1. INTRODUCTION

It is generally considered that the aim of Statistical Mechanics of many-body systems away from equilibrium is to determine their thermodynamic properties, and the evolution in time of their macroscopic observables, in terms of the dynamical laws which govern the motion of their constitutive elements. This implies, first, in the construction of an irreversible thermodynamics and a thermo-hydrodynamics (the latter meaning the particle and energy motion in fluids, rheological properties, etc., with the transport coefficients depending on the macroscopic thermodynamic state of the system). Second, we need to face the all-important derivation of a generalized nonlinear quantum kinetic theory and a response function theory, which are of fundamental relevance to connect theory with observation and experiment, basic for the corroboration of any theory [1], that is, the synthesis leg in the scientific method born in the seventeenth century.

Oliver Penrose [2] has noted that Statistical Mechanics is notorious for conceptual problems to which is difficult to give a convincing answer, mainly: what is the physical significance of a Gibbs' ensemble?; How can we justify the standard ensembles used in equilibrium theory?; What are the right ensembles for nonequilibrium problems?; How can we reconcile the reversibility of microscopic mechanics with the irreversibility of macroscopic behavior? Moreover, related to the case of many-body systems out of equilibrium, the late Ryogo Kubo, in the oppening addres in the Oji Seminar [3], told us that statistical mechanics of nonlinear nonequilibrium phenomena is just in its infancy and further progress can only be hoped by closed cooperation with experiment. Some progress has been achieved since then, and we try in this paper to describe, in a simple manner, some attempts in the direction to provide a path for one particular initial programme to face the questions posited above.

This is the so-called **Nonequilibrium Statistical Operator Method** (**NE-SOM** for short), which, however initially built on intuitive and heuristic arguments, apparently can be incorporated within an interesting approach to the rationalization of statistical mechanics, as contained in the Maximization of (informational-statistical) entropy (**MaxEnt** for short) and Bayesian methods. In that way, NESOM may be considered as covered under the umbrella of the so-called Jaynes' **Predictive Statistical Mechanics** [4]. In the present paper, we attempt a description of the MaxEnt-based NESOM (from now on MaxEnt-NESOM for short) however mainly from a, say, pragmatical point of view: In section **3**, we show its use as a variational principle which allows to codify the different Gibbs'

statistical operators for the traditional ensembles in equilibrium. In section **4**, the application to nonequilibrium situations is described, mainly on intuitive basis through analogy with the case of equilibrium, and the six fundamental steps required to have a complete reliable theory are presented and discussed. Previously, in next section **2**, some general considerations on the rationale of the approach are presented. In section **5** are briefly described some applications of the formalism, like a MaxEnt-NESOM-based Thermodynamics and Thermo-Hydrodynamics of irreversible processes, and an all important Response Function Theory. The latter allows to make contact with experiments, and some successful applications are summarized (they refer to the case of the highly excited photoinjected plasma in semiconductors and of polymers). Finally, in section **6**, are presented some concluding remarks together with a brief account of some associated epistemological aspects of the formalism and criticisms that have been labelled on some of its aspects.

2. GENERAL CONSIDERATIONS

In the study of the macroscopic state of nonequilibrium systems we face greater difficulties than those present in the theory of equilibrium systems. This is mainly due to the fact that a more detailed analysis is necessary to determine the temporal dependence of measurable properties, and to calculate transport coefficients which are time-dependent (that is, depending on the evolution in time of the nonequilibrium macrostate of the system where dissipative processes are unfolding), and which are also space dependent. That dependence is nonlocal in space and non-instantaneous in time, as it encompasses space and time correlations. Robert Zwanzig [5] has summarized the basic goals of nonequilibrium statistical mechanics as consisting of: (i) To derive transport equations and to grasp their structure; (ii) To understand how the approach to equilibrium occurs in natural isolated systems; (iii) To study the properties of steady states; and (iv) To calculate the instantaneous values and the temporal evolution of the physical quantities which specify the macroscopic state of the system. Also according to Zwanzig, for the purpose to face these items, there exist several approaches which can be classified as: (a) Intuitive techniques; (b) Techniques based on the generalization of the theory of gases; (c) Techniques based on the theory of stochastic processes; (d) Expansions from an initial equilibrium ensemble; (e) Generalization of Gibbs' ensemble formalism.

The last item (e) is connected with Penrose's question noticed in the Intro-

duction concerning if there are, and what are, right ensembles for nonequilibrium problems. In the absence of a Gibbs-style ensemble approach, for a long time different kinetic theories were used, with variable success, to deal with the great variety of nonequilibrium phenomena occurring in physical systems in nature. We describe here a proposition for a nonequilibrium statistical ensemble formalism, namely, the already mentioned Nonequilibrium Statistical Operator Method, or NESOM, which appears to provide grounds for a general prescription to choose appropriate ensembles for nonequilibrium systems. The formalim has an accompanying nonlinear quantum transport theory of a large scope (which encompasses as particular limiting cases Boltzmann's and Mori's approaches), a response function theory for arbitrarily-away-from-equilibrium systems, a statistical thermodynamics (the so-called Informational Statistical Thermodynamics), and an accompanying thermo-hydrodynamic for quantum fluids.

NESOM appears as a very powerful, concise, based on sound principles, and elegant formalism of a broad scope to deal with systems arbitrarily away from equilibrium. Zwanzig stated that the formalism "has by far the most appealing structure, and may yet become the most effective method for dealing with nonlinear transport processes" [5]. Later developments have confirmed Zwanzig's prediction. The present structure of the formalism consists in a vast extension and generalization of earlier pioneering approaches, among which we can pinpoint the works of Kirkwood [6], Green [7], Mori-Oppenheim-Ross [8], Mori [9], and Zwanzig [10]. NESOM has been approached from different points of view: some are based on heuristic arguments [8,11-14], others on projection operator techniques [15-17] (the former following Kirkwood and Green and the latter following Zwanzig and Mori). The formalism has been particularly systematized and largely improved by the Russian School of statistical physics, which can be considered to have been initiated by the renowned Nicolai Nicolaievich Bogoliubov [18], and we may also name Nicolai Sergievich Krylov [19], and more recently mainly through the relevant contributions by Dimitrii Zubarev [20,21], Sergei Peletminskii [12,13], and others.

These different approaches to NESOM can be brought together under a unique variational principle. This has been originally done by Zubarev and Kalashnikov [22], and later on reconsidered in Ref. [23] (see also Refs. [24] and [25]). It consists on the maximization, in the context of Information Theory, of Gibbs statistical entropy (to be called fine-grained informational-statistical entropy), subjected to certain constraints, and including non-locality in space, retro-effects, and irreversibility on the macroscopic level. This is the foundation of the nonequilibrium

statistical ensemble formalism that we describe in general terms in following sections. The topic has surfaced in the section "Questions and Answers" of the Am. J. Phys. [26,27]. The question by Baierlein [26], "A central organizing principle for statistical and thermal physics?", was followed by Semura's answer [27] that "the best central organizing principle for statistical and thermal physics is that of maximum [informational] entropy [...]. The principle states that the probability should be chosen to maximize the average missing information of the system, subjected to the constraints imposed by the [available] information. This assignment is consistent with the least biased estimation of probabilities."

As already noticed in Section **1**, the formalism may be considered as covered under the umbrella provided by the scheme of Jaynes' Predictive Statistical Mechanics [4,28]. This is a powerful approach based on the Bayesian method in probability theory, together with the principle of maximization of informational entropy (MaxEnt), and the resulting statistical ensemble formalism here described is the already referred-to as **MaxEnt-NESOM.** Jaynes' scheme implies in a predictive statistics that is built only on the access to the relevant information that there existis of the system [4,29-32]. As pointed out by Jaynes [28]. "How shall we best think about Nature and most efficiently predict her behavior, given only our incomplete knowledge [of the microscopic details of the system]? [...]. We need to see it, not as an example of the N-body equations of motion, but as an example of the logic of scientific inference, which by-passes all details by *going directly from our macroscopic information to the best macroscopic predictions that can be made from that information*" (emphasis is ours) [...]. "Predictive Statistical Mechanics is not a physical theory, but a method of reasoning that accomplishes this by finding, not the particular that the equations of motion say in any particular case, but the general things that they say in 'almost all' cases consisting with our information; for those are the reproducible things".

Again following Jaynes' reasoning, the constuction of a statistical approach is based on "a rather basic principle [...]: If any macrophenomenon is found to be reproducible, then it follows that all microscopic details that were not under the experimenters' control must be irrelevant for understanding and predicting it". Further, "the difficulty of prediction from microstates lies [..] in our own lack of the information needed to apply them. We never know the microstate; only a few aspects of the macrostate. Nevertheless, the aforementioned principle of [macroscopic] reproductibility convinces us that this should be enough; *the relevant information is there, if only we can see how to recognize it and use it*" [emphasis is ours].

As noticed, Predictive Statistical Mechanics is founded on the Bayesian approach in probability theory. According to Jaynes, the question of what are theoretically valid, and pragmatically useful, ways of applying probability theory in science has been approached by Sir Harold Jeffreys]33,34], in the sense that he stated the general philosophy of what scientific inference is and proceeded to carry both the mathematical theory and its implementations. Together with Jaynes and others, the Nobelist Philip W. Anderson [35] mantains that what seems to be the most appropriate probability theory for the sciences is the Bayesian approach. The Bayesian interpretation is that probability is the degree of belief which is consistent to hold in considering a proposition as being true, once other conditioning proposition are taken as true [36]. Or, also according to Anderson: "What Bayesian does is to focus one's attention on the question one wants to ask of the data. It says in effect, how do these data affect my previous knowledge of the situation? It is sometimes called *maximum likelihood thinking, but the essence of it is to clearly identify the possible answers, assign reasonable a priori probabilities to them and then ask which answers have been done more likely by the data"* [emphasis is ours].

The question that arises is, as stated by Jaynes, "how shall we use probability theory to help us do plausible reasoning in situations where, because of incomplete information we cannot use deductive reasoning?" In other words, the main question is how to obtain the probability assignment compatible with the available information, while avoiding unwarranted assumptions. This is answered by Jaynes who formulated the criterion that: the least biased probability assignment $\{p_j\}$, for a set of mutually exclusive events $\{x_l\}$, is the one that maximizes the quantity S_I, sometimes referred to as the *informational entropy*, given by

$$S_I = -\sum_j p_j \ln p_j \qquad , \qquad (1)$$

conditioned by the constraints imposed by the available information. This is based on Shannon's ideas in the mathematical theory of communications [37], who first demonstrated that, for an exhaustive set of mutually exclusive propositions, there exists a unique function measuring the uncertainty of the probability assignment. This is the already mentioned principle of maximization of the informational-statistical entropy, MaxEnt for short. It provides the variational principle which results in a unifying theoretical framework for the NESOM, thus introducing, as we have noticed, the MaxEnt-NESOM as a nonequilibrium statistical ensemble formalism. It should be stressed *that the maximization of S_I implies in making*

maximum the uncertainty in the information available (in Shannon-Brillouin's sense [37,38]), to have in fact the least biased probability assignment.

We proceed in the next two sections to describe the construction of the MaxEnt-NESOM: First we briefly review the case corresponding to Gibbs' equilibrium ensemble formalism, for, in continuation to consider the case of systems arbitrarily away from equilibrium presenting strong dissipative effects.

3. MaxEnt-NESOM IN EQUILIBRIUM CONDITIONS

Let us consider a many-body system in equilibrium with a given set of ideal reservoirs, and, to be specific, let us take the case of thermal and particle reservoirs, with the equilibrium between the system and the two reservoirs implying that they have equal temperature and chemical potential respectively. Moreover, because of Liouville theorem, in any case the statistical operator, designated by $\varrho(t)$, satisfies Liouville-Dirac equation, namely

$$\frac{\partial}{\partial t}\varrho(t) + \frac{1}{i\hbar}\left[\varrho(t), \hat{H}\right] = 0 \quad , \tag{2}$$

where $\hat{H}$ is the system Hamiltonian. In equilibrium ϱ does not depend on time, commutes with the Hamiltonian and, consequently, as well known, it must be a superoperator depending on the dynamical operators corresponding to constants of motion of the system.

The derivation in MaxEnt-NESOM of the equilibrium statistical operator [39] (and also in the local equilibrium approximation [40]) is already a textbook matter [41]. For that purpose, in Eq. (1), index j is to be interpreted as the complete set of quantum numbers which characterizes the eigenstates of the Hamiltonian $\hat{H}$, and p_j is the diagonal matrix element of ϱ in such states. In this case Eq. (1) can alternatively be written in the form

$$S_G = -Tr\left\{\varrho\ln\varrho\right\} \quad , \tag{3}$$

that is, in terms of the trace operator, what thus makes the calculation independent of the quantum representation. This S_G is denominated Gibbs' statistical entropy which multiplied by Boltzmann constant k_B provides in equilibrium the proper thermodynamic entropy in Clausius-Carnot sense [42]. According to Max-Ent, S_G is maximized however subjected to the appropriate normalization of ϱ, that is

$$Tr\left\{\varrho\right\} = 1 \quad , \tag{4}$$

and the other constraints consist into the choice of the relevant constants of motion to be used. But the *one and only information* we do have is the imposed macroscopic condition in the given experiment, namely, the preparation of the system in equilibrium with a thermal and a particle reservoirs. In these conditions are fixed the temperature T, the chemical potential μ, and, of course, the volume V is given. [We recall that the thermodynamic state is then fully described by a thermodynamic potential, which in this case is the so-called grand-canonical free energy $\mathcal{F}(T, V, \mu)$]. Therefore, on the basis of the information we do have, the constraints in the maximization process are the expected values for energy E and particle number N, at the given T and μ (for fixed V), namely

$$E = Tr\left\{\hat{H}\varrho\right\} \quad , \tag{5a}$$

$$N = Tr\left\{\hat{N}\varrho\right\} \quad , \tag{5b}$$

where $\hat{N}$ is the particle number operator. Resorting to the Lagrange variational method for the calculation of the ϱ which makes maximum S_G of Eq. (3) together with the constraints imposed by Eqs. (5a), one easily finds that (see Appendix **I**, first part)

$$\varrho = \exp\left\{-\Phi - F_1\hat{H} - F_2\hat{N}\right\} \quad , \tag{6}$$

where Φ, F_1 and F_2 are the *Lagrange multipliers* that the variational method introduces, and which are related to the three constraints in Eqs. (4), (5a) and (5b) respectively. Moreover, it is usually written

$$\Phi(T, V, \mu) = \ln Z(T, V, \mu) \quad , \tag{7}$$

introducing the grand-partition function Z. The other Lagrange multipliers are related to partial derivatives of the entropy, that is

$$F_1 = \partial S_G/\partial E \quad ; \quad F_2 = \partial S_G/\partial N \quad , \tag{8}$$

and are functions of the basic extensive variables E, V, N. Equations (8) are equations of state connecting extensive and intensive thermodynamic variables, since these Lagrange multipliers F_1 and F_2 are related to the temperature T and the chemical potencial μ: In fact, as known, building Gibbs statistical thermodynamics in terms of ϱ and comparing it with the results of phenomenological thermodynamics, it follows that

$$F_1 = \beta = 1/k_B T \quad ; \quad F_2 = -\mu/k_B T \quad . \tag{9}$$

Moreover, the third Lagrange multiplier Φ, which ensures the normalization of ϱ, determines the grand-canonical free energy

$$\mathcal{F}(T, V, \mu) = -k_B T \Phi(T, V, \mu) = -k_B T \ln Z(T, V, \mu). \tag{10}$$

Hence, the equilibrium statistical operator reads as

$$\varrho = Z^{-1}(T, V, \mu) \exp\left\{-\beta\left(\hat{H} - \mu\hat{N}\right)\right\}, \tag{11}$$

which is precisely Gibbs' grand-canonical statistical operator, with

$$\Phi(T, V, \mu) = \ln Z(T, V, \mu) = \ln Tr\left\{\exp\left[-\beta\left(\hat{H} - \mu\hat{N}\right)\right]\right\}. \tag{12}$$

Along a quite similar line of reasoning, we can derive any Gibbs' canonical statistical operator, simply introducing the appropriate *informational constraints* determined by the given macroscopic conditions of preparation of the system, meaning *the knowledge of the set of reservoirs with which the system is in contact and in equilibrium* (an equilibrium, we stress, defined by equal values of the corresponding intensive thermodynamic variables - the Lagrange multipliers in the formalism - in system and reservoir).

Without further considerations, we simply notice that the local equilibrium situation is described by the statistical operator

$$\varrho(t) = \exp\left\{-\Phi(t) - \int d^3r \ \beta(\vec{r}, t)\left[\hat{h}(\vec{r}) - \mu(\vec{r}, t)\hat{n}(\vec{r})\right]\right\}, \tag{13}$$

where $\hat{h}(\vec{r})$ and $\hat{n}(\vec{r})$ are the locally conserved densities of energy and particle number, $\beta(\vec{r}, t)$, the reciprocal of a field of local temperature and $\mu(\vec{r}, t)$ the field of a local-chemical potential [41]. The corresponding Gibbs' statistical thermodynamics gives microscopic foundations to Classical (sometimes called Linear or Onsagerian) Irreversible Thermodynamics, once the constitutive Fick and Fourier laws for the fluxes of matter and energy are introduced (see for example the classical textbook of Ref. [43]).

The associated Response Function Theory and Transport Theories for weak excitations near the equilibrium state, follow from perturbation theory applied on the equilibrium state described by Eq. (11) corresponding to the equilibrium state of initial preparation of the system in the given experiment [44-47].

4. MaxEnt-NESOM FOR DISSIPATIVE PROCESSES

We consider now a many-body system out of equilibrium, described by a statistical operator $\varrho(t)$, to be derived in MaxEnt-NESOM. It satisfies Liouville equation, Eq. (2), but differently to equilibrium it depends explicity on time, as it describes the evolution of the macroscopic state of the system while dissipative processes unfold in the isolated media. Hence, in this case, we do not have the information available in the case of equilibrium that ϱ is dependent only on constants of motion. Consequently, the first fundamental step in the present situation is to decide on the basic set of dynamical variables appropriate for the description of the macroscopic state of the nonequilibrium system. At this point enters the fundamental *Bogoliubov's principle of correlation weakening,* and the accompanying hierarchy of relaxation times [48,49]. According to this view, a series of successively contracted descriptions is possible because the existence, in many cases, of an array of relaxation times, say $\tau_\mu < \tau_1 < ...$, such that after each one has elapsed, correlations with lifetimes smaller that each one of these time lengths are damped out (that is, the associated dissipative processes have died down) and can be ignored. Then, an ever shortened set of dynamical variables can be used for a proper description of the macrostate of the system; at a sufficiently long time the equilibrium condition is approached (with all correlations being wiped out), and the most contracted descriptions is to be used (i.e., in terms of only $\hat{H}$ and $\hat{N}$ as shown in Section **2**). Uhlenbeck [50] has pointed out that it seems likely that successive contractions of the description are an essential feature of the theory of irreversile processes, and that such contraction must be a property of the basic equations of the system (illustrations in the case of a spin-lattice system and of the photoinjected plasma in semiconductors, are given in Refs. [51] and [52], respectively).

This is fundamental in MaxEnt-NESOM, and has been in practice introduced according to the proposal set forward by, among others, Mori [9,47], Zubarev [14,21], and Peletminskii [12,13]. It consists in the **basic first step** in the formalism consisting into introducing a separation of the total Hamiltonian into two parts, namely

$$\hat{H} = \hat{H}_o + \hat{H}' \qquad , \qquad (14)$$

where $\hat{H}_o$ is the so-called "relevant" (or secular, or quasi-conserving) part, composed by energy operators involving the kinetic energies and a part of the interactions, namely, those strong enough to be responsible for fast dissipative processes with *very short relaxation times,* meaning those smaller than the characteristic

time scale to be used for the description of the system, essentially the resolution time in any given experiment under consideration. Hence, as pointed out by Grandy [40], the ground level in the formulation of a theory is to properly describe the system and the kind of experiment(s) to be analized. It is worth noticing the nowadays impressive development of experimental techniques in ultrafast laser spectroscopy [53] in the pico- and femto-second time scale, and soon, resorting to atomic instead of molecular transitions, extended to the atto-second $[10^{-18}$ sec] scale, and also the development of means of detection with spatial resolution in the nanometer scale. The other contribution, $\hat{H}'$, in Eq. (14) contains the remainig interaction potentials, associated to interactions responsible for processes with *long-time relaxations times* (meaning larger than the experimental characteristic time), in the dissipative processes that develop in the system.

This leads to the **second basic step** in the formalism, namely, to introduce a basic set of dynamical variables, call them $\left\{ \hat{P}_j \right\}$, $j = 1, 2, ...$ (the triangular hat indicating Hermitian operator in Quantum Mechanics, or in Classical Mechanics a dynamical function defined over the phase space). This is done, in analogy with equilibrium, introducing those that are quasi-conserved (quasi-constants of motion) under the dynamics generated by the secular part of the Hamiltonian, namely, $\hat{H}_o$, that is, satisfying what we call *Zubarev-Peletminskii selection rule,* consisting in that the evolution of the basic variables under $\hat{H}_o$ produces linear combinations of the type

$$\frac{1}{i\hbar} \left[\hat{P}_j, \hat{H}_o \right] = \sum_k \alpha_{jk} \hat{P}_k \qquad , \qquad (15)$$

where $j, k = 1, 2, ...$, and, in an appropriate quantum representation (the use of reciprocal space) the α's are c-numbers. In other representations, quantities $\hat{P}$ can be dependent on the space variable, that is, when considering local densities of dynamical variables, and then the α's can depend on the space variable or be differential operators [54-56]. As already noticed, this introduces the quasi-conserved quantities $\hat{P}_j$, in the sense of having associated – at the macroscopic level defined by their average values over the nonequilibrium ensemble – a near dissipationless character, meaning that their relaxation times are much larger than the experimental resolution time (or the corresponding characteristic time in the theoretical analysis being performed). It also needs be stressed that Eq. (15) encompasses the case of quantities $\hat{P}$ for which all coefficients α's on the right are null, i.e. they are full constants of motion under the dynamics generated by $\hat{H}_o$, which itself falls under this condition, and, as a rule, must always be

taken as a basic variable. It is relevant to notice that Zubarev-Peletminskii law provides a kind of a *closure condition* in the accompanying nonlinear-nonlocal-memory dependent kinetic theory, that is, a closed set of equations of evolution, as shown later on as we proceed. As discussed elsewhere [57], this is the statistical counterpart (in Informational Statistical Thermodynamics) of the principle of equipresence in phenomenological Thermodynamics [58,59].

The practical use of the law of Eq. (15) runs as follows: First, the secular part of the Hamiltonian, viz. $\hat{H}_o$, is chosen in the particular problem and conditions under consideration (as noted, it contains the kinetic energies plus the interactions strong enough to produce damping of correlations, responsible for a certain set of dissipative processes, in times smaller than that of the characteristic time of the experiment one has in mind; hence, here Bogoliubov's principle of correlation weakening is fully at work). Second, one introduces a few dinamical variables $\hat{P}$ deemed relevant for the description of the physical problem in hands (typically are chosen the densities of energy and of particle number, to introduce - via the process described below - a kind of nonequilibrium generalized grand-canonical ensemble). Next, the commutator of these firstly chosen variables is performed and the new variables - which are different from those already introduced - appearing in the linear combination indicated by the right-hand side of Eq. (15) are incorporated to the basic set. This procedure is repeated until a closure is attained. For a first choice consisting of the energy density and particle number density, application of the law of Eq. (15) requires to introduce as basic variables the fluxes of all order of energy and mass [55], what constitutes the basis for the construction of a MaxEnt-NESOM-based Thermo-Hydrodynamics [54], that is, a nonclassical hydrodynamics founded in the nonequilibrium thermodynamic state described by IST [60-62].

