Generalization of the Boltzmann Approach in an Inforrnational Statistical Mechanics

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A statistical mechanical formalism, namely the nonequilibrium statistical operator method, admits a construction based on a variational principle associated to an informational theory approach within the context of what is referred to as Jaynes' Predictive Statistical Mechanics. We briefly describe this formalism at tlie classical level of mechanics. On the basis of the formalism it is possible to obtain a nonlinear generalizecl theory of large scope. Shis theory is applied to derive the equations of evolution for the single and two-particle distribution functions, and from them tliere follows a transport equation of the Boltzmann type introducing collisional processes to all order. We discuss the connection with phenomenological irreversible thermodynamics and the question of entropy production and an associated H-theorem

1. Introduction

The purpose of Statistical Mechanics of systems away from equilibrium is to determine their thermodynamic properties and the evolution in time of macroscopic observables of such systems in terms of tlie dynamical laws which govern tlie motioii of tlieir constitutive elements. The analysis of nonequilibrium systems presents far greater difficulties than those faced in the theory of equilibrium systems. This is mainly due to the fact that it is necessary a more detailed discussion to determine the temporal dependence of measurable properties, and to calculate the time-dependent (i.e. depending on the evolving macrostate of the system) and space-dependent transport coefficients associated with the irreversible processes that take place in these systems. It has been stated[1] that the basic goals of nonequilibrium statistical mechanics are: (i) to derive transport equations and to unclerstand tlieir structure; (ii) to understand how the approacli to equilibrium occurs in isolated natural systems; (iii) to study the properties of steady states; and (iv) to calculate the instantaneous values and tlie temporal evolution of tlie physical quantities which specify the macroscopic state of the system.

Nonequilibrium statistical mechanics has typically followed two directions: (1)The kinetic theory of dilute gases, where starting with a few, albeit controversial, liypotheses, one obtains a clescription of how simple systems evolve and approach equilibrium (the celebrated Boltzmann'ç transport theory and H-theorem). An extension of these ideas to dense systems follows several paths like, for example, the construction of a generalized theory of kinetic *equations*[2] and the equations of the BBGKY hierarchy[3]. (2) A generalization of tlie Brownian inotion, where the complicated dynamic equations - the generalized Newton-Langevin equations - that follows from tlie laws of Mechanics are accompanied by statistical assumptions. Belonging to this approacli are, for example tlie formalism of the correlation functions due to Mori[4], and the master equation method[5].

The approaches used to develop a theory encompassing tlie program described by items (i) to (iv) stated above, have been classified by Zwanzig[1] as: (a) intuitive techniques; (b) techniques based on the generalization of the kinetic theory of gases; (c) techniques based on tlie theory of stochastic processes; (d) expansions from an initial equilibrium ensemble; (e) generalizations of Gibbs' ensemble algorithm.

The last of them, viz. item (e), the so called

Nonequilibrium Statistical Operator Method (NSOM) is considered[1] to have an appealing structiire and seems to be a. very effective technique to deal with a large class of experimental situations. This formalism lias been formulated by several autliors, either using lieuristic arguments[6-9] or projection operator techniques[10-12]. These approaches can be brought togetlier under a unifying variational method[13]. Tlie present paper is clevoted to a description of tlie NSOM at the classical mechanical level, in order to try clarify its tenets and to provide within its coiitext a. generalization of Boltzmann transport approacli. I-Ience, tlie NSOM can be considered as a far-reaching generalization of statistical methods based on Boltzmann and Gibbs ideas.

Tlie organization of the paper is as follows: in tlie next sectioii we describe the construction of tlie classical nonequilibrium statistical operator, hence to be called tlie nonequilibrium statistical distribution (NSD), within tlie context of Jaynes' Predictive Statistical Mechanics[14], through tlie use of tlie formalism of tlie maximization of tlie statistical/informational entropy. Section III is clevoted to a brief description of tlie construction of a generalized transport tlieory based on tlie NSD built in section II. In section TV tlie transport theory of section III is used to derive tlie equation of evolution for tlie single-particle distribution, i.e. a generalized Boltzmann-like equation. In section V we consider thermodynamical aspects of the interacting gas of particles as clescribed by tlie NSOM. In last section we summarize tlie content of tlie paper.

II. Tlie nonequilibrium statistical distribution

When one resorts to a statistical mechanical approach like tlie NSOM, here in a classical description, as it is well known tlie macroscopic state of the system is described by a contracted descriptioii in terms of some set of dynamical variables, say $P_1(\Gamma)$, $P_2(\Gamma),...P_n(\Gamma)$, with tlie statistical distribution being a functional of tliese and only tliese variables, where Γ is a point in phase space characteriziiig tlie state of the system at tlie microscopic mechanical level. On the other hand, the state of the system at the macroscopic level is characterized by a poiiit in tlie thermodynamic phase space (soinetimes called Gibhs space or state space) composed by tlie values at time t of tlie macroscopic variables $Q_1(t),...,Q_n(t)$, that are tlie average values of the P_j in the macrostate defined by the NSD. It should be noted that quantities P_j and Q_j can depend on a space variable, namely in the case when they are densities, and also on a. momentum variable as in tlie case to be considered in section IV. Tlie quantities P_j change in time with the inicroscopic evolution of the mechanical state of tlie system, but an experiment does not follow tliis rnicroscopic evolution; it follows the numerical values of tlie Q_j. The result of such experiment are described by transport equations of the form[1]

