

On Nonequilibrium Many-Body Systems I: The Nonequilibrium Statistical Operator Method

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Abstract We discuss the theoretical aspects involved in the treatment of many-body systems strongly departed from equilibrium. We consider in detail the nonequilibrium statistical operator (NSO) method. Using Jaynes' maximum entropy formalism complemented with an ad hoc hypothesis a nonequilibrium statistical operator is obtained. Our approach introduces irreversibility from the outset and we recover statistical operators like those of Green-Mori and Zubarev as particular cases. The connection with Generalized Thermodynamics and the construction of nonlinear transport equations are briefly described.

1. INTRODUCTION

The purpose of the Statistical Mechanics of systems away from equilibrium is to determine the thermodynamic properties and evolution in time of macroscopic observables of such systems in terms of the dynamical laws which govern the motion of their constitutive particles. The basic goals of nonequilibrium statistical mechanics are: (a) to derive transport equations and to understand their structure, (b) to understand how the approach to equilibrium occurs in isolated natural systems; (c) to study the properties of steady states, and (d) to calculate the instantaneous values and the temporal evolution of the physical quantities which specify the macroscopic state of the system.

The analysis of nonequilibrium systems presents greater difficulties than those faced in the theory of equilibrium systems. This is due to the fact that a more detailed discussion to determine the temporal dependence of measurable properties, and the calculation of time-dependent transport coefficients associated with the irreversible pro-

cesses that take place in these systems, are necessary.

At present there exist several theoretical methods to study the macroscopic evolution of nonequilibrium systems. The usefulness of these methods can be ascertained through comparison of the results obtained by application of the theory with experimental data. However, the reason why these methods work well within their own dominions of application can not be properly understood until a profound insight of the basic conceptual problems associated to the irreversible processes is obtained. Existing formalisms have inherent difficulties: typically those related to, mainly, introduction of coarse-grained procedures, the question of irreversibility, and the definition of initial and boundary conditions. In any approach an overall important step is the derivation of nonlinear transport equations able to describe the temporal macroscopic evolution of nonequilibrium systems. It is worth noticing that the nonlinearity of the transport equations implies feedback mechanisms which may be the source of remarkable self-organization effects on a macroscopic scale in the system (synergesis).

In the next section we briefly describe the main questions that arise: in dealing with the Statistical Mechanics of far-from-equilibrium systems. Further, among the different available formalisms we single out for study the so called nonequilibrium statistical operator (NSO) method. It provides a very promising technique which is an advanced generalization of statistical methods based on Boltzmann and Gibbs' fundamental ideas. We derive a nonequilibrium statistical operator using Jaynes' maximum entropy formalism² complemented with an *ad hoc* hypothesis. Our approach allows us to introduce (forcibly) irreversibility from the outset, and to recover, as particular cases, statistical operators proposed in the available literature on the subject.

2. THE NONEQUILIBRIUM STATISTICAL OPERATOR METHOD

As is well known, since in any experiment there is no access to a complete knowledge of the microscopic dynamical state of a many-body system one resorts to statistical mechanics to obtain a description of the macroscopic state of the system in terms of a small set of dynamical quantities, say P_1, P_2, \dots, P_n , where n is much smaller than the number of degrees of freedom of the system under observation. Quan-

tities P_j are functions defined over the phase space in the classical limit or hermitian operators acting on the Hilbert space of the wavefunctions in the quantum case.

One of the main problems of nonequilibrium statistical mechanics is the choice of these quantities and the derivation of closed equations of evolution (nonlinear transport equations) for the macroscopic variables $Q_j(t)$, $j = 1, 2, \dots, n$, which are suitable averages $\langle P_j | t \rangle$ of the P_j , to be put in correspondence with the measurements obtained in a given experiment. For example, the set $\{P_j\}$ may be constituted by the mass density, momentum density and energy density when the hydrodynamics of a fluid is studied.

These quantities P_j change in time with the evolution of the dynamical state of the system; however the experiment does not follow this microscopic evolution, it only follows the numerical values $Q_j(t)$ of P_j . The results of such experiment are described by transport equations of the form

$$\frac{d}{dt} Q_j(t) = \phi_j\{Q_1(t), Q_2(t), \dots, Q_n(t); t\}, \quad (1)$$

where ϕ_j is a functional of the macrovariables Q_j which, in general, is expected to be nonlinear, non-local and with memory effects, i.e. depending on the past history of variables Q up to the time t when the measurement is performed. Several questions arise immediately and need be addressed

1) How to choose these variables? At present there seems to be no wholly satisfactory theory to generate this information allowing the making of a unique decision.

First we should recall Bogoliubov's assertion³ that a contracted description is possible if there exists a relaxation time for microinformation, τ_μ , such that after it has elapsed the system loses the memory of the initial distribution. For not too short delay times after excitation, i.e. for $t \gg \tau_\mu$, correlations with lifetime smaller than τ_μ can be ignored and the macroscopic state of the nonequilibrium system can be described by the reduced set of macrovariables $Q_j(t)$, $j = 1, 2, \dots, n$.

