instead, we briefly analyze the case of hot electrons which are characterized by $\ell_e \gg \ell_p$. Final comments are given in Section 4.

2 Model equations

In the realm of EIT [12, 13], in the present section we set up a mesoscopic theoretical model allowing a description of the heat transport in a rigid body, whenever the heat carriers are both phonons and electrons, including the contribution of the latter to the electric current. Our approach rests on the idea that the heat carriers form a gas-like mixture flowing through the crystal lattice [3–8], with each component obeying the same balance equations as a single heat carrier [9–11], namely:

$$\dot{u}^{(p)} + \nabla \cdot \mathbf{q}^{(p)} = C(T^{(e)} - T^{(p)}), \quad (2a)$$

$$\dot{u}^{(e)} + \nabla \cdot \mathbf{q}^{(e)} = -C(T^{(e)} - T^{(p)}) + \mathbf{E} \cdot \mathbf{I}, \quad (2b)$$

where $u^{(p)}$ and $u^{(e)}$ are the partial internal energies (of phonons and electrons, respectively), and \mathbf{E} is the electric field. The term $\mathbf{E} \cdot \mathbf{I}$ in Eq. (2b) represents the power expended by the Joule effect, while $C(T^{(e)} - T^{(p)})$, with C being an electron–phonon coupling factor, accounts for the rate of energy exchange between electrons and phonons. The coupling factor C was first analyzed within the free-electron gas model by Kaganov et al. [20]. For a detailed analysis of that coefficient, see Ref. [21].

The summation of Eqs. (2) yields

$$\dot{u} + \nabla \cdot \mathbf{q} = \mathbf{E} \cdot \mathbf{I}, \quad (3)$$

with $u = u^{(p)} + u^{(e)}$ as the total internal energy of the system, which is just the balance of energy derived in Ref. [22] in the absence of a magnetic field.

As we are assuming that each heat carrier has its own temperature, we postulate the following constitutive equations for the partial internal energies appearing in Eqs. (2):

$$u^{(p)} = c_v^{(p)} T^{(p)}, \quad u^{(e)} = c_v^{(e)} T^{(e)}, \quad (4)$$

with $c_v^{(p)}$ and $c_v^{(e)}$ as the phonon- and the electron-specific heats at constant volume [21], respectively. In order to emphasize the essential physical ideas, here we deal only with the simplest situation in which $c_v^{(p)}$ and $c_v^{(e)}$ are constant. Incorporation of additional effects, as, for instance, the temperature dependence of the specific heats, would be straightforward.

Recalling that the average internal energy of the system may be expressed through the average temperature T as $u = c_v T$, being

$$c_v = c_v^{(p)} + c_v^{(e)} \quad (5)$$

the specific heat at constant volume of the whole system [23], from Eqs. (4) we have

$$T = \frac{c_v^{(p)} T^{(p)} + c_v^{(e)} T^{(e)}}{c_v}. \quad (6)$$

Note that, from the practical point of view, $c_v^{(e)}$ is comparable to $c_v^{(p)}$ only at very low temperatures. Thus, in the usual applications one expects that the phonon heat capacity is dominant with respect to the electron heat capacity, and consequently the average temperature defined in Eq. (6) would be practically equal to the phonon gas temperature. Nevertheless, in Section 3 we show that in some cases our theoretical model allows an estimation of the difference between $T^{(p)}$ and $T^{(e)}$.

The rate of the electric charge density $\rho^{(e)}$ obeys the charge conservation law, i.e.,

$$\dot{\rho}^{(e)} + \nabla \cdot \mathbf{I} = 0, \quad (7)$$

which, together with Eqs. (2), determines the evolution of $u^{(p)}$, $u^{(e)}$, and $\rho^{(e)}$, once the evolution of the corresponding fluxes $\mathbf{q}^{(p)}$, $\mathbf{q}^{(e)}$, and \mathbf{I} is known. According to the basic principles of EIT [12, 13], we postulate for them the following balance equations:

$$\dot{\mathbf{q}}^{(p)} = -\nabla \cdot \Phi^{(p)} + \mathbf{r}^{(p)}, \quad (8a)$$

$$\dot{\mathbf{q}}^{(e)} = -\nabla \cdot \Phi^{(e)} + \mathbf{r}^{(e)}, \quad (8b)$$

$$\dot{\mathbf{I}} = -\nabla \cdot \Phi^{(I)} + \mathbf{r}^{(I)}, \quad (8c)$$

wherein $\Phi^{(p)}$, $\Phi^{(e)}$, and $\Phi^{(I)}$ denote the fluxes of the corresponding state variables, and $\mathbf{r}^{(p)}$, $\mathbf{r}^{(e)}$, and $\mathbf{r}^{(I)}$ are their productions.

EIT requires that suitable constitutive equations should be assigned to both fluxes and productions [12, 13]. Thus, in order to obtain a simple model accounting for nonlocal and nonlinear effects, for the sake of simplicity and along with the approach used in Refs. [3, 4], in the present section we assume the following constitutive relations:

$$\Phi^{(p)} = -(\Gamma_0^{(p)} \nabla \cdot \mathbf{q}^{(p)}) \mathbf{U} - \Gamma_2^{(p)} \mathbf{q}^{(p)} \otimes \mathbf{q}^{(p)} - \Gamma_1^{(p)} \nabla \mathbf{q}^{(p)}, \quad (9a)$$

$$\Phi^{(e)} = -(\Gamma_0^{(e)} \nabla \cdot \mathbf{q}^{(e)}) \mathbf{U} - \Gamma_2^{(e)} \mathbf{q}^{(e)} \otimes \mathbf{q}^{(e)} - \Gamma_1^{(e)} \nabla \mathbf{q}^{(e)}, \quad (9b)$$

$$\Phi^{(I)} = -(\Gamma_0^{(I)} \nabla \cdot \mathbf{I}) \mathbf{U} - \Gamma_2^{(I)} \mathbf{I} \otimes \mathbf{I} - \Gamma_1^{(I)} \nabla \mathbf{I}, \quad (9c)$$

where \mathbf{U} is the second-order unit tensor, and the symbol \otimes means the dyadic product between two vectors (i.e., $\mathbf{a} \otimes \mathbf{b} = a_i b_j$ once the index notation is used). Moreover, in Eqs. (9) $\Gamma_i^{(p)}$, $\Gamma_i^{(e)}$, and $\Gamma_i^{(I)}$ ($i = 0, 1, 2$) are phenomenological scalar coefficients which will be identified later on by comparison with other theoretical proposals.

It seems important to emphasize that the constitutive assumptions (9), which have been obtained following the way outlined in Refs. [24, 25], rest on both mathematical and physical motivations. In fact, under the hypothesis of isotropy of the heat conductor, $\Phi^{(p)}$, $\Phi^{(e)}$, and $\Phi^{(I)}$ have to be analytically represented by second-order isotropic tensor functions which, due to the chosen state space, depend on scalars, vectors, and second-order tensors. The first term in the right-hand side of Eqs. (9) is symmetric and its form has been chosen according to the representation theorem of isotropic symmetric second-order tensor functions proved in Ref. [26] (see eqs. (4.4) and (4.5) therein). Such a general representation has been simplified under the additional physical assumptions that each vectorial flux, due to the different carriers of heat or of electrical charge, enters its own tensorial flux only, and that this last is linear in the dyadic composition of the respective vectorial flux. Furthermore, the quantities $\Phi^{(p)}$, $\Phi^{(e)}$, and $\Phi^{(I)}$ are supposed to be linear in the gradients of $\mathbf{q}^{(p)}$, $\mathbf{q}^{(e)}$, and \mathbf{I} , respectively. Thus, the second and third terms in the right-hand side of Eqs. (9) have been chosen according to the general theorem of representation of linear isotropic tensor functions (see Ref. [27], p. 235, eq. (22) therein). From the considerations above, the constitutive equations (9) ensue.

Meanwhile, we also assume that the productions of each flux $\mathbf{q}^{(p)}$, $\mathbf{q}^{(e)}$, and \mathbf{I} are linear both in the thermodynamical force (related to the respective heat, or electrical-current, carrier), and in the flux itself, but do not depend on the thermodynamical forces (or fluxes) due to the other carriers. That way we get

$$\mathbf{r}^{(p)} = \gamma_0^{(p)} \nabla T^{(p)} + \gamma_1^{(p)} \mathbf{q}^{(p)}, \quad (10a)$$

$$\mathbf{r}^{(e)} = \gamma_0^{(e)} \nabla T^{(e)} + \gamma_1^{(e)} \mathbf{q}^{(e)} + \delta^{(Ie)} \mathbf{E}, \quad (10b)$$

$$\mathbf{r}^{(I)} = \gamma_0^{(I)} \nabla T^{(e)} + \gamma_1^{(I)} \mathbf{I} + \delta^{(eI)} \mathbf{E}, \quad (10c)$$

wherein $\gamma_i^{(p)}$, $\gamma_i^{(e)}$, $\gamma_i^{(I)}$ (with $i = 0, 1$), $\delta^{(Ie)}$, $\delta^{(eI)}$ are further suitable coefficients. It is easy to check that the equations above constitute a particular case of the general representation of isotropic vector functions proved in Ref. [26] (see eqs. (4.2) and (4.3) therein).