Briefly summarizing the points described above, we may say that in a first step are separated fast-relaxating processes from the slow ones. Next, on the basis of this, Zubarev-Peletminskii selection rule implies taking into account all dynamical quantities (mechanical observables) that, under the dynamics generated by $\hat{H}_o$, are kept in a subspace of the Hilbert space, and then are referred to as quasi-conserved variables. They are the relevant ones to be retained in the informational-based approach of MaxEnt-NESOM. As already noticed, the procedure is the analog of the choice of the basic variables in the case of systems in equilibrium when it is done on the basis of taking the wholly conserved ones. The point shall be better clarified as we proceed.

4.1. The Variational Method

Once the basic set of variables $\left\{\hat{P}_j\right\}$ has been chosen, in analogy with the case of equilibrium one should, in principle, proceed to obtain the nonequilibrium statistical operator by - according to MaxEnt - maximizing the informational-statistical entropy at time t, given by

$$\bar{S}(t) = -Tr\left\{\bar{\varrho}(t,0)\ln\bar{\varrho}(t,0)\right\} \qquad , \tag{16}$$

subjected to the constraints consisting in the requirement of its normalization

$$Tr\left\{\bar{\varrho}(t,0)\right\} = 1 \qquad , \tag{17}$$

and the chosen set of average values

$$Q_j(\mathbf{r},t) = Tr\left\{\hat{P}_j(\mathbf{r})\,\bar{\varrho}(t,0)\right\} \qquad , \tag{18}$$

where we have explicitly introduced a possible dependence on the space coordinate. Here, we are indicating by $\bar{\varrho}(t,0)$ the statistical operator to follow from application of the variational method in this instantaneous (at time t) procedure; the first t in the argument of $\bar{\varrho}$ stands for the time dependence of the basic thermodynamic variables, and the zero indicates that the dynamical operators are taken in Schroedinger representation (this point will be better clarify below). The set $\{Q_j(\mathbf{r},t)\}$ constitutes the one composed by the macrovariables that are the basic ones in the nonequilibrium thermodynamic description that the MaxEnt-NESOM provides (the so-called Informational Statistical Thermodynamics), or, in other words, they define Gibbs - or nonequilibrium thermodynamic - state space. As already noticed, the selection rule of Eq. (15) provides a set of macrovariables for a closed kinetic theory which accounts for the thermodynamic description of the system and its evolution, the equivalent, as indicated, of the principle of equipresence imposed in some phenomenological thermodynamic theories.

Using the Lagrange multipliers method, it follows that

$$\bar{\varrho}(t,0) = \exp\left\{-\Phi(t) - \sum_j \int d^3r\; F_j(\mathbf{r},t)\,\hat{P}_j(\mathbf{r})\right\} \;, \tag{19}$$

with

$$\Phi(t) = \ln Tr\left\{\exp\left[-\sum_j \int d^3r\; F_j(\mathbf{r},t)\,\hat{P}_j(\mathbf{r})\right]\right\} \;, \tag{20}$$

ensuring the normalization of $\bar{\varrho}$, and where $\{F_j(\mathbf{r}, t)\}$ are the set of Lagrange multipliers that the variational method introduces, and which are determined in terms of the basic macrovariables Q_j by Eq. (18). Moreover, interpreting $\Phi(t)$ as the logarithm of a nonequilibrium ensemble partition function $\bar{Z}(t)$ it follows that

$$Q_j(\mathbf{r}, t) = -\delta\Phi(t)/\delta F_j(\mathbf{r}, t) = -\delta\ln\bar{Z}(t)/\delta F_j(\mathbf{r}, t) , \qquad (21)$$

showing a close analogy with equilibrium, and where δ stands here for functional differential [63].

The statistical operator of Eq. (19) has the form of an instantaneous generalized canonical distribution, and an immediate question is if it properly provides a nonequilibrium statistical mechanics for dissipative systems. The answer is on the *negative.* Indeed: (1) it *does not* satisfy Liouville equation; (2) it *does not* describe the dissipative processes that develop in the system; (3) it *does not* provide a correct kinetic theory for the description of the dissipative processes which are unfolding in the medium; (4) it *does not* give the correct average values for observables, other than those corresponding to the basic dynamical variables in Eq. (18). Taking this statistical operator (whose meaning and relevance will be discussed below) as the one that may properly describe the full nonequilibrium state of the system and its dissipative evolution, has led to some unnecessary confusion and controversy in the past.

The question is then to find the proper nonequilibrium statistical operator that MaxEnt-NESOM should provide. The way out of the dificulties pointed out above is contained in the idea set forward by John Kirkwood in the decade of the forties [6]. He pointed out that the state of the system at time t is strongly dependent on all the previous evolution of the nonequilibrium processes that have been developing in it. Kirkwood introduces this fact, in the context of the transport theory he proposes, in the form of a so-called *time-smoothing procedure,* which is generalized in MaxEnt-NESOM as shown below.

Introducing in MaxEnt-NESOM [22-25] the idea that it must be incorporated all the past history of the system (or *historicity effects*), all along the time interval going from the initial condition of preparation of the sample in the given experiment at, say, time t_o up to time t when a measurement is performed (i.e., when we observe the macroscopic state of the system), we proceed to maximize Gibbs' entropy (sometimes called fine-grained entropy)

$$S_G(t) = -Tr\{\varrho(t)\ln\varrho(t)\} \qquad , \qquad (22)$$

with the normalization and constraints given at any time t' in the interval $t_o \leq$

$t' \leq t$, namely

$$Tr\left\{\varrho\left(t'\right)\right\} \;=\; 1 \quad , \tag{23a}$$

$$Q_j\left(\mathbf{r},t'\right) \;=\; Tr\left\{\hat{P}_j\left(\mathbf{r}\right)\varrho\left(t'\right)\right\} . \tag{23b}$$

Again resorting to Lagrange's procedure we find that (see second part of Appendix **I**)

$$\varrho\left(t\right) = \exp\left\{-\Psi\left(t\right) - \sum_j \int d^3r \int_{t_o}^{t} dt'\; \varphi_j\left(\mathbf{r};t,t'\right)\hat{P}_j\left(\mathbf{r};t-t'\right)\right\}, \tag{24}$$

where

$$\Psi\left(t\right) = \ln Tr\left\{\exp\left[-\sum_j \int d^3r \int_{t_o}^{t} dt'\; \varphi_j\left(\mathbf{r};t,t'\right)\hat{P}_j\left(\mathbf{r};t-t'\right)\right]\right\}, \tag{25}$$

and the φ_j are the corresponding Lagrange multipliers determined in terms of the basic macrovariables by Eq. (23b), and operators $\hat{P}_j$ are given in Heisenberg representation.

An important point to be remarked is that Eqs. (23b) introduce a dynamical character in the chosen information, differently to the case of Eqs. (17) which provide the macroscopic state at only a given time t. Both descriptions, namely the "historical one" via $\varrho\left(t\right)$ and the "instantaneous one", via $\bar{\varrho}\left(t,0\right)$, are related by the relevant fact that both describe at any time t the same macrostate [cf. Eqs. (18) and (23b)], that is, it must be satisfied that

$$Q_j\left(\mathbf{r},t\right) = Tr\left\{\hat{P}_j\left(\vec{r}\right)\bar{\varrho}\left(t,0\right)\right\} = Tr\left\{\hat{P}_j\left(\mathbf{r}\right)\varrho\left(t\right)\right\} . \tag{26}$$

Another relevant observation needs be antecipated at this point to avoid misunderstandings: The statistical operator depends on the information-gathering interval (t_o,t), but it must be kept in mind that this is the formal point consisting in that, as Kirkwood pointed out, the description to be built must contain all the previous history in the development of the macrostate of the system. This is later on translated to the accompanying nonlinear kinetic theory (a far-reaching generalization of those of Boltzmann and Mori), when the set of integro-differential transport equations for the basic variables require us to have access to *only* the value of the macrovariables at time t_o, the initial time of preparation of the system.

Hence, following the two basic steps for the building up of the formalism described in the first part of this section, a **third basic step** has just been introduced, namely, the inclusion of the past history (or, as sometimes called, *retro-effects* or *historicity*) of the macrostate of the dissipative system. A **fourth basic step** needs now be considered, being a generalization of Kirkwood's *time-smoothing procedure*. This is done introducing an extra assumption on the form of the Lagrange multipliers φ_j, in such a way, we stress, that (i) irreversible behavior in the evolution of the macroscopic state of the system is satisfied; (ii) the instantaneous state of the system is given by Eq. (26); (iii) both $\bar{\varrho}$ and ϱ are normalized at each time t, and (iv) it is introduced the set of quantities $\{F_j(\mathbf{r},t)\}$ as intensive variables thermodynamically conjugated to basic macrovariables $\{Q_j(\mathbf{r},t)\}$, what leads a *posteriori* to generate satisfactory Thermodynamic and Thermo-Hydrodynamic theories. This is accomplished introducing the definition

$$\varphi_j(\mathbf{r};t,t') = w(t,t')F_j(\mathbf{r},t) \qquad , \tag{27}$$

where $w(t,t')$ is an auxiliary weight function, which, to satisfy the four points just listed immediatly above, must have well defined properties which are discussed elsewhere [23], and it is verified that

$$\Psi(t) = \int\limits_{-\infty}^{t} dt' w(t,t')\phi(t') \qquad . \tag{28}$$

The function $w(t,t')$ introduces the *time-smoothing procedure*, and, because of the properties it must have to acomplish its purposes, it is acceptable any kernel that the mathematical theory of convergence of trigonometrical series and transform integrals provides. Kirkwood, Green, Mori and others have chosen what in mathematical parlance is Fejèr (or Cesàro-1) kernel, while Zubarev introduced the one consisting in Abel's kernel for w in Eq. (27) - which apparently appears to be the best choice, either mathematically but mainly physically - that is, taking $w(t,t') = \varepsilon \exp\{\varepsilon(t'-t)\}$, where ε is a positive infinitesimal that goes to zero after the calculation of averages has been performed, and with t_o going to minus infinite. Once this choice is introduced in Eq. (24), in Zubarev's approach the nonequilibrium statistical operator, designated by $\varrho_\varepsilon(t)$, after integration by parts in time, can be written in the form (see Appendix **II**)

$$\varrho_\varepsilon(t) = \exp\left\{-\hat{S}(t,0) + \int\limits_{-\infty}^{t} dt'\ e^{\varepsilon(t'-t)}\frac{d}{dt'}\hat{S}(t',t'-t)\right\} \ , \tag{29}$$

where

$$\hat{S}(t,0) = -\ln\bar{\varrho}(t,0) = \Phi(t)\,\hat{1} + \sum_j \int d^3r \; F_j(\mathbf{r},t)\,\hat{P}(\mathbf{r}) \;, \qquad (30)$$

with $\hat{1}$ being the unit operator, $\bar{\varrho}$ is defined in Eq. (19), and

$$\hat{S}(t',t'-t) = \exp\left\{-\frac{1}{i\hbar}(t'-t)\hat{H}\right\}\hat{S}(t',0)\exp\left\{\frac{1}{i\hbar}(t'-t)\hat{H}\right\}. \qquad (31)$$

The operator $\hat{S}(t,0)$ is designated as the *informational-entropy operator*, whose relevance and properties will be evidenced later on.

Several important points can be stressed in connection with the nonequilibrium statistical operator of Eq. (29). First, *the initial condition* at time $t_o \to -\infty$, is

$$\varrho_\varepsilon(t_o) = \bar{\varrho}(t_o,0) \qquad , \qquad (32)$$

what implies in a kind of initial *Stosszahlansatz*, in the sense that the initial state is defined by the instantaneous generalized canonical-like distribution $\bar{\varrho}$, thus ignoring correlations among the basic variables prior to time t_o. Second, $\varrho_\varepsilon(t)$ can be separated into two parts, namely (Refs. [14], [21-24], see also [8] and Appendix **II**)

$$\varrho_\varepsilon(t) = \bar{\varrho}(t,0) + \varrho'_\varepsilon(t) \qquad , \qquad (33)$$

where $\bar{\varrho}(t,0)$ is the instantaneous distribution of Eq. (19). This, and further results associated to the MaxEnt-NESOM-based IST and Kinetic Theory described later on, clarify the role of both $\bar{\varrho}$ and ϱ'_ε. The first one [cf. Eqs. (16) to (19)] defines an instantaneous, at time t, distribution, which describes a "frozen" equilibrium providing at such given time the macroscopic state of the system, and for that reason is sometimes dubbed as the *quasi-equilibrium statistical operator*. This distribution describes the macrostate of the system in a time interval, around t, much smaller than the relaxation times of the basic variables (implying in a "frozen" equilibrium or quasi-equilibrium in such interval). But, of course, for larger time intervals the effect of the dissipational processes comes into action. The dynamics that has led the system to that state at time t from the initial condition of preparation at time t_o [cf. Eq. (32)], as well as its continuing dissipative evolution from that state at time t to eventually a final full equilibrium, is contained in the fundamental contribution $\varrho'_\varepsilon(t)$. Third, there exists a time-dependent projection operator $\mathcal{P}(t)$ with the property that [23,24] (see Appendix **III**)

$$\mathcal{P}(t)\ln\varrho_\varepsilon(t) = \ln\bar{\varrho}(t,0) \qquad . \qquad (34)$$

This projection procedure, a generalization of those of Zwanzig (apparently the first to introduce projection techniques in statistical physics [10]), Mori [9], Zubarev and Kalashnikov [17], and Robertson [15], has interesting characteristics. We recall that the formalism involves the macroscopic description of the system in terms of the set of macrovariables $\{Q_j(\mathbf{r}, t)\}$, which are the average over the nonequilibrium ensemble of the set of dynamical quantities $\left\{\hat{P}_j(\mathbf{r})\right\}$. The latter, which, as already noticed, are quasi-conserved under the dynamics generated by $\hat{H}_o$ [cf. Eq. (14)], are called the "relevant" variables, and we denote the subspace they define as the *informational subspace* of the space of states of the system. The remaining quantities in the dynamical description of the system, namely, those absent from the informational space associated to the constraints in MaxEnt [cf; Eqs. (21)], are called "irrelevant" variables. The role of the projection operation is to introduce what can be referred to as a *coarse-graining procedure,* in the sense that it projects the logarithm of the "fine-grained" statistical operator $\varrho_\varepsilon(t)$ onto the subspace of the "relevant" (informational) variables, this projected part being the logarithm of the auxiliary (or quasi-equilibrium, or "instantaneous frozen", or "coarse-grained") distribution $\bar{\varrho}(t, 0)$, and consequently, the procedure eliminates the "irrelevant" variables, quite in the spirit of the Bayesian-based approach and MaxEnt. The "irrelevant" variables are "hidden" in the contribution $\varrho'_\varepsilon(t)$ to the full distribution $\varrho_\varepsilon(t)$ of Eq. (33), since it depends on the last term in the exponential of Eq. (29), where the differentiation in time drives $\ln\bar{\varrho}$ outside the subspace of "relevant" (informational) variables (see also Appendix **III)**. We stress that the projection operation is time dependent, such dependence corresponding to the fact that the projection $\mathcal{P}(t)$ is determined by the macroscopic state of the system at the time the projection is performed. Further considerations of this projection procedure will appear in the kinetic and thermodynamics theories based on this informational approach, which are briefly discussed later on. Moreover, geometrical-topological implications are derived and discussed in detail by Balian et al. [64].

Two further comments are of relevance. First, for a given dynamical quantity $\hat{A}$, its average value in MaxEnt-NESOM, that is, the expected value to be compared with the experimental measure, is given by

$$\langle \hat{A} \mid t \rangle = \lim_{\varepsilon \to +0} Tr\left\{\hat{A}\varrho_\varepsilon(t)\right\} = Tr\left\{\hat{A}\bar{\varrho}(t, 0)\right\} + \lim_{\varepsilon \to +0} Tr\left\{\hat{A}\varrho'_\varepsilon(t)\right\}, \qquad (35)$$

the last equality following after the separation given by Eq. (33) is introduced. This is the said generalization of Kirkwood time-smoothing averaging [6], and

we can see that the average value is composed of two contributions: one is the average with the quasi-equilibrium distribution (meaning the contribution of the state at the time t), plus the contribution arising out of the dynamical behavior of the system (the one that accounts for the past history and future dissipational evolution). Moreover, this operation introduces in the formalism the so-called *Bogoliubov's method of quasi-averages* [49,65]. Bogoliubov's procedure involves a symmetry-breaking process, which is introduced in order to remove degeneracies connected with one or several groups of transformations in the description of the system. According to Eq. (35) the regular average with $\varrho_\varepsilon(t)$ is followed by the limit of cancelling the *ad hoc* symmetry-breaking introduced by the presence of the weight function w in Eq. (27) (which is Abel's kernel in Zubarev approach, cf. Eq. (29), and follows for ε going to $+0$), which imposes a *breaking of the time-reversal symmetry* in the dynamical description of the system. This is mirrored in the Liouville equation for $\varrho_\varepsilon(t)$: Zubarev's nonequilibrium statistical operator *does* satisfy Liouville equation, but it must be reckoned the fact that the group of its solutions is composed of two subsets, the one corresponding to the retarded solutions and the one corresponding to the advanced solutions. The presence of the weight function w (Abel's kernel in Zubarev's approach) in the *time-smoothing or quasi-average procedure* that has been introduced *selects the subset of retarded solutions* from the total group of solutions of Liouville equation. We call the attention (as Zubarev had; see Appendix in the book of reference [14]) that this has a certain analogy with Gell-Mann and Goldberger [66] procedure in scattering theory, where these authors promote a symmetry-breaking in Bogoliubov's sense in Schroedinger equation, in order to represent the way in which the quantum mechanical state has been prepared during times $-\infty \leq t' \leq t$, adopting for the wave function a weighted time-smoothing as the one used in Zubarev's approach to NESOM (see Appendix **IV)**. More precisely, $\varrho_\varepsilon(t)$ satisfies a Liouville equation of a form that automatically, via Bogoliubov's procedure, selects the retarded solutions, namely

$$\frac{\partial}{\partial t} \ln \varrho_\varepsilon(t) + i\hat{\Lambda}_\varepsilon(t) \ln \varrho_\varepsilon(t) = 0 \qquad , \tag{36}$$

where $\hat{\Lambda}_\varepsilon$ is the modified Liouville operator

$$i\hat{\Lambda}_\varepsilon(t) = i\overset{\wedge}{\mathcal{L}} + \varepsilon\left[1 - \mathcal{P}(t)\right] \qquad , \tag{37}$$

with $\overset{\wedge}{\mathcal{L}}$ being the regular Liouville operator and $\mathcal{P}(t)$ the projection operator of Eq. (34). Equation (36) is of the form proposed by Ilya Prigogine [67], with

$\hat{\Lambda}_\varepsilon$ being composed of even and odd parts under time-reversal. Therefore, the time-smoothing procedure introduces a kind of *Prigogine's dynamical condition for dissipativity* [67,68].

Using Eq. (34) we can rewrite Eq. (36) in the form

$$\frac{\partial}{\partial t} \ln \varrho_\varepsilon\left(t\right) + \frac{1}{i\hbar}\left[\ln \varrho_\varepsilon\left(t\right), \hat{H}\right] = -\varepsilon\left[\ln \varrho_\varepsilon\left(t\right) - \ln \bar{\varrho}\left(t, 0\right)\right] , \qquad (38)$$

viz., a regular Liouville equation but with an infinitesimal source, which introduces Bogoliubov's symmetry breaking of time reversal, and is responsible for disregarding the advanced solutions. Equation (38) is then said to have Boltzmann-Bogoliubov-Prigogine symmetry. Following Zubarev [14], Eq. (38) is interpreted as the logarithm of the statistical operator evolving freely under Liouville operator $\overset{\wedge}{\mathcal{L}}$, from an initial condition at time t_o, and with the system undergoing random transitions, under the influence of the interaction with the surroundings. This is described by a Poisson distribution (w in the form of Abel's kernel), and the result at time t is obtained by averaging over all t' in the interval (t_o, t) [cf. Eq. (24)]. This is the time-smoothing procedure in Kirkwood's sense [cf. Eq. (35)], and therefore, it is introduced information related to the past history in the thermo-hydrodynamics macrostate of the system along its evolution from the inital t_o (further considerations are given in Appendix **IV).**

Two points need be considered here. One is that the initial t_o is usually taken in the remote past $(t_o \rightarrow -\infty)$, and the other that the integration in time in the interval (t_o, t) is weighted by the kernel $w(t, t')$ (Abel's kernel in Zubarev's approach, Fejér's kernel in Kirkwood, Green , Mori approaches; and others are possible). As a consequence the procedure introduces a kind of *evanescent history* as the system macrostate evolves toward the future from the initial condition at time t_o $(\rightarrow -\infty)$. Therefore, the contribution $\varrho'_\varepsilon(t)$ to the full statistical operator, that is, the one describing the dissipative evolution of the state of the system, to be clearly evidenced - as later described - in the resulting kinetic theory, clearly indicates that it has been introduced a *fading memory* process. This may be considered as the statistical-mechanical equivalent of the one proposed in phenomenological continuum-mechanical-based Rational Thermodynamics [58,69]. In Zubarev's approach this fading process occurs in an adiabatic-like form towards the remote past: as time evolves memory decays exponentially with lifetime ε^{-1}.

We may interpret this considering that as time evolves correlations established in the past fad away, and only the most recent ones strongly influence the evolution of the nonequilibrium system; here again is in action Bogoliubov's principle

of correlations weakening. This establishes *irreversible behavior* in the system introducing in a peculiar way a kind of Eddington's *time-arrow:* Colloquially speaking, we may say that because of its fading memory, the system can only evolve irreversibly towards the future and cannot "remember" how to retrive the mechanical trajectories that would return it to the past situations (what is attained when neglecting the advance solutions of Liouville equation). In a sense we may say that Boltzmann original ideas are here at work in quite general conditions [70,71], and in its evolution towards the future, once any external perturbating source is switched off, the system tends to a final state of equilibrium, described by the distribution of section **2**, irrespective of the nonequilibrium initial condition of preparation (this is shown in Refs. [57] and [72] and we simply mention the fact here).

