Constitutive equations for heat conduction in nanosystems and nonequilibrium processes: an overview

David Jou[1,2], Vito Antonio Cimmelli[3]*

[1]Departament de Física, Universitat Autònoma de Barcelona, Bellaterra, Catalonia, Spain

[2]Institut d'Estudis Catalans, Barcelona, Catalonia, Spain

[3]Department of Mathematics, Computer Science and Economics, University of Basilicata, Potenza, Italy

*Email address for correspondence: vito.cimmelli@unibas.it

Abstract

We provide an overview on the problem of modeling heat transport at nanoscale and in far-from-equilibrium processes. A survey of recent results is summarized, and a conceptual discussion of them in the framework of Extended Irreversible Thermodynamics is developed.

Keywords: Fourier law, heat transport equations, nanosystems, nonlocal effects, nonlinear effects, thermoelectric effects, nonequilibrium processes

AMS subject classification: 74A15, 74A20, 80A17, 80A20

1. Introduction

Heat transport is currently experiencing a true revolution, which is enlarging its domain of applicability and discovering new phenomenologies where the classical Fourier theory of heat conduction is no longer applicable [1,2]. This new epoch began with the miniaturization, since several new phenomena arise in connection to the relation between the heat carriers' mean-free path ℓ, and a relevant characteristic size of the system L, expressed by the Knudsen number $\mathrm{Kn} = \ell/L$. The Fourier law is valid in the limit of very small Knudsen number, i.e., when $\ell/L \ll 1$. Indeed, Kn may increase both because of an increase of ℓ (as in rarefied gases and in aerospace engineering), and because of a reduction of L (as in miniaturization technologies).

Nowadays, the analysis of heat transport in nanosystems stimulated new approaches to the foundations of thermodynamics, transport theory, statistical physics and computer simulations. The most current perspective on this topic starts from a microscopic basis (kinetic theory, computer simulations) and modifies it to incorporate the collisions of the heat carriers with the walls or, in very small systems, to take into account quantum confinement. Although, apparently, the topic is clearly settled, there are several fundamental open questions at this level.

One of them is the meaning of temperature and its relation with heat transport [3–7]. In fact, different degrees of freedom, far from equilibrium, may be associated with different "temperatures". For instance, in harmonic oscillators, and under a strong heat flux, the average kinetic energy is not the same as the average potential energy, and thus one may consider a kinetic temperature and a potential temperature. How do the gradients of these different temperatures contribute to heat transport?

A second open problem is that most of the microscopic evaluations of the thermal conductivity, based on the first-order expressions of kinetic theory, seem to be questionable. In fact, when the mean free path of heat carriers is comparable to the characteristic spatial range of variation of the distribution function, the kinetic theory leads to more complicated transport laws than the Fourier's one (namely, Burnett expansions in Chapman-Enskog approach, moment expansions in Grad's approach), but most of the analyses stick to the first-order approximation [8]. The success of the results may be due to the fact that most of these analyses are restricted to one-dimensional heat flow, rather than, for instance, radial heat flow or other situations.

Further conceptual problems arise from the thermodynamic point of view. Indeed, if generalized heat transport equations are used, it turns out that the analysis of their consistency with the second law of thermodynamics requires a generalized framework, where the entropy and the entropy flux are not known a priori. In fact, entropy and entropy flux are found to be, already in simple situations, more general than their local-equilibrium forms [9–11].

Considering more general heat transport equations and more general expressions of thermodynamic quantities, and comparing these last to more sophisticated models of microscopic theories, is a big stimulus for the conceptual progress of non-equilibrium thermodynamics.

2. Heat transport equations beyond the Fourier law and hydro-dynamic regime

Nowadays, there is a current interest for mesoscopic modelization based on generalized heat transport equations simpler than the much more complex and detailed microscopic approach. Three such approaches are the phonon hydrodynamics [5–7], the thermomass theory [12–14], and the dual-phase-lag model [15,16]. All these models consider the heat carriers as a fluid, whose hydrodynamic-like equations of motion describe the heat transport. The phonon hydrodynamics lays on the Guyer-Krumhansl transport equation [16–22] for the heat flux $\mathbf{q}$, i.e.,

$$\tau \dot{\mathbf{q}} + \mathbf{q} = -\kappa_0 \nabla T + \ell^2 \left(\nabla^2 \mathbf{q} + 2\nabla \nabla \cdot \mathbf{q} \right) \tag{1}$$

where τ is the relaxation time due to the resistive (quasi-momentum not conserved) scattering of phonons in the bulk, T the temperature, and ℓ the phonon mean-free path. Moreover, in Eq. (1) κ_0 represents the Ziman limit [23] for the bulk thermal conductivity, namely, $\kappa_0 = \varrho c_v \tau \bar{c}^2/3$, where ϱ is the mass density, c_v the specific heat per unit mass at constant volume, and $\bar{c}$ is the average speed of phonons.

Whenever nonlocal effects are negligible, Eq. (1) turns out the Maxwell-Cattaneo-Vernotte equation [24]

$$\tau \dot{\mathbf{q}} + \mathbf{q} = -\kappa_0 \nabla T \tag{2}$$

which accounts for heat conduction with finite speed of thermal disturbances [25,26].

Equation (2) generalizes the classical Fourier equation

$$\mathbf{q} = -\kappa_0 \nabla T \tag{3}$$

by including relaxation effects (characterized by the relaxation time τ), while Eq. (1) generalizes Eq. (2) by including nonlocal effects (characterized by the mfp ℓ).

Eqs. (1) and (2) have been derived in the linear regime and do not account for nonlinear effects, which instead are usual at the micro/nanoscale, since even small differences of temperature, over a reduced length-scale may produce strong gradients. Extensions of Eq. (1) to the nonlinear regime may be obtained in the framework of Extended Irreversible Thermodynamics (EIT) [6,7,21,27,28], a theory which upgrades the dissipative fluxes to the rank of independent thermodynamic variables [10,22,29–31], while nonlinear generalizations of Eq. (2) have been obtained either in EIT [5], or in the framework of the thermomass theory [12–14], which also pays a special attention to nonlinear terms in the heat transport equation.

198

At nanoscale the deformations of the heat conductor do not play any role, so that we may limit ourselves to consider rigid bodies. On the other hand, the analysis of heat conduction requires to complement Eq. (1) by the local balance of the energy which, for rigid bodies in the absence of external heat supply reads

$$\dot{u} + \nabla \cdot \mathbf{q} = 0 \tag{4}$$

with u as the internal energy per unit volume. When Eq. (4) is taken into account, in steady states Eq. (1) turns out the following nonlocal constitutive equation for the heat flux:

$$\mathbf{q} = -\kappa_0 \nabla T + \ell^2 \nabla^2 \mathbf{q} \tag{5}$$

In nanosystems one may have in several cases that $\ell^2 \nabla^2 \mathbf{q} \approx \mathrm{Kn}^2\, \mathbf{q} \gg \mathbf{q}$, since the Knudsen number can take values relatively higher than 1. Then, the nonlocal term in Eq. (5) may be more important than the heat flux itself [32–35], and that equation reduces to

$$\nabla^2 \mathbf{q} = \frac{\kappa_0}{\ell^2} \nabla T \tag{6}$$

Equation (6) is analogous to the Navier-Stokes equation in steady states when the nonlinear convective term is negligible, i.e.,

$$\nabla^2 \mathbf{v} = \frac{1}{\eta} \nabla p \tag{7}$$

η being the shear viscosity of the fluid, $\mathbf{v}$ the velocity of the fluid, and p the pressure. The analytical resemblance between Eqs. (6) and (7) motivates the definition of "hydrodynamic regime" for those situations in which the heat flux obeys Eq. (6), and allows one to identify the "viscosity" of phonons in terms of the thermal conductivity and of their mean-free path.

