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Nonequilibrium temperature versus local-equilibrium temperature

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We discuss the conceptual differences between a nonequilibrium absolute temperature (defined as the partial derivative of the steady-state nonequilibrium entropy) and the local-equilibrium absolute temperature. We explore two situations in which this difference could be observed in molecular-dynamical situations. By using a simple model for the nonequilibrium entropy, we compute the difference between both temperatures for gases, metals, and electromagnetic radiation. We analyze the compatibility of both temperatures in two simple examples in the kinetic theory of gases and in an information-theoretic analysis of harmonic chains. Finally, we compare with some other works which have proposed nonequilibrium temperatures on several different grounds.

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I. INTRODUCTION

Basic questions in nonequilibrium thermodynamics concern the definition and meaning of entropy and absolute temperature out of equilibrium. In classical irreversible thermodynamics [1–4], based on the local-equilibrium hypothesis, it is assumed that these concepts do not need a reformulation out of equilibrium, and that the usual equilibrium concepts may be applied locally in nonhomogeneous nonequilibrium situations.

When the assumption of local equilibrium is relaxed, one is faced with the problem of defining temperature and entropy in nonequilibrium conditions. In rational thermodynamics, the difficulty is circumvented by considering entropy and temperature as primitive quantities, the latter being measured by means of small and fast thermometers [5]. Such a temperature is related to the derivative of the entropy with respect to internal energy. Since the entropy in rational thermodynamics is not necessarily equal to the local-equilibrium entropy, as it may depend on nonequilibrium quantities (such as the temperature gradient or the velocity gradient) the absolute temperature in rational thermodynamics does generally not coincide with the local-equilibrium absolute temperature. However, in rational thermodynamics the problem of the difference between both temperatures has not been explicitly investigated.

Different concepts of "nonequilibrium temperatures" have been considered in other contexts by different authors. In that respect let us mention Meixner, who proposes the concept of a "dynamical temperature" [6–8], Müller, who introduces a "coldness" [9], Lambermont and Lebon [10] and Muschik [11], who postulate "contact temperatures," Keizer, who bases his analysis on statistical considerations of molecular fluctuations [12], Landauer, who works within the frame of electronic devices [13], and more recently Jou and Casas-Vázquez [14,15], Nettleton [16], and Sieniutycz and Berry [17], who revisited this concept in the context of extended irreversible thermodynamics (EIT). The meaning of temperature in nonequilibrium situations has also been discussed in information theory [18–24], kinetic theory of gases [25–30], and in computer simulations [31].

The aim of this paper is to present several considerations about nonequilibrium temperature by starting from a simple phenomenological model which presents the advantage to express the differences between nonequilibrium absolute temperature and local-equilibrium absolute temperature in an explicit form. In Sec. II two different definitions of absolute temperature are reviewed. Section III summarizes the macroscopic phenomenological model used to discuss the nonequilibrium temperature. In Sec. IV we recall a possible experiment that we suggested recently to make evident the difference between nonequilibrium and local-equilibrium absolute temperature. This difference is explicitly calculated by using simple kinetic considerations. Section V presents some explicit evaluations of the difference between both temperatures for three different systems: ideal gases, metals, and thermal radiation. Sections VI and VII underline several microscopic interpretations of nonequilibrium temperature in the context of information theory and kinetic theory of gases. Section VIII compares the present formulation with other works mentioned in this introduction.

II. DEFINITION OF TEMPERATURE

The standard thermodynamic definition for the equilibrium absolute temperature is [32]

$$T^{-1}=(\partial S/\partial U)_V , \tag{1}$$

where S is the entropy (or s the entropy per unit mass), U the internal energy (or u the internal energy per unit mass), and V the volume (or v the volume per unit mass).

Another way to define the temperature in nondegenerate systems of independent particles is through the mean value of the translational kinetic energy of the particles, namely,

$$\tfrac{3}{2}kT=\langle \tfrac{1}{2}m\mathbf{c}^2\rangle , \tag{2}$$

with k Boltzmann's constant, m the mass of particle, and $\mathbf{c}$ the peculiar velocity of the particle with respect to the barycentric motion. In equilibrium systems, both expressions (1) and (2) lead to the same value of T. Note, however, that (1) is more general than (2), as (2) is not valid for degenerate gases satisfying Bose-Einstein or Fermi-Dirac statistics and, furthermore, (2) does not allow for negative absolute temperatures, as those appearing, for instance, in magnetic systems when more than half of the population lies in the upper energy level.

Out of equilibrium, the problem is more complicated, as the entropy is not univocally defined. Definition (1) is not directly operative and relation (2) is used as a definition of temperature, both in kinetic theory of gases and in molecular-dynamics simulations. This definition of temperature is consistent with the local-equilibrium hypothesis, which postulates that in a nonequilibrium situation the entropy may be defined locally by identifying the entropy of small parts of the system with a given energy u and specific volume v with the entropy $s(u,v)$ of the system in an equilibrium state characterized by the same values of u and v. From a practical point of view the calculation of T according to (1) is very simple, as it is directly related to the mean translational kinetic energy, a quantity which is well defined either in equilibrium or out of equilibrium. However, the assumption that T is the temperature measured by a thermometer implies the hypothesis that T acts as a potential for heat transport, i.e., that heat flows according to ∇T^{-1}; this hypothesis is consistent in the framework of the local-equilibrium theory, but must be revised in a more general context, because the natural potential for heat transport is $(\partial S/\partial U)$ rather than the mean value of kinetic energy.

