



## Extended irreversible thermodynamics of heat transport A brief introduction

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**Abstract.** Current frontiers of technology require generalized transport equations incorporating memory, non-local effects, and non-linear effects. Extended Irreversible Thermodynamics provides such transport equations in a form compatible with the second law of thermodynamics, and that, for low frequency and short mean-free paths, reduce to the classical transport equations. Here we present the basic concepts of extended irreversible thermodynamics, namely, the fluxes as independent variables, and their evolution equations as generalized transport equations obeying the second law of thermodynamics. We show that these equations cover a rich phenomenology in heat transport, including thermal waves, phonon hydrodynamics, ballistic transport, and saturation in the fluxes for high values of the thermodynamic forces.

**Key words:** non-equilibrium thermodynamics, ballistic heat transport, extended irreversible thermodynamics, thermal waves.

### 1. INTRODUCTION. PHYSICAL MOTIVATIONS

Current frontiers in technology, e.g. in materials sciences and nanotechnology, require generalized transport equations beyond the classical theory. For instance, transport equations for miniaturized systems whose size is comparable to the mean free path have become an important topic because of the surge of nanotechnology. Analogously, the behaviour of systems submitted to high-frequency perturbations, comparable to the reciprocal of internal relaxation times, is necessary to optimize the operation of high-frequency devices. Equations for heat, mass, charge, and momentum transport have been actively explored in several situations: in miniaturized electronic devices, in nanotubes and nanowires, in theoretical models of energy transport in one-dimensional chains, in rarefied gases, etc. How far thermodynamic formalisms are helpful or necessary in this endeavour is an open question, because the mentioned situations clearly exceed the limits of validity of the classical local-equilibrium thermo-

dynamics. Therefore, their study is a challenge for non-equilibrium thermodynamics to better understand its basic concepts, its limits of application, and its frontiers.

Among the several thermodynamic theories going beyond the local-equilibrium approach, Extended Irreversible Thermodynamics (EIT) provides generalized transport equations that incorporate memory and non-local effects, that reduce to the classical transport equations for low frequency and short mean-free paths, and that are able to incorporate the high-frequency behaviour of dissipative signals as, for instance, a finite speed of propagation of heat pulses, and general features of ballistic behaviour for long mean-free paths. Thus, they provide not only small corrections to the usual transport equations, but they turn out to be useful even under extreme non-equilibrium situations where the classical equations completely fail.

In this paper, we introduce the basic concepts of EIT, namely, the idea of the fluxes as independent variables of the entropy and entropy flux, and the procedure to obtain their evolution equations, which provide generalized transport equations obeying the second law of thermodynamics. The reader interested in this topic and in its relation with other current frontiers

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of non-equilibrium thermodynamics may go to wider presentations such as Jou et al. (2001a, b) and Lebon et al. (2008).

Finite speed of propagation for dissipative signals was one of the starting stimuli for developing extended thermodynamics, but it appeared initially as an academic motivation because it was thought that the measurement of the relaxation times for the fluxes would be in general rather difficult. However, the development of light-scattering and neutron-scattering techniques showed not only that such relaxation times could be measured with accurateness, but that they were dependent on the wavevector in such a way that non-local effects should be taken into consideration.

Accordingly, we will incorporate memory and second-order non-local effects, and will show that this describes a rich phenomenology in heat transport, including thermal waves and phonon hydrodynamics. Though such transport equations had been proposed earlier on different bases, it was generally not realized that they were violating the classical formulation of the second law of thermodynamics, as they led in some cases to a negative entropy production. Extended Irreversible Thermodynamics was able to circumvent this problem by introducing a generalized entropy and entropy flux depending not only on the classical variables but also on the fluxes. Extended Irreversible Thermodynamics provides relevant models to explore the validity of thermodynamic ideas beyond their usual range of application.

However, the inclusion of memory and second-order non-local effects, interesting as it is, cannot cope with the ballistic regime, where most of the particles cross all the system without experiencing practically any collision, except with the walls. To deal with this situation, it is necessary to include an infinite number of higher-order fluxes. Continued-fraction expansions for the effective thermal conductivity are established, leading to the expected limiting behaviours in collisional and ballistic regimes, and providing an interpolation in the intermediate regimes. Systems whose dimensions are comparable to or smaller than the mean free path of the carriers are not necessarily small. For instance, multilayer materials and superlattices, constituted by the superposition of thin layers, may exhibit non-Fourier heat transport when the width of each layer is smaller than the mean free path of the carriers. Such a configuration is characterized by a combination of ballistic regime and a set of barriers separating the successive layers. In ultrafast solidification, a transition from diffusive to ballistic behaviour is also observed (Herlach et al. 2007).

The behaviour of small systems is strongly influenced by non-linear effects, because even a small difference in temperature over a small distance generates very high gradients. As a consequence, the

transport equations must explicitly incorporate non-linear effects. In the present analysis, the heat flux will always have a finite, limited value, which will be of the order of the energy density times the maximum speed of signal propagation. The non-linear transport equations studied here are characterized by saturation in the fluxes for high enough values of the temperature gradient.