3. Second-order nonlocal effects

When the Knudsen number becomes comparable to (or higher than) 1, the heat transport is no longer diffusive, but ballistic. Moreover, when the mean-free path between successive collisions becomes large, there is a direct connection among nonadjacent regions of the system with very different values of the temperature. Nonlocal effects are especially important to describe the transition from diffusive to ballistic regime. To this end in EIT it is possible to introduce a new extra variable, represented by a second-order tensor $\mathbf{Q}$, and write the balance of the heat flux in the following general form [36]

$$\tau_1 \dot{\mathbf{q}} + \mathbf{q} = -\lambda \nabla T + \nabla \cdot \mathbf{Q} \tag{8}$$

where τ_1 is still a relaxation time. The tensor $\mathbf{Q}$, assumed to be symmetric, may be split in the usual form $\mathbf{Q} = Q\mathbf{I} + \mathbf{Q}_s$, the scalar Q being one-third of the trace of $\mathbf{Q}$, and $\mathbf{Q}_s$ being the deviatoric part of $\mathbf{Q}$. In the relaxation time approximation [37], the evolution equations for Q and $\mathbf{Q}_s$ may be written as [37],

(9a) $$\tau_0 \dot{Q} + Q = \gamma_0 \nabla \cdot \mathbf{q}$$

(9b) $$\tau_2 \dot{\mathbf{Q}}_s + \mathbf{Q}_s = 2\gamma_2 \left[(\nabla \mathbf{q})^0 \right]_s$$

where $\left[(\nabla \mathbf{q})^0 \right]_s$ denotes the symmetric and traceless part of $\nabla \mathbf{q}$. Assuming that the relaxation times τ_0 and τ_2 are negligibly small, and considering only regular processes, for which the time derivatives appearing at the left hand side of Eqs. (9a) and (9b) do not diverge, the coupling of these equations with Eq. (8) yields the following evolution equation for the heat flux

(10) $$\tau_1 \dot{\mathbf{q}} + \mathbf{q} = -\lambda \nabla T + \gamma_2 \nabla^2 \mathbf{q} + \left(\gamma_0 + \frac{1}{3}\gamma_2 \right) \nabla \nabla \cdot \mathbf{q}$$

It is easy to recognize that the general heat-transport equation (10) reduces to the Eq. (1) under the following identifications

(11) $$\tau_1 = \tau_R, \quad \gamma_0 = \frac{5}{3}\ell_p^2, \, \gamma_2 = \ell_p^2$$

The thermodynamics underlying the transport equation (10) is easily derived by introducing extended constitutive equations for the specific entropy and for the entropy flux of the form, respectively, [22,38]

(12a) $$s = s_{\text{eq}}(u) - \frac{\tau_1}{2\lambda T^2}\mathbf{q} \cdot \mathbf{q} - \frac{\tau_2}{4\lambda T^2 \gamma_2}\mathbf{Q}_s : \mathbf{Q}_s - \frac{\tau_0}{2\lambda T^2 \gamma_0}Q^2$$

(12b) $$\mathbf{J}^s = \frac{\mathbf{q}}{T}\left(1 + \frac{Q}{\lambda T} \right) + \frac{\mathbf{Q}_s \cdot \mathbf{q}}{\lambda T^2}$$

where $s_{\text{eq}}(u)$ denotes the local-equilibrium entropy, the symbol : denotes the complete contraction of the corresponding tensors giving a scalar as result, and the symbol $\mathbf{Q}_s \cdot \mathbf{q}$ denotes the contraction over the last index of of $\mathbf{Q}_s$, giving a vector as result.

The absolute temperature is given by the reciprocal of the derivative of the entropy with respect to the internal energy (at constant values of the other extensive variables). When the extended entropy (12a) is used instead of the local-equilibrium entropy, the resulting absolute temperature is [3]

(13)
$$\frac{1}{T} = \frac{\partial s}{\partial u} = \frac{\partial s_{eq}}{\partial u} - \frac{\partial}{\partial u}\left(\frac{\tau_1}{2\lambda T^2} \right)\mathbf{q} \cdot \mathbf{q} - \frac{\partial}{\partial u}\left(\frac{\tau_2}{4\lambda T^2 \gamma_2} \right)\mathbf{Q}_s : \mathbf{Q}_s - \frac{\partial}{\partial u}\left(\frac{\tau_0}{2\lambda T^2 \gamma_0} \right)Q^2$$

Note that T differs from the local-equilibrium temperature

$$T_{eq} = \left(\frac{\partial s_{eq}}{\partial u} \right)^{-1}$$

and depends on the fluxes [3]. This is in accordance with the experimental evidence that the local-equilibrium temperature loses its validity in situations where the deviation from equilibrium ensemble is not negligible, as for example the heat propagation in nanosystems [22,30,36,39–41].

It is worth noticing that the dispersion relation of heat waves along nanowires (or thin layers) which are not isolated from the environment allows to compare different definitions of nonequilibrium temperature, since thermal waves are predicted to propagate with different phase speed, depending on the definition of nonequilibrium temperature being used [22,41].

4. Higher-order fluxes and hierarchy of nonlinear transport equations

We know from kinetic theory that the relaxation times of the higher-order fluxes are not always shorter than the collision time. Thus, the first-order flux as sole independent variable is not satisfactory to describe high-frequency processes, because when the frequency becomes comparable to the inverse of the relaxation time of the first-order flux, all the higher-order fluxes will also behave like independent variables [22,36,42]. In EIT it is possible to introduce higher-order variables, each one being defined as the flux of the preceding one, and being denoted as $\mathbf{J}_1, \mathbf{J}_2, \ldots, \mathbf{J}_n$, where $\mathbf{J}_k$ with $k = 1 \ldots n$, is a tensor of the order k and stands for the flux of the element of the hierarchy of order $\mathbf{J}_{k-1}$.

Up to the n-th order, a convenient constitutive equation for the specific entropy takes the form

$$(14) \qquad s = s\left(u, \mathbf{J}_1, \ldots, \mathbf{J}_n\right) = s_{\text{eq}}\left(u\right) + \frac{\alpha_1}{2}\mathbf{J}_1 : \mathbf{J}_1 + \ldots + \frac{\alpha_n}{2}\mathbf{J}_n : \mathbf{J}_n$$

while the entropy flux can be written as

$$(15) \qquad \mathbf{J}^s = \frac{\mathbf{J}_1}{T} + \beta_1 \mathbf{J}_2 \cdot \mathbf{J}_1 + \ldots + \beta_{n-1} \mathbf{J}_n \cdot \mathbf{J}_{n-1}$$

with $\alpha_1 \ldots \alpha_n$ and $\beta_1 \ldots \beta_n$ being suitable material functions which are supposed to depend on u, and the symbol $\mathbf{J}_k \cdot \mathbf{J}_{k-1}$ denotes the contraction over the last $k-1$ indices of $\mathbf{J}_k$, giving a vector as result. It is worth observing that, for the sake of formal simplicity, in the previous expressions of the entropy and of the entropy flux, cubic coupled contributions have not been taken into account.

The corresponding evolution equations compatible with a positive entropy production are written in the following hierarchy [43]

$$\tau_1\dot{\mathbf{J}}_1 + \mathbf{J}_1 = -\lambda\nabla T + \frac{\beta_1\tau_1}{\alpha_1}\nabla\cdot\mathbf{J}_2$$

(16)
$$\vdots$$

$$\tau_n\dot{\mathbf{J}}_n + \mathbf{J}_n = \frac{\beta_n\tau_n}{\alpha_n}\nabla\cdot\mathbf{J}_{n+1} + \frac{\beta_{n-1}\tau_n}{\alpha_n}\nabla\mathbf{J}_{n-1}$$

The compatibility of the system of equations (16) with the general balance law for the fluxes

$$\dot{\mathbf{J}}_k + \nabla\cdot\mathbf{J}_{k+1} = \mathbf{P}_k \tag{17}$$

where $k = 2\ldots n$, and $\mathbf{P}_k$ denotes the production of $\mathbf{J}_k$, implies

$$\beta_k = -\alpha_k, \mathbf{P}_k = -\frac{\mathbf{J}_k}{\tau_k} + \frac{\beta_{k-1}}{\beta_k}\nabla\mathbf{J}_{k-1} \tag{18}$$

In Ref. [44] several mathematical aspects of Eqs. (16) and related ones have been analyzed.