$$\frac{\partial}{\partial t}Q_j(\vec{r},t) = \Phi_j\{Q_1(\vec{r},t),...,Q_n(\vec{r},t);\vec{r},t\}\ , \quad (1)$$

where we have explicitly introduced tlie possible space dependence of tlie basic variables, witli tlie Φ_j being functionals of the macrovariables Q_j, which, in general, are expected to be nonlinear, nonlocal, and with memory effects, i.e. depending on tlie past history of tlie macroscopic state of the systein from time t_0 of initiation of tlic experiment up to time t when a measurement is performed.

These coiisiclerations rise immediately several questions tliat need be addressed[1]: (1) How to choose tlie basic variables? At present there seems to be no wholly satisfactory theory to generate this information allowing to make a. unique decision. It lias been snggested tliat this basic set of variables must include all approximate integrals of motion or quasi-invariant variables tliat change very slowly on a molecular time scale, as it is the case in NSOM as we sliall see. (2) How are tlie functionals in Eq. (1) obtained? or, in other words, wliat is the form of tlie nonlinear transport equations for macrovariables Q_j? Sliere are several approaches available associated to the different tecliniques corresponding, following Zwanzig[1], to the items (a) to (e) listed in tlie Introduction. In tlie NSOM tlie answer is straightforward: oiice tlie NSD is given the equation of evolution is tlie statistical average of the mechanical equation of motion, as sliall be described in next section. (3) The question of initial conclitions. The equations of evolution, Eqs. (1), are of first order in tlie time derivative and tlierefore require an initial condition for a unique solution to be obtained. Many times this is clone using initial conditions that appear reasonable and well suited to theoretical analysis. Tlie

ideal should be to have experimental access to these values, but this is selclom feasible. Thus, in any particular problem the sensitivity of the results to the details of tlie chosen initial state needs be carefully considered. Finally, it should be noticed that for isolated systems the NSD satisfies Liouville equation, which is reversible. This poses another fundamental question: (4) How to obtain irreversible behavior in the evolution of the macroscopic state of the system (sometiines referred to as the time-arrow problem[15])?. In NSOM, as shown later on, irreversibility is incorporated from the outset using an *ad hoc* non-mechanical hypothesis much in the way of a simulation of Prigogine's principle of dynamic condition for dissipativity[16].

Insofar we have stated the four main clifficulties associated to the construction of a statistical mechanical formulation for nonequilibrium processes, but we have not discussed the fundamental question of how to build the NSD, i.e. the classical level of tlie NSOM. As noted in the Introduction, several approaches have been developed, which can be encompassed in a unique variational approach, which we proceed to describe and discuss. As previously stated it can be related to tlie method of reasoning put forward in Jaynes' Predictive Statistical Physics[14]. Also according to Jaynes, the difficulty of prediction from microstates lies in our lack of the inforination needed to apply them, since we never know the microstate but a few aspects of tlie macrostate. However, tlie aforementioned principle of reproducibility implies that this shoulcl be enougli: tlie relevant information is there, if only we can see how to recognize it and use it.

This makes tlie connection witli questions **(1)** to **(3)** stated previously concerning the query related of the contraction of information and the choice of the macrovariables Q_j. At this point we can make contact with tlie relevant Bogoliubov's principle of correlation weakening[17], implying tliat there exists a hierarchy of relaxation times tliat leads to successive contractions in the macroscopic description of tlie system as it evolves in time. This principle is at the core of tlie NSOM.

The technical problem of construction of the NSD was enunciated by Jaynes as how shall we use probahility theory to help us do plausible reasoning in situations where, because of incomplete information, we cannot use deductive reasoning. This implies in how to obtain tlie probability assignment compatihle with the available information and avoiding unwarrantecl assumptions. As repeatedly emphasized by Jaynes this amounts to perform Bayesian inference[18]. The question is answered by tlie criterion that: the least biased probability assignnient $\{\|_i\}$ for a set of mutually exclusive events $\{x_j\}$ is the one that maximizes the statistical "entropy"

$$S = -\sum_i \|_i \ln \|_i \ , \tag{2}$$

subjected to the constraints imposed by available information. This is the result of assuming that tlie expression of Eq. *(2)* - which lias a similar form in Shannon's[19] so-called information entropy - is a unique function measuring tlie uncertainty of the probahility assignment. The criterion stated above is the principle of *maximization of* statistical entropy, or *MaxEnt* for short.

