

## **On the Foundations of Extended Irreversible Thermodynamics**

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A theory of macroscopic systems which takes as independent variables the slow (conserved) ones plus the fast dissipative fluxes is carefully analyzed at three levels of description: macroscopic (thermodynamic), microscopic (projection operators) and mesoscopic (fluctuation theory). Such a description is compared with the memory function approach based only on the conserved variables. We find that the first theory is richer and wider than the second one, and some misunderstandings in this connection are clarified and discussed.

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**KEY WORDS:** Extended irreversible thermodynamics; kinetic theory; fluctuations; memory functions; projection operators; flux relaxation.

### **1. INTRODUCTION**

While linear irreversible thermodynamics (LIT) has been undeniably useful for the analysis of many phenomena in nonequilibrium macroscopic systems, and in spite that it is a consistent and elegant formalism, it presents some very well-known limitations. The first one is that in LIT the response of the system is instantaneous; in fact, the systems have a certain inertia which produces a delay or retardation in their response to any driving force. The drastic simplification implied by the ignorance of such effects renders LIT inapplicable to high frequency phenomena. On the other side, LIT neglects nonlinear terms in the constitutive equations. This is known to be an excessive simplification from the experimental point of view.

The usual way to avoid the first limitation of LIT has been to restore to the memory function formalism, directly confirmed from a microscopic basis

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in the framework of linear-response theory. In this formalism the system is described locally by the conserved variables, whose evolution equations (conservation equations) are completed by constitutive equations for the fluxes with memory functions instead of simple phenomenological coefficients.

Recently, a phenomenological framework has been proposed, which includes in the set of independent variables the dissipative fluxes. The macroscopic version of this formalism constitutes what is called extended irreversible thermodynamics (EIT). In this theory, the evolution equations of the fluxes play the role of constitutive equations of the system. If a contraction of this level of description is carried out, by projecting the results onto the space of the conserved variables, the results of the memory function approach are recovered, with the additional advantage that the fast fluctuations of the fluxes provide in an immediate way the stochastic noise appearing in the stochastic version of the memory functions approach.

The underlying idea behind the attempts to describe situations which do not fit into the scheme of classical LIT is therefore to enlarge the space of state variables required to describe the system. For the sake of simplicity and because the basic physics involved is essentially the same for more complicated systems, we will consider as a prototype the case of a simple monoatomic fluid. In this case, one adds to the five conserved densities (local mean density  $\rho(\mathbf{r}, t)$ , local hydrodynamic velocity  $\mathbf{u}(\mathbf{r}, t)$  and local energy density  $e(\mathbf{r}, t)$ , the dissipative fluxes (heat flux  $\mathbf{q}$ , scalar viscous pressure  $\tau$ , and viscous pressure tensor  $\hat{\tau}$ , which is assumed to be a symmetric traceless tensor).

These lines of thought go back to Maxwell,<sup>(1)</sup> who in 1897 realized that in a viscous body the state of stress will disappear at a rate which depends on the value of the state of stress and on the nature of the body. In the language of LIT this implies that the Navier–Newton constitutive equation is no longer valid, but must be substituted by a relaxation equation of the type

$$\frac{d\hat{\tau}}{dt} = -\frac{1}{\theta_2} [\hat{\tau} + 2\eta(\text{grad } \mathbf{u})^s + \dots] \quad (1.1)$$

where  $\theta_2$  is the relaxation time measuring the way in which  $\hat{\tau}$  gradually disappears.

Later on it was realized that equations of this type are very useful for solving the already mentioned inconsistency which appears in LIT, namely, that of instantaneous response, which leads for instance to parabolic partial differential equations implying an infinite velocity for the propagation of thermal and viscous disturbances. This fact was first noticed by Grad,<sup>(2)</sup> who further developed the kinetic method devised by Maxwell, considering as

independent variables the successive moments of the microscopic distribution function. The first 13 moments are indeed the five conserved variables plus the fast relaxing dissipative fluxes. The idea was later pursued by Cattaneo,<sup>(3)</sup> Vernotte,<sup>(4)</sup> and others,<sup>(5,6)</sup> and equations of the kind of Eq. (1) are now known as Maxwell–Cattaneo–Vernotte equations. In 1967 Müller<sup>(7)</sup> proposed that one way of generalizing LIT was to modify the local equilibrium assumption by introducing an entropy dependent on both the classical variables and dissipative fluxes. This proposal has been taken and refined by a large number of workers<sup>(8)</sup> and has given rise to the present form of EIT.

The aim of this paper is to clarify firstly, the physical nature of the theory, and secondly, some misunderstandings which have arisen with respect to EIT. On the one side, it is often true that the microscopic approaches of nonequilibrium statistical mechanics do not take account of their macroscopic thermodynamic counterpart. Usually neither the entropy nor the restrictions imposed by the second law are even mentioned, so that one ignores completely whether the results of the different microscopic approximations are consistent with well-established results. On the other hand, the microscopic theories have been too rigidly tied to the local equilibrium hypothesis (LIT) or have been based on heavy mathematical artifacts without a sufficient physical interpretation (rational thermodynamics). This has motivated a number of prejudices against EIT both from the standard macroscopic and microscopic point of view.

The plan of the paper is as follows: in the next section we present briefly EIT from a macroscopic point of view. In Section 3, a microscopic approach is undertaken on the basis of projection operators dynamics. In Section 4, a mesoscopic approach is underlined based on the theory of thermodynamic fluctuations. Then, in Section 5 we introduce a general definition of non-equilibrium entropy, which in some special cases reduces to the standard version of nonequilibrium entropy used in EIT, and which allows to generalize the previous results concerning fluctuations. We conclude in Section 6 by making some pertinent physical implications of the theory.

## 2. EXTENDED IRREVERSIBLE THERMODYNAMICS

In this section we present a short survey of the macroscopic aspects of EIT in hydrodynamic systems. As has already been said, the space of state variables, which we shall denote by  $G$ , consists of the union of two subsets, the subset  $\mathcal{C}$  formed by the conserved local densities  $(\rho, \mathbf{u}, e)$ , and the subset  $\mathcal{R}$  of the the dissipative fluxes, or nonconserved variables  $(\mathbf{q}, \tau, \hat{\mathbf{v}})$ . The choice of the dissipative fluxes as additional variables is in a certain way obvious, since they appear in the conservation equations describing the

evolution of the conserved variables. Other nonequilibrium variables could in principle be taken, but the use of this set is in many respects more convenient than other possible choices.

