

Statistical Mechanics of Dissipative Systems: an Information-Theoretic Approach

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It is described a mechano-statistical formalism able to deal with dissipative processes in systems arbitrarily away from equilibrium. The method is considered to be encompassed in the context of Jaynes' Predictive Statistical Mechanics. The formalism allows for the construction of a nonlinear generalized transport theory of large scope. It also provides foundations for phenomenological thermodynamics in what is denominated Informational Statistical Thermodynamics, and an accompanying non-classical hydrodynamics (Informational Statistical Hydrodynamics). In the context of the latter, we derive generalized equations of evolution for the ordinary fluxes of Classical (Linear) Irreversible Thermodynamics. These time evolution equations for the fluxes are shown to be of the type of a large generalization of Mori-Langevin equations, which are nonlinear equations including space correlations, memory, and dissipation. We also consider how such equations reduce, taking a linear approximation in the fluxes and an instantaneous in time approach, to nonlocal in space constitutive-like equations for the fluxes.

I. Introduction

As it is well known, it is usually stated that the objective of statistical mechanics is to explain and predict the properties of macroscopic matter from the underlying microscopic dynamics of its constituents. It is divided into two parts, namely that associated to equilibrium states and that associated to nonequilibrium states. Within its own structure Statistical Mechanics possesses a number of quite difficult conceptual problems^[1]. Among them there is the question about the physical meaning of Gibbs ensemble algorithm. Also, one may wonder how to justify the use of the usual ensembles for systems in equilibrium. Is such

possibility feasible and, if so, what would their structure be like in order to deal with the case of systems arbitrarily out of equilibrium? Another question is how to reconcile the reversibility inherent in the equations of microscopic mechanics, with the irreversible behavior of macroscopic systems in nature. So we see that conceptual difficulties may be even associated to the well established and highly regarded equilibrium statistical mechanics. It is really a puzzling fact that Gibbs ensemble algorithm for systems in equilibrium works so stupendously well^[2].

It is then not surprising that the analysis of nonequilibrium systems presents far greater difficulties than

those faced in the theory of equilibrium systems. This is due firstly to the fact that non-equilibrium states are not uniquely defined and secondly because a more detailed discussion is necessary to determine the temporal dependence of measurable properties, and to calculate the time and space - dependent transport coefficients associated with the irreversible processes that take place in these systems. At present several theoretical methods exist for studying the macroscopic evolution of nonequilibrium systems. The usefulness of these methods can be assessed through comparison of the theoretical results with experimental data. However, the reason why these methods work well within their own domains of application cannot be properly understood until a profound insight on the basic conceptual problems associated to the irreversible processes is obtained. Existing formalisms have inherent difficulties, typically those related mainly to the introduction of coarse-graining procedures, the question of irreversibility, and the definition of initial and boundary conditions.

Those approaches can be grossly associated with two main directions of thought in nonequilibrium statistical mechanics: (1) The kinetic theory of gases where, starting with a few hypothesis although very controversial, one obtains a description of how simple systems approach equilibrium (e.g. the celebrated Boltzmann's \mathcal{H} -theorem). An extension of these ideas to dense systems has followed several paths like, for example, the construction of generalized kinetic theories^[3], and the equations of the BBGKY hierarchy^[4]. (2) A generalization of the theory of the Brownian motion, where the complicated dynamic equations - the generalized Newton-Langevin equations - that follow from the laws of mechanics (used to describe the microscopic dynamics of molecules, or atoms, or quasiparticles, that constitute the system) are accompanied by statistical assumptions. Belonging to this approach are, for example, the formalism of the correlation functions or memory functions due to Mori^[5], and some aspects of the master

equations method^[6].

This situation arose from stagnation: for a long time there was no general prescription for choosing appropriate ensembles to describe the behaviour of nonequilibrium systems. Hence the rise of kinetic theories, some more reliable than others, to deal with the great variety of nonequilibrium phenomena in physical, chemical, and biological (i.e. natural) systems. It has been rightly stated^[7] that: "The prototype and still most successful of all kinetic equations is Boltzmann's famous equation for the time evolution of the position and velocity distribution of atoms in a gas. The beautiful elegance of this equation, so easy to derive intuitively and so difficult to justify rigorously, is as impressive today as it was over a hundred years ago when it sprang like Minerva fully clothed from the head of Jupiter. It still stands today as a practical tool and a model of what a kinetic equation should be. The philosophical problems it raised and the heated arguments it engendered are also still with us today."

It has been considered^[8] that the basic goals of nonequilibrium statistical mechanics are: (i) to derive transport equations and to understand their structure; (ii) to understand how the approach to equilibrium occurs in natural isolated systems; (iii) to study the properties of steady states; (iv) to calculate the instantaneous values and the temporal evolution of the physical quantities which specify the macroscopic state of the system. The approaches to develop a theory encompassing the programme just stated have also been classified by Zwanzig^[8] as: (a) Intuitive techniques; (b) Techniques based on the generalization of the kinetic theory of gases; (c) Techniques based on the theory of stochastic processes; (d) Expansions from an initial equilibrium ensemble; (e) Generalizations of Gibbs ensemble algorithm.

The last of these items, (e), is placed among the long sought attempts to search for a generalized Gibbsian statistics for systems arbitrarily away from equilibrium, and encompassing as proper limiting cases the

successful theories of linear response (near equilibrium conditions) and finally equilibrium. A modality of this theory, that can be called the Nonequilibrium Statistical Operator Method (NSOM for short from now on), has been an object of interest and research in the last three decades. The NSOM is considered to have a quite appealing structure and seems to be a very effective technique to deal with a large class of experimental situations; we will return to this point in the last section. This formalism has been formulated by several authors, either using heuristic arguments^[9,10], or projection operator techniques^[11]. It has been shown^[12] that these approaches can be brought together under a unifying variational method, which is to be reviewed and further discussed in next Section.

The important point to stress here is that such unifying variational method seems to place the formalism within the scope of Edwin T. Jaynes predictive Statistical Mechanics (PSM)^[13], which seems to encompass a new paradigm in the scientific method. PSM is founded on the principles of Bayesian statistical inference^[14] along with a constructive criterion for setting up probability distributions, namely, the maximum entropy formalism (MaxEnt for short), based on an informational-theoretical approach^[15]. As pointed by Jaynes, we are beginning today to realize how much of all physical science is really only *information* organized in a particular way. However there remains a knotty question, namely, to what extent does this information reside in us, and to what extent it is a property of Nature. The point, mainly that the foundations of probability theory and the role of human information have to be brought in, is also considered by Jaynes in connection with the difficulties inherent to quantum measurement theory^[16]. According to Jaynes the question of what the theoretically valid, and pragmatically useful, ways of applying probability theory in science has been approached by Harold Jeffreys^[17], in the sense that he stated the general philosophy of what scientific inference is and proceeded to carry both the mathematical theory and its

practical implementations. Jeffreys^[17] indicates that "the fundamental problem of scientific progress, and a fundamental of everyday life, is that of learning from experience. Knowledge obtained in this way is partly merely description of what we have already observed, but part consists of making inferences from past experience to predict future experience. This part may be called generalization or induction. It is the most important part." Jeffreys also quotes James C. Maxwell as stating that the true logic for this world is the Calculus of probabilities, which takes into account the magnitude of the probability which is, or ought to be, in a reasonable man's mind.

Such approach can go beyond physics, chemistry, biology and other sciences, encompassing even the social ones. As a consequence a point of view adopted by several authors is that it provides an unifying scientific method for them - meaning that the different branches of science that seem to be far apart may, within such new paradigm, grow and be held together organically.

Jacob Bronowski^[18] conjectured that this may be the revolutionary thought in modern science. It replaces the concept of the inevitable effect for that of the probable trend. Further, Ilya Prigogine, in his quest for the meaning of time and the role of irreversibility in the emergence of complex behavior in the natural sciences, has stressed that it is not surprising that probability could play an even more relevant role, that the one so far provided, in the description of natural phenomena; the innovation being to introduce probability in physics not as a mean of approximation but rather as an *explanatory principle*^[19].

Also, following Jaynes^[14] and Anderson^[24], 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 it is consistent to hold in a proposition being true, according to which other conditioning propositions are taken as true. Or, according to Anderson^[20], "What Bayesian does is to focus one's attention on the ques-

tion one wants to ask of the data: It says in effect, How do these 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 made more likely by the data."

After these general considerations, let us return to the particular question we have in hands, namely to see how nonequilibrium statistical mechanics can become a predictive science. To proceed in that direction, as pointed out by Jaynes "How shall we best think about Nature and most efficiently predict her behavior, given only our incomplete knowledge? [...] 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 [...] 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 motions say in any particular case, but the general things that they say in "almost all" cases consistent with our information, for these are the reproducible things." The construction of the statistical approach should be based on a rather basic principle: "[...] if any macrophenomenon is found to be reproducible, then it follows that all microscopic details that are not under the experimenter's control must be irrelevant for understanding it. [...] We never know the microstate, only a few aspects of the macrostate. Nevertheless the aforementioned principle of reproducibility convinces us that this should be enough; the relevant information is there, if only we can see how to recognize it and use it."

Hence, in Jaynes approach, when the basic question of the physicist: How does the system behave? is asked, the physical theory instead of seeking to answer it by deductive reasoning from the known laws of physics, searches for an answer to the question: Given

the partial information that we do have, what are the best predictions we can make of observable phenomena? We cannot claim deductive certainty for its predictions, but it must ensure the objectivity. In a colloquial vein we can say that, to ensure the honesty of the predictions we do make, we ought to forbid ourselves from the use of extraneous assumptions beyond the data at hand. The formal device which accomplishes this relies on the idea of drawing inferences only from that probability distribution whose sample space represents what is known about the structure of microstates. PSM claims that considering that Gibbs standard of logical reasoning is powerful enough to give a formalism, that can be put under a unifying variational principle, of - as already stated - tremendous success in dealing in the realm of Physics and Chemistry for a century, then it also must be powerful enough to be appropriately generalized to irreversible processes^[13–15,21].