The generalized non-equilibrium entropy introduced by EIT, dependent on the fluxes, yields some insights into how to formulate a thermodynamic theory beyond local-equilibrium, an aim shared with other approaches (Eu 1992, 1998; Maugin and Muschik 1994a, b; Verhas 1997; Maugin 1999; Luzzi et al. 2001, 2002; Öttinger 2005). This implies a generalization of equations of state containing non-equilibrium contributions, which are useful to understand some open problems concerning the definition and meaning of temperature.

In summary, EIT is not only a conceptually interesting theory, with contributions to such basic questions as the form of the entropy and temperature in non-equilibrium states and the formulation of the second law in far-from-equilibrium situations, but it is also able to describe sophisticated experiments at micro- and nano-scales. Nowadays, a new area is open for EIT: the area of new technological applications.

## 2. MEMORY EFFECTS AND EXTENDED ENTROPY

The central relations in transport theories are the transport laws, describing the rate of transport of the basic variables in terms of the inhomogeneities of the system, yielding, for instance, the expressions of the fluxes of heat, mass, momentum, or charge as a function of the gradients of temperature, concentration, velocity, and electrical potential. In the classical transport theory, the fluxes  $\mathbf{J}$  and the conjugated thermodynamic forces  $\mathbf{X}$  are related by linear transport laws of the form  $\mathbf{J}(t) = \mathbf{L} \cdot \mathbf{X}(t)$  with  $\mathbf{L}$  being suitable phenomenological coefficients. For instance, one may identify  $\mathbf{J}$  with the heat flux  $\mathbf{q}$  and  $\mathbf{X}$  with the temperature gradient  $\mathbf{X} = \nabla T^{-1}$ , and  $\mathbf{L}$  as  $\mathbf{L} = \lambda T^2 \mathbf{I}$ , where  $\mathbf{I}$  denotes the identity tensor. This leads for isotropic systems to the Fourier law

$$\mathbf{q} = -\lambda \nabla T. \quad (2.1)$$

This equation implies an instantaneous response of the system. This is in general a good approximation, but it breaks down when the perturbation is very fast or when the response time is very long. In these situations, a flux  $\mathbf{J}(t)$  at a given time  $t$  is related to its respective conjugate force  $\mathbf{X}(t')$  at previous times  $t'$  through

$$\mathbf{J}(t) = \int_{-\infty}^0 \mathbf{K}(t-t') \cdot \mathbf{X}(t') dt', \quad (2.2)$$

where  $\mathbf{K}(t-t')$  is a memory function. When  $\mathbf{K}(t-t') = \mathbf{L}\delta(t-t')$  one recovers equations of the form (2.1); the next simplest possibility is to write

$$\mathbf{J}(t) = \int_{-\infty}^0 \frac{\mathbf{L}}{\tau} \exp[-(t-t')/\tau] \cdot \mathbf{X}(t') dt'. \quad (2.3)$$

In this case the memory decays exponentially, but it could also decay in other fast ways according to Coleman and Noll's fading memory principle (Wang 1964). The relation (2.3) is equivalent to assuming that the flux is described by a generalized transport equation of the form

$$\tau \frac{\partial \mathbf{J}}{\partial t} = -(\mathbf{J} - \mathbf{L} \cdot \mathbf{X}). \quad (2.4)$$

Indeed, integration of (2.4), and assuming that the initial value of the flux is zero, leads to (2.3). In the case of heat transport, (2.4) takes the explicit form

$$\tau \frac{\partial \mathbf{q}}{\partial t} = -(\mathbf{q} + \lambda \nabla T), \quad (2.5)$$

which is generally referred to as the Cattaneo or Maxwell–Cattaneo equation. The term containing the time  $\tau$  represents the heat flux relaxation. When  $\tau$  is negligible or when the time variation of the heat flux is slow, (2.5) will reduce to Fourier's law.

Analogous generalizations are known for other fluxes, but here we will focus our attention on the heat flux. To examine the physical consequences of (2.5), we first consider the behaviour of thermal waves in rigid solids and incompressible fluids at rest. To do this, we use the balance equation of the specific internal energy  $u$ , which can be cast in the form

$$\rho \frac{\partial u}{\partial t} = -\nabla \cdot \mathbf{q}, \quad (2.6)$$

where  $du = c_v dT$ , with  $c_v$  being the heat capacity per unit mass at constant volume. Introducing (2.5) into (2.6) one obtains

$$\tau \frac{\partial^2 T}{\partial t^2} + \frac{\partial T}{\partial t} - \chi \nabla^2 T = 0, \quad (2.7)$$

where  $\chi = \lambda/\rho c_v$  designates the heat diffusivity, wherein the coefficients  $\tau$  and  $\lambda$  are assumed to be constant. The solutions of (2.7) propagate with finite speed  $(\chi/\tau)^{1/2}$ , and the amplitude of the pulse decreases in time as a consequence of the irreversible term. For  $t \ll \tau$ , the first term of equation (2.7) is dominant, so that it reduces to

$$\tau \frac{\partial^2 T}{\partial t^2} = \chi \nabla^2 T. \quad (2.8)$$

This is a wave equation with the same wave speed as (2.7); it describes a reversible process as it is invariant with respect to time inversion. In contrast, for time scales longer than  $\tau$  ( $t \gg \tau$ ), the first term of (2.7) is negligible and one obtains the partial differential equation

$$\frac{\partial T}{\partial t} = \chi \nabla^2 T, \quad (2.9)$$

associated with diffusion of heat, which is an irreversible process as (2.9) is not invariant when  $t$  is changed into  $-t$ . Thus, at short times the transport equation (2.5) is reversible and heat propagates with a finite speed (which may be microscopically interpreted as a ballistic motion of the particles before experiencing a collision), whereas at longer times the process becomes irreversible and heat is diffused throughout the system. Then  $\tau$  can be interpreted as the characteristic time for the crossover between ballistic motion and the onset of diffusion. In the context of chaotic deterministic systems,  $\tau$  may be interpreted as the Lyapunov time beyond which predictivity is lost (Nicolis and Prigogine 1989). Thus, from a conceptual perspective, (2.5) is more suitable than the Fourier equation (corresponding to  $\tau=0$ ), as it describes the transition from reversible to irreversible behaviour.

