

Foundations and applications of a mesoscopic thermodynamic theory of fast phenomena

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A mesoscopic thermodynamic theory of fast phenomena is proposed. In principle, such a description should include an infinite number of moments of the velocity distribution; in a frequency–wave-number space the corresponding transport coefficients would be expressed in terms of a continued fraction expansion. Our objective is to eliminate from the description a maximum number of fast variables. This is achieved by deriving an asymptotic expression of the continued fraction. This procedure allows for a considerable reduction of the number of relevant variables, which are generally identified as the classical variables, such as energy and velocity, complemented by their corresponding dissipative fluxes, namely, the heat and the momentum fluxes. Two applications are investigated: ultrasound propagation in dilute gases and heat transport in dielectric crystals at very low temperature, where the phenomena of second sound is observed. It is shown that for ultrasound propagation, the influence of the fast variables can be described by introducing so-called effective relaxation times. This results in better agreement with experiments than earlier theoretical models and casts a light on the foundation of mesoscopic formalisms, such as extended irreversible thermodynamics. Concerning heat conduction in dielectric crystals, it is seen that the present description includes the three different modes of transport observed experimentally, namely, ballistic phonons, second sound waves, and diffusion. Our approach is a generalization of the models proposed by Cattaneo [Atti Sem. Univ. Modena **3**, 33 (1948)] and by Guyer and Krumhansl [Phys. Rev. **148**, 766 (1966); **148**, 778 (1966)].

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I. INTRODUCTION

The classical theory of irreversible processes [1], based on the local-equilibrium hypothesis, is valid at low frequencies and long wavelengths. In more specific terms, this formalism is applicable when the frequencies of the phenomena are much lower than the collision frequency between particles and when the wavelengths are much longer than the mean free path; it is tantamount to saying that the characteristic lengths describing the variation of the macroscopic parameters (such as, for instance, temperature, velocity, and density) must be much larger than the mean free path. It is of course highly desirable to extend the domain of validity of the classical theory of irreversible processes to high-frequency and short-wavelength phenomena. This has fostered the interest towards the formulation of theories with emphasis on non-locality, both in time and space, and nonlinearity. There is of course a limit that cannot be crossed and is characterized by frequencies larger than the collision frequency and wavelengths much shorter than the mean free path; under these conditions, the particles no longer behave collectively but individually.

There exists an interesting intermediate region when the frequency is of the order of 10^{-1} times the collision frequency, which should be open to a thermodynamic description. Of course, the task is not a trivial one as the validity of classical thermodynamics is guaranteed only when the frequency is much lower than the collision frequency (of the order of 10^{-2} or 10^{-3} times the collision

frequency or lower).

There are, however, two arguments to push the formalism beyond the classical limits. First, the experimental data on light scattering in gases and neutron scattering in liquids have received a decisive interpretation in molecular hydrodynamics [2]. This is a formalism that borrows its general structure from classical hydrodynamics, but with transport coefficients depending on the frequency and the wavelength. *A priori* it may be surprising that macroscopic concepts such as viscosity or thermal conductivity remain significant at the microscopic scale of atoms and molecules, because originally they were defined at different time and length scales. Since a macroscopic theory such as hydrodynamics turns out to be applicable at the molecular scale, it seems logical to ask whether thermodynamics, another macroscopic theory having a similar epistemological structure as hydrodynamics, could not be assessed the same status.

The second argument is inspired by the recent and intensive developments of the theory of chaos [3]. Because of the sensitivity of phase trajectories with respect to initial conditions, the microscopic information will be lost at an exponential rate. This means that after a short delay (say a few times the collision time), one should cross the frontier between reversibility and irreversibility and the system would be characterized by a thermodynamic behavior. Therefore, the attempt to generalize the domain of validity of thermodynamics to a range of frequencies comparable to the collision frequency falls in line with the mainstream of contemporary physics.

However, such an extension of classical thermodynamics faces serious problems. The first concerns the selection of the relevant variables. Thermodynamics, as well as hydrodynamics, uses a small number of well-defined macroscopic variables (density, momentum, internal energy, etc.), which obey well-known conservation laws. At a time scale much shorter than the collision time, the particles behave independently of each other and a detailed description should take into account $6N$ variables for N particles. Now the question is, how far can a thermodynamic description, using an intermediate number of variables much less than $6N$ but more than the five conserved hydrodynamic variables, provide sufficient information at the molecular scale?

To deal with this problem, consider a monatomic gas. It is known that at frequencies comparable to the collision frequency and wavelengths of the order of the mean free path, the gas may be described by the Boltzmann equation. The basic quantity in the Boltzmann equation is the velocity distribution function, from which one may determine any collective quantity. Unfortunately, there exists no analytical solution of the Boltzmann equation in nonequilibrium situations; only approximate solutions are available. The best known is the Chapman-Enskog approximation [4]: the system is assumed to be described by the five hydrodynamic variables and one performs an expansion in terms of the gradients of these quantities. Though very useful for computing the usual transport coefficients, this formalism is not very satisfactory at short wavelengths or high frequencies because it misses essential information that is not contained in the five hydrodynamic variables. Another approach was proposed by Grad [5], who expands the nonequilibrium distribution function in terms of higher-order moments, which behave as independent variables. Grad truncated his expansion after fourteen moments: the first five are related to the five conserved variables and the remaining nine components are identified as the heat flux and the viscous pressure tensor components (in reality, the viscous pressure tensor of an ideal gas contains only five, rather than six, independent variables and therefore Grad's original expansion was limited to thirteen moments, the fourteenth moment corresponding to the bulk viscous pressure, which is identically zero in ideal gases). The main difficulty raised by Grad's expansion is that it lacks a smallness parameter and therefore it is not clear at all whether this truncation after 13 or 14 moments is legitimate.

The aim of the present work is to examine under which conditions a thermodynamic description based on an intermediate number of variables is possible. As mentioned earlier, the problem is of fundamental importance in the development of modern thermodynamics; as an illustration of the procedure, wave propagation in dilute gases and heat transport in rigid solids at very low temperature are investigated.