The constructive criterion for deriving the probability assignment for the problem on the basis of the available information is the principle of maximization of informational entropy, the already mentioned MaxEnt for short. In other words, according to Jaynes' MaxEnt, the least biased probability assignment $\{p_j\}$ for a set of mutually exclusive events $\{x_j\}$ is the one that maximizes the quantity η , sometimes referred to as the informational entropy, given by the expression

$$\eta = - \sum_j p_j \ln p_j ,$$

subject to the constraints imposed by the available information. This is based on Shannon's ideas, who first demonstrated that, for an exhaustive set of mutually exclusive propositions, there exists a unique function measuring the uncertainty of the probability assignment, namely, the function η defined above^[22].

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 it a logical-mathematical viewpoint - the principle of economy in logic, known as Occam's razor, namely, *Entia non sunt multiplicanda praeter necessitatem* (Entities are not to be multiplied except of necessity). Jaynes' PSM predicts a thermodynamic behavior of a system, not on the basis of 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 distribution represents the best predictions we are able to make from the information we have^[13-15].

As described in next Section the NSOM can be brought under the variational principle just stated, and so we will refer to it as the MaxEnt-NSOM. We mean that in that way we recover, generalize and extend the existing NSOM in its heuristic and projection techniques approaches^[9-12]. Furthermore, the MaxEnt-NSOM recovers as a special case equilibrium statistical mechanics, and in particular, in the thermodynamic limit it is a manifestation of the second law of thermodynamics^[23,24]. Also it provides mechano-statistical basis for classical equilibrium thermodynamics, linear response theory, and classical hydrodynamics^[25]. We are considering an extension of these results to the case of irreversible thermodynamics and non-classical hydrodynamics for systems arbitrarily away from equilibrium. This seems to be possible when resorting to the MaxEnt-NSOM including nonlinearities and nonlocality in space and time (what implies in incorporating space correlations and memory), leading to what can be referred to as *Informational Statistical Thermodynamics*^[26,27,28].

In Section II we describe the construction of the MaxEnt-NSOM for a system in quite general nonequilibrium conditions. In this MaxEnt-NSOM the characteristic macrovariables describing the states of the system are defined from an appropriate set of basic dynamical variables, by taking the average of the latter

in terms of a "coarse-grained" probability density. The main gist behind this coarse-graining operation is to eliminate all the "irrelevant" information necessary to characterize the macrostate. The MaxEnt nonequilibrium statistical operator is obtained, and within the formalism a generalized nonlinear quantum transport theory is constructed. This is used to derive constitutive equations in non-classical hydrodynamics, and from them, together with the equations of continuity, the equations of propagation (damped wave motion) for the hydrodynamic modes. This is done in Section III in order to provide an illustrative application of the method. Concluding remarks are included in Section IV.

II. Theoretical background

The NSOM can be considered as a generalization of statistical formalisms based on Boltzmann and Gibbs fundamental ideas. Different approaches have been developed by several authors, relying on either heuristic arguments, or using projection operator techniques. A unifying approach based on a variational principle is described elsewhere^[12,29].

The NSOM is based, in any of its formulations, on Bogoliubov's assertion (principle of correlation weakening)^[30] that in general there exists a hierarchy of relaxation times such that as time goes on, the system keeps losing memory of the previous evolution, so that as equilibrium is approached an ever decreasing number of variables is enough for the description of the macroscopic state of the system. This contraction is connected with the separation from the total Hamiltonian of strong interactions with certain symmetries; such interactions are those related to the fast relaxing processes^[31]. In the contracted description the macroscopic state of the system is characterized by a reduced set of thermodynamic variables, say $Q_j(t)$ with $1, 2, \dots, n$, which are the average values, calculated with the use of the nonequilibrium statistical operator (NSO), of a corresponding set of dynamical variables P_j , the NSO being a functional of these variables. It

ought to be noticed that, for inhomogeneous systems, these variables should be locally defined (position dependent), that is one introduces the densities $P_j(\vec{r})$ and the thermodynamic fields $Q_j(r',t)$. The choice of these variables is not unique and one of the fundamental questions of the theory consists in defining their completeness in some sense^[31,32]. One way associated to the NSOM, which is shown to be closely connected with phenomenological irreversible thermodynamics^[27], is based on the separation of the total Hamiltonian into two parts, namely

$$H = H_0 + H' \quad (1)$$

where H_0 contains the kinetic energies and the contributions of the interactions that produce very *rapid* relaxation processes, and H' is related to the slow relaxation processes. Moreover, the quantities P_j and the relevant part of the Hamiltonian, H_0 , are connected by what we call the Peletminskii-Zubarev symmetry condition, namely

$$[P_j, H_0] = \sum_{k=1}^n \Omega_{jk} P_k, \quad (2)$$

in an appropriate quantum representation, and where Ω are c-numbers. In this way it may be said that the fast relaxing variables have been eliminated from the description and the macrostate of the system is characterized in terms of the contracted description generated by the set of slow relaxing variables.

As already mentioned, the NSOM can be put under a unifying approach resorting to a variational principle, namely Jaynes' principle of maximization of information entropy^[14-16], with memory effects and ad hoc hypothesis^[12,29]. The method consists in maximizing Gibbs functional

$$S_G(t) = -Tr\{\rho(t) \ln \rho(t)\}, \quad (3)$$

where ρ is the NSO, subject to the constraints that the set of macrovariables $Q_j(\vec{r},t)$ are those that properly describe the macroscopic state of the system, and that

$$Q_j(\vec{r},t) = Tr\{P_j(\vec{r})\rho(t)\}, \quad (4)$$

where $t_0 \leq t' \leq t$, with t_0 being the initial time of preparation of the system and t the time at which a measurement is performed. Eq. (4) introduces a dynamical character in the information (after-effects) since these conditions involve the evolution of the system from the initial time of preparation t_0 (to be understood as much larger than the relaxation times in Bogoliubov's hierarchy associated to the principle of correlation weakening) up to time t . It must also be noted the formal character of Eq. (4) where one makes the assumption that there is a knowledge of the values of variables Q_j on the time interval (t_0, t) . However, this information-gathering interval can and ought to be reduced to information recorded at a unique time: the formalism generates equations of evolution for variables $Q_j(\vec{r},t)$ which give their values at any time $t > t_0$, once initial values $Q_j(r',t_0)$ are provided.

We omit the details of the description of the variational procedure, and refer the reader to references [12,29]. It suffices to say that the Lagrange multipliers that the variational method introduces are specified in a special way in order to: (i) fix an initial condition from which the irreversible evolution of the macroscopic state of the nonequilibrium many-body system proceeds so that one is able to introduce from the outset a condition for dissipativity in an ad hoc manner; (ii) introduce a set of functions $F_j(\vec{r},t)$ such that they play the role of intensive variables thermodynamically conjugated to the intensive variables $Q_j(\vec{r},t)$, to generate a complete connection with phenomenological nonequilibrium thermodynamics; and (iii) separate the NSO into two parts

$$\rho(t) = \bar{\rho}(t) + \rho'(t), \quad (5)$$

where the first term, $\bar{\rho}(t)$, is an auxiliary generalized Gibbsian distribution which defines the instantaneous values of the macrovariables, and $\rho'(t)$ carries the information on the microscopic dynamics relevant to the

description of the irreversible evolution of the macroscopic state of the system. The auxiliary distribution is given by

$$\bar{\rho}(t) = \exp \left\{ \phi(t) - \sum_{j=1}^n \int d^3r F_j(\vec{r}, t) P_j(\vec{r}) \right\}, \quad (6)$$

where

$$\phi(t) = -\ln Tr \left\{ \exp \left(- \sum_{j=1}^n \int d^3r F_j(\vec{r}, t) P_j(\vec{r}) \right) \right\}, \quad (7)$$

ensures its normalization.

Condition (ii) stated above, applied to the variational Lagrange multipliers, requires the additional property that

$$Q_j(\vec{r}, t) = Tr \{ P_j(\vec{r}) \rho(t) \} = Tr \{ P_j(\vec{r}) \bar{\rho}(t) \}, \quad (8)$$

which stands for a *coarse-graining condition*. This property has a relevant role providing for the simultaneous normalization of both $\rho(t)$ and $\bar{\rho}(t)$, namely Eq. (7) in the latter case, and making of $\phi(t)$ a generating functional in the sense that

$$\frac{\delta \phi(t)}{\delta F_j(\vec{r}, t)} = -Q_j(\vec{r}, t), \quad (9)$$

where δ stands for functional derivative^[33]. Eq. (9) defines the conjugation of both kind of variables (F_j

and Q_j) in the sense of phenomenological irreversible thermodynamics^[27]. It is the generalization to nonequilibrium situations of the relation that stands in equilibrium and near equilibrium conditions; it also implies in the result provided by Eq. (32b) below which is a manifestation of the equations of state in nonequilibrium conditions.