A way out is to start from the Boltzmann definition, expressing the nonequilibrium entropy in terms of the velocity distribution function f,

$$\rho s(\mathbf{r})=-k\int f(\mathbf{r},\mathbf{c})\ln f(\mathbf{r},\mathbf{c})d\mathbf{c} \; . \tag{3}$$

Since the form of f in a nonequilibrium steady state is *a priori* unknown, the same is true for the nonequilibrium entropy. In a system in a steady state under a heat flux $\mathbf{q}$, the entropy will depend not only on u and v, but also on $\mathbf{q}$ or, if the system is submitted to a shear viscous pressure P_{12}, the entropy will depend on u, v, and P_{12}. Here we shall specialize our attention to a system under a heat flux. Thus the entropy will generally depend on the heat flux, so that one will have $s=s(u,v,\mathbf{q})$. If $s(u,v,\mathbf{q})$ is introduced into definition (1), one has

$$\theta^{-1}(u,v,\mathbf{q})=(\partial s/\partial u)_{v,\mathbf{q}} \; , \tag{4}$$

which is, formally speaking, one of the equations of state in this entropy representation. However, T only depends on u, as in kinetic theory one imposes on the nonequilibrium distribution function the auxiliary conditions

$$\int f\,d\mathbf{c}=\int f_{\text{eq}}d\mathbf{c}=n \; , \tag{5a}$$

$$\int f\mathbf{c}\,d\mathbf{c}=\int f_{\text{eq}}\mathbf{c}\,d\mathbf{c}=n\mathbf{v} \; , \tag{5b}$$

$$\int \tfrac{1}{2}mc^2 f\,d\mathbf{c}=\int \tfrac{1}{2}mc^2 f_{\text{eq}}d\mathbf{c}=\tfrac{3}{2}nkT \; , \tag{5c}$$

with f_{eq} the local-equilibrium Maxwellian distribution function corresponding to the number density n, the internal energy u, and barycentric velocity $\mathbf{v}$. Since f is different from f_{eq}, the higher-order moments of f, corresponding to nonconserved quantities, will in general differ from the corresponding moments of f_{eq}. As a consequence of (5), θ defined by (4) cannot be equal to T defined by (5) in nonequilibrium states. In this paper, we will call θ the nonequilibrium absolute temperature and T the local-equilibrium absolute temperature.

In order to be more specific, let us expand $s(u,v,\mathbf{q})$ around its local-equilibrium value up to a second-order approximation in $\mathbf{q}$. This will result in

$$s(u,v,\mathbf{q})=s_{\text{eq}}(u,v)-(\alpha/2)\mathbf{q}\cdot\mathbf{q} \; , \tag{6}$$

where $s_{\text{eq}}(u,v)$ is the local-equilibrium entropy. The coefficient α will be interpreted in the next section.

The relation between T and θ at this order of approximation, according to (4) and (6), is given by

$$\theta^{-1}=T^{-1}-\tfrac{1}{2}\left[\frac{\partial\alpha}{\partial u}\right]\mathbf{q}\cdot\mathbf{q} \; . \tag{7}$$

This explicit expression is the basis of our analysis about the conceptual and numerical differences between nonequilibrium absolute temperature and local-equilibrium absolute temperature. In general, $s(u,v,\mathbf{q})$ is a much more complicated function of $\mathbf{q}$ than (6), but this simplified expression is sufficient for the present purpose.

III. MACROSCOPIC THEORY

For simplicity, consider a rigid solid or an incompressible perfect fluid at rest, locally characterized by the internal energy u per unit mass and the heat flux vector $\mathbf{q}$ [33–43]. The energy balance equation reduces to

$$\rho\dot{u}=-\nabla\cdot\mathbf{q} \; , \tag{8}$$

where, for simplicity, no energy supply has been considered. To obtain an evolution equation for $\mathbf{q}$ compatible with the second law, one postulates the existence of a generalized entropy s which depends on u and $\mathbf{q}$, and whose total differential is given by

$$ds=\theta^{-1}du-\alpha\mathbf{q}\cdot d\mathbf{q} \; , \tag{9}$$

where $\theta^{-1}=(\partial s/\partial u)_{\mathbf{q}}$ is the generalized nonequilibrium absolute temperature. The time derivative of s may be obtained from (9) and written as

$$\rho\dot{s}=-\theta^{-1}\nabla\cdot\mathbf{q}-\rho\alpha\mathbf{q}\cdot\dot{\mathbf{q}} \; , \tag{10}$$

wherein use has been made of (8). The factor θ^{-1} in the first term on the right-hand side may be introduced into the divergent term so that

$$\rho\dot{s}+\nabla\cdot(\theta^{-1}\mathbf{q})=\mathbf{q}\cdot(\nabla\theta^{-1}-\rho\alpha\dot{\mathbf{q}}) \; . \tag{11}$$

Comparison with the general form of the entropy balance $\rho\dot{s}+\nabla\cdot\mathbf{J}^s=\sigma^s$ leads to identify the entropy flux $\mathbf{J}^s$ and the entropy production σ^s as

$$\mathbf{J}^s=\theta^{-1}\mathbf{q} \; , \tag{12}$$

$$\sigma^s=\mathbf{q}\cdot(\nabla\theta^{-1}-\rho\alpha\dot{\mathbf{q}}) \; . \tag{13}$$

To formulate an equation for the evolution of $\mathbf{q}$ compatible with the required positive definiteness of σ^s, the simplest hypothesis is to assume that

$$\nabla\theta^{-1}-\rho\alpha\dot{\mathbf{q}}=\mu\mathbf{q} \tag{14}$$

with $\mu\geq 0$. For small values of the heat flux, the contribution of order $\mathbf{q}\cdot\mathbf{q}$ to the absolute temperature may be neglected so that θ is equivalent to the local-equilibrium temperature T. Then, comparison of (14) with the Maxwell-Cattaneo equation [35,37,44]

$$\tau\dot{\mathbf{q}}=-(\mathbf{q}+\lambda\nabla T) \tag{15}$$

(with λ the thermal conductivity and τ the relaxation time) leads to the identifications

$$\alpha=\tau v/\lambda T^2,\quad \mu=(\lambda T^2)^{-1}\ . \tag{16}$$

We have written this short summary to emphasize that it is the generalized absolute temperature θ and not merely the local-equilibrium temperature T the relevant quantity appearing in the entropy flux and the evolution equation for the heat flux. In view of (9) and the first of relations (16), the generalized Gibbs equation takes the form

$$ds=\theta^{-1}du-(\tau v/\lambda T^2)\mathbf{q}\cdot d\mathbf{q}\ . \tag{17}$$

Integrability condition of (17) leads straightforwardly to expression (7).