Alvarez-Romero and Garcia-Colin [25] has presented an interesting alternative approach to the derivation of Zubarev's form of MaxEnt-NESOM, however, which differs from ours in the interpretation of the time-smoothing procedure, which they take as implying the connection of an adiabatic perturbation for $t' > t_o$ (we think that these authors mean adiabatic switch on of the interactions in H' responsible for the dissipative processes), instead of implying in a fading-memory interpretation. We need notice that both are interpretations which we feel are equally satisfactory and may be equivalent, but we side with the point of view of irreversible behavior following from - in Boltzmann-Bogoliubov-Prigogine's sense - adiabatic decorrelation of processes in the past. This is the fading-memory phenomenon, introduced in Zubarev's approach as a result of the postulated Poissonian random processes (on the basis that no real system can be wholly isolated), as already discussed. This interpretation aside, we agree with the authors in Ref. [25], in that the method provides adequate convergence properties (ensured by Abel's kernel in Zubarev' approach) for the equations of evolution of the system. These properly describe the irreversible processes unfolding in the media, with an evolution from a specific initial condition of preparation of the system and, after remotion of all external constraints - except thermal and particle reservoirs - tending to the final grand-canonical equilibrium distribution of Section **2.**

Moreover, the convergence imposed by Abel's kernel in Zubarev's approach appears as the most appropriate, not only for the practical mathematical advantages in the calculation it provides, but mostly important, by the attached physical meaning associated to the proposed adiabatic decoupling of correlations which surface in the transport equations in the accompanying MaxEnt-NESOM kinetic theory (see below). In fact, on the one hand this kinetic theory produces, when

restrictions are applied on the general theory, the expected collision operators (as those derived in other kinetic theories) introducing, after the time integration in the interval (t_o, t) has been done, the expected terms of energy renormalization and energy conservation in the collision events. Furthermore, as pointed out by Zubarev [14], Abel's kernel ensures the convergence of the integrals in the calculation of the transport coefficients, which in some cases show divergences when, instead, Fejèr kernel is used (as in Green, Mori, etc. approaches). The procedure also appears as having certain analogies with the so-called repeated randomness assumptions [73,74] as discussed by del Rio and Garcia-Colin [75]. In Appendix **IV** we present other alternative derivations, using a treatment akin to the textbook one for obtaining the ensemble algorithm in equilibrium, also following the ideas proposed by McLennan [11], and a connection with an earlier proposal by I. Prigogine is discussed.

A **fifth basic step** consists in the construction of a *MaxEnt-NESOM-based Nonlinear Kinetic Theory*, that is, the transport (evolution) equations for the basic set of macrovariables that describe the irreversible evolution of the macrostate of the system. They are, in principle, straightforwardly derived, consisting in Heisenberg equations of motion for the corresponding basic dynamical variables (mechanical observables) or Hamilton equations in the classical case, averaged over the nonequilibrium ensemble, namely

$$\frac{\partial}{\partial t} Q_j(\mathbf{r}, t) = Tr \left\{ \frac{1}{i\hbar} \left[\hat{P}_j(\mathbf{r}), \hat{H} \right] \varrho_\varepsilon(t) \right\} \quad . \tag{39}$$

Using the separation of the Hamiltonian as given by Eq. (14), the separation of the statistical operator as given by Eq. (33), the selection rule of Eq. (15), and the equivalence with an instantaneous description as given by Eq. (26), it follows that Eq. (39) can be written in the form [76,77]

$$\frac{\partial}{\partial t} Q_j(\mathbf{r}, t) = J_j^{(0)}(\mathbf{r}, t) + J_j^{(1)}(\mathbf{r}, t) + \mathcal{J}_j(\mathbf{r}, t) \ , \tag{40}$$

where

$$J_j^{(0)}(\mathbf{r}, t) = Tr \left\{ \frac{1}{i\hbar} \left[\hat{P}(\mathbf{r}), \hat{H}_o \right] \bar{\varrho}(t, 0) \right\} \quad , \tag{41a}$$

$$J_j^{(1)}(\mathbf{r}, t) = Tr \left\{ \frac{1}{i\hbar} \left[\hat{P}(\mathbf{r}), \hat{H}' \right] \bar{\varrho}(t, 0) \right\} \quad , \tag{41b}$$

$$\mathcal{J}_j\left(\mathbf{r},t\right) = Tr\left\{\frac{1}{i\hbar}\left[\hat{P}\left(\mathbf{r}\right),\hat{H}'\right]\varrho'_\varepsilon\left(t\right)\right\} \qquad . \tag{42}$$

As shown elsewhere [23,56,76,77] this Eq. (40) can be considered as a far-reaching generalization of Mori's equations [9,47]. It also contains a large generalization of Boltzmann's transport theory, with the original Boltzmann equation for the one-particle distribution retrived under stringent asymptotic limiting conditions; details and discussions are given in Refs. [24] and [78].

In this Eq. (40), in most cases of interest the contribution $J^{(1)}$ is null because of symmetry properties of the interactions in $\hat{H}'$, and the term $J^{(0)}$ provides a conserving part consisting in the divergence of the flux of quantity $Q_j\left(\mathbf{r},t\right)$ [55,56,79]. The last term, i.e. the one of Eq. (42), is the collision operator responsible for relaxation processes, which, evidently, cancels if $\hat{H}'$ or ϱ'_ε is null, what clearly indicates that dissipative phenomena are described by these contributions to the Hamiltonian in Eq. (14), and to the statistical operator in Eq. (33), respectively. Hence, as already anticipated, dissipation is not present in the instantaneous quasi-equilibrium operator $\bar{\varrho}\left(t,0\right)$ of Eq. (19), but in the nonequilibrium operator containing the history and time-smoothing characteristic of $\varrho'_\varepsilon\left(t\right)$ of Eqs. (29) and (33). We notice that if $\hat{H}'$ is null, so is $\varrho'_\varepsilon\left(t\right)$, when $\hat{H}_o$ coincides with the whole Hamiltonian corresponding to a full equilibrium condition, as already discussed.

The collision operator of Eq. (42) requires an, in general, quite difficult, and practically unmanageable, mathematical handling. But for practical use, it can be reformulated in the form of an infinite series of partial collison operators in the form

$$\mathcal{J}_j\left(\mathbf{r},t\right) = \sum_{n=2}^{\infty}\Omega_j^{(n)}\left(\mathbf{r},t\right) \qquad , \tag{43}$$

where quantities $\Omega^{(n)}$ for $n = 2, 3, ...$ can be interpretated as corresponding to describing two-particle, three-particle, etc., collisional processes. These partial collision operators, and then the transport equation (40), are highly nonlinear, with complete details given in Refs. [76,77].

An interesting limiting case is the Markovian approximation to Eq. (40), consisting into retaining in the collision operator of Eq. (43) the interaction $\hat{H}'$ strictly up to second order (limit of weak interactions) [80,81] to obtain for a density $Q_j\left(\mathbf{r},t\right)$ the equation [12,76,77,79]

$$\frac{\partial}{\partial t}Q_j\left(\mathbf{r},t\right) + div\vec{I}_j\left(\mathbf{r},t\right) = J_j^{(2)}\left(\mathbf{r},t\right) \qquad , \tag{44}$$

where $\vec{I}_j$ is the flux of Q_j, and

$$J_j^{(2)}(\mathbf{r}, t) = \int_{-\infty}^{t} dt' e^{\varepsilon(t'-t)} Tr \left\{ \left[\hat{H}'(t'-t)_0, \left[\hat{H}', \hat{P}_j(\mathbf{r}) \right] \right] \bar{\varrho}(t,0) \right\}, \qquad (45)$$

once $J_j^{(1)}$ is taken as null, and subindex nought indicates mechanical evolution under $\hat{H}_o$ alone (interaction representation). In Appendix **V** we present a derivation of a MaxEnt-NESOM generalized Mori-like equation, showing the role of the projection operator of Eq. (34) in the kinetic theory.

Finally, the **sixth basic step** is the construction of the all important MaxEnt-NESOM response function theory for systems arbitrarily away from equilibrium, to connect theory with observation and measurement in the experimental procedure. We do not describe it here, what is done elsewhere [23]. We simply notice that as in the traditional response function theory around equilibrium [44,45], the response of the system away from equilibrium to an external probe, is expressed in terms of correlation functions but defined over the nonequilibrium ensemble. Moreover, also in analogy with the case of systems in equilibrium it is possible to construct a double time nonequilibrium thermodynamic Green function formalism [28,82].

In this way, through the realization of the six basic steps we have described, a nonequilibrium statistical ensemble formalism - the MaxEnt-NESOM - can be built. The quite relevant case of a generalized nonequilibrium grand-canonical ensemble is described in Appendix **VI.** Applications of the theory are very briefly described in next section, and further considerations presented in last section.

5. APPLICATIONS OF THE FORMALISM

We briefly summarize in this section some applications of the formalism.

5.1. Theory and Experiment

Three areas of particular interest where the formalism has full and quite useful application are those which study ultrafast dissipative processes in polymers, biological systems, and in highly excited semiconductor systems. A large amount of very succesful experimental studies of these systems is available in the scientific literature on the subject, being centered mainly on measurement of ultrafast

transport and optical properties (see for example [53,83,84]). Before considering these cases, introducing a kind of historical recording we describe several earlier applications of the formalism, certainly incomplete and then we apologize to those authors whose works have been omitted. Moreover, the description of the different applications is in most cases summarized by writting the Abstract of the publication, and the articles are listed in the References.

Hydrodynamic-like equations were derived by L. A. Prokovskii in 1968 [85], and later on by Zubarev and V. Morosov [86], and **Kinetic equations** in a theory of relaxation phenomena by Prokovskii [87], Zubarev and A. G. Bashkirov [88-90], and others. A *double-time nonequilibrium Green function theory* is due to V. P. Kalashnikov [91-93]. Studies of **nuclear spin diffusion** were carried by L. L. Buishvili and Zubarev [94], Buishvili [95], G. R. Khutsishvili [96,97], and of **nuclear magnetic resonance** by Buishvili [98,99], Buishvili and M. D. Zvizdadze [100-105], Buishvili and N. P. Giogadze [106], etc. **Spin-lattice relaxation** was considered by V. G. Grachev [107], Kalashnikov [108-110], K. Walasek and A. L. Kuzemskii [111,112]. L. L Buishvili and M. D. Zviadadze [113] discuss the problem of the choice of the independent internal thermodynamic parameters for the description of nonequilibrium systems on the basis of Bogoliubov's idea concerning the hierarchy of relaxation times as well as successive reductions in the description of nonequilibrium states of the system when it tends to equilibrium. The set of parameters is shown to be specified, in principle, by the explicit form of the Hamiltonian of the system. General conclusions were used to analyse a number of difficulties in the phenomenological theory of magnetic relaxation in solids. Special attention was paid to a good choice of macroscopic parameters. The problem concerning the question why in some cases the application of Bloch equations is incorrect was discussed.

V. P. Kalashnikov and N. V, Kozhevnikov have dealt with a two-component spin system in [114], where the nonequilibrium statistical operator method is used to consider the dynamics of a two-component isothermal magnetic system in an alternating magnetic field. Exact coupled equations of motion were obtained for the small deviations from equilibrium of the magnetizations of the subsystems, together with dispersion relations for the spectra of the normal modes and exact general expressions for the matrix Green's functions, the dynamic magnetic susceptibility, and the power obsorbed in the external field. A self-consistent approach was formulated for the calculation of these quantities in terms of the exact characteristics of the noninteracting subsystems. More recently M. Yu. Kovalevskii and S. V. Peletminskii [115] have considered a hydrodynamic theory

in magnetic media, where a microscopic approach to the description of the dynamics of magnets with complete spontaneous symmetry breaking is proposed. The structure of the source that breaks the symmetry of the equilibrium Gibbs distribution was established, and additional thermodynamic parameters (Cartan forms) that characterize the equilibrium state were introduced. The quasiaverage representation was generalized to locally equilibrium states, and the thermodynamics of such systems is constructed. The flux densities of the additive integrals of the motion were represented in terms of the local-equilibrium thermodynamic potential. An expression was found for the orthogonal rotation matrix in terms of an arbritrary statistical operator. A method of reduced description is formulated, and "hydrodynamic" equations of the considered magnets were obtained.

Now going over to the relevant area of **semiconductor physics**, first applications seems to be due to V. P. Kalashnikov, in connection with the so-called **'hot' electrons in semiconductors.** His work using MaxEnt-NESOM was cited as a satisfactory approach by J. Brinkman in an invited talk in the 21st International Conference on the Physics of Semiconductors (Stuttgart, Germany, July 1994). In [116] we read in the Abstract that the nonequilibrium density matrix, obtained from quantum energy and momentum conservation laws, is used to describe the motion of hot carriers in semiconductors. In an earlier publication [117] the nuclear polarization resulting from the interaction of the nuclei with a nonequilibrium steady-state distribution of hot conduction electrons, generated by crossed static magnetic and strong electric fields, was investigated theoretically. The effect of a strong electric field on the spin-lattice relaxation times of the conduction electrons and the relaxation time of the nuclei by hyperfine interaction with hot carriers were considered for various types of semiconductors. Formulae for the field-enhanced nuclear magnetization, and for the relaxation times of the electronic and nuclear magnetic moments, were obtained as function of the current density of the conduction electrons. Later on, in [118] the many-electron nonequilibrium statistical operator was used to construct the equations of momentum and energy balance. These describe the kinetics of spatially homogeneous distributions of current carriers in conducting crystals in strong crossed electric and magnetic fields. A study was made of the case of high densities of the conduction electrons when their nonequilibrium state can be described by the average values of the total energy, total momentum, and particle number. In [119] the nonequilibrium statistical operator method was used to derive a system of balance equations for the momentum density and particle number in the energy space. This system determines the kinetics of hot electrons in strong crossed electric and magnetic

fields. For quasielastic scattering the equations are tranformed into differential equations that describe the diffusion of electrons in the energy space; they are integrated in the lowest approximation in the ratio of the relaxation frequency of the transverse momentum to the frequency of the cyclotron motion.

This topic of hot carriers incorporating the idea of Jaynes' Maxent, was further carried on by H. Sato [120], and by V. Christoph, G. Vojta, and R. Röpke [121], Röpke and Christoph [122], Röpke, Christoph, and Vojta [123], where a direct calculation of the electrical resistivity of an electron-phonon system was made by means of the force-force correlation function method. The coupling of the system being considered to a bath is essential for the correct physical and mathematical formulation of the theory. It was assumed that the conduction electrons interact with the longitudinal phonons (only normal processes were taken into account). The interaction of the longitudinal phonons with the bath was given by a relaxation term with a wave-vector dependent relaxation time. The corrections to the electrical resistivity caused by the finite coupling strength between phonons and bath were derived in lowest order and discussed; they are connected with the phonon drag.

V. P. Semiozhenko and A. A. Yatsenko considered the kinetic of systems in strong alternating fields [124], where an equation is obtained for the density matrix of a system of interaction particles in a strong alternating external field. For a system of electrons interactiong with impurities and phonons, the limit corresponding to an arbitrarily strong constant electric field was obtained. Examples considered were the problem of the high-frequency conductivity of the electron gas of semiconductors and the Cooper pairing of electrons in a strong electromagneitic field.

When dealing with transport phenomena is relevant considering the presence of the electron-phonon interaction in nonequilibrium conditions, with earlier studies due several authors, and we mention here Auslender and Kalashnikov [125], who obtained an explicit expression and an integral equation was derived for the generating functional of a nonequilibrium electron-phonon system. A closed non-Markov equation of motion was derived for the quasi-equilibrium generating functional, from which a system of exact kinetic equations was derived, and also an equation for the macroscopic displacement of the lattice. In the second order in the interaction, collision integrals were obtained for the one-particle density matrices. In the spatially homogeneous case and in the Markov limit approximate expressions were constructed for the collision integrals that take into account the nonsharp energy conservation law in collisions and renormalization of the inter-

action.

Kalashnikov [126] considered the interaction of carriers with an external electromagnetic field. In this work a study is made of the structure of the Hamiltonian for the interaction of conduction electrons with an electromagnetic field, and semiconducting crystals were considered whose Hamiltonian contains terms that depend on both the spin and the kinetic degrees of freedom of the electrons. It was shown that the previously constructed interaction Hamiltonians for such systems break the gauge invariance of the equations of motion of the physical quantities. By means of a time-dependent canonical transformation of the system's Hamiltonian, a new expression was found for the operator of the interaction with the field, and this preserves the gauge invariance of the equations of motion. Canonical transformations of the basis operators in the nonequilibrium statistical operator method were considered. Expressions that are exact with respect to the internal interactions of the subsystems were constructed for the power absorbed by the electrons in the second order in the strengths of the electric and the magnetic field.

This question was also considered by V. I. Emelyanov in [127] where a method is described for deriving kinetic equations for an electron subsystem with a band spectrum interacting with a photon subsystem. Kinetic equations with allowance for the polarization were obtained for the diagonal and nondiagonal (relative to the bands) elements of the density matrix. The polarization leads to renormalization of the photon frequencies and interaction of the electrons with one another through the exchange of virtual photons. The relaxation of the band populations and the polarization due to an external field were studied in the two-band approximation by means of the collision integrals obtained in the method.

This system of so-called 'hot' carriers in semiconductors belongs to the area of the **photoinjected highly excited two-component plasma in semiconductors (HEPS),** a physical phenomenon of large relevance reviewed in some of its aspects by V. S. Vorobev [128] (see also Proceedings of the International Conferences on Hot Carriers in Semiconductors [129]). In Vorobev's work are described the physical phenomena which result in the appearance of plasma near the surface of a solid heated by laser radiation. They include: the dynamics of heating and vaporization of the solid surface as a whole; separate defects of the surface, and aerosol particles; the hydrodynamics of the expansion of the vaporized material into the gas surrounding the target; and, the kinetics of ionization in the vapors or in their mixture with the surrounding gas. Plasma formation is linked, first, to the necessity of having sufficiently high vapor density in the interaction zone

or to heating of the target up to a definite temperature, which imposes definite requirements on the energy parameters of the laser pulse. It is also linked to the possibility of development of ionization in the vapors or their mixtures with the surrounding gas; this dictates a definite laser-pulse intensity. Starting from these requirements, the boundary of the plasma region is found in the energy-intensity plane. The moment at which plasma appears is determined as the point of intersection of this boundary by the laser pulse in the same plane. Different cases of plasma formation in diffusion and hydrodynamic regimes of vapor efflux, associated with heating and vaporization of the target as a whole and its microdefects or aerosol particles, are described on the basis of this approach for different materials, pressures, and composition of the gas surrounding the target, size of the focusing spot, and durations, shapes, and wavelengths of the laser pulses.

We notice that the statistical characteristics of a regular plasma was considered by M. V. Tokarchuk [130] in a paper in an issue of Teor. Mat. Fiz. dedicated in memory of D. N. Zubarev, who describes how Zubarev's nonequilibrium statistical operator method is used to give a statistical description of a nonequilibrium plasma in its electromagnetic self-field. Generalized transport equations were obtained for the charged particles and the oscillators of the electromagnetic field with allowance made for the local conservation laws. The case of a nonequilibrium plasma was considered.

On the question of optical properties in solid state matter A. Zehe and G. Röpke considered the radiative recombination of hot carriers in cathodo-excited semiconductors [131], where application of the theory of nonequilibrium processes was made to study the relaxation and recombination of high-excited electrons in semiconductors. Following the scheme of a hot-electron theory based on the method of nonequilibrium statistical operator developed by Zubarev and, independently, by McLennan, expressions for relaxation and recombination times of hot carriers has been established, resulting directly from a microscopical description of the system. As an example a free-to-bound transition is discussed (transitions between donor levels and the valence band or between acceptor levels and the conduction band) in (Ga,Al)As. With this, on the one hand, the concept of hot electrons is shown to be related to the general theoretical description and, on the other hand, intensity curves of time-resoved spectra, i.e. the time-variation of spectra after an excitation pulse, are given. Moreover, Röpke [132] uses Zubarev's nonequilibrium statistical operator method to obtain balance equations for a system of interacting electrons in the field of a scattered potential in which both localized and delocalized states are possible. An explicit expression for the con-

ductivity is obtained by calculating the correlation function by the method of thermal Green's functions. In [133] Röpke and Christoph derive a general linear response formula for the isothermal electrical resistivity by means of the nonequilibrium statistical operator formalism of Zubarev-McLennan. The coupling between system and heat bath is taken into account. Röpke and F. E. Höhne in [134] consider that the quantum transport theory of electrical conductivity of a model system of electrons interacting with fixed ions should unify the usual theories of electrical conductivity of doped semiconductors, liquid metals, and dense ion plasmas. Starting from the method of nonequilibrium statistical operator, the conductivity is expressed by correlation functions which can be evaluated using the Green's function technique. Especially, the influence of electron-electron scattering on the conductivity is considered. Results are given for arbitrary degree of degeneration and are compared with results obtained from the solution of the Boltzmann equation by standard methods.

We may mention at this point, on the question of **quantum transport** related to hot carriers, a couple of brief reviews and comments, one by J. R. Barker [135] and the other by L. Reggiani [136]. Furthermore, a **higher-order Einstein relation** for nonlinear charge transport in an approach of the type we are considering, is due to S. A. Hope, G. Feat, and P. T. Landsberg [137], who consider nonlinear terms in relations for current densities which are treated macroscopically, semi-microscopically and microscopically. In the macroscopic treatment, terms in ϕ^2, E^2, $(\nabla n)^2$, $\nabla^2 n$ and $\vec{E} \cdot \nabla n$ are included, where ϕ is the electrostatic potential, n is the carrier concentration and $\vec{E}$ is the electric field. The power series expansion of the current density is valid for equilibrium and yields conductivity-diffusion type Einstein relations. In the semi-microscopic approach a perturbation theory for the density matrix is used, and Einstein relations were then derived by equating the average of the current density operator to zero. In the microscopic approach a Kubo formalism is developed, based on a local nonequilibrium distribution function due to Mori. This leads to Einstein relations via correlation functions and Liouville's equation. A set of such relations which emerge consistently from such a treatment was given.

We notice the quite interesting phenomenon which is present in the photoinjected plasma in semiconductors - at very low temperatures and mainly for indirect gap semiconductors -, consisting in the so-called **Keldysh's condensation,** or formation of **metallic electron-hole droplets** (e.g. [138]). The question was treated by some authors within a scheme akin to MaxEnt-NESOM. We may mention the work of G. Mahler and J. L. Birman [139], where the gas-liquid transition

of an electron-hole plasma is studied under the influence of a donor electron system of density n_D^-. It is found that the density of holes within the drop decreases with increasing n_D^-. The width of the electron-hole recombination line calculated from the joint density of states, is found to go through a minimum in agreement with experiment. It is further shown that the behavior of the linewidth reflects the nature of the impurity-induced semiconductor-metal transition. It is therefore possible to construct the underlying change of the free-carrier density with doping which was demonstrated for Si:P. Condensation seems to occur up to high doping levels. It might also be expected in a number of heavily doped (metallic) semiconductors, for which the metallic phase is not stable with respect to excitation formation under normal conditions. This was followed by a theory of the electron-hole plasma in highly excited Si and Ge [140], where in a macroscopic-model calculation the electron-hole system was treated as an interacting free-carrier system in thermal equilibrium with a nonideal exciton gas. Renormalization of the excitons was approximately taken into account. The chemical potential as a function of the total electron-hole density was discussed with respect to possible unstable regions also in the low-density regime. Making simplifying assumptions, the phase diagram for the matallic condensation was derived for Ge and Si and compared to experimental data.