If one admits that in nonequilibrium situations the specific entropy is given by Eq. (14) while the evolution of the heat flux is ruled by an equation of the type (16), then the use of a dynamical nonequilibrium temperature β [4,20,21,45], allows to obtain a nonlinear generalization of the classical Maxwell-Cattaneo-vernotte and Guyer-Krumhansl equations [5–7]. For instance, Eq. (1) may be extended to the nonlinear case as [6,7]

$$\tau_R\dot{\mathbf{q}} + \mathbf{q} = -\lambda\nabla T + \left(\frac{2\tau}{Tc_v}\right)\nabla\mathbf{q}\cdot\mathbf{q} + \ell_p^2\left(\nabla^2\mathbf{q} + 2\nabla\nabla\cdot\mathbf{q}\right) \tag{19}$$

which can be further generalized in

$$\tau_R\dot{\mathbf{q}} + \mathbf{q} + \left(\mu\nabla\mathbf{q} + \mu'\nabla^t\mathbf{q}\right) = -\lambda\left(1 + \xi\mathbf{q}\cdot\mathbf{q}\right)\nabla T + \ell_p^2\left(\nabla^2\mathbf{q} + 2\nabla\nabla\cdot\mathbf{q}\right) \tag{20}$$

where μ, μ' and ξ are material parameters and $\nabla^t\mathbf{q}$ denotes the transpose of $\nabla\mathbf{q}$. This represents a nonlinear evolution equation for the heat flux which allows to consider in a simple way some nonlocal, nonlinear and memory effects, beside to study the propagation of heat waves, which is a well-known topic in current nonequilibrium thermodynamics [22,30,46–48].

5. Other generalized heat-transport equations

5.1. *The Thermomass Theory*

The Thermomass (TM) theory [13,49–51] provides a further example of nonlinear heat-transport equation with thermal lag. In TM theory the

heat transport is due to the motion of a gas-like collection of heat carriers, characterized by an effective mass density and flowing through the medium due to a thermomass-pressure gradient. This collection is made by quasi-particles of heat carriers, called thermons, which are representative of the vibrations of the molecules generated by heating the conductor and whose mass may be calculated from the Einstein's mass-energy duality. For crystals, the thermomass gas is just the phonon gas, for pure metals it will be attached on the electron gas, and for semi-metals it will be constituted by both these different gases [13,49–51].

In TM theory the evolution equation for the heat flux reads [52]

$$(21) \qquad \tau_{\mathrm{tm}}\dot{\mathbf{q}} - c_v \dot{T}\mathbf{L} + \nabla\mathbf{q}\cdot\mathbf{L} + \lambda\left(1 - \mathrm{M}_{\mathrm{tm}}^2\right)\nabla T + \mathbf{q} = \mathbf{0}$$

wherein

$$\tau_{\mathrm{tm}} = \frac{\lambda\rho}{2\gamma c_v^2 T}$$

with γ being the Grüneisen constant, is the relaxation time in the TM theory [49,53,54], and

$$\mathbf{L} = \frac{\mathbf{q}\lambda\rho}{2\gamma c_v\left(c_v T\right)^2}$$

denotes a characteristic-length vector [53,54]. Moreover

$$(22) \qquad \mathrm{M}_{\mathrm{tm}} = \frac{|\mathbf{q}|\sqrt{\rho}}{c_v T\sqrt{2\gamma c_v T}}$$

stands for a dimensionless number which is called thermal Mach number of the drift velocity relative to the thermal-wave speed in the thermon gas. By means of it, Eq. (21) introduces a nonlinear thermal conductivity

$$(23) \qquad \lambda_{\mathrm{nl}} = \lambda\left(1 - \mathrm{M}_{\mathrm{tm}}^2\right)$$

In steady states, when the spatial derivatives of the heat flux may be neglected with respect to the flux itself, Eq. (21) reduces to

$$\mathbf{q} = -\lambda_{\mathrm{nl}}\nabla T$$

Since second law of thermodynamics requires $\lambda_{\mathrm{nl}} \geq 0$, from Eqs. (22) and (23) it follows that the modulus of the local heat flux has to fulfill the following relation

$$(24) \qquad |\mathbf{q}| \leq c_v T\sqrt{\frac{2\gamma c_v T}{\rho}}$$

which implies an upper bound for the heat flux for increasing temperature gradient [55].

The experimental results in silicon nanowires, for a difference of temperature $\Delta T = 100\,\mathrm{K}$ on some $50nm$, confirm the existence of this upper bound [56]. Such a phenomenology, well-known in nonlinear heat conduction, is referred to as the presence of "flux limiters" [22,57].

Beside to describe relaxational effects, Eq. (21) incorporates information on the characteristic length of the system and accounts for nonlinear phenomena. In the linear case (i.e., when the terms containing the quantities $\dot{T}\mathbf{L}$ and $\nabla\mathbf{q}\cdot\mathbf{L}$ are negligible, as well as when $\mathrm{M}_{\mathrm{tm}}^2 \ll 1$), Eq. (21) takes the same form of the Maxwell-Cattaneo-Vernotte equation, but the relaxation time of TM theory is two orders of magnitude higher than that of the Maxwell-Cattaneo-Vernotte equation and, in silicon films, it predicts a slower response to the thermal perturbations [56].

5.2. *The Dual-Phase-Lag model*

Evolving from the Fourier law, in the dual-phase-lag model [15,58,59] the following constitutive equation (which provides a convenient approach in describing the ultra-fast physical response) is introduced

$$(25) \qquad \mathbf{q}\left(\mathbf{r}, t + \tau_q\right) = -\lambda\nabla T\left(\mathbf{r}, t + \tau_T\right)$$

where τ_T and τ_q are two phase lags due to the delayed response during the ultra-fast transient. In Eq. (25) the phase lag of the heat flux τ_q captures the small-scale response in time, while the phase lag of the temperature gradient τ_T captures the small-scale response in space.

Up to the second-order approximation in the relaxation times, Eq. (25) can be written as

(26)
$$\mathbf{q}\left(\mathbf{r}, t\right) + \tau_q\dot{\mathbf{q}}\left(\mathbf{r}, t\right) + \frac{\tau_q^2}{2}\ddot{\mathbf{q}}\left(\mathbf{r}, t\right) \approx -\lambda\nabla T\left(\mathbf{r}, t\right) - \tau_T\nabla\dot{T}\left(\mathbf{r}, t\right) + \frac{\tau_T^2}{2}\nabla\ddot{T}\left(\mathbf{r}, t\right)$$

By Eq. (26) we infer that the lagging response significantly deviates from Fourier law, due to involvement of the higher-order derivatives with respect to time. Moreover, it reduces to Maxwell-Cattaneo-Vernotte equation only when $\tau_T = 0$, and the terms proportional to τ_q^2 can be neglected. The combination of the divergence of Eq. (26) with the energy-balance equation (4) leads to

$$(27) \qquad \nabla^2 T + \tau_T\nabla^2\dot{T} + \frac{\tau_T^2}{2}\nabla^2\ddot{T} = \left(\frac{c_v}{\lambda}\right)\dot{T} + \left(\frac{c_v\tau_q}{\lambda}\right)\ddot{T} + \left(\frac{c_v\tau_q^2}{2\lambda}\right)\dddot{T}$$

which completely alters the fundamental characteristics of Fourier diffusion. If the effects related to τ_T^2 in Eq. (26) are neglected, Eq. (27) is able to describe the propagation of temperature waves with thermal speed

$$(28) \qquad U_T = \sqrt{\frac{2c_v\tau_T}{\lambda\tau_q^2}}$$

5.3. *Ballistic-diffusive model*

An alternative approach rests on the assumption that two types of phonon populations, namely, diffusive and ballistic, may coexist. Diffusive phonons undergo multiple collisions within the core of the system, while ballistic phonons, originating at the boundaries of the system, experience mainly collisions with the walls. This model is called ballistic-diffusive (BD) model [2], and allows for a more flexible description of the heat transfer at nanoscale than the single-population models considered above.

On a purely macroscopic approach, in the BD model both the specific internal energy per unit volume u, and the local heat flux $\mathbf{q}$ are split into a ballistic part and a diffusive one, in such a way that

$$(29) \qquad u = u_{\mathrm{bal}} + u_{\mathrm{dif}}, \quad \mathbf{q} = \mathbf{q}_{\mathrm{bal}} + \mathbf{q}_{\mathrm{dif}}$$

Owing to that decomposition, in EIT [22] the state variables are selected as follows:

- the couple $(u_{\mathrm{bal}}, \mathbf{q}_{\mathrm{bal}})$, accounting for the ballistic behavior of the heat carriers;
- the couple $(u_{\mathrm{dif}}, \mathbf{q}_{\mathrm{dif}})$, accounting for the diffusive behavior of the heat carriers.