This is the variational principle that provides a unifying theoretical framework to tlie NSOM. Let us consider a nonequilibrium many-body system which is tlie object of a given experiment, whose contracted description is made iii terms of a basic set of classical dynamical quantities $\{P_j(\Gamma)\}$, $j = 1, 2, ..., \mathrm{n}$, where, for the sake of simplicity, we omit to write down explicitly the eventual dependence on the space coorclinate $\vec{r}$ when tliese quantities are local densities. In this case, if we write $\rho(\Gamma|t)$ for tlie NSD, tlie equivalent of Eq. *(2)* is Gibbs' statistical entropy, namely

$$S_G(t) = -\int d\Gamma \rho(\Gamma|t) \ln \rho(\Gamma|t) \ , \tag{3}$$

witli p defined in tlie interval (t_0, t) and normalized at all times, i.e

$$\int d\Gamma \rho(\Gamma|t') = 1 \ , \ \text{for } t_0 \leq t' \leq t \ . \tag{4}$$

Here $\mathbf{\Gamma} = \{q_1, ..., q_{\nu N}, p_1, ..., p_{\nu N}\}$ is a point in phase space, q and p are the generalizecl coorclinate and conjugated momentum, N the number of particles and ν the number of internal degrees of freedom of each particle. Further we write $d\Gamma = \Pi dq_j \ \Pi dp_j / N! h^{\nu N}$ for indistinguishable particles and h is the usual scaling factor with dimension of sction.

Following MaxEnt we obtain the best choice for tlie NSD $\rho(\Gamma|t)$ looking for an extreme (maximum) of

Gibbs' entropy under the constraints of Eq. (4) and the conditions

$$Q_j(t') = \int d\Gamma \rho(\Gamma|t') P_j(\Gamma) \ , \tag{5}$$

for t $\leq t' \leq$ t.

Clearly, as stated, tliis implies that a choice of tlie basic variables lias been performed; we will return to this question later on. Eqs. (5) introduce a dynamical character in the imposed information, but it ought to be remarlzed that the information-gatliering interval (t_0, t) can (and should) be reduced to information recorded at a unique time, namely t_0, when are given the initial values $Q_j(t_0)$, to be used in the solution of the equations of evolution for variables $Q_j(t)$ that the method provicles, as shown in next section.

Following well known procedures, namely tlie method of Lagrange inultipliers, to solve the variational problem with constraints, we fiiid that

$$\rho(\Gamma|t) = \exp\left\{-\psi(t) - \sum_{j=1}^{n} \int_{t_0}^{t} dt' \varphi_j(t,t') P_j(\Gamma|t' - t)\right\} \ , \tag{6}$$

where ψ is the Lagrange multiplier that ensures the normalization of ρ, tliat is

$$\psi(t) = \ln \int d\Gamma \exp\left\{-\sum_{j=1}^{n} \int_{t_0}^{t} dt' \varphi_j(t,t') P_j(\Gamma|t' - t)\right\} \ , \tag{7}$$

and the φ_j are Lagrange multipliers associated to the conditions imposed by Eqs. (5). In Eq. (6) we have written

$$P_j(\Gamma|t' - t) = e^{i(t'-t)\mathcal{L}} P_j(\Gamma) \ , \tag{8}$$

where C is the Liouville operator of tlie system, meaning in this classical limit tliat $i\mathcal{L}A = \{A, \mathrm{H}\}$, where tlie last term is Poisson's bracket of quantity A witli tlie system Hainiltonian H.

Next, we malte an extra assumption, nainely tliat tlie Lagrange multipliers φ_j are of tlie forin

$$\varphi_j(t,t') = w(t,t') F_j(t') \ , \tag{9}$$

where w is an auxiliary weight function witli tlie following properties: given $w(t,t') = dW(t,t')/dt'$ it must be verified that

$$\lim_{t \to t'} W(t,t') = 1 \ , \tag{10a}$$

$$\lim_{t \to t_0'} W(t,t') = 0 \ , \tag{10b}$$

$$\lim_{t \to +0} \int d\Gamma \rho_w(\Gamma|t) A(\Gamma) = < A|t > \ , \tag{10c}$$

where in Eq. (10c) $< A|t >$ stands for the average value of quantity A ancl it needs be kept in mind tliat the limit is taken after tlie calculation of tlie integral, i.e., the regular average is followed by the limit, what introduces Bogoliubov's method of quasi-averages[20], and tlie thermoclynamic limit is implicit. Bogoliubov's quasi-averages method involves a symmetry-breaking procediire in case of degeneracies connected witli one or severa1 transformation groups. In the present case the syminetry breaking is tliat of time-reversal symmetry, where tlie presence of w selects the sub-group of retarded solutions from the total group of solutions of Liouville equation establishing from the outset evolution for increasing times from an initial value condition, as shall be better clarify later on in this section. Finally, we have used the notation ρ_w for tlie NSD for a given choice of w, the latter satisfying the conditions imposed by Eqs. (10).