The dynamical properties of equation (2.7) have been thoroughly analysed. For instance, by assuming a solution of the form  $T(x, t) = T_0 \exp[i(kx - \omega t)]$ , where  $\omega$  is a (real) frequency and  $k$  a (complex) wave-number, it is found that the solution is characterized by a phase speed  $v_p$  and an attenuation factor  $\alpha$ , respectively given by

$$v_p = \frac{\omega}{\text{Re} k} = \frac{\sqrt{2\chi\omega}}{\sqrt{\tau\omega + \sqrt{1 + \tau^2\omega^2}}}, \quad \alpha = \frac{2\chi}{v_p}. \quad (2.10)$$

In the high-frequency limit ( $\tau\omega \gg 1$ ), the phase speed and attenuation coefficient following from (2.10) are

$$v_{p\infty} \equiv U = (\chi/\tau)^{1/2}, \quad \alpha_\infty = 2(\chi\tau)^{1/2}. \quad (2.11)$$

The value of  $v_p$  diverges when the relaxation time vanishes, thus leading to an infinite speed of propagation. Therefore, the presence of the relaxation time is much more than a minor quantitative correction, as in the high-frequency regime it leads to a completely different behaviour than that predicted by the classical Fourier's law. The analysis of thermal waves has been the topic of much research (Joseph and Preziosi 1989, 1990; Dreyer and Struchtrup 1993; Tzou 1997; Jou et al. 2001a). After application of a thermal pulse, and according to (2.5), the front propagates at a speed  $v_p = (\chi/\tau)^{1/2}$ ; beyond the wavefront, located at  $x_f = v_p t$ , the temperature perturbation is not felt. The

temperature behind the wavefront will be higher than the one corresponding to Fourier's law, because the same amount of energy is confined into a smaller volume. For longer times, the difference between the hyperbolic and the parabolic temperature distributions becomes smaller and smaller. Long relaxation time of the heat flux is also typical of superfluids, another topic of interest for extended thermodynamics (Mongiovi and Jou 2007).

Cattaneo's equation (2.5) is appealing in practice, but it is not compatible with the positive definite character of the local-equilibrium entropy production (Jou et al. 2001a; Müller and Ruggeri 1997). Since (2.5) may be considered as an evolution equation for the heat flux, it becomes an independent quantity. To achieve a consistent thermodynamic framework where Cattaneo's equation becomes compatible with the second law, we consider  $\mathbf{q}$  as an independent variable and assume that the entropy density  $s$  is  $\mathbf{q}$ -dependent. More explicitly, we write:

$$ds = T^{-1}du - T^{-1}v\alpha_1\mathbf{q} \cdot d\mathbf{q}, \quad (2.12)$$

where  $v$  is the specific volume (the reciprocal of mass density  $\rho$ ) and  $\alpha_1$  a coefficient allowed to depend on  $T$  but not on  $\mathbf{q}$ . From (2.12) and the internal energy balance law (2.6), one obtains for the time derivative  $\dot{s}$  of the entropy

$$\rho\dot{s} = -T^{-1}\nabla \cdot \mathbf{q} - T^{-1}\alpha_1\mathbf{q} \cdot \dot{\mathbf{q}}, \quad (2.13)$$

or, equivalently,

$$\rho\dot{s} = -\nabla \cdot (T^{-1}\mathbf{q}) + \mathbf{q} \cdot (\nabla T^{-1} - T^{-1}\alpha_1\mathbf{q} \cdot \dot{\mathbf{q}}). \quad (2.14)$$

This equation can be cast in the general form of a balance equation, namely

$$\rho\dot{s} = -\nabla \cdot \mathbf{J}^s + \sigma^s, \quad (2.15)$$

with  $\mathbf{J}^s$  the entropy flux and  $\sigma^s$  the entropy production (a positive definite quantity as required by the second law of thermodynamics) given by

$$\mathbf{J}^s = T^{-1}\mathbf{q} \quad (2.16)$$

and

$$\sigma^s = \mathbf{q} \cdot (\nabla T^{-1} - T^{-1}\alpha_1\mathbf{q} \cdot \dot{\mathbf{q}}) \geq 0. \quad (2.17)$$

Relation (2.17) is a bilinear form  $\sigma^s = \mathbf{q} \cdot \mathbf{X}$  in the flux  $\mathbf{q}$  and the force  $\mathbf{X}$ , identified as the quantity within parentheses in (2.17); it differs from the classical thermodynamic force,  $\nabla T^{-1}$ , by the presence of a term in the time derivative of the heat flux.