The second assumption of EIT is that the entropy density of the system is now a function of all variables in  $G = \mathcal{E} \cup \mathcal{R}$ , i.e., ( $v = \rho^{-1}$ ),

$$S = S(e, v, \mathbf{q}, \tau, \overset{\circ}{\boldsymbol{\tau}}) \quad (2.1)$$

The velocity has not been included since we assume that a global uniform motion of the system has no effect on its macroscopic properties. The time evolution of the entropy density is governed by a generalized Gibbs equation (which replaces the local equilibrium assumption of LIT) of the form

$$T \frac{dS}{dt} = \frac{de}{dt} + p \frac{dv}{dt} + v \boldsymbol{\alpha}_1 \cdot \frac{d\mathbf{q}}{dt} + v \alpha_0 \frac{d\tau}{dt} + v \overset{\circ}{\boldsymbol{\alpha}}_2 : \frac{d\overset{\circ}{\boldsymbol{\tau}}}{dt} \quad (2.2)$$

where the quantities  $T$ ,  $p$ ,  $\boldsymbol{\alpha}_1$ ,  $\alpha_0$ , and  $\overset{\circ}{\boldsymbol{\alpha}}_2$  have been defined as the corresponding partial derivatives of  $S$ . Clearly,  $T$  and  $p$  are generalizations of the local equilibrium temperature and pressure in the full  $G$  space, but here we will neglect the nonequilibrium corrections, which are of second order in the nonconserved variables. The quantities  $\boldsymbol{\alpha}_1$ ,  $\alpha_0$ , and  $\overset{\circ}{\boldsymbol{\alpha}}_2$  are obtained formally as the most general isotropic tensors of rank one, zero, and two, respectively, that one can construct with  $e$ ,  $v$ , and the nonconserved variables. Here, we will restrict ourselves to the first order in these variables, so that

$$\boldsymbol{\alpha}_1 = \alpha_{10} \mathbf{q}, \quad \alpha_0 = \alpha_{00} \tau, \quad \overset{\circ}{\boldsymbol{\alpha}}_2 = \alpha_{20} \overset{\circ}{\boldsymbol{\tau}} \quad (2.3)$$

where  $\alpha_{10}$ ,  $\alpha_{00}$ , and  $\alpha_{20}$  depend only on  $e$  and  $v$ .

The time evolution equations for  $e$  and  $v$  are the well-known energy and mass conservation equations. In order to obtain the equations that govern the time dependence of  $\mathbf{q}$ ,  $\tau$ , and  $\overset{\circ}{\boldsymbol{\tau}}$  one recasts Eq. (2.2) into the form of an entropy balance equation. For this purpose it is necessary to define a generalized entropy flux vector  $\mathbf{J}_s$  which is the most general vector that can be constructed from  $e$ ,  $v$ , and the dissipative fluxes. Up to second order in the nonconserved variables, one has

$$\mathbf{J}_s = \frac{1}{T} \mathbf{q} + \beta_{01} \tau \mathbf{q} + \beta_{10} \overset{\circ}{\boldsymbol{\tau}} \cdot \mathbf{q} + \dots \quad (2.4)$$

where  $\beta_{01}$  and  $\beta_{10}$  are phenomenological coefficients which depend only on the slow variables  $e$  and  $v$ . From Eqs. (2.2), (2.3), (2.4) and the balance

equations for  $e$  and  $v$  one obtains an expression for the entropy production  $\sigma$ , defined as

$$\rho \dot{s} + \text{div } \mathbf{J}_s = \sigma \tag{2.5}$$

The entropy production turns out to be given by<sup>(9)</sup>

$$\begin{aligned} \sigma = \tau & \left[ \beta_{01} \text{div } \mathbf{q} - T^{-1} \text{div } \mathbf{u} + T^{-1} \alpha_{00} \frac{d\tau}{dt} \right] \\ & + \mathbf{q} \cdot \left[ \text{grad } T^{-1} + T^{-1} \alpha_{10} \frac{d\mathbf{q}}{dt} + \beta_{01} \text{grad } \tau + \beta_{10} \text{div } \dot{\boldsymbol{\tau}} \right] \\ & + \dot{\boldsymbol{\tau}} : \left[ -T^{-1} (\text{grad } \mathbf{u})^s + T^{-1} \alpha_{21} \frac{d\dot{\boldsymbol{\tau}}}{dt} + \beta_{10} (\text{grad } \mathbf{q})^s \right] \end{aligned} \tag{2.6}$$

where we have assumed that the coefficients  $\beta_{10}$  and  $\beta_{01}$  are constant, for the sake of simplicity. The extension to nonconstant coefficients is straightforward but tedious.

Equation (2.6) has the structure of a sum of products of the nonconserved variables and some expressions which contain the unknown time derivatives of the fluxes, among other quantities. Our aim is to obtain evolution equations for the time derivatives of the fluxes in terms of the variables of  $G$  and their spatial derivatives. Indeed,  $\sigma$  may be written as

$$\sigma = X_0 \tau + \mathbf{X}_1 \cdot \mathbf{q} + \mathbf{X}_2 : \dot{\boldsymbol{\tau}} \tag{2.7}$$

where  $X_0$ ,  $\mathbf{X}_1$ , and  $\mathbf{X}_2$  contain, respectively,  $\tau$ ,  $\mathbf{q}$ , and  $\dot{\boldsymbol{\tau}}$ . Although one can call  $X_0$ ,  $\mathbf{X}_1$ , and  $\mathbf{X}_2$  generalized thermodynamic “forces,” the notion of fluxes and forces is somewhat lost since both the conserved and nonconserved variables have the same status as independent variables. Here we will develop the quantities  $X_i$  in terms of the nonconserved variables up to second order:

$$\begin{aligned} X_0 &= \mu_{01} \tau + \mu_{02} \tau^2 + \mu_{03} \mathbf{q} \cdot \mathbf{q} + \mu_{04} \dot{\boldsymbol{\tau}} : \dot{\boldsymbol{\tau}} \\ \mathbf{X}_1 &= \mu_{01} \mathbf{q} + \mu_{11} \tau \mathbf{q} + \mu_{12} \mathbf{q} \cdot \dot{\boldsymbol{\tau}} \\ \mathbf{X}_2 &= \mu_{21} \dot{\boldsymbol{\tau}} + \mu_{22} (\dot{\boldsymbol{\tau}} \cdot \dot{\boldsymbol{\tau}})^s + \mu_{23} (\mathbf{q} \dot{\boldsymbol{\tau}})^s + \mu_{24} \tau \dot{\boldsymbol{\tau}} \end{aligned} \tag{2.8}$$

When Eqs. (2.8) are introduced into Eq. (2.7), the restriction  $\sigma > 0$  implies that  $\mu_{01} > 0$ ,  $\mu_{10} > 0$ , and  $\mu_{21} > 0$ , and no conclusions can be reached with respect to the other phenomenological coefficients  $\mu_{ij}$ , because in Eq. (2.8) we are omitting higher-order nonlinear terms. The coefficients  $\mu_{ij}$  are assumed to be functions of  $e$  and  $v$  only.