II. HIERARCHY OF HIGHER-ORDER FLUXES

We propose a way to extend the domain of application of classical nonequilibrium thermodynamics [1]. There-

fore, we consider a very simple situation, namely, heat conduction in rigid bodies at rest. The Fourier law for heat transport states that the heat flux \mathbf{q} is related to the temperature gradient ∇T by

$$\mathbf{q} = -\lambda \nabla T, \quad (1)$$

with λ the thermal conductivity, but a more general description is given by the Cattaneo equation [6]

$$\tau_1 \frac{\partial \mathbf{q}}{\partial t} + \mathbf{q} = -\lambda \nabla T, \quad (2)$$

where τ_1 is a relaxation time whose magnitude is of the order of the collision time. After eliminating \mathbf{q} between Cattaneo's relation and the energy balance equation

$$\rho \frac{\partial u}{\partial t} = -\nabla \cdot \mathbf{q}, \quad (3)$$

wherein u stands for internal energy per unit mass and ρ for the mass density, assuming that $du = c_v dT$ with c_v the specific heat at constant volume, one obtains for the temperature T the equation

$$\tau_1 \frac{\partial^2 T}{\partial t^2} + \frac{\partial T}{\partial t} = \chi \nabla^2 T, \quad (4a)$$

where the quantity $\chi = \lambda / \rho c_v$ stands for the thermal diffusivity. In contrast to the usual parabolic equation

$$\frac{\partial T}{\partial t} = \chi \nabla^2 T, \quad (4b)$$

derived by setting $\tau_1 = 0$, Eq. (4a) is hyperbolic. It possesses the following remarkable features: (a) it is reversible at frequencies much higher than τ_1^{-1} and is irreversible at frequencies lower than τ_1^{-1} ; (b) it predicts that thermal pulses propagate with a finite speed

$$U = \left[\frac{\chi}{\tau_1} \right]^{1/2}. \quad (5)$$

Many physical applications of Eq. (4a) have been studied, e.g., [7–14]. It is also important to realize that Eq. (2) or (4a) is not compatible with the local equilibrium hypothesis, because the corresponding local equilibrium entropy of isolated systems would decrease during the approach to equilibrium [15]. In contrast, expression (4a) is compatible with a generalized entropy given by

$$s(u, \mathbf{q}) = s_{\text{eq}}(u) - \frac{\tau_1}{2\rho\lambda T^2} \mathbf{q} \cdot \mathbf{q}, \quad (6)$$

wherein $s_{\text{eq}}(u)$ denotes the local equilibrium entropy. Both (2) and (6) reduce to the classical results when τ_1 tends to zero. Furthermore, Eqs. (2) and (6) have been justified microscopically [7,8] from Grad's procedure for monatomic gases.

To summarize, it can be stated that at frequencies comparable to τ_1^{-1} , a description based on the classical Fourier law is no longer valid and the heat flux \mathbf{q} becomes a new degree of freedom with its own evolution governed by Eq. (2). As a direct consequence, the space of variables must be enlarged: instead of considering only u as the single relevant variable, one must include \mathbf{q}

among the space of variables and this results in a mesoscopic thermodynamic description.

Although the above scheme is useful to extend the range of applicability of local equilibrium theory and to fix its limits of validity, it suffers from some drawbacks. (a) In general, a term having the form of the divergence of an extra flux $Q^{(2)}$ should appear in Cattaneo's equation (2):

$$\tau_1 \frac{\partial \mathbf{q}}{\partial t} + \mathbf{q} = -\lambda \nabla T - \nabla \cdot Q^{(2)}. \quad (7)$$

Indeed, a macroscopic balance equation should contain a term describing the exchange across the boundary surface besides a production term: in that respect, Eq. (2) is certainly not the most general way to extend Fourier's law because of the absence of a divergence term [16]. (b) From a microscopic point of view, the heat flux is related to the third moment of the distribution function; however, for completeness, one should include an infinite number of moments because all the higher-order moments (or higher-order fluxes, according to the macroscopic point of view) may also become independent variables besides the heat flux vector \mathbf{q} [7,8,17]. Of course, for some systems, for instance, superconductors, the relaxation time of \mathbf{q} is much longer than the relaxation time of the higher-order fluxes and a description based only on u and \mathbf{q} may be sufficient. Nevertheless, in some systems, such as monatomic gases, the relaxation times of the higher-order fluxes are of the order of the collision time and therefore it is not satisfactory to describe the system in terms of u and \mathbf{q} only. It can thus be concluded that, generally speaking, there exists no exact mesoscopic description that is intermediate between the macroscopic theory (five variables) and the microscopic theory (6N variables).

Fortunately, there are many situations in which most of the variables are irrelevant and an adequate model based on a limited number of variables may capture the essential physical features. For instance, the van der Waals equation for nonideal gases, the Weiss equation for ferromagnets, or the Debye-Hückel model of plasmas and electrolytes are not exact theories, but they grasp the essentials of the underlying physics. Similarly, in real gases or in liquids, it is sufficient to use only the distribution functions for one and two particles while a complete description should include the three-, four-, and N -particle distribution functions. Even if an exact mesoscopic thermodynamic should be conceivable, it would be intractable from a practical point of view and therefore it is justified to look towards a simplified but physically sound mesoscopic approach.

The main difference between Eqs. (1) and (2) is that the first one predicts that thermal pulses propagate with an infinite speed at high frequencies and does not allow for a second sound. These problems are circumvented by using Eq. (2), which was derived on thermodynamic bases by introducing the heat flux \mathbf{q} as extra variable in the formalism [7,8]. However, it is also known that Cattaneo's relation (2) is not sufficient to grasp some experimental data, for instance, the value of the phase velocity derived from Eq. (2) is not in agreement with measured values at

high frequencies [8]. Similarly, the van der Waals, Weiss, and Debye-Hückel equations are very useful for interpreting several phenomena, but at the same time they are unable to reproduce some results such as the ratio between the critical temperature and the inversion temperature, the compressibility ratio, or the critical exponents.

