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Microscopic approach to irreversible thermodynamics. I. General theory

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In this paper we show how an extension of the nonequilibrium-statistical-operator method, relying upon the maximum-entropy principle set up by Jaynes [Am. J. Phys. **33**, 391 (1965)], may be used to describe the time evolution of an arbitrary many-body system. The Gibbs space of the observables describing the macrostates of the system is extended to include not only the conserved variables, but additional ones whose origin is directly related to the microscopic nature of the system manifested in its Hamiltonian. This allows us to go beyond linear irreversible thermodynamics and enter into the domain of what is now known as extended irreversible thermodynamics (EIT). Transport equations for the extended basic set of macrovariables are derived, showing that the Maxwell-Cattaneo-Vernotte equations of EIT are obtained. The relaxation times and transport coefficients contained therein can be calculated from the microscopic dynamics of the system averaged over an appropriate nonequilibrium coarse-grained probability density. Other outstanding features of the methods are emphasized and related to already-established results for nonequilibrium systems.

I. INTRODUCTION

Nonequilibrium thermodynamics formulated at a phenomenological level has remained more or less an open subject beyond the linear approximation now referred to as linear irreversible thermodynamics[1] (LIT). In spite of the fact that several efforts have been made to extend the validity of this linear theory, none of them can be considered fully satisfactory.[2,3] One of the main reasons for this is that so far they lack a solid justification based on the general principles of statistical mechanics. The difficulty that arises in this task of deriving irreversible thermodynamics from the microscopic laws of physics resides in the choice of a basic set of variables appropriate to describe the nonequilibrium macroscopic states of the system under consideration. Next to it stands the question of the existence of a functional involving all of these variables which provides a fundamental relation able to generate the basic relations of the irreversible thermodynamics for such systems. Of course, the well-established laws of equilibrium thermodynamics and LIT must be recovered from such a fundamental relation as particular limiting cases. Since the entropy function enjoys a preferential status in those cases, one may seek a fundamental relation playing the role of an entropylike function for the restricted description to be used in the study of the macroscopic nonequilibrium states of a many-body system. Finally, to close the theory it is necessary to provide equations for the time evolution of the macroscopic variables.

The underlying ideas behind the question posed above go back to Maxwell[4] and Boltzmann.[5] Their analysis went beyond equilibrium thermodynamics and constructed evolution equations that have been successfully applied to a large variety of situations from gases to solids.[6] There is certainly a profound physical meaning in Boltzmann's equation, but the task of solving the full nonlinear equation and of clarifying its domain of validity has been rather insurmountable. Nevertheless, very general results are extracted from it such as the general conservation equations for the locally conserved densities and the H theorem.[7] The relationship between the function H and the equilibrium entropy of a dilute gas has also been clearly established.[8] Insofar as its relation with irreversible thermodynamics is concerned, it is also well known that the Chapman-Enskog solution of the Boltzmann equation leads to the laws of LIT (Ref. 1) and that the moments solution set forth by Grad 30 years ago[9] leads to one version of extended irreversible thermodynamics.[10,11]

In the hands of Gibbs[12] and Einstein,[13] the ideas of Maxwell and Boltzmann were finally brought into a full theory relating the laws of equilibrium thermodynamics to those of microscopic physics. Yet, as some authors have repeatedly emphasized,[14–16] the use of the concept of an ensemble to describe the time evolution of a system undergoing an irreversible process has not yet been fully exploited. There are a number of methods[14–21] that have been successful in describing nonequilibrium phenomena around the local equilibrium states of the system in consideration, thus providing a statistical basis for LIT and fluctuations around the equilibrium state. Others, such as the projection-operator methods first devised by Mori and Zwanzig[21–23] may be used to deal in principle with situations far from equilibrium, but the nature of the formalism is such that only in rather simple situations have concrete relations with real systems been reached.[24]

In this work we want to show how an appropriate extension of the nonequilibrium statistical operator method (NSOM) provides formal results with remarkable structural compactness and leads to natural and far-reaching generalizations of the formalisms referred to in the previous paragraph. To do so we shall work with a Gibbs space of macrovariables (G), which is extended to include fluxes of energy, momentum, mass, and others deemed necessary for the appropriate description of the nonequilibrium states of the system under study. Next, using the Gibbs definition of the H function (often but incorrectly referred to as an entropy), we construct a generalized entropy function using the maximum-entropy principle set forth by Jaynes.[16] This entropy is a function of all variables in G and has a linear differential form in G. Finally, we show how one can compute a generalized entropy production, thus arriving at a condition which allows the calculation of the time-evolution equations for the fluxes elevated to the status of independent variables in G. This procedure closely resembles the moment method devised by Grad to solve Boltzmann's equations, which was referred to before. As a consequence of the theory, nonlinear transport equations for the G variables are obtained, and with an appropriate mathematical treatment, the transport equations for the G variables agree, close to equilibrium with well-known results and far from equilibrium with equations which have the general structure of the Maxwell-Cattaneo-Vernotte (MCV) equations, often taken as the most elementary extension of LIT, to describe nonequilibrium states.[2,25]

However, we must point out that the underlying ideas of the maximum-entropy formalism (MEF) here applied to derive the basic macroscopic equations for systems in nonequilibrium are by no means new. After Jaynes's original papers were published,[26] a number of applications followed in which the general features about irreversibility[27–29] were discussed, as well as derivations of time-evolution equations for the macroscopic variables describing the states of the system given. In this latter line of thought closely connected with our work, kinetic and transport equations using the MEF were obtained for very specific cases[30,31] and afterward were brought together into a unifying scheme by Lewis.[32] More recently, Karkheck and co-workers[33–35] have successfully applied the method to generalize Enskog's kinetic theory for the dense hard-sphere fluid onto a kinetic theory of fluids which includes smooth potential tails. An H theorem may be extracted from the formalism, and although the correct equilibrium properties are predicted,[36] no discussion is given about the local entropy production in the way that arises in LIT and that is obtained by other methods.[37–39] Finally, we should also mention the use of the MEF to obtain time-evolution equations for the steady-state conduction of heat in dense fluids[40,41] and a generalized Grad-type foundation for extended irreversible thermodynamics (EIT) with altered thermodynamic forces.[42] These results seem to be encompassed and extended in the realm of the NSOM as put forward by Zubarev,[18] Peletminskii,[17] and others[14–16] when applied to the description of irreversible phenomenological thermodynamics, as described in this paper. In another publication[43] it has been shown that the NSOM contains a proper Gibbs equation, Prigogine minimum-entropy production law, Glansdorff-Prigogine universal criterion for evolution, and Glansdorff-Prigogine (in)stability criterion.