Taking into account the expressions of the  $X$ 's and omitting for simplicity the nonlinear terms in Eqs. (2.8) we obtain for the evolution equations of the fluxes

$$\begin{aligned} \frac{d\tau}{dt} &= \frac{T}{\alpha_{00}} [\mu_{01}\tau + T^{-1} \operatorname{div} \mathbf{u} - \beta_{01} \operatorname{div} \mathbf{q}] \\ \frac{d\mathbf{q}}{dt} &= \frac{T}{\alpha_{10}} [\mu_{01}\mathbf{q} + T^{-2} \operatorname{grad} T - \beta_{01} \operatorname{grad} \tau - \beta_{01} \operatorname{div} \dot{\mathbf{i}}] \quad (2.9) \\ \frac{d\dot{\mathbf{i}}}{dt} &= \frac{T}{\alpha_{21}} [\mu_{21}\dot{\mathbf{i}} + T^{-1}(\operatorname{grad} \mathbf{u})^s - \beta_{10}(\operatorname{grad} \mathbf{q})^s] \end{aligned}$$

In the first-order approximation, in the stationary state, and neglecting the space derivatives of the fluxes, Eqs. (2.9) must reduce to the classical Navier–Newton and Fourier laws. This implies that  $\mu_{01} = (\zeta T)^{-1}$ ,  $\mu_{10} = (\lambda T^2)^{-1}$ ,  $\mu_{21} = (2\eta T)^{-1}$ , with  $\zeta$ ,  $\eta$ , and  $\lambda$  being the bulk viscosity, shear viscosity, and thermal conductivity, respectively. When the space derivatives of the fluxes are neglected, Eqs. (2.9) must reduce to the relaxational Maxwell–Cattaneo–Vernotte equations, so that  $\alpha_{00} = -\theta_0/\zeta$ ,  $\alpha_{10} = -\theta_1/\lambda T$ , and  $\alpha_{21} = -\theta_2/2\eta$ . In this way we have obtained a physical interpretation of the parameters appearing in the generalized Gibbs equation and in the constitutive equations. Note that the restrictions of the second law imply, as usual, that  $\eta > 0$ ,  $\zeta > 0$ , and  $\lambda > 0$ , and the requirement that  $S$  must be a maximum in equilibrium implies that  $\theta_1 > 0$ ,  $\theta_2 > 0$ , and  $\theta_0 > 0$ . It is also worthwhile to stress the validity of reciprocal-like relations in the cross terms in Eq. (2.9), related with the coefficients  $\beta_{01}$  and  $\beta_{10}$ . These coefficients have an obvious physical meaning, but do not have classical counterparts comparable to the usual first-order coefficients.

It must be emphasized that our restriction to a linear theory is only for the sake of avoiding long and cumbersome expressions, but that is not essential. Equations (2.9) tell us how the fast variables affect the conserved variables in a coupling which in general turns out to be very complicated. The relaxation times of these equations depend on the conserved variables and the nature of the system, in much the same way as in the theory of chemical kinetics.<sup>(10)</sup> Also, the full evolution equations for the fluxes, i.e., Eqs. (2.9) plus all the omitted nonlinear terms in Eq. (2.8), have the same structure as the time evolution equations for higher moments of the distribution function obtained in Grad’s method of solution of the Boltzmann equation.<sup>(2)</sup> We remark that when the relaxation times vanish or one happens to be in a nonequilibrium steady state in which the time derivatives of  $\mathbf{q}$ ,  $\tau$ , and  $\dot{\mathbf{i}}$  are zero, the constitutive laws to every order in the gradients of the conserved variables are recovered, the local equilibrium assumption holds and we restrict to the subspace  $\mathcal{E}$  to describe the state of the system.<sup>(11)</sup> Note, finally, that nonlocal terms implying space derivatives of the fluxes could have been included in Eqs. (2.8). These considerations and refinements

are omitted in this very simple presentation of the main points of the macroscopic development, but will be discussed elsewhere.<sup>(12)</sup>

### 3. MICROSCOPIC APPROACHES

In this section we shall analyze the efforts that have been made to derive the phenomenological assumptions of EIT from a more microscopic basis. There are essentially two lines of thought, one which is due to Grad<sup>(2)</sup> and is based on the kinetic theoretical method provided by the Boltzmann equation for a dilute monatomic gas, and another one due to Nettleton,<sup>(13)</sup> which is based on the more general kinetic approach set forth by Zwanzig<sup>(14)</sup> applying projection operator techniques to the Liouville equation.

Grad's theory is the pioneering work giving a more microscopic basis for EIT. Since it was recently discussed at length<sup>(15)</sup> we shall content ourselves with pointing out only what the main ideas are. Recognizing that there are situations in which the state of a system, namely, a fluid, requires more information for its description than the one provided by the locally conserved densities, the Boltzmann equation is solved by using a method, referred to as the 13-moment method, in which the fluxes present in the gas are regarded as independent variables in the same way as it is done in the phenomenological theory. Thus one is able to describe the nonequilibrium state of the gas through a distribution function which depends on the conserved densities through a local Maxwellian distribution function and on the fast variables (fluxes) which appear in linear combinations with coefficients which involve the random velocities of the molecules and thermodynamic quantities. The nonconserved variables, i.e., the fluxes, obey relaxation-type equations whose relaxation times can be computed for specific models of intermolecular potentials. Furthermore the differential form for the extended entropy is identical to the one proposed in Section 2 [see Eq. (2.2)] and the unknown coefficients  $\alpha_{i0}$  ( $i = 0, 1, 2, \dots$ ) can be also computed from the molecular models. Thus, just as the Chapman-Enskog method for solving the Boltzmann equation provides for a kinetic theoretical justification of LIT, Grad's 13-moment method justifies the EIT. For further details about this theory the reader is urged to consult Ref. 15.