Particular cases of the NSOM given in the literature are recovered within the variational method (Cf. Ref. [12]). In particular Zubarev's NSO^[10], which is to be used in next section, is given by

$$\rho_\epsilon(t) = \exp \left\{ \epsilon \int_{-\infty}^t dt' e^{\epsilon(t'-t)} \ln \bar{\rho}(t', t'-t) \right\}, \quad (10)$$

where $\bar{\rho}$ is given by Eq. (6) with the first time in the argument referring to the time dependence of the thermodynamic variables $F_j(\vec{r}, t)$ and the second standing for the time evolution of operators $P_j(\vec{r}, t'-t)$ in Heisenberg representation. ϵ is a positive infinitesimal ensuring irreversibility in the description which goes to zero after the trace operation in the calculation of average values has been performed. Integration by parts in Eq. (10) yields

$$\rho_\epsilon(t) = \exp \left\{ \theta - \int_{-\infty}^t dt' e^{\epsilon(t'-t)} \frac{d}{dt'} \ln \bar{\rho}(t', t'-t) \right\}, \quad (11)$$

which can be put in the form of Eq. (5) (See Appendix A). It is worth noticing that Zubarev's NSO satisfies a modified Liouville equation of the form

$$\left[\frac{\partial}{\partial t} + i\mathcal{L} \right] \ln \rho_\epsilon(t) = -\epsilon [\ln \rho_\epsilon(t) - \ln \bar{\rho}(t, 0)], \quad (12)$$

where \mathcal{L} is the Liouville operator for the system. The presence of the infinitesimal source breaks the otherwise time reversal symmetry. In that way it has been introduced in the formalism, in an *ad hoc* manner, a condition for irreversible behavior in the evolution of the sys-

tem from an initial condition of preparation at time t_0 . This implies in the use of Bogoliubov's method of quasi-averages^[34], a procedure that involves a symmetry-breaking process to deal with the remotion of degeneracies connected with one or several transformation groups. In the present case the *symmetry-breaking* is that of *time-reversal* symmetry. Here the presence of ϵ selects the sub-group of retarded solutions from the total group of solutions of Liouville's equation for, as stated, establishing from the outset irreversible evolu-

tion for increasing times from an initial value condition. We note that the initial condition for the NSO is

$$\rho_\epsilon(-\infty) = \bar{\rho}(-\infty, 0), \quad (13)$$

or in words, the state characterized by the initial values $Q_j(-\infty)$ of the macrovariables with no correlation among them; for $t > t_0 (= -\infty)$ the term $\rho'(t)$ is present in ρ_ϵ and with it the irreversible evolution under the dynamics generated by the system's Hamiltonian.

The MaxEnt-NSOM proves to be a very powerful mechano-statistical formalism for the treatment of systems arbitrarily away from equilibrium. In particular it provides a mechano-statistical foundation for phenomenological irreversible thermodynamics and within its scope, it contains the Glansdorff-Prigogine universal criterion of evolution, Prigogine's theorem of minimum entropy production, and Glansdorff-Prigogine stability criterion^[12,35]. Also, within the framework of the MaxEnt-NSOM it is possible to construct a response function theory for far-from-equilibrium systems and an accompanying nonequilibrium thermodynamic

Green function formalism^[12].

On the other hand, the most important part of the MaxEnt-NSOM is the derivation of a nonlinear quantum transport theory for the basic variables, fundamental in all applications since they give the description of the irreversible evolution of the macroscopic state of the system. Such a theory follows from the general time evolution equation for the macrovariables, namely,

$$\frac{\partial}{\partial t} Q_j(\vec{r}, t) = Tr \left\{ \frac{1}{i\hbar} [P_j(\vec{r}), H] \rho_\epsilon(t) \right\}, \quad (14)$$

where, as usual, $[A, B]$ is the commutator of operators A and B. Using the separation of Eq. (5) and some mathematical manipulations we are lead to the result that^[36]

$$\frac{\partial}{\partial t} Q_j(\vec{r}, t) = Tr \left\{ \frac{1}{i\hbar} [P(\vec{r}), H] \rho_\epsilon(t, 0) \right\} + \mathcal{J}_j(\vec{r}, t). \quad (15)$$

where

$$\begin{aligned} \mathcal{J}_j(\vec{r}, t) = & \frac{1}{i\hbar} \int_{-\infty}^t dt' e^{\epsilon(t'-t)} Tr \left\{ \frac{1}{i\hbar} [H, [H'(t-t'), P_j(\vec{r}, t-t')]] \bar{\rho}(t', 0) \right\} + \\ & + \sum_{k=1}^n \int d^3 r' \frac{\partial Q_k(\vec{r}', t')}{\partial t'} [\delta Tr \{ [H'(t-t'), P_j(\vec{r}, t-t')] \bar{\rho}(t', 0) \} / \delta F_k(\vec{r}', t')] , \end{aligned} \quad (16)$$

where, we recall, δ stands for functional derivative, and the operators are given in Heisenberg representation.

The collision operator of Eq. (16) is clearly nonlocal in space and time and highly nonlinear in the state variables; also it is extremely complicated for use in practical calculations, in fact of unmanageable propor-

tions. However, the separation of the Hamiltonian as given by Eq. (1), and the use of the symmetry condition of Eq. (2) allows to write it in ways easier to handle. In fact, some mathematical manipulations allows to go from the Liouville equation for the NSO [Eq. (12)], to an integral equation, namely^[37]

$$\begin{aligned} \rho_\epsilon(t) = & \bar{\rho}(t, 0) + \frac{1}{i\hbar} \int_{-\infty}^t dt' e^{\epsilon(t'-t)} [\rho_\epsilon(t', t'-t)_0, H'(t'-t)_0] \\ & \frac{1}{i\hbar} \sum_{j=1}^n \int_{-\infty}^t dt' e^{\epsilon(t'-t)} Tr \{ [P_j, H'] \rho_\epsilon(t') \} \frac{\delta \bar{\rho}(t', t'_0)_0}{\delta Q_j(t')} . \end{aligned} \quad (17)$$

Here and in what follows, for the sake of simplicity, we have omitted writing explicitly the dependence on the space variables and, further, subindex naught defines the corresponding operator Heisenberg's representation with the partial Hamiltonian H_0 .

Eq. (17) is an integral equation for the operator $\rho_e p(t)$, which admits a solution by iteration that takes

the form

$$\rho_e p(t) = \sum_{m=0}^{\infty} \rho_e^{(m)}(t, 0), \quad (18a)$$

where

$$\rho_e^{(0)} p(t) = \bar{\rho}(t, 0), \quad (18b)$$

$$\begin{aligned} \rho_e^{(m)}(t, 0) = & \frac{1}{i\hbar} \int_{t_0}^t dt' e^{\epsilon(t'-t)} \left[H_1(t'-t)_0, \rho_e^{(m-1)}(t', t'-t)_0 \right] \\ & \frac{1}{i\hbar} \sum_{j=1}^n \int_{-\infty}^t dt' e^{\epsilon(t'-t)} \frac{\delta \bar{\rho}(t', t'_0)_0}{\delta Q_j(t')} \text{Tr} \{ [H_1, P_j] \rho_e^{(m-1)}(t', 0)_0 \}, \end{aligned} \quad (18)$$

for $M \geq 1$.

Using this result, the equations of evolution for the basic variables are

$$\frac{\partial}{\partial t} Q_j(t) = J_j^{(0)}(t) + J_j^{(1)}(t) + \sum_{m=2}^{\infty} \Omega_j^{(m)}(t), \quad (19)$$

where

$$J_j^{(0)}(t) = \text{Tr} \left\{ \frac{1}{i\hbar} [P_j, H_0] \bar{\rho}(t, 0) \right\}, \quad (20a)$$

$$J_j^{(1)}(t) = \text{Tr} \left\{ \frac{1}{i\hbar} [P_j, H_1] \bar{\rho}(t, 0) \right\}, \quad (20b)$$

$$\Omega_j^{(m)}(t) = \text{Tr} \left\{ \frac{1}{i\hbar} [P_j, H_0] \bar{\rho}_e^{-(m-1)}(t, 0) \right\}. \quad (20c)$$

Eq. (19) shows that the collision operator of Eq. (16) has been transformed in an infinite series of partial collision operators. We omit to write down the derivation of this equation and the expressions for the partial collision operators, leaving the details for the interested reader to follow in Ref. [37].

According to the formalism developed in Ref. [37] the complicated collision integrals $\Omega_j^{(m)}$ can be rewritten individually as a series of collision integrals $J_j^{(n)}$ each containing the interaction strength only to a given

order n and which are instantaneous in time. This simply means that they are given in the form of correlation functions defined over the ensemble characterized by the auxiliary distribution operator $\bar{\rho}(t, 0)$ given at the time when a measurement is performed. For that purpose, making use of Zubarev-Peletninskii symmetry condition of Eq. (4), we have been able to introduce an operator O which may be referred to as a memory propagation operator in the sense that

$$\bar{\rho}(t', t' - t)_0 = \Theta(t, t' - t) \bar{\rho}(t, 0) \quad (21)$$

(Cf. Eqs. (43), (47) and (51) in Ref. [37]. It ought to be noticed the relevance of this result once it is realized that in Eqs. (15) the use of the recurrence relation given by Eq. (13b) allows us to write any $\rho_e^{(m)}(t', t' - t)_0$ in terms of $\bar{\rho}(t', t' - t)_0$. Finally,

$$\Omega_j^{(m)}(t) = \sum_{n=m}^{\infty} (m) J_j^{(n)}(t), \quad (22)$$

for $m \geq 2$. Furthermore, we introduce the collision integral of a given order n in the interaction strength, namely

$$J_j^{(m)}(t) = \sum_{n=2}^{\infty} (m) J_j^{(n)}(t) \quad (23)$$

The connection between collision operators R and J is summarized in Table I, and we recall that details of the

Table I - Organization of the partial collision integrals.

m/n	$J^{(0)}$	$J^{(1)}$	$J^{(2)}$	$J^{(3)}$	$J^{(4)}$...
$\Omega^{(0)}$	$(0)^{J^{(0)}}$					
$\Omega^{(1)}$		$(1)^{J^{(1)}}$				
$\Omega^{(2)}$			$(2)^{J^{(2)}}$	$(2)^{J^{(3)}}$	$(2)^{J^{(4)}}$...
$\Omega^{(3)}$				$(3)^{J^{(3)}}$	$(3)^{J^{(4)}}$...
$\Omega^{(4)}$					$(4)^{J^{(4)}}$...
...						...

procedure and explicit expressions for them are given in Ref. [37].