When nonlinear terms in $\mathbf{q}\cdot\mathbf{q}$ are kept in the expression for θ, the Maxwell-Cattaneo equation (15) generalizes as follows:

$$\tau\dot{\mathbf{q}}+\mathbf{q}=-\lambda\nabla\theta \tag{18}$$

with $\alpha=\tau v/\lambda\theta^2$ and $\mu=(\lambda\theta^2)^{-1}$. The linear Maxwell-Cattaneo equation (15) has been used in many occasions to describe heat waves in solids at low temperatures [44]. For a detailed discussion of this equation and its thermodynamic consequences, the reader is referred to [34,35]. It is important to notice that (18) reduces to (15) when the term in $\mathbf{q}\cdot\mathbf{q}$ which appears in θ is neglected. The appearance of θ instead of T in (14) and (18) is imposed by thermodynamic requirements which are a direct consequence of the use of the generalized entropy (9) instead of the local-equilibrium entropy.

IV. THERMODYNAMIC AND KINETIC INTERPRETATION OF THE NONEQUILIBRIUM TEMPERATURE

The fact that the heat flux is proportional to $\nabla\theta$ rather than to ∇T suggests a possible experiment to check whether θ is a mathematical artifact arising from an undue extension of the classical definition (1), or whether it is an actual physical quantity [15(c)].

We connect by means of a good thermal conductor two thermodynamic systems. One of them is at equilibrium ($T_1=\theta_1=T$) whereas the other is in a nonequilibrium steady state characterized by a heat flux q_y perpendicular to the connection between both systems ($T_2\neq\theta_2=\theta$) (Fig. 1). The connection is installed in such a way that the local-equilibrium temperature of the nonequilibrium system at the position of the connection is equal to the temperature of the system at equilibrium. According to (18), one should observe in the steady state a heat flux given by

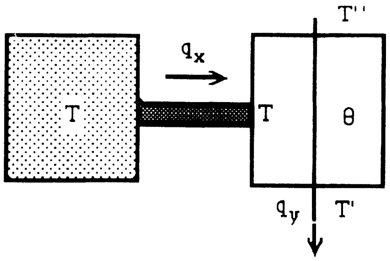

FIG. 1. The system on the left is at equilibrium at temperature T. The system on the right is in a nonequilibrium steady state under a heat flux q_y. Despite the fact that both ends of the conducting rod are at the same local-equilibrium absolute temperature T, a heat flow q_x from the left to the right is predicted to occur because θ in the nonequilibrium right-hand side system is less than T.

$$q_x=\lambda_m(\theta-T)/d \tag{19}$$

along the connecting rod. Here λ_m is the thermal conductivity of the thermal conductor connecting both systems and d is the separation between them. In contrast, in the local-equilibrium theory q_x should be given by $q_x=\lambda_m(T-T)/d=0$, because it is assumed that both ends of the connection are at the same local-equilibrium temperature T.

Expanding $\theta-T$ up to second order in $\mathbf{q}$, and taking into account that for system 1, $\mathbf{q}=0$, and in system 2 the flux $\mathbf{q}$ is directed along the y axis, we can write (19) as

$$q_x=(\lambda_m/d)\gamma T^2 q_y^2 \tag{20}$$

with $\gamma=\frac{1}{2}(\partial\alpha/\partial u)$.

The measurement of such a heat flux q_x between the two systems at the same local-equilibrium temperature T would offer strong support in favor of the generalized absolute temperature θ. However, a direct realization of such an experiment would require one to know whether a thermometer measures θ or T [45]. In fact, according to our reasoning, the thermometer measures θ rather than T, because the condition of no heat exchange between two systems (or between a system and a thermometer) is that they are at the same θ rather than at the same T. However, to avoid this problem, one may devise a microscopic interpretation of the experiment which does not require the use of a thermometer.

Suppose that the two systems in Fig. 1 consist of an ideal monatomic gas, and study the power delivered to both ends of the connecting rod. If the power arriving at one side is higher than the power arriving at the other side, it may be concluded that heat will flow from the end receiving more power to the end receiving less power, unless the bar is insulating. We will show, in a qualitative way, that even if both ends of the rod are at the same local-equilibrium temperature, the end corresponding to the nonequilibrium system is receiving less power than the end at equilibrium; as a consequence, heat will flow from the latter system to the former one, confirming our previous macroscopic prediction.

Consider the kinetic energy transferred to the wall due to collisions of particles whose trajectory makes an angle $\pm\phi$ with the normal to the surface of the wall (Fig. 2). A fraction of this energy will be delivered to the rod if it is heat conducting. The energy arriving at the wall will be proportional to $a(\phi)[n_+T_+\sqrt{T_+}+n_-T_-\sqrt{T_-}]$, where $a(\phi)$ is a geometrical factor depending on the angle ϕ and on the energy transfer coefficient between the molecules and the rod; n_+,n_- and T_+,T_- are the number densities of particles and the temperatures at the positions shown on Fig. 2. Indeed, $n\sqrt{T}$ is proportional to the flow of particles colliding with the wall (density times speed) whereas T is the mean energy carried per particle. Thus $nT\sqrt{T}$ is the flow of energy carried by the particles colliding with the wall. As is well known in kinetic theory, one may fix the values of the density, barycentric speed, and temperature independently of the value of the heat flux, so that neither n nor T are affected by the presence of the heat flux.