Some authors suggest that this basis set of variables must include all approximate integrals of motion, or quasi-invariant variables,

that change very slowly on a molecular time scale. Others argue that one should include enough variables to make the functionals ϕ_j "almost markoffian", or almost instantaneous in time. Another possibility consists in including only those variables which are measurable (directly or indirectly) in the experiment under consideration. This is in the spirit of Jaynes' maximum information entropy formalism², and it is the one we use to deal with the study of ultrafast relaxation phenomena in semiconductors to be described in a forthcoming article.

2) The *question of initial conditions*. Transport equations (1) are of first order in the time derivative and therefore require an initial condition for a unique solution to be obtained. Once the definition of the basis set of macrovariables has been decided, it becomes necessary to provide initial condition $Q_j(t_1)$, at a given time t_1 , which should show a large degree of reproducibility. Many times this is done using initial condition that appear to be reasonable and well suited to theoretical analysis. In our studies of ultrafast transients in semiconductors we used initial values obtained from the experimental data, either from direct measurements or through estimations based on information concerning the experimental setup and known properties of the sample. Clearly this incorporates a certain lack of reproducibility resulting from experimental indetermination. The sensitivity of the results to the details of the initial state needs to be carefully considered.

3) *How are the functionals ϕ_j in Eq.(1) obtained?* In other words, what is the form of the nonlinear transport equations for macrovariables $\{Q_j(t)\}$.

Several approaches to nonlinear transport are available at present. Following Zwanzig¹ they can be classified as:

- i) Intuitive techniques,
- ii) Techniques based on the generalization of the kinetic theory of gases,
- iii) Techniques based on the theory of stochastic processes,
- iv) Expansions from an initial equilibrium ensemble,
- v) Generalizations of Gibbs' ensemble algorithm.

The last of them, or nonequilibrium statistical operator method (NSO), has an appealing structure and seems to be a very effective technique to deal with a large class of experimental situations. Elegant

treatments are due to Robertson⁴ and Zubarev⁵, and a version of Zubarev's method adapted to deal with open systems was applied by us to the study of polar semiconductors under high degrees of excitation⁷. This statistical method is based on the construction of an ensemble of replicas of the system distributed with some a priori probability over all the microscopic states in accordance with the initial specifications and constraints imposed on the system. To the representative ensemble one associates a distribution function (statistical operator) $\rho(t)$, and the average over the ensemble of a dynamical quantity ,

$$\langle A | t \rangle = \text{Tr}\{A \rho(t)\},$$

is placed in correspondence with the result $\alpha(t)$ of a measurement performed on the actual physical system.

These methods are connected with a projection operator technique which separates the NSO $\rho(t)$ into two parts

$$\rho(t) = P(t) \rho(t) + [1-P(t)]\rho(t) = \rho_{cg}(t) + \rho'(t) . \quad (2)$$

The first term $\rho_{cg}(t)$, obtained by application of the time-dependent projection operator $P(t)$ on the complete NSO, is a non-dissipative term which defines the mean values of quantities P_j , i.e. the macrovariables

$$Q_j(t) = \text{Tr}\{P_j \rho(t)\} = \text{Tr}\{P_j \rho_{cg}(t)\} . \quad (3)$$

The second term, ρ' , carries the information on the dynamics relevant to the description of the irreversible evolution of the system^{4,5,8}. Therefore, $\rho'(t)$ must satisfy the relation

$$\text{Tr}\{\Omega \rho'(t)\} = 0 ,$$

where R is any linear combination of the quantities P_j . The NSO $\rho(t)$, and the coarse-grained statistical operator $\rho_{cg}(t)$, express the same macroscopic state but differ in details due to the microscopic processes developing in the media.

At present there exist several approaches used for the derivation of the nonequilibrium statistical operator like those due to Green-Mori⁸, Robertson⁴ and Zubarev⁵. We propose here a derivation of a general nonequilibrium statistical operator which allows us to recover

the approaches of refs.5 and 8 as particular cases.

First it should be noted that for an isolated system the NSO $\rho(t)$ must satisfy the Liouville equation

$$\frac{\partial}{\partial t} \rho(t) + iL \rho(t) = 0 \quad (4)$$

where L is the Liouvillian operator of the system ($iL\rho$ is the Poisson parenthesis $\{\rho, H\}$ in the classical limit and the commutator $(i\hbar)^{-1}[\rho, H]$ in the quantum case, where H is the total hamiltonian). Eq. (4) is Lt -invariant, i.e. it remains unaltered by the transformation $(t, iL) \rightarrow (-t, (iL)^\dagger)$.

This poses another fundamental question:

4) *How to obtain irreversible behavior in the evolution of the macroscopic state of the system?* This is sometimes referred to as the time arrow problem.