Replacing Eqs. (23) in Eq. (22), and the ensuing result into Eq. (19) we are left with the compact expression

$$\frac{\partial}{\partial t} Q_j(t) = \sum_{n=0}^{\infty} J_j^{(n)}(t) \quad (24)$$

It needs to be emphasized that Zubarev-Peletminskii symmetry condition of Eq. (2) is of fundamental relevance for the derivation of the ensuing nonlinear quantum transport theory in the framework of the MaxEnt-NSOM that lead to Eqs. (24). Such symmetry condition can be obtained in each case in an appropriate representation: For inhomogeneous systems, once local densities are introduced, say $P_j(\vec{r})$, its commutator with the kinetic energy operator contained in H_0 produces the divergence of a flux. This means that $\Omega_{j\ell}$ in Eq. (2) would be a differential operator and not a c-number. Hence, to recover the proper symmetry condition it is necessary to report to a transformation to momentum, or crystal momentum, representation, as it is clearly shown, for example, Ref. [27] when we dealt with the hydrodynamic approach to the photoinjected

plasma in semiconductors. After the calculations are performed according to the method, a transformation back to the local space can be performed if desired.

The form of the collision operator given by Eq. (24) allows us to introduce approximations by means of a truncation of the series of partial collision operators $J^{(n)}$ for a given order of interaction. The lowest order that introduces relaxation effects is a truncation in second order in the interaction strengths: it renders equations which are instantaneous in time (memory-less) which we have called in Ref. [37] the second order approximation in relaxation theory, SOART for short. This approximation is usually referred to in the literature as the linear theory of relaxation^[38], a name we avoid because of the misleading term linear that refers to a certain approximation in the operator ρ' in Eq. (5) and in the expression for the information-entropy production in MaxEnt-NSOM. In the SOART the equations of evolution are a set of coupled highly nonlinear integro-differential equations, namely

$$\frac{d}{dt} Q_j(t) \simeq J_j^{(0)}(t) + J_j^{(1)}(t) + J_j^{(2)}(t), \quad (25)$$

where $J^{(0)}$ and $J^{(1)}$ are given in Eqs. (20a) and (20b), and

$$\begin{aligned} J_j^{(2)}(t) = & (i\hbar)^{-2} \int_{-\infty}^0 dt' e^{\epsilon t'} \text{Tr} \{ [H'(t'-t)_0, [H^1, P_j]] \bar{\rho}(t, 0) \} \\ & + (i\hbar)^{-1} \sum_k \int_{-\infty}^0 dt' e^{\epsilon t'} \text{Tr} \{ [H'(t'_0, P_k] \bar{\rho}(t', 0)_0 \} \frac{\delta J_j^{(1)}(t)}{\delta Q_k(t)}, \end{aligned} \quad (26)$$

where $H'(t')_0$ is expressed in Heisenberg's representation with Hamiltonian H_0 .

It is worth noticing that the equations of evolution for the nonequilibrium thermodynamic variables can, through the use of the result of Appendix A, be alternatively written in the form

$$\begin{aligned}\frac{d}{dt}Q_j(t) &= Tr\left\{\frac{1}{i\hbar}[P_j, H_0 + H_1]\rho_\epsilon(t)\right\} = \\ &= \frac{1}{i\hbar}Tr\{[P_j, H_0 + H_1]\bar{\rho}_\epsilon(t)\} + \\ &+ \int_{-\infty}^t dt' e^{\epsilon(t'-t)} \frac{1}{i\hbar} \{[P_j, H_1]; \hat{\sigma}(t', t'-t)|t\} ,\end{aligned}\quad (27)$$

where $i?$ is the MaxEnt-NSOM-entropy production operator

$$\hat{\sigma}(t_1, t_2) = \frac{d\phi(T_1)}{dt_1} + \sum_{j=1}^n [F_j(t_1)\dot{P}_j(t_2) + \dot{F}_j(t_1)P_j(t_2)] , \quad (28)$$

(dots stand for time derivative) and we have introduced the super-correlation function

$$\{A(t_1); B(t_2)|t\} = \int_0^1 du Tr\{A(t_1)Y(\hat{\sigma}|u)\bar{\rho}(t, 0)^u \Delta_B(t_2)[\bar{\rho}(t, 0)]^{-u+1}\} , \quad (29)$$

with

$$\Delta_B = B - Tr\{\bar{\rho}(t, 0)\} . \quad (30a)$$

and the operator Y satisfies the equation

$$Y(\hat{\sigma}|u) = 1 + \int_0^u dx Y(\hat{\sigma}|x)[\bar{\rho}(t, 0)]^x \int_{-\infty}^t dt' e^{\epsilon(t'-t)} \hat{\sigma}(t', -t)[\bar{\rho}(t, 0)]^{-x} ; \quad (30b)$$

where we have made use of the fact that $Tr\{\hat{\sigma}\rho(t, 0)\} = 0$, meaning that there is no dissipation in the ensemble characterized by the auxiliary operator $\bar{\rho}$.

Since Eq. (38b) can be solved by an iterative process, we can see that the super-correlation function of Eq. (27) can be expressed as a series of infinite terms containing the MaxEnt-NSOM-entropy production operator in ever increasing orders. Thus, this allows for a classification of the series of collisions operators in orders of $\hat{\sigma}$, in what may be termed higher and higher orders in the relaxation processes. Putting $Y = 1$ in Eqs. (5), and making the approximation $F_j(t') \simeq F_j(t)$, what amounts to neglect terms of order higher than the second in H_1 , we obtain the already mentioned SOART, as explained before. The linearity arising in SOART refers to the order in $\hat{\sigma}$ in Eq. (27), namely by putting $Y = 1$, but the equations of evolution remain, in general, highly nonlinear in the state variables. In SOART the right hand side of Eqs. (27) reduces to three terms, namely the collision integrals given by Eqs. (20) and

(26).

The connection of the MaxEnt-NSOM with phenomenological irreversible thermodynamics proceeds through the definition of the MaxEnt-NSOM-statistical entropy namely,

$$\bar{S}(t) = -Tr\{\rho_w(t) \ln \bar{\rho}(t, 0)\} , \quad (31)$$

to be set in correspondence with the thermodynamical entropy. This function $\bar{S}(t)$ satisfies the Pfaffian form

$$d\bar{S}(t) = \sum_{j=1}^n \int d^3r F_j(\vec{r}, t) dQ_j(\vec{r}, t) , \quad (32a)$$

where

$$F_j(\mathbf{r}, t) = \delta \bar{S}(t) / \delta Q_j(\mathbf{r}, t) , \quad (32b)$$

we recall that δ stands for functional derivative and we have reintroduced explicitly the dependence on the space variable. Hence, the Lagrange multipliers F_j in the variational formulation of the MaxEnt-NSOM

are the differential coefficients of the MaxEnt-NSOM-entropy, in complete analogy with equilibrium thermodynamics and statistical mechanics.

The MaxEnt-NSOM-entropy production function is formally given by

$$\begin{aligned}\sigma(t) &= d\bar{S}(t)/dt = \sum_{j=1}^n \int d^3r F_j(\vec{r}, t) \frac{\partial}{\partial t} Q_j(\vec{r}, t) = \\ &= \text{Tr}\{\hat{\sigma}(t, 0)\rho_w(t)\} = \\ &= \int_{-\infty}^t dt' e^{\epsilon(t'-t)} \{\hat{\sigma}(t, 0); \hat{\sigma}(t', t' - 1)|t\}, \quad (33)\end{aligned}$$

where we have used the results of Appendix A, and the definition of Eq. (29). Eq. (33) clearly indicates that the MaxEnt-NSOM-entropy production function is a super-self-correlation function of the MaxEnt-NSOM-entropy production operator of Eq. (28). It should be noticed at this stage that there is at present no indication whatsoever that $\bar{\sigma}(t)$, as defined by Eq. (33) is non-negative. The super-correlation function of the entropy operator $\hat{\sigma}$ evaluated at different times is a quantity that contains only the dynamics of the system which is being included in the MaxEnt-NSOM probability distribution operator $\rho_w(t)$. Even though this probability distribution obeys a Liouville equation with sources that remove its, otherwise, time-reversal symmetry [Cf. Eq. (12)], its dynamics is complicated enough to prevent us from giving a clear cut answer to the above question. This fact is further sustained by just looking at the equally complicated structure of Eq. (33). As we have insisted before in I, this property is only known to hold true in SOART and close to the equilibrium state (Also, in SOART for systems where quantities Ω in Eq. (2) are zero). This very same conclusion has been recently obtained by Nettleton^[39] through a different method than ours. Indeed he shows that the entropy production calculated to all orders in the thermodynamic forces is only positive definite in the bilinear approximation. Deeper studies concerning the nature of $\sigma(t)$ are required before it can really be identified with the entropy production term as defined in nonequilibrium thermodynamics^[40,41].

III. Derivation of constitutive-like equations

We now undertake the derivation of the constitutive equations, namely those relating fluxes and forces, using the results for the MaxEnt-NSOM in Zubarev's approach as outlined in the previous section. Care must be exercised in using this terminology since within the scope of modern phenomenological thermodynamic theories^[26,42-44], the fluxes themselves are raised to the status of independent variables and in neither case they ought to be confused with Onsager's definition. We shall clarify the full meaning of this statement as we proceed along.