Our aim is to fill the gap between a microscopic description, which requires an infinite number of variables (here N is to be considered very high, practically infinite), and a macroscopic approach using a limited number of variables. This will be achieved in two steps: in the first one, we shall consider an infinite number of fluxes and check how far this attitude is tractable and applicable; in the second step, we shall perform an asymptotic expansion, allowing for a drastic reduction of the number of variables.

Besides the flux \mathbf{q} , we take as variables the flux of the flux, namely, the second-order tensor $Q^{(2)}$ and the successive higher-order fluxes $Q^{(n)}$. Here $Q^{(n)}$ is a tensor of order n , which is identified as the flux of $Q^{(n-1)}$, according to the equation

$$\frac{\partial Q^{(n)}}{\partial t} = -\nabla \cdot Q^{(n+1)} + \sigma^{(n)}, \quad (n=1, 2, \dots), \quad (8)$$

where $\sigma^{(n)}$ denotes the production term of $Q^{(n)}$ and $Q^{(1)}$ is identified as the heat flux \mathbf{q} . In Sec. III, particular examples of the hierarchy expressed by (8) are considered.

To remain on general bases but having in mind a simple physical phenomenon such as heat conduction, it is assumed [18] that for a rigid heat conductor, there exists a nonequilibrium entropy that is a function of the internal energy u and a set of fluxes of tensorial order n ranging from 1 to infinity, i.e., $s = s(u, Q^{(1)}, \dots, Q^{(n)}, \dots)$. In differential form, one has

$$ds = T^{-1} du - \sum_{n=1}^{\infty} \rho^{-1} \alpha_n Q^{(n)} \otimes dQ^{(n)}, \quad (9)$$

wherein the coefficients α_n may be temperature dependent and will be identified later on, the symbol \otimes denotes the n -fold product between tensors of order n , and the factor ρ^{-1} is introduced for convenience. In addition, a generalized entropy flux is defined as

$$\mathbf{J}^s = T^{-1} \mathbf{q} + \sum_{n=1}^{\infty} \beta_n Q^{(n+1)} \otimes Q^{(n)}, \quad (10)$$

wherein β_n may be temperature dependent and \mathbf{J}^s is the most general vector involving the product of two fluxes, which has been justified by Grad's 13-moment formalism in the case of $n=1$ [5-7].

The entropy production σ^s , a positive definite quantity, can be derived from the equation of evolution for s , namely,

$$\rho \frac{\partial s}{\partial t} + \nabla \cdot \mathbf{J}^s = \sigma^s. \quad (11)$$

In view of Eqs. (3), (9), and (10), the expression for σ^s turns out to be

$$\begin{aligned} \sigma^s = \mathbf{q} \cdot & \left[-\alpha_1 \frac{\partial \mathbf{q}}{\partial t} + \beta_1 \nabla \cdot \mathcal{Q}^{(2)} + \nabla T^{-1} \right] \\ & + \sum_{n=2}^{\infty} \mathcal{Q}^{(n)} \otimes \left[-\alpha_n \frac{\partial \mathcal{Q}^{(n)}}{\partial t} + \beta_n \nabla \cdot \mathcal{Q}^{(n+1)} \right. \\ & \left. + \beta_{n-1} \nabla \mathcal{Q}^{(n-1)} \right], \end{aligned} \quad (12)$$

wherein one has omitted third- and higher-order terms involving the products of the fluxes, their space and time derivatives, and the gradient of temperature. Equation (12) is a bilinear form in which each flux is multiplied by a conjugate generalized thermodynamic force containing the time derivative of the corresponding flux. The simplest form of the evolution equations satisfying the positiveness of the entropy production is obtained by assuming that each thermodynamic force is proportional to the corresponding flux. This results in

$$-\alpha_1 \frac{\partial \mathbf{q}}{\partial t} + \beta_1 \nabla \cdot \mathcal{Q}^{(2)} + \nabla T^{-1} = \mu_1 \mathbf{q}, \quad (13a)$$

$$-\alpha_n \frac{\partial \mathcal{Q}^{(n)}}{\partial t} + \beta_n \nabla \cdot \mathcal{Q}^{(n+1)} + \beta_{n-1} \nabla \mathcal{Q}^{(n-1)} = \mu_n \mathcal{Q}^{(n)}, \quad n=2,3,\dots \quad (13b)$$

Without loss of generality, we can identify the unknown coefficients μ_1 and μ_n , which generally depend on T , as

$$\mu_1 = \frac{\alpha_1}{\tau_1} = (\lambda T^2)^{-1}, \quad \mu_n = \frac{\alpha_n}{\tau_n},$$

wherein τ_n has the dimension of time and will be called a relaxation time. Since $\mathcal{Q}^{(n+1)}$ is the flux of $\mathcal{Q}^{(n)}$ for $n > 1$, it follows also that $\alpha_n = -\beta_n$ for $n > 1$. After substitution of Eqs. (13a) and (13b) in (12), one obtains the expression for the entropy production

$$\sigma^s = \frac{1}{\lambda T^2} \mathbf{q} \cdot \mathbf{q} + \sum_{n=2}^{\infty} \frac{\alpha_n}{\tau_n} \mathcal{Q}^{(n)} \otimes \mathcal{Q}^{(n)}, \quad (14)$$

which is clearly a quadratic expression in the fluxes. In virtue of the second law of thermodynamics, expression (14) of σ^s is positive definite and as a consequence the quantities λ and α_n/τ_n must be positive. On the other hand, it has been shown [7,8] that thermodynamic stability requires that α_n is positive, so that τ_n is also positive. We remark that since λ is proportional to τ_1 , the entropy production, for constant values of the fluxes, will tend to zero when the relaxation times $\tau_1, \tau_2, \dots, \tau_n$ are all diverging; such a result is not surprising because in that case there are no collisions among the particles and one has a purely mechanical motion of free independent particles, which is reversible.

