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Nonequilibrium Entropy and the Second Law of Thermodynamics: A Simple Illustration[1]

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The objective of this paper is twofold: first, to examine how the concepts of extended irreversible thermodynamics are related to the notion of accompanying equilibrium state introduced by Kestin; second, to compare the behavior of both the classical local equilibrium entropy and that used in extended irreversible thermodynamics. Whereas the former does not show a monotonic increase, the latter exhibits a steady increase during the heat transfer process; therefore it is more suitable than the former one to cope with the approach to equilibrium in the presence of thermal waves.

KEY WORDS: accompanying state; extended irreversible thermodynamics; heat transport; second law of thermodynamics.

1. INTRODUCTION

The formulation of the second law of thermodynamics in nonequilibrium states has been a challenge for scientists since Clausius and Lord Kelvin stated this law around 1850. Fifteen years later, the introduction by Clausius of the concept of entropy allowed for a rigorous mathematical formulation of the second law, at least for processes performed between equilibrium states. For instance, in an isolated system at equilibrium and in which several internal constraints are present, the removal of one of these constraints brings the system toward another equilibrium state whose entropy is equal to or higher than, but never lower than, that of the initial state.

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It is worthwhile pointing out that in equilibrium thermodynamics, time does not play any role: one compares the entropy of equilibrium states compatible with different internal and external constraints. Of course, problems involving time, as, for instance, how long the system will take to attain the final equilibrium state, are very important in practice, so that the status of the second law in nonequilibrium states is a topic of fundamental interest.

It was recognized by Meixner [1] some years ago that nonequilibrium thermodynamics has many faces. The same observation was made by Kestin [2], who speaks of a veritable tour of Babel. Nevertheless, in the course of time a small number of theories have survived. Undoubtedly, the most successful formalism was the so-called classical theory of irreversible processes proposed by Onsager in the year 1930 [3] and developed later by several people, such as Prigogine [4], Meixner and Reik [5], de Groot and Mazur [6], and Haase [7]. This theory is based on the local-equilibrium hypothesis, stating that "not too far from equilibrium" the system depends locally and instantaneously on the same variables as in equilibrium. This approach was generalized by Kestin and Bataille [8, 9], who introduced the notion of an accompanying equilibrium state.

Departing radically from the aforementioned description are the works regrouped under the generic title of *Rational Thermodynamics* [10]. This theory was proposed by Coleman, Noll, Truesdell, and Gurtin and is characterized by its mathematical rigor. In the spirit of its authors, rational thermodynamics is general and applicable to any system whatever its distance from equilibrium is. Although it has known interesting successes, its insufficient emphasis on the physical foundations of its basic concepts has restrained its expansion [11].

During the last two decades, another thermodynamic formalism, known as extended irreversible thermodynamics (EIT), has grown up under the impulsion of many people such as Lebon et al. [12], Müller [13], García-Colín [14], Nettleton [15], and Eu [16]. This theory was born out of the necessity to build a formalism which goes beyond the local-equilibrium hypothesis and would be less formal than rational thermodynamics with a wider physical support.

The several versions of nonequilibrium thermodynamics are faced with common problems: What is nonequilibrium temperature? How do we define a nonequilibrium entropy? How do we exploit the consequences of the second law of thermodynamics? We do not have the pretension of solving these fundamental questions in this note, but more modestly, we wish to shed some light on the concept of nonequilibrium entropy through the ideas underlying EIT.

This will be achieved by considering the simplest example found in any textbook on thermodynamics: namely, the problem of heat transfer between two homogeneous bodies subject to a temperature difference.

The aim of this paper is twofold: on one hand, to examine how the concepts of extended irreversible thermodynamics may be related to the conceptual idea of an accompanying equilibrium state proposed by Kestin in several publications [2, 8, 9] and, on the other, to compare the behavior of the entropy in local-equilibrium thermodynamics and in EIT.