The particular form of tlie Lagrange multipliers as given by Eqs. (9) lias been made, on tlie one hand to force irreversible behavior in the evolution of the macroscopic state of the system (as previously noticed it is one tliat mimics Prigogine's principle of dynamic condition for dissipativity). Furtlier, such choice allows (1) to introduce tlie set of variahles $F_j(t)$ that have the role of intensive variables tliermodynarnically con-

jugated to the extensive macróvariables Q_j(t) in order to generate a complete connection with phenomenological irreversible thermodynamics[13,21], and (2) to fix an initial condition from which proceeds the irreversible evolution of the macrostate of the system. To specify such condition it may be noticed that using Eq. (9) in the expression (6), we find that

$$\rho_w(\Gamma|t) = \text{enp}\left\{\int_{t_0}^{t} dt' w(t,\text{t}') \ln \bar{\rho}(\Gamma|t', t' - \text{t})\right\} \quad , \quad (11)$$

where it has been introduced an auxiliary NSD $\bar{\rho}$ given by

$$\bar{\rho}(\Gamma|t_1, t_2) = \exp\left\{-\phi(t_1) - \sum_{j=1}^{n} F_j(t_1) P_j(\Gamma|t_2)\right\} \quad , \quad (12)$$

where t_1 refers to the time dependence of variables ϕ and F_j, and t_2 to the time dependence of quantities P_j as given by Eq. (8). Moreover, ϕ is defined by the relation

$$\psi(t) = \int_{t_0}^{t} dt' w(t,t') \phi(t') \quad (13)$$

Integration by parts in Eq. (11) and using the properties (10) allow us to alternatively write

$$\ln \rho_w(\Gamma|t) = \ln \bar{\rho}(\Gamma|t,0) - \int_{t_0}^{t} \text{dt}^{1} \text{W}(\text{t},\text{t}^{1}) \frac{d}{\text{dt}'} \ln \bar{\rho}(\Gamma|t' - t' - t) \ , \quad (14)$$

Hence the initial condition is

$$\rho_w(\Gamma|t_0) = \bar{\rho}(\Gamma|t_0, 0) \quad (15)$$

Furthermore, Eq. (14) leads to the fact that the NDS can be separated into two parts, namely

$$\rho_w(\Gamma|t) = \bar{\rho}(\Gamma|t_0, 0) + \rho'_w(\Gamma|t) \ , \quad (16)$$

where $\bar{\rho}$ is the auxiliary distribution of Eq. (12), and

$$\rho'_w(\Gamma|t) = \sum_{k=1}^{\infty} \frac{1}{k!} \left[-\int_{t_0}^{t} dt' W(t,t') \frac{d}{dt'} \ln \bar{\rho}(\Gamma|t' - t' - t)\right]^k \bar{\rho}(t,0) \ . \quad (17)$$

Eq. (16) indicates that the NSD is composed of an instantaneous (*"frozen"*) generalized Gibbsian distribution, plus a deviation that accounts for the microscopic processes that produce the dissipative effects in the system[6-10], to be evidenced in next sections.

The initial condition of Eq. (15) amounts then to an initial description (preparation) of the system neglecting all previous (to time t_0) correlations among the basic variables. The connection with the approaches that resort to projection operator techniques follows from the identification of a time-dependent projection operator $P(t)$ such that[10-12]

$$\bar{\rho}(\Gamma|t,0) = P(t)\rho_w(\Gamma|t) \ ;$$

$$\bar{\rho}'_w(\Gamma|t) = [1 - P(t)]\rho_w(\Gamma|t) \ .$$

Finally, to complete the method it is introduced the *coarse-graining condition* defined by

$$\begin{aligned} Q_j(t) &= \int d\Gamma \rho_w(\Gamma|t) P_j(\Gamma) = \\ &= \int d\Gamma \bar{\rho}(\Gamma|t,0) P_j(\Gamma) \end{aligned} \quad (18)$$

which, on the one hand, defines the thermodynamic functions F_j(t) in complete accord with nonequilibrium phenomenological thermodynamics[13,21] and also ensures, together with the conditions (10), the simultaneous normalization of ρ_w and $\bar{\rho}$, i. e. it is verified

that

$$\phi(t) = \ln \int d\Gamma \exp\left[-\sum_{j=1}^{n} F_j(t) P_j(\Gamma)\right] . \qquad (19)$$

The MaxEnt-NSD thus obtained can be shown to satisfy a Liouville equation with a so-called Boltzmann-Prigogine symmetry, namely a Liouville equation with infinitesimal sources that breaks its otherwise time-reversal symmetry. Using Eqs. (10) and definition (13) we obtain that

$$\left[\frac{\partial}{\partial t} + i\mathcal{L}\right] \ln \rho_w(\Gamma|t) = R_w(t) \ln \rho_w(\Gamma|t) . \qquad (20)$$

where we have defined

$$R_w(t) \ln \rho_w(\Gamma|t) = w(t,t') \ln \bar{\rho}(\Gamma|t,0) + \\ + \int_{t_0}^{t} dt' \frac{\partial w}{}$$

Eq. (20) can also be written in the form proposed by Prigogine[22], namely

$$\left[\frac{\partial}{\partial t} + i\Lambda_w\right] \ln \rho_w(\Gamma|t) = 0 , \qquad (22)$$

where A is a modified Liouville operator composed of even and odd parts under time-reversal, i.e. $i\Lambda = i\mathcal{L} - R$.