Before considering the behavior of this hierarchy of higher-order fluxes, let us indicate how to obtain in a particular case an explicit expression for the coefficients α_n . Since the fluxes $\mathcal{Q}^{(n)}$ are absolutely general, one may, for example, take for $\mathcal{Q}^{(n)}$ the traceless symmetric parts $\mathcal{Q}_{\langle i_1 \dots i_n \rangle}$ of the tensors $\mathcal{Q}^{(n)}$. For a tensor of order 2, one has

$$\mathcal{Q}_{\langle i_1 i_2 \rangle} = \frac{1}{2} [\mathcal{Q}_{(i_1 i_2)} + \mathcal{Q}_{(i_2 i_1)}] - \frac{1}{3} \mathcal{Q}_{i_k i_k} \delta_{i_1 i_2},$$

wherein the summation rule on repeated indices k is used, angular brackets denote traceless symmetric tensors, and parentheses denote the usual tensor components.

Let us particularize the hierarchy of evolution equations (8) in the case of an n -order flux $\mathcal{Q}^n = \mathcal{Q}_{\langle i_1 \dots i_n \rangle}$, when the source term obeys Callaway's approximation [19], namely,

$$\sigma^n = -\frac{1}{\tau_n} \mathcal{Q}_{\langle i_1 \dots i_n \rangle}.$$

Equation (8) can then be written as

$$\frac{\partial}{\partial t} \mathcal{Q}_{\langle i_1 \dots i_n \rangle} + \frac{\partial}{\partial x_k} \mathcal{Q}_{\langle i_1 \dots i_n \rangle k} = -\frac{1}{\tau_n} \mathcal{Q}_{\langle i_1 \dots i_n \rangle}. \quad (15)$$

Moreover, it was shown by Dreyer and Struchtrup [19] that the $(n+1)$ th-order flux $\mathcal{Q}_{\langle i_1 \dots i_n \rangle k}$ is related to fluxes of lower order by the recurrence formula

$$\mathcal{Q}_{\langle i_1 \dots i_n \rangle k} = c_0^2 \frac{n}{2n+1} \mathcal{Q}_{\langle \langle i_1 \dots i_{n-1} \rangle \rangle \delta_{i_n \rangle k} + \mathcal{Q}_{\langle i_1 \dots i_n \rangle k}, \quad (16)$$

wherein c_0 is the speed of wave propagation through the medium; for a gas of particles, it is the sound velocity, for a phonon gas, it is Debye's speed. $\delta_{i_n \rangle k}$ means that the corresponding component is zero except for $i_n = k$.

For further purposes, let us consider one-dimensional heat propagation in the x_1 direction. After substitution of formula (16) in (15), it is checked that [19]

$$\begin{aligned} \frac{\partial \mathcal{Q}_{\langle i_1 \dots i_n \rangle}}{\partial t} + \frac{\partial \mathcal{Q}_{\langle i_1 \dots i_{n+1} \rangle}}{\partial x_1} + c_0^2 \frac{n^2}{4n^2-1} \frac{\partial \mathcal{Q}_{\langle i_1 \dots i_{n-1} \rangle}}{\partial x_1} \\ = -\frac{1}{\tau_n} \mathcal{Q}_{\langle i_1 \dots i_n \rangle} \quad (i_1, \dots, i_{n+1} = 1). \end{aligned} \quad (17)$$

Comparing Eqs. (17) and (13), wherein use is made of the result $\beta_{n-1} = -\alpha_{n-1}$, it is found that the ratio α_{n-1}/α_n is given by

$$\frac{\alpha_{n-1}}{\alpha_n} = \frac{n^2}{4n^2-1} c_0^2. \quad (18)$$

This expression will be used to determine the numerical values of some physical quantities in Sec. III.

In parallel with the above derivation, a hierarchy of equations for the moments of the distribution function has been established by Velasco and García-Colin [17] and Hess [20] in the case of ideal monatomic gases. Using the projection operator technique, Mori [21] proposed another hierarchy of equations to generalize the Langevin equations. Such results are important, as they assess that the hierarchy derived in this work rests on statistical bases.

In the present analysis, it is assumed that the set of evolution equations is linear. Of course, a more general study should contain nonlinear terms, but in this case, the corresponding entropy production would not allow for general conclusions about the sign of the coefficients of the higher-order terms. Therefore, we have refrained from including nonlinear terms; moreover, they are not essential for solving the problems treated in the following sections.

III. ASYMPTOTIC BEHAVIOR AND COMPARISON WITH EXPERIMENTAL RESULTS

In this section we establish the asymptotic expression of the hierarchy of evolution equations involving higher and higher-order thermodynamic fluxes and apply it in two particular cases: ultrasound propagation in monatomic gases and phonons propagation in dielectric crystals at low temperature. It is also shown that the formalism is considerably simplified by introducing so-called effective relaxation times.

A. High-frequency wave speed in monatomic gases

According to classical hydrodynamics, monatomic gases are univocally described by the velocity and temperature (or internal energy) fields. Working in the frame of extended irreversible thermodynamics, these quantities are completed by extra variables taking the form of a heat flux vector \mathbf{q} and a traceless symmetric viscous pressure tensor \mathbf{P}^ν , which are assumed to satisfy the evolution equations

$$\tau_1^{(\text{th})} \frac{\partial \mathbf{q}}{\partial t} + \mathbf{q} = -\lambda \nabla T \quad (19)$$

and

$$\tau_1^{(\nu)} \frac{\partial \mathbf{P}^\nu}{\partial t} + \mathbf{P}^\nu = -2\eta \mathbf{V} . \quad (20)$$

The quantity \mathbf{V} introduced in Eq. (20) represents the traceless symmetric velocity gradient tensor; in Cartesian coordinates, its components are

$$V_{ij} = \frac{1}{2} \left[\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} \right] - \frac{1}{3} \frac{\partial v_k}{\partial x_k} \delta_{ij} ,$$

