# An extended thermodynamic model of transient heat conduction at sub-continuum scales

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A thermodynamic description of transient heat conduction at small length and time scales is proposed. It is based on Extended Irreversible Thermodynamics, the main feature of this formalism is to elevate the heat flux vector to the status of independent variable at the same level as the classical variable, the temperature. The present model assumes the coexistence of two kinds of heat carriers: diffusive and ballistic phonons. The behavior of the diffusive phonons is governed by a Cattaneo-type equation to take into account the high frequency phenomena generally present at nano scales. To include non-local effects which are dominant in nano structures, it is assumed that the ballistic carriers are obeying a Guyer-Krumhansl relation. The model is applied to the problem of transient heat conduction through a thin nano film. The numerical results are compared to these provided by Fourier, Cattaneo, and recent models.

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# 1. Introduction

It is well recognized that Fourier's law of heat conduction $\boldsymbol{q} = -\lambda \nabla T$ with $\boldsymbol{q}$ the heat flux vector, $\nabla T$ the temperature gradient and $\lambda$ the heat conductivity is only valid at low frequencies and large space scales. To cope with high frequency processes, Fourier's law has been generalized by Cattaneo (1948) into the non-steady form

$$\tau \frac{\partial \boldsymbol{q}}{\partial t} + \boldsymbol{q} = -\lambda \nabla T, \tag{1.1}$$

wherein $\tau$ designates the heat flux relaxation time. Cattaneo's relation reduces to Fourier's law in the limit of vanishing values of $\tau$. However, Cattaneo's equation is not able to describe highly non-local effects characterizing small scale systems. To account for non-localities, a generalization has been proposed by Guyer and Krumhansl (1966a, 1966b) who derived the following equation on the basis of the kinetic theory:

$$\tau \frac{\partial \boldsymbol{q}}{\partial t} + \boldsymbol{q} = -\lambda \nabla T + l^2 (\nabla^2 \boldsymbol{q} + 2\nabla\nabla.\boldsymbol{q}), \tag{1.2}$$

the quantity $l$ stands for the mean free path of the heat carriers, namely phonons; non-locality is expressed though the second order space derivatives in $\nabla^2 \boldsymbol{q}$ and $\nabla\nabla.\boldsymbol{q}$. The objective of this work is to describe transient heat conduction at micro and nano scales based on Extended Irreversible Thermodynamics (Lebon *et al* 2008, Jou *et al* 2010). The main idea underlying this theory is to elevate the fast variables, like the heat flux, to the status of independent variables at the same level as the slow variables like energy, or temperature. In the next section, it is shown that the Cattaneo and Guyer-Krumhansl equations can be directly derived from the Extended Thermodynamics formalism. In the present paper, it is assumed that heat propagation is governed by two kinds of phonons: ballistic and diffusive ones. The idea is not new and was essentially initiated by G. Chen (2001, 2002) who proposed a so-called "ballistic-diffusion model" mixing kinetic theory and macroscopic considerations. In contrast, our approach is purely macroscopic and rests on the assumption that the motion of the diffusive phonons is governed by Cattaneo's equation while the ballistic phonons, which are dominant when the dimensions of the system are equal or smaller than the mean free path of the phonons, will obey Guyer-Krumhansl's relation.

The paper will run as follows. In Section 2, the main ingredients of Extended Irreversible Thermodynamics are recalled; in particular, it is shown under which conditions, the Cattaneo and Guyer-Krumhansl equations can be derived from this formalism. The ballistic-diffusion model is analyzed in Section 3 and is applied in Section 4 to the problem of transient heat conduction in nano films. The numerical results are analyzed and compared with these provided by Fourier's, Cattaneo's, and more recent descriptions by Joshi and Majumdar 1993, Chen 2002, Alvarez and Jou 2010. General conclusions are drawn in Section 5.

## 2. Brief review of Extended Irreversible Thermodynamics

The main idea underlying Extended Irreversible Thermodynamics (EIT) is to consider the dissipative fluxes, like the flux of heat in heat transport problems, as independent basic variables, on the same footing as the classical variables like energy, or temperature. Elevating the dissipative fluxes to the status of independent variables amounts to introduce memory and non-local effects into the formalism. It is also assumed that there exists a non-equilibrium entropy $s$ depending on the whole set of variables, including the fluxes. In the particular case of heat conduction, $s$ is assumed to be a function of the internal energy $u$ and the heat flux vector $\boldsymbol{q}$:

$$s = s\,(u,\, \boldsymbol{q}), \tag{2.1}$$

with $s$ and $u$ denoting quantities measured per unit volume. The entropy $s$ obeys a time evolution equation of the form

$$\frac{\partial s}{\partial t} + \nabla . \boldsymbol{J}^{s} = \sigma^{s} \geq 0,\,, \tag{2.2}$$

wherein $\boldsymbol{J}^s$ denotes the entropy flux vector, $\sigma^s$ the rate of entropy production per unit volume, a positive definite quantity according to the second law of thermodynamics. Since the global velocity of the material is supposed to be equal to zero, partial and material time derivatives are identical. It is well known that Fourier's law can directly be derived from the classical theory of irreversible processes based on the local equilibrium hypothesis and developed, among others, by Onsager (1931), Prigogine (1961) and De Groot and Mazur (1962). To illustrate the range of application of EIT, we now show that Cattaneo's and Guyer-Krumhansl's equations enter naturally into the framework of this formalism. In differential form, relation (2.1) takes the form

$$\frac{\partial s}{\partial t} = \frac{\partial s}{\partial u}\frac{\partial u}{\partial t} + \frac{\partial s}{\partial \boldsymbol{q}} . \frac{\partial \boldsymbol{q}}{\partial t} . \tag{2.3}$$

Define as usually the non-equilibrium temperature by $T^{-1} = \partial s / \partial u$ and assume moreover that $\partial s/\partial \boldsymbol{q} = -\alpha(T)\boldsymbol{q}$ with $\alpha(T)$ a material coefficient allowed to depend on $T$, the minus sign being introduced for convenience and non-linear contributions in $\boldsymbol{q}$ being omitted; substitution of these expressions in (2.3) yields

$$\frac{\partial s}{\partial t} = T^{-1}\frac{\partial u}{\partial t} - \alpha \boldsymbol{q} . \frac{\partial \boldsymbol{q}}{\partial t} . \tag{2.4}$$

The time derivative $\partial u/\partial t$ is given by the first law of thermodynamics, which for rigid heat conductors at rest and absence of internal heat sources, reads as

$$\frac{\partial u}{\partial t} = -\nabla . \boldsymbol{q}\ . \tag{2.5}$$

Our next task is to formulate the time-evolution equation of $\boldsymbol{q}$, as shown below, simple forms are provided by Cattaneo's and (or) Guyer- Krumhansl's equations.