The simplest way to obtain an evolution equation for  $\mathbf{q}$  compatible with the positiveness of  $\sigma^s$  is to assume that the force  $\mathbf{X}$  is linear in  $\mathbf{q}$ , namely

$$\nabla T^{-1} - T^{-1}\alpha_1\dot{\mathbf{q}} = \mu_1\mathbf{q}, \quad (2.18)$$

where the phenomenological coefficient  $\mu_1$  may depend on  $u$  but not on  $\mathbf{q}$  because, as previously, third-order contributions in  $\mathbf{q}$  are omitted. Introduction of (2.18) into (2.17) results in  $\sigma^s = \mu_1\mathbf{q} \cdot \mathbf{q} \geq 0$ , from which it infers that  $\mu_1 > 0$ .

Expression (2.18) contains two coefficients,  $\alpha_1$  and  $\mu_1$ , which must be identified on physical grounds. By comparing (2.18) with Cattaneo's equation (2.5), one is led to  $\mu_1 = (\lambda T^2)^{-1}$  and  $\alpha_1 = \tau/\lambda T$ . With these identifications, the generalized Gibbs equation (2.12) takes the form (Jou et al. 1988, 1999, 2001a)

$$ds = \frac{1}{T}du - \frac{\tau}{\rho\lambda T^2}\mathbf{q} \cdot d\mathbf{q}, \quad (2.19)$$

wherein it is important to observe that the coefficient of the new term in  $d\mathbf{q}$  is identified in terms of physical quantities, namely the relaxation time  $\tau$  and the heat conductivity  $\lambda$ . After integration of (2.19), the explicit expression for the entropy outside (local) equilibrium up to second-order terms in  $\mathbf{q}$  is

$$\rho s(u, \mathbf{q}) = \rho s_{\text{eq}}(u) - \frac{1}{2} \frac{\tau}{\lambda T^2} \mathbf{q} \cdot \mathbf{q}. \quad (2.20)$$

Note that when the relaxation time tends to zero, Cattaneo's equation (2.7) tends to Fourier's equation and (2.19) tends to the classical Gibbs equation of local-equilibrium theory. An alternative way to achieve thermodynamic consistency of the Maxwell–Cattaneo equation is by introducing a vectorial internal variable and obtaining its evolution equation; when the internal variable is proportional to the heat flux, the evolution equation for the latter is seen to be the Maxwell–Cattaneo equation (Coleman et al. 1982; Morro and Ruggeri 1987; Cimmelli and Kosinski 1991; Verhas 1997).

### 3. SECOND-ORDER NON-LOCAL EFFECTS

Non-local effects are especially important to describe the transition from diffusive to ballistic regime (Jou et al. 2005; Alvarez and Jou 2007). Indeed, when the mean-free path between successive collisions becomes long, there will be a direct connection between non-adjacent regions, with very different values of the temperature. The surge of interest in nanotechnology has raised new questions about heat transport. In particular, it may be asked whether laws like those of Fourier and Cattaneo remain applicable for nano-systems, where the ratio between the mean-free path  $\ell$  and the characteristic length  $L$  of the system, the Knudsen number ( $Kn \equiv \ell/L$ ), becomes comparable to

or higher than 1 and heat transport is no longer diffusive but ballistic. To formulate the problem in simple terms, consider a one-dimensional system of length  $L$ , whose opposite boundaries are at temperature  $T$  and  $T - \Delta T$ . Depending on the values of  $Kn$ , the heat flux  $q$  takes the following limiting forms

$$q = \lambda \frac{\Delta T}{L} \quad (Kn \ll 1, \text{ diffusive transport}), \quad (3.1)$$

$$q = \Lambda \Delta T \quad (Kn \gg 1, \text{ ballistic transport}). \quad (3.2)$$

The factor  $\lambda$  denotes the thermal conductivity and  $\Lambda$  is a heat conduction transport coefficient. In the diffusive limit, the heat flux is proportional to the temperature gradient, according to Fourier's law; in the ballistic regime, it depends only on the temperature difference, but not on the length  $L$  of the system.

A simple phenomenological modelling of the transition between the diffusive and the ballistic regimes can be achieved by introducing a heat conductivity  $\lambda(T, \ell/L)$  in such a way that in whole generality

$$q = \lambda(T, \ell/L) \frac{\Delta T}{L}. \quad (3.3)$$

The limiting values of this generalized conductivity should be

$$\lambda(T, \ell/L) \rightarrow \lambda(T) \quad \text{for } \ell/L \rightarrow 0, \quad (3.4a)$$

$$\lambda(T, \ell/L) \rightarrow \frac{\lambda(T) L}{a \ell} \equiv \Lambda(T) L \quad \text{for } \ell/L \rightarrow \infty, \quad (3.4b)$$

where  $a$  is a constant depending on the system. First of all, we introduce second-order non-local effects, which describe weak non-locality (Jou et al. 2001a; Lebon et al. 2008); we will see the possible advantages and the limitations of this situation, but we will show that it does not describe the transition to the ballistic regime. To deal with this transition, an infinite number of higher-order fluxes must be incorporated.