η stands for the dynamic viscosity, and $\tau^{(\text{th})}$ and $\tau^{(\nu)}$ are the relaxation times of the heat flux and the viscous pressure tensor, respectively, related to the speed of propagation of thermal and viscous waves, respectively, through

$$U_{\text{th}}^2 = \frac{\chi}{\tau_1^{(\text{th})}} , \quad U_\nu^2 = \frac{\nu}{\tau_1^{(\nu)}} , \quad (21)$$

where ν is the kinematic viscosity. Equations (19) and (20) are usually referred to as Maxwell-Cattaneo equations. However, as mentioned earlier, they do not present the general structure of evolution equations as divergence terms expressing the exchange with the external environment are missing. For this reason, Eqs. (19) and (20) will be replaced by the following more general equations derived in the simplest version of extended thermodynamics [7] and confirmed by Grad's kinetic approach [5]:

$$\tau_1^{(\text{th})} \frac{\partial \mathbf{q}}{\partial t} + \mathbf{q} = -\lambda \nabla T + \beta \lambda T^2 \nabla \cdot \mathbf{P}^\nu , \quad (22)$$

$$\tau_1^{(\nu)} \frac{\partial \mathbf{P}^\nu}{\partial t} + \mathbf{P}^\nu = -2\eta \mathbf{V} + 2\beta \eta T (\nabla \mathbf{q})^s , \quad (23)$$

where β is a coefficient that depends only on the equilib-

rium variables of the system, i.e., temperature T and pressure p , $(\nabla, \mathbf{q})^s$ stands for the symmetric traceless part of tensor $\nabla \mathbf{q}$. According to Grad's 13 moment approximation [5], the relaxation times $\tau_1^{(\text{th})}$ and $\tau_1^{(\nu)}$ as well as the coefficient β are expressed by

$$\tau_{1\text{Grad}}^{(\text{th})} = \frac{2m\lambda}{5k_B^2 T} , \quad \tau_{1\text{Grad}}^{(\nu)} = \frac{\eta}{p} , \quad \beta_{\text{Grad}} = -\frac{2}{5pT} , \quad (24)$$

where k_B is the Boltzmann constant and m the mass of the molecules.

Equations (19) and (20), from one side, and (22) and (23), from the other side, have been used to study ultrasound propagation in monatomic gases. From the results (24), it is found that within the high-frequency limit, ultrasounds propagate with a velocity v_p given by

$$\lim_{\omega \rightarrow \infty} \frac{v_p}{c_0} = 1.64 , \quad (25)$$

where $c_0 = (5k_B T/3m)^{1/2}$ is the adiabatic sound velocity in monatomic gases. However, experimental observations predict that [8,22,23]

$$\lim_{\omega \rightarrow \infty} \left[\frac{v_p}{c_0} \right]_{\text{expt}} = 2.1 , \quad (26)$$

indicating clearly that the above theoretical result (25) is approximative.

Carrassi and Morro [22a] analyzed ultrasound propagation in monatomic gases by using (22) and (23) with $\tau_1^{(\text{th})} = \tau_1^{(\nu)} = \tau_1$ and they adjusted τ_1 in order to fit (26). This leads to $\tau_1^{(\text{th})} = \tau_1^{(\nu)} = (3/5\pi) \tau_{1\text{Grad}}^{(\nu)}$ or, equivalently,

$$\tau_1^{(\text{th})} = \frac{2}{5\pi} \tau_{1\text{Grad}}^{(\text{th})} , \quad \tau_1^{(\nu)} = \frac{3}{5\pi} \tau_{1\text{Grad}}^{(\nu)} , \quad \beta = 0 . \quad (27)$$

Anile and Pluchino [22b] allowed both quantities $\tau_1^{(\text{th})}$ and $\tau_1^{(\nu)}$ to vary independently and found good agreement with experimental data by using for the relaxation times and β the values

$$\tau_1^{(\text{th})} = 0.40 \tau_{1\text{Grad}}^{(\text{th})} ,$$

$$\tau_1^{(\nu)} = 0.29 \tau_{1\text{Grad}}^{(\nu)} , \quad (28)$$

$$\beta = 0.015 \beta_{\text{Grad}} .$$

It follows from these results that the experimental values of the relaxation times are smaller than those derived from Grad's 13-moment formalism.

Our objective is to show that better agreement with experiment is achieved by introducing higher-order fluxes into the theoretical description. Since the values of the relaxation times are obtained respectively from the speed of propagation of thermal waves and shear waves, we will consider separately both kinds of waves in the next developments. The problem for the heat flux will be treated exhaustively whereas the analysis for the viscous pressure, which is completely parallel to the previous one, will be sketched only briefly.

In the Fourier-Laplace space (ω, k) with ω the frequency and k the complex wave number, the hierarchy of Eqs. (13) takes the form of a generalized transport law with a

(ω, k) -dependent heat conductivity. Denoting by $\bar{Q}(\omega, k)$ and $\bar{T}(\omega, k)$ the Fourier-Laplace transforms of $Q(x, t)$ and $T(x, t)$, respectively, one has

$$\bar{Q}(\omega, k) = -ik\lambda(\omega, k)\bar{T}(\omega, k).$$

At the n th order, the thermal conductivity is written as

$$\lambda_n(\omega, k) = \frac{\lambda_0(0, 0)}{1 + i\omega\tau_1 + \frac{l_1^2 k^2}{1 + i\omega\tau_2 + \frac{l_2^2 k^2}{1 + i\omega\tau_3 + \dots}}}, \quad (29)$$

where $\lambda_0(0, 0)$ is the zeroth-order classical Fourier approximation and

$$l_n^2 = \tau_n \tau_{n+1} \frac{\alpha_n}{\alpha_{n+1}}. \quad (30)$$

The asymptotic expression of Eq. (29) obtained by assuming $\tau_1 = \tau_2 = \dots = \tau_n$ and $l_1 = l_2 = \dots = l_n$ is given by

$$\lambda_\infty(\omega, k) = \frac{\lambda_0}{2l_\infty^2 k^2} \left\{ -(1 + i\omega\tau_\infty) + [(1 + i\omega\tau_\infty)^2 + 4l_\infty^2 k^2]^{1/2} \right\}, \quad (31)$$

where τ_∞ and l_∞ are the limits of τ_n and l_n for $n \rightarrow \infty$. To establish (31), we have used the general results established in Ref. [24].

