Irreversible-thermodynamic approach to nonequilibrium heat fluctuations

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Starting from a generalized nonequilibrium entropy, and from an extension of the Einstein formula for the probability of the fluctuations, we obtain the second moments of nonequilibrium fluctuations of the specific energy and the heat flux in rigid heat conductors. This approach leads to nonequilibrium corrections to the usual fluctuation-dissipation expressions for the heat fluctuations. The corresponding numerical corrections are found for phonon heat transport in dielectric solids and for electronic heat transport in metals. The macroscopic results share common features with those obtained for heat transport in harmonic chains by an information-theoretical approach.

I. INTRODUCTION

In the last years there has been a great interest in the description of the thermodynamic fluctuations near nonequilibrium steady states.[1-8] Two different aspects of this problem have to be considered: the dynamical and the statistical ones.[3] From the dynamical point of view, one has to solve the full nonlinear equations with the corresponding boundary conditions to find the steady-state value of the macroscopic variables, and afterwards one must find the equations of motion for small fluctuations by linearizing the previous nonlinear equations. In nonequilibrium problems, the statistical part is introduced through a Langevin force added to the linearized equations for the fluctuations. It is generally assumed that this Langevin force is described by the same correlation function as in equilibrium with local values of the temperature and of the transport coefficients. In so doing, it is argued that the corresponding random forces have such short correlation times that they have a chance to probe only a small region of the system, so that they are adequately characterized by a local-equilibrium average.[2-4] Starting from this prescription for the Langevin forces, one can obtain from the dynamical stochastic equations the corresponding nonequilibrium corrections to the classical formulas for the thermodynamic fluctuations.

The purpose of this paper is to provide a phenomenological analysis of the purely statistical part of the problem of nonequilibrium fluctuations, where the nonvanishing relaxation time of the Langevin forces is taken into account. In spite of its usual smallness, this relaxation time influences the whole thermodynamic framework: it modifies the usual definition of the nonequilibrium entropy, enters into the constitutive equations, and gives nonequilibrium corrections in the correlation function of the Langevin forces. For the sake of simplicity, we specify our analysis to the case of thermal fluctuations in rigid heat conductors, where the Langevin forces are usually identified as the divergence of a fluctuating heat flux. In this way, we obtain some nonequilibrium corrections to the usual Landau-Lifshitz formulas for the second moments of the fluctuating heat flux.[9] Our analysis is based on a generalized nonequilibrium entropy, which depends on the classical thermodynamic variables, as well on the dissipative fluxes, in the framework of extended irreversible thermodynamics.[10,11]

In Sec. II, we present a brief summary of extended irreversible thermodynamics and of its relation to equilibrium fluctuations. In Sec. III, we extend our previous calculations and we obtain the second moments of the nonequilibrium fluctuations. In Sec. IV, we apply these general results to heat fluctuations in dielectric materials, by considering the phonon heat conduction in one, two, and three dimensions, and in metals, where we deal with electronic heat conduction. In Sec. V, we compare our results with an exact model for the nonequilibrium fluctuations in a linear harmonic chain based on an information-theoretic approach.

II. EXTENDED IRREVERSIBLE THERMODYNAMICS AND EQUILIBRIUM FLUCTUATIONS OF DISSIPATIVE FLUXES

In the last decade, some authors[10-12] have tried to build a theory of irreversible thermodynamics which is not based on the classical local equilibrium hypothesis. Indeed, in the usual development of irreversible thermodynamics[13] one is led to the usual Fourier's law for heat conduction in solids, which gives a parabolic equation for the evolution of the temperature and therefore predicts the propagation of the thermal disturbances at infinite velocity, and which is not able to describe, for instance, the phenomenon of second sound observed in some solids at low temperatures.[14] The second-sound phenomenon brings an incompatibility with the definite positive character of the classical instantaneous entropy production, since it implies that, at some stages, the heat must flow from cold to hot regions in order to sustain the thermal wave. Our purpose has been to construct an extended irreversible thermodynamics based on a generalized entropy, compatible with the above-mentioned experimental facts. It is assumed that the dependence of the generalized entropy on the dissipative fluxes as well as on the classical thermodynamic variables may be expressed through a generalized Gibbs equation. This theory differs from the classical irreversible thermodynamics since in the latter theory the entropy depends only on the classical variables and the Gibbs equation retains locally its usual equilibrium form.[13] It also differs from the entropy-free theories of thermodynamics, since these avoid the use of an entropy in nonequilibrium.[15] Finally, though the so-called rational thermodynamics[16] also uses a nonequilibrium entropy, it has many important differences with the formalism presented here. In rational thermodynamics, one assumes the existence of a nonequilibrium entropy and a nonequilibrium temperature as primitive variables, no matter how far from equilibrium. These entropy and temperature are assumed to have the property of satisfying the Clausius-Duhem inequality for all imaginable processes. Though it is not sure that this nonequilibrium temperature is given by any physical thermometer, it is taken as a fundamental variable of the theory. As a consequence of the restriction of the Clausius-Duhem inequality, one obtains the constitutive equations as well as a generalized Gibbs equation which, in contrast to the present development, plays no essential role in the theory. In the present

formalism, the entropy and the temperature are the local equilibrium ones, which have a well-defined meaning, both theoretically and experimentally, plus some corrections depending on the dissipative fluxes, which can in turn be identified in terms of physical parameters. In principle, therefore, our theory is not valid arbitrarily far from equilibrium, in contrast with rational thermodynamics, which is claimed to be valid even in this situation.