To describe non-local effects, EIT introduces a new extra variable, the flux of the heat flux, described by a second-order tensor  $\mathbf{Q}$ , and writes instead of the Cattaneo equation (2.7) the following expression (Jou et al. 2001a):

$$\tau_1 \frac{\partial \mathbf{q}}{\partial t} = -(\mathbf{q} + \lambda \nabla T) + \nabla \cdot \mathbf{Q}. \quad (3.5)$$

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 its trace and  $\mathbf{Q}^s$  the deviatoric part. In a relaxational approach, the evolution equations for  $Q$  and  $\mathbf{Q}^s$  may be written as

$$\tau_0 \frac{\partial Q}{\partial t} = -Q + \beta' \nabla \cdot \mathbf{q}, \quad (3.6)$$

$$\tau_2 \frac{\partial \mathbf{Q}^s}{\partial t} = -\mathbf{Q}^s + 2\beta'' (\nabla \mathbf{q})^s. \quad (3.7)$$

Assuming that the relaxation times  $\tau_0$  and  $\tau_2$  are negligibly small and considering only regular solutions for which the time derivatives appearing at the left hand side of (3.6) and (3.7) do not diverge, and substituting (3.6–3.7) into (3.5), one obtains for the evolution of the heat flux

$$\tau_1 \frac{\partial \mathbf{q}}{\partial t} = -(\mathbf{q} + \lambda \nabla T) + \beta'' \nabla^2 \mathbf{q} + \left( \beta' + \frac{1}{3} \beta'' \right) \nabla (\nabla \cdot \mathbf{q}). \quad (3.8)$$

Equation (3.8) is comparable with that obtained by Guyer and Krumhansl (1966) from phonon kinetic theory. The phonons in a solid undergo two types of collisions: resistive  $R$ -collisions, with defects of the lattice or the boundaries of the crystal, and Umklapp phonon–phonon processes. The former conserve energy but not momentum and have a characteristic time  $\tau_R$ . The latter, referred to as normal  $N$  processes, conserve energy and momentum and have a characteristic time  $\tau_N$ . Starting from the Boltzmann equation, Guyer and Krumhansl (1966) derived an equation of the form (3.8) with the following identifications of the coefficients:

$$\tau_1 = \tau_R, \quad \frac{\lambda}{\tau_R} = \frac{1}{3} \rho c_v c_0^2, \quad \beta'' = \frac{1}{5} c_0^2 \tau_N \tau_R, \quad \beta' = \frac{1}{3} c_0^2 \tau_N \tau_R, \quad (3.9)$$

from which follows that  $\tau_1$  is associated with resistive collisions while the non-local contributions find their origin in the normal collisions. Equation (3.8) contains as particular cases the Fourier and the Cattaneo equations for heat transport, for  $\tau_R^{-1} \rightarrow \infty$  and  $\tau_N^{-1} \rightarrow \infty$ , and for  $1/\tau_R$  finite and  $1/\tau_N \rightarrow \infty$ , respectively. It becomes also clear that the flux of the heat flux  $\mathbf{Q}$  accounts for the presence of the momentum-preserving  $N$  phonon–phonon collisions. Equation (3.8) is also used to describe the so-called phonon hydrodynamics, which arises when the resistive collision time is very long and the normal relaxation time is the predominant one. In this case, (3.8) is analogous to the linearized Navier–Stokes equation, with the heat flux instead of the velocity,  $c_0^2 \tau_N / 5$  instead of the kinematic viscosity, and  $\nabla T$  playing a role analogous to the pressure gradient in hydrodynamics.

An equation of the form of (3.8) arises also in some other contexts, as for instance in systems composed of two subsystems, each of them with its own temperature. These subsystems are, for instance, the electrons and the lattice in a metal submitted to a short-pulse laser

heating, where the electron temperature is much higher than the lattice temperature. This problem is well described by the following evolution equations for the electron and lattice temperatures  $T_e$  and  $T_l$  respectively:

$$c_e \frac{\partial T_e}{\partial t} = \nabla \cdot (\lambda \nabla T_e) - C(T_e - T_l), \quad (3.10)$$

$$c_l \frac{\partial T_l}{\partial t} = C(T_e - T_l). \quad (3.11)$$

The constant  $C$  refers to the electron–phonon coupling, which accounts for the energy transfer from the electrons to the lattice, and  $c_e$  and  $c_l$  are the specific heats of the electrons and lattice per unit volume, respectively. When the solution of (3.11) is introduced into (3.10), one is led to

$$\nabla^2 T_l + \frac{c_l}{C} \frac{\partial \nabla^2 T_l}{\partial t} = \frac{c_l + c_e}{\lambda} \frac{\partial T_l}{\partial t} + \frac{c_e c_l}{\lambda C} \frac{\partial^2 T_l}{\partial t^2}. \quad (3.12)$$

Such an equation can also be obtained by eliminating  $\mathbf{q}$  between the energy balance equation (2.6) and equation (3.8) under the following identifications:  $c_l/C = (\beta''/\lambda)\rho c_v$ ,  $c_e c_l/C = 9\rho c_v \tau_R$ , and  $\beta' = 0$ .

Another context where an equation of the form of (3.8) may be derived is the so-called dual-phase-lag equation (Tzou 1997)

$$\tau_1 \dot{\mathbf{q}} + \mathbf{q} = -\lambda \left( \nabla T + \tau' \frac{\partial \nabla T}{\partial t} \right), \quad (3.13)$$

which takes into account relaxation effects in both the heat flux and the temperature gradient. However, such a procedure yields a parabolic equation, while by starting with the heat flux and the flux of the heat flux as independent variables one is led to a hyperbolic equation that contains the parabolic equation (3.8) in the limit of a vanishing relaxation time of the flux of the heat flux.