2. PHYSICAL STATE AND ACCOMPANYING EQUILIBRIUM STATE

According to Kestin's point of view [2, 8, 9], any nonequilibrium physical state may be associated with an equilibrium state. This "accompanying equilibrium state" is obtained by isolating the system suddenly with a rigid and adiabatic wall and letting it relax to equilibrium. This procedure allows for the introduction of supplementary variables with respect to the classical description of the Onsager–Prigogine school: these variables, called "internal variables," are associated with internal processes and are not controllable from the outside, contrary to temperature and stress. Internal variables are associated with chemical reactions, plastic deformations, etc., and do not participate in the mechanical external work and (or) heat input. Denoting by τ the relaxation time toward the accompanying equilibrium state, Kestin proposes to introduce the Deborah number defined as

$$D = \tau/\tau_M \tag{1}$$

to measure how far the system is out of equilibrium; τ_M stands for a macroscopic time scale given, for instance, by $a/\dot{a}$, where a denotes any local equilibrium variables, while $\dot{a}$ represents its time derivative. Kestin's theory coupled with the introduction of internal variables has proved successful especially in solid continuum mechanics.

The distinction between the physical state and the accompanying equilibrium state may be useful for a better understanding of the basic concepts underlying extended irreversible thermodynamics. In this theory, the thermodynamic fluxes (as heat flux, electric flux, mass flux, viscous pressure tensor, and so on) are included in the description of the nonequilibrium thermodynamic state, besides the classical variables (internal energy, electrical charge, volume, composition, and so on). It follows that in EIT, the nonequilibrium state is described by the set of variables formed by the classical ones and the thermodynamic fluxes. If, for the sake of simplicity, we consider a rigid heat conductor with internal energy U and a heat flux vector **q**, in EIT, the nonequilibrium state is described by U (or temperature T) and **q**, and in particular the entropy s is assumed to depend on both U and **q** (Fig. 1).

According to Kestin, the accompanying equilibrium state would be obtained by isolating the system suddenly and letting it reach thermal equilibrium. Since the system has been isolated, its energy will remain constant during the decay toward equilibrium, so that the final accompanying state will be characterized only by U (the same energy as the initial physical state) and by a vanishing value of the heat flux. Obviously, the entropy associated with the accompanying equilibrium state is simply the equilibrium entropy corresponding to the internal energy U. Concerning the entropy to be assigned to the initial physical state, it is given by

$$S_{\text{in}}(U, \mathbf{q}) = S_{\text{fin}}(U) - v \int \sigma \, dt \tag{2}$$

where σ is the entropy production per unit time and unit volume during the decay from the initial physical state to the final accompanying equilibrium state, v is the volume of the system.

If one takes into account that the entropy production is [12]

$$\sigma = (1/\lambda T^2) \, \mathbf{q} \cdot \mathbf{q} \tag{3}$$

and if one assumes that **q** decays exponentially according to the Vernotte–Cattaneo equation [12]

$$\tau \dot{\mathbf{q}} + \mathbf{q} = -\lambda \, \Delta T \tag{4}$$

i.e., $\mathbf{q}(t) = \mathbf{q}(0) \exp(-t/\tau)$, with τ the relaxation time, one finds from Eqs. (2) and (3) that

$$S_{\text{in}}(U, \mathbf{q}) = S_{\text{eq}}(U) - (\tau v / 2\lambda T^2) \, \mathbf{q} \cdot \mathbf{q} \tag{5}$$

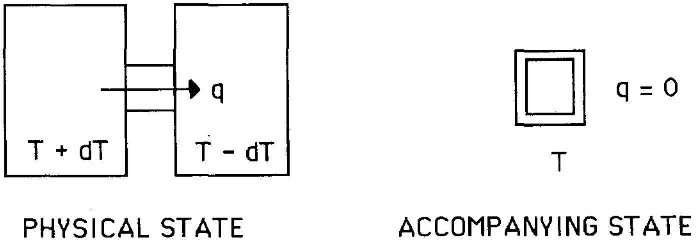

Fig. 1. The physical state is characterized by internal energy u and heat flux **q**, whereas the accompanying equilibrium state is described only by u, because the heat flux vanishes at equilibrium.

which is the usual expression for the generalized entropy of EIT for rigid heat conductors up to the second order in the heat flux.

It can thus be claimed that the entropy used in EIT corresponds to the entropy of the physical state, whereas the local-equilibrium entropy is the entropy of the accompanying equilibrium state. It must be observed that $\mathbf{q}$ is not necessarily related to the presence of internal variables: a heat flux may be present in an ideal monatomic gases which does not contain any internal variable at all. However, for more general systems, $\mathbf{q}$ may originate from several contributions, some coming from the molecular translational motion and others coming from internal degrees of freedom or internal variables. In that respect, EIT is more general than internal variable theories.