On the other hand, in a rather forgotten paper Nettleton<sup>(13)</sup> approached the problem of deriving a version of EIT using Zwanzig's projection operator technique<sup>(14)</sup> to derive exact kinetic equations from Liouville's equation. In his original approach, Zwanzig showed how one could recover Onsager's symmetry relationships from his general formalism when the set of dynamic phase space functions  $A_i(\Gamma)$ , whose ensemble averages define the corresponding set of macroscopic variables  $\{\alpha_i\}$ , contains only functions which are even with respect to time reversal. In his work Nettleton extends

this to include in the set  $A_i(I)$  also functions which *are* odd with respect to time reversal and specifies these functions by  $A_j$ . This implies that the corresponding set of observables are the  $\alpha_i$ 's and the  $\dot{\alpha}_i$ 's. It is that this point important to stress that this election lies within the Onsager-Machlup scheme of irreversible thermodynamics if one attempts to identify the  $\alpha$ 's with the observables associated to the locally conserved densities and other quasi-constants of the motion (the slow variables), and the  $\dot{\alpha}$ 's with the fluxes or non-conserved variables. The *essential* assumption introduced by Nettleton lies on the fact that whereas the distribution function for the numerical values of the even functions is taken to be a microcanonical one in phase space, the corresponding one for the odd functions is taken to be a Gaussian distribution.

Without going into any of the details of the derivation which is easily reconstructed from the original sources, the equations of motion for  $\dot{\alpha}_j = v_j$  and for  $\dot{v}_j = \dot{\alpha}_j$  are obtained and shown to be non-Markovian with a memory effect that constains essentially the exact dynamics of all those variables which are not in the set  $\{A_j, \dot{A}_j\}$ . The following step is to assume that this memory effects are either small or negligible in the time scales usually encountered in experimental situations and convert those non-Markovian equations in Markovian ones. When this is done the equations of motion reduce to their canonical form, namely,

$$\dot{\alpha}_j = \sum_{\nu=1}^n L_{j\nu} F_{\nu}^*, \quad j = 1, \dots, n \quad (3.1)$$

$$\dot{v}_j = \sum_{j=1}^n L_{\nu j}^{(3)} F_j + \sum_{\lambda=1}^n L_{\nu\lambda}^{(4)} F_{\lambda}^* \quad (3.2)$$

where

$$F_j = \frac{\partial S}{\partial \alpha_j}, \quad F_{\nu}^* = \frac{\partial S}{\partial \dot{\alpha}_{\nu}} \quad (3.3)$$

and  $S = k \ln W(\alpha, \dot{\alpha})$ . The function  $W$  corresponds to the phase space cell determined by the numerical values of  $\{A_j\}$  and  $\{\dot{A}_j\}$ . Further, it is also shown that

$$L_{\nu j}^{(3)} = -L_{j\nu}^{(3)}, \quad L_{\nu\lambda}^{(4)} = L_{\lambda\nu}^{(4)} \quad (3.4)$$

which are the Onsager-Casimir reciprocity relations.

In this way Nettleton provides a microscopic derivation of the full Onsager-Machlup version of linear irreversible thermodynamics. Since the rapidly varying variables  $\{\dot{\alpha}\}$  are included one would be tempted to identify this work as a microscopic basis for EIT. Indeed, this identification has been



made by Keizer<sup>(16)</sup> in a recent paper in which he attempts to relate fluctuating irreversible thermodynamics with the extended theories. Comparison of Eqs. (5) and (6) with Eqs. (13) and (14) of Ref. 16 clearly indicates that the former ones are just a very particular case of the latter when the memory function can be mimicked by an exponential function. However, in neither case one can conclude that the phenomenological basis of EIT conceived as an enlargement of the space of state variables by adding to it nonconserved variables has been explained. Concretely, the Grad scheme carried over in a general way by starting with Liouville's equation is still pending. We would like to complete this section by pointing out some of the difficulties encountered in carrying out this program.

One may begin by considering a set of macroscopic variables  $\{\alpha_j(t)\}$  in which both conserved (or slow) and nonconserved (or fast) variables are included. These variables may be expressed in terms of the Onsager-like quantities according to the definition<sup>(17)</sup>

$$\alpha_j(t) = \int d\mathbf{b} \overline{a_j(t)}^b g(\mathbf{b}, 0) \tag{3.5}$$

where  $\overline{a_j(t)}^b$  is the average value of the "number" associated with a measurement of the corresponding dynamic observable  $A_j(I)$ , weighted with the conditional probability  $P(\mathbf{a}, t/\mathbf{b})$ .  $g(\mathbf{b}, 0)$  is the distribution function of the set of numbers  $\{\mathbf{b}\}$  associated with measurements of the set  $\{\mathbf{A}\}$  at time  $t = 0$ . The time evolution equation for the  $\alpha$ 's is shown to be<sup>(17)</sup>

$$\frac{d\alpha(t)}{dt} = \int_0^t ds \int d\mathbf{a} K(\mathbf{a}, s) g_1(\mathbf{a}, t - s) \tag{3.6}$$

where

$$g_1(\mathbf{a}, t) = \int d\Gamma \rho(\Gamma) G(\mathbf{a}, t) \tag{3.7}$$

and  $G(\mathbf{a}, t) = \delta(\mathbf{A}(\Gamma') - \mathbf{a})$  is the characteristic function for the hypercell in phase space at time  $t$ .  $K(\mathbf{a}, s)$  is a rather complicated operator containing the full microscopic dynamics of the state variables  $\mathbf{A}$  whose explicit form will not be given here but may be found in Ref. 17 and 18.