### *2.1 The Cattaneo equation.*

Making use of (2.5), relation (2.4) writes as

$$\frac{\partial s}{\partial t} = -\nabla . \frac{\boldsymbol{q}}{T} + \boldsymbol{q} . (\nabla T^{-1} - \alpha \frac{\partial \boldsymbol{q}}{\partial t}). \tag{2.6}$$

By comparison with the general expression (2.2) of the evolution equation for *s*, one obtains for $\boldsymbol{J}^s$ and $\sigma^s$ the following results respectively:

$$\boldsymbol{J}^s = \frac{\boldsymbol{q}}{T}, \qquad \sigma^s = \boldsymbol{q} . (\nabla T^{-1} - \alpha \frac{\partial \boldsymbol{q}}{\partial t}) \geq 0 . \tag{2.7}$$

The simplest way to ensure the positiveness of $\sigma^s$ is to assume a linear relation between the flux $\boldsymbol{q}$ and the so-called thermodynamic force represented by the terms between parentheses:

$$\alpha \frac{\partial \boldsymbol{q}}{\partial t} - \nabla . T^{-1} = -\mu \, \boldsymbol{q} \ , \tag{2.8}$$

wherein $\mu$ is a positive definite coefficient. It is also shown within the general framework of EIT (Jou et al 2010) that $\alpha \geq 0$ to comply with the concavity property of entropy. By introducing the notation

$$\alpha/\mu = \tau, \qquad 1/\mu T^2 = \lambda \tag{2.9}$$

one recovers from expression (2.8) the familiar form of Cattaneo's equation, namely

$$\tau \frac{\partial \boldsymbol{q}}{\partial t} + \boldsymbol{q} = -\lambda \nabla T , \tag{2.10}$$

with $\tau$ designating the relaxation time of the heat flux and $\lambda$ the positive heat conductivity, both quantities are generally depending on the temperature.

### *2.2 The Guyer-Krumhansl equation.*

It is observed that expression (2.7a) of the entropy flux $\boldsymbol{J}^s$ is the same as in classical irreversible thermodynamics (i.e. the heat flux divided by the temperature). When non-localities become important, it is natural to expect that $\boldsymbol{J}^s$ will in addition depend on the gradients of $\boldsymbol{q}$. In that respect and without loss of generality, we find justified to write $\boldsymbol{J}^s$ in the following form involving terms in $\nabla \boldsymbol{q}$ and $\nabla . \boldsymbol{q}$:

$$\boldsymbol{J}^s = \frac{\boldsymbol{q}}{T} + \gamma ( \boldsymbol{q} . \nabla \boldsymbol{q} + 2 \boldsymbol{q} \nabla . \boldsymbol{q} ), \tag{2.11}$$

wherein $\gamma$ is a coefficient to be identified later on, the factor 2 in the last term is not essential but has been introduced to recover Guyer-Krumhansl's kinetic equation. Starting from relation (2.2) and replacing $\partial s/\partial t$ and $\boldsymbol{J}^s$ by their expressions (2.4) and (2.11) respectively, it is found that

$$\sigma^s = \boldsymbol{q}.\nabla T^{-1} - \alpha\, \boldsymbol{q}.\frac{\partial \boldsymbol{q}}{\partial t} + \gamma[\boldsymbol{q}.\nabla^2\boldsymbol{q} + \nabla\boldsymbol{q} : \nabla\boldsymbol{q} + 2\boldsymbol{q}.\nabla(\nabla.\boldsymbol{q}) + 2(\nabla.\boldsymbol{q})(\nabla.\boldsymbol{q})] \geq 0\,, \tag{2.12}$$

or, reassembling the terms containing the factor $\boldsymbol{q}$,

$$\sigma^s = \boldsymbol{q}.[\nabla T^{-1} - \alpha\frac{\partial \boldsymbol{q}}{\partial t} + \gamma(\nabla^2\boldsymbol{q} + 2\nabla\nabla.\boldsymbol{q})] + \gamma(\nabla\boldsymbol{q} : \nabla\boldsymbol{q} + 2\,(\nabla.\boldsymbol{q})(\nabla.\boldsymbol{q})). \tag{2.13}$$

The simplest way to guarantee that the entropy production is positive definite is to assume that there exists a linear relationship between the flux $\boldsymbol{q}$ and its conjugated force represented by the terms enclosed in the brackets and that $\gamma$ is a positive factor; as a consequence, one is led to

$$\boldsymbol{q} = \frac{1}{\mu}[\nabla T^{-1} - \alpha\frac{\partial \boldsymbol{q}}{\partial t} + \gamma(\nabla^2\boldsymbol{q} + 2\nabla\nabla.\boldsymbol{q})], \qquad \gamma \geq 0, \tag{2.14}$$

wherein $\mu$ is a positive phenomenological coefficient. Introducing the identifications

$$\mu=1/\lambda T^2, \quad \alpha/\mu=\tau, \quad \gamma/\mu=l^2, \tag{2.15}$$

one finds back Guyer-Krumhansl's original law

$$\tau\frac{\partial \boldsymbol{q}}{\partial t} + \boldsymbol{q} = -\lambda\nabla T + l^2(\nabla^2\boldsymbol{q} + 2\nabla\nabla.\boldsymbol{q}), \tag{2.16}$$

while the entropy production takes the form

$$\sigma^s = \frac{q^2}{\lambda T^2} + \frac{l^2}{\lambda T^2}[\nabla\boldsymbol{q} : \nabla\boldsymbol{q} + 2(\nabla.\boldsymbol{q})(\nabla.\boldsymbol{q})] \geq 0, \tag{2.17}$$

positivity of $\sigma^s$ demands that the heat conductivity $\lambda$ be positive definite. The derivation of the Guyer-Krumhansl equation given here is new and presents the advantage to be rather simple; it exhibits also clearly that not only Cattaneo's but also Guyer-Krumhansl's relation can been derived by assuming that the entropy $s$ depends, besides the classical variable $u$, of only one extra flux variable, the heat flux vector $\boldsymbol{q}$.

## 3. The ballistic-diffusion model

Micro and nano materials are characterized by the property that the ratio of the mean free path $l$ of the heat carriers and the mean dimension $L$ of the system, the Knudsen number $Kn = l/L$, is comparable or larger than unity. In the present work, we assume the coexistence of two kinds of heat carriers: diffusive phonons which undergo multiple collisions within the core of the system and ballistic phonons originating at the boundaries and experiencing mainly collisions with the walls. This model is called the ballistic–diffusion one and was initially introduced by Chen (2001). The main point underlying Chen's approach is to split the distribution function $f$ into two parts $f = f_b + f_d$, subscripts $b$ and $d$ referring to ballistic and diffusive phonons respectively.

Subsequently, the internal energy and the heat flux are decomposed into a ballistic and a diffusive component in such a way that

$$u = u_b + u_d, \quad \boldsymbol{q} = \boldsymbol{q}_b + \boldsymbol{q}_d. \tag{3.1}$$

The construction of the present model proceeds in three steps.