The structure of the paper is as follows: Section II contains an overview of nonequilibrium thermodynamics which we consider useful for later purposes. Section III is devoted to a discussion of the NSO formalism where we put all existing approaches under a unique derivation based on Jaynes's maximum-entropy principle, complemented with an additional assumption. The connection with nonequilibrium thermodynamics is pursued, and nonlinear transport equations are derived. In Sec. IV we discuss a plausible criterion for the determination of the basic set of dynamical variables appropriate for a class of experimental situations. The average values of these quantities over the nonequilibrium ensemble are interpreted as the macrovariables of EIT so that its quantum statistical-mechanical basis is thus provided. Next, we investigate how the general transport equations for the macrovariables obtained in the previous section reduce to well-known results close to equilibrium and to Mori-Langevin type of evolution equations for the fluxes beyond local equilibrium. The coefficients appearing in these equations are in principle calculable as averages over the nonequilibrium ensemble, which has an advantage over others still containing the N-body dynamics. Finally, Sec. V contains the main conclusions of this work.

II. OVERVIEW OF IRREVERSIBLE THERMODYNAMICS

Phenomenological irreversible thermodynamics is often associated with linear irreversible thermodynamics (LIT), which is founded in the ideas of Onsager and Machlup,[44] Glansdorf and Prigogine,[45] de Groot and Mazur,[1] and others.[46] These ideas resort to the basic concepts of thermostatics to describe the properties of the nonequilibrium states of any arbitrary system. The time evolution of the variables performing such description is drawn from their underlying conservation equations, which are complemented by prescribing a linear relationship between the thermodynamic forces, usually expressed as the gradients of intensive macroscopic quantities, and the fluxes or currents they produce in the system. Furthermore, the matrix formed by the coefficients appearing in these linear relations is proven to be symmetric a result now known as the Onsager reciprocity theorem.[47] As has been clearly established today, this theory is rather accurate in describing a large class of phenomena occurring near the equilibrium state. In a more descriptive language, LIT is useful to deal with nonequilibrium phenomena for very small wave vectors (large wavelengths) and small frequencies (long times). If one desires to incorporate into a phenomenological framework nonequilibrium phenomena which occur as both the wave vector and the frequency increase, it becomes clear that LIT has to be modified. As was mentioned in the Introduction, many efforts have been done in this direction in the past 20 years, although not a single satisfactory theory has been developed, at least in the same way that LIT has been rooted in more microscopic principles.

Among such efforts, EIT has had a partial success in carrying out the above-mentioned program.[48,49] It also has the advantage that one is able to prove how it stems out of kinetic theory,[9,10] much in the same way LIT is derived from the Chapman-Enskog solution to the Boltzmann equation.[1] It thus appears reasonable to ask if it is possible to relate the basic ideas of EIT to a deeper microscopic description of the time evolution of an arbitrary system. Since the results obtained in this paper clearly indicate that in fact such a relationship exists, it is convenient to summarize the main hypothesis on which EIT has been developed.

The first assumption of EIT concerns the nature of the variables chosen to describe the states of the system. For that purpose the space of state variables, to be denoted by G, consists of the union of two subsets, one formed by the locally conserved densities used in LIT, denoted by C, and another subset formed by the nonconserved variables and denoted by R. Thus $G=C\cup R$. The nature of the R variables has been a long-debated question.[50,51] From a deep physical point of view, these variables should represent the internal constraints of the system, not controllable by an external observer, which characterize the nature of the specific internal processes which take place in the system. The "degree of advancement" of a chemical reaction would be a typical example. Yet, for the overwhelming majority of the systems so far studied, it has been impossible to detect such variables. The only guide that has been available for this purpose is Grad's moments solution to the Boltzmann equation where the fluxes *per se* are raised to the status of independent variables.[10] In most of the systems dealt with by EIT, this prescription has been used rather successfully. We shall have more to say on it later on. The second assumption states that a certain function of the G variables exists, and is continuous and differentiable. Thus, for any infinitesimal irreversible process occurring in the system, this function, to be denoted by η, has a linear differential form whose coefficients will, in general, be tensorial fields, whose properties are determined by the structure of G.[52] To obtain the time-evolution equations for the set of independent variables in G, since the time derivatives of the R variables are unknown, one needs an additional assumption. The choice mad by Jou, Casas-Vazquez, and Lebon[48] is that the function η satisfies a balance equation, namely,

$$\frac{\partial}{\partial t}\eta(\mathbf{r},t)+\operatorname{div}\mathbf{J}_\eta(\mathbf{r},t)=\sigma_\eta(\mathbf{r},t)\ . \tag{1}$$

In Eq. (1), $\mathbf{J}_\eta$ is the most general vector that may be constructed in G,[52] and σ_η is a scalar function which may be computed in two ways. One is by carrying out the operations indicated in the left-hand side of Eq. (1). The second way is by recognizing that σ_η is the most general scalar which may be constructed in G. This defines a closure operation in space G (Ref. 53) and determines the full form of the equations of motion for the R variables. Furthermore, a compatibility requirement has to be imposed in Eq. (1), namely, that when the R variables prove to be irrelevant for the description of the states of the system, Eq. (1) must reduce to the ordinary entropy balance equation of LIT. The set of nonlinear differential equations composed by the conservation equations associated with the variables in C together with those derived from Eq. (1) for the R variables is the full set of equations governing the time evolution of the state variables for the system under study. These equations, like all others derived from phenomenological premises, contain a number of undetermined coefficients whose knowledge has to be drawn either from experiment or from a microscopic theory. Given such coefficients, the system may be solved in principle for given initial and well-defined boundary conditions. Some approximations are usually introduced; one is to regard all the coefficients appearing in the equations as constants, and the other is to neglect all terms which are of order higher than two in the R variables.[54] In this, referred to as the first approximation, one obtains linear differential equations for the R variables which are identical to those proposed by Maxwell[4] and Kohlrausch[55] and later derived by Grad.[9] For instance, in the case of a fluid, if we denote by $\mathbf{I}_q$ the heat flux and by $\mathring{\tau}$ the traceless part of the symmetric viscous tensor, the corresponding equations read as

$$-\Theta_q\frac{\partial}{\partial t}\mathbf{I}_q=\mathbf{I}_q+\kappa\,\mathrm{grad}T+\cdots\ , \tag{2a}$$

$$-\Theta_v\frac{\partial}{\partial t}\mathring{\tau}=\mathring{\tau}+2\eta(\mathrm{grad}\mathbf{u})^s+\cdots\ , \tag{2b}$$

where κ is the thermal conductivity, η the shear viscosity, and Θ_q,Θ_v two undetermined coefficients having dimensions of reciprocal time that are interpreted as the relaxation times associated with $\mathbf{I}_q$ and $\mathring{\tau}$, respectively. Equation (2a) is identical to that proposed by Cattaneo[56] and Vernotte[57] to contend with the nonphysical prediction of infinite propagation velocities for thermal disturbances arising from the fact that the heat conduction equation which comes from LIT is parabolic. On the other hand, Eq. (2b) is the Maxwell-Kohlrausch equation which describes how the shear stress evolves in time in elastic media. Equations (2a) and (2b) are now referred to as the Maxwell-Cattaneo-Vernotte equations (MCV) and have been applied to a variety of phenomena.[48,49]