Some additional work is also due to R. N. Silver in a series of papers: In [141] a theory of electron-hole condensation in germanium and silicon is developed in which recombination, evaporation, and exciton condensation are treated as random processes. An expression was derived for the probability distribution of the number of electron-hole pairs bound to a nucleation center. Consideration of the effects of lifetime, surface tension, and nucleation centers leads to: (i) the relation of multiexciton complexes to electron-hole droplets; (ii) stable droplet sizes which are strong functions of temperature but only weak functions of pair-generation rate; (iii) the possibility of determining the surface tension from size measurements; and (iv) deviations from the usual phase diagram for a liquid-gas transition at very low tempeatures. Detailed numerical calculations were carried out for uniform excitation of germanium and compared to data available from laser excitation experiments. In [142] the dominant relaxation rates in electron-hole condensation are calculated from the stochastic rate equations proposed in a previous paper. These govern the time scale for the nucleation of electron-hole droplets and for fluctuations in the number of electron-hole pairs bound to a nucleation center. The calculational procedure makes use of exact recursion relations for the temporal moments of the probability distribution. It was found

that metastable states of electrons and holes can exist at high temperatures ($T \gtrsim 2K$ in Ge), for a limited range of exciton densities. At low temperatures the finite carrier lifetimes lead to measurably short relaxation times. The importance of the time dependence of the exciton density in experiments at fixed generation rates was stressed.

Moreover, in [143] is shown that expressions for electron-hole droplet nucleation and decay currents, derived in earlier papers by Silver and others, can be applied to problems of time-dependent exciton densities only in restricted conditions. The induction time, which characterizes the response of nucleation and decay currents to changes in the exciton density, must be shorter than the inverse logarithmic time derivative of the nucleation and decay currents rising high-intensity pulses, and for most decay phenomena except for extremely slow changes in the laser intensity. Finally in [144] a hydrodynamic model for the nonequilibrium thermodynamics of electron-hole droplets in semiconductors was presented. It predicts droplet properties at densities and temperatures where the assumptions of nucleation kinetics fail. It is an extension to finite lifetimes of the Cahn-Hilliard theories of critical droplets and spinodal decomposition. As in finite-lifetime nucleation kinetics both critical and stable droplets are found to exist above a minimum supersaturation which must become large at low temperatures. However, stable droplets differ both quantitatively and qualitatively from the capillarity approximation commonly assumed in nucleation kinetics. For example, they may be characterixed by a velocity profile which peaks in the surface region. Among other novel predictions are that: (i) a maximum supersaturation before phase separation is given by the spinodal line; (ii) stable droplets continue to exist at temperatures approaching T_c but their properties are strongly affected by impurity and phonon scattering; and (iii) at very low temperatures critical droplets are too small for hysteresis, but stable droplet properties are calculated. Quantitative predictions are made by the principle of corresponding states.

Let us now proceed with a recollection of more recent applications of MaxEnt-NESOM in the case of the **photoinjected two-component plasma in semiconductors.**

Consider first the case of **quantum transport.** D. K. Ferry and collaborators have considered in Zubarev's approach the case of transient transport in bulk semiconductors and submicron devices. Ferry et al. [145] call the attention to the fact that essentially all investigations of hot-electron transport in semiconductors are based on a one-electron transport equation, usually the Boltzmann transport equation (BTE). Indeed, the overriding theoretical concern in such high-field

transport is primarily the solution of the transport equation to ascertain the form that the nonequilibrium distribution function takes in the presence of the electric field. However, for transport purposes, this is not an end product, since integrals must be carried out over the distribution function in order to evaluate the transport coefficients. In applications to semiconductor devices, however, the full solution of the BTE is usually too complicated to be determined at each spatial point within the device, and transport equations for relevant observables, such as energy and momentum, are preferred. Such transport equations are obtained by taking moments of the kinetic equation, and these often relate directly to the normal hydrodynamic semiconductor equations. In general, the complicated nature of the kinetic equation precludes solving it analytically, and the existence of the various moment equations is based upon a number of assumptions, the most common of which is that the distribution function can be represened as a displaced Maxwellian.

In small semiconductor devices, the time scales are such that the use of the most common kinetic equation, the BTE, must be questioned. Traditional semi-classical approaches, such as that of the BTE, assume that the response of the carriers to any applied force occurs simultaneously with the applied force, even though the system may undergo subsequent relaxation to a nonequilibrium steady state. On the short time scale of interest though, a truly causal theory introduces memory effects that lead to convolution integrals in the transport coefficients, so that the resultanting kinetic equation is not of the Markovian type. For the steady state, this results in a collision operator that depends upon the frequency of the driving field.

The concerns over the detailed form of the moment equations can be removed by deriving these equations directly from the quantum transport equations. The exact solutions of the Liouville equations describe the time evolution of a statistical ensemble at any time interval after an external field is applied. If the rate of intercarrier scattering is high, then after a short time interval τ_1, smaller than any appropriate time scale of interest, the evolution of the nonequilibrium density matrix must be independent of the initial distribution, and there should be a reduction in the number of parameters necessary to describe the nonequilibrium response of the system [52]. It is therefore possible to assume a nonequilibrium statistical operator that is smoothed in its microfluctuations and from the very beginning describes the slow evolution of the system for time intervals that are larger than τ_1 [21-24,76-78]. By utilizing such an approach, both the relevant moment equations and the form of the distribution function itself are obtained

directly prior to the extension to the semiclassical transport properties. When one introduces a retarded kinetic equation to describe the transport on a short time scale, this retarded equation is a significant deviation from the usual assumption of a simultaneous response to driving forces, and is a consequence of extending the concept of a causal response to the short time scale. Causal behavior is usually associated with ignoring a large percentage of the individual dynamic variables. This is covered by the MaxEnt-NESOM nonlinear quantum kinetic theory described in the previous section.

J. L. Birman and collaborators have used MaxEnt-NESOM for the study of **nonlinear (non-Ohmic) transport** by the carrier system in the photoinjected plasma. In [146] X. L. Ling et al. consider the balance-equation approach for hot-electron transport systems composed of two groups of carriers, each of different effective mass. This is the simplest model for a real band structure of a multivalley semiconductor. The separation of the center-of-mass (c.m.) motion from the relative motion of the electrons is incomplete due to the possibility of exchange of particle number between the two systems and this is taken into account in the Liouville equation for the density matrix. General expressions for the rates of change of the center-of-mass momenta, electron system energies, and particle numbers are obtained. These equations in their classical forms are used for a model calculation for the high-field steady-state transport in GaAs and the calculated results show reasonably good agreement with experiments.

This paper was followed by additional publications: Xing et al. in [147] employ the method of the nonequilibrium statistical operator developed by Zubarev to investigate steady-state hot-electron transport in a strong electric field. The momentum and energy balance equations which are nonlinear in the drift velocity v_e are derived to the lowest order in the electron-impurity and electron-phonon interactions. It is shown that these balance equations are exactly identical to those obtained by Ling et al. [146]. However, their equations cannot be reduced to those of Kalashnikov and Ferry, who previously applied a similar approach to study warm-electron transport. The origin of this difference was demonstrated in detail. These results yield better agreement with the experimental data in p-type Ge for hot heavy-hole transport. D. Y. Xing and C. S. Ting [148] present a Green's-function approach for steady-state hot-electron transport from the transient region: coupled differential and integral equations are constructed for the evolution of the drift velocity $v(t)$ and the electron temperature $T_e(t)$. The effect of current fluctuations on these equations was included and discussed qualitatively. When the evolution equation for $v(t)$ is linearized, a Langevin equation

is obtained for the drift velocity. For electric fields with moderate strengths, it is shown that the calculated values for $v(t)$ as a function of t with memory and without memory differ very little. Thus the memory effect is neglegible and the original evolution equations are reduced to a pair of differential nonlinear equations for $v(t)$ anf $T_e(t)$. Numerical computation has been carried out for hole transport in p-type Ge. Also, scatterings due to both acoustic and nonpolar-optical phonons were considered. For a step field at $t = 0$, $v(t)$ shows the well known ballistic and overshoot behavior. When a rectangular pulse field is applied, both overshoot and undershoot phenomena may appear in $v(t)$.

In [149] M. Liu et al. carry further the study of high-field carrier transport in many-valley semiconductors. They derive for steady states the balance equations for momenta, energies, and populations of the hot electrons in various valleys. Taking n-type silicon as an example, it is calculated the drift velocity, electron temperatures and repopulations of both cold and hot valleys as functions of electric field $(1-10^5 \text{ V/cm})$ at several temperatures between $T = 8\ K$ and $T = 300\ K$. By applying the electric field parallel to the $\langle 111 \rangle$, $\langle 100 \rangle$, and $\langle 110 \rangle$ crystallographic directions, the anisotropic effect for the drift velocity was investigated. Furthermore, when considering the transient repopulation effect for a given sample with a certain length, a negative-differential-mobility region was obtained. It was shown that these results are not only in excellent agreement with the results of Monte Carlo method but also quantitatively comparable with experimental data in all temperature ranges.

Also in this area of nonlinear transport, has also been considered time-dependent conductivity in HEPS, when under the action of a high-frequency oscillating field and in the presence of a constant electric field [150].

Ultrafast transient transport (in the picosecond time scale) has also been considered within the scope of MaxEnt-NESOM. In [151] a study of ultrafast transient transport in nonequilibrium direct-gap polar semiconductors under high levels of excitation is presented. The dynamic equation for the drift velocity was derived. A numerical application, appropriate for the case of photoexcited carriers distributed in the zone-center valleys of GaAs, was done. The time evolution of the momentum relaxation time and drift velocity is discussed, and it is shown that, depending on experimental conditions, a velocity overshoot may result. V. N. Freire et al. [152] present an analytical study of the ultrafast-mobility transient of central-valley nonequilibrium carriers in a highly photoexcited plasma in semiconductors. General expressions for the mobility of the photoinjected carriers were derived. Numerical results were obtained in the case of low to moderately

high fields in GaAs. It was shown that the mobility transient has a structure (maxima and minima) depending on the degree of photoexcitation and electric field intensity. Three different regimes are present, corresponding to (i) structure without overshoot and an Ohmic steady state, (ii) structure with overshoot and a non-Ohmic steady state, and (iii) normal evolution and an Ohmic steady state. A brief discussion of the diffusion coefficient was given.

Transport in HEPS also requires to look for a **generalization of Einstein relation,** linking conductivity and diffusivity, for far-from-equilibrium systems. The diffusion coefficient in a nonlinear transport theory has been considered by Hope et al. as already noticed [137]. Vasconcellos et al. 153] have presented a quasi-thermohydrodynamic theory built in the framework of MaxEnt-NESOM for the study of effects of diffusion in the photogenerated carrier system in highly photoexcited polar semiconductors. It was developed a quantum quasi-hydrodynamic description of the system based on the nonequilibrium statistical operator formalism. It was presented a generalized Fick's diffusion equation for the charge density of the carriers, with the ambipolar diffusion coefficient obtained at the microscopic level and depending on the evolving macroscopic (nonequilbrium thermodynamic) state of the sample. A detailed numerical calculation for the case of GaAs was done, obtaining good agreement with experimental data.

These conductivity and diffusion coefficient in HEPS, calculated in MaxEnt-NESOM, were used to derive a generalized Einstein relation for the nonequilibrium carriers (electrons and holes) for weak and intermediate electric field strengths. It was discussed the effect of the irreversible evolution of the system and of the non-Ohmic behavior on such generalized Einstein relation [154]. This is further analized in [155] where a MaxEnt-NESOM-based response theory to thermal perturbations was applied to a simple model. It was obtained the evolution equation for the particle density, which becomes of the form of a propagating wave with a damping dependent on the diffusion coefficient. The latter was calculated at the microscopic level. For a charged system it is obtained the mobility coefficient for arbitrarily intense electric fields, resulting in a generalized Ohm's law for nonlinear charge transport. Using the expressions for both transport coefficients an Einstein relation in the nonlinear nonequilibrium thermodynamic state of the system was derived.

We turn now our attention to the quite relevant area of **optical properties in HEPS.** The optical properties of semiconductors have been extensively studied, because of both the interest in the comprehension of their microscopic properties and their applications in devices. A considerable amount of information is

available on the subject, and presently the mounting interest in the areas of development of quantum generators and other devices based on semiconductors at high density of excitations has made this one of the dominant fields in the area of semiconductor optics. The hot excitation model has been applied to the study of these problems [the hot electron model has been amply used in the area of high field transport in semiconductors since the pioneering work of Fröhlich(see for example [156])], beginning with the concept of hot excitons at weak to moderate excitation densities, as reviewed by Permogorov [157], and going to some present work on solid state plasma in doped or photoinjected semiconductors at high excitation densities.

Plasmas in semiconductors are quite interesting physical systems, among other reasons, because of the flexibility in the choice of a number of parameters such as Fermi energy, plasma frequency, cyclotron frequency, energy dispersion relation, effective masses, different types of carriers, etc. [158,159]. Furthermore, the carrier concentration n can be controlled either by doping or by the excitation intensity of a pumping laser, producing a variation of n which permits the parameter r_s, the intercarrier spacing measured in units of the excitonic Bohr radius, run through the metallic region ($1 \lesssim r_s \lesssim 5$), which is of particular interest to the study of the electron gas many-body problem [160]. A nonequilibrium distribution of carriers and of optical phonons, with which they interact, can also be obtained in these semiconductor plasmas. The participation of nonequilibrium distributions of carriers and optical phonons and many-body effects in this "hot" high density gas are manifested in the behaviour and shape of optical spectra.

It ought to be noticed that such nonequilibrium distributions can be characterized by well defined Lagrange multipliers that the variational MaxEnt-NESOM introduces, and whose evolution while the experiment is being performed, evolution which is a consequence of the dissipative effects that are developing in the system, are completely determined within the scope of the nonlinear quantum kinetic theory based on MaxEnt-NESOM. It is worth recalling that the Lagrange multipliers associated with the energy operator can be interpreted as the reciprocal a nonequilibrium thermodynamic intensive variable playing the role of a temperature-like quantity, usually refered to as a *quasitemperature*. Hence, within MaxEnt-NESOM is given a more rigorous meaning to such concept which was introduced on phenomenological basis, and used in different contexts, by several authors: H. B. G. Casimir and F. K. du Pre [161] for nuclear spins; C. S. Wamg-Chang, G. E. Uhlenbeck, and J. de Boer [162] for molecules; L. D. Landau [163] for plasmas; H. Fröhlich [164] for electrons excited in strong electric fields; V.

A. Shklovskii [165] for electrons in superconductors; J. Shah and R. C. C. Leite [166] for photoexcited carriers; J. Shah, R. C. C. Leite, and J. F. Scott [167] for photoexcited phonons.

We also call the attention to the fact that HEPS are, at the microscopic quantum-mechanical level, dealt with in the Random Phase Approximation (RPA, sometimes referred to as the generalized time-dependent Hartree-Fock approach); on this we can highlight the books by D. Pines [160], Pines and Nozieres [168], Hedin and Lindquist [169], among others.

On the question of the optical properties of HEPS, we begin recalling that in [52] is provided an illustrative discussion of the role of **Bogoliubov hierarchy of relaxation times in HEPS**, that is, it is considered the question of the contraction of the macroscipic nonequilibrium thermodynamic description of dissipative dynamic systems. As argumented by Bogoliubov, this process is associated to the determination of a spectrum (hierarchy) of relaxation times. Studies of the irreversible evolution of highly photoexcited plasmas in polar semiconductors to provide a way to exemplify and test the existence of such a spectrum of characteristic times were presented. It was shown that, in fact, several kinetic stages can be characterized, each accompanied by a successive contraction in the description of the macroscopic state of the system. A proper choice, depending on the experimental conditions, leads to good agreement with observational data.

Moreover, in [170] is presented a description of the time-dependent thermodynamic properties of the carrier system in HEPS, but resorting to a quite simplified model for better visualization of the illustration: In that paper is described the nonequilibrium thermodynamics of a model for semiconductors under high levels of excitation using the nonequilibrim statistical operator method. The thermodynamic functions in terms of thermodynamic variables that are accesible to experimental measurements via ultrafast laser spectroscopy were obtained. Calculations of entropy production and the rate of entropy production were performed, kinetic equations for the relaxation processes derived and Onsager-like coefficients defined. It was shown that for the system what is considered Prigogine's theorem of minimum entropy production holds even in the non-linear regime, and the that Glansdorff-Prigogine thermodynamic (sometimes referred to as universal) evolution criterion is verified.

In **optical spectroscopy** we need to consider either time-integrated measurements, with collection of data in the, say, nanosecond scale, and time-resolved measurements, with collection of data in the pico- to femto-second scale. We begin with a description of application of MaxEnt-NESOM to the study of data

in **time-integrated experiments.** We summarize some earlier work which was based on a simplified application of MaxEnt-NESOM consisting in assuming an averaged - over the time-resolution of the detection apparatus - of the nonequilibrium statistical operator. That is, the details of the evolution of the system in such interval of time are not evaluated, paying the price of leaving as open parameters the averaged, over such time interval, nonequilibrium thermodynamic variables (the Lagrange multipliers in MaxEnt-NESOM).

In [171] is investigated the effect of plasmon-phonon coupling on the spectrum of laser light scattered by doped semiconductors under high-excitation conditions. A model consisting of the plasmon and LO-phonon subsystems in conditions of quasiequilibrium, characterized by uniform internal temperatures, was used. The scattering cross section was derived through an appropriate generalization of the fluctuation-dissipation theorem and the use of Bogoliubov's Green's-function formalism. The Coulomb interaction between electrons was treated within the random-phase approximation and the Fröhlich Hamiltonian was used to describe the electron-phonon interaction. The phonon lifetime and plasma lifetime, other than Landau damping, were introduced in a phenomenological way. Numerical calculations for the case of a nondegenerate conduction-electron gas in GaAs were presented. The analysis was completed with a discussion of resonant Raman scattering when "hot" polarons are considered for the intermediate states of the scattering amplitude.

The dependence of photoluminescence on hot excitations (in carrier and phonon systems) is considered in [172], where the high energy tail of the photoluminescence spectra of CdS in conditions of high photoexcitation intensities is studied. It was shown that the increasing excitation is a result of the simultaneous effect of nonequilibrium distribution of electrons and LO-phonons. This has also been further considered by E. A. Meneses et al. in [173], where experimental results concerning the photoluminescence spectrum of CdS under high excitation intensities were considered. With increasing excitation intensity the single emission band observed at $77K$ shows a peak displacement towards lower energies, an enhancement of its low-energy side as well as of its high-energy side. These effects increase with excitation intensity. It was described a complete model that can account for the above behavior and the emission band shape. The broadening is mainly due to nonequilibrium distributions of LO phonons, though contributions to the high-energy side from hot electrons is quite significant. Self-energy corrections account for the energy-gap reduction and consequently for the shift of the luminescence band peak towards lower energies.

The above and other resuts are described in [174], where progress (up to the end of the decade of the seventies) in the investigation of optical responses from highly photo-excited semiconductor plasma is reviewed. The theoretical interpretation of the spectroscopy data is outlined on the basis of the coupling of the usual scattering theory with Zubarev's nonequilibrium statistical operator method. Connection with appropriate extension to the nonequilibrium state of the thermodynamic double-time Green functions was also presented. **Magneto-optical effects** in HEPS have been also considered in the above mentioned simplified form of MaxEnt-NESOM and we can mention inelastic scattering of light from a hot magnetoplasma in direct-gap polar semiconductors [175], analized for an arbitrary experimental geometry; the geometry-dependent mixing between the hybrid-plasma first cyclotron mode and the first Berstein mode was studied. Also, field-dependent alternative effects are discussed. Moreover, in [176] is considered the inelastic scattering of light by single-particle spin-flip electron excitations and paramagnetic spin-wave in semiconductor magneto-plasmas. The generalized Landau quasiparticle picture was used to calculate the Raman cross section. Particular attention is given to n-doped GaAs for carrier concentrations in the metallic region ($r_s = 1$ to 6). Scattering of the carriers with lattice vibrations was considered to discuss the spin-diffusion coefficient, in uniform quasi-equilibrium conditions, as a function of the magnetic field and the electron effective temperature. Spin-flip magneto-Raman investigations in doped semiconductors can produce valuable information on the "hot metallic electron liquid" and its interactions.

S. Frota-Pessoa and R. Luzzi [177] have considered resonant Raman scattering of longitudinal optical phonons in HEPS in magnetic fields. The influence of the electron-phonon interaction on the Raman line was studied. It was shown that significant effects appear when, for certain experimental geometries, a harmonic of the cyclotron frequency equals the LO-phonon frequency. The frequency shift and line shape were discussed and application to GaAs made.

Another kind of resonant magneto-Raman scattering was considered by A. J. Sampaio and R. Luzzi [178], that is, direct gap, small effective mass, n-doped semiconductors were considered in conditions in which the laser and the scattered frequencies are of the order and larger than the harmonics of the cyclotron frequency. In these resonant and near resonant conditions the lifetime of the intermediate states gives important contribution to the scattered intensity. A calculation was presented of the scattering cross-section for the magneto-Raman scattering by LO phonons which includes the electron-phonon interaction contribution to the electron lifetimes. Numerical study in the case of InSb was done.

Let us now consider the case of **ultrafast laser spectroscopy** [53,83,84,179]. Inelastic scattering of light by 'hot' carriers is considered in [180], where a theoretical study of time-resolved Raman scattering by a highly photoexcited semiconductor plasma was described. The scattering cross-section was calculated with numerical results appropriate for GaAs presented as an illustration. These results were derived resorting to a MaxEnt-NESOM-based formalism to determine the response function of a sample in conditions far from thermal equilibrium [181]. The scattering cross section was expressed in terms of double-time correlation functions, which were related to appropriate nonequilibrium thermodynamic Green's functions.

These results were extended to include the phenomenon of hybridization of plasma waves and longitudinal optical phonon [182]. In this work the ultra-fast time-resoved Raman spectra of a highly photoexcited semiconductor plasma is calculated. Information is provided on the time-evolution of irreversible relaxation processes that develop in the system. It was described how plasmon-phonon interference effects in the Raman spectra are affected in the far-from-equilibrium state of the system. A numerical analysis appropriate for the case of GaAs samples was presented.

As already noticed ultrafast time-resolved Raman scattering, luminescence, reflectivity, etc., provide a notable amount of information on the dissipative relaxation processes in matter [53,83,84,179]. We do not go in length on a number of results presently available, simply mentioning the review article [183] to be followed by an up-to-date addendum [184]. Also general considerations are given in [185], where is presented a summarized discussion of the question of the very rapid relaxation processes that follow in the photoinjected plasma in semiconductors, phenomena that can be experimantally studied via ultrafast laser spectroscopy.

Moreover, in [186] is discussed the ultrafast kinetics of evolution of optical phonons in a photoinjected highly excited plasma in semiconductors. The state of the nonequilibrium ("hot") phonon system is described in terms of the concept of a nonequilibrium temperature, referred to as *quasitemperature*, per mode, which can be experimentally characterized and measured. The phonon emission time shows that optical phonons are preferentially produced, well in excess of equilibrium, in a reduced off-center region of the Brillouin zone. The phonons in this region are responsible for the phenomenon referred to as "hot-phonon temperature overshoot". Most of the phonons, namely, those outside such region, are only weakly to moderately excited, and mutual thermalization of the nonequilibrium carriers and optical phonons follows, typically, in the tenfold picosecond scale. All

these results are influenced by the experimental conditions, which were discussed on the basis of calculations specialized for GaAs. Comparison with experimental data was presented, showing good agreement.