It is also interesting to compare the expressions for the absolute temperature defined in the space of the physical state and in the space of the accompanying state; they are given, respectively, by [12]

$$\theta^{-1} = (\partial S_{\mathrm{phys}}(U, \mathbf{q})/\partial U)_q, \qquad T^{-1} = (\partial S_{\mathrm{eq}}(U)/\partial U) \tag{6}$$

The main difference is that the physical θ is a function of $\mathbf{q}$, while the "accompanying" T depends only on the internal energy U. We refer the reader interested in this topic to Ref. 17.

The aim of the next sections is to make as clear as possible the differences between the entropy in the physical space and the entropy in the accompanying equilibrium space.

3. LOCAL-EQUILIBRIUM THEORY

To be the most comprehensible, we address our attention to one of the simplest processes in thermodynamics: heat transfer between two rigid bodies at different temperatures. Initially, the two bodies are separated by an adiabatic and rigid wall. If at a given moment, only the adiabatic constraint is removed, heat will flow from one body to the other without either work performed or mass carried. In this section, the analysis is restricted to discontinuous systems, but it can easily be generalized to continuous media. We successively analyze the heat transfer problem in the framework of the classical and the extended descriptions of nonequilibrium thermodynamics.

Let us start with the *local-equilibrium formulation*. Consider an isolated system composed of two bodies (subsystems) at temperatures T_1 and T_2 $(< T_1)$, respectively. Each subsystem supposed isolated is in internal (local) equilibrium, which means that the internal temperature changes are negligible compared to the temperature difference $T_1 - T_2$ and that the only nonequilibrium region is the exchange wall. In virtue of the local-equilibrium hypothesis, the entropy S of the total system is the sum $S_1 + S_2$ of the entropies of each subsystem with S_1 and S_2 functions, respectively, of the internal energies U_1 and U_2 of subsystems 1 and 2 even during the heat transfer process: $S = S(U_1, U_2) = S_1(U_1) + S_2(U_2)$. When the adiabatic wall separating the two subsystems is replaced by a diathermal one, the time-rate variation of entropy of the total system is

$$\frac{dS}{dt} = \frac{dS_1}{dt} + \frac{dS_2}{dt} = T_1^{-1}\frac{dU_1}{dt} + T_2^{-1}\frac{dU_2}{dt} \tag{7}$$

Since the total system is isolated, one has $dU_1 + dU_2 = 0$, and from the first law of thermodynamics,

$$\frac{dU_1}{dt} = -\frac{dU_2}{dt} = -\dot{Q} \tag{8}$$

where $\dot{Q}$ is the amount of heat exchanged between subsystem 1 and subsystem 2 per unit time. In fact, $\dot{Q}$ is also the heat flux integrated over the surface separating the two bodies and can be related to the heat flux vector $\mathbf{q}$ by

$$\dot{Q} = -\int \mathbf{q} \cdot \mathbf{n} \, dA \tag{9}$$

where A is the bounding surface with unit normal $\mathbf{n}$ pointing outward from the system. By convention, energy input will be positive and energy release negative.

For an isolated system, Eq. (7) represents the rate of entropy produced inside the system; in virtue of Eq. (8), it can be written as

$$\frac{dS}{dt} = -(T_1^{-1} - T_2^{-1})\,\dot{Q} \tag{10}$$

which, according to the usual formulation of the second law, is nonnegative. This implies that the integrated heat flux $\dot{Q} > 0$ and, therefore, heat can flow only from the region of highest temperature to the region of lowest temperature, which is the original Clausius formulation of the second law.

The simplest hypothesis ensuring the positiveness of Eq. (10) is to assume that the heat flux $\dot{Q}$ is proportional to the driving force $(T_1^{-1} - T_2^{-1})$, so that

$$\dot{Q} = -K(T_1^{-1} - T_2^{-1}) \tag{11}$$

with K a positive coefficient. If the temperature difference is small, one may linearize this relation and give it the usual form

$$\dot{Q} = K'(T_1 - T_2) \tag{12}$$

with $K' = KT^{-2}$ assumed to be a constant and T an intermediate temperature between T_1 and T_2; Eqs. (11) and (12) are generally referred to as Fourier's law.