The crucial question is how can one derive a well-established phenomenology from these exact but rather complicated expressions. Although no completely satisfactory answer is yet available a preliminary analysis has shown<sup>(18)</sup> that under the following assumptions, namely, (a) that a process is slow, ( $\dot{A}_i(I) \sim \delta < 1$ ), (b) only those terms which are linear in

the  $\alpha$ 's are extracted from  $K(\mathbf{a}, s)$  one can transform Eq. (3.6) into a linear non-Markovian regression equation, namely,

$$\frac{d\alpha(t)}{dt} = - \int_0^t ds \mathbf{M}(t) \cdot \alpha(t-s) \quad (3.8)$$

where  $\mathbf{M}(t)$  is precisely the matrix of kinetic coefficients first proposed by Zwanzig,<sup>(19)</sup>

$$\mathbf{M}(t) = \left\{ \delta^2 \lim_{\delta \rightarrow 0} \frac{1}{\delta^2} \langle \dot{\mathbf{A}}(I, t) \dot{\mathbf{A}}(I, 0) \rangle \right\} \cdot \mathbf{C}^{-1}(0) \quad (3.9)$$

where

$$\mathbf{C}(0) = \langle \mathbf{A}(I, 0) \mathbf{A}(I, 0) \rangle$$

and  $\langle \rangle$  denotes an equilibrium average. In the Markovian limit one thus recovers LIT. In Eq. (3.8) the  $\alpha$ 's are even and *slow* variables. In order to extract from this formalism the time evolution equations for both slow and fast  $\alpha$ 's one has to find a way of decomposing the function  $K(\mathbf{a}, s)$  into the relevant part for this purpose and one irrelevant. But this analysis has never been performed and represents the main difficulty in generalizing the Grad's scheme dealing with the Boltzmann equation.

#### 4. FLUCTUATIONS IN EXTENDED IRREVERSIBLE THERMODYNAMICS

Up to now, the explicit expression for the entropy obtained in Section 2 has not been used. In fact, the entropy is neglected in many approaches of nonequilibrium statistical mechanics, which restrict their aim to the analysis of the constitutive equations for the fluxes.<sup>(20)</sup> In a macroscopic theory the entropy plays an important role because it restricts the possible forms of the constitutive equations, owing to the requirement of the second law. Furthermore, the entropy contains information on the fluctuations. In particular the entropy of EIT which includes the fluxes as independent variables, gives information on their fluctuations. This fact is usually neglected in microscopic theories and in macroscopic theories as well, where the classical entropy is of interest. The second moments of the fluctuations of the fluxes and the dissipative coefficients with the relaxation times may also be obtained from a macroscopic analysis based on the generalized entropy and on an immediate extension of the usual formalism of thermodynamic fluctuations. Such an analysis allows to reduce the number of independent parameters appearing in the macroscopic theory. Therefore, the interest in

fluctuations, both from a theoretical and practical point of view, is more than justified and constitutes an important part of EIT. In fact, it provides a mesoscopic approach, intermediate between the purely macroscopic on the Section 2, and the microscopic one of Section 3.

The fundamental idea in the analysis of equilibrium fluctuations in EIT is to use the second differential of the generalized entropy as a potential for the fluctuations of the variables in  $G$  space. In this way, one assumes that the probability of fluctuations is given by the Einstein–Smoluchowsky formula

$$W \sim \exp(\Delta S/k_B) \tag{4.1}$$

This method has been discussed in detail<sup>(21)</sup> and will not be pursued at length here, where we will restrict ourselves to a brief description of the main assumptions and results. In the fluctuations near the equilibrium state of an isolated system,  $\Delta S$  may be developed up to second order as  $\Delta S = (\delta S)^{eq} + \frac{1}{2}(\delta^2 S)^{eq}$  where  $(\delta S)^{eq} = 0$  and  $(\delta^2 S)^{eq} \leq 0$ , because the entropy is maximum in equilibrium. Here, we will use for  $S$  the generalized entropy of EIT, obtained in Section 2. In this approximation we have, therefore, the following Gaussian probability distribution function:

$$\begin{aligned}
 &W(\delta e, \delta v, \delta \mathbf{q}, \delta \tau, \delta \dot{\tau}) \\
 &\sim \exp \left\{ \frac{1}{2k_B} \left[ \frac{\partial^2 S}{\partial e^2} (\delta e)^2 + \frac{\partial^2 S}{\partial v^2} (\delta v)^2 + 2 \frac{\partial^2 S}{\partial e \partial v} \delta e \delta v \right. \right. \\
 &\quad \left. \left. - \frac{\theta_1 v}{\lambda T^2} \delta \mathbf{q} \cdot \delta \mathbf{q} - \frac{\theta_0 v}{\zeta T} (\delta \tau)^2 - \frac{\theta_2 v}{2\eta T} \delta \dot{\tau} : \delta \dot{\tau} \right] \right\} \tag{4.2}
 \end{aligned}$$

Note that the parameters  $\theta_1 v/\lambda T^2$ ,  $\theta_0 v/\zeta T$ , and  $\theta_2 v/2\eta T$  are considered to remain constant during the fluctuation, since the relaxation time of the conserved variables is much longer than that of the fast variables, so that it is reasonable to assume that their fluctuations are uncorrelated. The second moments are easily obtained from Eq.(4.2). While for the conserved variables the results are the classical ones, for the fast variables we obtain

$$\begin{aligned}
 \langle \delta q_i \delta q_j \rangle &= \frac{k_B \lambda T^2}{\theta_1 v} \delta_{ij} \\
 \langle \delta \tau \delta \tau \rangle &= \frac{k_B \zeta T}{\theta_0 v} \\
 \langle \delta \dot{\tau}_{ij} \delta \dot{\tau}_{kl} \rangle &= \frac{k_B \eta T}{\theta_2 v} \Delta_{ijkl}
 \end{aligned} \tag{4.3}$$

with

$$\Delta_{ijkl} = (\delta_{il}\delta_{jk} + \delta_{ik}\delta_{jl} - \frac{2}{3}\delta_{ij}\delta_{kl})$$

Equation (4.3) relates the coefficients  $\lambda$  and  $\theta_1$ ,  $\zeta$  and  $\theta_0$ , through the second moments of the fluctuations of the respective fluxes near equilibrium. In fact Eqs. (4.3) are a particular case of the Green–Kubo relations for the exponential decay of fluctuations of the fluxes as implied by the Maxwell–Cattaneo–Vernotte equations.<sup>(22)</sup>

In the present approach Eqs. (4.3) have the consequence of reducing the number of independent parameters. In this way, while in the macroscopic formalism of Eq. (2.9) there are eight independent parameters ( $\theta_0$ ,  $\theta_1$ ,  $\theta_2$ ,  $\zeta$ ,  $\lambda$ ,  $\eta$ ,  $\beta_{01}$ ,  $\beta_{10}$ ), in the mesoscopic level of the theory of fluctuations there are only five independent parameters ( $\theta_0$ ,  $\theta_1$ ,  $\theta_2$ ,  $\beta_{01}$ ,  $\beta_{10}$ ). In a purely microscopic theory, there would not be any independent parameters, because all of them are expressed as functions of the given interparticle potential. However, the microscopic description is explicitly feasible only in some simple cases, so that the intermediate level of fluctuations often constitutes a good approximation for practical purposes.