The aim of the extended irreversible thermodynamics is to provide a phenomenological mesoscopic description of thermodynamic systems, taking as independent variables not only the classical ones but also the dissipative fluxes. In terms of a widespread scheme,[17] we take as "slow" variables of our theory not only the usual conserved variables, but also the nonconserved fluxes, because we are interested in phenomena at relatively high frequency, whose characteristic time scale is comparable to the relaxation time of the dissipative fluxes. Such a set of "slow" variables has been used successfully, for instance, in the analysis of neutron scattering in fluids,[18] in the framework of Mori's formalism. While the evolution of the classical variables is related to general conservation laws and may therefore be described by the usual balance laws of mass, momentum, energy, and so on, one has to derive the evolution equations for the dissipative fluxes. A microscopic deduction of these equations is in general extremely involved, so that we have tried to obtain for them some simplified expressions starting from macroscopic hypotheses, in a general thermodynamic framework.

A. The generalized Gibbs equation and constitutive equation

We start our thermodynamic analysis with the assumption that there exists a generalized entropy s which, for the particular case of rigid heat conductors, is a function of the specific internal energy per unit mass u and of the heat flux $\vec{q}$. As with classical entropy, it is supposed that this entropy is locally a maximum in equilibrium, and that the corresponding entropy production must be locally and instantaneously definite positive for all imaginable processes. Furthermore, it is supposed to be differentiable enough, so that we can write[10,11]

$$ds = (\partial s/\partial u)_{\vec{q}}\,du + (\partial s/\partial \vec{q})_u \cdot d\vec{q} \;. \qquad (2.1)$$

In isotropic systems, the derivatives of the entropy may be written up to second order in the heat flux as

$$(\partial s/\partial u)_{\vec{q}}=T^{-1}(u)+O(\vec{q}^{2}) ,$$

$$(\partial s/\partial\vec{q})_{u}=T^{-1}v\alpha(u)\vec{q} ,$$

(2.2)

with T the local equilibrium absolute temperature, v the specific volume per unit mass, and α a parameter which can be easily identified in the framework of extended irreversible thermodynamics,[11] as we show below. Indeed, combining (2.1) with the balance equation of the internal energy

$$\rho\dot{u}=-\nabla\cdot\vec{q} ,$$

(2.3)

and assuming that the entropy flux $\vec{J}_{s}$ is given, as usually, by $\vec{J}_{s}=T^{-1}\vec{q}$, one can obtain the entropy production σ from the standard form of a balance equation

$$\rho\dot{s}+\nabla\cdot\vec{J}_{s}=\sigma .$$

(2.4)

One gets in this way

$$\sigma=\vec{q}\cdot(\nabla T^{-1}+T^{-1}\alpha\dot{\vec{q}}) .$$

(2.5)

The simplest expression for $\vec{q}$ compatible with our hypothesis that the instantaneous entropy production must be locally definite positive is to assume that

$$\nabla T^{-1}+T^{-1}\alpha\dot{\vec{q}}=\mu\vec{q} .$$

(2.6)

The coefficients α and μ may be identified by comparing (2.6) with the Maxwell-Cattaneo equation[10,11,14]

$$\dot{\vec{q}}=-\tau^{-1}(\vec{q}+\lambda\nabla T) ,$$

(2.7)

where λ is the thermal conductivity and τ the heat relaxation time. As is well known, when introduced into (2.3), this equation may be used to describe second sound in solids[14] and leads to a finite velocity for the propagation of thermal disturbances.[10,11] From (2.6) and (2.7) one gets $\mu=(\lambda T^{2})^{-1}$ and $\alpha=-\tau(\lambda T)^{-1}$, so that the derivatives (2.2) of the entropy may be finally identified as

$$(\partial s/\partial u)_{\vec{q}}=T^{-1}(u)$$
$$-\tfrac{1}{2}[\partial(\tau v\lambda^{-1}T^{-2})/\partial u]\vec{q}^{2} ,$$

(2.8)

$$(\partial s/\partial\vec{q})_{u}=-\tau v\lambda^{-1}T^{-2}\vec{q} .$$

(2.9)

The terms of order $\vec{q}^{2}$ in (2.8) may be obtained

from the equality of the mixed second-order derivatives of the entropy (2.1). The quantity defined in (2.8) may be considered in some aspects as the inverse of a generalized nonequilibrium absolute temperature Θ, which is essentially the local equilibrium absolute temperature plus small but in some points significative corrections.[19]

In view of (2.8) and (2.9), we can write (2.1) in the form of a generalized Gibbs equation[11,19]

$$ds=\Theta^{-1}du-(\tau v/\lambda T^{2})\vec{q}\cdot d\vec{q} .$$

(2.10)

It can be noted in (2.10) that the presence of a nonvanishing relaxation time τ in the constitutive equation for the evolution of the heat flux (2.7) influences the definition of a local entropy compatible with the second sound.