*Step 1. Definition of the space of state variables.* According to the decomposition (3.1) of $u$ and $\boldsymbol{q}$, the state variables are selected as follows:

i) the couple $u_d$, $\boldsymbol{q}_d$ to account for the diffusive behaviour of the heat carriers;

ii) the couple $u_b$, $\boldsymbol{q}_b$ to provide a description of the ballistic motion of the carriers.

For future use, we introduce also the diffusive and ballistic quasi-temperatures $T_d$ and $T_b$ defined respectively by $T_d = u_d / c_d$ and $T_b = u_b / c_b$, where $c_d$ and $c_b$ denote the heat capacities per unit volume and are positive quantities to guarantee stability of the equilibrium state. Admitting that the heat capacities are equal so that $c_d = c_b = c$, and defining the total quasi-temperature by $T = u/c$, it is verified that $T = T_d + T_b$. Although the quantities $T_d$, $T_b$, and $T$ bear some analogy with the classical definition of the temperature, it should however be realized that, strictly speaking, these quantities do not represent temperatures in the usual sense but must be considered as a measure of the internal energies, this justifies the use of the terminology "quasi-temperature".

*Step 2. Establishment of the evolution equations.* After having defined the sate variables, one must specify their behaviour in the course of time and space. The evolutions of the internal energies $u_d$ and $u_b$ are governed by the classical energy balance laws

$$\frac{\partial u_d}{\partial t} = -\nabla.\boldsymbol{q}_d + r_d, \quad \frac{\partial u_b}{\partial t} = -\nabla.\boldsymbol{q}_b + r_b, \tag{3.2}$$

while the total internal energy, $u = u_d + u_b$, satisfies the first law of thermodynamics (2.5), the quantities $r_d$, and $r_b$, designate source terms which may be either positive or negative. In virtue of the first law (2.5), one has to satisfy $r_d + r_b = 0$ in absence of energy sources, so that $r_d = - r_b$. Based on kinetic theory considerations (Chen 2001, 2002), it is shown that

$$r_b = -u_b / \tau_b, \tag{3.3}$$

the sign minus indicates that ballistic carriers can be converted into diffusive ones but that the inverse is not possible, $\tau_b$ is the relaxation time of the ballistic energy flux $\boldsymbol{q}_b$.

It remains to derive the evolution equation for the fluxes. Concerning the diffusive phonons, it is assumed that they satisfy Cattaneo's equation to cope with their high frequency properties, i.e.

$$\tau_d \frac{\partial \boldsymbol{q}_d}{\partial t} + \boldsymbol{q}_d = -\lambda_d \nabla T, \tag{3.4}$$

wherein the relaxation time $\tau_d$ and the heat conductivity coefficient $\lambda_d$ are positive quantities to meet the requirements of stability of equilibrium and positivity of the entropy production respectively (Lebon *et al* 2008, Jou *et al* 2010). However, expression (3.5) is not able to describe the ballistic regime which is mainly influenced by non-local effects as most of the ballistic carriers cross the system without experiencing collisions except with the boundaries. As shown before, this situation is satisfactorily described through Guyer-Krumhansl's equation

$$\tau_b \frac{\partial \boldsymbol{q}_b}{\partial t} + \boldsymbol{q}_b = -\lambda_b \nabla T + l_b^2 (\nabla^2 \boldsymbol{q}_b + 2\nabla\nabla . \boldsymbol{q}_b), \tag{3.5}$$

$l_b$ is the mean free path of the ballistic phonons, the terms involving the space derivatives of the heat flux vector account for the non-local effects and are important when the spatial scale of variation of the heat flux is comparable to the mean free path of the heat carriers. From the kinetic point of view, Guyer and Krumhansl have shown that $\tau_b$ can be identified with the collision time $\tau_R$ of the resistive phonons collisions (non-conserving momentum collisions), and that $l^2_b = (1/5)\, v^2\, \tau_R\, \tau_N$ with $v$ the mean velocity of phonons and $\tau_N$ the collision time of normal (momentum conserving) phonons collisions. Let us also mention that the relaxation times, the mean free paths and the heat conductivities are not independent but according to the phonon theory kinetic, they are related by

$$\lambda_d = \frac{1}{3} c\, v_d^2\, \tau_d \ , \ \lambda_b = \frac{1}{3} c\, v_b^2\, \tau_b \tag{3.6}$$

wherein $v_{d,} = l_d / \tau_d$ and $v_b = l_b / \tau_b$ designate the mean velocity of the diffusive and ballistic phonons, respectively. Expressions (3.2), (3.4) and (3.5) provide the basic set of the eight scalar evolution equations for the eight unknowns $u_d$ , $u_b$ ,$\boldsymbol{q}_d$ and $\boldsymbol{q}_b$.

*Step3.Elimination of the fluxes* $\boldsymbol{q}_d$ *and* $\boldsymbol{q}_b$.. This operation is easily achieved and is shown in the appendix. Assuming that all the transport coefficients are constant, one is led to the two second-order linear coupled differential equations :

$$\tau_d \frac{\partial^2 u_d}{\partial t^2} + \frac{\partial u_d}{\partial t} - (\tau_d / \tau_b) \frac{\partial u_b}{\partial t} - (1/\tau_b) u_b = (\lambda_d / c_d) \nabla^2 u_d , \tag{3.7}$$

$$\tau_b \frac{\partial^2 u_b}{\partial t^2} + 2\frac{\partial u_b}{\partial t} + u_b / \tau_b = (\lambda_b / c_b) \nabla^2 u_b + 3 l_b^2 \nabla . [\nabla \frac{\partial u_b}{\partial t} + (1/\tau_b) \nabla u_b]. \tag{3.8}$$

Expressions (3.7) and (3.8) are the key relations of our model. Setting $\tau_d = \tau_b = \tau$, $\lambda_d = \lambda_b = \lambda$, $c_d = c_b = c$, making use of the energy balance(3.2b) for the ballistic phonons, one recovers directly Chen's basic result from expression (3.7), namely

$$\tau \frac{\partial^2 u_d}{\partial t^2} + \frac{\partial u_d}{\partial t} + \nabla . \boldsymbol{q}_b = (\lambda \ / c \ ) \nabla^2 u_d , \tag{3.9}$$

this relation differs from the telegraph equation by the presence of the term $\nabla . \boldsymbol{q}_b$ . In Chen's formalism, the heat flux vector $\boldsymbol{q}_b$ has been obtained by using the kinetic definition of the heat flux and by solving Boltzmann's equation. Here, we do not refer to a kinetic approach but solve the problem exclusively at the macroscopic level. It should also be underlined that our model is more general than Chen's who introduced, without any justification, the simplifying assumptions that $\tau_d = \tau_b$. Moreover, Chen remains silent about the signs of $\tau_i$ , $\lambda_i$ and $c_i$ *(i=d, b).*