The thermal conductivity corresponding to Cattaneo's equation (2) is obtained from Eq. (29) by simply keeping the first relaxation time τ_1 , i.e., by setting $\tau_2 \dots = \tau_n = l_1 = \dots = l_n = 0$; the corresponding speed of propagation of heat waves is given by relation (5). From this expression, it is clear that the relaxation time τ_1 for \mathbf{q} is directly calculated from the measurements of the thermal diffusivity χ and the speed $U^{(\text{th})}$ of the thermal signal.

A more refined result is provided by combining the general expression (31) with the energy balance (3), written as

$$\rho c_\nu i\omega = -k^2 \lambda_\infty(\omega, k).$$

In the high-frequency limit ($\omega\tau \gg 1$), the speed of heat pulses defined as $U_{\text{th}} = \lim_{\omega \rightarrow \infty} (\omega/Rek)$ takes the form

$$U_{\text{th}}^2 = \frac{\chi}{\tau_\infty^{(\text{th})} - l_\infty^{(\text{th})2} \chi^{-1}}, \quad (32)$$

wherein χ stands for $\lambda_0/\rho c_\nu$. A comparison of expression (32) with Eq. (5) allows us to introduce an effective relaxation time $\tau_{\text{eff}}^{(\text{th})}$ given by

$$U_{\text{th}}^2 = \frac{\chi}{\tau_{\text{eff}}^{(\text{th})}}, \quad (33)$$

wherein $\tau_{\text{eff}}^{(\text{th})}$ is defined as

$$\tau_{\text{eff}}^{(\text{th})} = \tau_\infty^{(\text{th})} - l_\infty^{(\text{th})2} \chi^{-1}. \quad (34)$$

A similar development can be achieved for the viscous pressure tensor \mathbf{P}^ν and would result in the following ex-

pressions for the speed of viscous signals:

$$U_\nu^2 = \frac{\nu}{\tau_\infty^{(\nu)} - l_\infty^{(\nu)2} \nu^{-1}}. \quad (35)$$

Defining as before an effective relaxation time through

$$U_\nu^2 = \frac{\nu}{\tau_{\text{eff}}^{(\nu)}}, \quad (36)$$

one obtains

$$\tau_{\text{eff}}^{(\nu)} = \tau_\infty^{(\nu)} - l_\infty^{(\nu)2} \nu^{-1}. \quad (37)$$

To determine $\tau_{\text{eff}}^{(\text{th})}$ and $\tau_{\text{eff}}^{(\nu)}$, one needs the expression (30) of l_n^2 for $n = \infty$. Using the particular values (18) of α_n/α_{n+1} derived in Sec. II, it is directly checked that within the limit of high- n values

$$l_\infty^2 = \frac{1}{4} c_0^2 \tau_\infty^2. \quad (38)$$

It is known from the kinetic theory that $c_0 = \sqrt{3k_B T/m}$, from which it follows that

$$l_\infty^{(\text{th})2} = \frac{3k_B T}{4m} \tau_\infty^{(\text{th})2}, \quad l_\infty^{(\nu)2} = \frac{3k_B T}{4m} \tau_\infty^{(\nu)2}.$$

By introducing these expressions in Eqs. (34) and (37) and taking into account that for monatomic ideal gases, one has $\chi = (5k_B T/3m)\tau_\infty^{(\text{th})}$ and $\nu = (k_B T/m)\tau_\infty^{(\nu)}$, it is found that

$$\tau_{\text{eff}}^{(\text{th})} = \frac{11}{20} \tau_{1\text{Grad}}^{(\text{th})}, \quad \tau_{\text{eff}}^{(\nu)} = \frac{1}{4} \tau_{1\text{Grad}}^{(\nu)}. \quad (39)$$

An effective coefficient β cannot be introduced in a similar way, but one possibility is to use the expression for β derived from the fluctuation theory [2,23], namely,

$$\beta = -\tau^{(\text{th})} \tau^{(\nu)} (k_B \lambda \eta T^3)^{-1} \langle q_1(c) C_2 P_{12}^\nu(c) \rangle, \quad (40)$$

with $\langle \rangle$ standing for the equilibrium average and C_2 the x_2 component of the molecular peculiar velocity. Expression (40) suggests that the correction yielding the effective β would be the product of the corrections for $\tau^{(\text{th})}$ and $\tau^{(\nu)}$, thus leading to

$$\beta_{\text{eff}} = \frac{11}{80} \beta_{\text{Grad}}. \quad (41)$$

It is important to realize that the approach proposed here is an alternative to Grad's 13-moment approximation: in the latter, one cuts the continued fraction expansion (29) at the second level, by assuming $\tau_2 \neq 0$ but $l_n = 0$ ($n \geq 2$) and $\tau_n = 0$ ($n \geq 3$). Here, in contrast, we consider the whole set of relaxation times and all the correlation lengths, but we assume that they all are equal. Of course, this is not exactly true, but since the essential features are described by the lowest-order fluxes, it is reasonable to assume that by taking all the higher-order τ_n and l_n to be identical, one modifies only slightly the correct value of the propagation speed.

In summary, we have shown that by starting from a general formalism including an infinite number of fluxes, it is possible to construct a simple model involving only a reduced number of variables provided the relaxation times are defined in a suitable way. The description proposed here bears some analogies with the theory of criti-

cal points. Near critical points, the fluctuations are very important and become practically independent quantities. However, the fluctuations have the same importance whatever the wavelength and therefore one should, in principle, include the whole range of fluctuations corresponding to all the wavelengths. Since this would be impracticable, one uses a renormalization procedure that allows for a suitable redefinition of the parameters in terms of an effective Hamiltonian; this provides a way to obtain the values of the critical exponents, with no need to take into account the whole set of variables. In the present problem, the numerous extra variables are the higher-order fluxes, but they are incorporated into the description by introducing a kind of renormalization of the relaxation times.