The thermodynamics underlying the transport equations (3.5–3.7) is easily derived by following the same procedure as in Section 2, i.e. by introducing an extended Gibbs equation and entropy flux of the forms

$$ds = \frac{1}{\theta} du - \frac{\tau_1 v}{\lambda T^2} \mathbf{q} \cdot d\mathbf{q} - \frac{\tau_2 v}{2\lambda T^2 \beta''} \mathbf{Q}^s : d\mathbf{Q}^s - \frac{\tau_0 v}{\lambda T^2 \beta'} Q dQ, \quad (3.14)$$

and

$$\mathbf{J}^s = \frac{1}{\theta} \mathbf{q} + \frac{1}{\lambda T^2} \mathbf{Q}^s \cdot \mathbf{q} + \frac{1}{\lambda T^2} Q \mathbf{q}. \quad (3.15)$$

Note, incidentally, that (3.15) agrees with the general form derived by Verhas (1983), according to which the entropy flux is the sum of all fluxes each of them multiplied by the suitable intensive quantities appearing

in the entropy expression. Combining (3.8) with the energy balance equation and working in the Fourier space, the dispersion relation between the frequency  $\omega$  and the wavenumber  $k$  for thermal waves is

$$i\omega = \frac{-\chi k^2}{1 + i\omega\tau_R + \frac{l^2 k^2}{1 + i\omega\tau_N}}, \quad (3.16)$$

with  $l^2 = \frac{4}{3}\beta'' + \beta'$  for longitudinal waves and  $l^2 = \beta''$  for transverse waves. For  $\omega\tau_R \gg 1 \gg \omega\tau_N$  and  $\ell = 0$  equation (3.16) leads to the phase velocity  $v_p = (\chi/\tau_R)^{1/2}$ . This is the regime referred to as second sound. At higher frequencies, when  $\omega\tau_N \gg 1$  and  $\omega\tau_R \gg 1$ , the phase velocity obtained from (3.16) for longitudinal waves is

$$v_p = \left( \frac{\chi}{\tau_R} + \frac{l^2}{\tau_R \tau_N} \right)^{1/2}. \quad (3.17)$$

This regime is typical of ballistic propagation of phonons, i.e. a flow in which phonons travel through the whole crystal without suffering any collision.

Equation (3.16) may be interpreted in terms of an effective thermal conductivity given by

$$\lambda(T, \omega, k) = \frac{\lambda(T)}{1 + i\omega\tau_R + \frac{l^2 k^2}{1 + i\omega\tau_N}}. \quad (3.18)$$

To examine the transition to a ballistic regime in a steady regime, we assume a zero frequency, and consider that  $k$  is of the order of  $1/L$ . In this case, (3.18) becomes

$$\lambda(T, \ell/L) = \frac{\lambda(T)}{1 + a(\ell/L)^2}. \quad (3.19)$$

This reduces to  $\lambda(T)$  for small values of  $\ell/L$ , but it behaves as  $L^2$  for high values of  $\ell/L$ , in contrast with the observed data, showing that  $\lambda$  is proportional to  $L$  in the ballistic regime, as indicated by (3.4). Therefore, introduction of second-order non-local terms is not sufficient to describe the transition. We will see that the introduction of an infinite number of fluxes leads to the required behaviour.

#### 4. HIGHER-ORDER FLUXES, CONTINUED-FRACTION EXPANSIONS, AND BALLISTIC TRANSPORT

So far, we have taken as non-equilibrium variables the heat flux  $\mathbf{q}$  and the flux of the heat flux  $\mathbf{Q}$ . Now, we

will incorporate higher-order variables, each one being defined as the flux of the preceding one, and denoted as  $\mathbf{J}^{(1)}$ ,  $\mathbf{J}^{(2)}$ , ...,  $\mathbf{J}^{(n)}$ , where  $\mathbf{J}^{(n)}$ , a tensor of the order  $n$ , is the flux of  $\mathbf{J}^{(n-1)}$ . Indeed, it follows from the kinetic theory that the relaxation times of the higher-order fluxes are not shorter than the collision time. Therefore, using only the first-order fluxes as independent variables 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 behave also like independent variables and must be incorporated in the formalism.

Up to the  $n$ th-order moment, the Gibbs equation takes the form (Jou et al. 2001a)

$$ds = T^{-1}du - \alpha_1 v \mathbf{J}^{(1)} \cdot d\mathbf{J}^{(1)} - \dots - \alpha_1 v \mathbf{J}^{(n)} \otimes d\mathbf{J}^{(n)}, \quad (4.1)$$

and the entropy flux can be written as

$$\mathbf{J}^s = T^{-1}\mathbf{J}^{(1)} + \beta_1 \mathbf{J}^{(2)} \cdot \mathbf{J}^{(1)} + \dots + \beta_{n-1} \mathbf{J}^{(n)} \otimes \mathbf{J}^{(n-1)}. \quad (4.2)$$