## 4. Application: transient temperature distribution in thin films

The foregoing model will be applied to the study of transient heat conduction in a one dimensional thin film of thickness *L* which may be of the same order of magnitude or even smaller than the mean free path *l* of the phonons. Heat capacity and heat conductivity are assumed to be constant and to take the same values for the diffusive and ballistic phonons, internal energy sources are absent (*r=0*). Initially, the system is at uniform energy $u_0$ or, using an equivalent terminology, at the "quasi-temperature" $T_0$ related to $u_0$ by $u_0= cT_0$. The lower surface *z=0* is suddenly brought at *t=0* to the "quasi-temperature" $T_1 = T_0 + \Delta T$, while the upper surface *z=L* is kept at "quasi-temperature" $T_0$. For further purpose, we introduce the Knudsen numbers $Kn_i = l_i /L$ (*i=d, b*) which, in virtue of expression (3.6), can be given the more general form

$$(Kn_i)^2 = 3\lambda\tau_i / cL^2, \qquad (i=d,\ b). \tag{4.1}$$

Having in mind numerical solutions, it is convenient to use dimensionless quantities

$$t^* = t/\tau_b,\ z^* = z/L,\ \ \theta_d = [u_d - u_d(z=L)]/c\Delta T,\ \theta_b=[u - u_b(z=L)]/c\Delta T,$$
$$\theta = \left[u - cT(z=L)\right]/c\Delta T, \tag{4.2}$$

with $\theta_d$, $\theta_b$ and $\theta\ (=\theta_d+\theta_b)$ designating the non-dimensional energy (or temperature) associated to the ballistic, diffusive and total energy respectively. The corresponding evolution equations (3.7) and (3.8) take now the form

$$\frac{Kn_d^2}{Kn_b^2}\left(\frac{\partial^2\theta_d}{\partial t^{*2}} - \frac{\partial\theta_b}{\partial t^*}\right) - \frac{Kn_b^2}{3}\frac{\partial^2\theta_d}{\partial z^{*2}} + \frac{\partial\theta_d}{\partial t^*} - \theta_b = 0, \tag{4.3}$$

$$\frac{\partial^2\theta_b}{\partial t^{*2}} + 2\frac{\partial\theta_b}{\partial t^*} - \frac{10}{3}Kn_b^2\frac{\partial^2\theta_b}{\partial z^{*2}} - 3Kn_b^2\frac{\partial^3}{\partial z^{*2}\,\partial t^*}\theta_b + \theta_b = 0. \tag{4.4}$$

*Initial conditions*. At *t=0*, the sample is at uniform temperature $T_0$ which implies that the total energy is given by $u(z,\ 0) = u_d(z,\ 0) + u_b(z,\ 0) = cT_0$. But it is reasonable to suppose that at short times, the ballistic phonons are dominant so that the initial energy will be essentially of ballistic nature leading to $u_b(z,\ 0) = cT_0$, or in dimensionless notation :

$$\theta_b(z^*,\ 0) = 0, \qquad \theta_d(z^*,\ 0) = 0. \tag{4.5}$$

Throughout the sample, at time $t=0$, the heat flux $\boldsymbol{q}$ is also zero; as a consequence of the energy balance (2.5), it is checked that initially $\partial\theta(z^*,t^*)\partial t^* = 0$, this result remains, in particular, satisfied under the assumptions

$$\frac{\partial\theta_d(z^*,t^*)}{\partial t^*}\Big|_{t^*=0} = 0, \qquad \frac{\partial\theta_b(z^*,t^*)}{\partial t^*}\Big|_{t^*=0} = 0. \tag{4.6}$$

*Boundary conditions*. The formulation of the boundary conditions is a more delicate problem. Their importance has to be underlined because in nano materials, their influence is felt throughout the whole system. To satisfy the conditions $\theta(0,t^*)=1$ and $\theta(1,t^*)=0$, the simplest tentative would be to suppose that, at $z^*=0$, $\theta_b(0, t^*)=1$ together with $\theta_d(0,t^*)=0$ while at $z^*=1$, the temperature of both the ballistic and diffusive constituents would be zero. However, such expressions are too simple and do not, in particular, cope with temperature jumps due to thermal boundary resistance as discussed in several papers (Swartz and Pohl 1989, Joshi-Majumdar 1993, Chen 2002, Navqi and Waldenstrom 2005). This is the reason why we have considered the following boundary conditions for the ballistic carriers:

$$\theta_b(0,t^*) = a, \quad \theta_b(1,t^*) = 0 \tag{4.7}$$

The quantity $a$ which represents the temperature jump of the ballistic phonons at the face $z^*=0$ at $t^*=0$, is taken equal to ½. This value may be understood statistically: since the temperature boundary condition at $z^*=0$ actually represents an internal energy boundary condition, it can be said that the ballistic phonons which are generated at the heated face are formed, by half of the carriers at the initial internal energy $\theta_b=0$ and the other half at the value $\theta_b=1$ corresponding to the energy at the face where the temperature is suddenly increased.. This result is confirmed by Chen (2002) who was able to determine the explicit expression of $\theta_b(z^*, t^*)$ by solving Boltzmann's equation from which results that indeed $\theta_b(0, t^*)=1/2$, at the heated boundary $z^*=0$. A posteriori, it is shown later on that this value leads to results which match satisfactory well with other different approaches. Concerning the diffusive carriers, we assume with Chen (2002), that both of the interfaces are black phonons emitters and absorbers, implying that the boundaries are made of incident diffusive carriers only. Combining Cattaneo's equation and Marshak's boundary condition (Modest 1993) for black body thermal radiation, one obtains (Chen 2002)

at z=*0,1:*

$$\frac{Kn_d^2}{Kn_b^2}\frac{\partial\theta_d}{\partial t^*} + \theta_d = \pm\frac{2}{3}Kn_d\frac{\partial\theta_d}{\partial z^*}, \tag{4.8}$$

the positive and negative signs at the right hand side correspond to the lower z*=0 and upper $z^*=1$ faces respectively, the factor $(Kn_d/Kn_b)^2$ is not present in Chen's developments because of his hypothesis of equality of relaxation times.

*Discussion of the results*

In a first stage, we have assumed that $Kn_b = Kn_d = Kn$ because it is wanted to check the validity of our model by comparing with previous different approaches. In particular, we have compared our results with those of Joshi and Majumdar (1993) who solved Boltzmann's equation of phonon's radiative transfer (EPRT model), Chen's (2001, 2002) ballistic-diffusive model and Alvarez and Jou (2010) who used a modified Fourier law with a heat conductivity depending on the Knudsen number. A modified version of Alvarez and Jou's work was recently proposed by Xu and Hu (2011) who based their analysis on a coarse graining of Boltzmann equation. In addition, for the sake of completeness, we have solved the hyperbolic Cattaneo and the parabolic Fourier equations for the identical geometry and boundary conditions.