In the gas at equilibrium, n and T do not depend on the position, so that $n_+=n_-=n$ and $T_+=T_-=T$. In the nonequilbrium system $n(y)$ and $T(y)$ depend on the position, but the product $n(y)T(y)$ must be independent of y, in order to avoid convective motion (constant-pressure condition); thus $n_+T_+=n_-T_-$ and $T_+=T+\delta T$, $T_-=T-\delta T$, with $\delta T\approx l\nabla T\sin\phi$, l being the mean free path (in this qualitative discussion we simply assume that particles coming from longer distances will not arrive at the wall due to collisions with other particles). Thus the energy transferred to the wall per unit time will be, in the equilibrium system, and for a given angle ϕ.

$$J_u^{\rm eq}(\phi)=2a(\phi)nT\sqrt{T}\ . \tag{21}$$

In the nonequilibrium system it is given by

$$J_u^{\rm neq}(\phi)=a(\phi)nT\sqrt{T}\,\{[1+(\delta T/T)]^{1/2}+[1-(\delta T/T)]^{1/2}\} \tag{22}$$

or, expanding up to second order in $\delta T/T$,

$$\begin{aligned}J_u^{\rm neq}(\phi)&\approx 2a(\phi)nT\sqrt{T}\,[1-\tfrac{1}{8}(\delta T/T)^2]\\&=2a(\phi)nT\sqrt{T}\,[1-\tfrac{1}{8}(l\nabla\ln T)^2(\sin\phi)^2]\ .\end{aligned} \tag{23}$$

Thus $J_u^{\rm neq}(\phi)<J_u^{\rm eq}(\phi)$ and the net energy flow may be found by integrating (21) and (23) for $-\pi\le\phi\le\pi$, so that

$$\Delta J_u=J_u^{\rm neq}-J_u^{\rm eq}=-(A/4)l^2(\nabla\ln T)^2 \tag{24}$$

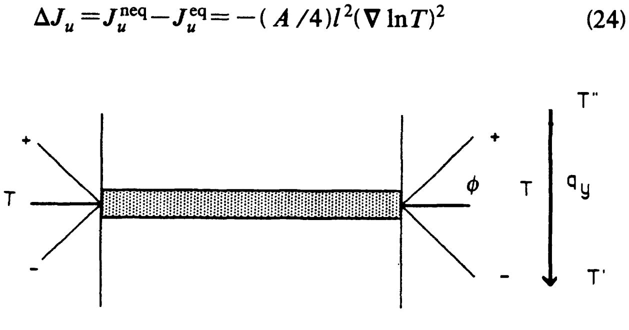

FIG. 2. The power delivered through molecular collisions to ends of the rod is less in the presence of the heat flux q_y than in the equilibrium system.

with

$$A=nT\sqrt{T}\int_{-\pi}^{\pi}a(\phi)\sin^2\phi\,d\phi\ .$$

Integration over all angles ϕ from $-\pi$ to π shows that the energy per unit time arriving at the end of the rod in contact with the system at equilibrium is higher than at the other end, in contact with the nonequilibrium system; this result has been established despite both systems being at the same local-equilibrium temperature, meaning that they are characterized by the same mean molecular energy.

This interpretation shows that the nonequilibrium temperature θ is not contradictory with the concepts of local-equilibrium temperature and ideal-gas temperature used in nonequilibrium computer simulations. The latter is related to the internal energy of the ideal gas, but it is not exactly the temperature measured by the thermometer, because, as we have seen in this section, two systems at the same T, but one in equilibrium and the other one out of equilibrium, have a net exchange of heat. The difference between θ and T is of second order in $l\nabla\ln T$, so that T and θ are identical in a first-order theory, i.e., in usual hydrodynamics and in classical irreversible thermodynamics. However, the difference between both concepts is of interest in second- and higher-order developments of the kinetic theory of gases as, for instance, in the Burnett and super-Burnett approximations [46,47].

V. EVALUATION OF THE NONEQUILIBRIUM TEMPERATURE

In this section an estimation of the order of magnitude of the difference $T-\theta$ is carried out. For a monatomic ideal gas one has, according to the kinetic theory of gases [46], $\lambda=\frac{5}{2}(k^2Tn/m)\tau$, so that $\tau v/\lambda T^2=2/(5p^2T)$ with $p=nkT$. Then, by integrating relation (17), the expression for the entropy up to second order in $\mathbf{q}$ is

$$s(u,\mathbf{q})=s_{\rm eq}(u)-[1/(5p^2T)]\mathbf{q}\cdot\mathbf{q}\ . \tag{25}$$

For a metallic conductor, the heat is carried out by electrons, and one has $\lambda=(\pi^2/3)(k^2Tn/m)\tau$ from which follows $(\tau v/\lambda T^2)=3/(\pi^2k^2T^3n^2)$ so that the entropy is

$$s(u,\mathbf{q})=s_{\rm eq}(u)-[3/(2\pi^2k^2T^3n^2)]\mathbf{q}\cdot\mathbf{q}\ . \tag{26}$$

Taking the derivatives of (25) and (26) with respect to u at constant $\mathbf{q}$ and bearing in mind that $du=c_v dT$ with c_v the specific heat [$c_v=3k/2m$ for monatomic gases and $c_v=(\pi^2kT/2m\epsilon_F)$ for an electron gas in metals] one obtains the respective explicit expressions of the generalized temperature, namely,

$$\theta^{-1}=T^{-1}+\tfrac{2}{5}(m/n^2k^3T^4)\mathbf{q}\cdot\mathbf{q}\ , \tag{27}$$

$$\theta^{-1}=T^{-1}+(9/\pi^4)(m\epsilon_F/n^2k^4T^5)\mathbf{q}\cdot\mathbf{q}\ , \tag{28}$$

where m is the mass of the molecules in (27) or the electron mass in (28), n the number particle density, ϵ_F the Fermi energy of the metal, and k the Boltzmann constant ($k=1.38\times10^{-23}$ J/K).

To estimate $T-\theta$, assume, for instance, that the subsystems are composed of CO_2 at 300 K and 0.1 atm.

Then $m=4\times10^{-26}$ kg and $n=2.6\times10^{24}$ particles/m^3 and we have from (27) $T-\theta=9.6\times10^{-12}q_y^2$, with q_y expressed in W/m^{2}K. Thus, for q_y of the order of 10^5 W/m^{2}K, the effective temperature difference $T-\theta$ would be of the order of 9.6×10^{-2} K. If the two subsystems are made of copper ($n=8.45\times10^{22}$ cm^{-3}, $T_F=\epsilon_F/k=8.12\times10^4$ K, $m=9.1\times10^{-31}$ kg), the difference $T-\theta$ for a temperature gradient in the y direction of the order of 10^4 K/m would be of the order of 2×10^{-3} K, less than for the gas of the previous example.