To proceed further with the method we are considering, we overcome this question by the introduction of Prigogine's principle of *dynamic condition for dissipativity*⁹. This is an *ad hoc* non-mechanical hypothesis consisting of a breaking of the time-reversal symmetry of the Liouville equation which casts it in the form

$$\frac{\partial \tilde{\rho}(t)}{\partial t} + A \tilde{\rho}(t) = 0 \quad (5)$$

where A is a modified Liouvillian composed of an odd and an even part under time-reversal and $\tilde{\rho}$ a transformed NSO in which an irreversible character for the evolution of the macroscopic state of the system has been built¹⁰.

To derive the complete NSO satisfying the separation obtained by projection technique [eq.(2)] and having the Boltzmann-Prigogine symmetry of eq. (5), we resort to the use of a variational principle, the *maximum entropy formalism* (MEF)^{2,11}. It is based on Jaynes' suggestions that Gibbs' ensemble algorithm allows the construction of statistical operators which fully describe nonequilibrium conditions. The main question associated with this approach is how to obtain the probability assignment compatible with the available information and avoiding unwarranted assumptions. This is answered by Jaynes who formulated the criterion that: The least biased probability assignment $\{p_i\}$ for a set of mutually exclusive events x_i is that which maximizes the

"entropy"

$$S = - \sum_i p_i \log p_i$$

subject to the constraints imposed by available information¹².

Let us make this explicit for a many-body physical system which is the object of a given experiment, and in the treatment we include memory effects and non-locality. First we introduce the Gibbs entropy

$$S_G(t) = -\text{Tr}\{\rho(t) \log \rho(t)\}, \quad (6)$$

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

$$\text{Tr}\{\rho(t')\} = 1, \quad \text{for } t_0 \leq t' \leq t. \quad (7)$$

Further, once the basis set of dynamical quantities $\{P_j(\vec{r})\}$ has been chosen¹³ the constraint conditions

$$Q_j(\vec{r}, t') = \text{Tr}\{P_j(\vec{r}) \rho(t')\} = \text{Tr}\{P_j(\vec{r}, t'-t) \rho(t)\} \quad (8)$$

are introduced, for $t_0 \leq t' \leq t$. To write the last equality we have used the fact that

$$\text{Tr}\{A \rho(t')\} = \text{Tr}\{A e^{-i(t'-t)L} \rho(t)\} = \text{Tr}\{A(t'-t) \rho(t)\}. \quad (9)$$

Eqs. (8) introduce a dynamical character in the information since they involve the evolution of the system from the initial time of preparation t_0 ($t_0 \gg \tau_H$) up to time t . Also to be noted is the formal character of eqs. (8) where we make the assumption that one has the knowledge of the values of variables Q in the time interval (t_0, t) . However, this information-gathering interval can be reduced to information recorded at a unique t : the formalism produces evolution equations for variables $Q_j(t)$ which give their values at any time $t_0 > t_1 \geq t$ once the initial values $Q(t_1)$ are provided (Cf. question (2) in the first part of this Section).

Next, according to the maximum entropy formalism we obtain the NSO that maximizes the Gibbs entropy of eq. (6), subject to the constraints imposed by eqs. (7) and (8). This corresponds to making extremal the functional

$$I\{\rho\} = -\text{Tr}\{\rho(t) \log \rho(t)\} - [\Psi(t) - 1] \text{Tr}\{\rho(t)\} \\ - \sum_{j=1}^n \int d^3r \int_{t_0}^t dt' \phi_j(\vec{r}, t, t'; t_0) \text{Tr}\{P_j(\vec{r}, t'-t) \rho(t)\} ,$$

where 1 and 4_3 are Lagrange multipliers. Following well known procedures we find

$$\rho(t) = \exp\{-\Psi(t) - \sum_{j=1}^n \int d^3r \int_{t_0}^t dt' \phi_j(\vec{r}, t, t'; t_0) P_j(\vec{r}, t'-t)\} , \quad (9)$$

where

$$\Psi(t) = \log\{\text{Tr}\{\exp - \sum_{j=1}^n \int d^3r \int_{t_0}^t dt' \phi_j(\vec{r}, t, t'; t_0) P_j(\vec{r}, t'-t)\}\} .$$

Next, we write the Lagrange multipliers ϕ_j in the following form

$$\phi_j(\vec{r}, t, t'; t_0) = w(t, t'; t_0) F_j(\vec{r}, t') , \quad (10)$$

where w is an auxiliary function. The form for the Lagrange multipliers given by eq. (10) is proposed in order:

- 1) To introduce the set of functions $F_j(\vec{r}, t)$ such that they will have the role of intensive variables (fields) thermodynamically conjugated to the extensive variables $Q_j(\vec{r}, t)$, in a way to be defined later on, to generate a complete connection with phenomenological generalized nonequilibrium thermodynamics¹¹, and
- 2) To define a function w permitting to include Prigogine's dynamical condition for dissipativity in the formalism, and to fix an initial condition from which the irreversible evolution of the macroscopic state of the nonequilibrium many-body system is obtained.