Note that $\mathbf{r}^{(e)}$ and $\mathbf{r}^{(I)}$ have a term proportional to \mathbf{E} , accounting for the relation between the electric field and the electric charges and allowing a description of the Seebeck effect and the Peltier effect [12, 28, 29]. Since \mathbf{E} does not belong to Σ , a constitutive equation for it must be assigned, too.

The system of equations (2), (7), and (8), together with the constitutive equations (4), (6), (9), and (10), set up our mesoscopic theoretical model.

2.1 Restrictions placed by the second law of thermodynamics

The constitutive assumptions in Eqs. (9) and (10) have been proposed from mathematical formal grounds, as the simplest generalizations of nonlocal and nonlinear constitutive equations previously used for phonons [3, 4]. In that case, constitutive equations of this kind (with suitable interpretation of the coefficients) may be obtained from the kinetic theory of phonons up to the second order in the fluxes [30]. However, to our knowledge, they have not yet been obtained simultaneously for electrons and phonons, because most of the kinetic-theory approaches to this problem do not go beyond first-order solutions.

At this step it is necessary to check their physical admissibility in order to avoid any possible violation of the basic principles of continuum physics.

The second law of thermodynamics accounts for the natural evolution of a system in any possible thermodynamic process and constitutes a useful tool for restricting the form of the constitutive equations [12, 13, 31, 32]. It states that the rate of entropy production per unit volume $\sigma^{(s)}$ cannot be negative along any admissible thermodynamic process. Locally it reads

$$\sigma^{(s)} = \dot{s} + \nabla \cdot \left(\frac{\mathbf{q}}{T} + \mathbf{k} \right) \geq 0, \quad (11)$$

where s is the entropy density, the ratio \mathbf{q}/T is the classical entropy-density flux [22, 33], and \mathbf{k} is an entropy-density extra flux due to long-range interactions [13, 34]. Since the average temperature T may be easily expressed in terms of the state variables by Eq. (6), it seems natural to introduce the Helmholtz free energy $\psi = u - Ts$. In terms of ψ , inequality (11) becomes [22]

$$\dot{\psi} + s\dot{T} - \mathbf{E} \cdot \mathbf{I} + \frac{\mathbf{q} \cdot \nabla T}{T} - T \nabla \cdot \mathbf{k} \leq 0, \quad (12)$$

once the term $\nabla \cdot \mathbf{q}$ has been expressed by means of the local balance of energy (3).

Referring the reader to the Appendix, wherein the consequences of inequality (12) are established, here we only summarize the most relevant results.

- (1) The constitutive assumptions in Eqs. (9) and (10) agree with the second law of thermodynamics.
- (2) The constitutive equation of the Helmholtz free energy ψ reads

$$\psi = \psi_{\text{eq}}(T) + \frac{\psi_p(T)}{2} \mathbf{q}^{(p)} \cdot \mathbf{q}^{(p)} + \frac{\psi_e(T)}{2} \mathbf{q}^{(e)} \cdot \mathbf{q}^{(e)} + \frac{\psi_I(T)}{2} \mathbf{I} \cdot \mathbf{I}, \quad (13)$$

where the subscript “eq” refers to the local-equilibrium value (characterized by $\mathbf{q}^{(p)} = \mathbf{q}^{(e)} = \mathbf{I} = \mathbf{0}$). In Eq. (13) ψ_p , ψ_e , and ψ_I are suitable positive-defined functions of the state variables, so that ψ reaches a minimum at equilibrium [12, 13, 31].

- (3) The entropy-density extra flux \mathbf{k} and the entropy production $\sigma^{(s)}$ are, respectively, given by

$$\begin{aligned} \mathbf{k} = & \frac{\psi_p}{T} [(\Gamma_0^{(p)} \nabla \cdot \mathbf{q}^{(p)}) \mathbf{q}^{(p)} + \Gamma_1^{(p)} \nabla^t \mathbf{q}^{(p)} \cdot \mathbf{q}^{(p)}] \\ & + \frac{\psi_e}{T} [(\Gamma_0^{(e)} \nabla \cdot \mathbf{q}^{(e)}) \mathbf{q}^{(e)} + \Gamma_1^{(e)} \nabla^t \mathbf{q}^{(e)} \cdot \mathbf{q}^{(e)}] \\ & + \frac{\psi_I}{T} [(\Gamma_0^{(I)} \nabla \cdot \mathbf{I}) \mathbf{I} + \Gamma_1^{(I)} \nabla^t \mathbf{I} \cdot \mathbf{I}], \end{aligned} \quad (14a)$$

$$T\sigma^{(s)} = \mathbf{E} \cdot \mathbf{I} - \frac{\mathbf{q} \cdot \nabla \mathbf{T}}{T} + f(\Sigma) \geq 0, \quad (14b)$$

wherein the superscript “t” means the transposed gradient of the indicated vector, and the scalar function f is a suitable function defined on the state space, the explicit form of which is given in Eq. (39) of the Appendix.

2.2 Identification of the phenomenological coefficients

In order to look for possible applications of our model, we have to express the coefficients entering the different constitutive equations in terms of well-known material functions. This is the aim of the following analysis, which will be pursued by comparisons with earlier theoretical mesoscopic models.

Let us put ourself for a while in the semi-linear approximation for the constitutive equations (9), i.e., let us assume that the terms $\Gamma_2^{(p)} \mathbf{q}^{(p)} \otimes \mathbf{q}^{(p)}$, $\Gamma_2^{(e)} \mathbf{q}^{(e)} \otimes \mathbf{q}^{(e)}$, and $\Gamma_2^{(I)} \mathbf{I} \otimes \mathbf{I}$ are vanishing. Then, once the constitutive assumptions in Eqs. (9) and (10) have been taken into account, Eqs. (8) reduce to

$$\dot{\mathbf{q}}^{(p)} - \gamma_1^{(p)} \mathbf{q}^{(p)} = \gamma_0^{(p)} \nabla T^{(p)} + \Gamma_0^{(p)} \nabla \nabla \cdot \mathbf{q}^{(p)} + \Gamma_1^{(p)} \nabla^2 \mathbf{q}^{(p)}, \quad (15a)$$

$$\dot{\mathbf{q}}^{(e)} - \gamma_1^{(e)} \mathbf{q}^{(e)} = \gamma_0^{(e)} \nabla T^{(e)} + \Gamma_0^{(e)} \nabla \nabla \cdot \mathbf{q}^{(e)} + \Gamma_1^{(e)} \nabla^2 \mathbf{q}^{(e)} + \delta^{(Ie)} \mathbf{E}, \quad (15b)$$

$$\dot{\mathbf{I}} - \gamma_1^{(I)} \mathbf{I} = \gamma_0^{(I)} \nabla T^{(e)} + \Gamma_0^{(I)} \nabla \nabla \cdot \mathbf{I} + \Gamma_1^{(I)} \nabla^2 \mathbf{I} + \delta^{(eI)} \mathbf{E}. \quad (15c)$$

These equations may be compared with those discussed in Ref. [4] to analyze the thermoelectric effects and the size dependency of the figure-of-merit in cylindrical nanowires (see eqs. (5) therein). Those equations, in fact, have a form which is very similar to the form of Eqs. (15), the only difference being the presence of the average temperature in the former, while two different temperatures are introduced in Eqs. (15). Recalling the previously discussed difference between $T^{(p)}$ and $T^{(e)}$ in the usual practical applications, that comparison allows us the following identifications:

$$\left\{ \begin{array}{lll} \gamma_1^{(p)} = -\tau_p^{-1}; & \gamma_1^{(e)} = -\tau_e^{-1}; & \gamma_1^{(I)} = -\tau_I^{-1}; \\ \gamma_0^{(p)} = -\lambda_p \tau_p^{-1}; & \gamma_0^{(e)} = -(\lambda_e + \epsilon \Pi \sigma_e) \tau_e^{-1}; & \gamma_0^{(I)} = -\epsilon \sigma_e \tau_I^{-1}; \\ \Gamma_1^{(p)} = \ell_p^2 \tau_p^{-1}; & \Gamma_1^{(e)} = \ell_e^2 \tau_e^{-1}; & \Gamma_1^{(I)} = \ell_I^2 \tau_I^{-1}; \\ \Gamma_0^{(p)} = 2\ell_p^2 \tau_p^{-1}; & \Gamma_0^{(e)} = 2\ell_e^2 \tau_e^{-1}; & \Gamma_0^{(I)} = 2\ell_I^2 \tau_I^{-1}; \\ \delta^{(Ie)} = \Pi \sigma_e \tau_e^{-1}; & \delta^{(eI)} = \sigma_e \tau_I^{-1}; & \end{array} \right. \quad (16)$$

where $(\tau_p; \ell_p)$, $(\tau_e; \ell_e)$ and $(\tau_I; \ell_I)$ are the relaxation time and mean-free path of phonons, electrons, and electric-current density [3, 4, 35–37], respectively, ϵ is the Seebeck coefficient, σ_e is the electrical conductivity, λ_p and λ_e are the thermal conductivity due to phonons and electrons, respectively [38], and Π is the Peltier coefficient.