The nonequilibrium entropy for thermal radiation under a heat flux $\mathbf{q}$ is given by

$$S(U,V,\mathbf{q})=\tfrac{4}{3}a^{1/4}U^{3/4}V^{1/4}-\tfrac{3}{8}a^{1/4}c^{-2}V^{9/4}U^{-5/4}\mathbf{q}^2\ , \tag{29}$$

where the first term is the usual local-equilibrium entropy. This is obtained from (6) by taking into account that $\lambda=\tfrac{4}{3}c^2aT^3\tau$, where c is the speed of light in vacuum and a the blackbody constant. Differentiating this expression with respect to U at constant V and $\mathbf{q}$ yields

$$\theta^{-1}=T^{-1}[1+\tfrac{15}{32}c^{-2}U^{-2}V^2\mathbf{q}^2]\ . \tag{30}$$

In order to roughly estimate this nonequilibrium temperature θ we assume that at the surface of a star the radiation flux is given by the Stefan-Boltzmann law, $q=\tfrac{1}{4}c(U/V)$, and then expression (30) yields $\theta^{-1}=1.031T^{-1}$. Thus the modification in the temperature in this region is of the order of 3%. On the other hand, substitution of the above expression for q into (29) and use of the definition of the local-equilibrium temperature T in terms of internal energy $U=aT^4V$, yield for the entropy of nonequilibrium radiation $S=1.31aT^3V$, a value which is less than the corresponding value for the entropy of the radiation in equilibrium at the same temperature, $S=\tfrac{4}{3}aT^3V$. Rather than being related to the energy content, temperature θ refers to the rate of change of energy with entropy at constant $\mathbf{q}$ (see Fig. 4).

VI. LAGRANGE MULTIPLIERS AND INFORMATION THEORY

Information theory is a field where the question about a nonequilibrium absolute temperature arises in a natural way. One could assume, for instance, a homogeneous system with a total internal energy U and a given heat flux Q. In this case, maximum-entropy arguments lead for the probability distribution function to an expression of the form

$$f=Z^{-1}\exp[-\beta H-\gamma J]\ , \tag{31}$$

where Z is the partition function, H the Hamiltonian of the system, J the microscopic heat flux operator, and β and γ Lagrange multipliers determined by the conditions

$$\langle H\rangle=U,\quad \langle J\rangle=Q\ . \tag{32}$$

In equilibrium statistical mechanics the Lagrange multiplier β is identified as $\beta=(kT)^{-1}$, with T the absolute temperature; therefore it is logical to ask whether in nonequilbrium β may be identified as $\beta=(k\theta)^{-1}$, with θ the generalized absolute temperature. From a formal point of view, the latter interpretation coincides with $\theta^{-1}=(\partial s/\partial u)_{\mathbf{q}}$. To check if it is physically realistic to interpret β as a quantity proportional to the inverse of a temperature, we consider the problem of heat propagation in a harmonic chain treated by Miller and Larson [24], and we propose a possible experiment analogous to the previous one discussed in Sec. IV.

In a harmonic chain, the phonon mean free path is infinite, so that the energy flux along it is not proportional to the temperature gradient but to the temperature difference between the reservoirs located at its ends. To avoid complications associated with the boundary conditions, Miller and Larson eliminate the boundaries by considering that chain ends are linked together to form a ring. In this case, the system turns out to be a "superconductor" of thermal energy, because of its infinite heat conductivity: a heat flux lasts indefinitely, without appealing to boundary reservoirs to sustain it.

The system consists of a linear chain of N particles, each of mass m. Each particle is connected to its nearest neighbors by Hookean springs with stiffness κ. The Nth particle is connected by a spring to the first particle, so that the chain forms a closed ring. One may choose a system of units where the mass is expressed in terms of m, time in units of $(m/\kappa)^{1/2}$, and energy in units of $(h/2\pi)(\kappa/m)^{1/2}$, h being Planck's constant.

The Lagrange multipliers β and γ may be explicitly found in terms of U and Q through the constraints (32), which may be expressed by

$$U=\langle H\rangle=-\partial\ln Z/\partial\beta,\quad Q=\langle J\rangle=-\partial\ln Z/\partial\gamma\ . \tag{33}$$

The final result for the partition function Z reads [24]

$$Z=[\epsilon(1-x)^2]^N \tag{34}$$

with $\epsilon=U/N$ and $x=Q/\epsilon$. In particular, β and γ are given by

$$\beta=\frac{1+x^2}{\epsilon(1-x^2)},\quad \gamma=-\frac{2N}{\epsilon}\frac{x}{1-x^2}\ . \tag{35}$$

For $x=0$ one recovers the usual equilibrium results, whereas for $x^2\to1$, both β and γ diverge.

The entropy and the generalized Lagrange multiplier β deserve special comments. According to (31) and the usual relation

$$S=-k\int f\ln f\,d\Gamma_{N-1}\ , \tag{36}$$

where $d\Gamma_{N-1}$ is the volume element of the phase space, the entropy may be written as

$$S=k(\beta U+\gamma Q+\ln Z)\ . \tag{37}$$

In the thermodynamic limit when N tends to infinity, the entropy per particle turns out to be, in view of the explicit form (34) of Z,

$$s=\lim_{N\to\infty}(S/N)=k[1+\ln\epsilon+\ln(1-x^2)]\ . \tag{38}$$

As expected, the presence of the heat flux modifies the value of s. For small values of the heat flux, (38) reduces to

$$s(\epsilon,Q)=s_{\mathrm{eq}}(\epsilon)-(k/\epsilon^2)Q^2 \ . \tag{39}$$

The dependence of this expression on the heat flux Q was obtained from arguments drawn from information theory; it provides a further corroboration of the basic assertions of extended irreversible thermodynamics, stating that the entropy is a function of the heat flux out of equilibrium.

If the Lagrangian multiplier β can be interpreted in terms of a generalized absolute temperature θ defined as $\theta=1/(k\beta)$, it follows from the definition $\theta^{-1}=(\partial s/\partial\epsilon)_Q$ that

$$\theta^{-1}=T^{-1}+(2k/\epsilon^3)Q^2 \ , \tag{40}$$

indicating that the generalized temperature θ differs from the usual local equilibrium T by terms of order Q^2. This is a supplementary argument that supports the introduction of a generalized absolute temperature.