Replacing eq. (10) in eq. (9), we obtain

$$\rho(t) = \exp\left\{- \int_{t_0}^t dt' w(t, t'; t_0) S(t', t'-t)\right\} = \\ = \exp\left\{ \int_{t_0}^t dt' w(t, t'; t_0) \log \rho_{eq}(t', t'-t)\right\} \quad (11)$$

where we have introduced the operators

$$\rho_{cg}(t_1, t_2) = \exp\{-\phi(t_1) - \sum_{j=1}^n \int d^3r F_j(\vec{r}, t_1) P_j(\vec{r}, t_2)\} \quad (12)$$

$$S(t_1, t_2) = -\log \rho_{cg}(t_1, t_2) \quad , \quad (13)$$

and the function $\phi(t)$ such that

$$\psi(t) = \int_{t_0}^t dt' w(t, t'; t_0) \phi(t') \quad (14)$$

The first term in the argument of S or $\log \rho$ refers to the time-dependence on variables F_j and the second to the time-dependence of operators P_j in the Heisenberg representation.

The ρ_{cg} of eq. (12) has the role of the coarse-grained statistical operator of eq. (2) [cf. eq. 25], and S of eq. (13) is termed the coarse-grained statistical entropy. The average value of S over the nonequilibrium ensemble will be put in correspondence with the entropy function of generalized thermodynamics this giving a statistical foundation for the latter; this question will be addressed in detail in a future article. The coarse-grained statistical operator is normalized, i.e.

$$\phi(t) = \log \text{Tr}\{\exp(-\sum_{j=1}^n \int d^3r F_j(\vec{r}, t) P_j(\vec{r}))\} ;$$

which can be proved from eq. (14) (Appendix 1).

Performing a partial integration in eq. (11) we get

$$\begin{aligned} \log \rho(t) &= W(t, t'; t_0) \log \rho_{cg}(t', t'-t) \Big|_{t_0}^t \\ &- \int_{t_0}^t dt' W(t, t'; t_0) \frac{d}{dt'} \log \rho_{cg}(t', t'-t) \quad , \end{aligned} \quad (15)$$

where W is given by

$$\frac{d}{dt'} W(t, t'; t_0) = w(t, t'; t_0) \quad , \quad (16)$$

and we impose the following properties on it:

a) $W(t, t; t_0) = 1$

b) $\lim_{t' \rightarrow t_0} W(t, t'; t_0) \equiv W(t, t_0; t_0) = 0$

c) W is taken equal to 1 after the trace operation in the calculation of averages has been performed.

Hence, eq. (15) becomes

$$\log \rho_w(t) = \log \rho_{cg}(t, 0) - \int_{t_0}^t dt' W(t, t'; t_0) \frac{d}{dt'} \log \rho_{cg}(t', t'-t) , \quad (17)$$

or after integration by parts

$$\log \rho_w(t) = \int_{t_0}^t dt' w(t, t'; t_0) \log \rho_{cg}(t', t'-t) . \quad (18)$$

This expression can be interpreted as a time-smoothing of the operator S (or $\log \rho_{cg}$) weighted by the function w . By a proper choice of w we recover nonequilibrium statistical operators already proposed in the literature on the subject.

1. Green-Mori NSO: The function

$$W(t, t'; t_0) = 1 - \frac{t-t'}{\tau}$$

satisfies condition (a), condition (b) fixes the initial time at the delay time $t = t - \tau$, and to comply with (c) τ goes to $+\infty$ at the end of the calculations of averages. The function w is τ^{-1} and then it follows Green-Mori NSO^e

$$\log \rho_{\tau}(t) = \frac{1}{\tau} \int_{t-\tau}^t ds \log \rho_{cg}(s, s-t) \quad (19)$$

2. Zubarev NSO: It is obtained by the choice

$$W(t, t'; t_0) = \exp\{\epsilon(t'-t)\} ,$$

which satisfies condition (a), and condition (b) follows for $t_0 \rightarrow -\infty$. A change of variables allows us to write it in the form⁵

$$\log \rho_{\epsilon}(t) = \epsilon \int_{-\infty}^0 dt' e^{\epsilon t'} \log \rho_{cg}(t+t', t') , \quad (20)$$

since $w(t, t', t_0) = \epsilon \exp\{\epsilon(t'-t)\}$; $\epsilon (> 0)$ is an infinitesimal parameter which goes to zero after the trace operation in the calculation of averages has been performed to satisfy requirement (c) .

3. Among other choices of the weight function we could mention

$$W(t, t'; t_0) = \exp\{-\alpha^2 (t'-t)^2\} ,$$

which satisfies condition (a); condition (b) requires that $t_0 \rightarrow -\infty$, and α is taken equal to zero at the end of calculation of averages to satisfy condition (c). Since

$$w(t, t'; t_0) = -2\alpha^2 (t'-t) \exp\{-\alpha^2 (t'-t)^2\} ,$$

we obtain

$$\log \rho_\alpha(t) = -2\alpha^2 \int_{-\infty}^0 dt' t' e^{-\alpha^2 t'^2} \log \rho_{cg}(t+t', t') . \quad (21)$$

We remark that the construction of NSO in this way resembles the methods of the theory of summability of trigonometrical series and integral transforms:¹⁵ Case (1) is related to Fejèr- (or Cesàro-I), case (2) to Abel-, and case (3) to Gauss- summability procedures. Up to the present time we do not have interpretations for time-smoothing integral procedures other than those of eqs. (19) and (20) .