The evolutions of u_{bal} and u_{dif} are provided by the following classical balance laws [2]

$$(30a) \qquad \dot{u}_{\mathrm{bal}} = -\nabla \cdot \mathbf{q}_{\mathrm{bal}} + r_{\mathrm{bal}}$$
$$(30b) \qquad \dot{u}_{\mathrm{dif}} = -\nabla \cdot \mathbf{q}_{\mathrm{dif}} + r_{\mathrm{dif}}$$

wherein r_{bal} and r_{dif} denote, respectively, the heat supply due to the ballistic population and to the diffusive one. These quantities describe the energy exchange (per unit volume and time) between both phonon populations. It is easy to see that the summation of Eqs. (30a) and (30b) turns out the well-known energy-balance law for u, with heat supply $r = r_{\mathrm{bal}} + r_{\mathrm{dif}}$. It reduces to Eq. (4) whenever $r_{\mathrm{bal}} = -r_{\mathrm{dif}}$.

The evolution of $\mathbf{q}_{\mathrm{bal}}$ and $\mathbf{q}_{\mathrm{dif}}$, instead, is governed by the balance laws [2]

$$(31a) \qquad \tau_{\mathrm{bal}}\dot{\mathbf{q}}_{\mathrm{bal}} + \mathbf{q}_{\mathrm{bal}} = -\lambda_{\mathrm{bal}}\nabla T + \ell_{\mathrm{bal}}^2 \left(\nabla^2 \mathbf{q}_{\mathrm{bal}} + 2\nabla\nabla \cdot \mathbf{q}_{\mathrm{bal}} \right)$$

$$(31b) \qquad \tau_{\mathrm{dif}}\dot{\mathbf{q}}_{\mathrm{dif}} + \mathbf{q}_{\mathrm{dif}} = -\lambda_{\mathrm{dif}}\nabla T$$

wherein τ_{bal} and τ_{dif} are the relaxation times of two phonon populations, λ_{bal} and λ_{dif} are their thermal conductivities, respectively, and ℓ_{bal} is the mean-free path of ballistic phonons. The relaxation times, the thermal conductivities and the phonon mean-free paths of two populations are not independent, but they are such that

$$(32) \qquad \lambda_{\mathrm{bal}} = \frac{1}{3}c_v \mathrm{v}_{\mathrm{bal}}^2 \tau_{\mathrm{bal}}, \quad \lambda_{\mathrm{dif}} = \frac{1}{3}c_v \mathrm{v}_{\mathrm{dif}}^2 \tau_{\mathrm{dif}}$$

wherein $\mathrm{v}_{\mathrm{bal}} = \ell_{\mathrm{bal}}/\tau_{\mathrm{bal}}$ and $\mathrm{v}_{\mathrm{dif}} = \ell_{\mathrm{dif}}/\tau_{\mathrm{dif}}$ are the mean velocities of the ballistic and diffusive phonons, respectively, with ℓ_{dif} being the mean-free path of diffusive phonons [2]. The coupling of Eqs. (31) leads to the Guyer-Krumhansl equation (1) under the following identifications

$$\lambda = \lambda_{\mathrm{bal}} + \lambda_{\mathrm{dif}}, \;\; \tau = \tau_{\mathrm{dif}}, \;\; \ell = \ell_{\mathrm{bal}}$$

6. Heat conduction in thermoelectric systems

Thermoelectric effects involve a fundamental interplay between electric and thermal properties of some materials. The two primary thermoelectric effects are the Seebeck effect and the Peltier one, which can be used to derive all other thermoelectric effects when combined with the laws of thermodynamics. The Seebeck effect describes how a temperature difference creates a charge flow, while the Peltier effect describes how an electrical current can create a heat flow.

Thermoelectric devices offer an attractive source of energy since they do not have moving parts, do not create pollution, do not make noise [60,61].

In practical applications, the thermodynamic efficiency of a thermoelectric device is determined by the dimensionless parameter ZT, with T being the operating temperature, and Z the figure-of-merit, defined as

$$(34) \qquad Z = \frac{\epsilon^2 \sigma_e}{\lambda}$$

wherein ϵ is the Seebeck coefficient, σ_e the electrical conductivity. Although the thermal conductivity λ of thermoelectric materials is usually dominated by that of the electrons, in several cases the lattice heat conductivity, due

to the phonons, has to be added [62]. Therefore, in the denominator of Eq. (34) the total thermal conductivity is such that

$$\lambda = \lambda_p + \lambda_e \tag{35}$$

with λ_p being the phonon contribution to the thermal conductivity, and λ_e the electron contribution to it [63–65].

Since the higher ZT, the higher the efficiency of a thermoelectric device [60,61], one of the primary challenges in developing advanced thermoelectric materials is increasing the power factor $\epsilon^2\sigma_e$ and reducing the thermal conductivity λ. To achieve that task, it is needed to decouple ϵ, σ_e and λ, which are typically strongly interdependent, in such a way that an increase in ϵ usually results in a decrease in σ_e, and a decrease in σ_e produces a decrease in the electronic contribution to λ, following from the Wiedemann-Franz law.

Nanomaterials provide an interesting avenue to obtain more performing thermoelectric devices, for example, making nanocomposites, adding nanoparticles to a bulk material, or using one-dimensional nanostructures [66,67].

However, the research in this field is still in progress, since the physics of thermoelectric nanomaterials presents several points which are not well-understood, as for instance the exact role played by nonlocal and nonlinear effects [15,22,30,68,69]. In the classical form, thermoelectric effects are described by the following constitutive equations

$$\mathbf{q} = -\lambda\nabla T + \left(\Pi + \frac{\mu_e}{z_e}\right)\mathbf{I} \tag{36a}$$

$$\mathbf{I} = -\sigma_e\epsilon\nabla T + \sigma_e\left[\mathbf{E} - \nabla\left(\frac{\mu_e}{z_e}\right)\right] \tag{36b}$$

wherein Π is the Peltier coefficient, $\mathbf{I}$ the electric-current density, $\mathbf{E}$ the electric field, μ_e the chemical potential due to the electrons, and z_e the electric charge per unit mass of the electrons (which should be not confused with the electric charge per unit volume $\varrho_e = c_e z_e$, with c_e being the mass fraction of electrons).

From Eq. (36a) it is possible to see that, even in absence of a temperature gradient, a heat flux may be generated due to an electrical current: this is the so-called the Peltier effect. The coefficient $\Pi = \pm\left(|q|/|I|\right)_{\Delta T=0}$ measures the amount of heat absorbed (or rejected) at the junction of two conductors of different materials kept at uniform temperature and crossed by an electric current of unitary density [30]. Equation (36b), instead, shows that, even in absence of an electric current, an electrical field $\mathbf{E}$ can be

created by a temperature difference: this is known as Seebeck effect. The Seebeck coefficient ϵ (also known as thermoelectric power coefficient) measures the electrical potential produced by a unit temperature difference, in absence of electric current [30].

7. Two-temperature thermoelectric systems

Eqs. (36) may be extended to the case in which phonons and electrons have no longer the same temperature. Accounting for two different temperatures may be important, for instance, in the following physical situations

   i. **Hot electrons**. When the electron mean-free path corresponding to electron-phonon collisions is long, one may have a population of "hot electrons", whose kinetic temperature is higher than that of the phonons [70].
   ii. **Nonequilibrium temperatures**. As the electron mean-free path is usually shorter than the phonon mean-free path, when the longitudinal distance is bigger than the electron mean-free path but smaller than the phonon mean-free path, there will be a very high number of electron collisions, and only scant phonon collisions. As a consequence, the electron temperature may reach its local-equilibrium value, whereas the phonon temperature may be still far from it.
   iii. **Fast laser pulses**. When a laser pulse hits a system, initially the electrons capture the main amount of the incoming energy and subsequently, through electron-phonon collisions, they give a part of such energy to the phonons.

We assume that the heat carriers behave as a mixture of gases flowing through the crystal lattice [71], so that the internal energy of phonons per unit volume u_p, the internal energy of electrons per unit volume u_e and the electrical charge per unit volume of electrons ϱ_e belong to the state space. These variables are ruled by the following evolution equations:

(37a) $$\dot{u}_p = -\nabla \cdot \mathbf{q}^{(p)}$$

(37b) $$\dot{u}_e = -\nabla \cdot \mathbf{q}^{(e)} + \mathbf{E} \cdot \mathbf{I}$$

(37c) $$\dot{\varrho}_e = -\nabla \cdot \mathbf{I}$$

A further basic assumption is that in thermoelectric materials the local heat flux $\mathbf{q}$ has two different contributions: the phononic partial heat flux $\mathbf{q}^{(p)}$ and the electronic partial heat flux $\mathbf{q}^{(e)}$. In the simplest situation, those contributions are such that

(38) $$\mathbf{q} = \mathbf{q}^{(p)} + \mathbf{q}^{(e)}$$

Thus, if the total internal energy per unit volume of the system u is supposed to be given by the constitutive relation

$$(39) \qquad u = u_p + u_e$$

and Eq. (38) is taken into account, then the summation of Eqs. (37a) and (37b) turns out the well-known energy-balance equation

$$\dot{u} + \nabla \cdot \mathbf{q} = \mathbf{E} \cdot \mathbf{I}$$

obtained in Ref. [72] in the absence of a magnetic field.