Recently an interesting phenomenon was observed in experiments measuring time-resolved changes in the reflectivity of GaAs and others materials, in which a distinct oscillation of the signal in real time was observed [187]. Such phenomenon was attributed to the generation of coherent lattice vibrations, and some theoretical approaches were presented. The question is reconsidered in [188] on the basis of a description in the framework of MaxEnt-NESOM, where it is shown that the phenomenon originates in nonlinear coupling of plasma waves and coherent lattice vibrations, in the nonequilibrium conditions created in the pump-probe experiment. The plasma waves are strongly excited through coupling with the coherent photons in the laser-electromagnetic field, and become the source for the creation of the coherent phonons.

Besides the above mentioned pump-probe experiments, which allow to follow the ultrafast development of dissipative processes in the medium, we can also mention the case of continuous excitation leading to **nonequilibrum dissipative-steady states.** In the same vein used to describe the topics above, we summarize several results in this area which have been treated in MaxEnt-NESOM.

S. A. Hassan et al. [189] have developed an analysis of the nonequilibrium thermodynamics of a dissipative system, dealt with at the mechano-statistical level provided by informational-statistical thermodynamics. In particular the case of a highly excited photoinjected plasma in a polar semiconductor was considered. Under continuous constant illumination, a steady state sets in, whose macroscopic state was characterized, and the main mechanisms for pumping and dissipation that are involved were discussed. It is shown that such evolution displays a phenomenon of quasitemperature overshoot.

The influence of nonlinear contributions in the kinetic equations that govern the evolution of the macrostate in HEPS under continuous laser illumination, which appear as one considers higher order collision processes in the nonlinear kinetic theory in MaxEnt-NESOM, are considered in [190]. It was analized how dissipative nonlinear processes influence the photoproduction of optical phonons in n-doped polar semiconductors. It was demonstrated that such nonlinear effects may lead to interesting and remarkable results. First it was shown that, through free-carrier absorption processes, LO phonons in excess of equilibrium are produced in a small off-center region of reciprocal space, second, that nonlinear relaxation effects are unimportant at weak to intermediate laser intensities

but come to play a role in the range of strong excitations. On the one hand, they reduce the amplification of the preferentially pumped modes, and at very strong levels of photoexcitation the nonlinear contributions are responsible for a channeling of energy from the pumped modes to the modes with lowest frequency which grow enormously: it follows a phenomenon akin to a nonequilibrium Bose-Einstein condensation. Even though this effect is hardly accessible experimentally in real semiconductors under laser-light excitation, it may follow in other system, like biological polymers.

The possible emergence of complex behavior in HEPS under constant excitation is considered in [191] where the nonequilibrium steady state of a direct gap semiconductor is studied under high levels of photoexcitation by continuous laser light. The stability of the uniform steady state of itinerant carriers is probed resorting to linear normal mode analysis of the nonlinear equations of evolution for the carrier charge density. Such analysis leads to the determination of the wavevector dependent electronic contribution to the dielectric function. Examination of its behavior allows us to show that in the extremely degenerate regime the carrier system becomes nonmetallic, and displays a coexistence of metallic and nonmetallic phases on leaving that regime: itinerant carriers move in the background of an extended state of bounded electron and hole charge densities. This introduces a new view of Mott transition in photoinjected semiconductors. This complex behavior is a result of collective together with dissipative effects in the far from equilibrium carrier system governed by nonlinear dynamic laws.

The elementary excitations in the carrier's system in HEPS has been determined [192] resorting to MaxEnt-NESOM. It is calculated of the Raman spectrum of the double (electrons and holes) photoinjected plasma in direct-gap polar semiconductors. It allows to identify four types of elementary excitations in the photoinjected carrier system. Besides the expected two Raman bands corresponding to single quasi-particle excitations and a higher frequency plasma wave (labelled optical), there appears a low-frequency band. It shows linear energy dispersion relation and is labelled an acoustic plasma oscillation. While the optical plasma branch is ascribed to the out of phase collective movement of both types of carriers interacting through the bare Coulomb interaction, the acoustic branch is ascribed to the in-phase oscillation of each type of carriers interacting through the screened part of Coulomb interaction. This type of excitation has been experimentally evidenced.

The interesting possibility of spatial ordering - formation of a steady-state charge density wave - in the carrier's system in HEPS is considered in [193]. The

case of n-doped direct-gap polar semiconductors under continuous laser illumination was studied. It is shown that the solution consisting of the homogeneous population of electrons and holes, that develops from the equilibrium state with increasing values of the laser power flux, presents a bifurcation point. A new solution emerges from it corresponding to the formation of a steady-state spatially organized structure in the carrier charge density in the form of a polarization wave. This dissipative structure occurs beyond a critical distance from equilibrium, when a fluctuation drives the carrier system to such self-organized macroscopically ordered state. It is stabilized by the joint action of collective and dissipative effects.

The physics of low-dimensional semiconductors is acquiring continuous relevance (see for example [194]). On the basis of MaxEnt-NESOM, Hassan et al. [195] describe the production and the optical properties of the nonequilibrium photoinjected plasma in semiconductor quantum wires under continuous UV-light illumination. The wavenumber-dependent dynamic dielectric function of this system was derived and the Raman scattering cross-section calculated. From the latter it is identified the contributions from different types of elementary excitations. They are composed of, besides the single-particle excitations, two types of collective oscillations: An upper one, consisting of an intrasubband-like plasmon and a lower one, identified as an acoustic-like plasmon. The dependence of both on the nonequilibrium (dissipative) macroscopic state of the system is evidenced and discussed.

The case of steady states far from equilibrium also encompasses an area of particular interest, namely systems that may display the so-called **complex behavior**, which can arise in systems whose evolution is governed by nonlinear kinetic laws (see for example [196]). A possible role of Predictive Statistical Mechanics in the realm of Complexity Theory is considered in [196,197], where some aspects of the physics of dissipative phenomena are analized. Attention is called to its connection with the emerging theory of complexity, and its place in the realm of nonlinear physics. This nonlinearity has a fundamental role in determining complex behavior in open systems far away from equilibrium. In many cases it shall lead to the formation of *self-organized synergetic behavior* at the macroscopic level, in the form of the so called Prigogine's dissipative structures. Dissipation is then not a source of decay but has a constructive role, maybe including the emergence of life, natural evolution, and the astounding functioning of living systems. This is the question of order out of chaos in complex system, i.e. synergetic processes leading to self-organization in open systems far-from-equilibrium, when, as noticed, are governed by nonlinear kinetic laws.

Such kind of complex behavior can arise in solid state matter, and we briefly summarized a few examples in semiconductors, polymers, and biological system. In [198] is given an overview of the role of the irreversible thermodynamics based on MaxEnt-NESOM in dealing with biosystems. On the question of the relation of Biology and Physics we may say that the sometimes mentioned gap between both disciplines has been slowly shrinking along recent decades. The old difficulty with this sought after connection, which resided into looking exclusively at the microscopic mechanistic level of Physics, becomes to disappears when one begins to consider the macroscopic level of Physics. An important role is played by the thermodynamics of nonlinear nonequilibrium open dissipative systems. In that paper it was succinctly described a statistical approach to irreversible thermodynamics of nonlinear nonequilibrium dissipative systems. MaxEnt-NESOM is applied in the determination of the complex behavior that may result in biopolymers, namely, Fröhlich-Bose-Einstein-like condensation and propagation of Davidov's solitary-wave-like excitations, which are of relevance in Bioenergetics. The question of the lifetime of the latter at physiological conditions was discussed, and the case was illustrated in a comparison with experiments performed in the case of an organic molecular polymer.

The interesting phenomenon of the so-called Fröhlich-Bose-Einstein-like condensation - as viewed from the MaxEnt-NESOM angle - has been considered in several articles. Mesquita et al. [199] have considered the nonequilibrium and dissipative evolution, and the steady state of the population of vibrational polar modes in a chain of biomolecules. These polar modes are excited through a coupling with a pumping source metabolic energy and are in anharmonic interaction with an elastic continuum. Groups of polar modes are coupled in this way through nonlinear terms in the kinetic equations. This nonlinearity is shown to be the source of an unexpected phenomenon characterizing complex behavior in this kind of system: after a threshold of intensity of the pumping source is achieved, polar modes with the lowest frequencies increase enormously their population in a way reminiscent of a *Bose-Einstein condensation (Fröhlich effect)*. The transient time for the steady-state condensate to follow is very short (picosecond time scale) and the condensation appears even for weak values of the anharmonic coupling strength responsible for its occurrence. Further, it seemingly requires accessible levels of pumping power of metabolic energy in order to be produced and sustained.

The question was pursued in [200-202], where the above mentioned *Fröhlich effect* - consisting, as noticed, of a coherent behavior of boson-like excitations

in biological and molecular polymers - is fully derived and analyzed in terms of MaxEnt-NESOM. It was shown that when double (or multiple) processes of excitation of the boson system are possible there follows a *positive -feedback phenomenon* that greatly favors and enhances the effect.

The transient regime in Fröhlich condensation phenomenon was considered by M. A. Tenan et al. [203]. It was analyzed the dynamics of (i) the transient stage before the establishment of the steady state and (ii) the relaxation to the final thermodynamic equilibrium state after the pumping source is turned off.

An alternative possibility for Fröhlich condensation to follow due to higher order relaxation processes mediated by carriers - as for example in proteins -, was considered by L. Lauck et al. [204], who take into account a model of a biological system, for example, a long chain of proteins possessing polar modes of vibration and where energy is pumped through metabolic processes. It was considered the effect produced by free electrons that are usually present as hole carriers in proteins with electron-donor molecules. MaxEnt-NESOM was used for the derivation of the kinetic equations and introducing non-linearities due to interactions of the polar vibrations with the carriers and with the thermal bath. These non-linearities arising out of high order relaxation processes lead to the emergence of the Fröhlich effect in the polar modes, i.e., as noticed, the occurence of a peculiar (nonequilibrium) Bose-Einstein-like condensation. It also points to an instability of the system that seems to be followed by a morphological transformation in the form of a spatially ordered dissipative structure.

Another phenomenos is closely related to this phenomenon of Fröhlich-Bose-Einstein condensation in a nonequilibrium phase, in the sense that it is a result of the same many-body system microdynamics being governed by the same Hamiltonian operator, and nonlinear kinetic effects, which consists in the propagation of solitary waves in several systems. Solitary waves are ubiquitous and of relevance in a number of situations in applied science [205]. They play a fundamental role in the case of conducting polymers (for use in electric car batteries, microcircuits, etc.) [206-209]. In biological systems, the so-called Schroedinger Davydov's solitary waves [210] may have a relevant role; they have been considered within MaxEnt-NESOM in [211], where it was analized Davydov's biolophysical model in the context of a nonequilibrium statistical thermodynamics. It is shown that excitations of the Davydov-soliton type that can propagate in the system, which are strongly damped in near-equilibrium conditions, become near dissipation-free in the Fröhlich-Bose-Einstein-like condensate and that this occurs after a certain threshold of pumped metabolic energy is reached. This implies in the propagation

of excitations at long distances in such biosystems. The question have been further analyzed and extended in [212], and in [213] is considered the case of the organic polymer acetanilide, which mimics some aspects of certain biopolymers and has been subjected to extensive experimental analysis. In that letter it is presented an analysis of the behavior of the macroscopic thermodynamic state of polymers, however, as noticed, centering on acetanilide. The nonlinear equations of evolution for the populations and the statistically averaged field amplitudes of polar modes of vibration are derived. The existence of excitations of the solitary wave type was evidenced. The infrared spectrum was calculated and compared with the experimental data of Careri et al. [214], resulting in a good agreement. It was also considered the situation of a nonthermally highly excited sample, predicting the occurence of a large increase in the lifetime of the solitary wave excitation, as we have already noticed above.

The case of acetanilide and biopolymers involve the study of the polar vibrations resulting of the so-called CO-stretching, corresponding to frequencies in the infrared. But it is also of relevance to consider the case of acoustical vibrations (propagation of sound): Mesquita et al. [215] have shown that accoustic vibronic excitations propagating in highly excited matter present, as a result of nonlinear interactions, a large increase in the populations of the normal modes lowest in frequency, the above mentioned Fröhlich effect. This phenomenon makes the solitary waves which can be produced in the medium to have associated three relevant phenomena when in sufficiently away-from-equilibrium conditions:(1) A large increase in the populations of the normal modes lowest in frequency, (2) a large increase of the solitary wave lifetime, and (3) emergence of a Cherenkov-like effect, consisting in a large emission of phonons in privileged directions, when the velocity of propagation of the soliton is larger than the group velocity of the normal vibrations. Comparison with experiments was presented, which points out to the corroboration of the theory. The eventual relevance of the phenomenon in medical imaging is considered in [216], in conection with some recent research in ultrasonography evidencing the propagation of a peculiar kind of excitation in water [217]. Such excitation, dubbed a X-wave, has characteristics resembling that of a solitary-wave type. Considering its possible relevance for improving ultrasound medical imaging, the probem in a medium consisting of a biological material of the like of α-helix proteins was reconsidered. It can be shown that in this case is expected an excitation of the Davidov's solitary wave type, however strongly damped in normal conditions. The case of acoustic (sound) vibrations was considered, where, as in the case of polar vibrations, a damped Davidov-like

solitary wave may be excited, which when traveling in conditions sufficiently away from equilibrium, has its lifetime largely enhanced. Moreover, a soliton moving in bulk with a velocity larger than that of the group velocity of the normal vibrational wave would produce a Cherenkov-like emission of phonons giving rise to the observed X-wave-like pattern.

We close this subsection mentioning some applications of MaxEnt-NESOM to the study of complex behavior - of the type of formation of Prigogine's dissipative structures - in far-from-equilibrium many-body systems. Morphological ordering of the reaction-diffusion Turing type is considered in [218], where is analysed the dissipative thermodynamic regime of a electron system in bulk matter under the action of an external source of energy, which generate electron-hole pairs with a nonequilibrium distribution in energy space. It was shown that with increasing values of the source power (furthering the distance from equilibrium), and strictly in the case of a p-doped material, the carrier system displays complex behavior characterized by undergoing a succession of transitions between synergetically self-organized dissipative structures. The sequence goes from the homogeneous steady state (or stochastic thermal chaos), to sinusoidal spatial deviations (morphological ordering), to an intricate ordered states (subharmonic bifurcations), and finally to deterministic turbulent-like-chaos (large amount of nonlinear periodic spatial organization of the Landau-Prigogine's type). The phenomenon may arise, for example, in semiconductor systems, molecular polymers, and protein molecular chains in biosystems.

Moreover, in [219] is considered the nonlinear kinetics of evolution of the carrier system in the photoinjected plasma in semiconductors under the action of constant illumination with ultraviolet light. It was shown that the spatially homogeneous steady-state becomes unstable, and a charge density wave emerges after a critical intensity of the incident radiation is achieved. For intensities beyond this critical threshold an increasing number of modes provide further contributions (subharmonics) to the space inhomogeneity, leading the system to display chaotic-like behavior, as it is in [211]. It was shown that this phenomenon can only follow in doped p-type materials as semiconductors and some molecular and biological polymers, the latter when under dark biochemical excitation.

5.2. Informational Statistical Thermodynamics

Meixner has stated that Thermodynamics of Irreversible Processes has many faces [69]. This has been reinforced by Tisza [220], who catalogued its main

four approaches, one of them being the mechanical-statistical-based Gibbs' Thermodynamics. In Tisza's words the latter is considered to be by itself richer, and to constitute a point of departure of a whole away of generalizations. Evidently, as Gibbs'ensemble algorithm in equilibrium gives microscopic (mechanical-statistical) bases for Thermostatics, the nonequilibrium statistical ensemble formalism MaxEnt-NESOM so does for the Thermodynamics of Irreversible Processes. This is the so-called *Informational Statistical Thermodynamics* (IST), sometimes also referred-to as Information-theoretic Thermodynamics. IST originated with the pioneering work of Hobson [221], after publication of Jaynes' seminal papers on Statistical Mechanics founded on Information Theory [39] (a brief and partial reviews are given in Refs. [60,61]; see also Ref. [222]; a more detailed account in Refs. [60-62] and in Refs. [223,224]).

IST is the statistical thermodynamics in which the space of states is defined by the set of macrovariables $\{Q_j(\mathbf{r}, t)\}$ of Eq. (21) [also (23b) and (26)]. In Thermostatics a fundamental state function is the entropy, defined over the Gibbs space consisting of the energy, particle numbers (or molar fractions) of the chemical species that are present, and the volume, which is given at the mechanical-statistical level by the Gibbs entropy of Eq. (3) (in units of Boltzmann constant). But Gibbs entropy, as given by Eq. (22), the straight forward generalization of the case in equilibrium, cannot represent an appropriate entropy-like function for dissipative systems since it is a constant of motion, that is $dS_G(t)/dt = 0$. This is a consequence that $\varrho_\varepsilon(t)$ satisfies Liouville equation (we recall that the inhomogenous term on the right of Eq. (38) does not introduce any spurious external mechanical perturbation, but simply selects the retarded solutions, and goes to zero - in the spirit of Boguliobov's quasi-averages - after the calculation of averages has been performed), what can be considered as a manifestation of the fact that S_G is a fine-grained entropy in the sense that it preserves information. This is the *information provided at the initial time of preparation of the system* [as given by the initial condition of Eq. (32)], which defines, via Eq. (26) at time t_o, the initial point for trajectories in Gibbs (nonequilibrium thermodynamic) space of states $\{Q_j(\mathbf{r}, t_o)\}$. The IST-entropy that is introduced needs be a coarse-grained one which is associated, at each time $t \geq t_o$, to the information provided by the constraints of Eq. (28). This is accomplished by the use of the projection operator of Eq. (34), that is, we introduce

$$\bar{S}(t) \;\; = \;\; -Tr\{\varrho_\varepsilon(t)\,\mathcal{P}(t)\ln\varrho_\varepsilon(t)\} = -Tr\{\varrho_\varepsilon(t)\ln\bar{\varrho}(t,0)\} =$$

$$= -Tr\left\{\varrho_\varepsilon(t)\,\hat{S}(t,0)\right\} = \Phi(t) + \sum_j \int d^3r F_j(\mathbf{r},t)\,Q_j(\mathbf{r},t) \ , \quad (46)$$

where we have used $\bar{\varrho}$ as given by Eq. (19), and $\hat{S}$ as given by Eq. (31). This last quantity, namely $\hat{S}$, is called the informational-entropy operator, whose properties are discussed in Ref. [225], and its connection with a Rosenfeld-Prigogine's complementary principle between micro- and macro-descriptions [67,226], in Bohr's sense [227], is considered elsewhere [228].

Consequently, the difference between IST-entropy $\bar{S}(t)$ and Gibbs entropy $S_G(t)$ is a kind of measurement of the information lost when the macroscopic state of the system is described at any time t by the reduced set of basic macroscopic variables (the "relevant" or informational ones), that is, in terms of what we have called the informational subspace of the full space of states. The point is illustrated in Figure 1: Starting from the inital condition of Eq. (32) (which defines the point $\{Q_j(\mathbf{r},t_o)\}$ in the nonequilibrium-thermodynamic space) the fine-grained informational-statistical Gibbs entropy remains constant in the full space of states (the union of the informational and supplementary subspaces), while the IST-entropy is its projection over the informational subspace; see also the topological-geometrical approach of Balian et al. [64].

Without going into further details (given in the Ref. [62]), we summarize the main properties of the IST-entropy. First, defining a local entropy density $\bar{s}(\vec{r},t)$, such that

$$\bar{S}(t) = \int d^3r\ \bar{s}(\mathbf{r},t) = \int d^3r\left[\varphi(\mathbf{r},t) + \sum_j F_j(\mathbf{r},t)\,Q_j(\mathbf{r},t)\right] \ , \quad (47)$$

with [54]

$$\Phi(t) = \int d^3r\ \varphi(\mathbf{r},t) \qquad , \quad (48)$$

there follows a generalized Gibbs' relation [57,60-62]

$$d\bar{s}(\mathbf{r},t) = \sum_j F_j(\mathbf{r},t)\ dQ_j(\mathbf{r},t) \qquad , \quad (49)$$

introducing the important fact that the Lagrange multipliers are the functional differentials of the IST-entropy, that is

$$F_j(\mathbf{r},t) = \delta\bar{S}(t)\,/\delta Q_j(\mathbf{r},t) \qquad , \quad (50)$$

where, we recall, δ stands for functional differential [63].

These Eqs. (50) constitute the set of equations of state for nonequilibrium situations, and go over those in equilibrium when the latter is attained. We stress the fact that $\bar{S}(t)$, given in terms of $\bar{\varrho}$ of Eq. (19), is the quasi-entropy associated at time t with the instantaneous or "frozen" equilibrium described by this quasi-equilibrium distribution, as already discussed in the previous section.

The IST-entropy density satisfies a continuity equation, which, once Eqs. (40) and (44) are taken into account, takes the form [57,60-62]

$$\frac{\partial}{\partial t}\bar{s}(\mathbf{r},t) + div\vec{I}_{\bar{s}}(\mathbf{r},t) = \sigma_{\bar{s}}(\mathbf{r},t) \qquad , \qquad (51)$$

where $\vec{I}_{\bar{s}}$ is the flux of IST-entropy,

$$\vec{I}_{\bar{s}}(\mathbf{r},t) = \sum_j F_j(\mathbf{r},t)\,\vec{I}_j(\mathbf{r},t) \qquad , \qquad (52)$$

and $\sigma_{\bar{s}}$ is the IST-entropy production density

$$\sigma_{\bar{s}}(\mathbf{r},t) = \sum_j \left[\vec{I}_j(\mathbf{r},t)\cdot\nabla F_j(\mathbf{r},t) + F_j(\mathbf{r},t)\,\mathcal{J}_j(\mathbf{r},t)\right] \;, \qquad (53)$$

obtained after some calculus and the use of Eqs. (40).

We call the attention to the fact that for the sake of brevity, we have oversimplified the presentation including only the densities Q_j and their first (vectorial) fluxes, but, as shown elsewhere [55,56,79] the selection law of Eq. (15) requires to introduce the full set or fluxes of all order $r = 2, 3, ...$, of these densities, besides the first vectorial one.