B. Second sound and ballistic heat transport in dielectric crystals

Another interesting problem is provided by the response of dielectric crystals to a heat pulse. The experiments describing the behaviour of thermal pulses across crystals at very low temperature, of the order of 10 K, exhibit the presence of a wave propagating with a speed ranging from c_0 (the Debye speed) to $c_0/\sqrt{3}$, depending on the temperature of the sample. As is well known, transport of heat in dielectric crystals is well described by means of the phonon model.

One distinguishes generally three mechanisms of transport of phonons. At very low temperature, phonons travel freely through the crystal without being scattered: they received the name of ballistic phonons. When temperature is increased, collisions occur and one observes a wavelike energy transport similar to sound waves in gases. During such a process, energy as well as momentum is conserved; this process is referred to as a second sound and is characterized by a collision relaxation time τ_N , wherein index N means "normal" collisions. When the temperature is still raised, one promotes collisions that do not conserve momentum. The wave nature property of energy transport is quickly damped and heat will propagate by diffusion; the corresponding time scale associated with diffusion will be denoted τ_R , where R stands for "resistive" processes. In passing, it should be recalled that τ_R is the single relaxation time appearing in Cattaneo's description.

The classical Fourier equation is only able to describe the diffusive regime; the Cattaneo equation predicts the presence of a second sound propagating at constant speed $c_0/\sqrt{3}$. However, Cattaneo's relation is silent about the ballistic behavior and is unable to determine the dependence of the second sound velocity with respect to temperature.

The simplest way to describe these effects is to introduce the extra variable $Q^{(2)}$, the flux of the heat flux besides the usual variables u and q . By doing so, one finds for the speed of ballistic phonons the value $\sqrt{3/5}c_0$ instead of c_0 [19]. Here we will show how the renormalization procedure developed in Sec. II is able to yield satisfactory values for both the second sound and the ballistic signal.

For the sake of simplicity, we limit our analysis to one-dimensional heat propagation. The hierarchy of evolution equations for the fluxes $Q_{\langle i_1 \dots i_n \rangle}$ was established earlier and is given by the set (17). Moreover, since phonons interact via R and N processes, it is natural to introduce both relaxation times τ_R and τ_N into the description. Referring to Callaway's kinetic theory of phonons, we shall make the identification [19]

$$\tau_n^{-1} = \tau_R^{-1} \quad \text{for } n = 1, \quad (42)$$

$$\tau_n^{-1} = \tau_R^{-1} + \tau_N^{-1} = \tau_\infty^{-1} \quad \text{for } n > 1. \quad (43)$$

Since $n = 1$ corresponds to Cattaneo's formalism, it is natural to take τ_1 equal to τ_R . The hypothesis (43) expressing that all the relaxation times are identical for $n > 1$ reflects the property that within a good approximation, the relaxation times of the higher-order moments are of the same order of magnitude [17,19].

It is easily checked that the hierarchy (17) leads to the following dispersion relation, when use is made of (42) and (43):

$$-\frac{1}{3\omega} ic_0^2 k^2 + i\omega + \frac{1}{\tau_R} + \frac{\frac{4}{15}c_0^2 k^2}{i\omega + \frac{1}{\tau_\infty} + \frac{\frac{9}{35}c_0^2 k^2}{i\omega + \frac{1}{\tau_\infty} + \dots}} = 0 \quad (44)$$

and after that solutions taking the form of plane waves

$$Q_{ij} \sim \exp(i\omega t + kx_1)$$

are introduced in the set (17). To compare with previous works, let us formulate expression (44) in the particular cases corresponding to one single flux ($Q^{(1)} = q$) and two fluxes (q and $Q^{(2)}$), respectively. In the first case the dispersion relation is simply

$$-\frac{1}{3} ic_0^2 k^2 \frac{1}{\omega} + i\omega + \frac{1}{\tau_R} = 0, \quad (45)$$

which is the result that should have been directly obtained from Cattaneo's equation. With two fluxes in mind, expression (44) reduces to

$$-\frac{1}{3\omega} ic_0^2 k^2 + i\omega + \frac{1}{\tau_R} + \frac{\frac{4}{15}c_0^2 k^2 \tau_\infty}{1 + i\omega \tau_\infty} = 0, \quad (46)$$

which can be given the form

$$-\frac{1}{3\omega} ic_0^2 k^2 + i\omega + \frac{1}{\tau_R} + \frac{3}{5} \tau_\infty c_0^2 k^2 + i\omega \frac{\tau_\infty}{\tau_R} - \tau_\infty \omega^2 = 0. \quad (47)$$

This equation contains in particular the Guyer-Krumhansl dispersion relation [16]

$$-\frac{1}{3\omega} ik^2 c_0^2 + i\omega + \frac{1}{\tau_R} + \frac{3}{5} \tau_\infty c_0^2 k^2 = 0.$$

As in Sec. II A, we now establish the asymptotic expression of Eq. (44), which is given by [24]

$$\left[-\frac{1}{3\omega} ic_0^2 k^2 + i\omega + \frac{1}{\tau_R} \right] \left[1 + i\omega\tau_\infty + \frac{18}{35} [-(1 + i\omega\tau_\infty) \pm \sqrt{(1 + i\omega\tau_\infty)^2 + c_0^2 k^2 \tau_\infty^2}] \right] + \frac{4}{15} c_0^2 k^2 \tau_\infty = 0. \quad (48)$$

It is of particular interest to examine the two following limiting cases, corresponding, respectively, to an undamped ($\text{Im}k=0$) second-sound signal ($\tau_R^{-1} \rightarrow 0$, $\tau_N^{-1} \rightarrow \infty$) and to the ballistic behavior ($\tau_R^{-1} \rightarrow 0$, $\tau_N^{-1} \rightarrow 0$). The first case describes situations where the frequency of resistive processes tends to zero while the second case corresponds to zero-frequency collisions.