From the theoretical point of view, we may postulate the following further constitutive equations which relate the partial internal energies appearing in Eqs. (37) to the phononic and electronic temperatures T_p and T_e

$$(40a) \qquad u_p = c_v^{(p)} T_p$$
$$(40b) \qquad u_e = c_v^{(e)} T_e$$

wherein $c_v^{(p)}$ and $c_v^{(e)}$ are the volumetric phonon and the electron heat capacities at constant volume [73], respectively. In other words, since we regard phonons and electrons as a mixture of gases flowing through the crystal lattice [32,71], each of which is endowed with its own temperature, according with the theory of fluid mixtures with different temperatures [74–76], we assume that each constituent obeys the same balance laws as a single fluid. The average temperature of the mixture may introduced by the consideration that the internal energy of the mixture is the same as in the case of a single-temperature mixture [75]. Thus, when the total internal energy u can be expressed through the average temperature T as $u = c_v T$, being $c_v = c_v^{(p)} + c_v^{(e)}$ the volumetric heat capacity at constant volume of the whole system [77], the coupling of Eqs. (39) and (40) yields

$$(41) \qquad T = \frac{c_v^{(p)} T_p + c_v^{(e)} T_e}{c_v}$$

This equation gives a link between T_p, T_e and T, the latter being a measurable quantity in practical applications. Although in the general case $c_v^{(p)}$ and $c_v^{(e)}$ should be temperature-dependent functions, here we deal only with the simplest situation in which those material functions are constant.

7.1. *Efficiency of thermoelectric energy generators*

Let us now investigate the consequences of accounting for two different temperatures for phonon and electrons on the efficiency of thermoelectric

systems. Here we consider a cylindrical thermoelectric nanodevice whose longitudinal length L is much larger than the characteristic size of the transversal section. In this case we may represent it as a one-dimensional system and determine the position of its points by only one Cartesian component, namely, the longitudinal one y. We assume that the hot side of this system (i.e., that at $y = L$) is kept at the temperature T^h, and its cold side (i.e., that at $y = 0$) at the temperature T^c. Moreover, we suppose that an electric current $\mathbf{I}$ and a quantity of heat per unit time $\dot{Q}_{\text{tot}}$ enter uniformly into the hot side of the device and flow through it. In such situation, the thermoelectric efficiency of this device reads

$$(42) \qquad \eta = \frac{P_{\text{el}}}{\dot{Q}_{\text{tot}}}$$

wherein P_{el} is the electric-power output, and $\dot{Q}_{\text{tot}}$ is the total heat supplied per unit time to the system.

For the sake of simplicity, let us suppose that $\mathbf{q}^{(p)}$, $\mathbf{q}^{(e)}$ and $\mathbf{I}$ are parallel to the nanowire, and that $\mathbf{E}$ takes a constant value on each of the planes orthogonal to the nanowire.

In these conditions, for vanishing values of μ_e/z_e, Eqs. (36) read

$$(43a) \qquad q = q^{(p)} + q^{(e)} = -\Lambda_p \nabla_y T_p - \Lambda_e \nabla_y T_e + \Pi I$$

$$(43b) \qquad I = -\sigma_e \epsilon \nabla_y T_e + \sigma_e E$$

wherein $\Lambda_p = \lambda_p + \lambda_{ep}$, and $\Lambda_e = \lambda_e + \lambda_{pe}$. Moreover, by lengthy but straightforward calculations, it can be proven that the thermoelectric efficiency is given by

$$(44) \qquad \eta = \left(1 - \frac{T^c}{T^h}\right) \left(\frac{\epsilon x - \dfrac{\lambda x^2}{\sigma_e \beta_1}}{\dfrac{\gamma + 1}{T^h} + \epsilon x} \right) = \eta_c \eta_r$$

wherein $\lambda = \Lambda_p + \Lambda_e$, $\beta_1 = T_e/T$, $\beta_2 = T_p/T$, $\gamma = (\Lambda_p/\lambda)(\beta_2/\beta_1 - 1)$, and

$$(45) \qquad x = \frac{IL}{\lambda(T^h - T^c)}$$

In Eq. (44) $\eta_c = 1 - T^c/T^h$ is the usual Carnot efficiency, and η_r is a *reduced efficiency*. Therefore, in practical applications one should enhance η_r in order to improve the thermoelectric efficiency. It is easy to see that whenever the ratio x defined above gets the value

$$(46) \qquad x_{\text{opt}} = \left(\frac{\gamma + 1}{\epsilon T}\right) \left(\sqrt{1 + \frac{Z_{\text{eff}} T \beta_1}{\gamma + 1}} - 1 \right)$$

with $Z_{\text{eff}} = \epsilon^2 \sigma_e / \lambda$ as an effective figure-of-merit, then the reduced efficiency gets its maximum value, and the thermoelectric efficiency becomes

$$(47) \qquad \eta_{\text{max}} = \eta_c \left[\frac{Z_{\text{eff}}T\beta_1 + 2\left(\gamma + 1\right)\left(1 - \sqrt{1 + \dfrac{Z_{\text{eff}}T\beta_1}{\gamma + 1}}\right)}{Z_{\text{eff}}T\beta_1} \right]$$

Finally, it reduces to the classical form for the maximum thermoelectric efficiency [30,78]

$$(48) \qquad \eta_{\text{max,cl}} = \eta_c \left[\frac{ZT + 2\left(1 - \sqrt{1 + ZT}\right)}{ZT} \right]$$

whenever T_p and T_e coincide, i.e., when $\beta_1 = \beta_2 = 1$ and $\gamma = 0$. From Eq. (47) it follows the usual result that the larger the figure-of-merit, the higher the efficiency of a thermoelectric device.

8. Thin tubes filled with superfluid helium

As well as thermal waves, phonon hydrodynamics was first discovered in superfluid liquid helium [79–82]. Here we give a brief introduction to the problem of heat transport along thin tubes, which is in fact one of the most challenging topics in heat transfer [81,83,84].

In EIT, superfluid helium is considered as a single fluid with the heat flux as an internal variable [85]. In the more usual two-fluid model by Landau and Tisza [86–89], instead, it is considered to be composed of a normal viscous component and a superfluid one. Their densities, respectively, are ρ_n and ρ_s in such a way that $\rho = \rho_n + \rho_s$. The velocities of two components, instead, are $\mathbf{v}_n$ and $\mathbf{v}_s$, and are related to the barycentric velocity $\mathbf{v}$ as $\mathbf{v} = \rho_n \mathbf{v}_n + \rho_s \mathbf{v}_s$.

In steady states, the heat transfer in turbulent liquid helium [85,89–92] may be described by an equation analogous to Eq. (6), taking the form

$$(49) \qquad \alpha L k \mathbf{q} = -A\nabla T + B\nabla^2 \mathbf{q}$$

where $A = \rho_n \rho T s^2$ with ρ_n as the mass density of the normal component of the fluid and ρ the total mass density, and $B = \eta_n$ as the viscosity of the normal component. Moreover, in the coefficient A in Eq. (49) s means the specific entropy carried out by the normal component, and the heat flux is identified as $\mathbf{q} = \rho_n T s \mathbf{v}_n$.

The term at the left-hand side of Eq. (49) accounts for the internal friction between normal fluid and the quantized vortices arising in the turbulent regime. Therein, L is the vortex length density, k is the quantum of vorticity (given by $k = h/m_{\text{He}}$ with h being the Planck constant, and m_{He} the atomic mass of helium), and α is a friction coefficient. The value of L is zero for small velocities, namely, when $v_n d/k < \text{Re}_{q1}$ with d as the diameter of the channel and Re_{q1} a critical value of the quantum Reynolds number.