In case (1), eq. (19) defines a time average over interval τ , and it is based on the assumption that correlations damp out in times much smaller than τ . After the calculation of averages the limit $\tau \rightarrow \infty$ is taken; it has been argued that this time-smoothing procedure leads to difficulties in the definition of integrals associated with transport coefficients¹⁶.

In case (2), [eq. (20)] $\log \rho_\epsilon(t)$ is interpreted as the logarithm of ρ evolving freely with Liouvillian L from time t' up to time t , and then the system undergoes a random transition under the influence of the interaction with the surroundings with a Poisson distribution $\epsilon \exp\{\epsilon(t-t')\}$; the NSO is obtained averaging over all initial times t' ¹⁷. The NSO of eq. (18) satisfies the Liouville equation the sources (See Appendix 2)

$$\left[\frac{\partial}{\partial t} + iL \right] \log \rho_w(t) = \int_{t_0}^t dt' \frac{\partial w(t, t', t_0)}{\partial t} \log \rho_{cg}(t', t'-t) + w(t, t; t_0) \log \rho_{cg}(t, 0), \quad (22)$$

and therefore in Green-Mori's method we find

$$\left[\frac{\partial}{\partial t} + iL \right] \log \rho_\tau(t) = \frac{1}{\tau} \log \rho_{cg}(t, 0), \quad (23)$$

and in Zubarev's method

$$\left[\frac{\partial}{\partial t} + iL \right] \log \rho_\varepsilon(t) = -\varepsilon \{ \log \rho_\varepsilon(t) - \log \rho_{cg}(t, 0) \}, \quad (24)$$

where we observe the presence of an infinitesimal source which breaks tL -symmetry and introduce Boltzmann-Prigogine symmetry.

Next we derive the connection of our results with *projection operator techniques*. For that purpose we first note that using the operator identity

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

where

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

the NSO $\rho_w(t)$ can be written as

$$\rho_w(t) = \rho_{cg}(t) + \rho'(t) \equiv \exp\{-\log \rho_{cg}(t, 0) + \zeta_w(t)\} \quad (25)$$

with

$$\rho_{cg}(t) = \exp\{-\phi(t) - \sum_{j=1}^n F_j(t) P_j\} = e^{-S(t, 0)}, \quad (26a)$$

$$\zeta_w(t) = - \int_{t_0}^t dt' W(t, t'; t_0) \frac{d}{dt'} \log \rho_{cg}(t', t'-t) \quad (26b)$$

$$\rho'(t) = D_w(t) \rho_{cg}(t), \quad (26c)$$

$$D_w(t) = \int_0^1 du Y(\zeta_w|u) e^{-uS(t, 0)} \zeta_w(t) e^{uS(t, 0)} \quad (26d)$$

$$Y(\zeta_w | x) = 1 + \int_0^{\infty} du Y(\zeta_w | u) e^{-uS(t,0)} \zeta_w(t) e^{uS(t,0)} \quad (26e)$$

The NSO of eq. (25) is composed of two additive parts as in eq. (2) and, because of eq. (3) we find that

$$\text{Tr}\{\rho'(t)\} = \text{Tr}\{D_w(t) \rho_{cg}(t)\} = 0, \quad (27a)$$

$$\text{Tr}\{P_3 \rho'(t)\} = \text{Tr}\{P_3 D_w(t) \rho_{cg}(t)\} = 0. \quad (27b)$$

Eq. (27a) is a manifestation of the fact that $\rho_{cg}(t)$ is assumed to be normalized and, since $D_w(t)$ is directly related to the entropy production operator $-\frac{d}{dt} \log \rho_{cg}(t,0)$ (Cf. eq. (38)), it also reflects that there are no dissipation effects in the ensemble characterized by $\rho_{cg}(t)$.

In eq. (26a), as well as in the following equations we have dropped the space dependence of quantities P and variables Q and F , in order to avoid cumbersome expressions.

Consider now quantities P_j as vectors of an n -dimensional Banach space with a metric defined by the inner product

$$\{P_i; P_j | t\} = \tilde{C}_{ij}(t) = \text{Tr}\{P_i \Delta \tilde{P}_j \rho_{cg}(t)\}, \quad (28)$$

where $\Delta P = P - \text{Tr}\{P \rho_{cg}(t)\}$ and

$$\tilde{A} = \int_0^1 du Y(\zeta_w | u) e^{-uS(t,0)} A e^{uS(t,0)} \quad (29)$$

Definition (28) allows us to introduce the time-dependent projection operator

$$P(t) A = \sum_{i,j} P_i \tilde{C}_{ij}^{-1}(t) \{P_j; A | t\}, \quad (30)$$

which is linear

$$P(t) (aB+bB) = a P(t) A + b P(t) B, \quad (31a)$$

hermitian

$$\{A; P(t) B | t\} = \{P(t) A; B | t\}, \quad (31b)$$

and idempotent

$$P(t') P(t) A = P(t) A . \quad (31c)$$

Further, $P(t)$ projects the logarithm of the NSO $\rho_w(t)$ over minus the coarse-grained entropy $S(t,0)$, i.e. the operator $\log \rho_{cg}(t,0)$. In fact using eqs. (25) and (30) we find

$$\begin{aligned} P(t) \log \rho_w(t) &= P(t) \log \rho_{cg}(t) - P(t) \zeta_w(t) = \\ &= \log \rho_{cg}(t) - \sum_{i,j} P_i \tilde{C}_{ij}^{-1}(t) \{P_j; \zeta_w(t) | t\} . \end{aligned}$$