B. Equilibrium fluctuations

The analysis of nonequilibrium dissipative phenomena is intimately related to the analysis of the fluctuations of dissipative fluxes, since both the dissipative coefficients and the fluctuations have as a common origin the collisions amongst the particles of the system. This close relation between the two phenomena has found in equilibrium a mathematical expression in the fluctuation-dissipation theorem.[20] It is therefore of interest to study the consequences of (2.10) in the description of the thermodynamic fluctuations. For an isolated system in equilibrium, the probability of the fluctuations is given by the Boltzmann-Einstein relation $W\sim\exp(\Delta S/k)$, where k is the Boltzmann constant. If the system is not isolated, but it is at constant temperature, constant pressure, and so on, the expression for the probability distribution function of the fluctuations is more general. As in the classical theory, we assume that the probability of the fluctuations at constant temperature and constant temperature gradient—or mean heat flux—is given by (see Ref. 21, Chap. 15)

$$W\sim\exp((1/k)\{S(\hat{u},\hat{\vec{q}})-\Theta_{0}^{-1}\hat{u}+(\tau v/\lambda T^{2})\vec{q}_{0}\cdot\hat{\vec{q}}$$
$$-S[\Theta_{0}^{-1},-(\tau v/\lambda T^{2})\vec{q}_{0}]\}) ,$$

(2.11)

where $\hat{u}$ and $\hat{\vec{q}}$ are the instantaneous values of u and $\vec{q}$ while Θ_{0}^{-1} and $(\tau v/\lambda T^{2})\vec{q}_{0}=-(\tau v/\lambda T^{2})\times(\nabla T)_{0}$ are the fixed values of the corresponding parameters, $\Theta^{-1}=\partial s/\partial u$ and $(\tau v/\lambda T^{2})\vec{q}$ $=-\partial s/\partial\vec{q}$. On the other hand, $S[\Theta_{0}^{-1},$

$-(\tau v/\lambda T^2)\vec{q}_0]$ is the corresponding Legendre transform of s which generalizes in our case the concept of the Massieu-Planck functions, and is given by

$$S[\Theta_0^{-1}, -(\tau v/\lambda T^2)\vec{q}_0]=S-\Theta_0^{-1}u$$
$$+(\tau v/\lambda T^2)\vec{q}_0\cdot\vec{q} \ .$$

(2.12)

As it is usual, we may expand $s(\hat{u},\hat{\vec{q}})$ around the mean value $s(u_0,\vec{q}_0)$ in powers of the deviations $\delta u = \hat{u}-u_0$, $\delta\vec{q}=\hat{\vec{q}}-\vec{q}_0$,

$$s(\hat{u},\hat{\vec{q}})=s(u_0,\vec{q}_0)+\Theta_0^{-1}\delta u-(\tau v/\lambda T^2)\vec{q}_0\cdot\delta\vec{q}$$
$$+\tfrac{1}{2}\delta^2 s + \cdots \ ,$$

(2.13)

where $\delta^2 s$ stands for the second differential of the entropy. Inserting this development into (2.11) and recalling (2.12), the first-order linear terms in δu and δq cancel and we find approximately, if we neglect higher-order terms,

$$W\sim\exp[(1/2k)\delta^2 s] \ .$$

(2.14)

It is well known (Ref. 21, Chap. 15) that this approximate Gaussian distribution function, the so-called Einstein relation, predicts the second moments correctly, but it does not predict third and higher moments accurately. However, since we are only interested in the second moments, we restrict ourselves to the use of the simple Einstein formula (2.14).

The second differential of the entropy, as obtained from (2.10), is given by

$$\delta^2 s = -[(cT^2)^{-1}+\tfrac{1}{2}\vec{q}_0^2(\partial^2 a/\partial u^2)](\delta u)^2$$
$$-a\delta\vec{q}\cdot\delta\vec{q}-2\vec{q}_0(\partial a/\partial u)\delta u\cdot\delta\vec{q} \ ,$$

(2.15)

where c is the specific heat per unit mass and $a=\tau v/\lambda T^2$. In equilibrium, taking into account that the mean heat flux $\vec{q}_0$ vanishes, and introducing the corresponding simplified form of (2.15) into (2.14), we get for the probability distribution function

$$W(\delta u,\delta q)\sim\exp\{-(1/2k)[(cT^2)^{-1}(\delta u)^2$$
$$+(\tau v/\lambda T^2)\delta\vec{q}\cdot\delta\vec{q}]\} \ .$$

(2.16)

This expression gives for the second moments of the fluctuations

$$\langle \delta u\,\delta u \rangle = kcT^2 \ ,$$

(2.17)

$$\langle \delta q_i\,\delta q_j \rangle = k\lambda T^2\tau^{-1}v^{-1}\delta_{ij} \ ,$$

(2.18)

$$\langle \delta u\,\delta q_i \rangle = 0 \ .$$

(2.19)