Once Eqs. (16) hold, relaxing the hypothesis of semi-linear approximation for the constitutive equations (9), when the terms proportional to the second-order spatial derivatives may be neglected (this is the case, for example, when the mean-free paths are very short), as well as both the dissipation due to the Joule effects (i.e., the term $\mathbf{E} \cdot \mathbf{I}$ in the time rate of $\dot{u}^{(e)}$), and the coupling between $\dot{u}^{(p)}$ and $\dot{u}^{(e)}$ (i.e., the term $C(T^{(e)} - T^{(p)})$),

in steady states, up to the second-order approximation, Eqs. (8) become, instead,

$$\frac{\mathbf{q}^{(p)}}{\tau_p} = \Gamma_2^{(p)} \nabla \mathbf{q}^{(p)} \cdot \mathbf{q}^{(p)} - \frac{\lambda_p}{\tau_p} \nabla T^{(p)}, \quad (17a)$$

$$\frac{\mathbf{q}^{(e)}}{\tau_e} = \Gamma_2^{(e)} \nabla \mathbf{q}^{(e)} \cdot \mathbf{q}^{(e)} - \frac{\lambda_e + \epsilon \Pi \sigma_e}{\tau_e} \nabla T^{(e)} + \frac{\Pi \sigma_e}{\tau_e} \mathbf{E}, \quad (17b)$$

$$\frac{\mathbf{I}}{\tau_I} = \Gamma_2^{(I)} \nabla \mathbf{I} \cdot \mathbf{I} + \frac{\sigma_e}{\tau_I} (\mathbf{E} - \epsilon \nabla T^{(e)}), \quad (17c)$$

since from Eqs. (2) and (7) one has $\nabla \cdot \mathbf{q}^{(p)} = \nabla \cdot \mathbf{q}^{(e)} = \nabla \cdot \mathbf{I} = \mathbf{0}$ and, moreover, the temperature gradients, as well as the fluxes and their spatial derivatives, have been considered as first-order quantities.

Looking at Eq. (17a), it is easy to recognize that it is very similar to the nonlinear evolution equation for the phonon contribution to the heat flux obtained in Ref. [19] (see eq. (27) therein), which has been used to analyze second-sound propagation in silicon nanowires. Thus, by the analysis of eq. (27) in Ref. [19], and the very close relation between $\mathbf{q}^{(p)}$ and $\mathbf{q}^{(e)}$, we may also infer

$$\Gamma_2^{(p)} = \frac{2}{c_v^{(p)} T^{(p)}}, \quad \Gamma_2^{(e)} = \frac{2}{c_v^{(e)} T^{(e)}}. \quad (18)$$

The physical identification of the coefficient $\Gamma_2^{(I)}$, instead, is not so direct. Recalling that we only aim to introduce a first simple model of thermoelectric coupling in nanosystems, a dimensional analysis, together with the balance equation (7) for the electric charge, allow the further identification,

$$\Gamma_2^{(I)} = \frac{1}{\varrho^{(e)}}. \quad (19)$$

Our further step will be to identify on physical grounds the remaining functions ψ_p , ψ_e , and ψ_I . In particular we are looking for identifications which, by design, are simple and in accordance with the principles of minimum free energy [39] and maximum entropy [13] at the equilibrium. As will be seen, linking the Helmholtz free energy (13) with well-defined material functions allows us to also make a conceptual distinction between the local-equilibrium temperature (characteristic of slow processes) and the non-equilibrium temperature (characteristic of fast regimes). Indeed, the meaning of temperature out of the equilibrium is a fundamental open problem in modern irreversible thermodynamics and statistical physics [17],

and it becomes especially acute in nanosystems experiencing fast processes [12, 18].

The simplest identifications which comply with the requirements above are

$$\psi_p = \frac{\tau_p T^2}{\lambda_p T_{\text{ref}}^3}, \quad \psi_e = \frac{\tau_e T^2}{(\lambda_e + \epsilon \Pi \sigma_e) T_{\text{ref}}^3}, \quad \psi_I = \frac{\tau_I T^2}{\epsilon \sigma_e T_{\text{ref}}^3}, \quad (20)$$

where T_{ref} denotes a given reference temperature, as, for instance, the working temperature of the system. The introduction of such a temperature is important, since at nanoscale it influences the thermal properties of the system. For example, in the analysis of nanosystems, the phonon–wall interaction must be incorporated in the usual description of phonon hydrodynamics, as surface effects become comparable to bulk effects. The material parameters describing the specular, diffusive, and backscattering collisions in silicon nanowires have been proved to depend on the working temperature [8]. This dependence is important because it strongly influences the temperature dependence of the effective thermal conductivity of nanosystems [8].

That way, the Helmholtz free energy (13) takes the form

$$\begin{aligned} \psi = \psi_{\text{eq}}(T) &+ \frac{\tau_p T^2}{2\lambda_p T_{\text{ref}}^3} \mathbf{q}^{(p)} \cdot \mathbf{q}^{(p)} \\ &+ \frac{\tau_e T^2}{2(\lambda_e + \epsilon \Pi \sigma_e) T_{\text{ref}}^3} \mathbf{q}^{(e)} \cdot \mathbf{q}^{(e)} + \frac{\tau_I T^2}{2\epsilon \sigma_e T_{\text{ref}}^3} \mathbf{I} \cdot \mathbf{I}. \end{aligned} \quad (21)$$

Then, by using the classical thermodynamic relation $s = -\partial\psi/\partial T$ (see Eqs. (36a) in the Appendix), it follows that

$$\begin{aligned} s = s_{\text{eq}}(T) &- \frac{\tau_p T}{\lambda_p T_{\text{ref}}^3} \mathbf{q}^{(p)} \cdot \mathbf{q}^{(p)} \\ &- \frac{\tau_e T}{(\lambda_e + \epsilon \Pi \sigma_e) T_{\text{ref}}^3} \mathbf{q}^{(e)} \cdot \mathbf{q}^{(e)} - \frac{\tau_I T}{\epsilon \sigma_e T_{\text{ref}}^3} \mathbf{I} \cdot \mathbf{I}, \end{aligned} \quad (22)$$

wherein $s_{\text{eq}} = -\partial\psi_{\text{eq}}/\partial T$. From the expression above it is evident that the entropy takes its maximum at the equilibrium.

According to the local-equilibrium hypothesis, the non-equilibrium temperature may be defined, as in equilibrium, by the relation

$$\frac{1}{T} = \frac{\partial s}{\partial u}, \quad (23)$$

whenever the internal energy u replaces the temperature T as state variable [12, 13, 40]. Thus, from Eqs. (22) and (23) we have the following constitutive equation for the non-equilibrium temperature:

$$\frac{1}{T} = \frac{1}{T_{\text{eq}}} - \frac{\tau_p}{\lambda_p c_v T_{\text{ref}}^3} \mathbf{q}^{(p)} \cdot \mathbf{q}^{(p)} - \frac{\tau_e}{(\lambda_e + \epsilon \Pi \sigma_e) c_v T_{\text{ref}}^3} \mathbf{q}^{(e)} \cdot \mathbf{q}^{(e)} - \frac{\tau_I}{\epsilon \sigma_e c_v T_{\text{ref}}^3} \mathbf{I} \cdot \mathbf{I}, \quad (24)$$

with $T_{\text{eq}}^{-1} = \partial s_{\text{eq}} / \partial u$ as the local-equilibrium temperature of the mixture of phonons and electrons. Equation (24) clearly shows that the non-equilibrium temperature may differ from the local-equilibrium temperature. For a detailed discussion on the different temperatures arising in non-equilibrium systems, see for instance Ref. [17].

Before going further, it seems important to remark on the following considerations regarding Eq. (24):

- (a) In Eq. (24), the non-equilibrium terms are independent of both the non-equilibrium temperature and the local-equilibrium one, but they depend on the intensities of the fluxes, as well as on the reference temperature. This is logical, since the temperature at which a device is working influences the non-equilibrium states.
- (b) The local-equilibrium temperature should not be considered as a constant temperature, but as the temperature following by thermodynamic restriction $s = -\partial \psi / \partial T$, with s defined according to the local-equilibrium hypothesis.
- (c) Both T and T_{eq} must be non-negative. Such a problem will be considered in Section 3.1.