As we shall see in Sec. IV, a mechanism is here provided to derive MCV-type equations from a microscopic point of view based on the NSOM. In fact, for a given Hamiltonian, time-evolution equations are obtained for the dynamic state variables containing transport coefficients whose value depends on the dynamic interactions between the atoms or molecules (or quasiparticles) composing the system. These equations are far more general than the linear approximation in the R variables requires. In fact, their general structure is nonlocal in both space and time, thus indicating the existence of higher-order approximations not yet explored even within the context of EIT. Their implications will be discussed in a separate paper.

III. REVIEW OF THE NONEQUILIBRIUM-STATISTICAL-OPERATOR METHOD

The NSO formalism has its sources in Boltzmann and Gibbs ideas, and it has been considered a far-reaching generalization of the Chapman-Enskog method in the kinetic theory of gases.[64] Several methods, some of them based on general arguments,[14,17,18] others based on projection-operator techniques,[15,20–23] are currently available to obtain an appropriate form for the statistical operator $\rho(t)$. In all cases $\rho(t)$ is separated into two parts:

$$\rho(t)=\rho_{\rm CG}(t)+\rho'(t)\ , \tag{3}$$

where $\rho_{\rm CG}$ is a coarse-grained (CG) nondissipative term that defines the mean values of the quantities P_j, $j=1,2,\ldots,n$, the dynamical variables which we assume that form the basic set appropriate for the description of the phenomenon under consideration. The average values of the P_j's are the macrovariables

$$Q_j(t)={\rm Tr}[P_j\rho(t)]={\rm Tr}[P_j\rho_{\rm CG}(t)]\ , \tag{4}$$

which characterize the macroscopic state of the system.[58] Further, it is chosen as initial condition that at the initial time t_0 one has $\rho(t_0)=\rho_{\rm CG}(t_0)$, from which ρ evolves under the action of the total Hamiltonian of the system. At any subsequent time $t>t_0$, both ρ and $\rho_{\rm CG}$ differ by ρ', the second contribution in Eq. (3), a contribution that carries the information on the dynamics relevant to the description of the relaxation processes that develop in the system.

The second equality in Eq. (4) clearly implies that the subsidiary condition ${\rm Tr}(P_j\rho')=0$ must be obeyed for all P_j's. The relevance of this condition will appear later [cf. Eq. (20)].

We proceed to derive a family of NSO using a variational principle based on Jaynes's maximum-entropy formalism (MEF),[16] including memory effects.[43] For that purpose we first introduce the Gibbs entropy

$$S_G(t)=-{\rm Tr}[\rho(t)\ln\rho(t)]\ , \tag{5}$$

with $\rho(t)$ defined in the interval (t_0,t) and normalized at all times, i.e.,

$${\rm Tr}[\rho(t')]=1\ , \tag{6}$$

for $t_0\le t'\le t$.

Next, S_G is made maximum subject to the constraints

$$Q_j(\mathbf{r},t')={\rm Tr}[P_j(\mathbf{r})\rho(t')]={\rm Tr}[P_j(\mathbf{r},t'-t)\rho(t)]\ , \tag{7}$$

for $t_0\le t'\le t$ and $j=1,2,\ldots$.

Following well-known procedures,[16] we find that

$$\rho(t)=\exp\left[-\psi(t)-\sum_{j=1}^{n}\int d^3r\int_{t_0}^{t}dt'\varphi_j(\mathbf{r},t,t';t_0)P_j(\mathbf{r},t'-t)\right]\ , \tag{8}$$

where ψ and φ are Lagrange multipliers, with

$$\psi(t)=\ln{\rm Tr}\left[\exp\left[-\sum_{j=1}^{n}\int d^3r\int_{t_0}^{t}dt'\varphi_j(\mathbf{r},t,t';t_0)P_j(\mathbf{r},t-t')\right]\right]\ , \tag{9}$$

ensuring the normalization condition (6).

Equations (8) and (9) are the general solution to the variational problem underlying the calculation of $\rho(t)$. We now introduce an extra assumption, namely, that the Lagrange multipliers are of the form

$$\varphi_j(\mathbf{r},t,t';t_0)=w(t,t';t_0)F_j(\mathbf{r},t')\ , \tag{10}$$

which is proposed in order (1) to define the set of functions $F_j(\mathbf{r},t)$ as intensive variables (fields) thermodynamically conjugated to the extensive variables $Q_j(\mathbf{r},t)$ [in the way defined by Eq. (23)], to generate a complete connection with phenomenological nonequilibrium thermodynamics, and (2) to define a function w in such a way to fix the initial condition $\rho_w(t_0)=\rho_{\rm CG}(t_0)$, from which the macroscopic state of the system evolves irreversibly. Here $\rho_w(t)$ is the NSO $\rho(t)$ for the specific choice given by Eq. (10).

In fact, given that $w(t,t';t_0)=dW(t,t';t_0)/dt'$, items (1) and (2) follow from the conditions

$$\lim_{t'\to t}W(t,t';t_0)=1\ , \tag{11a}$$

$$\lim_{t'\to t_0}W(t,t';t_0)=0\ , \tag{11b}$$

$$\lim_{w\to 0}{\rm Tr}[A\rho_w(t)]=\langle A|t\rangle\ . \tag{11c}$$

In Eq. (11c) the limit $w\to 0$ is taken after the trace operation in the calculation of averages of any dynamical operator A has been performed [Eq. (11c) defines a quasiaverage in Bogoliubov's sense].

If one now substitutes Eq. (10) into Eq. (8) and carries out a number of algebraic steps, one is led to the result that

$$\ln\rho_w(t) = \ln\rho_{\mathrm{CG}}(t,0) - \int_{t_0}^{t} dt'\, W(t,t';t_0)\frac{d}{dt'}\ln\rho_{\mathrm{CG}}(t',t'-t) , \tag{12}$$

where

$$\rho_{\mathrm{CG}}(t_1,t_2) = \exp\left[-\phi(t_1) - \sum_{j=1}^{n}\int d^3r\, F_j(\mathbf{r},t_1)P_j(\mathbf{r},t_2)\right] \tag{13}$$

and

$$\phi(t) = \ln \mathrm{Tr}\left[\exp\left[-\sum_{j=1}^{n}\int d^3r\, F_j(\mathbf{r},t)P_j(\mathbf{r})\right]\right] . \tag{14}$$

The first term in the argument of ρ_{CG} refers to the time dependence on variables F_j and the second to the time dependence of operators P_j in the Heisenberg representation. Note should be made of the fact that because of Eqs. (7), (13), and (14), ρ_w is really a time-dependent functional of the macroscopic variables Q_j.