In the course of time, the evolution equation for the temperature of each subsystem is easily found by recalling that $dU_1 = C_1\, dT_1$ and $dU_2 = C_2\, dT_2$, with C_1 and C_2 the heat capacities of the respective subsystems. Combining this result with Eq. (8), it is found that the temperature difference $\varepsilon = T_1 - T_2$ varies as

$$\frac{d\varepsilon}{dt} = -\dot{Q} C_{\text{eff}}^{-1} \tag{13}$$

with $C_{\text{eff}}^{-1} = C_1^{-1} + C_2^{-1}$. When Eq. (12) is introduced into Eq. (13), one finds

$$\frac{d\varepsilon}{dt} = -K''\varepsilon \tag{14}$$

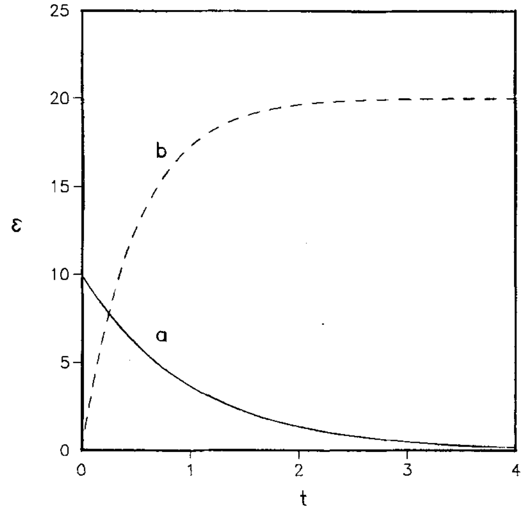

Fig. 2. Time evolution of the temperature difference ε calculated from expression $\varepsilon = \varepsilon_0 \exp(-K''t)$ (curve a) and time evolution of the corresponding local-equilibrium entropy S as given by Eq. (8) (curve b). Time is expressed in terms of $1/K''$, while $\varepsilon_0 = 10$ and $T^{-2}K' = 0.4$.

with $K'' = K'C_{\text{eff}}^{-1}$. Thus, ε decays exponentially like $\varepsilon = \varepsilon_0 \exp[-K''t]$, and after an infinite lapse of time the temperature inside the system is uniformized. In view of Eqs. (10) and (13) the rate of evolution of entropy may be written in terms of the temperature difference ε as

$$\frac{dS}{dt} = -T^{-2}\frac{K'}{K''}\varepsilon\frac{d\varepsilon}{dt} \tag{15}$$

It is thus seen that the entropy is a monotonically increasing function of time. The evolution of ε and of S is presented in Fig. 2.

4. HEAT CONDUCTION WITH INERTIAL EFFECTS

So far with the classical theory. Consider now the more general situation in which heat transfer is not described by a Fourier law [Eq. (11)] but, rather, by

$$\tau\frac{d\dot{Q}}{dt} + \dot{Q} = -K(T_1^{-1} - T_2^{-1}) \tag{16}$$

where τ is the positive relaxation time of the heat flux $\dot{Q}$. The generalization of Eq. (16) to continuous media is the Vernotte–Cattaneo equation (4). Equation (16) has several motivations. Fourier's law leads to infinite speed of propagation of thermal signals, whereas the Vernotte–Cattaneo equation predicts finite speed of propagation. From a practical point of view, this is not an important drawback and Fourier's equation is known to provide a very good description of thermal phenomena in most circumstances. Nevertheless, it must be kept in mind that Fourier's law is an approximation which is not valid at high frequencies. Equation (16) is the simplest way to incorporate high-frequency effects. More general descriptions including such effects are provided by the memory-function formalism: Eq. (16) corresponds simply to an exponential memory function [12].

The interest in high-frequency phenomena in condensed matter has been fostered by light-scattering experiments in gases, neutron scattering in liquids and solids, and numerical simulations of molecular dynamics. A wide field of research known as generalized hydrodynamics [18] is presently concerned with the study of such phenomena. High-frequency effects in heat conduction may be of interest for interpreting explosions, laser-induced nuclear fusion, or fast collapse of supernovae. More particularly, Eq. (16) and some generalizations have proven useful for describing heat waves in solids at low temperatures [19]. Note that an indiscriminate use of the Vernotte–Cattaneo equation is not possible in any circumstance, because it does not preclude negative absolute temperatures. However, in practice, both τ and K depend on the temperature and a nonlinear analysis should be taken into account.