As a conclusive summary, by comparing our model with earlier theoretical models, we have obtained the following nonlocal transport equations for phonon and electron contributions to the heat flux, and for the electron contribution to the electric-current density, including thermoelectric effects:

$$\begin{aligned} \tau_p \dot{\mathbf{q}}^{(p)} - \frac{2\tau_p}{c_v^{(p)} T^{(p)}} (\nabla \mathbf{q}^{(p)} \cdot \mathbf{q}^{(p)} + \mathbf{q}^{(p)} \nabla \cdot \mathbf{q}^{(p)}) + \mathbf{q}^{(p)} \\ = -\lambda_p \nabla T^{(p)} + \ell_p^2 (\nabla^2 \mathbf{q}^{(p)} + 2\nabla \nabla \cdot \mathbf{q}^{(p)}), \end{aligned} \quad (25a)$$

$$\begin{aligned} \tau_e \dot{\mathbf{q}}^{(e)} - \frac{2\tau_e}{c_v^{(e)} T^{(e)}} (\nabla \mathbf{q}^{(e)} \cdot \mathbf{q}^{(e)} + \mathbf{q}^{(e)} \nabla \cdot \mathbf{q}^{(e)}) + \mathbf{q}^{(e)} \\ = -(\lambda_e + \epsilon \Pi \sigma_e) \nabla T^{(e)} + \ell_e^2 (\nabla^2 \mathbf{q}^{(e)} + 2\nabla \nabla \cdot \mathbf{q}^{(e)}) + \Pi \sigma_e \mathbf{E}, \end{aligned} \quad (25b)$$

$$\begin{aligned} \tau_I \dot{\mathbf{I}} - \frac{\tau_I}{\rho^{(e)}} (\nabla \mathbf{I} \cdot \mathbf{I} + \mathbf{I} \nabla \cdot \mathbf{I}) + \mathbf{I} \\ = \sigma_e (\mathbf{E} - \epsilon \nabla T^{(e)}) + \ell_I^2 (\nabla^2 \mathbf{I} + 2\nabla \nabla \cdot \mathbf{I}). \end{aligned} \quad (25c)$$

Equations (25) comply with the experiments since, in the linear case they are capable of working out interesting results about the figure-of-merit in metallic nanowires when phonons are the sole heat carriers [3, 4]. In principle, the nonlinear terms appearing in Eqs. (25) may be used to study a further way of improving the efficiency of thermoelectric devices.

The first term on the left-hand side of Eqs. (25) describes the finite-time non-vanishing relaxational effects in the temporal response of the fluxes after a thermodynamic force is suddenly imposed on the system. The second and third terms on the left-hand side of Eqs. (25), which are proportional, respectively, to the gradient and to the divergence of the flux times the flux itself, are nonlinear terms which have not yet been studied in much detail, but which may be relevant for instance in conical geometries, where there are strong gradients of the flux (in contrast to cylindrical devices, where the gradient of the flux along the axis vanishes). On the right-hand side of Eqs. (25) the terms containing the square of the mean-free path account for nonlocal effects, which manifest themselves when some characteristic system's size becomes comparable to (or smaller than) the mean-free path; otherwise, they become negligible. The remaining terms are the usual ones in thermoelectric phenomena, but with the total heat flux split into the phonon and the electron contributions, which allows more flexibility in the analysis of nanosystems when the mean-free paths of phonons and electrons are considerably different.

Note that in the absence of a source, in purely one-dimensional steady-state situations, the nonclassical terms containing gradients in Eqs. (25) vanish, because the fluxes must be homogeneous along the system.

Equation (25a), but without the nonlinear terms, has been applied to phonon heat transport in nanowires, and it describes a reduction in the thermal conductivity [6–8]. This is because nanowires are not strictly a one-dimensional system, and the heat flux may change from a maximum value at the center to a small value along the walls. This effect is successfully described by a linear version of Eqs. (25), see Ref. [4].

However, a purely one-dimensional case would need a different approach, taking into account that the probability of collisions after a flight of length x is of the order of $1 - \exp^{-x/\ell_p}$. Thus, for $x \ll \ell_p$ the regime would be ballistic, and for $x \gg \ell_p$ it would become diffusive. This behavior is recovered if one makes the ansatz of a space-dependent effective thermal conductivity of the form $\lambda_p^{\text{eff}}(x) = \lambda_p(1 - \exp^{-x/\ell_p})$. Indeed, for $x \gg \ell_p$ one recovers the usual thermal conductivity, while for $x \ll \ell_p$ the effective thermal conductivity takes the form $\lambda_p^{\text{eff}} = \lambda(x/\ell_p)$. This implies that for such small distances the heat flux does not depend on temperature gradient, but on temperature difference, as is usual in ballistic regimes. Of course, it would be elegant to incorporate this feature in a set of macroscopic equations for the heat flux, generalizing Eqs. (25), instead of deriving it from a microscopic ansatz.

For the sake of illustration of the relation of the present model with other heat conduction theories, let us consider a one-dimensional system in which the heat flow is drawn by the effective thermal conductivity instead of the usual one, in the absence of electric field and current circulation, under the hypothesis that the phonons are the sole heat carriers. Moreover, let us suppose that the terms proportional to the second-order spatial derivatives may be neglected, namely, the mean-free path is very short. Then, the evolution of the one-dimensional heat flux q is governed by the first of the Eqs. (25), which takes the form

$$\tau \dot{q} - Lqq_{,x} + c_v L \dot{T} + \lambda_p^{\text{eff}} T_{,x} + q = 0, \quad (26)$$

where τ is the overall relaxation time, and $L = 2\tau q/c_v T$ is said to be the “characteristic length of the heat conduction” [41].

An enhanced heat-transport equation of the type (26) has been obtained in the framework of thermomass (TM) theory [41, 42], a thermodynamic model in which the heat-transfer process is regarded as a gas-like collection flowing through the medium due to a TM pressure gradient. In that theory, the heat carriers are the thermons, the mass of which may be calculated from Einstein’s mass–energy duality. The continuity and momentum equations for thermons assume the usual forms of fluid mechanics, and their combination yields an evolution equation for the heat flux similar to Eq. (26).

If instead the nonlocal effects are not negligible, namely, the mean-free path is comparable to (or bigger than) the physical dimensions of the system, Eq. (25a) yields

$$\tau \dot{q} - Lqq_x + c_v L \dot{T} + \lambda_p^{\text{eff}} T_{,x} + q = \ell^2 q_{,xx}, \quad (27)$$

already derived as a particular case in the framework of a more general model of nonlocal and nonlinear anisotropic heat transport [43, 44].

The physical identifications in Eqs. (16), merged with the thermodynamic restriction in Eq. (14a), also leads to the following form for the entropy flux $\mathbf{J}^{(s)}$:

$$\begin{aligned} \mathbf{J}^{(s)} = & \frac{\mathbf{q}}{T} + \frac{2\ell_p^2 T}{T_{\text{ref}}^3} \left[\frac{(\nabla \cdot \mathbf{q}^{(p)})\mathbf{q}^{(p)} + (\nabla^t \mathbf{q}^{(p)}) \cdot \mathbf{q}^{(p)}}{\lambda_p} \right] \\ & + \frac{2\ell_e^2 T}{T_{\text{ref}}^3} \left[\frac{(\nabla \cdot \mathbf{q}^{(e)})\mathbf{q}^{(e)} + (\nabla^t \mathbf{q}^{(e)}) \cdot \mathbf{q}^{(e)}}{\lambda_e + \epsilon \Pi \sigma_e} \right] \\ & + \frac{2\ell_I^2 T}{T_{\text{ref}}^3} \left[\frac{(\nabla \cdot \mathbf{I})\mathbf{I} + \nabla^t \mathbf{I} \cdot \mathbf{I}}{\sigma_e \epsilon} \right]. \end{aligned} \quad (28)$$

Recalling that the overall entropy flux is defined as $\mathbf{J}^{(s)} = \mathbf{q}/T + \mathbf{k}$, Eq. (28) clearly shows that it has a nonlinear form. A similar result has been obtained in Ref. [45] (see eqs. (2) and (35) therein), in the case of phonon transport only. Following the way paved in that paper, Eq. (28) may be used to study the influence of nonlocal terms on the temperature profile in thermoelectric devices.

While the application of our theoretical model to the analysis of thermoelectric phenomena, as well as to a comparison with the quasi-classic models of thermoelectricity discussed by Ziman [46], will have to be deferred to future work, in the following we focus our attention on two illustrations in which it would be interesting to account for different temperatures.

3 Phonon and electron temperature

In this section, for the sake of illustration, we consider two extreme situations, corresponding to $\ell_p \gg \ell_e$ and $\ell_e \gg \ell_p$, respectively. In the former case the phonons are out of local equilibrium, whereas electrons are in local-equilibrium states. The latter situation, instead, is characteristic of the hot electrons.

3.1 Non-equilibrium phonon temperature and local-equilibrium electron temperature

The possibility of accounting for two different temperatures (that is, the phonon temperature and the electron temperature) is one of the main assumptions of our theoretical model. If one would be able to measure both

of them, then one would also be able to obtain the average temperature T of the system by Eq. (6). Indeed, in Section 2 we already observed that in the standard applications T is practically coincident with $T^{(p)}$. Thus, at this step a natural question is how it is possible to measure, or to estimate, those temperatures in situations which may be extreme, but accessible to current experimental possibilities. We answer that question in the next lines. To this end, let us restrict ourselves to non-equilibrium situations in which the electron heat flux and the electric current are negligible with respect to the phonon heat flux.