For the sake of clarity, it is worth mentioning that the Green-Mori NSO (Ref. 14) follows for $W(t,t';t_0) = 1-(t-t')/\tau$, $t_0 = t-\tau$, and $\tau \to \infty$, thus satisfying Eqs. (11). Also, Zubarev's NSO (Ref. 18) is obtained putting $W(t,t;t_0) = \exp[\epsilon(t'-t)]$, $t_0 \to -\infty$, and $\epsilon \to +0$. The equivalence with NSO's obtained using projection-operator techniques has been discussed elsewhere.[43] That indeed the NSO of Eq. (12) satisfies a Liouville equation with infinitesimal sources, which break its time-reversal symmetry and introduces Prigogine's dynamical condition for dissipativity,[59] has been also shown in Ref. 43. Finally, using the operator identity[19]

$$e^{-A+B} = Y(B|1)e^{-A} , \tag{15a}$$

$$Y(B|x) = 1 + \int_0^x du\; Y(B|u)e^{-uA}Be^{uA} , \tag{15b}$$

the NSO of Eq. (13) can be written in the form of Eq. (3) as

$$\rho_w(t) = \exp[\ln\rho_{\mathrm{CG}}(t,0) + \zeta_w(t)] = \rho_{\mathrm{CG}}(t,0) + \rho'(t) , \tag{16}$$

where ρ_{CG} is given in Eq. (13), and

$$\zeta_w(t) = -\int_{t_0}^{t} dt'\, W(t,t';t_0)\frac{d}{dt'}\ln\rho_{\mathrm{CG}}(t',t'-t) , \tag{17a}$$

$$\rho'(t) = D_w(t)\rho_{\mathrm{CG}}(t,0) , \tag{17b}$$

$$D_w(t) = \int_0^1 du\; Y(\zeta_w|u)[\rho_{\mathrm{CG}}(t,0)]^u \zeta_w(t)[\rho_{\mathrm{CG}}(t,0)]^{-u} , \tag{17c}$$

$$Y(\zeta_w|x) = 1 + \int_0^x du\; Y(\zeta_w|u)[\rho_{\mathrm{CG}}(t,0)]^u \zeta_w(t)[\rho_{\mathrm{CG}}(t,0)]^{-u} . \tag{17d}$$

Because of the condition imposed by Eq. (4), it follows that

$$\mathrm{Tr}[\rho'(t)] = \mathrm{Tr}[D_W(t)\rho_{\mathrm{CG}}(t,0)] = 0 , \tag{18a}$$

$$\mathrm{Tr}[P_j\rho'(t)] = \mathrm{Tr}[P_jD_w(t)\rho_{\mathrm{CG}}(t,0)] = 0 . \tag{18b}$$

Equation (18a) is a result of the normalization of ρ_{CG}, and Eq. (18b) reflects the fact that there are no dissipation effects in the ensemble characterized by ρ_{CG}.

The connection with irreversible thermodynamics is done, following Jaynes, through the identification of the function $\mathcal{S}(t)$, to be called the NSOM-entropy function, namely,

$$\mathcal{S}(t) = -\mathrm{Tr}[\rho_w(t)\ln\rho_{\mathrm{CG}}(t,0)] = -\mathrm{Tr}[\rho_{\mathrm{CG}}(t,0)\ln\rho_{\mathrm{CG}}(t,0)] = \phi(t) + \sum_{j=1}^{n}F_j(t)Q_j(t) , \tag{19}$$

defined over the G space, with the entropy of the phenomenological nonequilibrium thermodynamics. In Eq. (19) the second equality is a consequence of Eqs. (4), and hereafter for the sake of brevity we omit the dependence on the space variables. From Eq. (14),

$$-\frac{\delta\phi(t)}{\delta F_j(t)} = Q_j(F_1(t),\ldots,F_n(t)) = Q_j(t) , \tag{20}$$

and then $\mathcal{S}$ and ϕ satisfy the Pfaffian forms

$$d\phi(t) = -\sum_{j=1}^{n}Q_j(t)dF_j(t) , \tag{21}$$

$$d\mathcal{S}(t) = \sum_{j=1}^{n}F_j(t)dQ_j(t) , \tag{22}$$

where use has been made of Eq. (19) to obtain Eq. (22).

Therefore, the Lagrange multipliers F_j are the differential coefficients of the NSOM-entropy function of Eq. (19):

$$\frac{\delta\mathcal{S}(t)}{\delta Q_j(t)} = F_j(Q_1(t),\ldots,Q_n(t)) = F_j(t) . \tag{23}$$

Because of Eq. (23), the intensive variables $F_j(t)$ are then canonically conjugate, in the sense of nonequilibrium thermodynamics, to the intensive basic variables $Q_j(t)$.

The rate of change of quantity $\mathcal{S}(t)$, which we call the NSOM-entropy production, plays a very important role in the formalism. It is obtained by time differentiation of Eq. (19), namely,

$$\sigma(t) = \frac{d\mathcal{S}(t)}{dt} = \sum_{j=1}^{n}F_j(t)\frac{d}{dt}Q_j(t) . \tag{24}$$

Defining the NSOM-entropy production operator $\hat{\sigma}(t,0) = -d\ln\rho_{\mathrm{CG}}(t,0)/dt$, and the generalized correlation function of operators A and B,

$$\{A;B|t\}=\mathrm{Tr}\left[A\int_0^1 du\, Y(\zeta_w|u)[\rho_{\mathrm{CG}}(t,0)]^u \Delta B[\rho_{\mathrm{CG}}(t,0)]^{-u+1}\right] , \qquad (25)$$

where $\Delta B = B - \mathrm{Tr}[B\rho_{\mathrm{CG}}(t,0)]$, and using Eqs. (17a)–(17d), we can write Eq. (24) in the form

$$\begin{aligned}\sigma(t)&=\mathrm{Tr}[\hat{\sigma}(t)\rho_w(t)]=\mathrm{Tr}[\hat{\sigma}(t)D_w(t)\rho_{\mathrm{CG}}(t)]\\ &=\{\hat{\sigma}(t,0);\zeta_w(t)|t\}=\int_{t_0}^{t}dt'W(t,t',t_0)\{\hat{\sigma}(t,0);\hat{\sigma}(t',t'-t)|t\} . \qquad (26)\end{aligned}$$