In this Eq. (53) the first term on the right takes the traditional form of a product of fluxes and thermodynamics forces, the latter given by the gradient of the Lagrange multipliers, which are fields of nonequilibrium intensive variables in IST as defined by the nonequilibrium equations of state, Eqs. (50). The other term is the one associated to the interactions that are contained in $\hat{H}'$ of Eq. (14), present in the collision operator of Eq. (42), and, as noticed, accounted for the presence of the contribution $\varrho'_{\varepsilon}(t)$ in Eq. (33). When in Eq. (53) we perform integration in space over the volume of the system, the first contribution (the one involving fluxes and forces), which arises from the term $J^{(0)}$ in Eq. (40), cancels out, only remaining the second one which constitutes the IST-entropy production

$$\bar{\sigma}(t) = d\bar{S}(t)/dt = \sum_j \int d^3r \; F_j(\mathbf{r},t)\,\mathcal{J}_j(\mathbf{r},t) \qquad . \qquad (54)$$

This reinforces our previous observation that no dissipation is present in the description given by the quasi-equilibrium distribution $\bar{\varrho}(t, 0)$, the dissipative evolution being described by $\varrho'_\varepsilon(t)$ in Eq. (33). We close the description of IST by simply pointing some additional results, consisting in that the IST-entropy satisfies generalizations of Glansdorff-Prigogine's criteria for thermodynamic evolution and (in)stability, and, in the strictly linear regime, can be derived a Prigogine-like theorem of minimum production of IST-entropy [62]. Moreover, it is derived a generalized Clausius relation (introducing a generalized heat-density function), and a Boltzmann-like relation stating that, in the thermodynamic limit, is given by [57]

$$\bar{S}(t) = -\ln W(t) \qquad . \tag{55}$$

In this Eq. (55) $W(t)$ is the number of complexions (number of quantum mechanical states, or volume in phase space in the classical level) corresponding, at time t, to the microscopic states compatible with the constraints imposed by the information introduced by Eq. (23b), quite in analogy with the case in equilibrium described in section **2** (se also Appendix **VI**).

Finally, at present we cannot make any definitive statement on the sign of the local in space IST-entropy production density of Eq. (53). However. it is possible to derive what we call a *weak principle of non-negative informational-entropy production,* namely [57,62]

$$\Delta S(t) = \bar{S}(t) - \bar{S}(t_o) = \bar{S}(t) - S_G(t) =$$

$$= \int_{t_o}^{t} dt' \int d^3r \ \sigma_{\bar{s}}(\mathbf{r}, t) \geq 0 \qquad , \tag{56}$$

which is an expression indicating that the global IST-entropy of the dissipative system always increases in time, from its initial value, along the trajectory of evolution of the nonequilibrium macrostate of the system. This result is equivalent to the one obtained by del Rio and Garcia-Colin [229], who have interpreted the resulting inequality as the fact that a sequence of observations performed, within a specific time interval, results in a loss of information in Shannon-Brillouin's sense [37,38] This is illustrated in Figure **1**: The average of the difference of both kinds of entropy, namely the fine-grained and the coarse-grained, ones, represents the increase in the statistical-informational entropy along the irreversible evolution of the system namely the average of $[1 - \mathcal{P}(t)] \ln \varrho_\varepsilon(t)$ [we recall that S_G is

conserved and equal to $\bar{S}(t_o)$, what justifies the second equal sign in Eq. (55)]. Of course, it is equal to zero in Eq. (56) when $\varrho'_\varepsilon(t) = 0$, for example in equilibrium conditions, but care should be taken to noticed that $\varrho'_\varepsilon(t)$ is non-null in any nonequilibrium steady-state: This is a condition different from equilibrium, and, precisely, responsible for the possible complex behavior consisting into the emergence of Prigogine-like dissipative structures, as commented in subsection **4.1**. It is relevant to call the attention to the fact that we do not make any attempt to relate the law of Eq. (56) to the second law of Thermodynamics; in its own right it can be only considered as a $\mathcal{H}-$theorem in Jancel's sense [230]. As an ending observation in this section, we notice that IST is accompanied by a MaxEnt-NESOM nonclassical hydrodynamics, which may be dubbed as Informational Thermo-Hydrodynamics [54-56,79]. A quite simplified form of it applied to the analysis of a techno-industrial problem is presented elsewhere [231].

6. SOME OPEN QUESTIONS AND CRITICISMS

Let us briefly consider some general questions and criticisms associated to the formalism. Further considerations are presented in Ref. [25], and extensive ones can be found in Jaynes' ouvre (see for example Refs. [4,28-32] and [232]).

Rolf Landauer [233] has argued that "advocacy of MaxEnt is perpertuated by selective decision making in the generation of papers [...] MaxEnt is likely to be sound, but often it is dreadfully difficult to understand what the constraints are" (see Apendix **VI**). Mario Bunge stated [234] that "when confronted with a random or seemingly random process, one attempts to build a probabilistic model that could be tested against empirical data, no randomness, no probability. Moreover, as Poincaré pointed out long ago, talk of probability involves some knowledge; it is not a substitute for ignorance [and Bunge adds, not correctly, in what refers to predictive statistical mechanics as we are discussing here, that] this is not how the Bayesian or personalists view the matter: when confronted with ignorance or uncertainty, they use probability – or rather their own version of it. This allows them to assign prior probabilities to facts and propositions in an arbitrary manner [again, this is not the case in MaxEnt-NESOM] – which is a way of passing off mere intuition, hunch, or guess for scientific hypothesis [...]; it is all a game of belief rather than knowledge".

Sometimes arguments against MaxEnt in terms of playing dices have been advanced. To this, it must be recalled that the question we are addressing here does not deal with gambling, but with many-body theory. That is, we deal with

systems with very many degrees of freedom, and then is necessary to have in mind the distinction between interpretations in terms of microscopic and macroscopic variables.

Concerning the arguments that knowledge arises out of ignorance, this is simply unnecessary confusion coming from a wrong interpretation of, maybe, a sometimes not correct phrasing used by some practitioners of MaxEnt in areas other than Many-Body Physics. Quite to the contrary, the spirit of the formalism is to make use of the restricted knowledge available, but without introducing any spurious one. Quoting Laplace [235], "the curve described by a molecule of air or of vapor is following a rule as certainly as the orbits of the planets: the only difference between the two is our ignorance. Probability is related, in part to this ignorance, in part to our knowledge". Also, as pointed out by Bricmont [236], "the part 'due to our ignorance' is simply that we *use* probabilistic reasoning. If we were omniscient, it would not be needed (but the averages would remain what they are, of course). The part 'due to our knowledge' is what makes reasoning work [...]. But this is the way things are: our knowledge *is* incomplete, and we have to live with that. Nevertheless, probabilistic reasoning is extraordinarily sucessful in practice, but, when it works, this is due to our (partial) knowledge. It would be wrong to attribute any constructive role to our ignorance. And it is also erroneous to assume that the system must be somehow indeterminate when we apply probabilistic reasoning to it." (See also Ref. [35]).

Moreover, we stress a point illustrated in section **2**: To derive the behavior of the macroscopic state of the system from partial knowledge has been already present in the original genial work of Gibbs. This is at the roots of the well established, fully accepted, and exceedingly successful statistical mechanics in equilibrium; as noted, the statistical distribution which should depend on all constants of motion is built, in any of the canonical ensembles, in terms of the available information we do have, namely, the preparation of the sample in the given experimental conditions in equilibrium with a given (and quite reduced) set of reservoirs. Werner Heisenberg wrote [237], "Gibbs was the first to introduce a physical concept which can only be applied to an object when our knowledge of the object is incomplete".

Finally on this point, the dismissal of a theoretical approach in Physics cannot (and should not) be done on the basis of general verbal arguments, which may or may not be sensible, but which need be strongly fundamented on the scientific method. In other words, the merits, or rather dismerits, of a theory reside in establishing its domain of validity (see for example Refs. [1,238,239]), when tested

against the experimental results it predicts. This point has recently been forcefully stressed by Stephen Hawkings as we stress in next section. Moreover, as we have already described in section **4**, MaxEnt-NESOM appears to provide a successful statistical mechanics and thermodynamics of a very large scope (that is, of a large domain of validity accompained with good intuitive physical interpretations) for the Physics of many-body system arbitrarily away from equilibrium. In this way, as antecipated in the Introduction, it confirms Zwanzig's prediction about the merits of the formalism.

Returning to the question of the Bayesian approach in statistical mechanics, Sklar [241 has summarized that Jaynes firstly suggested that equilibrium statistical mechanics can be viewed as a special case of the general program of systematic inductive reasoning, and that, from this point of view, the probability distributions introduced into statistical mechanics have their bases not so much in an empirical investigation of occurences in the world, but, instead in a general procedure for determining appropriate *a priori* subjective probabilities in a systematic way. Also, Jaynes' prescription was to choose the probability distribution which maximizes the statistical entropy (now thought in the information-theoretic vein) relative to the known macroscopic constraints, using the standard measure over the phase space to characterize the space of possibilities. This probability assignment is a generalization of the probabilities determined by the *Principle of Indifference* (or Bernoulli's "principle of insufficient reason", Maynard Keynes' "principle of ignorance", Tolman's "principle of equal *a priori* probabilities"), specifying one's rational choice *of a priori* probabilities. In equilibrium this is connected with ergodic theory, as known from classical textbooks. Of course it is implied to accept the justification of identifying averages with measured quantities using the time in the interval of duration of the experiment. This cannot be extended to nonequilibrium conditions involving ultrafast relaxation processes. Therefore, there remains the explanatory question: Why do our probabilistic assumptions work so well in giving us equilibrium values? [241].

The Bayesian approach attempts an answer which, apparently, works quite well in equilibrium, and then it is tempting to extend it to nonequilibrium conditions. Jaynes rationale for it is, again, that the choice of probabilities, being determined by a Principle of Indifference, should represent maximum uncertainty relative to our knowledge as exhausted by our knowledege of the macroscopic constraints with which we start [31]. This has been described in previous sections.

At this point, it can be rised the question of the possibility of situations when the Principle of Indifference may be seen as not applying. This seems to be the

case of some phenomena said to follow Lévy's distributions [242]. In condensed matter, Fick (or Fourier) diffusion equations are, for certain systems, nonvalid and a so-called anomalous Lévy-like diffusion is present. A generalized concept of entropy has been proposed to deal with these cases [243]. According to this approach the Principle of Indifference is violated in a nontrivial way. The motion is in some sense fractal, what is thought to explain the appeerence of the many fractal structures in nature. It is considered that many, if not all, fractal structures could emerge through a self-organized criticality [242]. An accompanying, say, statistics for fractal classical systems, sometimes called Tsallis' statistics, is being proposed and devised along some kind of an informational MaxEnt approach (see for example Refs. [244,245]).

We call the attention fo the fact that the principle of maximization of informational entropy in Shanon-Jaynes sense, can be alternatively covered by the principle of Minimization of cross-entropy distances [246] (the "distance" appropriately defined of two types of distributions adjudicated to a given statistical problem), *MinxEnt* for short. MaxEnt-NESOM follows from minimization of the so-called Kullback-Leibler measure (distance from the sought after distribution to the uniform distribution). But some problems can require non-exponential distributions, such that additivity - or better to say Euler homogeneity of order one - in the statistical functions is not satisfied. We have already mentioned Levy distributions, requiring generalized measures of cross-entropy. The case of the above cited Tsallis statistics is based on a particular case of Csiszer's measure [247], namely Havrada-Charvat measure [248].

We also call the attention to an attempt to derive, mainly on topological-geometrical bases, a fundamental theory for the realm of the physics of macroscopic systems by unifying, and properly characterizing, the levels of description involving micro- and macro-physics. The approach called Generics aspires to be all-embracing and multifarious. Its implicit programme is in development in the general aspects and in what regards its practicality [249].

Another point of contention is the long standing question about *macroscopic irreversibility in nature*. As discussed in section **3**, it is introduced in the formalism via the generalization of Kirkwood's time-smoothing procedure, after a specific initial condition [cf. Eq. (32)] – implying in a kind of generalized *Stosszahlansatz* – has been defined. This is a working proposal that goes in the direction which was essentially suggested by Boltzmann, as quoted in Ref. [236]: "Since in the differential equations of mechanics themselves there is absolutely nothing analogous to the second law of thermodynamics, the latter can be mechanically represented

only by means of assumptions regarding initial conditions". Or, in other words [236], that the laws of physics are always of the form: given some initial conditions, here is the result after some time. But they never tell us how the world *is or evolves*. In order to account for that, one always needs to assume something, first on the initial conditions and, second, on the distinction of the description being macroscopic and the system never isolated (damping of correlations). In this vein Hawkings [240] has manifested that "It is normally assumed that a system in a pure quantum state evolves in a unitary way through a succession of [such] states. But if there is loss of information through the appearence and disappearance of black holes, there can't be a unitary evolution. Instead, the [...] final state [...] will be what is called a *mixed quantum state*. This can be regarded as an ensemble of different pure quantum states, each with its own probability" (see Appendix **IV**).

Needless to say that this question of Eddington's time-arrow problem has produced a very extensive literature, and lively controversies. We do not attempt here to add any considerations to this difficult and, as said, controversial subject. We simply list in the references [67,70,71,240,250-264] some works on the matter which we have selected. As commented by Sklar [241], Nicolai S. Krylov (the Russian scientist unfortunately prematurely deceased) was developing an extremely insightful and careful foundational study of nonequilibrium statistical mechanics [19]. Krylov believed that he could show that in a certain sense, neither classical nor quantum mechanics provide an adequate foundation for statistical mechanics. Krylov's most important critical contribution is precisely his emphasis on the importance of initial ensembles. Also, that we may be utterly unable to demonstrate that the correct statistical description of the evolution of the system will have an appropriate finite relaxation time, much less the appropriate exact evolution of our statistical correlates of macroscopic parameters, unless our statistical approach includes an appropriate constraint on the initial ensemble with which we choose to represent the initial nonequilibrium condition of the system in question. Moreover, it is thought that the interaction with the system from the outside at the single moment of preparation, rather than the interventionists ongoing interaction, is what grounds the asymmetric evolution of many-body systems. It is the ineluctable interfering perturbation of the system by the mechanism that sets it up in the first place that guarantees that the appropriate statistical description of the system will be a collection of initial states sufficiently large, sufficiently simple in shape, and with a uniform probability distribution over it. Clearly, a question immediatly arises, namely: Exactly how does this initial interference lead to an

initial ensemble of just the kind we need? [241] We have seen in section **3** how MaxEnt-NESOM, mainly in Zubarev's approach, tries to heuristically address the question. Also something akin to these ideas seems to be in the earlier work of the Russian-Belgian Nobel Prize Ilya Prigogine [67,250,265], and also in the considerations in Refs. [241,259-261,266,267]. Certain kind of equivalence - at least partial - seems to exists between Prigogine's approach and MaxEnt-NESOM, as pointed out by Dougherty [268,269], and we side with Dougherty's view [270] (see also Appendix **IV**). More recently, Prigogine and his School have extended those ideas incorporating concepts, at the quantum level, related to dynamical instability and chaos (see for example Refs. [271,272]). In this direction, some attempts try to incorporate time-symmetry breaking, extending quantum mechanics to a general space state, a "rigged" (or "structured") Hilbert space or Gelfand space, with characteristics (superstructure) mirroring the internal structure of collective and cooperative macroscopic systems [273-275]. This formulation of dynamics constitutes an effort towards including the second law of thermodynamics, as displayed explicitly by a $\mathcal{H}$-function of the Boltzmann type, which decreases monotonically and takes its minimum value when unstable systems have decayed or when the system reaches equilibrium [276,277].

Finally, and in connection with the considerations presented so far, we stress that in the formalism as by us described in previous sections, no attempt is made to establish any direct relation with thermodynamic entropy in, say, the classical Clausius-Carnot style, with its increase between initial and final equilibrium states defining irreversibility. Rather, it has been introduced a statistical-informational entropy with an evolution as given by the laws of motion of the macrovariables, as provided by the MaxEnt-NESOM-based kinetic theory. Irreversible transport phenomena are described by the fluxes of energy, mass, etc..., which can be observed, but we do not see entropy flowing. We have already stressed in subsection **5.2** that the increase of IST-entropy amounts to a $\mathcal{H}$-like theorem, that is, a manifestation on the irreversible character of the transport equations, in close analogy with Boltzmann's $\mathcal{H}$-theorem which does so for Boltzmann equation. Moreover, as stated in other papers (see for example Ref. [57]), we side with Meixner's point of view [69,278] that, differently to equilibrium, does not exists a unique and precisely defined concept of thermodynamic entropy out of equilibrium. The one of subsection **5.2**, is the one peculiar to IST, and depending on the nonequilibrium thermodynamic state defined by Zubarev-Peletminskii selection law altogether with the use of Bogoliubov's principle of correlation weakening. The IST entropy, we recall, has several properties listed in section **5.2**, and one is that it takes

(in the thermodynamic limit) a typical Boltzmann-like expression [cf. Eq. (55)], implying that the macroscopic constraints imposed on the system (the informational bases) determine the vast majority of microscopic configurations that are compatible with them and the initial conditions. It is worth noticing that then, according to the weak principle of increase of the IST-entropy, as the dissipative system evolves, such number of microscopic configurations keeps increasing up to a maximum when final full equilibrium is achieved. Further, MaxEnt-NESOM recovers in the appropriate limit the distribution in equilibrium, and in IST one recovers the traditional Clausius-Carnot results for increase of thermodynamics entropy between an initial and a final equilibrium states, as shown in Ref. [72,279].

7. CONCLUDING REMARKS

In the preceding sections we have described, in terms of a general overview, a theory that attempts a particular answer to the long-standing sought-after question about the existence of a Gibbs-style statistical ensemble formalism for nonequilibrium systems. Such formalism, providing microscopic (mechanical-statistical) bases for the study of dissipative processes, heavily rests on the fundamental ideas and concepts devised by Gibbs and Boltzmann. It consists into the so-called MaxEnt-NESOM formalism, which, as noticed in the Introduction, appears to be covered under the theoretical umbrella provided by Jaynes' Predictive Statistical Mechanics. We have already called the attention to the fact that it is grounded on a kind of scientific inference approach, Jeffrey's style, based on Bayesian probability and information theory in Shannon-Brillouin's sense [33,34]. It has been improved and systematized mainly by the Russian School of Statistical Physics, and the different approaches have been brought under a unified description based on a variational procedure. It consists in the use of the principle of maximization of the informational entropy, meaning to rely exclusively on the available information and avoiding to introduce any spurious one. The aim is to make predictions on the behavior of the dynamics of the many-body system on the basis of only that information. On this, Jeffreys, at the begining of Chapter I in the book of reference [279], states that: "The fundamental problem of scientific progress, and the fundamental of everyday life, is that of learning from experience. Knowledge obtained in this way is partly merely discription of what we have already observed, but part consists of making inferences from past experience to predict future experience. This may be called generalization of induction. It is the most important part." Jeffreys also quotes J. C. Maxwell who stated that the true logic for this

world is the Calculus of Probability which takes account of the magnitude of the probability that is, or ought to be, in a reasonable man's mind.

Some authors conjecture that this may be the revolutionary thought in modern science (see for example Refs. [33,34,250,280]): It replaces the concept of inevitable effects (trajectories in a mechanicist point of view of many-body (large) systems) by that of the probable trend (in a generalized theory of dynamical systems). Thus, the different branches of science that seem to be far apart, may, within such new paradigm, grow and be hold together organically [281]. These points of view are the subject of controversy, mainly on the part of the adepts of the mechanicist-reduccionist school. We call the attention to the subject but we do not take any particular position, simply adhering to the topic here presented from a pragmatical point of view. In that sense, we take a position coincident with the one clearly stated by Stephen Hawkings [282]: "I do not demand that a theory corresponds to reality. But that does not bother me. I do not demand that a theory correspond to reality because I do not know what reality is. Reality is not a quality you can test with litmus paper. All I am concerned with is that the *Theory should predict the results of measurement*" [emphasis is ours].

MaxEnt-NESOM is the construtive criterion for deriving the probability assignment for the problem of dissipative processes in many-body systems, on the bases of the available information (provided, as Zwanzig pointed out [5], on the knowledge of measured properties and of sound theoretical considerations). The fact that a certain probability distribution maximizes the informational entropy, subject to certain constraints representing our incomplete information, is the fundamental property which justifies the use of that distribution for inference; it agrees with everything that is known, but carefully avoids assuming anything that is not known. In that way it enforces - or gives a logico-mathematical viewpoint - to the principle of economy in logic, known as Occam's Razor, namely "Entities are not to be multiplied except of necessity". Particularly, in what concerns Statistical Thermodynamics (see subsection **5.2**), MaxEnt-NESOM, in the context of Jaynes' Predictive Statistical Mechanics, allows to derive laws of thermodynamics, not on the usual viewpoint of mechanical trajectories and ergodicity of classical deductive reasoning, but by the goal of using inference from incomplete information rather than deduction: the MaxEnt-NESOM distribution represents the best prediction we are able to make from the information we have [4,28-32].

In Section **3,** we have briefly described the use of MaxEnt-NESOM to rederive the old-vintage equilibrium statistical mechanics. That is, to retrive the original Gibbs-ensemble canonical distributions, and where - what is considered to be

already contained in the work of Gibbs [30] - it is clearly visualized the use of the specific information used, and only this, consisting into the knowledge of the existence of equilibrium with well specified reservoirs.

In section **4,** we have, along general lines, shown how to derive a nonequilibrium ensemble formalism, in the MaxEnt-NESOM framework, which unifies and gives basic structure to the different approaches attempted on either heuristic arguments or projection operator techniques. Without entering into details, given in the references in each case indicated, we have described the main six basic steps that the formalism requires. Summarizing them:

- i) On the basis of Bogoliubov's principle of correlation weakening one chooses the basic set of dynamical variables, introducing the separation of the total Hamiltonian in the form of Eq. (14), eliminating fast variables (associated to correlations that have died down), and retaining only the slow variables (with relaxation times larger than the characteristic time for the description of the evolution of the nonequilibrium macroscopic state of the system).

- ii) Introduction of the rule of Eq, (15), which selects the relevant set of slow variables.

- iii) Introduction of retro-effects, making the state at time t be dependent on the past history of evolution of the system from a well established initial condition of preparation.

- iv) Introduction of an *ad hoc* time-smoothing procedure, with properties which allow to complete the construction of a satisfactory nonequilibrium statistical operator. In particular, the fading-memory characteristic it produces leads to the irreversible evolution of the macrostate of the system, from the initial condition of preparation (the information available to build the formalism) and to obtain the description of the system on the basis of such information and its evolution to a final state of equilibrium in the future.

And two final steps, those indispensable to obtain the macroscopic properties of the system, namely,

- v) A nonlinear quantum kinetic theory; and

- vi) A response function theory for system arbitrarily away from equilibrium.

In section **5**, we listed (given the corresponding references) some applications of MaxEnt-NESOM to the analysis and interpretation of experimental studies in the photoinjected plasma in highly excited semiconductors. Also, some considerations concerning complex behavior in biopolymers and organic polymers were briefly mentioned. In subsection **5.2**, we have described the construction, on the basis of the MaxEnt-NESOM, of a Statistical Thermodynamics, the so-called

Informational Statistical Thermodynamics, and its main aspects have been described. Moreover, one can develop a nonclassical Thermo-Hydrodynamics, and, it may be noticed, the scope of the formalism makes it suitable for applications in many areas other than that of the physics and chemistry of semiconductors and polymers, as in rheology, chemical engineering, food engineering, hydraulics etc...., and we have already mentioned the particular cases of the techno-industrial processes of laser-thermal estereo-lithography and medical imaging.

As ending considerations, we stress that, in this paper we have given a brief descriptional presentation of the MaxEnt-NESOM, which is an approach to a nonequilibrium statistical ensemble algorithm in Gibbs' style, seemingly as a very powerful, concise, soundly based, and elegant formalism of a broad scope apt to deal with systems arbitrarily away from equilibrium. We may say that it constitutes a promising tentative to fulfill a Programme for nonequilibrium statistical mechanics and thermodynamics, consisting of the itens:

• I. Construction of a relevant statistical operator corresponding to a nonequilibrium ensemble formalism, which can provide a satisfactory description of the *irreversible evolution* of macroscopic many-body systems.