In such a case, the non-equilibrium temperature (24) reduces to

$$\frac{1}{T} = \frac{1}{T_{\text{eq}}} - \frac{\tau_p}{\lambda_p c_v T_{\text{ref}}^3} \mathbf{q}^{(p)} \cdot \mathbf{q}^{(p)}, \quad (29)$$

and, consequently, one has

$$\begin{aligned} T &= T_{\text{eq}} \left(1 - \frac{T \tau_p}{\lambda_p c_v T_{\text{ref}}^3} \mathbf{q}^{(p)} \cdot \mathbf{q}^{(p)} \right) \approx T_{\text{eq}} \left(1 - \frac{\tau_p}{\lambda_p c_v T_{\text{ref}}^2} \mathbf{q}^{(p)} \cdot \mathbf{q}^{(p)} \right) \\ &\approx T_{\text{ref}} \left(1 - \frac{\tau_p}{\lambda_p c_v T_{\text{ref}}^2} \mathbf{q}^{(p)} \cdot \mathbf{q}^{(p)} \right), \end{aligned} \quad (30)$$

under the hypothesis of small deviations of T and T_{eq} from T_{ref} . This approximation is true if we are restricted to values of the heat flux which do not exceed a given threshold, in such a way that both T and T_{eq} are non-negative. Such a situation is effectively observed in nonlinear heat conduction, and in the literature it is referred to as the presence of “flux limiters” [13, 47, 48].

The electrons generally reach their local-equilibrium temperature earlier with respect to the phonons, since $\tau_e \ll \tau_p$ and $\ell_e \ll \ell_p$ in several practical applications. Then, in these situations we may take for $T^{(e)}$ the local-equilibrium value T_{eq} , whereas for the phonons we have to introduce a non-equilibrium value, which can be identified with T . In this way, in view of Eq. (30), for the non-equilibrium phonon temperature we may assume

$$T^{(p)} = T_{\text{ref}} \left(1 - \frac{\tau_p}{\lambda_p c_v^{(p)} T_{\text{ref}}^2} \mathbf{q}^{(p)} \cdot \mathbf{q}^{(p)} \right). \quad (31)$$

In principle, Eq. (31) may be used for a first rough estimation for the phonon temperature in situations wherein both the phonon relaxation time, and the phonon mean-free path are much larger than the corresponding electron quantities.

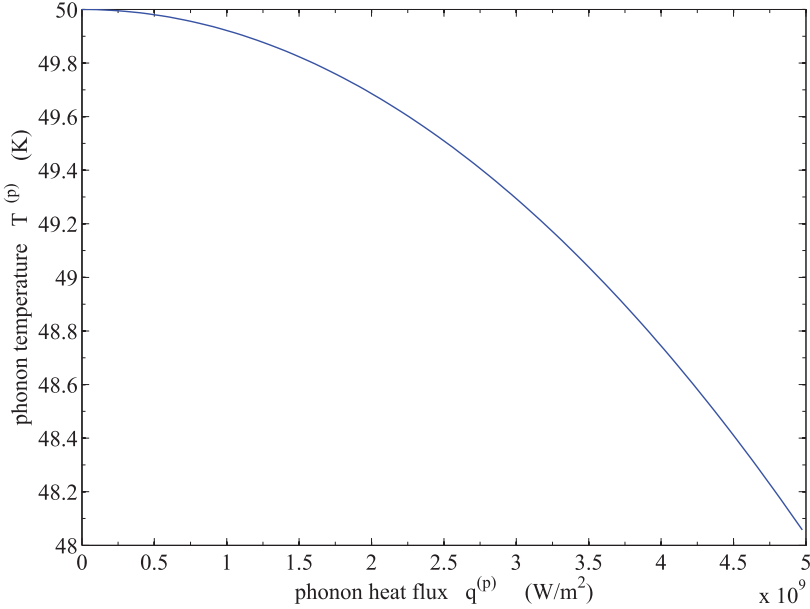


Figure 1. Non-equilibrium phonon temperature versus local phonon heat flux in a silicon sample at 50 K: theoretical estimation, as a result of Eq. (31).

As a simple illustration, Eq. (31) is used in Figure 1 to estimate the non-equilibrium phonon temperature in the case of a silicon sample at the average reference temperature of 50 K ($\lambda_p = 2680 \text{ Wm}^{-1}\text{K}^{-1}$ and $\ell_p = 6681 \times 10^{-9} \text{ m}$) as a function of $\mathbf{q}^{(p)}$. For the sake of computation, we estimate $c_v^{(p)} \approx c_v = (12/5)\pi^4(T/T_D)(R\rho_{\text{Si}}/M_{\text{Si}})$ (with $T_D = 645 \text{ K}$ being the Debye temperature for silicon, ρ_{Si} the silicon mass density, R the gas constant, and M_{Si} the silicon molar mass) and the phonon relaxation time as $\tau_p = \ell_p/v$ (with $v = 8.43 \times 10^3 \text{ ms}^{-1}$ being the phonon speed).

3.2 Hot electrons

The term hot electrons is used to indicate either holes or electrons that have gained very high kinetic energy, after having been accelerated by a strong electric field in areas of high field intensities within a semiconductor device (especially Metal-Oxide-Semiconductors) [49]. Because of their high kinetic energy, hot electrons can be injected and trapped in areas of the device where they should not be, forming a space charge that causes the device to degrade or become unstable. In the hot electron case, which is characterized by $\ell_e \gg \ell_p$, in Eq. (2b), one has $|\mathbf{E} \cdot \mathbf{I}| \gg |C(T^{(e)} - T^{(p)})|$, since

the energy gained by the electrons (between successive collisions under the action of the electric field) is higher than that communicated to the lattice, and the electron temperatures will be higher than the phonon temperature in an amount of

$$\Delta T \simeq \frac{\mathbf{E} \cdot \mathbf{I}}{nk_B} \tau_e = e \frac{\mathbf{E} \cdot \mathbf{V}}{k_B} \tau_e, \quad (32)$$

with k_B being the Boltzmann constant, n the electron number density per unit volume, e the absolute value of the electric charge, and \mathbf{V} the electric potential.

In such a condition, we can suppose that the electron heat flux is predominant with respect to the others, and that the phonon temperature and the lattice temperature coincide with the reference temperature, while the electron temperature is

$$T^{(e)} = T_{\text{ref}} \left[1 - \frac{\tau_e}{(\lambda_e + \epsilon \Pi \sigma_e) c_v^{(e)} T_{\text{ref}}^2} \mathbf{q}^{(e)} \cdot \mathbf{q}^{(e)} \right]. \quad (33)$$

It is worth observing that τ_e (or ℓ_e) may have two different contributions: that corresponding to electron–electron interactions, which is very short, and that corresponding to electron–lattice interaction (or electron–phonon interaction) which may be considerably large. The time of interest for hot electrons is the latter one, because it is the time during which the electrons gain energy under the action of the external electric field before giving it to the lattice. Having a short electron–electron collision time means that the electrons will have a distribution close to that of equilibrium, but with a kinetic temperature higher than that of the lattice.

A good understanding of hot-electron phenomena is very important for all modern semiconductor devices. In fact, in many occasions, these phenomena are a nuisance that should be avoided, as for example the hot-electron injection into the gate dielectric in silicon field-effect transistors, which produces a degradation of the transistor characteristics and may lead to a failure of the circuit.

4 Conclusions

In the present paper we have proposed a system of enhanced field equations for thermoelectricity, taking into account the different mean-free path of phonons and electrons, which leads to different nonlocal contributions, under the hypothesis that phonons and electrons have different temperatures. Energy exchanges between the phonons and the electrons are also

possible. In Section 1 we briefly discussed the importance of accounting for the differences between the phonon temperature and the electron one. It is worth observing, indeed, that a two-temperature model (TTM) was also proposed in previous papers [50,51] and, for example, has been widely employed both in theoretical and/or computational studies of laser interactions in metals [52]. That model describes the temporal and spatial evolution of the lattice and electron temperatures in the irradiated target by two coupled nonlinear differential equations [21], which are very similar to Eqs. (2) once the constitutive assumptions (4) are taken into account. The TTM relies on the notion of separation of relaxation time-scales in the electron and phonon distributions.

The model proposed in the present paper, instead, follows from the idea that the heat carriers (i.e., the electrons and the phonons) behave as a gas-like collection. In this way, we have taken advantage of a phonon-hydrodynamic approach to developing a theoretical model which introduces enhanced time rates for the phonon and electron heat flux, as well as for the electric-current density flux, in view of describing thermoelectric effects. Although no experimental evidence may be invoked to justify the use of Eqs. (25), the thermodynamic analysis performed in Section 2 ensures that they agree with the basic principles of continuum physics.

Note, incidentally, that in Eq. (11) we have taken for the classical part of the entropy flux the expression \mathbf{q}/T , with T being the average temperature defined by Eq. (6); an alternative possibility worthy of exploration would be to take $\mathbf{q}^{(e)}/T^{(e)} + \mathbf{q}^{(p)}/T^{(p)}$, instead of the former expression. We think it is an interesting, albeit academic, point whose discussion would require a specific paper, and we do not deal with it here.