This result clearly points out at the fact that the operator $D_w(t)$ defined by Eq. (17c) is directly related to the NSOM-entropy production. Since $\zeta_w(t)$ depends linearly on $\hat{\sigma}$, using for the generalized correlation function that defines σ its expression as given by Eq. (26), it follows that the NSOM-entropy production function is a superposition of the variances in all orders of the NSOM-entropy production operator in the ensemble characterized by $\rho_{\mathrm{CG}}(t,0)$. In the so-called NSOM-linear theory of relaxation (LTR),[60] σ reduces to the self-correlation function of the NSOM-entropy production operator and around equilibrium is positive definite.[18] Further, in LTR around stationary states it follows that the fluctuations of quantities Q_j are Gaussian, and the Glansdorff-Prigogine universal evolution criterion[45] as well as Prigogine's minimum-entropy production law[61] are verified.[43]

Finally, to close the formalism and to perform calculations of thermodynamic functions and response functions,[43,62] one needs to obtain the evolution equations for macrovariables $Q_j(t)$. Using the definition of $\dot{Q}_j$ and Eqs. (17b) and (17c), we see that

$$\begin{aligned}\frac{d}{dt}Q_j(t)&=\frac{d}{dt}\mathrm{Tr}[P_j\rho_w(t)]\\ &=\mathrm{Tr}\left[\frac{1}{i\hbar}[P_j,H]\rho_w(t)\right]\\ &=\mathrm{Tr}\left[\frac{1}{i\hbar}[P_j,H]\rho_{\mathrm{CG}}(t,0)\right]+\mathrm{Tr}\left[\frac{1}{i\hbar}[P_j,H]\rho'(t,0)\right]\\ &=\langle\dot{P}_j|t\rangle_{\mathrm{CG}}+\{\dot{P}_j;\zeta_w(t)|t\}\\ &=\langle\dot{P}_j|t\rangle_{\mathrm{CG}}+\int_{t_0}^{t}dt'W(t,t';t_0)\{\dot{P}_j;\hat{\sigma}(t',t'-t)|t\} , \qquad (27)\end{aligned}$$

where H is the total Hamiltonian of the system, and $(i\hbar)^{-1}[P_j,H]=\dot{P}_j$. Using Eqs. (17a), (17c), and (13), it follows that

$$\begin{aligned}\frac{d}{dt}Q_j(t)=\mathrm{Tr}[\dot{P}_j\rho_{\mathrm{CG}}(t,0)]&+\sum_{k=1}^{n}\int_{t_0}^{t}dt'W(t,t';t_0)\{\dot{P}_j;\dot{P}_k(t'-t)|t\}F_k(t')\\ &+\sum_{k=1}^{n}\int_{t_0}^{t}dt'W(t,t';t_0)\{\dot{P}_j;\dot{P}_k(t'-t)|t\}\frac{d}{dt'}F_k(t') . \qquad (28)\end{aligned}$$

It can be shown[43] that in the linear regime around equilibrium Eqs. (28) go over to the set of equations obtained by Mori.[21] This suggests that Eqs. (28) may be considered a generalization of Mori's formalism for systems arbitrarily away from equilibrium, and the last two terms in Eqs. (28) combine to produce a collision operator that depends, in Mori's terminology, only on the correlation of the rapidly fluctuating generalized forces.[43] In particular cases, those to be discussed in Sec. IV, the right-hand side of Eq. (28) can be written in the form of a series expansion of collision integrals, of ever-increasing power in the interaction strengths, involving only the calculation of averages over the coarse-grained ensemble.[43,63]

IV. BASIC VARIABLES AND THEIR EQUATIONS OF EVOLUTION

In the description of the NSO formalism of Sec. III, we have left aside the question of the choice of the basic set of dynamical quantities $\{P_j\}$, the associated set of macrovariables $\{Q_j(t)\}$, and their conjugated $\{F_j(t)\}$. At present there is no wholly satisfactory theory to generate the basic set of variables appropriate for the description of the macroscopic nonequilibrium state of a many-body system. Some authors suggest that it must include all approximate integrals of motion (quasi-invariant variables); others also claim that one should include enough variables that the collision operators in Eqs. (28) are almost instantaneous in time.[64] The adherents of EIT maintain that the subset of quasi-invariant variables should be expanded to include additional variables which, as explained in Sec. II, have so far been selected as the dissipative fluxes. It ought to be noted that, whichever set Q_j, we must be able to obtain their equations of evolution, and to integrate them initial and boundary conditions need be provided, generally not an easy or sometimes a not-so-feasible task. Further, Bogoliubov's principle must always be kept in mind, namely, that a contracted macroscopic description of a many-body system would be possible if there exists a relaxation time for microinformation, τ_μ, such that after it has elapsed the system loses the memory of the distribution that describes the initial state immediately after it has been driven arbitrarily away from equilibrium. For $t \gg \tau_\mu$ correlations with lifetime smaller than τ_μ can be ignored and a description in terms of a reduced set $\{Q_j(t)\}$ $(j=1,2,\ldots,n)$ may be possible.[58] Thus it is not always feasible to start with the equilibrium distribution (or equilibrium values of the variables) as an initial condition, but to specify what the distribution $\rho(Q_j(t_0))$ is for $t_0 > \tau_\mu$. Also, once the actual physical system and the experiment to be performed on it have been clearly defined, the interaction mechanisms, relaxation channels, and the instrumental resolution time Δt influence the choice of the space G and t_0, the latter because one can only use a description, appropriate in Bogoliubov's hierarchy of relaxation times, with a τ_μ smaller than or at least of the order of Δt.

In the NSOM, following the path set forward among others by Zubarev[18] and Peletminskii and Yatsenko,[17] the choice of the set of variables $\{P_j\}$ is connected with the separation of the total Hamiltonian of the system in a "relevant" part H_0 composed of the Hamiltonians of the free subsystems and some of the interactions, and a second part containing the interactions related to the *long-time relaxation mechanisms* H'. The former one is related to those interactions strong enough to have associated *very short relaxation times* and possessing certain symmetry properties. By very short relaxation times is meant those much smaller than the characteristic time scale of the experiment (typically, the instrumental resolution time). Clearly, the symmetry characteristics of the "relevant" part of the interactions also depend on the physical problem under consideration. The required symmetry (which we shall call Peletminskii-Zubarev symmetry condition) is that, in an adequate quantum representation [usually provided by the $(\mathbf{k},\omega)$ space],

$$[P_j,H_0]=\sum_{l=1}^{n}\Omega_{jl}P_l \ , \tag{29}$$

where Ω_{jl} are c numbers determined by H_0. Note should be made of the fact that this condition is consistent with Eq. (4), which defines the macrovariables under the same prescription involved in Eq. (29), since ρ' is associated precisely with H', the weak interactions. Further, this symmetry condition becomes of fundamental relevance for the purpose of writing the equations of evolution in a practical way consisting in putting the complicated supercorrelation functions on the right-hand side of Eq. (27) [or Eq. (28)] in the form of an infinite series of collision integrals which are instantaneous in time.[63] These equations of evolution can be considered[43] far-reaching generalizations of Mori-Langevin equations,[21] derivable from the Liouville equation by the coarse-graining procedure associated to the NSOM. As noted, in one approach (that associated to LIT) the macrovariables $Q_j(t)$ are conserved and/or nearly conserved quantities, but this approach requires additional constitutive equations. The Peletminskii-Zubarev closure condition implies taking into account all dynamical quantities that are conserved under H_0, and their equations of motion contain collision operators describing the evolution generated by H' that are the manifestation of the microscopic degrees of freedom that are suppressed in the coarse-graining procedure. We recall that this separation is allowed when there is a distinct hierarchy of time scales in Bogoliubov's sense.[58]