We consider a system whose macrostates are described by means of a basic set of variables (generically called Q_j in Section II) spanning the thermodynamic phase space G . We consider G in this case as formed by the union of two independent subspaces, one consisting of the macrovariables, say, $\{A_j(\vec{r}, t)\}$, $j = 1, 2, \dots, n$, defined as appropriate averages of a set of corresponding dynamical variables $\{P_j(\vec{r})\}$, and the subspace which consists of the set of fluxes $\{\vec{I}_j(\vec{r}, t)\}$, with the corresponding dynamical variables indicated by $\{U_j(\vec{r})\}$. This set of dynamical variables is generated in the way explained in Section II: the total Hamiltonian is divided into two parts $H_0 + H'$ [Cf. Eq. (1)], where H_0 contains the kinetic energies and the part of the interactions that produce very rapid relaxation processes, and H' is related to the slow relaxation processes, with quantities A_j and \vec{U}_j evolving under H_0 in the precessing form indicated by Zubarev-Peletminskii symmetry condition of Eq. (2). This is illustrated in the study of a plasma in semiconductors in Ref. [27], where we also emphasize the need, in general, to introduce a truncation procedure. The latter implies in a forced contracted description, and, therefore, an approximation to the characterization of the macroscopic state of the system in terms of the selected set of basic macrovariables. This is the case here when we select the set $\{A_j(\vec{r}, t)\}$, $\{\vec{I}_j(\vec{r}, t)\}$ of variables A_j and only their vector fluxes \vec{I}_j .

For the given choice of basic variables, the MaxEnt-NSOM-auxiliary coarse-grained statistical operator of Eq. (6) is

$$\bar{\rho}(t, 0) = \exp \left\{ -\phi(t) - \sum_{j=1}^n \int d^3r \left[F_j(\vec{r}, t) A_j(\vec{r}) + \vec{\alpha}_j(\vec{r}, t) \cdot \vec{U}_j(\vec{r}) \right] \right\}, \quad (34)$$

where $\{F_j, \vec{\alpha}_j\}$ are the Lagrange multipliers, or intensive thermodynamic variables, conjugated to A_j and \vec{I}_j , respectively, as defined by Eq. (32b). Zubarev's NSO, based on $\vec{\rho}$ of Eq. (34), given by Eq. (10) or, equivalently, Eq. (11).

To derive the generalized constitutive equations for the fluxes we start with Eq. (27) for $\vec{I}_j(\vec{r}, t)$, that is to say

$$\frac{\partial}{\partial t} \vec{I}_j(\vec{r}, t) = \vec{J}_j^{(1)}(\vec{r}, t) + \vec{J}_j^{(1)}(\vec{r}, t) + \vec{\lambda}_j(\vec{r}, t), \quad (35)$$

where now

$$\vec{J}_j^{(0)}(\vec{r}, t) = Tr \left\{ \frac{1}{i\hbar} [\vec{U}_j(\vec{r}), H_0] \bar{\rho}(t, 0) \right\}, \quad (36a)$$

$$\vec{J}_j^{(1)}(\vec{r}, t) = Tr \left\{ \frac{1}{i\hbar} [\vec{U}_j(\vec{r}), H_1] \bar{\rho}(t, 0) \right\}, \quad (36b)$$

$$\vec{\lambda}_j(\vec{r}, t) = \int_{-\infty}^t dt' e^{\epsilon(t'-t)} \frac{1}{i\hbar} \left\{ [\vec{U}_j(\vec{r}), H'] ; \bar{\sigma}(t', t'-t) | t \right\}, \quad (36c)$$

Next, in Eqs. (36) we separate in the auxiliary operator of Eq. (34) its homogeneous and inhomogeneous parts, as indicated below. Next, through the use of the operator identity

$$e^{-A+B} = Y(B|1)e^{-A}, \quad (37)$$

where

$$Y(B|x) = 1 + \int^{\parallel} du Y(B|u) e^{-uA} B e^{uA}, \quad (38)$$

we obtain that

$$\begin{aligned} \bar{\rho}(t, 0) &= \exp \left\{ -\phi(t) - \sum_j F_j(t) P_j - \sum_j \vec{\alpha}_j(t) \cdot \vec{U}_j - \right. \\ &\quad \left. - \sum_j \int d^3r [\Delta F_j(\vec{r}, t) P_j(\vec{r}) + \Delta \vec{\alpha}_j(\vec{r}, t) \cdot \vec{U}_j(\vec{r})] \right\} \\ &\simeq \bar{\rho}_h(t, 0) - \sum_j \int d^3r \int_0^1 dx [\bar{\rho}_h(t, 0)]^x \\ &\quad [\Delta F_j(\vec{r}, t) \Delta P_j(\vec{r}) + \Delta \vec{\alpha}_j(\vec{r}, t) \cdot \Delta \vec{U}_j(\vec{r})] [\bar{\rho}_h(t, 0)]^{-x+1}, \end{aligned} \quad (39)$$

where

$$\Delta F_j(\vec{r}, t) F_j(\vec{r}, t) = F_j(t); \quad \Delta \vec{\alpha}_j(\vec{r}, t) = \vec{\alpha}_j(\vec{r}, t) - \alpha_j(t) \quad (40)$$

$\Delta\theta = \theta - Tr\{\theta\bar{\rho}_u(t, 0)\}$, for any operator θ , and

$$\bar{\rho}_h(t, 0) = \exp\{-\phi_h(t) - \sum_j F_j(t)P_j - \sum_j \vec{\alpha}_j(t) \cdot \vec{U}_j\} \quad (41)$$

is the auxiliary NSO that describes the homogeneous state of the system. The approximate sign before the last term in Eq. (39) means that we are taking only the linear term in the inhomogeneities. Next we relate the fluxes to the nonequilibrium thermodynamic variables A , F and $\Delta\vec{\alpha}$, namely

$$\begin{aligned} \bar{I}_j(\vec{r}, 0) &= Tr\{\vec{U}_j(\vec{r})\bar{\rho}(t, 0)\} \simeq Tr\{\vec{U}_j\bar{\rho}_h(t, 0)\} - \\ &- \sum_k \int d^3r' \int_0^1 dx Tr\{\vec{U}_j(\vec{r})[\bar{\rho}_h(t, 0)]^x [\Delta F_k(\vec{r}', t) \Delta P_k(\vec{r}') + \\ &+ \Delta\vec{\alpha}_k(\vec{r}', t) \cdot \Delta\vec{U}_k(\vec{r}')] [\bar{\rho}_h(t, 0)]^{x+1}\} \equiv \\ &\equiv \sum_k \int d^3r' [\vec{A}_{jk}(\vec{r}, \vec{r}'; t) \Delta F_k(\vec{r}', t) + \vec{B}_{jk}(\vec{r}, \vec{r}'; t) \Delta\vec{\alpha}_k(\vec{r}'; t)], \end{aligned} \quad (42)$$

where we have taken into account that the average value of the flux vanishes in the homogeneous state. From Eq. (42) we find that

$$\begin{aligned} \Delta\vec{\alpha}_k(\vec{r}, t) &= - \sum_j \int d^3r' \vec{B}_{kj}^{-1}(\vec{r}, \vec{r}'; t) \vec{I}_j(\vec{r}', t) + \\ &+ \sum_{j\ell} \int d^3r' \int d^3r'' \vec{B}_{kj}^{-1}(\vec{r}, \vec{r}'; t) \vec{A}_{j\ell}(\vec{r}', \vec{r}'', t) \Delta F_\ell(\vec{r}'', t), \end{aligned} \quad (43)$$

an expression that relates the thermodynamic variable $\vec{\alpha}$ to the fluxes and also to A , F .

Consider now the collision operators $\vec{J}^{(0)}$ and $J^{(1)}$ in Eq. (36). For simplicity we neglect the latter which usually vanishes in a variety of practical cases as a result of symmetry considerations. Operator $\vec{J}^{(0)}$ involves the time variation of the flux under the action of the secular (or conservative) part of the Hamiltonian, namely H_0 . It gives rise to the divergence of a second rank tensor (which can be interpreted as the divergence of the flux of the flux, or second order flux of the density, and so is the contribution to the equation of conservation for \vec{I}_j). We write it as

$$\vec{J}_j^{(0)}(\vec{r}, t) = -div \vec{\Psi}_j(\vec{r}, t). \quad (44)$$

We now work the case of an isotropic material, so that the divergence of a tensor in Eq. (44) becomes the gradient of a scalar

$$\vec{J}_j^{(0)}(\vec{r}, t) = -\nabla \Psi_j(\vec{r}, t), \quad (45a)$$

or in reciprocal space we can write

$$\vec{J}_j^{(0)}(\vec{q}, t) = i\vec{q} \Psi_j(\vec{q}, t), \quad (45b)$$

Also, on account of isotropy, tensor \vec{B} in Eqs. (42) and (43) is a scalar quantity. Further, because the averages are over the homogeneous macrostate, the dependence on positions \vec{r} and \vec{r}' becomes a dependence on the relative coordinate $\vec{r} - \vec{r}'$. In reciprocal space the auxiliary NSO of Eq. (39) now becomes

$$\bar{\rho}(t, 0) = \exp\left\{-\phi(t) - \sum_{j=1}^n (F_j(t)P_j + \vec{\alpha}_j(t) \cdot \vec{U}_j)\right\}$$

$$\begin{aligned}
& - \sum_{j=1}^n \sum'_{\vec{q}} (F_j(\vec{q}, t) P_j(\vec{q}) + \vec{\alpha}_j(\vec{q}, t) \cdot \vec{U}_j(\vec{q})) \Big\} = \\
& \simeq \bar{\rho}_h(t, 0) - \sum_{j=1}^n \sum'_{\vec{q}} \int_0^1 dx [\bar{\rho}_h(t, 0)]^x (F_j(\vec{q}, t) \Delta P_j(\vec{q}) + \\
& + \vec{\alpha}_j(\vec{q}, t) \cdot \Delta \vec{U}_j(\vec{q})) [\bar{\rho}_h(t, 0)]^{-x-1} .
\end{aligned} \tag{46}$$

In Eq. (46) $\bar{\rho}_h$ is given by Eq. (41) and the prime over the sum in \vec{q} indicates that the term $\vec{q} = 0$ is not included (it corresponds to the homogeneous part).