But

$$\begin{aligned} \{P_j; \zeta_w(t)\} &= \text{Tr} \left\{ P_j \int_0^1 du Y(\zeta_w | u) e^{-uS(t,0)} \zeta_w(t) e^{uS(t,0)} \rho_{cg}(t) \right\} = \\ &= \text{Tr} \{ P_j D_w(t) \rho_{cg}(t) \} \end{aligned}$$

which is null because of eq. (27b).

Therefore, we have proved that

$$P(t) \log \rho_w(t) = \log \rho_{cg}(t) \quad (32)$$

for any NSO $\rho_w(t)$.

Using these results, for the specific case of Zubarev's method, eq. (24) can be alternatively written in the form

$$\left[\frac{\partial}{\partial t} + i\Lambda(t) \right] \log \rho_\epsilon(t) = 0 \quad (33)$$

where

$$i\Lambda = iL + \epsilon [1 - P(t)] , \quad (34)$$

and we have obtained a modified Liouville equation in the spirit of Prigogine's proposal.

To make connection with Generalized Thermodynamics we define the function of macrovariables $Q_3(t)$

$$\begin{aligned} \bar{S}(t) &= -\text{Tr}\{\rho_w(t) \log \rho_{cg}(t)\} = \text{Tr}\{S(t,0) \rho_w(t)\} = \\ &= \phi(t) + \sum_{j=1}^n F_j(t) Q_j(t) \quad , \end{aligned} \quad (35)$$

called the coarse-grained entropy. The Lagrange multipliers $F_j(t)$ are defined by eq. (3): using the normalization property

$$\begin{aligned} \phi(t) &= \phi[F_1(t), \dots, F_n(t)] = \\ &= \log \text{Tr}\{\exp[-\sum_{j=1}^n F_j(t) P_j]\} \quad , \end{aligned} \quad (36)$$

it follows that

$$Q_j(t) = -\frac{\partial \phi(t)}{\partial F_j(t)} = Q_j[F_1(t), \dots, F_n(t)] \quad (37a)$$

Further, \bar{S} and ϕ satisfy the Pfaffian forms

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

and

$$d\bar{S}(t) = \sum_{j=1}^n F_j(t) dQ_j(t) \quad ,$$

and therefore the $F_j(t)$ are the differential coefficients of the coarse-grained entropy

$$F_j(t) = \frac{\partial \bar{S}(t)}{\partial Q_j(t)} = F_j[Q_1(t), \dots, Q_n(t)] \quad . \quad (37b)$$

Equations (37a,b) can be considered as nonequilibrium equations of state connecting the set of macrovariables, $Q_j(t)$, on which the coarse-grained entropy depends, and the differential coefficients of the latter, or intensive variables $F_j(t)$.

The connection with Generalized Thermodynamics¹⁴ follows from the identification of the coarse-grained entropy of eq. (35) with the generalized thermodynamical entropy. The irreversible production of entropy, which plays an essential role in the thermodynamics of irreversible processes, is obtained by time differentiation of eq. (35)

$$\sigma(t) = - \frac{d}{dt} \text{Tr} \{ \rho_w(t) \log \rho_{cg}(t) \} = \sum_{j=1}^n F_j(t) \frac{d}{dt} Q_j(t) \quad , \quad (38)$$

and in the so-called quasi-linear relaxation regime ($Y = 1$ in eq. (26d)) it can be written as the autocorrelation of the entropy production operator - $\frac{d}{dt} \log \rho_{cg}(t)$ over the ensemble characterized by the coarse-grained statistical operator. The Glansdorff-Prigogine universal evolution criterion and Prigogine's minimum entropy production theorem¹⁴ are contained in the formalism¹⁸.