Expression (2.17) is the classical formula for the energy fluctuations, while (2.18) relates the equilibrium fluctuations of the heat flux with the corresponding dissipative coefficient λ, in accordance to the fluctuation-dissipation theorem.[20] Taking into account the evolution equation (2.7) and assuming, as Onsager,[22] that the evolution of the fluctuations is governed on the average by the same equations that describe the response of the system to external perturbations one obtains for the heat fluctuations $\delta\vec{q}$,

$$(\delta\dot{\vec{q}})=-\tau^{-1}\delta\vec{q} \ .$$

(2.20)

Then, for the spectral function of the fluctuations of the heat flux we get

$$\langle \delta q_i\,\delta q_j \rangle_\omega=2k\lambda T^2 v^{-1}(1+\omega^2\tau^2)^{-1}\delta_{ij} \ .$$

(2.21)

For low frequencies such that $(\omega\tau)^2 << 1$, this expression reduces to the usual Landau-Lifshitz formula for the fluctuations of the heat flux.[9]

Note that in this formalism we have dealt only with the purely statistical part of the problem, and that we have deduced simultaneously the expressions for $\langle \delta u\,\delta u \rangle$, $\langle \delta q_i\,\delta q_j \rangle$, and $\langle \delta u\,\delta q_i \rangle$, while in the usual treatments[23] of this problem the expression for $\langle \delta q_i\,\delta q_j \rangle$ is obtained from $\langle \delta u\,\delta u \rangle$ and from the dynamical equation for the evolution of the internal energy (2.3). This approach has been used in the analysis of heat fluctuations in rigid conductors,[24] electrical current fluctuations,[25] and hydrodynamical fluctuations.[26] It unifies into a single expression the formulas for energy and heat fluctuations, and it places some restrictions on the second derivative of the nonequilibrium entropy through the requirement that, in equilibrium, it must give a correct description of the heat fluctuations and of the fluctuations of the other dissipative fluxes. To our knowledge, this restriction has not been analyzed in other formulations of irreversible thermodynamics based on a priori nonequilibrium entropies as, for instance, rational thermodynamics.[16]

III. STATISTICAL ASPECTS OF NONEQUILIBRIUM FLUCTUATIONS

In view of the success of (2.14) in describing the equilibrium fluctuations, some authors have pro-

posed to extend its validity to nonequilibrium fluc-
tuations, at least not very far from equilibrium, in
the context of the local-equilibrium theory.[27] In
fact, the most common procedure in the analysis
of nonequilibrium fluctuations has been to employ
the local-equilibrium form for the nonequilibrium
static correlation functions as initial conditions for
the dynamical correlation functions. It has been
shown, however, that some new results may arise
in nonequilibrium, owing to the local variation of
the thermodynamic parameters or to nonlinear ef-
fects.[1,3,5] However, even these more refined
theories keep the local-equilibrium form of the
Langevin noise. As has been said, the reason for
this starting hypothesis is the vanishing correlation
time of the noise. If, however, this correlation
time is small but nonvanishing, the fast fluctua-
tions will have some time to "know" that the sys-
tem is not in equilibrium and, consequently, some
nonequilibrium corrections to the usual Langevin
noise can be expected. Our purpose in this section
is to evaluate these nonequilibrium corrections in
the framework of the present theory.

From another point of view, some authors[5–7]
have proposed to start from the knowledge of the
second moments of the fluctuations in nonequili-
brium, which can be found, again, from some sta-

tistical hypotheses about the Langevin noise and
from the dynamical equations, in order to define
nonequilibrium thermodynamic potentials. In this
way, in the relation (2.14) one knows the probabili-
ty W of the fluctuations and one looks for the cor-
responding generalized potential. Our situation is
rather the opposite one: We have a generalized
thermodynamic potential (2.10) which can be used
in nonequilibrium, since it has the dissipative
fluxes as independent variables, and we want to ex-
plore the consequences of (2.14) in the probability
of nonequilibrium fluctuations.

Here, we assume that the purely statistical as-
pect of the problem of nonequilibrium fluctuations
may be described by the corresponding nonequili-
brium extension of the Einstein relation (2.14).
One has to keep in mind, however, that when this
statistical prescription is introduced into the
dynamical equations, one can obtain significant
corrections of nonlocal or nonlinear origin for both
the static and the dynamical correlation functions.

For a nonequilibrium steady state, and according
to (2.7), the mean value of the heat flux $\vec{q}_0$ is given
by the classical Fourier law $\vec{q}_0 = -\lambda(\nabla T)_0$. In this
case, when the corresponding expression of (2.15) is
introduced into (2.14), one obtains

$$W(\delta u, \delta \vec{q}) \sim \exp(-(1/2k)\{ [(cT^2)^{-1} + (\lambda^2/2)(\nabla T)_0^2(\delta^2 a/\partial u^2)](\delta u)^2$$

$$+ a(\delta \vec{q})\cdot(\delta \vec{q}) - 2\lambda(\nabla T)_0(\partial a/\partial u)\delta u \cdot \delta \vec{q} \}) . \tag{3.1}$$