The symbol  $\otimes$  denotes the complete contraction of the corresponding tensors. We have limited ourselves to the simplest form of the entropy and the entropy flux and have not taken into account cubic coupled contributions. The corresponding evolution equations compatible with positive entropy production are

$$\tau_1 \dot{\mathbf{J}}^{(1)} = -(\mathbf{J}^{(1)} + \lambda \nabla T) + \frac{\beta_1 \tau_1}{\alpha_1} \nabla \cdot \mathbf{J}^{(2)}, \quad (4.3a)$$

$$\tau_n \dot{\mathbf{J}}^{(n)} = -\mathbf{J}^{(n)} + \frac{\beta_n \tau_n}{\alpha_n} \nabla \cdot \mathbf{J}^{(n+1)} + \frac{\beta_{n-1} \tau_n}{\alpha_n} \nabla \mathbf{J}^{(n-1)} \quad (n = 2, 3, \dots, N). \quad (4.3b)$$

Since  $\mathbf{J}^{(n)}$  is the flux of  $\mathbf{J}^{(n-1)}$ , this implies, by the very definition of a flux requiring that  $\rho \dot{\mathbf{J}}^{(n-1)} = \nabla \cdot \mathbf{J}^{(n)} + \dots$ , that the coefficient of  $\nabla \cdot \mathbf{J}^{(n)}$  in the equation for  $\rho \dot{\mathbf{J}}^{(n-1)}$  must be equal to  $-1$ . As a consequence,  $\rho \beta_n = -\alpha_n$ . Several mathematical aspects of these equations and related ones have been dealt with by Cimmelli and Van (2005).

In the  $(\omega, k)$ -Fourier space the hierarchy (4.3a, b) may be written as a generalized thermal conductivity  $\lambda(\omega, k)$  given by

$$\lambda(\omega, k) = \frac{\lambda_0}{1 + i\omega\tau_1 + \frac{k^2 l_1^2}{1 + i\omega\tau_2 + \frac{k^2 l_2^2}{1 + i\omega\tau_3 + \frac{k^2 l_3^2}{1 + i\omega\tau_4}}}}, \quad (4.4)$$

with  $l_n^2 = \beta_n^2 (\mu_n \mu_{n+1})^{-1} > 0$ . The result (4.4) allows us to define a  $k$ -dependent thermal conductivity  $\lambda(k)$  in

the steady state. An especially compact expression for  $\lambda(k)$  may be obtained when  $l_n$  does not depend on  $n$ , as for instance assuming  $l_n^2 = (1/4)l^2$ , it is found that for  $\omega = 0$ ,

$$\lambda(k) = \frac{2\lambda_0}{(lk)^2} \left[ \sqrt{1 + (lk)^2} - 1 \right]. \quad (4.5)$$

From (4.5) and in the steady state  $\omega = 0$ , one obtains a  $k$ -dependent thermal conductivity  $\lambda(T, k)$ . Since in the situation investigated here the system is characterized by one single length scale, the length  $L$ , it seems natural to identify  $k$  with the inverse of the length of the system,  $1/L$ . This yields the following for  $\lambda(T, \ell/L)$  (Jou et al. 2005):

$$\lambda(T, \ell/L) = \frac{2\lambda(T)L^2}{\ell^2} \left[ \left( 1 + \frac{\ell^2}{L^2} \right)^{1/2} - 1 \right], \quad (4.6)$$

which exhibits the required asymptotic behaviours (3.4). This result is in agreement with the experimental data for nanotubes and in some theoretical unidimensional models of heat transport (Alvarez and Jou 2007). The above considerations confirm that EIT provides a consistent modelling for heat transfer processes taking place not only in short times but also at micro- and nanoscales.

## 5. NON-LINEAR HIERARCHY OF TRANSPORT EQUATIONS AND FLUX LIMITERS

A direct consequence of the finite speed of thermal signals is that, for a given energy density, the heat flux cannot reach arbitrarily high values but will be bounded by a saturation value of the order of the energy density times the maximum speed of propagation. Typical situations arise, for instance, in radiative heat transfer, where the speed of photons is the speed of light  $c$ , and where the maximum heat flux is  $aT^4 c$ , or in plasma physics, where the maximum heat flux is  $k_B T (k_B T/m)^{1/2}$ . Such bounds on heat transfer imply a drastic reduction with respect to the values predicted by Fourier's law at high temperature gradients and play an important role, for instance, in laser-plasma interaction in laser-induced nuclear fusion, or in the collapse of stars.

This saturation effect cannot be described by the classical Fourier law, but can be interpreted by introducing an effective thermal conductivity  $\lambda(T, \nabla T)$ , which depends not only on the temperature but also on the temperature gradient. For instance, a typical dependence giving rise to a limited heat flux is

$$\mathbf{q} = -\frac{\lambda_0(T)}{\sqrt{1+a(\ell\nabla\ln T)^2}}\nabla T, \quad (5.1)$$

with  $\ell$  the mean-free path and  $a$  a numerical factor. This law reduces to Fourier's law for small temperature gradients and yields a saturation value in the limit of very high temperature gradients. The form of  $\lambda(T, \nabla T)$  has been the subject of many works in radiation hydrodynamics, and several expressions have been proposed (Levermore 1996; Jou et al. 2001a; Anile et al. 2003).