It is legitimate to ask for the implications of Eq. (16) on the formulation of the second law. After combining Eqs. (13) and (16), one finds for the evolution of the temperature difference ε

$$\tau \frac{d^2\varepsilon}{dt^2} + \frac{d\varepsilon}{dt} + K''\varepsilon = 0 \tag{17}$$

This equation is similar to the equation of motion of a damped pendulum. The decay is not always exponential but may exhibit an oscillatory behavior (Fig. 3), when the condition $4\tau K'' > 1$ is satisfied. In continuous systems, the exponential decay would correspond to heat diffusion perturbation, whereas an oscillation in ε would correspond to a propagating heat wave.

It is interesting to examine the behavior of the entropy S as a function of time in the case of an oscillatory decay of ε. According to Eq. (15), S behaves as a nonmonotonic function as represented by curve b in Fig. 3.

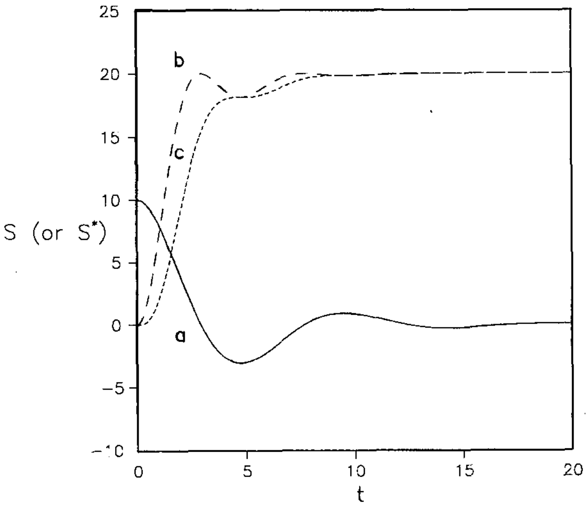

Fig. 3. Evolution of the temperature difference ε (curve a), the local-equilibrium entropy $S[U_1(t), U_2(t)]$ (curve b), and the generalized entropy $S^*[U_1(t), U_2(t), \dot{Q}(t)]$ (curve c) as a function of time during the oscillatory approach to equilibrium; curve c has been calculated for $\tau = 2/K''$. Note the monotonical increase in S^* compared with the nonmonotonical increase in S.

A most interesting situation is now displayed. Whereas the Clausius statement that the final equilibrium entropy is higher than the initial equilibrium entropy is still satisfied, in contrast, the local-equilibrium entropy is no longer a monotonically increasing function of time. In virtue of the local-equilibrium hypothesis, the evolution Eq. (16) should therefore be rejected. However, such an equation is confirmed experimentally, as it has been mentioned earlier. We thus remain confronted with the fundamental problems of the definition of entropy and the formulation of the second law in nonequilibrium situations.

In that respect, two questions arise. First, is the second law, as formulated in most textbooks, able to cope with the temporal evolution of processes? Second, does an expression of the nonequilibrium entropy compatible with the transport equation [Eq. (16)] exist?

5. EXTENDED IRREVERSIBLE THERMODYNAMICS DESCRIPTION

Let us discuss the answers provided by extended irreversible thermodynamics. In this formalism the heat flux $\dot{Q}$ is considered as an independent variable and is included among the set of independent variables appearing in the expression of the entropy. The proposed form of the generalized entropy in extended irreversible thermodynamics is therefore $S^*(U_1, U_2, \dot{Q})$, wherein an asterisk refers to the generalized entropy. The rate of variation of S^* is

$$\frac{dS^*}{dt} = T_1^{-1}\frac{dU_1}{dt} + T_2^{-1}\frac{dU_2}{dt} - \alpha(\dot{Q})\frac{d\dot{Q}}{dt} \tag{18}$$

where $-\alpha(\dot{Q})$, an undetermined function of $\dot{Q}$, is defined as the derivative of S^* with respect to $\dot{Q}$. For simplicity, $\alpha(\dot{Q})$ is assumed linear in $\dot{Q}$: $\alpha(\dot{Q}) = a\dot{Q}$, where a is a constant. After using the law of conservation of energy expressed by Eq. (8), Eq. (18) becomes

$$\frac{dS^*}{dt} = -(T_1^{-1} - T_2^{-1})\,\dot{Q} - a\dot{Q}\frac{d\dot{Q}}{dt} \tag{19}$$

For small temperature differences, dS^*/dt takes the form

$$\frac{dS^*}{dt} = \left(T^{-2}\varepsilon - a\frac{d\dot{Q}}{dt}\right)\dot{Q} \tag{20}$$