Taking into account that for a multivariant Gaussian probability distribution of the form

$$W \sim \exp[-(1/2)E_{jk}\delta x_j \delta x_k] , \tag{3.2}$$

the second moments are given by $\langle \delta x_i \delta x_j \rangle = E_{ij}^{-1}$, the second moments of the nonequilibrium fluctuations
are

$$\langle \delta u \delta u \rangle = kcT^2[1 + A(\nabla T)_0^2]^{-1} , \tag{3.3}$$

$$\langle \delta q_i \delta q_j \rangle = (k\lambda T^2/\tau v)[\delta_{ij} + (\lambda^2 cT^2/2)(\partial^2 a/\partial u^2)(\partial T/\partial x_i)_0(\partial T/\partial x_j)_0][1 + A(\nabla T)_0^2]^{-1} , \tag{3.4}$$

$$\langle \delta u \delta q_i \rangle = k\lambda^2 cT^4\tau^{-1}v^{-1}(\partial a/\partial u)(\partial T/\partial x_i)_0[1 + A(\nabla T)_0^2]^{-1} , \tag{3.5}$$

with

$$A = \lambda^2 cT^2[(1/2)(\partial^2 a/\partial u^2) - (1/a)(\partial a/\partial u)^2] .$$

These expressions show the nonequilibrium correc-
tions to the equilibrium formulas (2.17)—(2.19). In
particular, it can be noted that the generalized
Landau-Lifshitz formula (2.18) exhibits some none-
quilibrium modifications, owing to the nonvanish-
ing relaxation time, and that the energy-heat flux
correlation, which is null in equilibrium, does not

vanish in nonequilibrium states. One can also ob-
serve in (3.3)—(3.5) that if the coefficient A is neg-
ative, the fluctuations may become infinite when
$(\nabla T)_0^2 = -A^{-1}$. In Sec. V, in the comparison of
our results with an exact model, we will again find
this feature. In this limit, the validity of our for-
malism becomes highly questionable, but the possi-
bility of some kind of non-equilibrium instability
remains somewhat analogous to the Rayleigh
Bénard instability in fluids[4] or to other kinds of

nonequilibrium transitions.

Amongst the formulations of the problem of nonequilibrium fluctuations, Keizer's theory has received a great deal of attention in the last years. This author starts from a canonical form of the transport equations in terms of "elementary processes" and assumes a generalized fluctuation-dissipation expression for the Langevin forces. In the problem of heat conduction, his results[5] are however the classical ones, in contrast with our more general expressions. This is due to its starting point, which assumes that the heat conduction is described by Fourier's law. As may be seen here, a more general assumption for the constitutive equation for heat conduction leads to different results for the nonequilibrium noise, in spite of the new terms of the constitutive equation (2.7) only accounting for transient effects and, therefore, not influencing the stationary distribution of the temperature.

IV. NONEQUILIBRIUM FLUCTUATIONS OF SOME PHYSICAL SYSTEMS

In order to gain a further insight and understanding into the problem we are dealing with, we apply in this section our formal expressions (3.3)—(3.5) to some specific physical systems and for small temperature gradients. In particular, we consider here two models for heat conduction: phonon transport in dielectric solids at low temperatures and electronic heat transport in metals at room temperature.

In order to achieve further simplification, we restrict our attention to heat fluctuations $\delta \vec{q}$ parallel to the temperature gradient. There is no difficulty in obtaining the corresponding expressions for the transverse heat fluctuations. For small temperature gradients, we may develop the term $[1+A\,(\nabla T)_0^2]^{-1}$ up to the first order in $(\nabla T)_0^2$, and the expressions (3.3)—(3.5) lead in this case to

$$\langle \delta u\, \delta u \rangle = kcT^2\{1 - \lambda^2 cT^2[(1/2)(\partial^2 a/\partial u^2) - (1/a)(\partial a/\partial u)^2](\nabla T)_0^2\} \,, \tag{4.1}$$

$$\langle \delta q\, \delta q \rangle = k\lambda T^2\tau^{-1}v^{-1}[1 + \lambda^2 cT^2(1/a)(\partial a/\partial u)^2(\nabla T)_0^2] \,, \tag{4.2}$$

$$\langle \delta u\, \delta q \rangle = k\lambda^2 cT^4\tau^{-1}v^{-1}(\partial a/\partial u)(\nabla T)_0\{1 - \lambda^2 cT^2[(1/2)(\partial^2 a/\partial u^2) - (1/a)(\partial a/\partial u)^2](\nabla T)_0^2\} \,. \tag{4.3}$$

In what follows, and for the sake of illustration, we use simplified microscopic expressions for the evaluation of the coefficient $a = \tau v/\lambda T^2$ appearing in (4.1)—(4.3) in the physical systems previously mentioned.

A. Heat fluctuations in dielectric solids

In the usual elementary kinetic method and in the relaxation-time approximation, the thermal conductivity is given by[28]

$$\lambda = (1/d)\rho c c_0^2\tau \,, \tag{4.4}$$

where c is the specific heat per unit mass, c_0 an average velocity, and τ a mean collision time. In the case of phonon transport, and in the Debye approximation, the phonon specific heat is well known and c_0 is related to the linear phonon dispersion relation $\omega = c_0 k$, with ω the angular frequency and k the wave vector of the phonons. Starting from a linearized Boltzmann equation for the pure phonon field in three dimensions, Guyer

and Krumhansl have obtained for the heat flux at low temperatures a constitutive equation of the form[14(a)]