As a simple illustration of our model, we have considered two different extreme situations: the situation wherein $\ell_p \gg \ell_e$, and that characterized by $\ell_e \gg \ell_p$. In the former case nonlocal effects are neglected for electrons, whose temperature is identified with the local-equilibrium temperature, while nonlocal effects are kept for phonons whose temperature is different from the local-equilibrium temperature. In the special case of a silicon sample at very low temperature, we have estimated the difference between the phonon temperature and the electron one.

In the latter case, instead, which characterizes the hot electrons, the electron temperature is higher than the phonon temperature.

As a further point of interest, in this paper we have also explicitly related the several nonlocal contributions in Eqs. (25) to extra terms in the entropy flux (28), thus proving the relevance of the nonclassical form of the entropy flux in the analysis of nonlocal effects. This is a fundamental topic

in non-equilibrium thermodynamics, where the entropy flux generally has not received sufficient attention [45]. These contributions are expected to play a relevant role in the thermodynamic analysis of generalized transport equations, which is currently an active field of research.

A Consequences of the entropy inequality

In the inequality (12) both ψ and \mathbf{k} have to be expressed by constitutive functions, since they do not belong to Σ . According to the principle of equipresence, we assume $\psi = \psi(\Sigma)$ and $\mathbf{k} = \mathbf{k}(\Sigma)$. Then, by the chain rule one may write inequality (12) in the following explicit form:

$$\begin{aligned}
& \left(\frac{\partial \psi}{\partial T^{(p)}} + \frac{c_v^{(p)}}{c_v} s \right) \dot{T}^{(p)} + \left(\frac{\partial \psi}{\partial T^{(e)}} + \frac{c_v^{(e)}}{c_v} s \right) \dot{T}^{(e)} + \frac{\partial \psi}{\partial \nabla T^{(p)}} \cdot \nabla \dot{T}^{(p)} \\
& + \frac{\partial \psi}{\partial \nabla T^{(e)}} \cdot \nabla \dot{T}^{(e)} + \frac{\partial \psi}{\partial \mathbf{q}^{(e)}} \cdot \dot{\mathbf{q}}^{(e)} + \frac{\partial \psi}{\partial \nabla \mathbf{q}^{(e)}} : \nabla \dot{\mathbf{q}}^{(e)} + \frac{\partial \psi}{\partial \mathbf{q}^{(p)}} \cdot \dot{\mathbf{q}}^{(p)} \\
& + \frac{\partial \psi}{\partial \nabla \mathbf{q}^{(p)}} : \nabla \dot{\mathbf{q}}^{(p)} + \frac{\partial \psi}{\partial \mathbf{I}} \cdot \dot{\mathbf{I}} + \frac{\partial \psi}{\partial \nabla \mathbf{I}} : \nabla \dot{\mathbf{I}} - T \left(\frac{\partial \mathbf{k}}{\partial T^{(p)}} \cdot \nabla T^{(p)} \right. \\
& + \frac{\partial \mathbf{k}}{\partial T^{(e)}} \cdot \nabla T^{(e)} + \frac{\partial \mathbf{k}}{\partial \mathbf{q}^{(e)}} : \nabla \mathbf{q}^{(e)} + \frac{\partial \mathbf{k}}{\partial \mathbf{q}^{(p)}} : \nabla \mathbf{q}^{(p)} + \frac{\partial \mathbf{k}}{\partial \mathbf{I}} : \nabla \mathbf{I} \\
& + \frac{\partial \mathbf{k}}{\partial \nabla T^{(p)}} : \nabla \nabla T^{(p)} + \frac{\partial \mathbf{k}}{\partial \nabla T^{(e)}} : \nabla \nabla T^{(e)} + \frac{\partial \mathbf{k}}{\partial \nabla \mathbf{q}^{(p)}} \odot \nabla \nabla \mathbf{q}^{(p)} \\
& \left. + \frac{\partial \mathbf{k}}{\partial \nabla \mathbf{q}^{(e)}} \odot \nabla \nabla \mathbf{q}^{(e)} + \frac{\partial \mathbf{k}}{\partial \nabla \mathbf{I}} \odot \nabla \nabla \mathbf{I} \right) - \mathbf{E} \cdot \mathbf{I} + \frac{\mathbf{q} \cdot \nabla T}{T} \leq 0, \quad (34)
\end{aligned}$$

wherein the colon stands for the double inner product of two matrices (i.e., $\mathbf{A} : \mathbf{B} = A_{ij} B_{ij}$, once Einstein's summation convention over repeated indices is used), and the symbol \odot means the triple inner product of two third-rank tensors (that is, $\mathbf{A} \odot \mathbf{B} = A_{ijk} B_{ijk}$).

Our aim here is to determine necessary and sufficient conditions for the physical consistency of Eqs. (8) (together with the constitutive assumptions in Eqs. (9) and (10)), which are represented by a set of thermodynamic restrictions on the constitutive functions of ψ and \mathbf{k} , ensuring that the inequality (34) is never violated. To achieve that task, at first it is useful to rewrite Eqs. (8) in explicit form. Owing to the constitutive equations (9) and (10), they read

$$\begin{aligned}
\dot{\mathbf{q}}^{(p)} = & \gamma_0^{(p)} \nabla T^{(p)} + \gamma_1^{(p)} \mathbf{q}^{(p)} + \Gamma_0^{(p)} \nabla \nabla \cdot \mathbf{q}^{(p)} + \Gamma_1^{(p)} \nabla^2 \mathbf{q}^{(p)} \\
& + \Gamma_2^{(p)} (\nabla \mathbf{q}^{(p)} \cdot \mathbf{q}^{(p)} + \mathbf{q}^{(p)} \nabla \cdot \mathbf{q}^{(p)}), \quad (35a)
\end{aligned}$$

$$\begin{aligned} \dot{\mathbf{q}}^{(e)} &= \gamma_0^{(e)} \nabla T^{(e)} + \gamma_1^{(e)} \mathbf{q}^{(e)} + \Gamma_0^{(e)} \nabla \nabla \cdot \mathbf{q}^{(e)} + \Gamma_1^{(e)} \nabla^2 \mathbf{q}^{(e)} \\ &\quad + \Gamma_2^{(e)} (\nabla \mathbf{q}^{(e)} \cdot \mathbf{q}^{(e)} + \mathbf{q}^{(e)} \nabla \cdot \mathbf{q}^{(e)}) + \delta^{(Ie)} \mathbf{E}, \end{aligned} \quad (35b)$$

$$\begin{aligned} \dot{\mathbf{I}} &= \gamma_0^{(I)} \nabla T^{(e)} + \gamma_1^{(I)} \mathbf{I} + \Gamma_0^{(I)} \nabla \nabla \cdot \mathbf{I} + \Gamma_1^{(I)} \nabla^2 \mathbf{I} \\ &\quad + \Gamma_2^{(I)} (\nabla \mathbf{I} \cdot \mathbf{I} + \mathbf{I} \nabla \cdot \mathbf{I}) + \delta^{(eI)} \mathbf{E}. \end{aligned} \quad (35c)$$

According to the classical Coleman–Noll procedure [33, 53, 54] for the exploitation of the second law, thermodynamic restrictions on the constitutive functions may be obtained by replacing in inequality (34) the time derivatives of $\mathbf{q}^{(p)}$, $\mathbf{q}^{(e)}$, and \mathbf{I} through Eqs. (35). This yields a generalized entropy inequality containing both the time derivatives of some of the state variables (i.e., $\dot{T}^{(p)}$, $\dot{T}^{(e)}$, $\nabla \dot{T}^{(p)}$, $\nabla \dot{T}^{(e)}$, $\nabla \dot{\mathbf{q}}^{(p)}$, $\nabla \dot{\mathbf{q}}^{(e)}$, $\nabla \dot{\mathbf{I}}$) and the second-order spatial derivatives of the unknown fields (i.e., $\nabla \nabla T^{(p)}$, $\nabla \nabla T^{(e)}$, $\nabla \nabla \mathbf{q}^{(p)}$, $\nabla \nabla \mathbf{q}^{(e)}$, $\nabla \nabla \mathbf{I}$). All these quantities may assume arbitrary values in each point of the system at any time [32, 33]. Since the generalized entropy inequality is linear in those derivatives, their coefficients must vanish, otherwise the inequality could be easily violated [32, 33]. By nullifying the coefficient of each time derivative, the following first set of thermodynamic restrictions ensues:

$$s = -\frac{c_v}{c_v^{(p)}} \frac{\partial \psi}{\partial T^{(p)}}, \quad s = -\frac{c_v}{c_v^{(e)}} \frac{\partial \psi}{\partial T^{(e)}}, \quad (36a)$$

$$\frac{\partial \psi}{\partial \nabla T^{(p)}} = \mathbf{0}, \quad \frac{\partial \psi}{\partial \nabla T^{(e)}} = \mathbf{0}, \quad (36b)$$

$$\frac{\partial \psi}{\partial \nabla \mathbf{q}^{(p)}} = \mathbf{0}, \quad \frac{\partial \psi}{\partial \nabla \mathbf{q}^{(e)}} = \mathbf{0}, \quad \frac{\partial \psi}{\partial \nabla \mathbf{I}} = \mathbf{0}, \quad (36c)$$