The nonequilibrium statistical operator method can also be used to deal with the study of dissipative structures in far-from-equilibrium systems (morphological transitions, transitions between multiple steady states, macroscopic periodic oscillations)¹⁴, which involve synergetic processes. This is a result of the nonlinear character of the generalized transport equations that can be derived within the framework of the NSO method. This question deserves a detailed discussion, which will be presented in a forthcoming article. Here it suffices to say that the separation of the NSO in the form of eq. (25) allows us to write

$$\begin{aligned} \frac{d}{dt} Q_j(t) &= \text{Tr} \left\{ \frac{1}{i\hbar} [P_j, \bar{H}] \rho_w(t) \right\} = \text{Tr} \left\{ \frac{1}{i\hbar} [P_j, \bar{H}] \rho_{cg}(t) \right\} \\ &+ \sum_{\ell=1}^{\infty} \text{Tr} \left\{ \frac{1}{i\hbar} [P_j, H] D_w^{(\ell)}(t) \rho_{cg}(t) \right\} \quad , \quad (39) \end{aligned}$$

where $D_w^{(\ell)}(t)$ are the terms of the expansion of $D_w(t)$ of eq. (26d) corresponding to the successive contributions to the iterated solution of Y in eq. (26e).

For the specific case of Zubarev's method one has

$$\rho_{\epsilon}(t) = \rho_{cg}(t) + \rho'_{\epsilon}(t) \quad , \quad (40)$$

where

$$\rho'_{\epsilon}(t) = D_{\epsilon}(t) \rho_{cg}(t) \quad , \quad (41a)$$

$$D_{\epsilon}(t) = \int_0^1 du Y(\zeta_{\epsilon}|u) e^{-uS(t,0)} \zeta_{\epsilon}(t) e^{uS(t,0)} \quad , \quad (41b)$$

$$\zeta_{\epsilon}(t) = - \int_{-\infty}^0 dt' e^{\epsilon t'} \frac{d}{dt'} \log \rho_{cg}(t+t', t') \quad , \quad (41c)$$

$$Y(\zeta_\epsilon | u) = 1 + \int_0^u dx Y(\zeta_\epsilon | x) e^{-xS(t,0)} \zeta_\epsilon(t) e^{xS(t,0)} ; \quad (41d)$$

and an arduous mathematical handling of eqs. (39) permits us to rewrite them in the form^{5,19,20}

$$\frac{d}{dt} Q_j(t) = \sum_{\ell=0}^{\infty} J_j^{(\ell)}(t) \quad (42)$$

where the collision operators $J_j^{(n)}$ are

$$J_j^{(0)}(t) = \frac{1}{i\hbar} \text{Tr} \{ [P_j, H] \rho_{cg}(t) \} , \quad (43a)$$

$$J_j^{(1)}(t) = \frac{1}{i\hbar} \text{Tr} \{ [P_j, H^1] \rho_{cg}(t) \} , \quad (43b)$$

$$J_j^{(2)}(t) = \left(\frac{1}{i\hbar}\right)^2 \int_{-\infty}^0 dt' e^{\epsilon t'} \text{Tr} \{ [H^1(t'), [H^1, P_j]] \rho_{cg}(t) \} + \quad (43c)$$

$$+ \frac{1}{i\hbar} \int_{-\infty}^0 dt' e^{\epsilon t'} \sum_{\ell=1}^n \frac{\partial J_j^{(1)}(t)}{\partial Q_\ell(t)} \text{Tr} \{ [H^1(t'), P_\ell] \rho_{cg}(t) \}$$

...

Here H is the hamiltonian of the free subsystems and H^1 is the sum of the energy operators corresponding to the interactions among them.

Beyond the quadratic term in the interaction strengths the calculations become messy. When one truncates the series expansion in second order ($\ell=2$) the quasi-linear approximation is introduced in the relaxation processes²¹. This is equivalent to writing $Y=1$ in eq. (26d), and the collision operators contain the interaction coupling strengths up to second order only.

The NSO method permits us to obtain nonlinear transport equations in the form of expansions in terms of deviations from the nonequilibrium macroscopic state described by $\rho_{cg}(t)$. For this reason the method is considered a far reaching generalization of the Chapman-Enskog method in the kinetic theory of gases¹. The hydrodynamics of fluid systems arbitrarily away from equilibrium is within the scope of the NSO method, including systems with large fluctuations²².

A particular case of hydrodynamics is that of nonequilibrium plasma in semiconductors. The study of highly excited semiconductors

has become an important part of Solid State Physics. A considerable amount of experimental and theoretical information on the subject is available at present and the growing interest in the development of devices based on semiconductors keeps this area alive and active. Further, nonequilibrium plasma in semiconductors is an important testing ground for theoretical ideas in the physics of nonequilibrium many-body systems. In a forthcoming article we will discuss the application of the NSO method to the study of ultrafast relaxation phenomena in highly photoexcited semiconductors.

APPENDIX 1: Normalization of the coarse-grained statistical operator.