The simplest way to ensure the positiveness of the entropy production dS^*/dt is to assume the linear relation

$$\dot{Q} = K\left(T^{-2}\varepsilon - a\frac{d\dot{Q}}{dt}\right) \tag{21}$$

with K a positive constant. In the steady state, $d\dot{Q}/dt = 0$ and Eq. (21) reduces to Fourier's law given by Eq. (12). A further comparison of Eq. (21) with the Vernotte–Cattaneo equation [Eq. (16)] indicates that $aK = \tau$. Collecting these results, one obtains

$$\frac{dS^*}{dt} = -(T_1^{-1} - T_2^{-1})\,\dot{Q} - \left(\frac{\tau}{K}\right)\dot{Q}\,\frac{d\dot{Q}}{dt} \tag{22}$$

or, in an integrated form,

$$S^*(U_1, U_2, \dot{Q}) = S_1(U_1) + S_2(U_2) - \left(\frac{\tau}{2K}\right)\dot{Q}^2 \tag{23}$$

Observe that in the limiting case $\tau = 0$, the above expression reduces to the local-equilibrium entropy. The last term in the right-hand side of Eq. (23) may be viewed as expressing the interaction between subsystem 1 and subsystem 2. The minus sign in the nonclassical term in Eq. (23) is introduced to ensure that S^* is maximum at equilibrium, i.e., for $\dot{Q} = 0$.

According to Eqs. (20) and (21), the time variation of S^* may simply be written as

$$\frac{dS^*}{dt} = K^{-1}\dot{Q}^2 = K^{-1}C_{\text{eff}}^2\left(\frac{d\varepsilon}{dt}\right)^2 = \frac{T^{-2}K'}{K''^2}\left(\frac{d\varepsilon}{dt}\right)^2 \geqslant 0 \tag{24}$$

This expression is either positive or zero but never negative.

6. CONCLUDING REMARKS

The evolution of $S^*[U_1(t), U_2(t), \dot{Q}(t)]$ as a function of time is presented in Fig. 3 (curve c) for the exponential approach to equilibrium; it is compared with the time evolution of the classical local-equilibrium entropy (curve b).

It is seen that the entropy of extended irreversible thermodynamics never exceeds the corresponding values of the local-equilibrium entropy, but more important and in contrast with the latter, it monotonically increases in the course of time. This result suggests to define a rather general nonequilibrium entropy which is not the local-equilibrium entropy but which reduces to it in equilibrium. The presence of the fluxes influences not only the expression of entropy but also the intensive parameters, such as temperature and pressure, defined as derivatives of entropy with respect to the extensive internal energy and volume respectively.

Clearly, local-equilibrium thermodynamics is too restrictive as it leads to the rejection of some evolution equations such as the Vernotte–Cattaneo expression which are experimentally observed. This has motivated our attitude to include the dynamics of the system into the definition of a nonequilibrium entropy.

It may thus be concluded that, as asserted by Clausius in 1865, it is possible to formulate the second law in terms of a macroscopic entropy whose evolution in the course of time is never negative.

It is worth noting that this is not equivalent to the first Clausius formulation of the second law, expressing the impossibility of a spontaneous heat flow from a cold to a hot body. It follows from Eq. (16) that, due to inertial effects, a heat flux may run spontaneously from a cold to a hot region during relatively short instants of time. Of course, the total amount of heat exchanged during the whole process will indeed proceed from the initially hot toward the initially cold body, but this result cannot be interpolated to any interval of time.

Extended irreversible thermodynamics has been applied to a wide variety of topics such as hydrodynamics, electromagnetism, rheology, cosmology, and biophysics. The basic ideas underlying EIT have been confirmed by microscopic theories such as the kinetic theory of gases and the projection-operator method in nonequilibrium statistical mechanics [12]. Extended irreversible thermodynamics is not limited to simple relaxational equations such as Eq. (16) but can cope with a much wider range of evolution equations involving several relaxation schemes and nonlinearities [12].

Finally, it is pertinent to mention that, from a phenomenological point of view, the existence of nonequilibrium processes beyond the local-equilibrium regime is a fact of experience that legitimates an approach like that of EIT. By no means does it imply that this formalism constitutes a universal and unique receipt for describing irreversible processes, but in our opinion, it provides a promising step toward the formulation of a unified nonequilibrium thermodynamics.

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