The Peletminskii-Zubarev condition of Eq. (29) provides a closure condition for the choice of the basic set of variables: First, the secular part H_0 of the Hamiltonian has to be adequately chosen (as noted, it contains the kinetic energies plus the interactions strong enough to produce damping of correlations in times of the order of the experimental resolution time). Second, one introduces a few dynamical variables P_j deemed relevant for the description of the physical problem in hand, and next their commutator with H_0 is performed. The dynamical variables—different from those already introduced—that appear in the linear combination indicated on the right-hand side of Eq. (29) are incorporated to the basic set. The procedure is then repeated until closure is attained.

In a followup paper we illustrate the procedure by applying it to the study of the hydrodynamics of a photoexcited plasma in semiconductors.[65] In that case the closure condition leads to an infinite set of basic variables, consisting of the quasiconserved densities and their tensorial fluxes to all orders. Such a case calls for a truncation procedure leading to a partial closure in the choice of the basic variables that will depend on each specific problem; a particular one is indicated for the aforementioned example in the hydrodynamic limit. Such illustration shows that the fluxes of the quasiconserved densities are in fact to be taken as basic variables as repeatedly stressed in EIT theory. For example, consider the energy-density operator $\hat{h}(\mathbf{r})$ in a fluid of quasiparticles and let H_0 be the kinetic energy; then

$$\frac{1}{i\hbar}[\hat{h}(\mathbf{r}),H_0]=-\mathrm{div}\hat{\mathbf{I}}(\mathbf{r}) \ ,$$

where $\hat{\mathbf{I}}(\mathbf{r})$ is the Hermitian operator for the energy flux. In the representation provided by the reciprocal space of vectors $\mathbf{q}$,

$$[\hat{h}(\mathbf{q}),H_0]=\hbar\mathbf{q}\cdot\hat{\mathbf{I}}(\mathbf{q}) \ ,$$

which is precisely of the form of Eq. (29), and then $\hat{\mathbf{I}}(\mathbf{q})$ is to be included in the basic set according to the rule. Next, $[\hat{\mathbf{I}}(\mathbf{q}),H_0]$ will produce a term proportional to a rank-two tensorial flux and so on; in this way we have the microscopic approach of the treatment in EIT put forward by Perez-Garcia and Jou.[66]

Once the basic set of dynamical quantities P_j, and therefore of variables Q_j (the G space), has been established, the description of the irreversible evolution of the macrostate of the system is given by the equations of evolution for the basic macrovariables, which may be called generalized nonlinear quantum transport equations. These equations are given by Eqs. (28). The right-hand side of this formal expression can be put in the form of a series of collision operators of ever-increasing order in the interaction strength coupling constants.[63] In the so-called NSOM-linear theory of relaxation (LTR), this series of collision operators is truncated to second order to produce Markoffian transport equations given by

$$\frac{d}{dt}Q_j(\mathbf{r},t)=J_j^{(0)}(\mathbf{r},t)+J_j^{(1)}(\mathbf{r},t)+J_j^{(2)}(\mathbf{r},t)\ , \tag{30}$$

where, in Zubarev's approach to the NSOM,[18]

$$J_j^{(0)}(\mathbf{r},t)=\mathrm{Tr}\left[\frac{1}{i\hbar}[P_j(\mathbf{r}),H_0]\rho_{\mathrm{CG}}(t,0)\right]\ , \tag{31a}$$

$$J_j^{(1)}(\mathbf{r},t)=\mathrm{Tr}\left[\frac{1}{i\hbar}[P_j(\mathbf{r}),H']\rho_{\mathrm{CG}}(t,0)\right]\ , \tag{31b}$$

$$\begin{aligned}J_j^{(2)}(\mathbf{r},t)=&\left[\frac{1}{i\hbar}\right]^2\int_{-\infty}^{0}dt'e^{\epsilon t'}\mathrm{Tr}\{[H'(t'),[H',P_j(\mathbf{r})]]\rho_{\mathrm{CG}}(t,0)\}\\&+\frac{1}{i\hbar}\int_{-\infty}^{0}dt'e^{\epsilon t'}\sum_{k=1}^{n}\frac{\delta J_j^{(1)}(\mathbf{r},t)}{Q_k(\mathbf{r},t)}\mathrm{Tr}\{[H'(t'),P_k(\mathbf{r})]\rho_{\mathrm{CG}}(t,0)\}\ .\end{aligned} \tag{31c}$$

Consider now a set of basic variables (fields) $\{Q_j(\mathbf{r},t),\mathbf{I}_j(\mathbf{r},t)\}$, $j=1,\ldots,n$, composed of the secular variables Q_j and the set of their fluxes $\mathbf{I}_j$ (for the sake of simplicity we omit higher-order tensorial fluxes). The auxiliary statistical operator is in this case

$$\rho_{\mathrm{CG}}(t,0)=\exp\left[-\phi_0(t)-\sum_{j=1}^{n}\int d^3r\,F_j(\mathbf{r},t)P_j(\mathbf{r})+\Pi(t)\right]\ , \tag{32}$$

where

$$\Pi(t)=\phi_1(t)+\sum_{k=1}^{n}\int d^3r\,\boldsymbol{\alpha}_k(\mathbf{r},t)\cdot\hat{\mathbf{I}}_k(r,t)\ , \tag{33}$$

with $\phi_0(t)+\phi_1(t)$ ensuring the normalization of ρ_{CG}, and $\phi_0(t)$ normalizes the statistical operator

$$\rho_0(t,0)=\exp\left[-\phi_0-\sum_{j=1}^{n}\int d^3r\,F_j(\mathbf{r},t)P_j(\mathbf{r})\right]\ , \tag{34}$$

i.e., the auxiliary statistical operator in the absence of fluxes $\hat{\mathbf{I}}_k$. Further, according to the NSOM,

$$Q_j(\mathbf{r},t)=\mathrm{Tr}[P_j(\mathbf{r})\rho_\epsilon(t)]=\mathrm{Tr}[P_j(\mathbf{r})\rho_{\mathrm{CG}}(t,0)]\ , \tag{35a}$$

$$\mathbf{I}_k(r,t)=\mathrm{Tr}[\hat{\mathbf{I}}_k(\mathbf{r})\rho_\epsilon(t)]=\mathrm{Tr}[\hat{\mathbf{I}}_k(\mathbf{r})\rho_{\mathrm{CG}}(t,0)]\ , \tag{35b}$$

with F_j and $\boldsymbol{\alpha}_k$ being the thermodynamic conjugate parameters of Q_j and $\mathbf{I}_k$, and ρ_ϵ is Zubarev's NSO.