The normalization of ρ_{cg} implies that

$$\phi(t) = \log \text{Tr} \left\{ \exp \left(- \sum_j F_j(t) P_j \right) \right\}, \quad (1.1)$$

which together with equations (3) defines ϕ and the n quantities F_j . Also, since $\rho_w = \rho_{cg} + \rho'$ it follows that $\text{Tr}\{\rho'\} = 0$, which, as noted in the main text, is a manifestation of the fact that there is no dissipation in the coarse-grained ensemble. The normalization of ρ_w is given by

$$\psi(t) = \log \text{Tr} \left\{ \exp \left(- \int_{t_0}^t dt' w(t, t'; t_0) \sum_j F_j(t') P_j(t'-t) \right) \right\}; \quad (1.2)$$

integrating (1.2) by parts we obtain

$$\psi(t) = \log \text{Tr} \left\{ \exp \left(-S(t) + \phi(t) + \int_{t_0}^t dt' w(t, t'; t_0) \frac{d}{dt'} \left[F_j(t') P_j(t'-t) \right] \right) \right\}$$

where we have added and subtracted ϕ in the exponent to make explicit the coarse-grained entropy operator S . Recalling that $\rho_{cg} = \exp\{-S\}$, and using the expansion of operators of the form $\exp\{A+B\}$ given in the main text we find

$$\psi(t) = \phi(t) + \log \text{Tr} \left\{ \rho_{cg}(t) \left[1 + D_w(t) \right] - \exp \int_{t_0}^t dt' w(t, t'; t_0) \frac{d}{dt'} \phi(t') \right\}$$

But

$$\begin{aligned} \log \text{Tr}\{\rho_{cg}(t) + \rho_{cg}(t)D_w(t)\} &= \log \text{Tr}\{\rho_{cg} + \rho'\} = \\ &= \log \text{Tr}\{\rho_{cg}\} = 0, \end{aligned}$$

and then

$$\psi(t) = \phi(t) - \int_{t_0}^t dt' w(t, t'; t_0) \frac{d}{dt'} \phi(t') = \int_{t_0}^t dt' w(t, t'; t_0) \phi(t')$$

which verifies eq. (14).

Furthermore, using eqs. (3) and the expressions for ψ and ϕ we obtain

$$-\frac{\delta\psi(t)}{\delta F_j(t)} = \langle P_j | t \rangle_w = Q_j(t) = \langle P_j | t \rangle_{cg} = -\frac{\delta\phi(t)}{\delta F_j(t)}, \quad (1.3)$$

i.e. ψ and ϕ have the same differential coefficients, which are the macrovariables Q .

APPENDIX 2: Verification of eq. (22) and boundary condition.

Multiplying both sides of eq. (22) by $\exp\{itL\}$ we obtain on the left hand side

$$e^{itL} \left[\frac{\partial}{\partial t} + iL \right] \log \rho(t) = \frac{d}{dt} \log \rho(t, t), \quad (2.1)$$

where

$$\log \rho(t, t) = e^{itL} \log \rho(t, 0)$$

Besides, on the right hand side of eq. (22) we obtain

$$\begin{aligned} \int_{t_0}^t dt' \frac{\partial w(t, t'; t_0)}{\partial t} \log \rho_{cg}(t', t') + w(t, t; t_0) \log \rho_{cg}(t, t) = \\ = \frac{d}{dt} \int_{t_0}^t dt' w(t, t'; t_0) \log \rho_{cg}(t', t'). \end{aligned} \quad (2.2)$$

Therefore, from (2.1) and (2.2) we obtain

$$\log \rho(t, t) = \int_{t_0}^t dt' w(t, t'; t_0) \log \rho_{cg}(t', t') + \text{const.}$$

The integration constant is determined by the Boundary condition

$$\lim_{t \rightarrow t_0} \log \rho(t, t) = \log \rho_{cg}(t_0, t_0) \quad ,$$

i.e. the system is initially prepared as in contact with idealized reservoirs characterized by intensive parameters $F_3(t_0)$, and next it evolves freely from this initial situation under the action of the total Liouville operator L . Comparison with eqs. (11) and (18) tells us that the integration constant is null and

$$\lim_{t \rightarrow t_0} \int_{t_0}^t dt' w(t, t'; t_0) \log \rho_{cg}(t', t' - t) = \log \rho_{cg}(t_0, 0) \quad .$$

This is verified for the cases of eqs. (19), (20) and (21), and holds for any w such that

$$\text{i) } \lim_{t \rightarrow t_0} \int_{t_0}^t dt' w(t, t', t_0) = 1 \quad ,$$

which is a straightforward consequence of the properties (a) and (b) of w , and

ii) w tends to zero when W tends to 1 (τ^{-1} , E , and a go to zero in eqs. (19)-(21))

i.e. w behaves as a singular kernel in the limits of time going to the initial time t_0 and w to zero.

Thus, the infinitesimal source on the right hand side of Liouville equation (22) ensures the breaking of time-reversal symmetry and evolution of the nonequilibrium many-body system from the initial condition determined by $\rho_{cg}(t_0, 0)$.²³

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Resumo

São discutidos aspectos teóricos envolvidos no tratamento de sistemas de muitos corpos afastados do equilíbrio. Consideramos, em detalhe, o método do operador estatístico de não-equilíbrio. Usando o formalismo da maximização da "entropia" juntamente com uma hipótese *ad hoc*, desenvolvemos um método para obter operadores estatísticos de não-equilíbrio. Nosso tratamento recupera, como casos particulares, os operadores de Green-Morí e de Zubarev. Descrevemos sumariamente a conexão com a Termodinâmica Generalizada e a construção das equações de transporte não-lineares.