• II. To build a *Statistical Irreversible Thermodynamics* derived from this nonequilibrium ensemble formalism.

• III. To derive a confiable nonlinear quantum *Kinetic Theory*, providing for a description of the evolution of the nonequilibrium system (the trajectory in the nonequilibrium thermodynamic state space).

• IV. To derive a *Response Function Theory*, for systems arbitrarily away from equilibrium, the all important step to establish the connection between theory and experiment.

• V. The final closing step of *applying the theory to real situations* in laboratory conditions for comparison with experimental data.

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Appendix I:. The variational procedure

Consider a many-body system in contact and in equilibrium with a set of n reservoirs with which exchange the physical quantities $\hat{P}_1$, ..., $\hat{P}_n$ (e.g. energy, particles, etc.). The equilibrium is characterized by the equalization of the corresponding intensive thermodynamic variables, say, F_1, ..., F_n (e.g. temperature, chemical potential, etc.), which determine the average value of the former, Q_1, ..., Q_n. In the variational method to Gibbs' ensemble formalism the statistical operator ϱ for the system in equilibrium follows from the maximization of Gibbs' entropy

$$S_G = -Tr\{\varrho \ln \varrho\} \tag{I.1}$$

under the constraints of (1) normalization

$$Tr\{\varrho\} = 1 \quad , \tag{I.2}$$

and (2) the average values fixed by the condition of equilibrium with the reservoirs, namely

$$Q_j = Tr\left\{\hat{P}_j \varrho\right\} \tag{I.3}$$

for $j = 1, 2, ..., n$, which of course depend on the intensive variables F_j.

As known, the method of Lagrange multipliers requires to make extremal the functional

$$I\{\varrho\} = Tr\left\{\varrho\left[\ln \varrho + (\phi - 1) + \sum_{j=1}^{n} F_j \hat{P}_j\right]\right\} \quad , \tag{I.4}$$

what produces Gibbs' generalized canonical distribution

$$\varrho = \exp\left\{-\phi - \sum_{j=1}^{n} F_j \hat{P}_j\right\} \quad , \tag{I.5}$$

with

$$\phi = \ln Z = \ln Tr\left\{\exp\left[-\sum_{j=1}^{n} F_j \hat{P}_j\right]\right\} \tag{I.6}$$

ensuring the normalization of ϱ and where Z is the corresponding partition function. The usual canonical distribution follows for the case of a thermal reservoir when $\hat{P}_1 = \hat{H}$ and $F_1 = \beta = 1/k_B T$; the grand-canonical distribution for the case of a thermal and a particle reservoir when $\hat{P}_1 = \hat{H}$, $\hat{P}_2 = \hat{N}$, and $F_1 = 1/k_B T$, $F_2 = -\mu/k_B T$.

For nonequilibrium conditions, as noticed in the main text, once the choice of the set of basic variables $\left\{ \hat{P}_j \left(\mathbf{r} \right) \right\}$ has been done according to the procedure we have described, and the initial condition at time t_o has been set, and following Kirkwood time-smoothing procedure, we maximize the time-dependent Gibbs' entropy

$$S_G \left(t \right) = -Tr \left\{ \varrho \left(t \right) \ln \varrho \left(t \right) \right\} \qquad , \tag{I.7}$$

under the constraints

$$Tr \left\{ \varrho \left(t' \right) \right\} = 1 \qquad , \tag{I.8}$$

$$Q_j \left(\mathbf{r}, t' \right) = Tr \left\{ \hat{P}_j \left(\mathbf{r} \right) \varrho \left(t' \right) \right\} \qquad , \tag{I.9}$$

for $t_o \leq t' \leq t$, that is, keeping the information on the history of evolution of the system from the inital condition of preparation at time t_o time up to the time t when the measurement is performed. Hence, following the spirit of the method of Langrange multipliers, we need to make extremal the functional

$$I \left\{ \varrho \left(t \right) \right\} = Tr \left\{ \varrho \left(t \right) \ln \varrho \left(t \right) + \int_{t_o}^{t} dt' \left[\psi \left(t' \right) - \delta \left(t - t' \right) \right] \varrho \left(t' \right) + \right.$$

$$\left. + \sum_{j=1}^{n} \int_{t_o}^{t} dt' \int d^3 r \; \varphi_j \left(\mathbf{r}, t, t' \right) \hat{P}_j \left(\mathbf{r} \right) \right\} \qquad , \tag{I.10}$$

leading to the result that

$$\varrho \left(t \right) = \exp \left\{ -\Psi \left(t \right) - \sum_{j=1}^{n} \int_{t_o}^{t} dt' \int d^3 r \; \varphi_j \left(\mathbf{r}, t, t' \right) \hat{P}_j \left(\mathbf{r} \right) \right\} \qquad , \tag{I.11}$$

where

$$\Psi \left(t \right) = \int_{t_o}^{t} dt' \psi \left(t' \right) = \ln Tr \left\{ \exp \left[-\sum_{j=1}^{n} \int_{t_o}^{t} dt' \int d^3 r \; \varphi_j \left(\mathbf{r}, t, t' \right) \hat{P}_j \left(\mathbf{r} \right) \right] \right\} \tag{I.12}$$

ensures the normalization of $\varrho \left(t \right)$.

The Lagrange multipliers $\varphi_j \left(\mathbf{r}, t, t' \right)$ are determined by the conditions of Eq. (I.9), which, as indicated in the main text, are redefined in the form

$$\varphi_j \left(\mathbf{r}, t, t' \right) = w \left(t, t' \right) F_j \left(\mathbf{r}, t' \right) \qquad , \tag{I.13}$$

introducing the weight function w in the integration in time, with the properties discussed in Ref. [23].

Appendix II:. Zubarev's NESOM

Zubarev's approach to MaxEnt-NESOM follows from the choice of the weight function $w(t, t')$ of Eq. (I.13) in the form of Abel's kernel $\varepsilon \exp\{\varepsilon(t' - t)\}$ and t_o taken in the remote past, Hence,

$$\varrho_\varepsilon(t) = \exp\left\{-\varepsilon \int_{-\infty}^{t} dt' \, e^{\varepsilon(t'-t)} \, \hat{S}(t', t' - t)\right\} \quad , \tag{II.1}$$

which after part integration takes the form

$$\varrho_\varepsilon(t) = \exp\left\{-\hat{S}(t, 0) + \hat{\zeta}_\varepsilon(t)\right\} \quad , \tag{II.2}$$

where

$$\hat{\zeta}_\varepsilon(t) = \int_{-\infty}^{t} dt' \, e^{\varepsilon(t'-t)} \frac{d}{dt'} \, \hat{S}(t', t' - t) \quad . \tag{II.3}$$

Using the operator identity

$$e^{-\hat{A}+\hat{B}} = Y\left(\hat{B} \mid 1\right) e^{-\hat{A}} \quad , \tag{II.4}$$

where

$$Y\left(\hat{B} \mid x\right) = 1 + \int_{0}^{x} du \, Y\left(\hat{B} \mid u\right) e^{-u\hat{A}} \, B \, e^{u\hat{A}} \quad , \tag{II.5}$$

the statistical operator of Eq. (II.2) can be written as

$$\varrho_\varepsilon(t) = \bar{\varrho}(t, 0) + \varrho'_\varepsilon(t) \quad , \tag{II.6}$$

where

$$\bar{\varrho}(t, 0) = \exp\left\{-\hat{S}(t, 0)\right\} \quad , \tag{II.7}$$

$$\varrho'_\varepsilon(t) = \hat{D}_\varepsilon(t) \, \bar{\varrho}(t, 0) \quad , \tag{II.8}$$

$$\hat{D}_\varepsilon(t) = \int_{0}^{1} du \, Y\left(\hat{\zeta}_\varepsilon(t) \mid u\right) [\bar{\varrho}(t, 0)]^u \, \hat{\zeta}_\varepsilon(t) \, [\bar{\varrho}(t, 0)]^{-u} \quad , \tag{II.9}$$

$$Y\left(\hat{\zeta}_\varepsilon(t) \mid u\right) = 1 + \int_0^x du\, Y\left(\hat{\zeta}_\varepsilon(t) \mid u\right) [\bar{\varrho}(t,0)]^u\, \hat{\zeta}_\varepsilon(t)\, [\bar{\varrho}(t,0)]^{-u} \;, \qquad \text{(II.10)}$$

and we recall that

$$\hat{S}(t,0) = \phi(t)\,\hat{1} + \sum_{j=1}^n \int d^3r\; F_j(\vec{r},t)\,\hat{P}_j(\vec{r}) \qquad . \qquad \text{(II.11)}$$

We call the attention to the fact that because of Eq. (26)

$$Tr\{\varrho'_\varepsilon(t)\} = Tr\left\{\hat{D}_\varepsilon(t)\,\bar{\varrho}(t,0)\right\} = 0 \qquad , \qquad \text{(II.12)}$$

$$Tr\left\{\hat{P}_j\varrho'_\varepsilon(t)\right\} = Tr\left\{\hat{P}_j\hat{D}_\varepsilon(t)\,\bar{\varrho}(t,0)\right\} = 0 \qquad . \qquad \text{(II.13)}$$

Moreover, we notice that the statistical operator in Green-Mori's approach follows from the choice

$$\varrho_\tau(t) = \exp\left\{-\frac{1}{\tau}\int_{t-\tau}^t dt'\,\hat{S}(t',t'-t)\right\} \qquad , \qquad \text{(II.14)}$$

with τ going to infinity after the trace operation in the calculation of averages has been performed. We may see that Eq. (II.14) implies in a kind of time average over the time interval of extension of τ, while the one in Eq. (II.1) is the so-called causal average. We stress that *a posteriori* the latter introduces in the kinetic equations a fading memory and produces finite transport coefficients, while the use of the statistical operator of Eq. (II.14) may produce divergent integrals in the calculation of transport coefficients.

Appendix III:. Time-Dependent Projection Operator

Let us consider the set of dynamical variables $\hat{P}_j$, to which we further add $\hat{P}_o = \hat{1}$ whose associated Lagrange multiplier is $F_o(t) = \phi(t)$, in terms of which we define the supercorrelation functions

$$\mathcal{C}_{ij}(t) = \left\{\hat{P}_i, \hat{P}_j \mid t\right\} \qquad , \qquad \text{(III.1)}$$

with $i, j = 0, 1, 2, ..., n$, and where for any pair of operators A and B

$$\left\{ \hat{A}, \hat{B} \mid t \right\} = Tr \left\{ \int_0^1 du \ \hat{A} \ Y \left(\hat{\zeta}_\varepsilon \mid u \right) [\bar{\varrho}(t,0)]^u \ \hat{B} \ [\bar{\varrho}(t,0)]^{-u} \ \varrho(t,0) \right\} \quad ,$$

(III.2)

where Y is given in Eq. (II.10).

In terms of this particular metric - in the informational subspace of quantities $\hat{P}_j$ - we define the time-dependent projection operator

$$\mathcal{P}_\varepsilon(t) \hat{A} = \sum_{i,j=0}^n \hat{P}_i \mathcal{C}_{ij}^{(-1)}(t) \left\{ \hat{P}_j, \hat{A} \mid t \right\} \quad ,$$

(III.3)

where $\mathcal{C}^{(-1)}$ is the inverse of the matrix with elements given by Eq. (III.1). This projection operator has the property that

$$\mathcal{P}_\varepsilon(t) \ln \varrho_\varepsilon(t) = \ln \bar{\varrho}(t,0) \quad .$$

(III.4)

In fact,

$$\mathcal{P}_\varepsilon(t) \ln \varrho_\varepsilon(t) = \mathcal{P}_\varepsilon(t) \left[\ln \bar{\varrho}(t,0) + \hat{\zeta}_\varepsilon(t) \right] \quad ,$$

(III.5)

because of Eq. (II.2), and

$$\begin{aligned}
\mathcal{P}_\varepsilon(t) \ln \bar{\varrho}(t,0) &= \sum_{i,j,k=0}^n \hat{P}_i \mathcal{C}_{ij}^{(-1)}(t) \left\{ \hat{P}_j, F_k(t) \hat{P}_k \mid t \right\} = \\
&= \sum_{i,j,k=0}^n F_k(t) \hat{P}_k \mathcal{C}_{ij}^{(-1)}(t) \mathcal{C}_{jk}(t) = \\
&= \sum_{k=0}^n F_k(t) \hat{P}_k = \ln \bar{\varrho}(t,0) \quad ,
\end{aligned}$$

(III.6)

$$\mathcal{P}_\varepsilon(t) \hat{\zeta}_\varepsilon(t) = \sum_{i,j,k=0}^n \hat{P}_i \mathcal{C}_{ij}^{-1}(t) \left\{ \hat{P}_j, \hat{\zeta}_\varepsilon(t) \mid t \right\} \quad .$$

(III.7)

But

$$\begin{aligned}
\left\{ \hat{P}_j, \hat{\zeta}_\varepsilon(t) \mid t \right\} &= Tr \left\{ \int_0^1 du \ \hat{P}_j \ Y \left(\hat{\zeta}_\varepsilon \mid u \right) [\bar{\varrho}(t,0)]^u \ \hat{\zeta}_\varepsilon(t) [\bar{\varrho}(t,0)]^{-u} \ \varrho(t,0) \right\} = \\
&= Tr \left\{ \hat{P}_j \ \varrho'_\varepsilon(t) \right\} = 0
\end{aligned}$$

(III.8)

because of Eq. (26).

Appendix IV:. Alternative Derivations in NESOM

We present some alternative derivations of the statistical operator, beginning with one following a path completely similar to that used to obtaining the usual Liouville equation, but first introducing only the retarded solutions of Schroedinger equation as proposed by Gell-Mann and Goldberger in scattering theory [66]

    We recall that in Gell-Mann and Goldberger approach the wavefunction satisfies a modified Schroedinger equation for the state function $\mid \psi(t) \rangle$, namely

$$i\hbar \frac{\partial}{\partial t} \mid \psi(t) \rangle - \hat{H} \mid \psi(t) \rangle = f_\eta(t) \qquad , \qquad (\text{IV.1})$$

where f_η is an infinitesimal source which selects the retarded solutions of the equation, which is

$$f_\eta(t) = \eta \left(\mid \psi(t) \rangle - \mid \phi(t) \rangle \right) \qquad , \qquad (\text{IV.2})$$

and η is an infinitesimal positive real number which goes to zero after the calculation of averages over the quantum state of observables of the system, and $\mid \phi(t) \rangle$ is the unperturbed state function. Given the initial condition at $t_o = -\infty$, $\mid \psi(t_o) \rangle = \mid \phi(t_o) \rangle$, and the evolution operator $U(t)$, i.e. $\mid \psi(t) \rangle = U(t) \mid \phi(t_o) \rangle$, which in the interaction representation is $U(t) = U_o(t) U'(t)$ with $U_o(t)$ being the unperturbed evolution operator, i.e. $U_o(t) \mid \phi(t_o) \rangle = \mid \phi(t) \rangle$, after some algebra we find that

$$f_\eta(t) = \eta \left[\hat{1} - \hat{K}(t) \right] \mid \psi(t) \rangle \qquad , \qquad (\text{IV.3})$$

where

$$\hat{K}(t) = U_o(t) U'^\dagger(t) U_o^\dagger(t) \qquad . \qquad (\text{IV.4})$$

On the basis of these results we can write for the retarded solutions that the modified Schroedinger Eq. (IV.1) can be written as a normal Schroedinger equation, but for the modified wavefunction

$$\mid \psi_\eta(t) \rangle = \mathcal{U}_\eta(t) \mid \psi(t) \rangle \qquad , \qquad (\text{IV.5})$$

where we have defined the operator

$$\mathcal{U}_\eta(t) = \exp \left\{ -\eta \int_{-\infty}^{t} dt' \hat{M}(t') \right\} \qquad (\text{IV.6})$$

and

$$\hat{M}(t') = \hat{1} - \hat{K}(t') \tag{IV.7}$$

Let us consider next the statistical ensemble which can be built on the basis of these wavefunctions. We designate by $\mid \psi_j(t) \rangle$ the wavefunction of the j-th replica, and by $\mathbf{P}_j(t) = \mid \psi_j(t) \rangle\langle \psi_j(t) \mid$ the corresponding statistical operator in pure space. The normal (reversible) statistical operator is given by

$$\varrho(t) = \sum_j p_j \mathbf{P}_j(t) \qquad , \tag{IV.8}$$

where p_j is the statistical weight of the j-th replica compatible with the macroscopic constraints imposed on the system. Normalization needs be verified, implying in that $\sum_j p_j = 1$.

Let us now introduce for each replica a caracterization in terms of the wavefunction of Eq. (IV.5), that is, the retarded wavefunctions of Gell-Mann and Goldberger proposal. Then

$$\varrho_\eta(t) = \sum_j p'_j \mathcal{U}_\eta(t) \mathbf{P}_j(t) \mathcal{U}_\eta^\dagger(t) \tag{IV.9}$$

with the statistical weight p'_j ensuring its normalization. This statistical operator satisfies the modified Liouville equation

$$\frac{\partial}{\partial t}\varrho_\eta(t) + \frac{1}{i\hbar}\left[\varrho_\eta(t), \hat{H}\right] = -\eta\left[\hat{1} - \mathbb{P}(t)\right]\varrho_\eta(t) \quad , \tag{IV.10}$$

where we have introduced the definition

$$\left[\hat{1} - \mathbb{P}(t)\right]\varrho_\eta(t) = \left[\hat{1} - \hat{K}(t)\right]\varrho(t) + \varrho(t)\left[\hat{1} - \hat{K}^\dagger(t)\right] \quad . \tag{IV.11}$$

Hence, we can rewrite Eq. (IV.10) in the form

$$\frac{\partial}{\partial t}\varrho_\eta(t) + \frac{1}{i\hbar}\left[\varrho_\eta(t), \hat{H}\right] = -\eta\left[\varrho_\eta(t) - \tilde{\varrho}(t)\right] \quad , \tag{IV.12}$$

where

$$\tilde{\varrho}(t) = \mathbb{P}(t)\varrho_\eta(t) \qquad , \tag{IV.13}$$

and whose solution is

$$\varrho_\eta(t) = \tilde{\varrho}(t) - \int_{-\infty}^{t} dt' e^{\eta(t'-t)}\frac{d}{dt'}\tilde{\varrho}\left(t' - t\right) \quad . \tag{IV.14}$$

This statistical operator differs from the one of Eq. (38) in two points. One is the difference in the form of the time-dependent projection operator, and the other that it is the logarithm of $\varrho_\varepsilon(t)$ which satisfied a modified Liouville equation.

However, we notice first that if in Eq. (IV.10) we replace $\mathbb{P}_\eta(t)$ for $\mathbb{P}(t)$, such that

$$\mathbb{P}_\eta(t)\,\varrho_\eta(t) = \bar{\varrho}(t,0) \qquad\qquad (IV.15)$$

we obtain Zubarev's modified Liouville equation

$$\frac{\partial}{\partial t}\varrho_\eta(t) + \frac{1}{i\hbar}\left[\varrho_\eta(t),\hat{H}\right] = -\eta\left[\varrho_\eta(t) - \bar{\varrho}(t,0)\right] \qquad . \qquad (IV.16)$$

Second, as shown by Zubarev and Kalashnikov [283] and by Tishenko [284] (see also the books of Refs. [14] and [21]), the description provided by the statistical operator of Eqs. (IV.16) and the one of Eq. (38) are identical in the sense of providing the same average values of observables.

Consequently, the nonequilibrium statistical operator of Section **4** can be considered as resulting also from an equivalent alternative construction via a nonequilibrium ensemble in the traditional style, but postulating an *ad hoc* hypothesis consisting in requiring evolution of the system towards the future from a given initial condition of preparation. Moreover, besides introducing irreversibility in the evolution of the macroscopic state of the system – built resorting to Boltzmann's proposal by the use of kind of generalized Stosszahlansatz in the initial conditions – the form of the projection operator ensures a description in terms of only the states contained in the informational subspace, as described in Fig. **1**. The infinitesimal contribution on the right of the modified Liouville equation, we stress, discards the advanced solutions responsible for the reversibility: Its particular form - analogous to the one in Gell-Mann and Goldberger's Schroedinger equation - introduces a fading memory effect accounted for the use of Abel's kernel (in Zubarev's approach; see Appendix **II**) in the definition of the Lagrange multipliers incorporated by the variational formalism, which, we recall, express the intensive nonequilibrium thermodynamic variables. Thus, the particular construction of the statistical operator is a result of deriving it in terms of wavefunctions, or better to say statistical operators for the pure state, for the different replicas in the statistical ensemble satisfying a modified equation of evolution which selects the retarded solutions and, for these, the part contained in the informational subspace, that is, giving a description based only on the basic set of informational (or "relevant") variables.

Let us consider Eq. (38). Introducing Gibbs-entropy operator in MaxEnt-NESOM and the informational-entropy operator, respectively

$$\hat{S}_\varepsilon(t) = -\ln \varrho_\varepsilon(t) \qquad and \qquad \hat{S}(t,0) = -\ln \bar{\varrho}(t,0) \qquad ,$$

then Eq. (38) reads as

$$\frac{\partial}{\partial t}\hat{S}_\varepsilon(t) + \frac{1}{i\hbar}\left[\hat{S}_\varepsilon(t),\hat{H}\right] = -\varepsilon\left[\hat{1} - \mathcal{P}_\varepsilon(t)\right]\hat{S}_\varepsilon(t) \qquad , \tag{IV.17}$$

where, we recall, $\mathcal{P}_\varepsilon(t)\hat{S}_\varepsilon(t) = \hat{S}(t,0)$. This Eq. (IV.17) also follows from Liouville equation for the regular Gibbs entropy operator, $S_G(t) = -\ln\varrho(t)$, after noticing that

$$\hat{S}_\varepsilon(t) = \mathcal{U}_\varepsilon(t)\hat{S}_G(t) \qquad , \tag{IV.18}$$

with

$$\mathcal{U}_\varepsilon(t) = \exp\left\{\varepsilon\int_{-\infty}^{t}dt'\hat{M}_\varepsilon(t')\right\} \tag{IV.19}$$

and

$$\hat{M}_\varepsilon(t') = \hat{1} - \mathcal{P}_\varepsilon(t') \tag{IV.20}$$

It is worth mentioning that there exists a certain analogy with earlier proposals by I. Prigogine [67], namely, that irreversible behavior at the macroscopic level may follow modifying the theory of representation in microscopic mechanic, by introducing the so-called star-unitary transformations $\mathcal{U}_p^\star(t)$ instead of the regular unitary ones, in that way the statistical operator to be used takes the form

$$\varrho_p(t) = \mathcal{U}_p^\star(t)\varrho(t) \qquad , \tag{IV.21}$$

where $\varrho(t)$ is the regular statistical operator, and

$$\mathcal{U}_p^\star(t) = \exp\left\{\frac{1}{i\hbar}\hat{V}\{\mathcal{L}\}\hat{\tau}\right\} \qquad , \tag{IV.22}$$

where $\hat{V}$ is a superoperator depending on the Liouvillian operator $\mathcal{L}$ and $\hat{\tau}$ is an operator with the property that $[\hat{\tau},\mathcal{L}] = \hbar$. The analogy with, for example, Eq. (IV.18), or with

$$\varrho_\eta(t) = \exp\left\{\eta\int_{-\infty}^{t}dt'\left[\hat{1} - \mathbb{P}_\eta(t)\right]\right\}\varrho(t) \qquad , \tag{IV.23}$$

is evident. However, it can be noticed that while in Eq. (IV.23) the projection operator depends on the state of the system at any time t, Prigogine's star-unitary transformation introducing irreversibility is a universal one.