To check the physical content of θ, an experiment analogous to that exposed in Sec. IV could be considered. A harmonic chain ring is at equilibrium with energy U and another identical chain has the same energy U but it sustains a nonzero energy flux J (Fig. 3). If both systems are put in contact through a thermal conducting string, the classical theory predicts that no heat will flow between them because they both have the same local-equilibrium temperature $T=U/kN$. In contrast, EIT predicts that some heat should flow from the first (equilibrium) system to the second (nonequilibrium system), because the generalized temperature of the latter is less than that of the former.

It is interesting to calculate the energy distribution in the final steady state when no more energy flows between systems 1 and 2. In this situation, one has, according to EIT,

$$\theta_1=\theta_2$$

or, equivalently,

$$\beta_1=\beta_2 \tag{41}$$

rather than $T_1=T_2$, but recalling that β is related to the energy per particle by means of the first of expressions (35), one may write

$$\frac{1}{\epsilon_1}\frac{1+(Q/\epsilon_1)^2}{1-(Q/\epsilon_1)^2}=\frac{1}{\epsilon_2} \ . \tag{42}$$

Since the total system is isolated, one has $\epsilon_1+\epsilon_2=\epsilon$, where $\epsilon=\epsilon_{1\ \mathrm{initial}}+\epsilon_{2\ \mathrm{initial}}$. Up to the second order in (Q/ϵ), Eq. (42) yields, in the steady state.

$$\begin{aligned}\epsilon_1&=(\epsilon/2)[1+4(Q/\epsilon)^2] \ ,\\ \epsilon_2&=(\epsilon/2)[1-4(Q/\epsilon)^2] \ .\end{aligned} \tag{43}$$

When $Q=0$, $\epsilon_1=\epsilon_2=\epsilon/2$, but for $Q\neq 0$ the steady state does not correspond to $T_1=T_2$.

It must be noted that an analysis of energy transport in continuous systems based on maximum entropy arguments was carried out by Robertson [18] and Luzzi and co-workers [21]. In these works, it is found that the heat flux is related to the gradient of the Lagrange multiplier β, which then does play the role of a temperature, as the heat transfer between two bodies will be zero only when β has the same value for two systems.

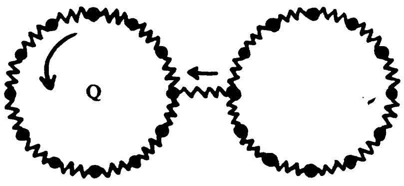

FIG. 3. Two circular harmonic chains are thermally connected. Both chains are assumed to have the same energy per particle (i.e., the same local-equilibrium temperature T). However, a steady heat flux Q flows along one of the chains, so that the generalized absolute temperature θ in this chain is less than T. As a consequence, some heat is predicted to flow from the equilibrium to the nonequilibrium system.

VII. MICROSCOPIC INTERPRETATION

The definition of temperature in kinetic theory has been also widely discussed in the case of dense gases with intermolecular interactions [25–28]. Two definitions of temperature are generally used: the first one relates the temperature to the molecular kinetic translational energy, the second expresses the temperature in terms of the total molecular energy. The two definitions yield the same result in equilibrium, but out of equilibrium they differ by quantities which are proportional to the velocity gradient and they lead to different values for the bulk viscosity. In the present work, where the velocity gradient is assumed to vanish, these corrections do not appear, but we think it is worthwhile to mention them. It must be added that García-Colín and Green [28] have shown that the two descriptions yield equivalent results at the macroscopic level.

To our knowledge not much attention has been paid to the definition of absolute temperature as the derivative of the entropy in dilute monatomic gases in nonequilbrium situations [29]. In this section we show that expression (2) of entropy is confirmed by the kinetic theory of gases in the 13-moment Grad approximation [46]. In the kinetic theory of monatomic gases, the temperature is usually defined through the expression $u=\frac{3}{2}kT/m$, u being the mean kinetic energy per unit mass, whereas the thermodynamic definition (1) is not used. It is worth noting that the notion of a local-equilibrium absolute temperature T related to the mean kinetic energy does not preclude the possibility to formulate other definitions of the temperature. To show that let us ask the following question: What is the energy u^* of a gas in equilibrium to which corresponds the same entropy as a gas with energy u but subject to a heat flux $\mathbf{q}$? In other words, we seek an energy u^* such that

$$s_{\mathrm{eq}}(u^*)=s(u,\mathbf{q})=s_{\mathrm{eq}}(u)-(\alpha/2)\mathbf{q}\cdot\mathbf{q} \ , \tag{44}$$

where expression (6) for the generalized entropy has been used. The expression for $s(u,\mathbf{q})$ used in (44) may be derived from the kinetic theory of gases as follows. In the Grad approach, the nonequilibrium distribution function under a heat flux $\mathbf{q}$ is given by

$$f = f_{\text{eq}} \left\{ 1 + \frac{2m}{5pk^2T^2} [\tfrac{1}{2} m \mathbf{c}^2 - \tfrac{5}{2} kT] \mathbf{c} \cdot \mathbf{q} \right\} . \tag{45}$$

Introduction of this expression into the Boltzmann formula (3) for the entropy yields, as indicated in Sec. V,

$$\rho s = \rho s_{\text{eq}} - \frac{m}{5pkT^2} \mathbf{q} \cdot \mathbf{q} . \tag{46}$$

Expanding $s_{\text{eq}}(u^*)$ up to the first order in $u^* - u$, one obtains

$$s_{\text{eq}}(u^*) = s_{\text{eq}}(u) + \left[\frac{\partial s_{\text{eq}}}{\partial u} \right]_{u = u^*} (u^* - u) + \cdots \tag{47}$$

and after comparing with (44), it follows that

$$u^* = u - \tfrac{1}{2} T \alpha \mathbf{q} \cdot \mathbf{q} \tag{48}$$

with $T = [(\partial s_{\text{eq}} / \partial u)_{u = u^*}]^{-1}$. Since for a monatomic gas, energy and temperature are related according to the expression $u = \frac{3}{2}(k/m)T$, relation (48) can be formulated in terms of the temperatures

$$T^* = T[1 - (m/3k)\alpha \mathbf{q} \cdot \mathbf{q}] . \tag{49}$$

The meaning of the temperature T^* is the following. We know from Eq. (44) that in the nonequilibrium state with energy u and heat flux $\mathbf{q}$, the gas is characterized by less entropy and then more order, than in equilibrium with the same energy. Thus not all the energy u contributes to the molecular disorder; the part of u which contributes to this molecular disorder is precisely u^*, so that T^*/T expresses the fraction of internal energy which really contributes to the molecular disorder.