Using this linear approximation in $\bar{\rho}(t, \mathbf{0})$ we can express, Ψ of Eq. (45) as

$$\begin{aligned}
\Psi_j(\vec{q}, t) &= Tr \left\{ -\hat{\Psi}_j(\vec{q}) \rho_\epsilon(t) \right\} \simeq Tr \left\{ \hat{\Psi}_j(\vec{q}) \bar{\rho}_h(t, 0) \right\} \\
&- \sum_{j=1}^n \sum'_{\vec{q}'} \int_0^1 dx Tr \left\{ \hat{\Psi}_j(\vec{q}) [\bar{\rho}_h(t, 0)]^x (F_j(\vec{q}', t) P_j(\vec{q}') [\bar{\rho}_h(t, 0)]^{-x+1} \right\} - \\
&- \sum_{j=1}^n \sum'_{\vec{q}'} \int_0^1 dx Tr \left\{ \hat{\Psi}_j(\vec{q}) [\bar{\rho}_h(t, 0)]^x \vec{\alpha}_j(\vec{q}', t) \cdot \vec{U}_j(\vec{q}') [\bar{\rho}_h(t, 0)]^{-x-1} \right\} ,
\end{aligned} \tag{47}$$

where the hat over Ψ stands for the corresponding dynamical operator. It should be noticed that the dissipative effects accounted for ρ'_ϵ in $\rho_\epsilon = \bar{\rho} + \rho'_\epsilon$ [cf. Eq. (5)] have been neglected.

Since Ψ is related to a local (tensorial) flux, its av-

erage value over the homogeneous state vanishes. Also, in the homogeneous and isotropic system in Eq. (47) all contributions to the super-correlation functions with $\vec{q}' \neq \vec{q}$ vanish so that we may set $\sum_{\vec{q}'} \rightarrow \sum_{\vec{q}} \delta_{\vec{q}, \vec{q}'}$. Then,

$$\Psi_j(\vec{q}, t) = \sum_k a_{jk}(\vec{q}, t) F_k(\vec{q}, t) + \sum_k \vec{b}_{jk}(\vec{q}, t) \cdot \vec{\alpha}_k(\vec{q}, t) , \tag{48}$$

where

$$a_{jk}(\vec{q}, t) = \int_0^1 dx Tr \left\{ \hat{\Psi}_j(\vec{q}) [\bar{\rho}_h(t, 0)]^x P_k(\vec{q}) [\bar{\rho}_h(t, 0)]^{-x-1} \right\} , \tag{49a}$$

$$\vec{b}_{jk}(\vec{q}, t) = \int_0^1 dx Tr \left\{ \hat{\Psi}_j(\vec{q}) [\bar{\rho}_h(t, 0)]^x \vec{U}_k(\vec{q}) [\bar{\rho}_h(t, 0)]^{-x-1} \right\} . \tag{49b}$$

Eq. (43) in reciprocal space becomes

$$\vec{\alpha}_j(\vec{q}, t) = \sum_k B_{jk}^{-1}(\vec{q}, t) \vec{I}_k(\vec{q}, t) + \sum_{k\ell} B_{jk}^{-1}(\vec{q}, t) \vec{A}_{k\ell}(\vec{q}, t) F_\ell(\vec{q}, t) , \tag{50}$$

which replaced in Eq. (48) and this in Eq. (45b) yields

$$\vec{J}_j^{(0)}(\vec{q}, t) = \sum_k L_{jk}(\vec{q}, t) i\vec{q} F_k(\vec{q}, t) + \sum_k i\vec{q} [\vec{\mu}_k(\vec{q}, t) \cdot \vec{I}_k(\vec{q}, t)] , \tag{51}$$

where

$$L_{jk}(\vec{q}, t) = a_{jk}(\vec{q}, t) + \sum_{mn} \vec{b}_{jm}(\vec{q}, t) B_{mn}^{-1}(\vec{q}, t) \vec{A}_{nk}(\vec{q}, t) , \quad (52a)$$

$$\vec{\mu}_{jk}(\vec{q}, t) = \sum_m B_{mk}^{-1}(\vec{q}, t) \vec{b}_{jm}(\vec{q}, t) . \quad (52b)$$

In direct space it follows that

$$\begin{aligned} \vec{J}_j^{(0)}(\vec{r}, t) &= \sum_k \int d^3 r' L_{jk}(\vec{r} - \vec{r}', t) \nabla' F_k(\vec{r}', t) + \\ &+ \sum_k \int d^3 r' \text{div}' \mu_{jk}(\vec{r} - \vec{r}', t) \vec{J}_k(\vec{r}', t) + \\ &+ \sum_k \int d^3 r' \mu_{jk}(\vec{r} - \vec{r}', t) \text{div}' \vec{J}_k(\vec{r}', t) . \end{aligned} \quad (53)$$

We consider now the collision operator λ given by Eq. (36c), where $\bar{\rho}$ is still given by the complete expression of Eq. (34). Recalling that the MaxEnt-NSOM-entropy production operator takes the form

$$\begin{aligned} \hat{\sigma}(t_1, t_2) &= \sum_j \int d^3 r [F_j(\vec{r}, t_1) P_j(\vec{r}, t_2) + F_j(\vec{r}, t_1) \Delta \dot{P}_j(\vec{r}, t_2)] + \\ &+ \sum_j \int d^3 r [\vec{\alpha}_j(\vec{r}, t_1) \vec{U}_j(\vec{r}, t_2) + \vec{\alpha}_j(\vec{r}, t_1) \cdot \Delta \vec{U}_j(\vec{r}, t_2)] \end{aligned} \quad (54)$$

where the upper dot stands for time derivative, we obtain that

$$\begin{aligned} \vec{\lambda}_j(\vec{r}, t) &= \sum_k \int_{-\infty}^t dt' \int d^3 r' \vec{\Lambda}_{jk}(\vec{r} - \vec{r}'; t - t') \dot{F}_k(\vec{r}', t') + \\ &+ \sum_k \int_{-\infty}^t dt' \int d^3 r' \vec{\Lambda}_{jk}^{(2)}(\vec{r} - \vec{r}'; t - t') F_k(\vec{r}', t') + \\ &+ \sum_k \int_{-\infty}^t dt' \int d^3 r' \vec{\Lambda}_{jk}^{(3)}(\vec{r} - \vec{r}'; t - t') \vec{\alpha}_k(\vec{r}', t') + \\ &+ \sum_k \int_{-\infty}^t dt' \int d^3 r' \vec{\Lambda}_{jk}^{(4)}(\vec{r} - \vec{r}'; t - t') \vec{\alpha}_k(\vec{r}', t') \end{aligned} \quad (55)$$

where

$$\vec{\Gamma}_{jk}^{(1)}(\vec{r} - \vec{r}'; t - t') = e^{\epsilon(t' - t)} \{ \vec{U}_j(\vec{r}); P_k(\vec{r}', t' - t) | t' - t \} , \quad (56a)$$

$$\vec{\Gamma}_{jk}^{(2)}(\vec{r} - \vec{r}'; t - t') = e^{\epsilon(t' - t)} \{ \vec{U}_j(\vec{r}); \dot{P}_k(\vec{r}', t' - t) | t' - t \} , \quad (56b)$$

$$\vec{\Gamma}_{jk}^{(3)}(\vec{r} - \vec{r}'; t - t') = e^{\epsilon(t' - t)} \{ \vec{U}_j(\vec{r}); \vec{U}_k(\vec{r}', t' - t) | t' - t \} , \quad (56c)$$

$$\vec{\Gamma}_{jk}^{(4)}(\vec{r} - \vec{r}'; t - t') = e^{\epsilon(t' - t)} \{ \vec{U}_j(\vec{r}); \vec{U}_k(\vec{r}', t' - t - t) | t' - t \} \quad (56d)$$

Eq. (55) is an extremely complicated expression that contains non-local *effects* in space and *in* time namely *correlations* in space and *memory effects*. Moreover, as already noticed, through the NSO of Eq. (32) it involves in its expression the fluxes to all orders.