$$\partial \vec{q}/\partial t + \tfrac{1}{3}c_0^2\rho c\nabla T$$

$$+ [\tau_z^{-1} - \tfrac{1}{5}\tau_N c_0^2(\nabla^2 + 2\nabla\nabla\cdot)]\vec{q} = 0 \,, \tag{4.5}$$

where τ_z is the relaxation time of the resistive collisions (umklapp scattering, impurity scattering) and τ_N is the relaxation time of the normal (momentum-conserving) collisions. When the normal collisions predominate ($\tau_N \rightarrow 0$), this equation reduces to the Maxwell-Cattaneo equation (2.7) and shows that in these circumstances, the relaxation time of the heat flux appearing in (2.7) is indeed equal to the mean collision time appearing in the expression (4.4) for the thermal conductivity. The physical essence and the complexities of calculating the thermal conductivity are included precisely in the relaxation time τ, while c_0 and c are given by the usual equilibrium theory. In our case, however, we are interested in $a = \tau v/\lambda T^2$, where the relaxation time and the conductivity enter through the combination τ/λ, and therefore we may avoid

the complexities of calculating τ.

At low temperatures, the phonon specific heat in the Debye model is proportional to T^d, where d is the dimensionality of the lattice.[28] Therefore, the terms $(\partial a/\partial u)$ and $(\partial^2 a/\partial u^2)$ appearing in (4.1)—(4.3) are found to be

$$\langle \delta u \delta u \rangle = kcT^2[1+(1/2d)(d+2)(l/T)^2(\nabla T)_0^2] , \tag{4.7}$$

$$\langle \delta q \delta q \rangle = k\lambda T^2\tau^{-1}v^{-1}[1+(1/d)(d+2)^2(l/T)^2(\nabla T)_0^2] , \tag{4.8}$$

$$\langle \delta u \delta q \rangle = -(d+2)k\lambda T(\nabla T)_0[1+(1/2d)(d+2)(l/T)^2(\nabla T)_0^2] . \tag{4.9}$$

In particular, the formula (4.8) gives the nonequilibrium correction to the usual Landau-Lifshitz expression (2.18) at low temperatures, where they may have more significance.

Note also that the expressions (3.3)—(3.5) predict infinite fluctuations when $(\nabla T)_0^2 = -A^{-1}$. In the case of phonon heat conduction, this critical temperature gradient is

$$(\nabla T)_0^2 = 2d(d+2)^{-1}(T/l)^2 . \tag{4.10}$$

In terms of the heat flux $q_0 = -\lambda(\nabla T)_0$, of the internal energy u per unit mass, and of the velocity c_0, this critical value is reached when

$$q_0^2 = (2/d)(d+1)^2(d+2)^{-1}u^2c_0^2\rho^2 . \tag{4.11}$$

B. Heat fluctuations in metals

Another rigid heat-conducting system of practical significance and with a well-studied microscopic model is provided by solid metals. In a metal at room temperature, a big fraction of the heat flux is carried by electrons, and the lattice phonon transport becomes negligible. In this case, the thermal conductivity is given by (4.4) with $c_0 = v_F$, the Fermi velocity of the electrons in the metal, and c is the electronic specific heat per unit mass, given by

$$c = (\pi^2/2)(k^2T/m\epsilon_F) , \tag{4.12}$$

with ϵ_F the Fermi energy and m the electron mass. As in the case of phonon transport at low temperatures, it can be shown that the relaxation time of Eq. (2.7) is equal to the mean collision time of expression (4.4). Indeed, starting from a relaxational Boltzmann equation, one gets for the complex thermal conductivity[29]

$$\lambda(\omega) = (\pi^2/3)(n/m)k^2T\tau(1+i\omega\tau)^{-1} , \tag{4.13}$$

$$\partial a/\partial u = -(d+2)a/cT , \tag{4.6}$$

$$\partial^2 a/\partial u^2 = (d+2)(2d+3)a/c^2T^2 .$$

When this results is introduced into (4.1)—(4.3) and using the mean free path l defined as $l = c_0\tau$, the following results are obtained:

where ω is the angular frequency of the perturbation and n the electronic density. This expression is precisely the Fourier image of (2.7) and shows the equality of the relaxation time of (2.7) and the mean collision time of (4.4). Therefore, we may obtain from this microscopic expression the following values for the derivatives of the parameter a:

$$\partial a/\partial u = -3a/cT , \quad \partial^2 a/\partial u^2 = 15a/c^2T^2 . \tag{4.14}$$

Consequently, the second moments of the fluctuations (4.1)—(4.3) are given by

$$\langle \delta u \delta u \rangle = kcT^2[1+\tfrac{1}{2}(l'/T)^2(\nabla T)_0^2] , \tag{4.15}$$

$$\langle \delta q \delta q \rangle = k\lambda T^2\tau^{-1}v^{-1}[1+3(l'/T)^2(\nabla T)_0^2] , \tag{4.16}$$

$$\langle \delta u \delta q \rangle = -3k\lambda T(\nabla T)_0[1+\tfrac{1}{2}(l'/T)^2(\nabla T)_0^2] , \tag{4.17}$$

where l' is the mean free path defined by $l' = v_F\tau$. In this case, (3.3)—(3.5) lead to infinite fluctuations when the heat flux reaches the critical value

$$q_0^2 = \tfrac{8}{9}v_F^2u^2\rho^2 . \tag{4.18}$$

For a metal, one can obtain in a similar way the nonequilibrium corrections to the classical Nyquist formula for the fluctuations of the electric current, when the sample is exposed to an electric field.[30] In this case, the results obtained by this method are qualitatively similar to some microscopic estimates obtained through nonequilibrium diagrammatic expansions, if one neglects, in a first approximation, the heating effect, which produces some divergences in the diagrammatic method.[3(c)]