If the decay of fluctuations is described by the Maxwell–Cattaneo laws, one obtains for the two-time correlation function of the fluxes<sup>(21)</sup>

$$\begin{aligned} \langle \delta q_i(t) \delta q_j(t+t') \rangle &= \frac{k_B \lambda T^2}{\theta_1 v} \delta_{ij} \exp(-|t'|/\theta_1) \\ \langle \delta \tau(t) \delta \tau(t+t') \rangle &= \frac{k_B \zeta T}{\theta_0 v} \exp(-|t'|/\theta_0) \\ \langle \delta \hat{\tau}_{ij}(t) \delta \hat{\tau}_{kl}(t+t') \rangle &= \frac{k_B \eta T}{\theta_2 v} \Delta_{ijkl} \exp(-|t'|/\theta_2) \end{aligned} \quad (4.4)$$

Clearly, in the limit of vanishing relaxation times  $\theta_i$ , these correlations reduce to the classical results of Landau–Lifshitz<sup>(23)</sup> and Fox–Uhlenbeck,<sup>(24)</sup> for the hydrodynamic stochastic noise. Note, however, that in EIT the fluctuations of the fluxes have a very clear physical meaning, while in stochastic hydrodynamics the noise is a mathematical expression of the uncertainty which hopefully one should be able to obtain from the contraction in the description of a molecular system.

Equations (4.4) imply that the hydrodynamic noise is not white, but colored, since it has an exponential memory related with the relaxation times. It should also be stressed that the spatial behavior of the correlations of the fast variables has been ignored, or rather, it has been implicitly assumed that their fluctuations are  $\delta$ -correlated in space. This is reasonable if the system is away from a critical point.

Another advantage of this formulation of fluctuations is that it allows for computation of the correlation of the fluxes associated with nonconserved variables for which the Landau–Lifshitz scheme is no longer applicable.<sup>(24)</sup> Such are the cases of chemical reactions,<sup>(24,25)</sup> magnetic fluids, polarizable media, and others.

Let us mention finally that the present formalism has also been confirmed from a different point of view based on the Onsager–Machlup approach<sup>(5)</sup> to the probability of paths in phase space.<sup>(26)</sup> For a survey of additional work in the field of equilibrium and nonequilibrium fluctuations of dissipative fluxes, the reader may consult Ref. 27.

## 5. MEMORY FUNCTIONS AND GENERALIZED ENTROPY

The results for the fluctuations obtained in Section 4 are limited to a particular kind of dynamics, namely, exponential dynamics implied by the Maxwell–Cattaneo equations. From this point of view, the results (4.3) do not share the generality of the corresponding expressions for the second moments of the fluctuations of the classical, conserved variables. This is not surprising, of course, since the dynamical processes allow for a much wider variety of phenomena than that implied by the equilibrium features. When dealing with such an amazing variety two main possibilities arise: the use of specific, concrete, clear models and the resource to general, but abstract and formal expressions. The analysis of the previous sections has been based on a specific model. The aim of this section is, in contrast, to show how more general, but more formal results may be obtained within the framework of EIT.

In Section 2 we were able to identify explicitly the coefficients appearing in the generalized Gibbs equation defining a generalized entropy. In Section 3, it was mentioned that the same result may be obtained from kinetic theory. Then in Section 4, such an identification of the nonclassical coefficients has been shown to be fully consistent with the theory of fluctuations. So many, exact coincidences do clearly reinforce the role and credibility of such a generalized entropy. Our purpose here is to provide yet another example of the use of the generalized entropy concept from a general macroscopic point of view.

In the classical equilibrium theory, the entropy of a state  $B$  is defined by means of the relation

$$S(B) = S(A) + \int_A^B \frac{1}{T} dQ_{\text{rev}} \quad (5.1)$$

where  $A$  is a reference state,  $T$  the absolute temperature, and  $dQ_{\text{rev}}$  the heat exchanged by the system with its surroundings in an idealized reversible

process. Perhaps one of the clearest and most direct definitions of the entropy of a nonequilibrium state is the following one:

$$S(B) = S(A) + \int_{A(t=0)}^{B(t=\infty)} \sigma dV dt \quad (5.2)$$

Here,  $A$  is the initial nonequilibrium state whose entropy we want to define. The system is suddenly isolated at  $t=0$  and is allowed to relax to the corresponding equilibrium state  $B$  at  $t = \infty$ . Since the relaxation is adiabatic, there is no entropy flow between the system and its surroundings, and the only difference between the well-known equilibrium entropy of the equilibrium state  $B$  and the unknown entropy of the initial nonequilibrium state  $A$  due to the entropy production integrated along the relaxation adiabatic path.

In this way definitions (5.1) and (5.2) are complementary and in fact, particular cases of the well-known inequality

$$S(B) \geq S(A) + \int_A^B \frac{dQ}{T} \quad (5.3)$$

where  $dQ$  is the actual heat flow and  $T$  the temperature at which the exchange is performed. This inequality can be rewritten as an equality through the introduction of the noncompensated heat Clausius  $dQ'$ :

$$S(B) = S(A) + \int_A^B \frac{dQ}{T} + \int_A^B \frac{dQ'}{T} \quad (5.3b)$$

In the absence of heat flow, the second term of the right-hand side drops out and Eq. (5.3b) becomes identical with Eq. (5.2). On the other hand, when the process is reversible so that the irreversible entropy production (or noncompensated heat) vanishes, the entropy change is due exclusively to the flow across the boundaries of the system and Eq. (5.3b) reduces to Eq. (5.1). Furthermore, all the states involved in Eq. (5.1) are equilibrium states, while Eq. (5.2) involves a time integral over a dynamical (i.e., nonstatic) process along nonequilibrium states traversed by the system during its adiabatic relaxation.