Consider the NSOM-transport equations for the fluxes [cf. Eqs. (31)], namely,

$$\frac{\partial}{\partial t}\mathbf{I}_k(\mathbf{r},t)=\mathbf{J}_k^{(0)}(\mathbf{r},t)+\left[\frac{1}{i\hbar}\right]^2\int_{-\infty}^{0}dt'e^{\epsilon t'}\mathrm{Tr}\{[H'(t'),[H',\hat{\mathbf{I}}_k(\mathbf{r})]]\rho_{\mathrm{CG}}(t,0)\}\ , \tag{36}$$

where we have taken $J^{(1)}$ null for the sake of simplicity. We proceed next to reorganize Eqs. (36) in order to put into clear evidence the contribution of the fluxes $\mathbf{I}_j$ to the collision operators. For this purpose we expand the auxiliary statistical operator in a series of powers in the quantity $\Pi(t)$ of Eq. (33). In order to do this, we rewrite Eq. (32), using the operator identity of Eq. (15), in the form

$$\rho_{\mathrm{CG}}(t,0)=[1+K(t)]\rho_0(t,0)\ , \tag{37}$$

where ρ_0 is given by Eq. (34), and

$$K(t)=\int_0^1du\;Y(\Pi|u)[\rho_0(t,0)]^u\Pi(t)[\rho_0(t,0)]^{-u+1}\ , \tag{38a}$$

with Y satisfying the integral equation

$$Y(\Pi|u)=1+\int_0^u dx\;Y(\Pi|x)[\rho_0(t,0)]^x\Pi(t)[\rho_0(t,0)]^{-x}\ . \tag{38b}$$

Hence

$$\frac{\partial}{\partial t}\mathbf{I}_k(\mathbf{r},t)=J_k^{(0)}(\mathbf{r},t)+\left[\frac{1}{i\hbar}\right]^2\int_{-\infty}^{0}dt'e^{\epsilon t'}\mathrm{Tr}\{[H'(t'),[H',\hat{\mathbf{I}}_k(\mathbf{r}')]][1+K(t)]\rho_0(t,0)\}\ . \tag{39}$$

We now take the *linear approximation in the fluxes,* i.e., the case of small deviations of ρ_0, which consists in taking $Y=1$ in Eq. (38a) to obtain

$$K(t)=\int_0^1 du[\rho_0(t,0)]^u \sum_{k=1}^{n} \int d^3r\, \boldsymbol{\alpha}_k(\mathbf{r},t)\cdot\Delta\hat{\mathbf{I}}_k(\mathbf{r})[\rho_0(t,0)]^{-u} , \tag{40}$$

where $\Delta\hat{\mathbf{I}}=\hat{\mathbf{I}}-\mathrm{Tr}(\hat{\mathbf{I}}\rho_0)$.

Further, a linear relationship between the fluxes $\mathbf{I}$ and parameters $\boldsymbol{\alpha}$ can be obtained: Starting from the definition of $\mathbf{I}_k(\mathbf{r},t)$ and using the operator relationship of Eq. (15), we find

$$\mathbf{I}_k(\mathbf{r},t)=\mathrm{Tr}[\hat{\mathbf{I}}_k(\mathbf{r})\rho_{CG}(t,0)]=\mathrm{Tr}\{\hat{\mathbf{I}}_k(\mathbf{r})[1+K(t)]\rho_0(t,0)\} ,$$

and, in linear approximation in the fluxes,

$$\mathbf{I}_\mathbf{k}(\mathbf{r},t)\simeq\mathbf{I}_k^{(0)}(\mathbf{r},t)+\sum_{l=1}^{m}\int d^3r'\Lambda_{kl}(\mathbf{r},\mathbf{r}';t)\boldsymbol{\alpha}_l(\mathbf{r}',t) , \tag{41}$$

where

$$\mathbf{I}_k^{(0)}(\mathbf{r},t)=\mathrm{Tr}[\hat{\mathbf{I}}_k(\mathbf{r})\rho_0(t,0)] , \tag{42a}$$

and

$$\Lambda_{kl}(\mathbf{r},\mathbf{r}';t)=\int_0^1 du\ \mathrm{Tr}\{\hat{\mathbf{I}}_k(\mathbf{r})[\rho_0(t,0)]^u\Delta\hat{\mathbf{I}}_l(\mathbf{r}')[\rho_0(t,0)]^{-u+1}\} \tag{42b}$$

is a correlation function of the fluxes $\hat{\mathbf{I}}_k$ over the flux-free macrostate. Defining $\Delta\mathbf{I}=\mathbf{I}-\mathbf{I}^{(0)}$, we have that

$$\Delta\mathbf{I}_k(\mathbf{r},t)=\sum_l\int d^3r'\Lambda_{kl}(\mathbf{r},\mathbf{r}';t)\boldsymbol{\alpha}_l(\mathbf{r}',t) , \tag{43}$$

and inverting it we obtain

$$\boldsymbol{\alpha}_k(\mathbf{r},t)=\sum_l\int d^3r'\Lambda_{kl}^{-1}(\mathbf{r},\mathbf{r}';t)\Delta\mathbf{I}_l(\mathbf{r}',t) . \tag{44}$$