V. COMPARISON WITH EXACT RESULTS

Up to now, we have dealt with a hypothesis which is well justified in equilibrium but which

lacks a firm basis in nonequilibrium. In spite of our formalism taking account of the nonvanishing mean heat flux, and, in consequence, describing nonequilibrium features, it would be desirable to have some more solid grounds on which to build a theory of nonequilibrium fluctuations. In fact, a rigorous statistical theory of nonequilibrium thermodynamic fluctuations should be based on the definition and counting of nonequilibrium microstates compatible to each macrostate. In this section, we compare our results with those of an information-theoretical description of heat conduction in linear harmonic chains, and we note the fundamental accordance of the respective results. This essential agreement with the statistical results reinforces the credibility of our starting hypothesis concerning the nonequilibrium fluctuations in absence, for the moment, of a more direct and rigorous proof of its validity and limitations.

While some nonequilibrium processes can be represented as the response of the system to external mechanical perturbations, some other nonequilibrium processes occur as a result of thermal perturbations, i.e., they are due to internal inhomogeneities of the system. The statistical analysis of the first kind of processes is based in general on the dynamical interpretation of the perturbation under conditions of statistical equilibrium at some initial time. However, the analysis of the thermal perturbations is more difficult, since they are not directly referred to any perturbative Hamiltonian. In order to describe these latter perturbations, many different methods have been proposed. Amongst them, some authors have tried to build a nonequilibrium ensemble theory parallel to the Gibbs treatment of equilibrium states representing the macroscopic conditions in which the systems are found.[31−34] The simplest method of constructing the corresponding nonequilibrium statistical ensemble is based on information theory. In this line, Miller and Larson[35] have analyzed the heat flux in a linear harmonic chain. While this is one of the simplest problems one can deal with, it has the inconvenience that a harmonic chain has in fact an infinite thermal conductivity. Some analyses[36] of the steady heat flow in a linear harmonic chain of finite length with nearest-neighbor interactions, and with each end in contact with a reservoir maintained at different temperatures, lead to a heat flux proportional to the temperature difference but independent of the chain length. In their analysis, Miller and Larson have avoided this kind of complication by assuming that the chain

ends are linked together to form a ring. For such a "superconductor" of thermal energy, no boundary reservoirs are needed to maintain a nonequilibrium state. In this case, the heat flux itself is a constant of the motion and can be chosen, as well as the constant total energy E, as a parameter of the macrostates.

If one fixes the position and velocity of the center of mass of the ring, the macrostate of the system can be specified by the ensemble average of the energy E and of the heat flux Q,

$$E = \langle H \rangle , \quad Q = \langle J \rangle , \quad (5.1)$$

where H is the Hamiltonian and J the microscopic heat flux operator. In terms of this set, the probability distribution function p can be obtained by maximizing the Shannon entropy

$$S = -k \int d\Gamma\, p \ln(p h^{1-N}) , \quad (5.2)$$

where $d\Gamma$ is the volume differential, h the Planck constant, and N the number of particles of the system. In this way, one obtains for the dimensionless partition function[35]

$$Z = h^{1-N} \int d\Gamma \exp(-\beta H - \gamma J) . \quad (5.3)$$

The undetermined multipliers β and γ must be chosen to satisfy the constrains (5.1). They can be obtained from the equations

$$E = \langle H \rangle = -\partial \ln Z / \partial \beta ,$$
$$\hspace{4cm} (5.4)$$
$$Q = \langle J \rangle = -\partial \ln Z / \partial \gamma .$$

By solving these equations and performing the corresponding integrations, one is led finally to[35]

$$Z = [\epsilon(1 - x^2)]^N , \quad (5.5)$$

$$\beta = \epsilon^{-1}(1 + x^2)(1 - x^2)^{-1} , \quad (5.6)$$

and

$$\gamma = -(N/\epsilon)2x(1 - x^2)^{-1} . \quad (5.7)$$

Here ϵ is the average energy per particle, $\epsilon = E/N$, and x is the relative heat flux $x = Q/\epsilon$. When $x = 0$, the usual equilibrium results are obtained. For x^2 different from zero, but small, one can observe that the generalized nonequilibrium temperature defined by $\Theta = (k\beta)^{-1}$ in (5.6) exhibits some corrections owing to the nonvanishing heat flux. Indeed, for small values of the heat flux Q, (5.6) may be rewritten as

$$\Theta^{-1} = T^{-1} + 2T^{-1}(Q/\epsilon)^2 . \quad (5.8)$$

This expression may be compared to our phenomenological formula (2.8) or with the more specific expression of (2.8) in the case of dielectric solids at low temperatures where, according to (4.6), it reduces to

$$\Theta^{-1} = T^{-1}$$
$$+ (d/2)(d+2)(d+1)^{-2} T^{-1} (q/c_0 u\rho)^2 .$$
$$(5.9)$$