Let us now take the following expression for  $\sigma$ :

$$\sigma = \frac{q^2}{\lambda T^2} + \frac{\dot{\tau} : \dot{\tau}}{2\eta T} + \frac{\tau^2}{2\zeta T} \quad (5.4)$$

When Eq. (5.4) is introduced into Eq. (5.2) we find

$$S(e, v, \mathbf{o}, o, o) = S(e, v, \mathbf{q}, \tau(0), \mathring{\mathbf{t}}(0)) + v \int_0^\infty \left[ \frac{\mathbf{q}^2(t)}{\lambda T^2} + \frac{\tau^2(t)}{\zeta T} + \frac{\mathring{\mathbf{t}}(t) : \mathring{\mathbf{t}}(t)}{2\eta T} \right] dt \quad (5.5)$$

Note that since the system is isolated during the relaxation,  $e$  and  $v$  remain constant, so that the final equilibrium state reached from the initial nonequilibrium state characterized by  $(e, v, \mathbf{q}(0), \tau(0), \mathring{\mathbf{t}}(0))$  will be precisely  $(e, v, \mathbf{o}, o, \mathring{\mathbf{o}})$ . If in addition one assumes that the evolution of the fluxes is described by the Maxwell–Cattaneo equations, then  $\mathbf{q}(t) = \mathbf{q}(0) \exp(-t/\theta_1)$ ,  $\mathring{\mathbf{t}}(t) = \mathring{\mathbf{t}}(0) \exp(-t/\theta_2)$ , etc. and when this is substituted into Eq. (5.5), it leads directly to

$$S(e, v, \mathbf{q}, \tau, \mathring{\mathbf{t}}) = S^{eq} - \frac{\theta_1 v}{2\lambda T^2} \mathbf{q}^2 - \frac{\theta_0 v}{2\zeta T} \tau^2 - \frac{\theta_2 v}{2\eta T} \mathring{\mathbf{t}} : \mathring{\mathbf{t}} \quad (5.6)$$

in complete agreement with the results of Section 2.

This derivation of the generalized entropy consolidates the meaning of such a nonclassical quantity, and suggests some ways of generalizing it to other physical situations. Here, we will deal with the linear expression for the entropy production:

$$\sigma = -T^{-2} \text{grad } T \cdot \mathbf{q} - T^{-1} \zeta \text{div } \mathbf{u} - T^{-1} \mathring{\mathbf{t}} : (\text{grad } \mathbf{u})^s \quad (5.7)$$

Introducing this expression into Eq. (5.2) we obtain

$$S(e, v, \mathbf{q}, \tau, \mathring{\mathbf{t}}) = S^{eq}(e, v) + vT^{-1} \int_0^\infty \text{grad } T(t) \cdot \mathbf{q}(t) dt + vT^{-1} \int_0^\infty \tau(t) \text{div } \mathbf{u}(t) dt + vT^{-1} \int_0^\infty \mathring{\mathbf{t}}(t) : (\text{grad } \mathbf{u}(t))^s dt \quad (5.8)$$

In the memory function approach the instantaneous constitutive equations are substituted by the more general expressions

$$\begin{aligned} \mathbf{q}(t) &= - \int_0^t \lambda(t-t') \text{grad } T(t') dt' \\ \tau(t) &= - \int_0^t \zeta(t-t') \text{div } \mathbf{u}(t') dt' \\ \mathring{\mathbf{t}}(t) &= - \int_0^t 2\eta(t-t') [(\text{grad } \mathbf{u}(t'))^s] dt' \end{aligned} \quad (5.9)$$

In the case when  $\lambda(t-t') = \lambda\delta(t-t')$ ,  $\zeta(t-t') = \zeta\delta(t-t')$  and  $\eta(t-t') = \eta\delta(t-t')$ , Eqs. (5.9) reduce to the classical Fourier and Navier–Newton constitutive equations, and if the memories are exponential in time we recover the Maxwell–Cattaneo equations. The memory functions incorporate all the rapid and very complicated processes that occur in the system as a consequence of the initial perturbation.

It is not our purpose here to work out explicitly the corresponding form of the entropy. Rather, our aim is to use the theory of thermodynamic fluctuations in order to obtain from Eq. (5.8) some information concerning the memory functions and their relation with the fluctuations of the fluxes.

Recall that according to the classical theory of thermodynamic fluctuations,<sup>(28)</sup> when  $dS = \sum_i X_i dY_i$ ,  $X_i$  being the natural variable of the entropy and  $Y_i$  its respective thermodynamic conjugate, the second moments of the fluctuations of  $X_i$  near equilibrium, are given by

$$\langle \delta X_i \delta X_j \rangle = -k_B \left( \frac{\partial X_i}{\partial Y_j} \right)_Y \tag{5.10}$$

In our case, expression (5.8) for the entropy shows clearly that the thermodynamic conjugate variables corresponding to  $\mathbf{q}(t')$ ,  $\tau(t')$ , and  $\overset{\circ}{\mathbf{t}}(t')$  are, respectively,  $vT^{-2}\nabla(T(t'))$ ,  $vT^{-1}\nabla \cdot \mathbf{u}(t')$ ,  $vT^{-1}(\nabla\mathbf{u}(t'))^s$ . We have, therefore,

$$\begin{aligned} \langle \delta \mathbf{q}(t) \delta \mathbf{q}(t') \rangle &= -\frac{k_B T^2}{v} \frac{\partial \mathbf{q}(t)}{\partial \nabla T(t')} \\ \langle \delta \tau(t) \delta \tau(t') \rangle &= -\frac{k_B T}{v} \frac{\partial \tau(t)}{\partial \text{div } \mathbf{u}(t')} \\ \langle \delta \overset{\circ}{\mathbf{t}}(t) \cdot \delta \overset{\circ}{\mathbf{t}}(t') \rangle &= -\frac{k_B T}{v} \frac{\partial \overset{\circ}{\mathbf{t}}(t)}{\partial (\text{grad } \mathbf{u}(t'))^s} \end{aligned} \tag{5.11}$$

Taking into account the constitutive equations (5.9) we finally obtain

$$\begin{aligned} \langle \delta q_i(t) \delta q_j(t') \rangle &= \frac{k_B T^2}{v} \lambda_{ij}(t-t') \\ \langle \delta \tau(t) \delta \tau(t') \rangle &= \frac{k_B T}{v} \zeta(t-t') \\ \langle \delta \overset{\circ}{t}_{ij}(t) \delta \overset{\circ}{t}_{kl}(t') \rangle &= \frac{k_B T}{v} \Delta_{ijkl} \eta(t-t') \end{aligned} \tag{5.12}$$