When $L = 0$, i.e. in the laminar regime, Eq. (49) has the same form as Eq. (6), but with different parameters, and one has the phonon-hydrodynamic regime, leading to an effective thermal conductivity proportional to the square of the radius of the channel. At temperatures lower than $1K$, the phonon mean-free path in liquid helium is of the order of $0.5mm$; in this case, and in absence of vortex lines ($L = 0$), the flux becomes increasingly ballistic and a slip heat flow along the wall must be incorporated [90], in such a way that the effective thermal conductivity becomes proportional to the radius, instead than to the square of the radius.

9. Outlook

The formulation of mesoscopic heat-transport equations, well characterized for technologically useful materials, and well connected with microscopic understanding of transport in such materials and with generalized constitutive equations of entropy and entropy flux, seems to be truly one of the current most exciting frontiers in nonequilibrium thermodynamics. Then, let's close this brief review with some perspectives on open problems to be further analyzed. The first of them is, of course, a more detailed microscopic understanding of the generalized transport equations, starting from phonon kinetic theory.

A second open problem is the detailed comparison with experiments for a variety of relevant materials. Besides nanoporous materials, other two kinds of systems of much interest are nanocomposites and nanofluids, namely, systems which are composed of a heat-conducting matrix (solid in the former case, and liquid in the latter case) and a dispersion of heat-conducting nanoparticles. Depending on the radius, size, number density and spatial distribution of the nanoparticles (in the case of nanocomposites), one may achieve a considerable degree of control on the transport properties of the system, either of heat, electric or thermoelectric transport coefficients.

Some of the most well-known nanocomposites are superlattices [93], in which the particles are distributed in a spatially ordered pattern, and

the nanoparticles may be so small as to behave as quantum dots [94–98]. In metals and semiconductors, where electrons and holes also contribute to thermal conductivity, superlattices may be designed in such a way to strongly reduce phonon transport without reducing electron transport, because of the widely different values of phonon and electron wavelengths. This is especially relevant in enhancing the efficiency of thermoelectric energy conversion, which requires to reduce as much as possible the thermal conductivity. Hence, more attention to thermoelectricity should also be paid. To this end, not only the heat conductivity, but also the electrical conductivity, the Seebeck and Peltier coefficients, as well as their possible nonlinear contributions, should be explored in depth.

Another tipe of nanocomposites is represented by graded systems [99], in which the composition of the system is not homogeneous, but changes along some directions. These systems are increasingly used in technology [100–104]. In thermoelectricity, for instance, the alloys $Bi_{2-2x} Te_{3-2x} Pb_x$, or $(Bi_{1-x} Sb_x)_2 Te_3$, with the stoichiometric index x changing from 0 to 1, are of interest in thermoelectric energy generators [103]. For $Bi_2 Te_3$ and $Pb Te$ (two of the best thermoelectric materials), ZT is maximum around 370 K and 670 K, respectively. Thus, to maximize that product along a system between 670 K and 370 K is better to use $Pb Te$ at the hot side, $Bi_2 Te_3$ at the cold side, and $Bi_{2-2x} Te_{3-2x} Pb_x$ in the middle (with x changing from 1 in the hot side to 0 in the cold side).

The heat transport in two-dimensional systems (graphene, silicon thin layers, microporous thin layers) should also be explored with more detail, because of the increased relevance of these systems as compared to the three-dimensional ones [105,106]. Radial heat transport from hot spots, and its application to temperature measurements (or to nanodevice refrigeration) is also an interesting topic, since it offers important hints on some basic problems of nonequilibrium thermodynamics. It would be interesting to deal with time-dependent phenomena, for a wide range of frequencies. The use of thermal waves (not necessarily the very high-frequency ones) could be useful for characterizing some properties of the materials, as for instance the porosity, or the distribution of the radii of particles embedded in a heat conducting matrix.

An interesting modern topic is the phononics whose aim is to control phonon flow in a way similar to the control of electron flow in electronics. The essential devices of electronics are diodes and transistors. Diodes rectify electric current and transistors may amplify electric signals, or act as commuters. The nanoscopic engineering of materials is allowing the control of phonon heat flow. Heat rectification is already well-known (although with small rectification effects, as compared to those of electrical rectifi-

cation); heat transistors require negative differential thermal conductivity, and some of them have been achieved. By combining these devices one may speculate about logic gates and with memories. Related to that there are also interesting projects on the heat cloaking and thermal metamaterials, which imply new and imaginative situations for heat transport.

Acknowledgments

REFERENCES

1. A. Sellitto, V. A. Cimmelli and D. Jou, *Mesoscopic Theories of Heat Transport in Nanosystems.* Berlin: Springer, 2016. DOI 10.1007/978-3-319-27206-1

2. G. Lebon, Heat conduction at micro and nanoscales: A review through the prism of Extended Irreversible Thermodynamics, *Journal of Non-Equilibrium Thermodynamics*, vol. 39, pp. 35–59, 2014.

3. J. Casas-Vázquez and D. Jou, Temperature in nonequilibrium states: a review of open problems and current proposals, *Reports on Progress in Physics*, vol. 66, pp. 1937–2023, 2003.

4. V. A. Cimmelli and K. Frischmuth, Determination of material functions through second sound measurements in a hyperbolic heat conduction theory, *Mathematical and Computer Modelling*, vol. 24, pp. 19–28, 1996.

5. V. A. Cimmelli, A. Sellitto, and D. Jou, Nonlocal effects and second sound in a nonequilibrium steady state, *Physical Review B*, vol. 79, p. 014303 (13 pages), 2009.

6. V. A. Cimmelli, A. Sellitto, and D. Jou, Nonequilibrium temperatures, heat waves, and nonlinear heat transport equations, *Physical Review B*, vol. 81, p. 054301 (9 pages), 2010.

7. V. A. Cimmelli, A. Sellitto, and D. Jou, Nonlinear evolution and stability of the heat flow in nanosystems: Beyond linear phonon hydrody-

namics, *Physical Review B*, vol. 82, p. 184302 (9 pages), 2010.

8. H. Struchtrup, *Macroscopic transport equations for rarefied gas flows: approximation methods in kinetic theory - Interaction of Mechanics and Mathematics*. New York: Springer, 2005.

9. V. A. Cimmelli, A. Sellitto, and V. Triani, A new thermodynamic framework for second-grade Korteweg-type viscous fluids, *Journal of Mathematical Physics*, vol. 50, p. 053101 (16 pages), 2009.

10. V. A. Cimmelli, D. Jou, T. Ruggeri, and P. Ván, Entropy Principle and Recent Results in Non-Equilibrium Theories, *Entropy*, vol. 16, pp. 1756–1807, 2014.

11. P. Ván and T. Fülöp, "Universality in heat conduction theory: weakly nonlocal thermodynamics," *Annalen der Physik*, vol. 524, pp. 470–478, 2012.

12. Z.-Y. Guo, Motion and Transfer of Thermal Mass - Thermal Mass and Thermon Gas, *Journal of Engineering Thermophysics*, vol. 27, pp. 631–634, 2006.

13. B.-Y. Cao and Z.-Y. Guo, Equation of motion of a phonon gas and non-Fourier heat conduction, *Journal of Applied Physics*, vol. 102, p. 053503 (6 pages), 2007.

14. Z.-Y. Guo and Q.-W. Hou, Thermal wave based on the thermomass model, *ASME Journal of Heat Transfer*, vol. 132, p. 072403 (6 pages), 2010.

15. D. Y. Tzou, *Macro-to Microscale Heat Transfer: The Lagging Behaviour*. United Kingdom: Wiley, second ed., 2014.

16. D. Y. Tzou, Nonlocal behavior in phonon transport, *International Journal of Heat and Mass Transfer*, vol. 54, pp. 475–481, 2011.

17. R. A. Guyer and J. A. Krumhansl, Solution of the linearized phonon Boltzmann equation, *Physical Review*, vol. 148, pp. 766–778, 1966.

18. R. A. Guyer and J. A. Krumhansl, Thermal conductivity, second sound and phonon hydrodynamic phenomena in nonmetallic crystals, *Physical Review*, vol. 148, pp. 778–788, 1966.

19. C. C. Ackerman and R. A. Guyer, Temperature pulses in dielectric solids, *Annals of Physics*, vol. 50, pp. 128–185, 1968.

20. V. A. Cimmelli and K. Frischmuth, Nonlinear effects in thermal wave propagation near zero absolute temperature, *Physica B*, vol. 355, pp. 147–157, 2005.