Replacing Eqs. (41) and (44) in Eqs. (39), we find that

$$\frac{\partial}{\partial t}\mathbf{I}_k(\mathbf{r},t)=\mathbf{J}_k^{(0)}(\mathbf{r},t)+\mathbf{J}_{k,0}^{(2)}(\mathbf{r},t)-\sum_{l=1}^{m}\int d^3r'\theta_k^{-1}(\mathbf{r},\mathbf{r}';t)\Delta\mathbf{I}_l(\mathbf{r}',t) , \tag{45}$$

where

$$\mathbf{J}_{k,0}^{(2)}(\mathbf{r},t)=\left[\frac{1}{i\hbar}\right]^2\int_{-\infty}^{0}dt'e^{\epsilon t'}\mathrm{Tr}\{[H'(t'),[H',\hat{\mathbf{I}}_k(\mathbf{r})]]\rho_0(t,0)\} \tag{46}$$

and

$$\theta_{kl}^{-1}(\mathbf{r},\mathbf{r}';t)=\frac{1}{\hbar^2}\sum_r\int_{-\infty}^{0}dt'e^{\epsilon t'}\mathrm{Tr}\{[H'(t'),[H',\hat{\mathbf{I}}_k(\mathbf{r})]]\int_0^1 du[\rho_0(t,0)]^u\Delta\hat{\mathbf{I}}_r(\mathbf{r}')[\rho_0(t,0)]^{-u+1}\}\Lambda_{rl}^{-1}(\mathbf{r},\mathbf{r}';t) . \tag{47}$$

Equation (45) is a linear Mori-Langevin-like equation of a particular type: It consists of three terms: (a) a precession term $\mathbf{J}_k^{(0)}$, related to the modes of evolution in the dynamics generated by H_0, (b) a term $\mathbf{J}_{k,0}^{(2)}$ involving relaxation effects of the flux while the macrostate of the system is evolving in the subspace of the secular variables, and (c) a term containing a nonlocal, time-dependent relaxation-time matrix $\theta(\mathbf{r},\mathbf{r}';t)$. The term $\mathbf{J}_k^{(0)}$ is the part that corresponds to the conservation equation (interaction free) for $\mathbf{I}$ and should take the form of the divergence of a tensorial flux (see paper II, following article).

Equation (45) may also be considered an equation of evolution for the fluxes of the Maxwell-Vernotte-Cattaneo type, as those obtained in EIT. This is explicitly shown in the particular case worked out in paper II. Multiplying Eq. (45) by the matrix θ, we find

$$\int d^3r'\theta(\mathbf{r},\mathbf{r}';t)\frac{\partial\mathbf{I}_j(\mathbf{r}',t)}{\partial t}=\int d^3r'\theta(\mathbf{r},\mathbf{r}';t)\mathbf{J}_j^{(0)}(\mathbf{r}',t)-\Delta\mathbf{I}_j(\mathbf{r},t) , \tag{48}$$

where we omitted the term with $J^{(2)}$. In the quasistatic regime, the right-hand side equals zero and corresponds to the usual constitutive equations (in a nonlocal version), e.g., Fick's or Fourier's ones for the fluxes of matter and energy, respectively. The term on the left, let us call it Maxwell's term, leads to partial differential equations for the corresponding quasiconserved quantities that are of the hyperbolic type (telegraphistlike equation) instead of the parabolic one in the usual theory (e.g., Fourier's heat equation), thus removing the problem of propagation of thermal perturbations with infinite velocity.

V. CONCLUSIONS

As described in Sec. III, Jaynes's predictive statistical physics[8,67] allows for the construction of a general approach to the nonequilibrium statistical operator method. The NSOM, on its own, seems to have an important role in the generation of the statistical-mechanic foundation for phenomenological irreversible thermodynamics. It provides a way to rederive the basic theorems regarding evolution and (in)stability of dissipative many-body systems[43] and retrieves the results of LIT, Kubo's transport theory, and linear response function theory.[68] In this paper we showed that it also covers the case of extended irreversible thermodynamics. This is possible as a result of the application of Bogoluibov's[58] principle of correlation weakening, fundamental for the construction of the NSOM together with the separation in the system Hamiltonian of a secular part H_0 plus the weak interactions, in H', responsible for the dissipative collisional processes, and the iterative application of the Peletminskii-Zubarev symmetry condition of Eq. (29). Moreover, we also construct the statistical NSOM entropy of the system which contains the coarse-grained probability distribution function suitably expressed in terms of the intensive conjugate variables to the set of macro-observables. The main properties of this NSOM entropy is that it is a linear differential term in G space and that its time derivative, the NSOM-entropy production, may be regarded as the natural extension of the entropy production of LIT, which is semipositve definite in the linear regime around equilibrium.[18] It should be stressed that at present there is no way to show such character for the general case of systems arbitrarily away from equilibrium, i.e., for its expression as given by Eq. (26).[69]

The accompanying nonlinear quantum transport theory of the NSOM provides the equations of evolution for the variables of G space. These equations, in their general form, have the structure of transport equations nonlinear and nonlocal in space and time. This structure is too complicated to be analyzed in general, but we know that for small deviations around equilibrium they reduce to those derived by other methods. In this paper (Sec. IV) we have restricted their calculation to the case of weak dependence on the R variables (linear approximation) and the so-called linear theory of relaxation that renders these equations Markoffian in character. In that way they fit into a natural extension of LIT as it has been conceived by some authors.[10,11,25] In particular, the Maxwell-Cattaneo-Vernotte-type equations are recovered with relaxation times and transport coefficients that may, in principle, be calculated from the microscopic dynamics of the system averaged over the coarse-grained probability density $\rho_{CG}(t)$. In fact, Eqs. (48) are the statistical-mechanic version of the phenomenological equations (2). An extension of the calculations including nonlinearity in the fluxes and memory effects, based on the formalism of Ref. 63, is under way and will be reported elsewhere.

Summarizing, it is our belief that the NSOM seems to be a rather adequate formalism to extend the macrovariable space G of ordinary LIT in a way similar to that first formulated by Grad for a dilute gas. The structure of the transport equations for the additional variables is a complicated one, but the equations do resemble the Mori-Langevin equations obtained using projection operator techniques. Yet there is a drastic difference between them, because in the latter ones the computation requires full knowledge of the N-body dynamics, whereas in those obtained by the NSOM the relevant quantities involve taking averages over the nonequilibrium ensemble characterized by $\rho_w(t)$, whose explicit form in G space is known.

Recently, Sieniutycz and Berry[70] have also addressed the question of deriving the conservation laws for nonlocal thermodynamic equilibrium fluids with heat flow from a Hamilton-like variational principle which are compatible with those obtained from kinetic theory up to a certain approximation. The rather interesting results of this work is the role played by the energy and entropy representations in nonequilibrium thermodynamics as well as the role played by the thermal momentum as the natural nonequilibrium variable in the Gibbs equation describing the fluid with heat, instead of the heat flux itself. The relevance of this result in the light of previous formulations of EIT remains to be studied with care.

Finally, we stress that the foundation of EIT provided by the NSOM, besides its conceptual aspects, allows one to obtain explicit expressions for the kinetic coefficients at the microscopic level, i.e., in terms of the molecular dynamics averaged over the nonequilibrium ensemble: Paper II provides an example based on the treatment of a simple physical model. A detailed study of the MCV equations of EIT that the NSOM provides, and the presence of certain novel aspects, is planned to be reported in future papers.

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