Now, since in the thermodynamic approach^[26,28,42–44]

the fluxes are taken as MaxEnt-NSOM-basic variables we can apply to the collision operator λ the approximate treatments already available. In particular, we resort to SOART, described in section II [cf. Eq. (25)]. In SOART, neglecting $\vec{J}_j^{(1)}$ reduces to the collision operator

$$\vec{J}_j^{(2)}(\vec{r}, t) = (i\hbar)^{-2} \int_{-\infty}^0 dt' e^{i t'} \text{Tr} \{ [H'(t')]_{0'} [\mathbf{H}', \vec{U}_j(\vec{r})] \} \bar{\rho}(t, 0) \quad (57)$$

The details of the calculations are given in the Appendix B and as shown there we find that the equations of evolution for the fluxes take the form

$$\begin{aligned} \frac{\partial}{\partial t} \vec{I}_j(\vec{r}, t) &= \vec{J}_j^{(0)}(\vec{r}, t) + \sum_k \int d^3 r' E_{jk}(\vec{r} - \vec{r}', t) \Delta F_k(\vec{r}', t) + \\ &+ \sum_k \int d^3 r' \Theta_{jk}^{-1}(\vec{r} - \vec{r}'; t) \vec{I}_k(\vec{r}', t) + \vec{\lambda}^{(h)}(\vec{r}, t). \end{aligned} \quad (58)$$

After multiplying by the inverse of Θ^{-1} we find alternatively that

$$\begin{aligned} \sum_k \int d^3 r' \Theta_{jk}(\vec{r} - \vec{r}', t) \frac{\partial}{\partial t} \vec{I}_k(\vec{r}', t) &= \\ \sum_k \int d^3 r' \Theta_{jk}(\vec{r} - \vec{r}', t) \vec{J}_k^{(0)}(\vec{r}', t) &+ \\ \sum_{k\ell} \int d^3 r' \int d^3 r'' \Theta_{jk}(\vec{r} - \vec{r}', t) \vec{E}_{k\ell}(\vec{r}'' - \vec{r}', t) \Delta F_\ell(\vec{r}', t) &+ \\ \vec{I}_j(\vec{r}, t) + \sum_+ \int d^3 r' \Theta_{jk}(\vec{r} - \vec{r}'; t) + \vec{\lambda}_k^{(h)}(\vec{r}', t) \end{aligned} \quad (59)$$

Replacing $\vec{J}^{(0)}$ of Eq. (53) in Eq. (59) and considering the quasi-static case, which implies setting $\partial \vec{I} / \partial t \simeq 0$, we find the equivalent of a constitutive *equation* for the *flux*, namely

$$\begin{aligned} \vec{I}_j(\vec{r}, t) &= \sum_k \int d^3 r' \Lambda_{jk}(\vec{r} - \vec{r}', t) \nabla' F_k(\vec{r}', t) + \\ &+ \sum_k \int d^3 r' \mathcal{L}_{jk}(\vec{r} - \vec{r}', t) \vec{I}_k(\vec{r}', t) + \\ &+ \sum_k \int d^3 r' \vec{\mathcal{M}}_{jk}(\vec{r} - \vec{r}', t) \text{div}' \vec{I}_k(\vec{r}', t) + \\ &+ \sum_k \int d^3 r' \vec{\mathcal{N}}_{jk}(\vec{r} - \vec{r}', t) \Delta F_k(\vec{r}', t) + \\ &+ \sum_k \int d^3 r' \Theta_{jk}(\vec{r} - \vec{r}', t) \vec{\lambda}_k^{(h)}, \end{aligned} \quad (60)$$

where

$$\Lambda_{jk}(\vec{r} - \vec{r}', t) = \sum_m \int d^3 r'' \Theta_{jm}(\vec{r} - \vec{r}'', t) L_{mk}(\vec{r}' - \vec{r}'', t), \quad (61a)$$

$$\vec{\mathcal{L}}_{jk}(\vec{r} - \vec{r}', t) = \sum_m \int d^3 r' \Theta_{jm}(\vec{r} - \vec{r}', t) \text{div}' \vec{\mu}_{mk}(\vec{r}'' - \vec{r}', t), \quad (61b)$$

$$\vec{\mathcal{M}}_{jk}(\vec{r} - \vec{r}', t) = \sum_m \int d^3 r'' \Theta_{jm}(\vec{r} - \vec{r}'', t) \vec{\mu}_{mk}(\vec{r}'' - \vec{r}', t), \quad (61c)$$

$$\vec{\mathcal{N}}_{jk}(\vec{r} - \vec{r}', t) = \sum_m \int d^3 r'' \Theta_{jm}(\vec{r} - \vec{r}'', t) \vec{E}_{mk}(\vec{r}'' - \vec{r}', t), \quad (61d)$$

which play the role of kinetic coefficients. Eq. (60) is invariant under the change $\vec{\Gamma} \rightarrow -\vec{\Gamma}$ and $\mathbf{V} \rightarrow -\mathbf{V}$, as expected.

Thus, we have obtained constitutive-like that are non-local in space equations although they are instantaneous in time (memoryless) because of the use of SOART. It can be seen that these constitutive equations for the fluxes consist, each one, of five terms. The first is the expected one that relates linearly the flux to the thermodynamic forces (gradients of \mathbf{F}). This term and the next two have their origins in $\vec{J}_j^{(0)}$, as shown by Eq. (51). The fourth and fifth come from the collision operator $\vec{J}_i^{(2)}$ [cf. Eq. (B2)]. The second and third term on the right hand side of Eq. (60) have their origin in the fact that the fluxes have been raised to the hierarchy of basic variables, and therefore produce "driving forces" acting on themselves. The fourth term depends on the inhomogeneities of the quasi-conserved basic variables, being a result of the expansion we have performed around the homogeneous state. The last term involves relaxation processes in the homogeneous state. Introducing a Fourier transform in the space coordinate, Eq. (60) becomes

$$\begin{aligned} \vec{I}_j(\vec{q}, t) &= i\vec{q} \sum_k \Lambda_{jk}(\vec{q}, t) F_k(\vec{q}, t) + \\ &+ \sum_k [\mathcal{L}_{jk}(\vec{q}, t) + i\vec{q} \cdot \vec{\mathcal{M}}_{jk}(\vec{q}, t)] \vec{I}_k(\vec{q}, t) \\ &+ \sum_k \vec{\mathcal{N}}_{jk}(\vec{q}, t) \Delta F_k(\vec{q}, t) + \\ &+ \sum_k \Theta_{jk}(\vec{q}, t) \vec{\lambda}_k^{(h)}(\vec{q}, t). \end{aligned} \quad (62)$$

Defining the matrix

$$M_{jk}(\vec{q}, t) = \delta_{jk} - \mathcal{L}_{jk}(\vec{q}, t) - i\vec{q} \cdot \vec{\mathcal{M}}_{jk}(\vec{q}, t), \quad (63)$$

and its inverse, M^{-1} , Eq. (62) can be written as

$$\vec{I}_j(\vec{q}, t) = \sum_k \tilde{\Lambda}_{jk}(\vec{q}, t) [i\vec{q} F_k(\vec{q}, t)] + \tilde{\Omega}_j(\vec{q}, t), \quad (64)$$

where

$$\tilde{\Lambda}_{jk}(\vec{q}, t) = \sum_m M_{jm}^{-1}(\vec{q}, t) \Lambda_{mk}(\vec{q}, t), \quad (65a)$$

and

$$\begin{aligned} \tilde{\Omega}_j(\vec{q}, t) &= \sum_{km} M_{jm}^{-1}(\vec{q}, t) \vec{\mathcal{N}}_{mk}(\vec{q}, t) \Delta F_k(\vec{q}, t) + \\ &= \sum_{km} M_{jm}^{-1}(\vec{q}, t) \Theta_{mk}(\vec{q}, t) \vec{\lambda}_k^{(h)}(\vec{q}, t), \end{aligned} \quad (65b)$$

Eqs. (65) tell us that the compact expression of Eq. (64) is expressed in terms of new kinetic coefficients that are the original kinetic coefficients Λ , \mathcal{N} , Θ , modified by the presence of the matrix M^{-1} . Finally, in direct space Eq. (64) acquires the form

$$\vec{I}(\vec{r}, t) = \sum_k \int d^3 r' \tilde{\Lambda}_{jk}(\vec{r} - \vec{r}', t) \nabla' F_k(\vec{r}', t) + \tilde{\Omega}_j(\vec{r}, t). \quad (66)$$

The results contained in Eq. (66) can be summarized as follows:

1. The nonlocality of the constitutive equations arises in a straight-forward manner from the method. As far as the time dependence is concerned they are

instantaneous in time (no memory effects) because we used SOART approximation. As demonstrated in Ref. [37], memory effects, present in Eq. (55), are obtained when going beyond SOART, and are contained in contributions in H of order higher than two. The Procedure to handle the collision operator described in such reference allows one to write it as an infinite series of collision operators instantaneous in time. That is, they are evaluated in terms of the macroscopic state of the system at the time a measurement is performed, and containing H' in ever higher orders, as summarized in Eq. (24). Because of this construction we briefly comment, without any further extension of this paper, that going beyond SOART using such approach we retrieve equations of the type of Eqs. (64) (or Eqs. (66) in direct space), except that the coefficients $\tilde{\Lambda}$ and $\tilde{\Omega}$ are composed of a series of terms corresponding to the different successive contributions by the series of partial collision operators (scattering of two, three, and so on, particles).

2. We have shown that within the context of Informational Statistical Thermodynamics wherein in the approach just described the fluxes are raised to the rank of basic thermodynamic variables, it is possible, first, to relate the kinetic coefficients to a characteristic time tensor θ_{jm} (whose diagonal terms are a kind of time between collisions of kinetic theory). They are given through an explicit form of calculation in terms of the microscopic dynamics averaged over the nonequilibrium ensemble. Second, the kinetic coefficients contain corrections due to the effect of the presence of the same fluxes in the macroscopic description of the system (the matrix M^{-1} in $\tilde{\Lambda}$). Thirdly, an additional term, $\tilde{\Omega}$, is in principle also present in the otherwise usual form of the constitutive equations, playing the role of a dissipative force.