In Figs. 1 to 3 are represented the non-dimensional temperature profiles for different $Kn$ values ($Kn=0.1$; $1$ and $10$) versus the distance at different times. To emphasize the specific roles of the two constituents, we have made explicit the contributions of the total, ballistic and diffusive components. The region close to the hot side is mainly dominated by the ballistic component contribution which decreases with space while the diffusive one is increasing up to a maximum, after which one observes a descent towards zero, the descent is the steepest as $Kn$ becomes smaller. As expected, the influence of the ballistic constituent becomes more important as $Kn$ is increased while the role of the diffusive one is dominant for small and intermittent $Kn$'s and is growing with time.. This observation reflects the conversion of the ballistic internal energy into the diffusive one as time is going on. It is also shown that for $Kn=10$, the steady state is reached rather soon (after $t^*=1$) and is decreasing linearly with space (see Fig. 3). The results are in qualitative accord with the aforementioned formalisms with however small discrepancies at small times ($t^*<0.1$) especially for $Kn = 10$. To avoid overloaded graphs, we have deliberately not plotted the results of the EPRT, Chen, Alvarez-Jou models as they are very close to ours. It is concluded that our description matches the results derived from various points of view, ranging from macroscopic, microscopic and mixed micro-macro approaches. Note also that for increasing values of $Kn$ (especially $Kn = 10$), a temperature jump is observed at the cold face. This indicates that the ballistic part exhibits a strong wall resistance not only at the hot but also at the cold face (especially at large $Kn$'s, see Fig. 3). The small bump just before the temperature jump is caused by numerical errors due to the abrupt temperature change.

It is clearly seen that both Cattaneo and Fourier descriptions lead to unrealistic results. Neither of these models predicts the temperature jumps at the boundary, moreover, they yield overestimated values for the temperature profiles as they do not integrate the specific properties of heat transport at nano scales, this particularly true at large $Kn$'s. This is not surprising as Cattaneo and Fourier laws give rise to an overestimated heat conductivity (Zhang 2007, Alvarez-Jou 2008). As observed in Figs. 2.b and 3.a, the Cattaneo equation exhibits a temperature discontinuity, propagating as a attenuating wave, the attenuation being due to the diffusion; at large time values, both Cattaneo's and Fourier's limits show the same linear behaviour with respect to the spatial coordinate (see Figs. 1c, 2c, 3c).

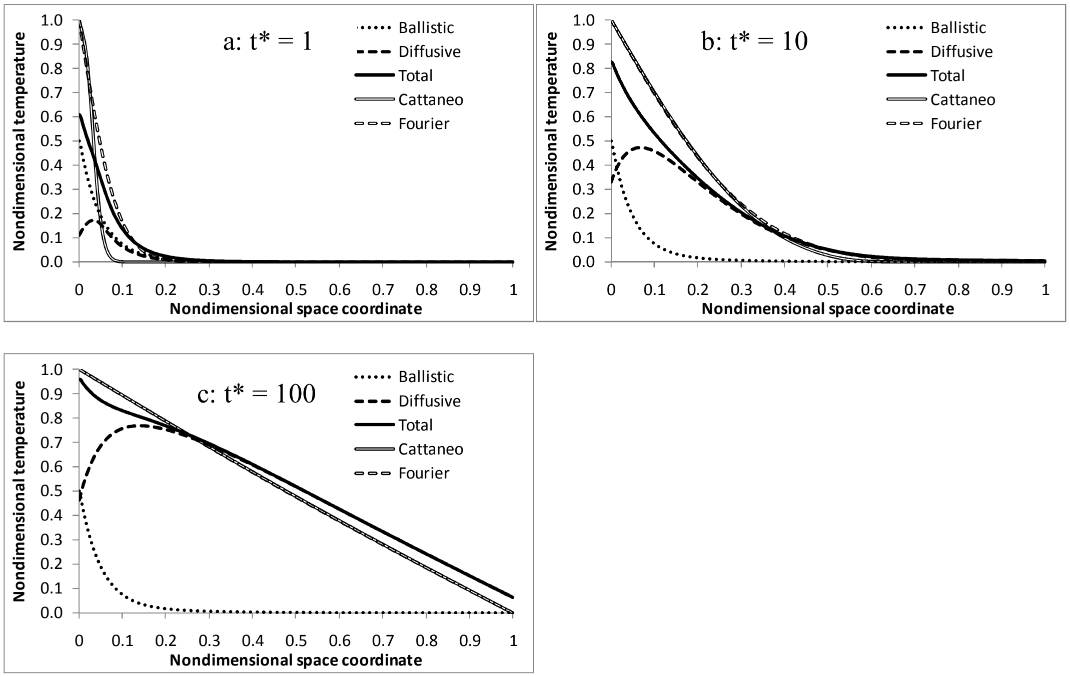


Fig.1. Non-dimensional temperature) profiles *θ (z*, t*)* as a function of distance *z*=z/L* at different times *t*= t/$\tau_b$* (*t** = 1, 10 and 100 respectively) for $Kn_d = Kn_b = Kn = 0.1$. The respective contributions of the ballistic, diffusive and total temperatures are shown and compared to the ones obtained from Cattaneo's and Fourier's equations.