which yields useful information about the strict relation between the form of s and ψ , as well as the independence of the latter on the gradients entering the state space. In particular, Eqs. (36b)–(36c) together with the theory of the representation of isotropic scalar functions depending on scalars and vectors [26], suggest that a possible form of the Helmholtz free energy is Eq. (13). Since ψ has to be minimum at equilibrium [12, 13, 31], from Eq. (13) it is easy to infer that ψ_p , ψ_e , and ψ_I are suitable positive-defined functions. Once the form of ψ given by Eq. (13) is taken into account, by nullifying the coefficients of the above second-order spatial derivatives of the unknown fields, we further find that the tensors

$$\frac{\partial \mathbf{k}}{\partial \nabla T^{(p)}}, \quad \frac{\partial \mathbf{k}}{\partial \nabla T^{(e)}}, \quad (37a)$$

$$T \frac{\partial \mathbf{k}}{\partial \nabla \mathbf{q}^{(p)}} - \psi^{(p)} (\Gamma_0^{(p)} \mathbf{q}^{(p)} \mathbf{U} + \Gamma_1^{(p)} \mathbf{U} \mathbf{q}^{(p)}), \quad (37b)$$

$$T \frac{\partial \mathbf{k}}{\partial \nabla \mathbf{q}^{(e)}} - \psi^{(e)} (\Gamma_0^{(e)} \mathbf{q}^{(e)} \mathbf{U} + \Gamma_1^{(e)} \mathbf{U} \mathbf{q}^{(e)}), \quad (37c)$$

$$T \frac{\partial \mathbf{k}}{\partial \nabla \mathbf{I}} - \psi^{(I)} (\Gamma_0^{(I)} \mathbf{I} \mathbf{U} + \Gamma_1^{(I)} \mathbf{U} \mathbf{I}) \quad (37d)$$

are skew-symmetric as regards the indices with respect to which the corresponding second-order gradient in the generalized entropy inequality is symmetric [19]. On the other hand, the relations

$$\frac{\partial \mathbf{k}}{\partial \nabla T^{(p)}} = \mathbf{0}, \quad \frac{\partial \mathbf{k}}{\partial \nabla T^{(e)}} = \mathbf{0}, \quad (38a)$$

$$T \frac{\partial \mathbf{k}}{\partial \nabla \mathbf{q}^{(p)}} = \psi^{(p)} (\Gamma_0^{(p)} \mathbf{q}^{(p)} \mathbf{U} + \Gamma_1^{(p)} \mathbf{U} \mathbf{q}^{(p)}), \quad (38b)$$

$$T \frac{\partial \mathbf{k}}{\partial \nabla \mathbf{q}^{(e)}} = \psi^{(e)} (\Gamma_0^{(e)} \mathbf{q}^{(e)} \mathbf{U} + \Gamma_1^{(e)} \mathbf{U} \mathbf{q}^{(e)}), \quad (38c)$$

$$T \frac{\partial \mathbf{k}}{\partial \nabla \mathbf{I}} = \psi^{(I)} (\Gamma_0^{(I)} \mathbf{I} \mathbf{U} + \Gamma_1^{(I)} \mathbf{U} \mathbf{I}) \quad (38d)$$

are sufficient to satisfy the restrictions above. Equations (38a) render \mathbf{k} independent both of $\nabla T^{(p)}$ and of $\nabla T^{(e)}$. Equations (38b)–(38d), instead, may be integrated in order to obtain the form of \mathbf{k} . Straightforward calculations allow us to obtain Eq. (14a).

Finally, once Eqs. (36) and (38) have been taken into account, the generalized entropy inequality reduces to (14b). Therein $f(\Sigma)$ summarizes all the remaining terms of the reduced entropy inequality which do not vanish, that is,

$$\begin{aligned} f(\Sigma) = & -\frac{\partial \psi}{\partial \mathbf{q}^{(p)}} \cdot [\Gamma_2^{(p)} (\nabla \mathbf{q}^{(p)} \cdot \mathbf{q}^{(p)} + \mathbf{q}^{(p)} \nabla \cdot \mathbf{q}^{(p)}) \\ & + \gamma_0^{(p)} \nabla T^{(p)} + \gamma_1^{(p)} \mathbf{q}^{(p)}] \\ & -\frac{\partial \psi}{\partial \mathbf{q}^{(e)}} \cdot [\Gamma_2^{(e)} (\nabla \mathbf{q}^{(e)} \cdot \mathbf{q}^{(e)} + \mathbf{q}^{(e)} \nabla \cdot \mathbf{q}^{(e)}) \\ & + \gamma_0^{(e)} \nabla T^{(e)} + \gamma_1^{(e)} \mathbf{q}^{(e)} + \delta^{(Ie)} \mathbf{E}] \\ & -\frac{\partial \psi}{\partial \mathbf{I}} \cdot [\Gamma_2^{(I)} (\nabla \mathbf{I} \cdot \mathbf{I} + \mathbf{I} \nabla \cdot \mathbf{I}) \\ & + \gamma_0^{(I)} \nabla T^{(e)} + \gamma_1^{(I)} \mathbf{I} + \delta^{(eI)} \mathbf{E}] \end{aligned}$$

$$\begin{aligned}
& + T \left(\frac{\partial \mathbf{k}}{\partial T^{(p)}} \cdot \nabla T^{(p)} + \frac{\partial \mathbf{k}}{\partial T^{(e)}} \cdot \nabla T^{(e)} + \frac{\partial \mathbf{k}}{\partial \mathbf{q}^{(e)}} : \nabla \mathbf{q}^{(e)} \right. \\
& \quad \left. + \frac{\partial \mathbf{k}}{\partial \mathbf{q}^{(p)}} : \nabla \mathbf{q}^{(p)} + \frac{\partial \mathbf{k}}{\partial \mathbf{I}} : \nabla \mathbf{I} \right). \quad (39)
\end{aligned}$$

Acknowledgments. D. Jou acknowledges the financial support from the *Dirección General de Investigación* of the Spanish Ministry of Economics and Competitiveness under grant FIS No. 2012-33099, the *Consolider Project NanoTherm* (grant CSD-2010-00044), and the *Direcció General de Recerca* of the Generalitat of Catalonia under grant No. 2009-SGR-00164.

A. Sellitto acknowledges the University of Basilicata for funding the research project *Modeling heat and electric transport in nanosystems in the presence of memory, nonlocal and nonlinear effects*, and the Italian *Gruppo Nazionale per la Fisica Matematica – GNFM* for financial support under grant *Progetto Giovani 2012*.

V. A. Cimmelli acknowledges the financial support from the Italian *Gruppo Nazionale per la Fisica Matematica – GNFM*. Thanks are given to the University of Basilicata for financial support and for funding the research subject in mathematical physics *Equazioni costitutive per la conduzione del calore nei nanosistemi*.

Bibliography

- [1] Rowe, D. M., *Thermoelectrics Handbook: Macro to Nano*, Taylor & Francis, New York, 2006.
- [2] Hochbaum, A. I., Chen, R., Delgado, R. D., Liang, W., Garnett, E. C., Najarian, M., Majumdar, A. and Yang, P., Enhanced thermoelectric performance of rough silicon nanowires, *Nature*, 451 (2008), 163–167.
- [3] Jou, D., Cimmelli, V. A. and Sellitto, A., Nonlocal heat transport with phonons and electrons: Application to metallic nanowires, *Int. J. Heat Mass Transfer*, 55 (2012), 2338–2344.
- [4] Sellitto, A., Cimmelli, V. A. and Jou, D., Thermoelectric effects and size dependency of the figure-of-merit in cylindrical nanowires, *Int. J. Heat Mass Transfer*, 57 (2013), 109–116.
- [5] Chen, G., *Nanoscale Energy Transport and Conversion – A Parallel Treatment of Electrons, Molecules, Phonons, and Photons*, Oxford University Press, Oxford, 2005.