Consider a dynamical quantity $A(\Gamma)$; in the NSOM its average value is given by the expression [Cf. Eq. (10c)]

$$< A|t >= \int d\Gamma A(\Gamma) \exp\left\{\int_{t_0}^{t} dt' w(t,t') \ln \bar{\rho}(\Gamma|t' - t' - t)\right\} , \qquad (23)$$

being implied the limit of w going to zero. This is akin to a generalization of Kirkwood's time-smoothing theory of measurement[24] that requires the identification of a macroscopic quantity through a time-smoothing-like procedure as in Eq. (23), when the macroscopic state is changing with time. It implies a two step operation: the statistical average from an initial distribution followed by the weighted time average up to the time a measurement is performed. It ought to be noticed that in the NSOM the time-smoothing procedure involves a kind of convolution in time - present in $\bar{\rho}$ in Eq. (23) - connecting the values of the thermodynamic parameters (Lagrange multipliers) $F_j(t')$ at time t' with the values of the dynamical basic variables $P_j(t' - t)$ at the shifted time $t' - t$. Further, using Eq. (16) we can alternatively write

$$< A|t >=< A|t >_0 + < A|t >' , \qquad (24)$$

where

$$< A|t >_0 = \int d\Gamma \bar{\rho}(\Gamma|t,0) A(\Gamma) , \qquad (25a)$$

$$< A|t >' = \int d\Gamma \rho'_w(\Gamma|t) A(\Gamma) , \qquad (25b)$$

implying that the average value of quantity A is composed of two terms, one is the average value with the auxiliary (coarse- grained non-dissipative) distribution $\bar{\rho}$ and the other associated to the dissipative effects through ρ'_w. (We recall that for the basic variables P_j the contribution given by Eq. (25b) is null: (Cf. Eqs. (18) and the arguments thereafter)

Already proposed NSD's are recovered with particular choices of the weight function $w(t,t')$. Green-Mori NSD[6,23] follows from the choice

$$W(t,t') = 1 - \frac{t - t'}{\tau} , \qquad (26)$$

which satisfies Eq. (10a); Eq. (10b) fixes the initial time at the delay-time $t_0 = t - r$; and to comply with condition (10c) r goes to infinity after the calculations of averages have been performed. Function $w(t,t')$ is $1/\tau$. Zubarev NSD[9] follows from the choice

$$W(t,t') = \exp\{\epsilon(t' - t))\} \qquad (27)$$

which satisfies Eq. (10a); Eq. (10b) requires that $t_0 \to -\infty$; $\epsilon(> 0)$ is an infinitesimal parameter that

goes to zero after the calculation of averages have been performed, thus satisfying condition (10c), where now $w(t,t') = \epsilon \exp\{\epsilon(t'-t)\}$. Other (very many) choices of the weight function w are possible; it should be noticed that these types of w in the time-smoothing procedure of Eq. (11) resemble particular summation procedures in the theory of integral transforms, for example the summation procedures of Fejèr (or Cesaro-1) and Abel in the cases above [Eqs. (26) and (27)][25].

Green-Mori approach implies a time average over interval r, and it is based on the assuinption that correlations damp out in times much smaller than r[']. After the calculation of averages the limit $r \to \infty$ is taken; it lias been argued that this time smoothing procedure leacls to difficulties in the definition of integrals associatecl with transport coefficients[26]. In Zubarev's case we have

$$\ln \rho_\epsilon(\Gamma|t) = \epsilon \int_{-\infty}^{0} dt' e^{\epsilon t'} \ln \bar{\rho}(\Gamma|t+t',t') \,, \tag{28}$$

where we have introduced the change of variable $t' \to t'+t$, and

$$\left[\frac{\partial}{\partial t} + i\mathcal{L}\right] \ln \rho_\epsilon(\Gamma|t) = -\epsilon[\ln \rho_\epsilon(\Gamma|t) - \ln \bar{\rho}(\Gamma|t,0)] \,. \tag{29}$$

In this case lnp, is interpreted as the logarithm of $\bar{\rho}$ evolving freely under Liouville operator C, from time t' up to time t, and then the system undergoes a random transition under the influence of the interaction with the surroundings described by a Poisson clistribution, w, and the NSD is obtained averaging over all t' [27]. It is worth noticing that Eq. (29) can be rewritten in the form proposed by Prigogine, Eq. (22), namely

$$\left[\frac{\partial}{\partial t} + i\Lambda_\epsilon(t)\right] \ln \rho_\epsilon(t) = 0 \,, \tag{30a}$$

with

$$i\Lambda_\epsilon(t) = i\mathcal{L} + \epsilon[1 - \mathcal{P}_\epsilon(t)] \,, \tag{30b}$$

wliere $\mathcal{P}_\epsilon(t)$ is a time-dependent projection operator for the case of Zubarev's approach to the NSOM, which for a general weight function w is

$$\mathcal{P}_w(t)A(\Gamma) = \sum_{i,j=0}^{n} P_i(\Gamma)\tilde{C}_{ij}^{-1}(t)\{P_j(\Gamma); A(\Gamma)|t\} \,, \tag{31}$$

including P_0 as the unit operator and $F_0 = \phi$, and where

$$\tilde{C}_{ij}(t)\{P_j(\Gamma); P_j(\Gamma)|t\} \,, \tag{32a}$$

introducing the super-correlation function for any pair of dynamical quantities A and P given by

$$\{A(\Gamma); B(\Gamma)|t\} = \int d\Gamma A(\Gamma) Y_w(\Gamma) B(\Gamma) \bar{\rho}(\Gamma|t,0) \,, \tag{32b}$$

witli

$$Y_w(\Gamma) = 1 + \sum_{k=1}^{\infty} \frac{1}{k!} \left[-\int_{t_0}^{t} dt' W(t,t') \frac{d}{dt'} \ln \bar{\rho}(\Gamma|t', t'-t)\right]^k \,. \tag{32c}$$