IV. Concluding remarks

We have described how a mechano-statistical formalism, that is a generalization of Gibbs and Boltzmann ideas, can be derived - and different approaches unified - using a variational method. This theory is based on an attempted new paradigm in the scientific method, which is encompassed in Jaynes' Predictive

Statistical Mechanics. The formalism introduces the variational procedure MaxEnt, but in such a way to include memory effects and an ad hoc hypothesis to ensure irreversible behavior in the evolution of the macroscopic state of the system from an initial condition. In the Introduction we have already presented some comments on Jaynes' PSM and its foundations on Bayesian theory of probability. We restate that, according to Jaynes, the question of what are the theoretically valid, and pragmatically useful, ways of applying probability theory in science has been approached by Jeffreys, in the sense that he stated the general philosophy of what scientific inference is, and its connection with probability theory. Also, according to Jaynes and Anderson, what seems to be the most appropriate probability theory is the Bayesian approach. The formulation of the MaxEnt-NSOM on this basis is described in Section II. We have also noticed that the MaxEnt-NSOM provides a framework for the construction of a nonequilibrium nonlinear transport theory of large scope, with its general aspects briefly reviewed in Section II. As already remarked, the collision operators involved require a quite difficult mathematical handling. However, a practical method can be devised which allows for an expression for the collision operators in the form of a series of simpler ones, organized in ever increasing order in the strengths of the interactions responsible for the dissipative processes that develop in the media. Within the extent covered by the informational constraints used in each case, we are then in possession of a transport theory of a quite large scope. It involves nonlinearity and nonlocality in space and time (that is, space correlations and memory, respectively, are included), providing a description of the evolution of the macrostate of systems arbitrarily away from equilibrium. The condition of nonlinearity permits that the theory, when applied to open systems far-away-from equilibrium, may provide microscopic foundations and an accompanying macroscopic description to self-organizing synergetic processes, usually dealt with on the basis of phenomenological thermodynamic and kinetic theories.

We have also briefly considered, in the last part of Section II, how the MaxEnt-NSOM can provide

microscopic (mechano-statistical) foundations to phenomenological irreversible thermodynamics in a theory of large scope dubbed Informational Statistical Thermodynamics. Hence, the MaxEnt-NSOM should contain an hydrodynamic theory, that may be called Non-Classical Informational Statistical Hydrodynamics. One aspect of it is illustrated in Section III. We have shown how, within such formalism, one can derive quite general equations of evolution for the fluxes of a certain set of dynamical densities. These equations of evolution have several particular aspects: (1) The kinetic coefficients are given in terms of the microscopic mechanics - at the quantum level - of the system averaged over the nonequilibrium ensemble; (2) Nonlocal in space and memory effects are encompassed by them, but at a certain step we introduced the approximation SOART that makes them instantaneous in time; (3) We considered a weakly inhomogeneous system and used a linear expansion in the fluxes and in the spatial inhomogeneity of the basic variables. The resulting equations are given by Eq. (58), and we have shown that in the quasi-static limit (meaning movement involving low frequencies, in the sense that $\omega \Theta_{jk} \ll 1$) one obtains constitutive-like equations for the fluxes, that are generalizations of the usual ones of Classical (Linear)

Irreversible Thermodynamics.

As final words we comment that the MaxEnt-NSOM constitutes an excellent method to provide a powerful and practical theory to the study of experimental data in far-from-equilibrium systems. A few examples are (i) the case of semiconductors under high intense electromagnetic fields^[45]; (ii) ultrafast time-resolved laser spectroscopy of the plasma in highly photoexcited semiconductors^[46]; (iii) charge transport by photogenerated carriers in semiconductors^[47]; (iv) self-organization (Prigogine's style) in plasmas in highly photoexcited semiconductors^[48], and in modelled biological systems^[49]. A particular application of Informational Statistical Thermodynamics to describe the nonequilibrium thermodynamics in the case of a simplified model of semiconductor is reported in Ref. [50].

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Appendix A: The separation of the NSO according to Eq. (5)

Consider the expression for the statistical operator ρ_ϵ given by Eq. (11), namely

$$\rho_\epsilon(t) = e^{-A+B} , \quad (A1)$$

where

$$A = \ln \bar{\rho}(t, 0) , \quad (A2a)$$

and

$$B = - \int_{-\infty}^0 dt' e^{\epsilon t'} \frac{d}{dt'} \ln \bar{\rho}(t+t', t') \quad (A2b)$$

Using the well known operator identity of Eq. (37) we obtain

$$\rho_\epsilon(t) = -\bar{\rho}(t, 0) + \rho'_\epsilon(t) , \quad (A3)$$

i.e. having the form of Eq. (5), where

$$\rho'_\epsilon(t) = D_\epsilon(t) + \bar{\rho}(t, 0) , \quad (A4a)$$

$$D_\epsilon(t) = \int_0^1 dx Y(\zeta_\epsilon | x) [\bar{\rho}(t, 0)]^x \zeta_\epsilon(t) [\bar{\rho}(t, 0)]^{-x} , \quad (A4b)$$

$$Y(\zeta_\epsilon|x) = 1 + \int_0^1 du Y(\zeta_\epsilon|u) [\bar{\rho}(t, 0)]^u \zeta_\epsilon(t) [\bar{\rho}(t, 0)]^{-u} , \quad (A4c)$$

$$\zeta_\epsilon(t) = - \int_{-\infty}^0 dt' e^{\epsilon t'} \frac{d}{dt'} \ln \bar{\rho}(t + t', t) = \int_{-\infty}^0 dt' e^{\epsilon t'} \hat{\sigma}(t + t', t) . \quad (A4d)$$

In Eq. (A.4d) $\hat{\sigma}$ is the MaxEnt-NSOM-entropy production operator of **Eq.** (28); this clearly points out to the fact that ρ'_ϵ contains the dynamics associated to dissipation in the nonequilibrium system on the other hand, as already noted in the main text, the ensemble characterized by $\bar{\rho}$ is dissipation free.

Appendix B: Calculation of **Eq.** (58)

The collision operator $\vec{\lambda}$ of **Eq.** (55) takes in SOART the form

$$\begin{aligned} \vec{\lambda}_j(\vec{r}, t) \simeq & \left(\frac{1}{i\hbar} \right)^2 \int_{-\infty}^0 dt' e^{\epsilon t'} Tr \left\{ \left[H'(t'), \left[H', \vec{U}_j(\vec{r}) \right] \right] \bar{\rho}_h(t, 0) \right\} + \\ & + \left(\frac{1}{i\hbar} \right)^2 \int_{-\infty}^0 dt' e^{\epsilon t'} \sum_k Tr \left\{ \left[H'(t'), \left[H', \vec{U}_j(\vec{r}) \right] \right] \right. \\ & \left. + \int d^3 r' \int_0^1 dx [\bar{\rho}_h(t, 0)]^x \left[\Delta F_k(\vec{r}', t) \Delta P_k(\vec{r}') + \vec{\alpha}_k(\vec{r}', t) \cdot \Delta \vec{U}_k(\vec{r}') \right] \bar{\rho}_h(t, 0) \right]^{-x+1} \right\} . \end{aligned} \quad (B.1)$$

Replacing in this Eq. (B1) the expression for $\Delta \vec{\alpha}$ given by Eq. (44), and using that the averages are taken over the homogeneous state, we obtain that

$$\begin{aligned} \vec{\lambda}_j(\vec{r}, t) \simeq & \vec{\lambda}_j^{(h)}(\vec{r}, t) + \sum_k \int d^3 r' \vec{E}_{jk}(\vec{r} - \vec{r}'; t) \Delta F_k(\vec{r}', t) + \\ & - \sum_k \int d^3 r' \Theta_{jk}^{-1}(\vec{r} - \vec{r}'; t) \vec{I}_k(\vec{r}', t) , \end{aligned} \quad (B.2)$$

where

$$\vec{\lambda}_j^{(h)}(\vec{r}, t) = \left(\frac{1}{i\hbar} \right)^2 \int_{-\infty}^0 dt' e^{\epsilon t'} Tr \left\{ \left[H'(t'), \left[H', \vec{U}_j(\vec{r}) \right] \right] \bar{\rho}_h(t, 0) \right\} , \quad (B.3)$$

$$\begin{aligned} \Theta_{jk}^{-1}(\vec{r} - \vec{r}', t) = & \sum_m \int_{-\infty}^0 dt' e^{\epsilon t'} \int d^3 r'' \int_0^1 dx Tr \left\{ \left[H'(t'), \left[H', \vec{U}_j(\vec{r}) \right] \right] \right. \\ & : [\bar{\rho}_h(t, 0)]^x \Delta \vec{U}_m(\vec{r}'') [\bar{\rho}_h(t, 0)]^{-x-1} \left. \right\} B_{mk}^{-1}(\vec{r}'' - \vec{r}', t) , \end{aligned} \quad (B.4)$$

$$\begin{aligned} \vec{E}_{jk}(\vec{r} - \vec{r}', t) = & \left(\frac{1}{i\hbar} \right)^2 \int_{-\infty}^0 dt' e^{\epsilon t'} \int_0^1 dx Tr \left\{ \left[H'(t'), \left[H', \vec{U}_j(\vec{r}) \right] \right] \right. \\ & \cdot [\bar{\rho}_h(t, 0)]^x \Delta P_k(\vec{r}') [\bar{\rho}_h(t, 0)]^{-x-1} \left. \right\} + \\ & \left(\frac{1}{i\hbar} \right)^2 \sum_{mn} \int_{-\infty}^0 dt' e^{\epsilon t'} \int d^3 r_1 \int d^3 r_2 \int_0^1 dx Tr \left\{ \left[H'(t'), \left[H', \vec{U}_j(\vec{r}) \right] \right] \right. \\ & \left. [\bar{\rho}_h(t, 0)]^x \Delta \vec{U}_m(\vec{r}_2) [\bar{\rho}_h(t, 0)]^{-x-1} \right\} \cdot B_{nm}^{-1}(\vec{r}_2 - \vec{r}_1, t) \vec{A}_{mk}(\vec{r}_1 - \vec{r}', t) , \end{aligned} \quad (B.5)$$

where Θ is a second rank tensor (double dots stand for a dyadic product), $\vec{\lambda}^{(h)}$ and \vec{I} are vectors; in the last term in the expression for \vec{E} it should be understood that it is present the scalar product $\Delta \vec{U} \cdot B^{-1} \vec{A}$. Finally, replacing **Eq.** (B2) into Eq. (55) we find Eq. (58).

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