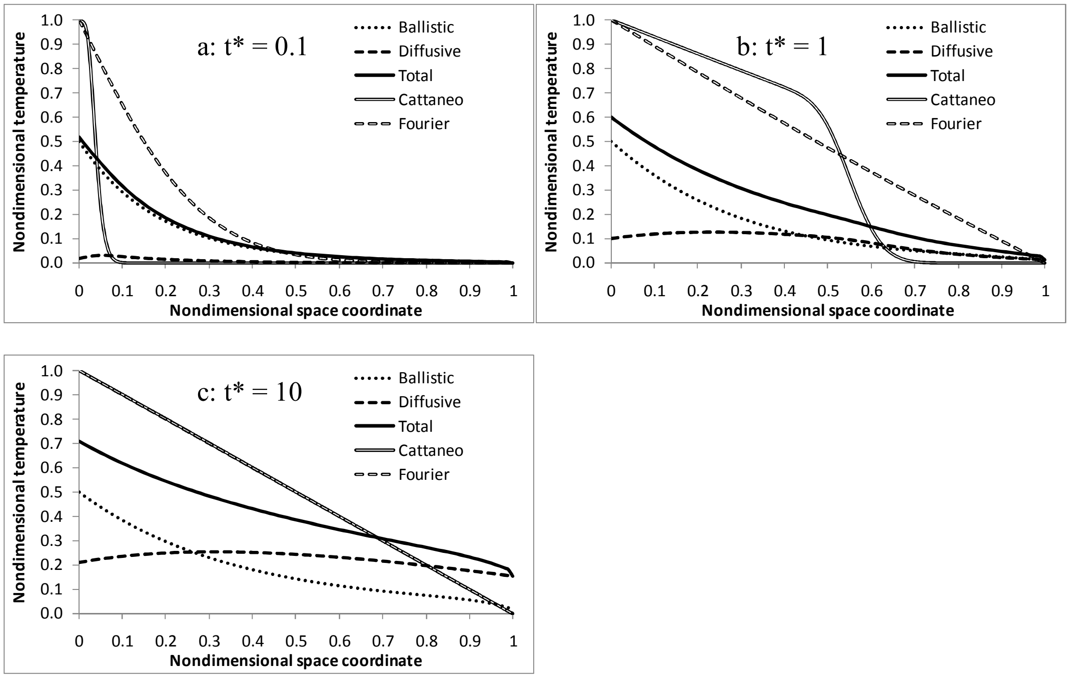


Fig. 2. Non-dimensional temperature profiles *θ (z*,t*)* as a function of distance *z*=z/L* at different times *t*= t/$\tau_b$* (*t** = 0.1, 1 and 10) for $Kn_d = Kn_b = Kn = 1$. The respective contributions of the ballistic, diffusive and total temperatures are shown and compared to the ones obtained by Cattaneo's and Fourier's equations.

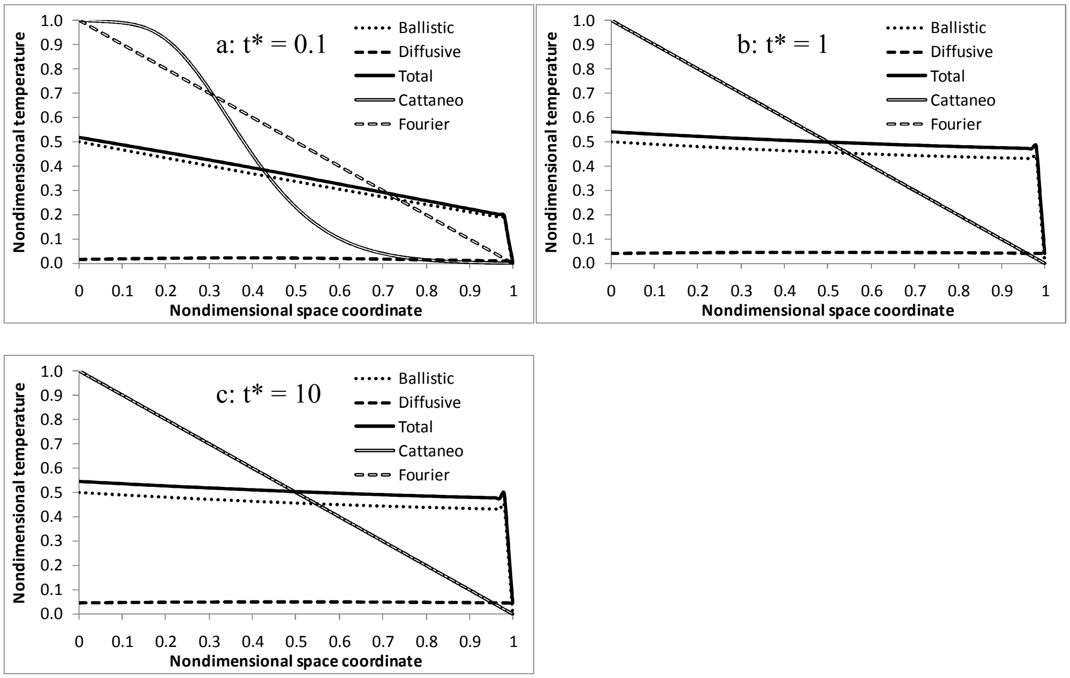
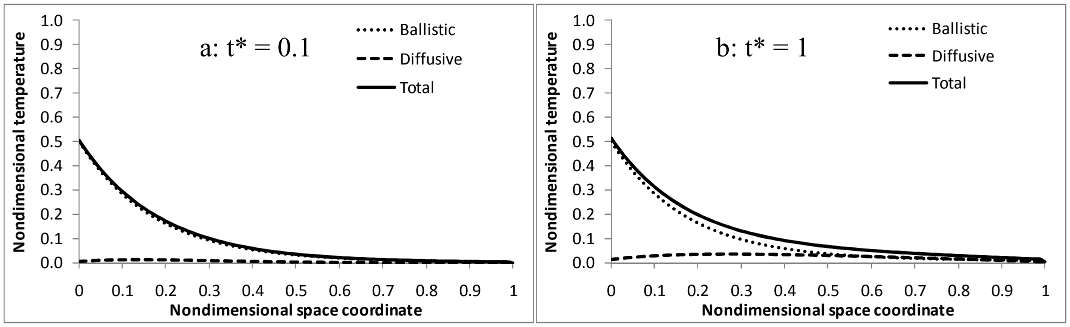


Fig. 3. Non-dimensional temperature profiles $\theta(z^*,t^*)$ as a function of distance $z^*=z/L$ at different times $t^*= t/\tau_b$ ($t^*$ = 0.1, 1 and 10) for $Kn_d = Kn_b = Kn = 10$. The respective contributions of the ballistic, diffusive and total temperatures are shown and compared to the ones obtained by Cattaneo's and Fourier's equations.

To better apprehend the specific contributions of the ballistic and diffusive constituents when the corresponding relaxation times are unequal, we have in a second step considered different values of $Kn_d$ and $Kn_b$. To be explicit, we have fixed $Kn_d =0.1$ with $Kn_b$ taking the values *1* and *10*. The results which are plotted on Figs. 4 and 5 exhibit the same general tendency as in the case of equal *Kn* values with the ballistic contribution being dominant at the $z^*=0$ heated face while the diffusive carriers tends to play a more important role at the cold face $z^*=1$ as time and $Kn_b$ are becoming larger. We notice also that the peak in the diffusive distribution (see Fig. 1.c) is disappearing. It is not surprising to observe that the diffusive contribution becomes minute at large $Kn_b /Kn_d$ ratios (see fig.5 for which $Kn_b/Kn_d=100$). We note also that at these values, the distribution of the temperature is practically linear and reaches quickly its stationary value after $t^*=1$, indeed, calculated curves at $t^*=10$ indicate no change.



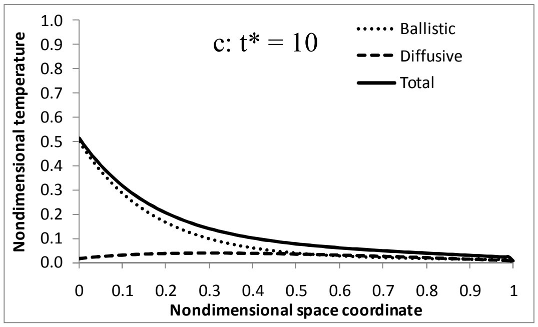


Fig.4. Non-dimensional temperature profiles *θ(z*,t*)* as a function of distance $z^*=z/L$ at different times $t^*= t/\tau_b$ ($t^*$ = 0.1, 1 and 10) for $Kn_d$ = 0.1 and $Kn_b$ = 1. The respective contributions of the ballistic, diffusive and total temperatures are shown.