It is important to realize that the temperature T^* is not exactly equal to the absolute nonequilibrium temperature θ given by (27), which can be rewritten as $\theta^{-1} = T^{-1}[1 + (m/k)\alpha \mathbf{q} \cdot \mathbf{q}]$. In Fig. 4 are sketched $s_{\text{eq}}(u)$ and $s(u, \mathbf{q})$ in terms of u, and θ^{-1}, T^{-1}, and T^{*-1} are represented as the slopes of the curves at the points A, B, and C, respectively. From (27) and (49) it follows that for small $\mathbf{q}$, $T^{-1} < T^{*-1} < \theta^{-1}$. It must be noted that, according to what has been said earlier, T is related to the internal energy by means of the definition (1), θ is the temperature measured by the thermometer, and T^* is related to the fraction of the internal energy which contributes to molecular disorder.

The value of the generalized temperature depends on the constraints acting on the system. For instance, the value of the temperature calculated at constant heat flux $\mathbf{q}$ is different from the value at the constant-temperature gradient. To be explicit, consider a monatomic ideal gas with purely repulsive power-law potentials. For this system, one has $\tau = aT^{-b}$, with a a constant and $0 < b < \frac{1}{2}$, the limiting values $b = 0$ and $b = \frac{1}{2}$ corresponding, respectively, to Maxwell molecules and to hard spheres. The entropy in the steady state takes the form

$$s = s_{\text{eq}} - (\tau / 2\rho\lambda T^2) \mathbf{q} \cdot \mathbf{q} = s_{\text{eq}} - (\tau\lambda / 2\rho T^2) \nabla T \cdot \nabla T . \tag{50}$$

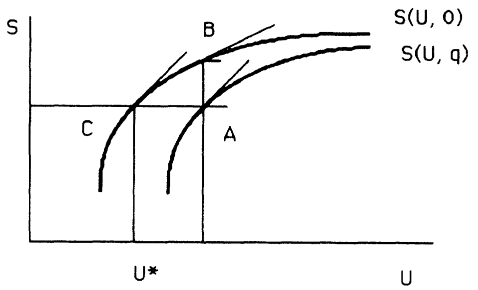

FIG. 4. The local-equilibrium entropy $S_{\text{eq}}(U)$ (upper curve) and the generalized equilibrium $S(U, \mathbf{q})$ (lower curve) are shown. The three temperatures θ, T, and T^* mentioned in the text are given by the inverse of the slopes of the curves at points A, B, and C, respectively.

Now we take into consideration two alternative definitions of the generalized temperature, namely,

$$\theta^{-1} = \left[\frac{\partial s}{\partial u} \right]_{\mathbf{q}} , \quad \theta^{*-1} = \left[\frac{\partial s}{\partial u} \right]_{\nabla T} , \tag{51}$$

which correspond to two different choices of independent variables. In the framework of the kinetic theory, the first choice is related to the Grad method and the second one to the Chapman-Enskog expansion. The Grad method is more suitable than the Chapman-Enskog expansion for situations characterized by fast changes of variables describing the system. As in both developments the problem of a nonequilibrium temperature arises, our aim here is restricted to a comparison of these generalized temperatures emerging in two different physical situations, namely, $\mathbf{q}$ or ∇T are kept fixed during the change of internal energy. Recalling that $\lambda = \frac{5}{2}(k^2 T n / m)\tau$, expression (50) reads

$$\begin{aligned} s &= s_{\text{eq}} - (5n^2k^2T^3) \mathbf{q} \cdot \mathbf{q} \\ &= s_{\text{eq}} - (5k^2a^2/4m^2) T^{-(1+2b)} \nabla T \cdot \nabla T . \end{aligned} \tag{52}$$

Observe that when s is written in terms of $\mathbf{q}$ does not depend explicitly on τ and, as a consequence, is independent of the particular form of the intermolecular potential. In contrast, expression $s(u, \nabla T)$ at constant ∇T is related to the intermolecular potential through the parameter b. By differentiating $s(u, \nabla T)$ at constant ∇T with respect to u we obtain

$$\theta^{*-1} = T^{-1} + (1 + 2b)(\tau\lambda / 2\rho c_v T^3) \nabla T \cdot \nabla T . \tag{53}$$

For Maxwell molecules ($b = 0$) and for hard spheres ($b = \frac{1}{2}$), one has, respectively,

$$\theta^{*-1} = \begin{cases} T^{-1} + (\tau\lambda / 2\rho T^2 c_v) \nabla T \cdot \nabla T & \text{(Maxwell)} \\ T^{-1} + (\tau\lambda / \rho T^2 c_v) \nabla T \cdot \nabla T & \text{(hard spheres)} . \end{cases} \tag{54}$$

Similar remarks can be repeated concerning the definition of the nonequilibrium temperature in systems under shear, for which the EIT entropy is [34,35]

$$s = s_{\text{eq}} - (\tau / 2\eta T \rho) P_{12}^2 = s_{\text{eq}} - (\tau\eta / 2T\rho) \dot{\gamma}^2 ,$$

where P_{12} is the shear stress and $\dot{\gamma}$ the shear rate, related to P_{12} by $P_{12}=\eta\dot{\gamma}$. In a monatomic gas, one has $\eta=nkT\tau$, so that

$$s=s_{\text{eq}}-(2n^2kT^2m)^{-1}P_{12}^2=s_{\text{eq}}-(k\tau^2/2m)\dot{\gamma}^2 \ . \tag{55}$$

The corresponding temperature is

$$\theta^{-1}=\left[\frac{\partial s}{\partial u}\right]_{P_{12}}=T^{-1}+(n^2kT^3mc_v)^{-1}P_{12}^2 \tag{56}$$

whatever the form of the intermolecular potential. In contrast, at constant $\dot{\gamma}$ one has

$$\theta^{*-1}=T^{-1}+(2bk\tau^2/2c_vTm)\dot{\gamma}^2 \tag{57}$$

so that $\theta^*=T$ for Maxwell molecules, but

$$\theta^{*-1}=T^{-1}+(k\tau^2/2c_vTm)\dot{\gamma}^2 \tag{58}$$

for hard spheres. Brey and Santos [29] have used the definition θ^* at constant $\dot{\gamma}$ in their analysis of the influence of the shear rate on the nonequilibrium temperature, and they found that $\theta^*=T$ for Maxwell molecules.