21. V. A. Cimmelli and K. Frischmuth, Gradient generalization to the

extended thermodynamic approach and diffusive-hyperbolic heat conduction, *Physica B*, vol. 400, pp. 257–265, 2007.

22. D. Jou, J. Casas-Vázquez, and G. Lebon, *Extended Irreversible Thermodynamics*. Berlin: Springer, fourth revised ed., 2010.

23. J. M. Ziman, *Electrons and Phonons*. Oxford: Oxford University Press, 2001.

24. C. Cattaneo, Sulla conduzione del calore, *Atti del Seminario Matematico e Fisico dell'Universitá di Modena*, vol. 3, pp. 83–101, 1948.

25. V. A. Cimmelli, Different thermodynamic theories and different heat conduction laws, *Journal of Non-Equilibrium Thermodynamics*, vol. 34, pp. 299–333, 2009.

26. B. Straughan, *Heat waves*. Berlin: Springer, 2011.

27. G. Lebon, D. Jou, J. Casas-Vázquez, and W. Muschik, Weakly nonlocal and nonlinear heat transport in rigid solids, *Journal of Non-Equilibrium Thermodynamics*, vol. 23, pp. 176–191, 1998.

28. V. A. Cimmelli, An extension of Liu procedure in weakly nonlocal thermodynamics, *Journal of Mathematical Physics*, vol. 48, p. 113510 (13 pages), 2007.

29. D. Jou, J. Casas-Vázquez, and G. Lebon, Extended irreversible thermodynamics revisited (1988-1998), *Reports on Progress in Physics*, vol. 62, pp. 1035–1142, 1999.

30. G. Lebon, D. Jou, and J. Casas-Vázquez, *Understanding nonequilibrium thermodynamics*. Berlin: Springer, 2008.

31. G. Lebon, H. Machrafi, M. Grmela, and C. Dubois, An extended thermodynamic model of transient heat conduction at sub-continuum scales, *Proceedings of the Royal Society of London, Section A*, vol. 467, pp. 3241–3256, 2011.

32. F. X. Alvarez, D. Jou, and A. Sellitto, Phonon hydrodynamics and phonon-boundary scattering in nanosystems, *Journal of Applied Physics*, vol. 105, p. 014317 (5 pages), 2009.

33. A. Sellitto, F. X. Alvarez, and D. Jou, Second law of thermodynamics and phonon-boundary conditions in nanowires, *Journal of Applied Physics*, vol. 107, p. 064302 (7 pages), 2010.

34. A. Sellitto, F. X. Alvarez, and D. Jou, Temperature dependence of boundary conditions in phonon hydrodynamics of smooth and rough nanowires, *Journal of Applied Physics*, vol. 107, p. 114312 (7 pages), 2010.

35. F. X. Alvarez, D. Jou, and A. Sellitto, Phonon boundary effects and thermal conductivity of rough concentric nanowires, *ASME Journal of Heat Transfer*, vol. 133, p. 022402 (7 pages), 2011.

36. D. Jou, J. Casas-Vázquez, and G. Lebon, Extended irreversible thermodynamics of heat transport. A brief introduction, *Proceedings of the Estonian Academy of Sciences*, vol. 57, p. 118–126, 2008.

37. M. Lundstrom, *Fundamentals of Carrier Transport*. Cambridge: Cambridge University Press, 2000.

38. D. Jou and L. Restuccia, Mesoscopic transport equations and contemporary thermodynamics: an introduction, *Contemporary Physics*, vol. 52, pp. 465–474, 2011.

39. 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.

40. J. M. Criado-Sancho, D. Jou, and J. Casas-Vázquez, Nonequilibrium kinetic temperatures in flowing gases, *Physics Letters A*, vol. 350, pp. 339–341, 2006.

41. D. Jou, V. A. Cimmelli, and A. Sellitto, Nonequilibrium temperatures and second-sound propagation along nanowires and thin layers, *Physics Letters A*, vol. 373, pp. 4386–4392, 2009.

42. S. I. Serdyukov, Higher order heat and mass transfer equations and their justification in extended irreversible thermodynamics, *Theoretical Foundations of Chemical Engineering*, vol. 47, pp. 89–103, 2013.

43. M. Ferrer and D. Jou, Higher-order fluxes and the speed of thermal waves, *International Journal of Heat and Mass Transfer*, vol. 34, pp. 3055–3060, 1991.

44. V. A. Cimmelli and P. Ván, The effects of nonlocality on the evolution of higher order fluxes in nonequilibrium thermodynamics, *Journal of Mathematical Physics*, vol. 46, p. 112901 (15 pages), 2005.

45. V. A. Cimmelli and W. Kosiński, Non-equilibrium semi-empirical temperature in materials with thermal relaxation, *Archives of Mechanics*, vol. 47, pp. 753–767, 1991.

46. D. D. Joseph and L. Preziosi, Heat waves, *Reviews in Modern Physics*, vol. 61, pp. 41–73, 1989.

47. W. Dreyer and H. Struchtrup, Heat pulse experiments revisited, *Continuum Mechanics and Thermodynamics*, vol. 5, pp. 3–50, 1993.

48. I. Müller and T. Ruggeri, *Rational Extended Thermodynamics.* New York: Springer, second ed., 1998.

49. Y. Dong, B.-Y. Cao, and Z.-Y. Guo, Generalized heat conduction laws based on thermomass theory and phonon hydrodynamics, *Journal of Applied Physics*, vol. 110, p. 063504 (6 pages), 2011.

50. Y. Dong, B.-Y. Cao, and Z.-Y. Guo, General expression for entropy production in transport processes based on the thermomass model, *Physical Review E*, vol. 85, p. 061107 (8 pages), 2012.

51. Y. Dong, B.-Y. Cao, and Z.-Y. Guo, Temperature in nonequilibrium states and non-Fourier heat conduction, *Physical Review E*, vol. 87, p. 032150 (8 pages), 2013.

52. D. Y. Tzou and Z.-Y. Guo, Nonlocal behavior in thermal lagging, *International Journal of Thermal Sciences*, vol. 49, pp. 1133–1137, 2010.

53. M. Wang, N. Yang, and Z.-Y. Guo, Non-Fourier heat conductions in nanomaterials, *Journal of Applied Physics*, vol. 110, p. 064310 (7 pages), 2011.

54. A. Sellitto and V. A. Cimmelli, A continuum approach to thermomass theory, *ASME Journal of Heat Transfer*, vol. 134, p. 112402 (6 pages), 2012.

55. A. Sellitto and V. A. Cimmelli, Flux limiters in radial heat transport in silicon nanolayers, *ASME Journal of Heat Transfer*, vol. 136, p. (8 pages), 2014.

56. M. Wang, B.-Y. Cao, and Z.-Y. Guo, General heat conduction equations based on the thermomass theory, *Frontiers in Heat and Mass Transfer*, vol. 1, p. 013004 (8 pages), 2010.

57. 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.

58. D. Y. Tzou, A unified field approach for heat conduction from micro-to-macro-scales, *ASME Journal of Heat Transfer*, vol. 117, pp. 8–16, 1995.

59. D. Y. Tzou, Longitudinal and transverse phonon transport in dielectric crystals, *ASME Journal of Heat Transfer*, vol. 136, p. 042401 (5 pages), 2014.

60. D. M. Rowe, *Thermoelectrics Handbook: Macro to Nano.* Boca Raton: CRC Press, 2005.

61. D. M. Rowe (ed.), *CRC Handbook of Thermoelectrics.* Florida: Boca

Raton: CRC Press LLC, 1995.

62. F. Koechlin and B. Bonin, Parametrisation of the Niobium thermal conductivity in the superconducting state, in *Proceedings of the 1995 Workshop on RF Superconductivity, Gif-sur-Yvette, France* (B. Bonin, ed.), (New York), pp. 665–669, Gordon and Breach, 1996.

63. K. E. Goodson and M. I. Flik, Electron and Phonon Thermal Conduction in Epitaxial High-T_c Superconducting Films, *ASME Journal of Heat Transfer*, vol. 115, pp. 17–25, 1993.

64. N. Stojanovic, D. H. S. Maithripala, J. M. Berg, and M. Holtz, Thermal conductivity in metallic nanostructures at high temperature: electrons, phonons, and the Wiedemann-Franz law, *Physical Review B*, vol. 82, p. 075418 (9 pages), 2010.

65. A. Sellitto, V. A. Cimmelli, and D. Jou, Thermoelectric effects and size dependency of the figure-of-merit in cylindrical nanowires, *International Journal of Heat and Mass Transfer*, vol. 57, pp. 109–116, 2013.