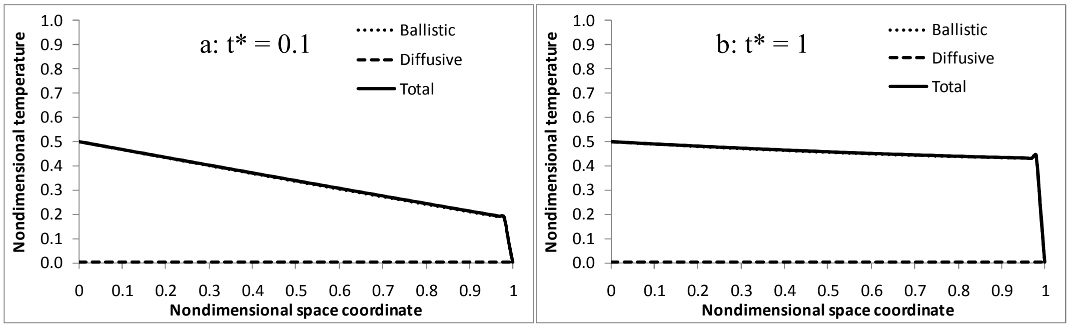


Fig.5. Non-dimensional temperature profiles *θ(z*,t*)* as a function of distance $z^*=z/L$ at different times $t^*= t/\tau_b$ ($t^*$ = 0.1 and 1 ) for $Kn_d$ = 0.1 and $Kn_b$ = 10. The respective contributions of the ballistic, diffusive and total temperatures are shown.

## Final comments and conclusion

A thermodynamic description of transient heat transport at nano scales based on Extended Irreversible Thermodynamics is proposed. The problem is important in the context of nano-electronics and heat transport in new materials. The model is original and purely macroscopic. The central assumption of the present work is that, contrary to previous approaches, the set of variables, namely the internal energy and the energy flux is split into contributions of diffusive and ballistic nature. Heat transport is viewed as a two-fluid diffusion-reaction process with ballistic particles converting into diffusive ones. The latter are obeying a Cattaneo equation while the behaviour of the ballistic phonons is governed by a Guyer-Krumhansl relation.This choice is motivated by the property that non-local effects are dominating in ballistic collisions.

The most important results of the present work are embodied in the differential equations (4.2) and (4.3) describing the behaviour of the diffusive and ballistic internal energies, These relations have been derived after elimination of the ballistic and diffusive heat fluxes from the basic set of time-evolution equations constituted by the balance of energies, Cattaneo and Guyer-Krumhnsl's equations. The choice of the initial and boundary conditions is inspired by earlier works by several authors (Joshi and Majumdar 1993, Chen 2001, Alvarez and Jou 2010).

One of our objectives was to convince the reader of the flexibility and wide range of applicability of Extended Irreversible Thermodynamics. It is shown that a rather simple model is able to cope with much of the results derived from more sophisticated approaches. It should however be kept in mind that the present work rests on several simplifying assumptions: for instance, from a fundamental point of view, questions may be raised about the definition of temperature at nano-scales. To circumvent this problem, in our analysis, temperature was understood as a measure of internal energy, the quantities $\theta_d$ and $\theta_b$ of the diffusive and ballistic components must therefore be understood as quasi- temperatures, defined as a measure of the corresponding energies $u_d$ and $u_b$ to which they are related by the simple expressions $\theta_d = u_d / c$, $\theta_b = u_b / c$ with $c$ designating the heat capacity. Moreover, our approach is restricted to the linear domain as all non-linear contributions are omitted. In addition, coupling between diffusive and ballistic heat fluxes has been neglected. It should be realized that the formalism discussed above represents only a first step towards a more elaborate description of heat transport at micro- and nano-scales. In particular, it is expected that higher order fluxes (the flux of the heat flux, the flux of the flux of the heat flux,…) (Jou *et al* 2010) should be introduced from the start to cope with the particulate behaviour of heat carriers at short wave lengths, but the difficulty is then the physical interpretation of these new variables coupled to the complexity of the mathematical formalism. The selection of the most appropriate set of state variables remains an open problem. Finally, as shown in the previous section, the establishment of appropriate boundary conditions remains a delicate task. In that respect, recent works (Jou *et al* 2010, Jou *et al* 2011) describe interesting and original prospective.

In spite of the above limitations, application of the model to the problem of transient heat conduction in materials with thickness of the order of magnitude of the mean free path of heat carriers has led to satisfactory results. Indeed, after comparison with earlier results derived from several works based on completely different approaches, one has obtained results exhibiting a qualitative accord.

The present study is supported by a project of collaboration between Wallonie-Bruxelles and Quebec under grant 06-809 (period 2009-2011). Discussions on an earlier version with professors A. Valenti (University of Catania) and A. Palumbo (University of Messina) were highly appreciated. Useful comments by professors P.C. Dauby and Th. Desaive (Liege University) are also acknowledged.

## Appendix: derivation of equations (3.7) and (3.8)

Application of operator $\nabla.$ on Cattaneo's equation (3.4) and use of $T_d = u_d / c_d$ yields

$$\tau_d \nabla.(\partial_t \boldsymbol{q}_d) = -\nabla.\boldsymbol{q}_d - (\lambda_d / c_d)\nabla^2 u_d , \tag{A.1}$$

wherein $\partial_t$ denotes the time derivative. Moreover, the balance of the total energy (2.5) can be written in the form

$$\nabla.\boldsymbol{q}_d = -\partial_t u - \nabla.\boldsymbol{q}_b = -\partial_t u_d - \partial_t u_b - \nabla.\boldsymbol{q}_b\,. \tag{A.2}$$

After differentiating (A.2) with respect to time and substituting in (A.1), one is led to

$$-\tau_d \partial_t^2 (u_d + u_b) - \tau_d \nabla.(\partial_t \boldsymbol{q}_b) = -\nabla.\boldsymbol{q}_d - (\lambda_d / c_d)\nabla^2 u_d = \nabla.\boldsymbol{q}_b + \partial_t u_d + \partial_t u_b - (\lambda_d / c_d)\nabla^2 u_d\,, \tag{A3}$$

wherein $\nabla.\boldsymbol{q}_d$ has been eliminated by means of (A.2). We now eliminate $\tau_d \partial_t^2 u_b$ by taking the time derivative of (3.2b) with $r_b = -u_b / \tau_b$ and we multiply this equation by $\tau_d$, the result is

$$\tau_d \partial_t^2 u_b = -\tau_d \nabla.(\partial_t \boldsymbol{q}_b) - (\tau_d / \tau_b)\partial_t u_b\,. \tag{A.4}$$