This time-clependent projection operator has the property that, used in conjunction with Eq. (18), projects tbe logarithm of the NSD over the logarithm of the auxiliary distribution, namely

$$\mathcal{P}_w(t) \ln \rho_w(\Gamma|t) = \ln \bar{\rho}(\Gamma|t,0) \,, \tag{33a}$$

since, because of Eqs. (18) and definition (32b), one has that

$$\mathcal{P}_w(t)\ln\bar{\rho}(\Gamma|t,0)=\sum_{i,j=0}^{n}P_i(\Gamma)\tilde{C}_{ij}^{-1}(t)\sum_{k=0}^{n}F_k(t)\{P_j(\Gamma);P_k(\Gamma)|t\}=$$

$$=\sum_{i,j,k=0}^{n}F_k(t)P_i(\Gamma)\tilde{C}_{ij}^{-1}(t)\tilde{C}_{jk}(t)=\sum_{k=0}^{n}F_k(t)P_k(\Gamma)=\ln\ \bar{\rho}(\Gamma|t,0)\ . \tag{33b}$$

$$\{P_k(\Gamma);-\int_{t_0}^{t}dt'W(t,t')\frac{d}{dt'}\ln\bar{\rho}(\Gamma|t',t'-t))|t\}=\int d\Gamma P_k(\Gamma)\rho'_w(\Gamma|t)=0\ . \tag{33c}$$

Concerning the question of the basic set of variables, in the NSOM, following the path set forward among others by Mori[4], Zubarev[9], and Peletminskii[8], the choice of the basic set of dynamical quantities $\{P_j\}$ is connected with the separation of the total Hamiltonian of the system into two parts, say

$$H=H_0+H'\ , \tag{34}$$

where H_0 is a "relevant" part composed of tlie Hamiltonians of the free subsystems and some of tlie interactions, namely those interactions strong enough to have associated *very short relazation times* and possessing certain symmetry properties. By very short relaxation times is meant those much smaller than the characteristic time scale of the experiment, typically, the instrumental resolution time. The other term, H', contains the interactions related to *long-time relaxation mechanisms.* The symmetry characteristics of the strong interactions depend on tlie problem under consideration: The required symmetry, to be called *Zubarev-Peletminskii symmetry condition,* is that

$$\{P_j,H_0\}=\sum_k\alpha_{jk}P_k \tag{35}$$

where α_{jk} are c-numbers determined by H_0. It can be generalized to the case of locally dependent quantities, say $P_j(\vec{r})$, when coefficients α are allowed to be differential operators.

The Peletminskii-Zubarev relation provides a closure condition for the choice of the basic set of variables: First, the secular part H_0 of the Hamiltonian has to be chosen in each particular problem under consideration (as noted, it contains the kinetic energies plus the interactions strong enough to produce damping of correlations in times smaller than that of the experimental resolution time). Second, one introduces a few dynamical variables P deemed relevant for the description of the physical problem in hands, and next the Poisson bracket with H_0 is calculated. The dynamical variables - different from those already introduced - that appear in the linear combination indicated by the right-hand-side of Eq. (35) are incorporated to tlie basic set. This procedure is then repeated until a closure is attained. In Eq. (35) the particular case of coefficients α being zero is admisible, that is, dynamical quantities conserved under the dynamics generated by H_0 are to be included, and that implies the presente of H_0 itself. Recently L.S. Garcia-Colin and two of the present authors[21] have discussed how this procedure provides statistical mechanical foundations to the questiou of the choice of basic variables in phenomenological irreversible thermodynamics, arid its role as a generalization of Grad's[28] moments approach. As shown in the second of references 21, in certain circumstances the closure procedure does not follow in a finite number of steps and then an appropriate truncation procedure needs be introduced. In summary, Peletminskii-Zubarev closure condition implies in taking into account all dynamical quantities that, under the dynamics generated by H_0, are kept in the subspace of Hilbert space spanned by tliem. Their equations of motion contain collision operators (see next section) generated by H' that are the manifestation of tlie microscopic degrees of freedom that are suppressed in the coarse-graining procedure that tlie method involves. As a final word we recall that the process of separation is based upon the existence of a distinct hierarchy of

time scales in Bogoliubov's sense[17].

We proceed next to describe the nonlinear generalized transport theory that can be derived from the MaxEnt-NSOM that was outlined in this section.

III. NSOM-nonlinear generalized transport theory

Transport phenomena in matter have been treated for a long time within the framework of Boltzmann transport theory, which constitutes a landmark in the field of statistical mechanics, providing deep conceptual ideas and a method for the mathematical handling of the problem[29]. In the area of solid-state physics it yielded a vast number of results, however requiring to be used in conjunction with a quasi-particle picture[30]. The original Boltzmann transport equation is derived using several restrictions on the characteristics of the scattering processes, driving forces, and relaxation effects. Extension of the method requires to incorporate the possibility to deal with dense systems, strong scattering, high intensity external fields, non-local scattering processes, strong relaxation effects, quantal effects of driving fields, etc. These questions have been addressed by many authors, and a concentration of efforts have been directed towards the aim of deriving elaborate transport theories[31]. We proceed here to show that the MaxEnt-NSOM allows for the construction of a nonlinear transport theory of large scope.