VIII. CONCLUDING REMARKS

We recall here some results obtained by other authors on the definition of a nonequilibrium temperature. Regarding the difficulties of finding a rigorous and unique definition of entropy in nonequilibrium, Meixner [6–8] tried to avoid the use of the entropy in his formulation of an entropy-free thermodynamics. However, he was not able to avoid the introduction of a dynamical temperature by means of a kind of entropy flux in the Clausius inequality. No operational definition of the dynamical temperature is given, but only its existence is assumed. The values of the dynamical temperature on the surface of a part of the body are supposed to be given by the temperatures of fictive heat baths in contact with the surface of the body. The fundamental inequality of this thermodynamics is then written as

$$\int dt[(T_{\text{eq}}^{-1}-T^{-1})\dot{u}+\rho^{-1}\mathbf{q}\cdot\nabla T^{-1}]\geq 0 \tag{59}$$

with T the dynamical temperature and T_{eq} the local-equilibrium temperature. Equation (59) follows from the Clausius inequality in which the entropy flux from the equilibrium heat bath to the nonequilibrium system is given by $\mathbf{q}/T$. The difference between T and T_{eq} is expressed by a constitutive relation as a function of u, v, $\dot{u}$, and $\mathbf{q}$. However, to our knowledge explicit expressions for this difference have not been worked out [7]. In our case, expressions (27), (28), and (30) are not particular examples of a general constitutive equation but equations of state in the entropy representation of some model systems [34].

Müller [9] introduced a nonequilibrium entropy η depending not only on the empirical temperature θ_e but also on its time derivative. Accordingly, he defined the coldness Λ as the derivative of the entropy with respect to internal energy. Such a coldness depends on the empirical temperature and on its time derivative, that is, $\Lambda=\Lambda(\theta_e,\dot{\theta}_e)$ and it must be continuous at the wall of a perfect thermometer. For steady states, in which the time derivative of the empirical temperature is zero, the coldness reduces to the usual temperature.

Keizer's approach [12] starts from the analysis of fluctuations in nonequilibrium steady states. He defines an entropy S by using the Einstein relation between the second moments of fluctuations and the second differential of the entropy, namely,

$$\langle \delta u\, \delta u \rangle \sim \exp[(\delta^2 S)/2k] \ . \tag{60}$$

If the second moments of the fluctuations depend on nonequilibrium parameters (as, for instance, on the mean heat flux applied to the system), the entropy S defined by (60) will also depend on the fluxes and therefore its derivative with respect to the internal energy will also depend on the fluxes. However, for the case of heat conduction. Keizer takes the classical Fourier law, so that he has not considered modifications to the entropy in simple heat conduction. Accordingly, he has identified in this case the local-equilibrium temperature with the nonequilibrium temperature. In principle, the difference between both temperatures could be seen by experimentally measuring the fluctuations in a nonequilibrium steady state.

Temperature is not the only thermodynamic quantity to contain nonequilibrium corrections: they should also arise in the pressure or in the chemical potential. These corrections may be of especial interest, because of their consequences on phase diagrams, electromotive forces, and coligative quantities in general. Keizer has studied theoretically and experimentally the corrections to the electromotive force in a nonequilibrium situation [47]. The experimental consequences of the nonequilibrium contributions to the chemical potential in polymeric solutions have been analyzed in the framework of extended irreversible thermodynamics [48]. In both works, the corrections turn out to be measurable.

In the case of mixtures (electrons and ions, or matter and radiation) the problem of temperature measurement presents other kind of subtleties, such as the fact that different thermometers may respond to different constituents and therefore may indicate different temperatures. In contrast, our analysis has been concerned with the more basic concept of the definition of temperature in the simplest situations, for instance, in a single-species monatomic gas.

In summary, in the present paper we have emphasized the need of a more thorough discussion of the concept of temperature in nonequilibrium situations, and contributed to this aim with a special, but explicit, model which is helpful in obtaining expressions for several definitions of absolute temperature in nonequilibrium steady states. We have pointed out that $(\partial S/\partial U)$ is not equal to the inverse of the local-equilibrium temperature when second-order nonequilibrium terms are considered into the nonequilibrium entropy. We have emphasized that whereas T retains its meaning as the measure of the mean translational kinetic energy in nonequilibrium states, it is θ rather than T the temperature which acts as a potential for heat transfer in nonequilibrium situations. The difference between θ and T may be attributed to the fact that the nonequilibrium state has less molecular disorder than the equilibrium state. Also we have examined some specific examples which could be amenable to dynamic computer simulation and helpful in deciding which of the several temperatures is measured by a thermometer immersed in an ideal gas.

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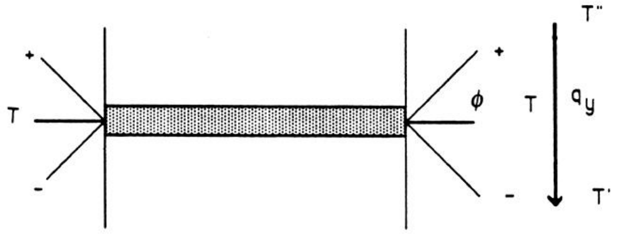

FIG. 2. The power delivered through molecular collisions to ends of the rod is less in the presence of the heat flux q_y than in the equilibrium system.