- [6] Alvarez, F. X., Jou, D. and Sellitto, A., Phonon hydrodynamics and phonon-boundary scattering in nanosystems, *J. Appl. Phys.*, 105 (2009), 014317 (5 pages).
- [7] Sellitto, A., Alvarez, F. X. and Jou, D., Second law of thermodynamics and phonon-boundary conditions in nanowires, *J. Appl. Phys.*, 107 (2010), 064302 (7 pages).
- [8] Sellitto, A., Alvarez, F. X. and Jou, D., Temperature dependence of boundary conditions in phonon hydrodynamics of smooth and rough nanowires, *J. Appl. Phys.*, 107 (2010), 114312 (7 pages).
- [9] Gouin, H. and Ruggeri, T., Identification of an average temperature and a dynamical pressure in a multitemperature mixture of fluids, *Phys. Rev. E*, 78 (2008), 016303 (7 pages).
- [10] Ruggeri, T. and Lou, J., Heat conduction in multi-temperature mixtures of fluids: The role of the average temperature, *Phys. Lett. A*, 373 (2009), 3052–3055.
- [11] Ruggeri, T., Multi-temperature mixture of fluids, *Theoret. Appl. Mech.*, 36 (2009), 207–238.
- [12] Lebon, G., Jou, D. and Casas-Vázquez, J., *Understanding Nonequilibrium Thermodynamics*, Springer, Berlin, 2008.
- [13] Jou, D., Casas-Vázquez, J. and Lebon, G., *Extended Irreversible Thermodynamics*, 4th rev. edn., Springer, Berlin, 2010.
- [14] Cimmelli, V. A., Different thermodynamic theories and different heat conduction laws, *J. Non-Equilib. Thermodyn.*, 34 (2009), 299–333.
- [15] Cimmelli, V. A., Sellitto, A. and Jou, D., Nonlocal effects and second sound in a nonequilibrium steady state, *Phys. Rev. B*, 79 (2009), 014303 (13 pages).
- [16] Luzzi, R., Vasconcellos, A. R., Casas-Vázquez, J. and Jou, D., On the selection of the state space in nonequilibrium thermodynamics, *Physica A*, 248 (1998), 113–137.
- [17] Casas-Vázquez, J. and Jou, D., Temperature in nonequilibrium states: A review of open problems and current proposals, *Rep. Prog. Phys.*, 66 (2003), 1937–2023.
- [18] Jou, D., Cimmelli, V. A. and Sellitto, A., Nonequilibrium temperatures and second-sound propagation along nanowires and thin layers, *Phys. Lett. A*, 373 (2009), 4386–4392.

- [19] Cimmelli, V. A., Sellitto, A. and Jou, D., Nonequilibrium temperatures, heat waves, and nonlinear heat transport equations, *Phys. Rev. B*, 81 (2010), 054301 (9 pages).
- [20] Kaganov, M. I., Lifshitz, I. M. and Tanatarov, M. V., Relaxation between electrons and crystalline lattices, *Sov. Phys. JETP*, 4 (1957), 173.
- [21] Lin, Z., Zhigilei, L. V. and Celli, V., Electron-phonon coupling and electron heat capacity of metals under conditions of strong electron–phonon nonequilibrium, *Phys. Rev. B*, 77 (2008), 075133 (17 pages).
- [22] Coleman, B. D. and Dill, E. H., Thermodynamic restrictions on the constitutive equations of electromagnetic theory, *ZAMP*, 22 (1971), 691–702.
- [23] Benedict, L. X., Louie, S. G. and Cohen, M. L., Heat capacity of carbon nanotubes, *Solid State Commun.*, 100 (1996), 177–180.
- [24] Lebon, G., Jou, D., Casas-Vázquez, J. and Muschik, W., Weakly nonlocal and nonlinear heat transport in rigid solids, *J. Non-Equilib. Thermodyn.*, 31 (1984), 149–160.
- [25] Jou, D., Cimmelli, V. A. and Sellitto, A., Dynamical temperature and renormalized flux variable in extended thermodynamics of rigid heat conductors, *J. Non-Equilib. Thermodyn.*, 36 (2011), 373–392.
- [26] Smith, G. F., On isotropic functions of symmetric tensors, skew-symmetric tensors and vectors, *Int. J. Eng. Sci.*, 9 (1971), 899–916.
- [27] Gurtin, M. E., *An Introduction to Continuum Mechanics*, Academic Press, New York, 1981.
- [28] De Groot, S. R. and Mazur, P., *Nonequilibrium Thermodynamics*, North-Holland, Amsterdam, 1962.
- [29] Gyarmati, I., *Nonequilibrium Thermodynamics*, Springer, Berlin, 1970.
- [30] Jou, D., Casas-Vázquez, J. and Criado-Sancho, M., *Thermodynamics of Fluids Under Flow*, Springer, Berlin, 2011.
- [31] Müller, I. and Ruggeri, T., *Rational Extended Thermodynamics*, Springer, Berlin, 1998.
- [32] Cimmelli, V. A., Sellitto, A. and Triani, V., A generalized Coleman–Noll procedure for the exploitation of the entropy principle, *Proc. R. Soc. A*, 466 (2010), 911–925.

- [33] Coleman, B. D. and Noll, W., The thermodynamics of elastic materials with heat conduction and viscosity, *Arch. Ration. Mech. Anal.*, 13 (1963), 167–178.
- [34] Müller, I., On the entropy inequality, *Arch. Rational Mech. Anal.*, 26 (1967), 118–141.
- [35] Guyer, R. A. and Krumhansl, J. A., Solution of the linearized phonon Boltzmann equation, *Phys. Rev.*, 148 (1966), 766–778.
- [36] Guyer, R. A. and Krumhansl, J. A., Thermal conductivity, second sound and phonon hydrodynamic phenomena in nonmetallic crystals, *Phys. Rev.*, 148 (1966), 778–788.
- [37] Hopkins, P. E., Norris, P. M., Phinney, L. M., Policastro, S. A. and Kelly, R. G., Thermal conductivity in nanoporous gold films during electron–phonon nonequilibrium, *J. Nanomaterials*, (2008), 418050 (7 pages).
- [38] Stojanovic, N., Maithripala, D. H. S., Berg, J. M. and Holtz, M., Thermal conductivity in metallic nanostructures at high temperature: Electrons, phonons, and the Wiedemann–Franz law, *Phys. Rev. B*, 82 (2010), 075418 (9 pages).
- [39] Callen, H. B., *Thermodynamics and an Introduction to Thermostatistics*, 2nd edn., John Wiley and Sons, New York, 1985.
- [40] Serdyukov, S. I., Generalized temperature and non-classical heat conduction in rigid bodies, *J. Non-Equilib. Thermodyn.*, 38 (2013), 81–96.
- [41] Sellitto, A. and Cimmelli, V. A., A continuum approach to thermomass theory, *J. Heat Trans. – T. ASME*, 134 (2012), 112402 (8 pages).
- [42] Dong, Y., Cao, B.-Y. and Guo, Z.-Y., Generalized heat conduction laws based on thermomass theory and phonon hydrodynamics, *J. Appl. Phys.*, 110 (2011), 063504 (6 pages).
- [43] Cimmelli, V. A., Weakly nonlocal thermodynamics of anisotropic rigid heat conductors revisited, *J. Non-Equilib. Thermodyn.*, 36 (2011), 285–309.
- [44] Triani, V. and Cimmelli, V. A., Anisotropic heat transport in rigid solids, *J. Non-Equilib. Thermodyn.*, 37 (2012), 377–392.
- [45] Sellitto, A., Cimmelli, V. A. and Jou, D., Entropy flux and anomalous axial heat transport at nanoscale, *Phys. Rev. B*, 87 (2013), 054302 (7 pages).
- [46] Ziman, J. M., *Electrons and Phonons*, Oxford University Press, Oxford, 2001.

- [47] Levermore, C. D., Relating Eddington factors to flux limiters, *J. Quant. Spec. Rad. Transfer.*, 23 (1998), 176–191.
- [48] Anile, A. M., Pennisi, S. and Sammartino, M., A thermodynamical approach to Eddington factors, *J. Math. Phys.*, 32 (1991), 544–550.
- [49] Balkan, N., *Hot Electrons in Semiconductors – Physics and Devices*, Clarendon Press, Oxford, 1998.
- [50] Anisimov, S. I., Kapeliovich, B. L. and Perel'man, T. L., Electron emission from metal surfaces exposed to ultrashort laser pulses, *Sov. Phys. JETP*, 39 (1974), 375.
- [51] Hertel, T. and Moos, G., Electron–phonon interaction in single–wall carbon nanotubes: A time-domain study, *Phys. Rev. Lett.*, 84 (2000), 5002–5005.
- [52] R. H. M. Groeneveld, Sprik, R. and Lagendijk, A., Femtosecond spectroscopy of electron–electron and electron–phonon energy relaxation in Ag and Au, *Phys. Rev. B*, 51 (1995), 11433–11445.
- [53] Muschik, W. and Ehrentraut, H., An amendment to the second law, *J. Non-Equilib. Thermodyn.*, 21 (1996), 175–192.
- [54] Cimmelli, V. A., Sellitto, A. and Triani, V., A new perspective on the form of the first and second laws in rational thermodynamics: Korteweg fluids as an example, *J. Non-Equilib. Thermodyn.*, 35 (2010), 251–265.

Received July 25, 2013; accepted October 8, 2013.

Author information

David Jou, Departament de Física, Universitat Autònoma de Barcelona, 08193 Bellaterra, Catalonia; and Institut d'Estudis Catalans, Carme 47, 08001 Barcelona, Catalonia, Spain.
E-mail: david.jou@uab.cat

Antonio Sellitto, Department of Mathematics, Computer Science and Economics, University of Basilicata, Viale dell'Ateneo Lucano, 10, 85100 Potenza, Italy.
E-mail: ant.sellitto@gmail.com

Vito A. Cimmelli, Department of Mathematics, Computer Science and Economics, University of Basilicata, Viale dell'Ateneo Lucano, 10, 85100 Potenza, Italy.
E-mail: vito.cimmelli@unibas.it