Moreover, we introduce another derivation of MaxEnt-NESOM-Zubarev's statistical operator following a line akin to the one proposed by McLennan [11]. Consider the nonequilibrium system with the Hamiltonian H of Eq. (14), weakly interacting with all the surrounding media via a potential energy operator V, and let H_R be the Hamiltonian of these surroundings ("the rest of the universe"). We write $R(t)$ for the whole statistical operator, depending on the degrees of freedom of the system and surroundings. It satisfies - for the closed system - Liouville equation

$$\frac{\partial}{\partial t}R(t) + \frac{1}{i\hbar}\left[R(t), \hat{H} + \hat{H}_R + \hat{V}\right] = 0 \quad . \tag{IV.24}$$

Definig the reduced statistical operator

$$\varrho(t) = Tr_R\{R(t)\} \quad , \tag{IV.25}$$

where the trace is taken over the space of states of the surroundings, and introducing the definition

$$R(t) = \frac{1}{2}\left[\varrho(t)\,\Xi(t) + \Xi(t)\,\varrho(t)\right] \quad , \tag{IV.26}$$

we find for $\varrho(t)$ the Liouville equation with sources

$$\frac{\partial}{\partial t}\varrho(t) + \frac{1}{i\hbar}\left[\varrho(t), \hat{H}\right] = \hat{\Phi}(t)\,\varrho(t) \quad , \tag{IV.27}$$

where

$$\hat{\Phi}(t)\,\varrho(t) = Tr_R\left\{\frac{1}{2}\left(\frac{1}{i\hbar}\left[V, \varrho(t)\,\Xi(t)\right] + \frac{1}{i\hbar}\left[V, \Xi(t)\,\varrho(t)\right]\right)\right\} \quad . \tag{IV.28}$$

In the classical limit Eq. (IV.27) goes over the equation derived by McLennan [11]. Furthermore, we may observe that the procedure we have used parallels the one proposed to build the BBGKY chain of equations for reduced density matrices [48]. Equation (IV.27) involves on the left the evolution of the system under its internal interactions, while the right side accounts for the action of the surroundings. As pointed out by Bogoliubov there are two ways to deal with this equation: in the weak coupling case one can use perturbation theory or one can

introduce propositions for the form of this term. A detailed study is left for a future publication, here suffice it to say that in the weak coupling limit and using some assumptions it can be obtained an expression of the type of a relaxation-time approximation, namely

$$\hat{\Phi}(t)\varrho(t) \simeq -\frac{1}{\tau}\left[\varrho(t) - \bar{\varrho}(t,0)\right] \qquad , \tag{IV.29}$$

where the reciprocal of the relaxation time τ is proprtional to the square modulus of the interaction potential V. Clearly, writing $\varepsilon = \tau^{-1}$ and taking the limit of V going to zero we obtain a modified Liouville equation for $\varrho(t)$ of the type of Eq. (IV.16).

In the spirit of this point of view we can then say that in Zubarev's approach to MaxEnt-NESOM the infinitesimal source in Eq. (38), which selects the retarded solutions of the regular Liouville equation and introduces irreversible evolution from an initial condition of preparation of the nonequilibrium system, is a result of the inevitable interaction of the system with the surroundings in the weak coupling limit. Irreversible dissipative behavior is, in this interpretation, a result of such interaction, that is, that a *system in nature is never isolated.*

Appendix V:. Generalized Nonlinear Mori-Heisenberg-Langevin Equations for the Lagrange Multipliers

Taking into account that because of the nonequilibrium equations of state

$$Q_j(t) = -\delta\phi(t)/\delta F_j(t) \qquad , \tag{V.1}$$

and that

$$\frac{d}{dt}Q_j(t) = \sum_{k=1}^{n}\frac{\delta Q_j(t)}{\delta F_j(t)}\frac{d}{dt}F_j(t) = -\sum_{j,k=1}^{n}\left[\frac{\delta^2\phi(t)}{\delta F_j(t)\,\delta F_k(t)}\right]\frac{d}{dt}F_j(t) =$$

$$= -\sum_{j,k=1}^{n}C_{jk}(t)\frac{d}{dt}F_j(t) \qquad , \tag{V.2}$$

where

$$C_{jk}(t) = Tr\left\{\int_{0}^{1}du\,\hat{P}_j\,[\bar{\varrho}(t,0)]^u\,\Delta\hat{P}_k\,[\bar{\varrho}(t,0)]^{-u+1}\right\} \tag{V.3}$$

with

$$\Delta \hat{P}_k = \hat{P}_k - Tr\left\{\hat{P}_k \ \bar{\varrho}(t,0)\right\} \qquad , \qquad (\text{V.4})$$

being the elements of a correlation matrix which we designate by $\hat{\mathbf{C}}(t)$, we find that Eq. (39), after neglecting the dependence on the space variable for simplicity, can be written as

$$\frac{d}{dt}\mathbf{Q}(t) = \hat{\mathbf{C}}(t)\ \frac{d}{dt}\mathbf{F}(t) = Tr\left\{\dot{\mathbf{P}}\ \bar{\varrho}(t,0)\right\} + \left\{\dot{\mathbf{P}}, \zeta_\varepsilon(t)\ |\ t\right\} \quad , \qquad (\text{V.5})$$

where we have introduced

$$\dot{\mathbf{P}} = \frac{1}{i\hbar}\left[\mathbf{P}, \hat{H}\right] \qquad , \qquad (\text{V.6})$$

Eq. (33) has been used and the fact that

$$Tr\left\{\dot{\mathbf{P}}\ \varrho_\varepsilon'(t)\right\} = \left\{\dot{\mathbf{P}}, \zeta_\varepsilon(t)\ |\ t\right\} \qquad , \qquad (\text{V.7})$$

using the supercorrelation function defined in Eq. (III.2), and finally $\mathbf{Q}$, $\mathbf{F}$, $\mathbf{P}$, and $\dot{\mathbf{P}}$ are vectors with components Q_j, F_j, P_j, and $\dot{P}_j$, $j = 1, 2, ..., n$. From this Eq. (V.5) we obtain that

$$\frac{d}{dt}\mathbf{F}(t) = \hat{\mathbf{C}}^{-1}(t)\ Tr\left\{\frac{1}{i\hbar}\left[\mathbf{P}, \hat{H}\right]\ \bar{\varrho}(t,0)\right\} + \hat{\mathbf{C}}^{-1}(t)\ \left\{\dot{\mathbf{P}}, \zeta_\varepsilon(t)\ |\ t\right\} \quad . \quad (\text{V.8})$$

But

$$Tr\left\{\frac{1}{i\hbar}\left[\mathbf{P}, \hat{H}\right]\ \bar{\varrho}(t,0)\right\} = Tr\left\{\mathbf{P}\ \frac{1}{i\hbar}\left[\hat{H}, \bar{\varrho}(t,0)\right]\right\} = \left(\mathbf{P}, \dot{\mathbf{P}}\ |\ t\right) \quad , \qquad (\text{V.9})$$

where

$$\left(\mathbf{P}, \dot{\mathbf{P}}\ |\ t\right) = Tr\left\{\int_0^1 du\ \mathbf{P}\ [\bar{\varrho}(t,0)]^u\ \Delta\dot{\mathbf{P}}\ [\bar{\varrho}(t,0)]^{-u+1}\right\} \qquad (\text{V.10})$$

is a tensor acting on the n-component vector on the right of it, and

$$\Delta\dot{\mathbf{P}} = \dot{\mathbf{P}} - Tr\left\{\dot{\mathbf{P}}\ \bar{\varrho}(t,0)\right\} \qquad . \qquad (\text{V.11})$$

Using Eq. (V.9) and the expression for $\zeta_\varepsilon(t)$ as given by Eq. (II.2), we can write Eq. (V.8) in the form

$$\frac{d}{dt}\mathbf{F}(t) = -\hat{\mathbf{C}}^{-1}(t)\left(\mathbf{P},\dot{\mathbf{P}}\mid t\right)\mathbf{F}(t) -$$

$$- \int_{-\infty}^{t} dt'\, e^{\varepsilon(t'-t)}\hat{\mathbf{C}}^{-1}(t)\left[\left\{\dot{\mathbf{P}},\mathbf{P}(t'-t)\mid t\right\}\frac{d}{dt'}\mathbf{F}(t') + \right.$$

$$\left. + \left\{\dot{\mathbf{P}},\dot{\mathbf{P}}(t'-t)\mid t\right\}\mathbf{F}(t')\right] \qquad . \qquad (V.12)$$

This Eq. (V.12) implies in a set of coupled highly nonlinear integrodifferential equations for the Lagrange multipliers (intensive nonequilibrium thermodynamic variables) $F_j(t)$, the nonlinearity being present in the correlation functions which are defined in terms of the statistical operator $\bar{\varrho}(t,0)$.

At this point we introduce an approximation consisting into retaining in the supercorrelation functions the lowest order in the dissipative relaxation processes, that is, we take in them [cf. eq. (II.5)] $Y(\zeta_\varepsilon\mid u)=1$, and then

$$\left\{\hat{A},\hat{B}\mid t\right\} \simeq \left(\hat{A},\hat{B}\mid t\right) \equiv Tr\left\{\int_0^1 du\,\hat{A}\,[\bar{\varrho}(t,0)]^u\,\hat{B}\,[\bar{\varrho}(t,0)]^{-u+1}\right\} \quad . \quad (V.13)$$

In this approximation the projection operator of Eq. (III.3) becomes

$$\mathcal{P}_\varepsilon(t)\,\hat{A} = \mathbf{P}\,\mathbf{C}^{-1}(t)\left(\mathbf{P},\hat{A}\mid t\right) \qquad . \qquad (V.14)$$

Moreover, in Eq. (V.12) we keep the time derivations of the basic variables P only up to second order in the interactions, introducing in the second term on the right of Eq. (V.12)

$$\frac{d}{dt'}\mathbf{F}(t') \simeq -\hat{\mathbf{C}}^{-1}(t')\left(\mathbf{P},\dot{\mathbf{P}}\mid t\right)\mathbf{F}(t') \qquad , \qquad (V.15)$$

and further taking into account the form of the projection operator of Eq. (III.3) and its property that

$$\mathcal{P}_\varepsilon(t)\,\hat{\zeta}_\varepsilon(t) = 0 \qquad , \qquad (V.16)$$

we can write Eq. (V.12) in the compact form

$$\frac{d}{dt}\mathbf{F}(t) = i\,\hat{\Omega}(t)\,\mathbf{F}(t) + \int_{-\infty}^{t} dt'\, e^{\varepsilon\left(t'-t\right)}\hat{\Gamma}\left(t'-t\mid t\right)\mathbf{F}(t') \qquad , \qquad (V.17)$$

where

$$\hat{\Omega}\left(t\right) = i\ \hat{\mathbf{C}}^{-1}\left(t\right)\left(\mathbf{P}, \mathbf{P} \mid t\right) \qquad , \tag{V.18}$$

$$\hat{\Gamma}\left(t' - t \mid t\right) = \hat{\mathbf{C}}^{-1}\left(t\right)\left(\dot{\mathbf{P}}\left[\hat{1} - \mathcal{P}_{\varepsilon}\left(t\right)\right] e^{i\left(t' - t\right)\mathcal{L}}\left[\hat{1} - \mathcal{P}_{\varepsilon}\left(t\right)\right]\dot{\mathbf{P}}|t\right) \quad , \tag{V.19}$$

where

$$\hat{A}\left(t' - t\right) = \exp\left\{i\left(t' - t\right)\mathcal{L}\right\}\hat{A} \qquad , \tag{V.20}$$

with $\mathcal{L}$ being the Liouvillian operator.

We can see that Eq. (V.17) for the Lagrange multipliers takes the form of a generalized nonlinear Mori-like equation [9], where, following Mori's terminology, the first term on the right is a precession term and the second contains the memory function $\hat{\Gamma}$ (a fading memory in this case because the presence of the exponential in the time integration). The nonlinearity is hidden in the fact that both Ω and Γ are highly nonlinear expressions in the intensive nonequilibrium thermodynamic variables $F_j\left(t\right)$, which are contained in the operator $\bar{\varrho}$.

The presence in Eq. (IV.21) of the projection operators $\left[1 - \mathcal{P}_{\varepsilon}\right]$ at left and right of the correlation function in the "memory function" Γ cancels the contribution $\left[\mathbf{P}, H_o\right]$ to the change in time of variables $\mathbf{P}$, leaving only at both ends of the correlation function only the contribution $\left[\mathbf{P}, H'\right]$. Thus, the operator $\left[1 - \mathcal{P}_{\varepsilon}\left(t\right)\right]$ projects $\mathbf{P}$ on the subspace which is complementary to the informational subspace containing the basic set of variables $\{P_j\}$: In Mori's words, Γ is a nonequilibrium correlation matrix of the rapidly fluctuating forces $\dot{\mathbf{P}} = \left(1/i\hbar\right)\left[\mathbf{P}, H'\right]$. This is achieved through the difference between the nonequilibrium correlation matrix of the total generalized forces [last contribution on the right of Eq. (V.12)] minus the projection of these generalized forces over the informational subspace [a contribution that arises from the second contribution on the right of Eq. (V.12)]. This point has been stressed by V. P. Kalashnikov who showed that the use of the total generalixed forces $\dot{\mathbf{P}}$, i.e. not corrected by the substraction of the contributions of their secular parts (the change under H_o), leads to wrong results like the so-called paradox of vanishing damping at zero frequency in the Markovian limit of this equation [80].

Equation (V.17) is similar to the one obtained by B. Robertson [15], and also to those of Kawasaki and Gunton [285] and of Grabert [16], because of the equivalence of these with that of Robertson. However, it must be stressed a difference consisting in the presence in the correlation matrix (or memory matrix) of the weight function $\exp\left\{\varepsilon\left(t' - t\right)\right\}$, which, we recall, fixes the inital state of prepara-

tion of the system (characterized by $\bar{\varrho}(t,0)$) and provides irreversible behavior for the evolution of the macroscopic state of the system.

As final words in this Appendix, we call the attention to the fact that a more practical and manageable way to calculate the equations of evolution of the basic variables is the one provided by the MaxEnt-NESOM kinetic theory [76,77], and then using Eqs. (43) and (V.6) we can write

$$\frac{d}{dt}\mathbf{F}(t) = \hat{\mathbf{C}}^{-1}(t)\left[\mathbf{J}^{(o)}(t) + \mathbf{J}^{(1)}(t)\right] + \sum_{n=2}^{\infty}\hat{\mathbf{C}}^{-1}(t)\ \mathbf{\Omega}^{(n)}(t) \quad , \qquad (V.21)$$

where $\mathbf{J}^{(o)}$, $\mathbf{J}^{(1)}$, and $\mathbf{\Omega}^{(n)}$ are vectors with components $J_j^{(o)}$, $J_j^{(1)}$, and $\Omega_j^{(n)}$ respectively, with $j = 1, 2, ..., n$, all of these quantities defined in [23].

Appendix VI:. Nonequilibrium Grand-Canonical Ensemble

For the study of many-body systems out of equilibrium, particularly the case of solid state matter, and in its realm the area of semiconductor physics, the relevant ensemble to consider is the grand-canonical one generalized to nonequilibrium conditions. It is described in Ref. [55], with applications in Ref. [56] where, on its foundations is derived a kinetic theory appropriate for giving bases to a nonequilibrium thermo-hydrodynamics. We briefly describe it here.

On the basis of the relevance for almost all problems in many-body physics of considering energy and particle numbers, we begin selecting the densities of particles $\hat{n}(\mathbf{r})$ and of energy $\hat{h}(\mathbf{r})$ for the set of basic variables. But Zubarev-Peletminskii selection rule of Eq. (15) requires that the fluxes of all order of these densities needs be added to the set of basic variables, which is then composed of

$$\left\{\hat{n}(\mathbf{r}),\ \hat{h}(\mathbf{r}),\left\{\hat{I}_n^{[r]}(\mathbf{r})\right\},\ \left\{\hat{I}_h^{[r]}(\mathbf{r})\right\}\right\} \qquad , \qquad (VI.1)$$

where $\hat{I}_{n(h)}^{[r]}(\mathbf{r})$ is the flux of order r (which is also its tensorial rank) of particle number (energy). As discussed in Ref. [55] these fluxes are Hermitian operators expressed in terms of single-particle dynamical operators, and are a functional of a generating velocity of the wavepacket of the particles involved.

We stress that in the case of solid state physics, and particularly of semiconductor physics, the description of the system can be done in terms of only single-particle operators, i.e. in terms of independent quasiparticles like phonons, Bloch-band electrons, plasmons, magnons, polarons, polaritons, plasmaritons, etc.

Because of this fact there follows an important consequence, namely, that since the fluxes – which are imposed as basic variables by Zubarev-Peletminskii selection rule of Eq. (15) – are linear combination of the single-particle Wigner-Landau-Dirac density matrices (that is, the average over the nonequilibrium ensemble of the single-particle dynamical operators), the latter can, in principle, be obtained once the equations of evolution for the fluxes are solved. In this way, and we reinforce that only for systems amenable to be described by a single-particle representation, we may say that Zubarev-Peletminskii rule consists into a *closure condition* for the nonequilibrium thermodynamic description of the system: Once the single-particle density matrices have been obtained we can calculate any macroscopic observable of the system. This is not the case for liquids, when two-particle density matrices are required to be added to the description (see for example [24]). But in this case a closure condition cannot be obtained since the two-particle potential, which differently to Coulomb interaction in solids, cannot be dealt with in a molecular field approximation, couples the reduced density matrices of all order leading to a kind of BBGKY hierarchy in nonequilibrium conditions requiring the introduction at a certain point of a decoupling approximation like in the theory of Green functions.

The basic set of dynamical quantities (mechanical observables) of Eq. (IV.1), in this case the basic P_j of the general theory of Section **3,** has associated the set of macrovariables (or nonequilibrium thermodynamic variables in IST)

$$\left\{ n\left(\mathbf{r}, t\right), \ h\left(\mathbf{r}, t\right), \left\{ I_n^{[r]}\left(\mathbf{r}, t\right)\right\}, \ \left\{ I_h^{[r]}\left(\mathbf{r}, t\right)\right\}\right\} \tag{VI.2}$$

and the Lagrange multipliers

$$\left\{ F_n\left(\mathbf{r}, t\right), \ F_h\left(\mathbf{r}, t\right), \left\{ F_n^{[r]}\left(\mathbf{r}, t\right)\right\}, \ \left\{ F_h^{[r]}\left(\mathbf{r}, t\right)\right\}\right\} \tag{VI.3}$$

and the auxiliary ("frozen" or instantaneous quasi-equilibrium) statistical operator in the nonequilibrium grand-canonical ensemble is

$$
\begin{aligned}
\bar{\varrho}\left(t, 0\right) \ = \ & \exp\left\{ -\phi\left(t\right) - \int dr^3 \left[F_h\left(\mathbf{r}, t\right) \hat{h}\left(\vec{r}\right) + F_n\left(\mathbf{r}, t\right) \hat{n}\left(\mathbf{r}\right) + \right.\right. \\
& \left. + \mathbf{F}_h\left(\mathbf{r}, t\right) \cdot \overset{\wedge}{\mathbf{I}}_h\left(\mathbf{r}\right) + \mathbf{F}_n\left(\mathbf{r}, t\right) \cdot \overset{\wedge}{\mathbf{I}}_n\left(\mathbf{r}\right) \right] + \\
& \left. + \sum_{r \geq 2} \int dr^3 \left[F_h^{[r]}\left(\mathbf{r}, t\right) \times \hat{I}_h^{[r]}\left(\mathbf{r}\right) + F_n^{[r]}\left(\mathbf{r}, t\right) \times \hat{I}_n^{[r]}\left(\mathbf{r}\right) \right] \right\} \tag{VI.4}
\end{aligned}
$$

where $\times$ stands for fully contracted product of tensors.

The nonequilibrium grand-canonical statistical operator $\varrho_\varepsilon(t)$ is the one given by Eq. (29) once we use in this expression the grand-canonical instantaneous quasi-equilibrium operator of Eq. (VI.4). As shown in Ref. [72] such nonequilibrium grand-canonical operator goes over Gibbs' grand-canonical distribution in equilibrium when the latter is achieved after the perturbing external sources are switched off while the contact with the thermal and particle reservoirs is maintained. This suggests to rewrite the Lagrange multipliers in a particular form, namely,

$$F_h(\mathbf{r}, t) = \beta(\mathbf{r}, t) = 1/k_B T^\star(\mathbf{r}, t) \qquad , \tag{VI.5}$$

$$F_n(\mathbf{r}, t) = -\beta(\mathbf{r}, t)\mu(\mathbf{r}, t) \qquad , \tag{VI.6}$$

$$\mathbf{F}_h(\mathbf{r}, t) = -\beta(\mathbf{r}, t)\boldsymbol{\alpha}_h(\mathbf{r}, t) \qquad , \tag{VI.7}$$

$$\mathbf{F}_n(\mathbf{r}, t) = -\beta(\mathbf{r}, t)\boldsymbol{\alpha}_n(\mathbf{r}, t) \qquad , \tag{VI.8}$$

$$F_h^{[r]}(\mathbf{r}, t) = -\beta(\mathbf{r}, t)\alpha_h^{[r]}(\mathbf{r}, t) \qquad , \tag{VI.9}$$

$$F_n^{[r]}(\mathbf{r}, t) = -\beta(\mathbf{r}, t)\alpha_n^{[r]}(\mathbf{r}, t) \qquad , \tag{VI.10}$$

introducing a field of nonequilibrium temperature (usually referred to as *quasitemperature*) $T^\star(\mathbf{r}, t)$, a field of nonequilibrium chemical potential (dubbed quasi-chemical potential) $\mu(\mathbf{r}, t)$, the vectorial fields of drift velocities of particles and of energy, $\boldsymbol{\alpha}_n(\mathbf{r}, t)$ and $\boldsymbol{\alpha}_h(\mathbf{r}, t)$ respectively, and some kind of fields of tensorial drift velocities also of particles and energy $\alpha_n^{[r]}(\mathbf{r}, t)$ and $\alpha_h^{[r]}(\mathbf{r}, t)$, with $r = 2, 3, \ldots\ldots$, associated to the fluxes with an order higher that one.

We call the attention to the fact that in nonequilibrium conditions we can find situations requiring to define different quasitemperatures for different sets of quasiparticles, a point apparently originally stressed by Lev Landau [163]. This is for example the case in highly excited semiconductors as described in Section **5**, where we have also mentioned some studies of a partial thermo-hydrodynamics for the fluid of carriers and phonons in the photoinjected plasma in semiconductors.

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