Substituting this result in (A.3) and replacing in the right-hand side of (A.3) the two terms $\nabla.\boldsymbol{q}_b + \dot{u}_b$ by $-u_b / \tau_b$ in virtue of (3.2b), we finally find back (3.7) after multiplying by (-1):

$$\tau_d \partial_t^2 u_d + \partial_t u_d - (\tau_d / \tau_b)\partial_t u_b - u_b / \tau_b = (\lambda_d / c_d)\nabla^2 u_d\,. \tag{A.5}$$

To derive expression (3.8), we start from the time derivative of the energy balance (3.2b), which multiplied by $\tau_b$, takes the form

$$\tau_b \partial_t^2 u_b = -\tau_b \nabla.(\partial_t \boldsymbol{q}_b) - \partial_t u_b\,. \tag{A.6}$$

To eliminate the term $\nabla.(\partial_t \boldsymbol{q}_b)$, we will use Guyer-Krumhansl's equation (3.6) to which we apply operator ∇., from which follows that

$$\tau_b \nabla.(\partial_t \boldsymbol{q}_b) + \nabla.\boldsymbol{q}_b = -(\lambda_b / c_b)\nabla^2 u_b + l_b^2 (\nabla.\nabla^2 \boldsymbol{q}_b + 2\nabla^2 \nabla.\boldsymbol{q}_b)\,. \tag{A.7}$$

After substitution of (A.7) in (A.6) and use of (3.2b) to eliminate $\nabla.\boldsymbol{q}_b$, one obtains, after some elementary arithmetic, relation (3.8), namely

$$\tau_b \partial_t^2 u_b + 2\partial_t u_b + u_b / \tau_b = (\lambda_b / c_b)\nabla^2 u_b + 3 l_b^2 \nabla.[\nabla(\partial_t u_b) + (1/\tau_b)\nabla u_b]\,. \tag{A.8}$$

## References

Alvarez, F.X. & Jou, D. 2008 Size and frequency dependence of effective thermal conductivity in nanosystems. *J. Appl. Phys.* **103**, 094321.

Alvarez, F.X. & Jou, D. 2010 Boundary condition,s and evolution of ballistic heat transport tr. *ASME J. Heat Transfe*r **132**, 0124404.

Cattaneo, C. 1948 Sulla conduzione del calore. *Atti del Seminario Matematico e Fisico delle Università di Modena* **3**, 83-101.

Chen, G. 2001 Ballistic-diffusion heat-conduction equation. *Phys.Rev. Lett.* **86**, 2297-2300.

Chen, G. 2002 Ballistic-diffusion equations for transient heat conduction from nano- to macroscales. *ASME J. Heat Transfer* **124**, 320-329.

De Groot, S.R. & Mazur, P. 1962 *Non-equilibrium thermodynamics.* North-Holland, Amsterdam.

Guyer, R.A.& Krumhansl, J.A. 1966 Solution of the linearized phonon Boltzmann equation. *Phys. Rev.* **148**, 766-777.

Guyer, R.A. & Krumhansl, J.A. 1966 Thermal conductivity, second sound, and phonon hydrodynamic phenomena in nonmetallic crystals. *Phys. Rev.* **148**, 778-788.

Joshi, A.A. & Majumdar, A. 1993 Transient ballistic and diffusive phonon heat transport in thin films. *J. Appl. Phys.* **74**, 31-39..

Jou, D., Casas-Vazquez, J. & Lebon, G. 2010 *Extended irreversible thermodynamics*, 4th ed. Springer, Berlin.

Jou, D., Lebon, G. & Criado-Sancho, M. 2010 Variational principles for thermal transport in nano systems with heat slip flow. *Phys. Rev. E* **82** 031128.

Jou, D., Sellito, A. & Alvrez, F.X. 2011 Heat waves and phonon-wall collisions in nanowires. *Proc. R. Soc. A* (doi:10.1098/rspa 2010. 0645)

Lebon, G. & Dauby P.C. 1990 Heat transport in dielectric crystals at low temperature: a variational formulation based on extended irreversible thermodynamics. *Phys. Rev.* **A 42**, 4710-4715.

Lebon, G., Jou, D. & Casas-Vazquez, J. 2008 *Understanding non-equilibrium thermodynamics*. Springer, Berlin.

Modest, M.F. 1993 *Radiative heat transfer*. McGraw-Hill, New York.

Naqvi, K.R. & Waldenstrom, S. 2005 Brownian Motion description of Heat conduction by Phonons. *Phys. Rev. Lett.*, **95**, 06590.

Onsager, L. 1931 Reciprocal relations in irreversible processes. *Phys. Rev.* **37**, 405-426.

Prigogine, I. 1961 *Introduction to thermodynamics of irreversible processes*. Interscience, New York.

Swartz, E.T. & Pohl, R.O. 1989 Thermal boundary resistance. *Rev. Mod. Phys.* **61**, 605-668.

Valenti, A.,Torrisi M. & Lebon, G. 1997 Heat pulse propagation by second sound in dielectric crystals. *J. Phys. Condens. Matter* **9**, 3117-3127.

Xu, M. & Hu, H. 2011 A ballistic-diffusive heat conduction model extracted from Boltzmann transport equation. *Proc. R. Soc. A* **467**1851-1854

Zhang, Z.M. 2007 *Nano/microscale heat transfer.* McGraw-Hill, New York.

**Short title** : Heat conduction at sub-scales.

**Figure captions**

Fig.1. Non-dimensional energy (temperature) profiles $\theta(z^*,t^*)$ as a function of distance $z^*= z/L$ at different time $t^*= t/\tau_b$ ($t^*= 1, 10 , 100$) for $Kn_d = Kn_b = Kn = 0.1$. The respective contributions of the ballistic (………) , diffusive (----------) and total ( __________) temperatures are shown.

Fig.2. The same temperature profiles as in Fig. 1 for $Kn_d=Kn_b= 1$. The contribution of the diffusive temperatures is perceptibly decreased compared to the case $Kn=0.1$.

Fig. 3. The same temperature profiles as in Figs.1 and 2 for $Kn_d = Kn_b= 10$. The diffusive component is considerably reduced and the total temperature is characterized by a quasi linear decrease with a temperature jump at each boundary .

Fig.4. Ballistic, diffusive and total temperature distributions $\theta$ versus distance $z^*$ for different times $t^*$ and Knudsen numbers $Kn_d= 0.1, Kn_b=1$.

Fig.5. The same as in fig. 4 but for $Kn_d=0.1, Kn_b = 10$. Profiles are quasi linear and the steady state is reached very rapidly after $t^*=1$. Similar curves were obtained for $Kn= =1$, $Kn=100$ and have not been represented.