1. Undamped second sound: $\tau_R^{-1} \rightarrow 0$, $\tau_N^{-1} \rightarrow \infty$, $\text{Im}k = 0$

In this limit, the frequency of resistive collisions is vanishing while the frequency of momentum preserving processes is very high. For undamped waves ($\text{Im}k=0$), the dispersion relation (48) reduces to

$$\frac{1}{3\omega} ic_0^2 k^2 = i\omega \quad (49)$$

and the second sound velocity v_s is given by

$$v_s = \frac{\omega}{\text{Re}k} = \frac{c_0}{\sqrt{3}}. \quad (50)$$

In fact, a second sound with velocity $c_0/\sqrt{3}$ has never, as far as we know, been observed in experiments in dielectric solids. In the temperature range where a second sound occurs, i.e., $\tau_R^{-1} \rightarrow 0$, which means the absence of diffusion, the requirement $\tau_N^{-1} \rightarrow \infty$ is never met. Instead of the requirements $\tau_R \rightarrow \infty$ and $\tau_N \rightarrow 0$, one should use the less restrictive inequalities $\omega\tau_R \gg 1$ and $\omega\tau_N \ll 1$, or $1/\tau_R < \omega < 1/\tau_N$, which is Guyer-Krumhansl window condition. When this condition is introduced in the dispersion relation (48), one finds a second sound velocity larger than $c_0/\sqrt{3}$ and given by $v_s = (c_0/\sqrt{3})[1 + \frac{2}{5}(\tau_N/\tau_R)]$. By decreasing the temperature of the sample, the frequency of normal collisions decreases and the phonons no longer behave collectively but individually: we are then in the ballistic regime.

2. Ballistic regime: $\tau_R^{-1} \rightarrow 0$, $\tau_N^{-1} \rightarrow 0$

Ballistic phonons are observed when the frequencies of both resistive and normal processes are vanishing. The dispersion relation (48) is now written as

$$\frac{3}{7} c_0^2 k^2 - \frac{17}{35} \omega^2 \pm \frac{18}{35} \left[-\frac{1}{3\omega} ik^2 c_0^2 + i\omega \right] \sqrt{k^2 c_0^2 - \omega^2} = 0. \quad (51)$$

Setting $\alpha = k^2 c_0^2 / \omega^2$, Eq. (51) can be expressed in the more attractive form

$$\alpha^3 - \frac{3}{4} \alpha^2 + \frac{5}{6} \alpha - \frac{35}{36} = 0. \quad (52)$$

The two complex solutions of relation (52) are characterized by a very large damping coefficient and therefore the corresponding waves cannot be observed experimentally and only the real solution of (52) is relevant. The corresponding phase speed is found to be

$$v_b = \frac{\omega}{\text{Re}k} = \frac{1}{\sqrt{\alpha}} c_0 = 1.026 c_0,$$

while the damping is zero, as it should be. The above result is in good agreement with the experimental Debye velocity c_0 for the propagation of ballistic pulses. The error of 2.6% may arise from the fact that the continued fraction expression (44) is approximated by its asymptotic expansion and because all the relaxation times δ_n ($n > 1$) are supposed to be identical.

The above results indicate that extended thermodynamics is able to cope with a wide variety of phenomena running from irreversible and collective processes to reversible and individual motions. A comparison with results obtained by Dreyer and Struchtrup [19], who used u , q , and $Q^{(2)}$ as variables, reveals another interesting result. It was found [19] that heat propagates with a velocity running from $c_0/\sqrt{3}$ ($\approx 0.58c_0$), which is the lowest limit for an undamped second sound, to $\sqrt{3/5}c_0$ ($\approx 0.77c_0$) in the ballistic regime; this latter value being different from c_0 indicates a shortcoming of the theory. Now, by increasing the numbers of variables up to 30 in a one-dimensional theory, Dreyer and Struchtrup [19] were able to recover the correct ballistic velocity, namely, $v_b = c_0$. By working with more and more fluxes, one covers situations further and further away from local equilibrium, but the theory becomes quickly inapplicable, in practice.

It is worth stressing that the formalism presented in the present paper is of a different nature as it is based on an asymptotic development of the continued fraction expansion and does not appeal to a high number of variables. Indeed, it is sufficient to introduce besides the relaxation time τ_R for q another extra relaxation time τ_∞ and to perform an asymptotic development to obtain satisfactory agreement with experiments.

IV. CONCLUSION

The present paper was essentially concerned with a mesoscopic formulation of nonequilibrium fast processes such as ultrasound propagation in gases and phonon hydrodynamics. It is true that an exact description should require an infinite number of variables; furthermore, in most problems, the relaxation times associated with the extra nonconserved variables are of the order of magnitude of the mean collision time. On the other hand, a theory involving an excessively high number of variables is practically intractable. The question is then how to find the best description using the smallest number of variables and subsidiary, how to describe high-frequency

phenomena that fall outside the scope of the classical theory of irreversible processes. To achieve this goal, a procedure has been proposed that consists of eliminating most of the redundant fast variables by introducing so-called effective or renormalized relaxation times for the few remaining fast variables.

Another motivation of the present paper was to provide a microscopic basis for extended irreversible thermodynamics (EIT). In the past, it had generally been admitted that the foundations of EIT are deeply rooted in Grad's 13-moment method [7–10]. Here we have shown that EIT covers a much wider range than that spanned by Grad's formalism, as it extends from the description of highly irreversible phenomena, such as pure heat diffusion to reversible processes such as propagation of ballistic phonons. This is achieved by using a limited number of slow variables; the effects of the remaining fast variables are taken into account by introducing a redefinition of some relevant quantities, such as the relaxation times.

Two examples have served as illustrations: wave propa-

gation in dilute gases and heat waves in dielectric crystals at very low temperature. Only small amplitude waves are considered so that the analysis is purely linear. It follows that the entropy production can be proved to be semipositive definite because it is a quadratic expression in the fluxes. Nonlinear developments would raise interesting and fundamental problems because the nonlinear terms may give positive as well as negative contributions to the entropy production and destroy its semipositive property [25]. Nonlinear developments are planned to be investigated in a future work.

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