These expressions generalize the previous ones, Eqs. (4.4) which were restricted to the exponential dynamics of the fluxes. Finally, if the memory is



short enough so that the slow parameters  $\nabla T$ ,  $\nabla \mathbf{u}$ , and  $(\nabla \mathbf{u})^s$  may be considered as constant during the relaxation of the fast variables, Eqs. (5.9) become greatly simplified and give

$$\begin{aligned}\mathbf{q}(t) &= - \left( \int_0^\infty \lambda(t') dt' \right) \cdot \text{grad } T(t) \\ \tau(t) &= - \left( \int_0^\infty \zeta(t') dt' \right) \text{div } \mathbf{u}(t) \\ \dot{\mathbf{t}}(t) &= - \left( \int_0^\infty 2\eta(t') dt' \right) (\text{grad } \mathbf{u}(t))^s\end{aligned}\quad (5.13)$$

Since the decay of the memory function is very fast, we may extend the integration in time up to infinity without any appreciable effect on the integral. From Eqs. (5.13) and (5.12) one obtains

$$\begin{aligned}\lambda_{ij} &= \frac{v}{k_B T^2} \int_0^\infty \langle \delta q_i(0) \delta q_j(t) \rangle dt \\ \zeta &= \frac{v}{k_B T} \int_0^\infty \langle \delta \tau(0) \delta \tau(t) \rangle dt \\ \eta \Delta_{ijkl} &= \frac{v}{k_B T} \int_0^\infty \langle \delta \tau_{ij}(0) \delta \tau_{kl}(t) \rangle dt\end{aligned}\quad (5.14)$$

These are indeed the well-known Green–Kubo formulas for the dissipative coefficients. We have shown, therefore, that the formalism of EIT is not restricted to the exponential model, but it has a generality comparable at least with linear response theory. Such a generalization may be obtained at the price of a more formal, but less evident development.

## 6. DISCUSSION

A number of misunderstandings have arisen with respect to the meaning and nature of EIT. In this last section we proceed to discuss some of them appeared in the recent literature.

Recently Keizer<sup>(16)</sup> has examined in some detail the process of contraction of variables, resulting in the elimination of the fast variables, i.e., the dissipative fluxes, in the particular case when the fluxes are the time derivatives ( $\dot{\alpha}$ ) of the conserved variables ( $\alpha$ ). This restrictive assumption is the basis of Onsager's method for the deduction of reciprocal relations and of many other valuable features of linear nonequilibrium thermodynamics. It must be stressed, however, that in many cases, for instance in

hydrodynamics, the dissipative fluxes are not in general the time derivatives of the conserved variables. They may be interpreted in this way in some particular circumstances, which generally suffice to state the symmetry of the thermal conductivity or the diffusion matrix or the electrical conductivity, but this is only a useful simplification of no general validity.<sup>(29)</sup>

The conclusions of Keizer's particular analysis have been used as unfounded criticisms toward the use of the fluxes as independent variables by arguing that in practice the same results are obtained with a memory function formalism. Indeed, as we have shown in Section 3 this is far from being the case. The memory function formalism hardly leads to equations such as Eq. (6) in Ref. 16 for the macroscopic variables. In fact this is an artificial memory function equation arising from the ordinary solution of an inhomogeneous linear differential equation in which the term  $\alpha(0)$  is interpreted as a statistical distribution. From there on use is made of the general formalism of stochastic processes to achieve some results on the properties of the "fluctuating force" appearing in the Langevin-type equation obeyed by the  $\alpha$ 's. It is even argued in the proof that the correlation matrix of  $\alpha(0)$  involving an average over conditional probability densities is connected with Zwanzig's equation for  $M(t)$  [see Eq. (3.9)]. This is clearly incorrect since the latter one contains the ensemble average of the time rate of change of the phase space functions associated with the observables of the system and *not* a conditional average over the time rate of change of the macroscopic (stochastic) variables. Thus, the validity of Eq. (20) in Ref. 13 is strongly questioned.

On the other hand, the formalism of EIT includes information on the stochastic noise due to the independence of the fluxes. The fact that upon a contraction of these fast variables one is lead to some very particular cases of a memory function approach reinforces rather than invalidates the extended theory.

It could be argued that EIT is limited to an exponential memory function. As we have seen in Section 5, this is not true, because EIT is able to deal with more general dynamics. In fact, the memory function, according to relations (5.12), very well known in statistical mechanics, is related to the dynamics of the fluxes in a very direct way. Moreover, since the memory function is so intimately related to the time correlation of the fluxes, it must obey the same equations that describe the evolution of the fluctuations of the fluxes around equilibrium. Therefore the evolution equations of the fluxes may provide a sounder and more physical basis for the analysis of the memory functions. In this respect such a basis seems preferable, very directly related with a dynamical physical process, than the purely mathematical game of inventing fanciful memories. Even in the case of having a very useful memory, one should try to explain its meaning and

success instead of taking for granted the process of physical understanding as a mere mathematical fitting of data.

“Finally, Keizer’s analysis only deals explicitly with the case where the relaxation times of the fast variables are much shorter than the time scale in which the conserved variables change. There are systems, however, (e.g., polymer solutions), where both time scales may become comparable and for their description the use of EIT is crucial. Also, when making the connection between his version of EIT—i.e., the one in which the fluxes are the time derivatives of the conserved variables—and fluctuating hydrodynamics (cf. Section 2 of Ref. 16), there is no reference to the generalized entropy and this is, of course, surprising since the entropy plays an important role in EIT as in any other phenomenological theory. Thus neglect of the entropy implies that, in order to find an expression for the second moments of the noise, Keizer has to return to the use of a microscopic theory. EIT, on the contrary, gives very directly such an information. The general interest of this particular point is that EIT is not strictly equivalent to the memory function approach, but it contains some further information which concerns the mathematical (approximated) properties and the physical meaning of the stochastic noise appearing in that formalism. In summary, EIT at its three levels of description: macroscopic (thermodynamic), mesoscopic (fluctuations), and microscopic (kinetic theory, projection operators), contains a richer description of the physical macroscopic systems than that provided by the usual theories, based only on the conserved variables as independent variables. This statement seems true even in the case when the classical description is formulated in terms of memory functions.

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