In NSOM the equations of evolution for the variables follow immediatly from time differentiation of Eqs. (18) to obtain

$$\frac{\partial}{\partial t}Q_j(\vec{r},t) = \int d\Gamma \rho_w(\Gamma|t)\{P_j(\Gamma;\vec{r}), H(\Gamma)\} \equiv < \{P_j(\Gamma;\vec{r}), H(\Gamma)\}|t > \tag{36}$$

Using Eq. (34) and the closure condition of Eq. (35), the contribution to the last term in Eq. (36) from the "relevant" part of the Hamiltonian, viz. H_0, becomes

$$< \{P_j(\Gamma;\vec{r}), H_0(\Gamma)\}|t >= \int d\Gamma \bar{\rho}(\Gamma|t,0)\{P_j(\Gamma;\vec{r}), H_0(\Gamma)\} \equiv J_j^{(0)}(\vec{r},t)\ , \tag{37}$$

once it is taken into account the coarse-graining condition of Eq. (18). Further, using the separation of p given by Eq. (16), we obtain that

$$\frac{\partial}{\partial t}Q_j(\vec{r},t) = J_j^{(0)}(\vec{r},t) + J_j^{(1)}(\vec{r},t) + \mathcal{J}_j(\vec{r},t)\ , \tag{38}$$

where $J_j^{(0)}$ is defined by Eq. (37), and

$$J_j^{(1)}(\vec{r},t) = \int d\Gamma \bar{\rho}(\Gamma|t,0)\{P_j(\Gamma;\vec{r}), H'(\Gamma)\} \tag{39a}$$

$$\mathcal{J}_j(\vec{r},t) = \int d\Gamma \rho'_w(\Gamma|t)\{P_j(\Gamma;\vec{r}), H'(\Gamma)\}\ . \tag{39b}$$

Clearly, $J_i^{(0)}$ is a precession-like term (evolution of P_j under H_0) while the others are related to tlie slow dynamical effects produced by the interactions contained in H'. As we shall see in section V, $\mathcal{J}$ is a collision integral associated to dissipative processes, on the other hand $J^{(0)}$ as $J^{(1)}$ - which are averages with the auxiliary distribution $\bar{\rho}$ - are dissipationless terms.

Use of Eq. (17) in Eq. (39b) leads us to rewrite the collision integral in a series of contributions of partial collision integrals, namely

$$\mathcal{J}_j(\vec{r},t) = \sum_{k=1}^{\infty}\int_{t_0}^{t} dt' W(t,t')(\{P_j(\Gamma;\vec{r}), H'(\Gamma)\}; \hat{\sigma}(t',t'-t)|t)^{(k)}\ , \tag{40}$$

where we have defined

$$(\{P_j(\Gamma;\vec{r}),H'(\Gamma)\};\hat{\sigma}(t',t'-t)|t)^{(k)}=\frac{1}{k!}\int d\Gamma\{P_j(\Gamma;\vec{r}),H'(\Gamma)\}\hat{\sigma}(\Gamma|t',t'-t)$$

$$\times\int_{t_0}^{t}dt_1W(t,t_1)\hat{\sigma}(\Gamma|t_1,t_1-t)...\int_{t_0}^{t}dt_{k-1}W(t;t_{k-1})\hat{\sigma}(\Gamma|t_{k-1},t_{k-1}-t)\bar{\rho}(\Gamma|t,0)\ , \tag{41a}$$

with

$$\hat{\sigma}(\Gamma|t',t'-t)=-\frac{d}{dt'}\ln\bar{\rho}(\Gamma|t',t'-t)\ . \tag{41b}$$

Since the average value of $\hat{\sigma}(\Gamma)$ is the NSOM-entropy-production function (see section V), the collision integral hecomes a series of contributions of liiglier and higher order in the dissipation processes that develop in the system while in nonequilibrium conditions. This collision integral is extremely clifficult to handle; we anticipate (to he shown in a forthcoming article specified for tlie case of a classical system[32], that $\mathcal{J}$ can he rewritten in a practical and relatively manageahle way through tlie use of the symmetry condition of Eq. (35) in the form

$$\mathcal{J}_j(\vec{r},t)=\sum_{n=2}^{\infty}J_j^{(n)}(\vec{r},t) \tag{42}$$

Here, $J_j^{(n)}$ are partial contributions tliat are of the form of correlations over the auxiliary distribution $\bar{\rho}$, which are instantaneous in time and organized in increasing order n in the interaction strengths included in H'. It is worth noticing that these contributions are composed of several terms, consisting of (1) the mechanical effects of collisions (in order n) averaged over tlie auxiliary ensemble. (2) terms that account for the evolution of the thermodynamic state of the system, and (3) terms arising from inemory effects.