The idea of continued-fraction expansions presented in sections 3 and 4 may be generalized as follows, by taking into account that, in the presence of a temperature gradient, the fluxes of order  $m$ ,  $m+1$ , and  $m-1$  may be coupled not only by the wave-vector  $k$  but also by the temperature gradient itself; as a consequence the hierarchy of equations (4.3) may be generalized as follows (Zakari 1997):

$$\tau_m \dot{\mathbf{J}}^{(m)} + \mathbf{J}^{(m)} = \lambda_m \nabla \mathbf{J}^{(m-1)} + \gamma_m \nabla \cdot \mathbf{J}^{(m+1)} + \lambda'_m \nabla T \cdot \mathbf{J}^{(m-1)} + \gamma'_m \nabla T \cdot \mathbf{J}^{(m+1)}. \quad (5.2)$$

In the Fourier–Laplace transform one may write (5.2) as

$$\tau_m \dot{\mathbf{J}}^{(m)} + \mathbf{J}^{(m)} = \mathbf{B}_m \cdot \mathbf{J}^{(m+1)} + \mathbf{C}_m \mathbf{J}^{(m-1)}, \quad (5.3)$$

wherein  $\mathbf{B}_m = \gamma'_m \nabla T + i\gamma_m \mathbf{k}$ ;  $\mathbf{C}_m = \lambda'_m \nabla T + i\lambda_m \mathbf{k}$ . This results in a continued-fraction expansion, analogous to that found in the previous section, of the form

$$\lambda(\omega, k, \nabla T) = \frac{\lambda_0}{1+i\omega\tau_1 + \frac{B_1 C_2}{1+i\omega\tau_2 + \frac{B_2 C_3}{1+i\omega\tau_3 + \dots}}}. \quad (5.4)$$

If all the terms  $B_i$  and  $C_{i+1}$  are equal, and considering vanishing values for the frequency and the wavevector, (5.4) will yield the following asymptotic expression for the constitutive equation for the heat flux:

$$\mathbf{q} = -\frac{\lambda \nabla T}{\frac{1}{2} + \sqrt{\frac{1}{4} + \ell^2 (\nabla \ln T)^2}}. \quad (5.5)$$

This equation predicts a finite value for the heat flux even when the temperature gradient diverges. The corresponding finite value is given by  $q_{\max} \approx \lambda/\ell = \rho u V$ , where  $\rho u$  is the energy density per unit volume and  $V$  the maximum speed for heat pulses.

## 6. CONCLUSIONS

The current frontiers of technology ask for transport equations far more general than the classical ones, incorporating memory, non-local, and non-linear terms. On the other hand, physical consistency demands that

these equations be compatible with the second law of thermodynamics, but this requires understanding how to formulate the second law in the extreme situations considered in technology. Extended Irreversible Thermodynamics provides a limited but fruitful framework to cope with these topics. In this formalism, the fluxes are upgraded to the status of independent variables, and one obtains for them evolution equations satisfying the second law of thermodynamics, formulated in terms of an extended entropy and an extended entropy flux depending themselves on the fluxes. This hierarchy may be expressed as a continued-fraction expansion, which, in the asymptotic case of an infinite number of fluxes leads to a general description ranging from collision-dominated to ballistic dominated regimes. The theoretical predictions agree fairly well with experimental data on heat transport in nanotubes and thin plates.

The consideration of non-local effects requires paying more attention to the boundary conditions and to the meaning of temperature out from equilibrium. Indeed, when non-local effects are important, the influence of the walls is expected to be felt at a considerable distance, and the fact that the mean-free path is long will imply that at each point there is a superposition of populations having different temperatures, thus breaking equipartition. The generalization of the entropy implies also the generalization of the equations of state for temperature, pressure, and chemical potential.

Deeper conceptual questions are found in the case of temperature, which is seen to be a subtler concept than in the classical theory. Indeed, different definitions of temperature in equilibrium may be extrapolated as definitions of effective non-equilibrium temperatures. In equilibrium, all of these temperatures tend to the same value, but out of equilibrium they are different from each other, and a deeper understanding of their relation should be achieved (Casas-Vázquez and Jou 2003).

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## Sojusülekande pöördumatute protsesside laiendatud termodünaamika. Lühike sissejuhatus

David Jou, Jose Casas-Vázquez ja Georgy Lebon

Tehnoloogia progress nõuab üldistatud transpordivõrrandeid, mis arvestavad mälu ja mittelokaalseid ning mitte-lineaarseid efekte. Pöördumatute protsesside laiendatud termodünaamika pakub sellist transpordivõrrandit kujul, mis ühildub teise termodünaamika seadusega ja mis madalal sagedusel ning lühikesel keskmestusvabal rajal taandub klassikaliseks transpordivõrrandiks. Artiklis on esitatud pöördumatute protsesside laiendatud termodünaamika põhi-idee: on vaadeldud alalisi muutusi kui sõltumatuid muutujaid ja neid kirjeldavaid evolutsioonivõrrandeid kui üldis-  
tatud transpordivõrrandeid, mis arvestavad teist termodünaamika seadust. On näidatud, et need võrrandid kirjeldavad laialdase valiku sojusülekanedega seotud nähtusi: termilised lained, foononite hüdrodünaamika, ballistiline transport ja termodünaamiliste jõudude suurtel väärtustel toimuv voogude küllastumine.