In the model of Miller and Larson, $c_0 = 1$ and the nearest neighbor distance a is $a = 1$; therefore ρu, the energy per unit length, in one dimension can be identified with ϵ, the energy per particle, since there is a particle per unit length. Concerning the numerical factor in (5.9), it reduces to unity when one considers, as Miller and Larson, a one-dimensional chain in the high-temperature limit, in which the specific heat is a constant. In this case, however, one cannot assure that the relaxation times in (2.7) and in (4.4) may be identified, and therefore, the numerical coefficients of (5.8) and (5.9) cannot be reliably compared. One can observe, however, the close parallelism of (5.8) and (5.9), and therefore it can be seen that in nonequilibrium states the local-equilibrium temperature is only a first approximation to a more complex "temperature," both from macroscopic and microscopic points of view.

From the partition function (5.5) one can easily obtain the second moments of the fluctuations of the energy and of the heat flux, which are given by[35]

$$\langle (\delta E)^2 \rangle = \partial^2 \ln Z / \partial \beta^2$$
$$= N\epsilon^2 (1+x^2)(1-x^2)^{-1} , \qquad (5.10)$$
$$\langle (\delta Q)^2 \rangle = \partial^2 \ln Z / \partial \gamma^2$$
$$= (\epsilon^2 / 2N)(1+4x^2 - x^4)(1-x^2)^{-1} , \quad (5.11)$$
$$\langle (\delta E)(\delta Q) \rangle = -2N\epsilon^2 x (1-x^2)^{-1} . \qquad (5.12)$$

These expressions may be compared with our phenomenological results (3.3)—(3.5). We note that, in both cases, when $Q = 0$ one recovers the classical result for the energy fluctuations and, simultaneously, an expression for the heat fluctuations, while the energy-heat flux correlations vanish. In a steady nonequilibrium state, the nonvanishing mean heat flux produces a nonvanishing energy-heat flux correlation proportional to the mean heat flux, and introduces some corrections in the second moments of the energy-energy and heat-heat fluctuations. Finally, in comparing

(5.10)—(5.12) with (3.3)—(3.5), it can be noted the common feature of divergent fluctuations when the heat flux approaches to a limiting value. In (5.10)—(5.12), this limit is reached when $x^2 = 1$. In the microscopic model, when the maximum energy flux is approached, the ensemble members "condense" into a macrostate with vanishing restoring force against displacements.[35] As a consequence of this condensation, the fluctuations become divergent, as it is usual and well known in critical points. On the contrary, no simple explanation can be given concerning the possible physical meaning, if any, of the divergences predicted by our model.

This comparison confirms some essential points of our phenomenological development. The existence of a nonequilibrium entropy which depends on the heat flux is seen to have a statistical basis, related to a nonequilibrium ensemble. The fluctuations of energy and of heat flux in this ensemble may be related to the nonequilibrium entropy, as well as the energy fluctuations can be related to the equilibrium entropy in the classical theory. The basic agreement with such a different approach indicates that some physical features are indeed contained in our phenomenological formalism.

VI. CONCLUSIONS

We have explored the consequences of a generalized entropy and a generalized Einstein relation in the statistical aspects of nonequilibrium fluctuations. In this way we have obtained some corrections to the usual expressions of the Langevin stochastic noise in the equation for the energy fluctuations, i.e., we have obtained nonequilibrium corrections to the usual Landau-Lifshitz formula for the fluctuations of the heat flux. As it has been seen, these corrections arise from a nonvanishing heat relaxation time, whose consideration modifies the whole thermodynamic formalism. Our generalized entropy depends on the dissipative fluxes and therefore it may be valid in nonequilibrium states, at least for small values of the fluxes. A rigorous foundation for this nonequilibrium entropy should be based on a statistical analysis of nonequilibrium states. In simple cases, some explicit statistical results can be obtained, but this is not the case for general systems. It seems therefore convenient to explore from a macroscopic and phenomenological point of view the role, behavior, definition, and consequences of possible nonequilibrium entropies[10–12] and to relate these macroscopic points of view with some general statistical

theories.[31-33]

The present macroscopic theory accounted for in the first section of this paper has been used to obtain second-order (linear and nonlinear) constitutive equations[10-11] similar, for instance, to the Burnett or Grad's thirteen-moments equations of the kinetic theory. These phenomenological equations can be used, for instance, in the analysis of second sound in solids, of the dispersion and absorption of ultrasonic waves in monatomic fluids, or for a simplified interpretation of neutron scattering experiments in fluids. While in the usual developments of these areas no reference is made to the entropy, a number of generalized constitutive equations are in fact not compatible with the positive definite character of the local-equilibrium entropy, and it seems convenient to look for a more general entropy. This is not merely a philosophical point of view, but can bring additional physical information. Indeed, we have seen here that from a generalized entropy compatible with second sound, one can obtain new information on the nonequilibrium fluctuations which generalizes the usual fluctuation-dissipation expressions.

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