66. A. I. Boukai, Y. Bunimovich, J. Tahir-Kheli, J.-K. Yu, W. A. Goddard-III, and J. R. Heath, Silicon nanowires as efficient thermoelectric materials, *Nature*, vol. 451, pp. 168–171, 2008.

67. G. Joshi, H. Lee, Y. Lan, X. Wang, G. Zhu, D. Wang, R. W. Gould, D. C. Cuff, M. Y. Tang, M. S. Dresselhaus, G. Chen, and Z. Ren, Enhanced Thermoelectric Figure-of-Merit in Nanostructured p-type Silicon Germanium Bulk Alloys, *Nano Letters*, vol. 8, pp. 4670–4674, 2008.

68. Z. M. Zhang, *Nano/Microscale Heat Transfer*. New York: McGraw-Hill, 2007.

69. S. Volz (ed.), *Thermal Nanosystems and Nanomaterials (Topics in Applied Physics)*. Berlin: Springer, 2010.

70. N. Balkan, *Hot Electrons in Semiconductors - Physics and Devices*. New York: Oxford University Press, 1998.

71. G. Chen, *Nanoscale Energy Transport and Conversion - A Parallel Treatment of Electrons, Molecules, Phonons, and Photons*. Oxford: Oxford University Press, 2005.

72. B. D. Coleman and E. H. Dill, Thermodynamic restrictions on the constitutive equations of electromagnetic theory, *Zeitschrift für angewandte Mathematik und Physik*, vol. 22, pp. 691–702, 1971.

73. Z. Lin, L. V. Zhigilei, and V. Celli, Electron-phonon coupling and elec-

tron heat capacity of metals under conditions of strong electron-phonon nonequilibrium, *Physical Review B*, vol. 77, p. 075133 (17 pages), 2008.

74. H. Gouin and T. Ruggeri, Identification of an average temperature and a dynamical pressure in a multitemperature mixture of fluids, *Physical Review E*, vol. 78, p. 016303 (7 pages), 2008.

75. T. Ruggeri and J. Lou, Heat conduction in multi-temperature mixtures of fluids: the role of the average temperature, *Physics Letters A*, vol. 373, pp. 3052–3055, 2009.

76. T. Ruggeri, Multi-temperature mixture of fluids, *Theoretical and Applied Mechanics*, vol. 36, pp. 207–238, 2009.

77. L. X. Benedict, S. G. Louie, and M. L. Cohen, Heat capacity of carbon nanotubes, *Solid State Communications*, vol. 100, pp. 177–180, 1996.

78. G. Benenti, K. Saito, and G. Casati, Thermodynamic bounds on efficiency for systems with broken time-reversal symmetry, *Physical Review Letters*, vol. 106, p. 230602 (4 pages), 2011.

79. S. J. Putterman, *Superfluid Hydrodynamics*. Amsterdam: North Holland, 1974.

80. D. Benin and H. J. Maris, Phonon heat transport and Knudsen's minimum in liquid helium at low temperatures, *Physical Review B*, vol. 18, pp. 3112–3125, 1978.

81. R. J. Donnelly, *Quantized vortices in helium II*. Cambridge, UK: Cambridge University Press, 1991.

82. D. Jou, G. Lebon, and M. S. Mongioví, Second sound, superfluid turbulence, and intermittent effects in liquid helium II, *Physical Review B*, vol. 66, p. 224509 (9 pages), 2002.

83. J. Wilks, *The properties of Liquid and Solid Helium*. Oxford: Clarendon Press, 1967.

84. S. W. Van Sciver, *Helium Cryogenics*. Berlin: Springer, second ed., 2012.

85. M. S. Mongioví, Extended Irreversible Thermodynamics of liquid helium II, *Physical Review B*, vol. 48, pp. 6276–6283, 1993.

86. L. D. Landau, The theory of superfluidity of He II, *Journal of Physics*, vol. 60, pp. 356–358, 1941.

87. D. S. Greywall, Thermal-conductivity measurements in liquid ^{4}He below 0.7K, *Physical Review B*, vol. 23, pp. 2152–2168, 1981.

88. L. D. Landau and E. M. Lishitz, *Mechanics of fluids*. Oxford: Perga-

mon, 1985.

89. M. Sciacca, A. Sellitto, and D. Jou, Transition to ballistic regime for heat transport in helium II, *Physics Letters A.*, vol. 378, pp. 2471–2477, 2014.

90. M. S. Mongioví and D. Jou, Thermodynamical derivation of a hydro-dynamical model of inhomogeneous superfluid turbulence, *Phys. Rev. B*, vol. 75, p. 024507 (14 pages), 2007.

91. M. Sciacca, M. S. Mongioví, and D. Jou, A mathematical model of counterflow superfluid turbulence describing heat waves and vortex-density waves, *Mathematical and Computer Modelling*, vol. 48, pp. 206–221, 2008.

92. L. Saluto, M. S. Mongioví, and D. Jou, Longitudinal counterflow in turbulent liquid helium: velocity profile of the normal component, *Zeitschrift für angewandte Mathematik und Physik*, vol. 65, pp. 531–548, 2014.

93. F. X. Alvarez, J. Alvarez-Quintana, D. Jou, and J. Rodriguez-Viejo, Analytical expression for thermal conductivity of superlattices, *Journal of Applied Physics*, vol. 107, p. 084303 (8 pages), 2010.

94. T. C. H. P. J. Taylor, M. P. Walsh, and B. E. La Forge, Quantum dot superlattice thermoelectric materials and devices, *Science*, vol. 297, pp. 2229–2232, 2002.

95. O. L. Lazarenkova and A. A. Balandin, Electron and phonon energy spectra in a three-dimensional regimented quantum dot superlattice, *Physical Review B*, vol. 66, p. 245319 (9 pages), 2002.

96. A. A. Balandin and O. L. Lazarenkova, Mechanism for thermoelectric figure-of-merit enhancement in regimented quantum dot superlattices, *Nature Materials*, vol. 82, p. 415 (3 pages), 2003.

97. J. Alvarez-Quintana, F. X. Alvarez, J. Rodriguez-Viejo, D. Jou, P. D. Lacharmoise, A. Bernardi, A. R. Goñi, and M. I. Alonso, Cross-plane thermal conductivity reduction of vertically uncorrelated Ge/Si quantum dot superlattices, *Applied Physics Letters*, vol. 93, p. 013112 (3 pages), 2008.

98. A. Sellitto, A phonon-hydrodynamic approach to thermal conductivity of Si-Ge quantum dot superlattices, *Applied Mathematical Modelling*, vol. 39, pp. 4687–4698, 2015.

99. V. Birman and L. W. Byrd, Modeling and Analysis of Functionally Graded Materials and Structures, *Applied Mechanics Reviews*, vol. 60,

pp. 197–216, 2007.

100. V. L. Kuznetsov, Functionally graded materials for termoelectric applications, in *Thermoelectrics Handbook: Macro to Nano – Sec. 38*, D. M. Rowe Ed., CRC Press, Boca Raton, 2005.

101. V. L. Kuznetsov, L. A. Kuznetsova, A. E. Kaliazin, and D. M. Rowe, High performance functionally graded and segmented Bi_2Te_3-based materials for thermoelectric power generation, *Journal of Materials Science*, vol. 37, pp. 2893–2897, 2002.

102. E. Müller, Č. Drašar, J. Schilz, and W. A. Kaysser, Functionally graded materials for sensor and energy applications, *Materials Science and Engineering*, vol. A362, pp. 17–39, 2003.

103. G. Jeffrey Snyder and E. S. Toberer, Complex thermoelectric materials, *Nature Materials*, vol. 7, pp. 105–114, 2008.

104. D. Jou, I. Carlomagno, and V. A. Cimmelli, A thermodynamic model for heat transport and thermal wave propagation in graded systems, *Physica E*, vol. 73, pp. 242–249, 2015.

105. A. Sellitto, V. A. Cimmelli, and D. Jou, Entropy flux and anomalous axial heat transport at the nanoscale, *Physical Review B*, vol. 87, p. 054302 (7 pages), 2013.

106. V. A. Cimmelli, I. Carlomagno, and A. Sellitto, Non-Fourier heat transfer with phonons and electrons in a circular thin layer surrounding a hot nanodevice, *Entropy*, vol. 17, pp. 5157–5170, 2015.