We proceed next to apply this NSOM-generalized transport theory for classical systems to obtain the equation for tlie single-particle distribution function, in order to arrive at a generalized Boltzmann equation.

IV. Generalized Boltzmann-type formalism

Let us consider a system of $\mathcal{N}$ interacting particles whose Hamiltonian is

$$\begin{aligned}H &= \int d^3rd^3p\left[\frac{p^2}{2m}+v(\vec{r},t)\right]n_1(\Gamma|\vec{r},t\vec{p})+\\ &+ \int d^3rd^3pd^3p'd^3p,V(|\vec{r}-\vec{r}\,'|)n_2(\Gamma|\vec{r}.\vec{p},\vec{r}\,',\vec{p}\,')\ ,\end{aligned} \tag{43}$$

where we call H_0 the part containing the ltinetic energy and H' includes the interactions hetween particles through the central force two particle potential V, and v is the interaction with externa1 sources, to have the separation of H into two parts as required hy Eq. (34). Here n_1 and n_2 are the one-particle and two-particle density matrices, namely

$$n_1(\Gamma|\vec{r},\vec{p})=\sum_{j=1}^{\mathcal{N}}\delta(\vec{r}-\vec{r}_j)\delta(\vec{p}-\vec{p}_j)\ , \tag{44a}$$

$$n_2(\Gamma|\vec{r},\vec{p},\vec{r}\,',\vec{p}\,')=\sum_{j\neq k=1}^{\mathcal{N}}\delta(\vec{r}-\vec{r}_j)\delta(\vec{p}-\vec{p}_j)\delta(\vec{r}\,'-\vec{r}_k\,')\delta(\vec{p}\,'-\vec{p}_k\,')\ . \tag{44b}$$

For the statistical description of this system in NSOM we choose as basic dynamical variahles H_0, n_1, and n_2. They satisfy the closure condition of Eq. (34) since the Poisson bracket of H_0 with itself is null, and

$$\{n_1(\Gamma|\vec{r},\vec{p},H_0) = -\frac{1}{m}(\vec{p}\cdot\nabla)n_1(\Gamma|\vec{r},\vec{p}) \ , \tag{45a}$$

$$\{n_2(\Gamma|\vec{r},\vec{p};\vec{r}\,',\vec{p}\,')H_0\} = -\frac{1}{m}(\vec{p}\cdot\nabla+\vec{p}\,'\cdot\nabla')n_2(\Gamma|\vec{r},\vec{p},\vec{r}\,',\vec{p}\,') \ , \tag{45b}$$

As it was remarked in section II there is no wholly satisfactory way to make a unique choice of the basic variables. The choice we have made here is of course a truncated one involving on the one hand H_0, as a consequence of taking into account the closure condition of Eq. (34), implying to consider quantities that are quasi-conserved under the dynamics generated by H_0 (we recall that relaxation processes are related to H'), and besides it the one-particle and two-particle density matrices since they are the two that take part in the calculation of any property of the system involving individual particles or two-particle correlations.

The auxillary probability distribution is then

$$\bar{\rho}(\Gamma|t,0) = \exp\left\{-\phi(t) - \beta(t)H_0 + \int d^3r d^3p \varphi_1(\vec{r},\vec{p};t)n_1(\Gamma|\vec{r},\vec{p}) + \right.$$
$$\left. \int d^3r d^3p d^3r', d^3p' \varphi_2(\vec{r},\vec{p},\vec{r}\,',\vec{p}\,';t)n_2(\Gamma|\vec{r},\vec{p};\vec{r}\,',\vec{p}\,')\right\} \tag{46}$$

where, we recall, ϕ ensures the normalization of $\bar{\rho}$, and β, φ_1 and φ_2 are the Lagrange multipliers (intensive nonequilibrium thermodynamic variables) conjugated to the basic macrovariables, which we call

$$U_0(t) = < H_0(\Gamma)|t> \ , \tag{47a}$$

$$f_1(\vec{r},\vec{p};t) = < n_1(\Gamma|\vec{r},\vec{p})|t> \ , \tag{47b}$$

$$f_2(\vec{r},\vec{p},\vec{r}\,',\vec{p}\,';t) = < n_2(\Gamma|\vec{r},\vec{p};\vec{r}\,'\vec{p}\,')|t> \ , \tag{47c}$$

where $< ...|t >$ stands for statistical average calculated with the NSD given by Eq. (46), and we recall that the basic variables satisfy the condition required by Eq. (18).

We proceed next to derive their equations of evolution; they are [Cf. Eqs. (38)]

$$\frac{d}{dt}U_0(t) = J_0^{(0)}(t) + J_0^{(1)}(t) + \mathcal{J}_0 \ , \tag{48a}$$

$$\frac{\partial}{\partial t}f_1(\vec{r},\vec{p};t) = J_1^{(0)}(\vec{r},\vec{p};t) + J_1^{(1)}(\vec{r},\vec{p};t) + \mathcal{J}_1(\vec{r},\vec{p};t) \ , \tag{48b}$$

$$\frac{\partial}{\partial t}f_2(\vec{r},\vec{p},\vec{r}\,',\vec{p}\,',;t) = J_2^{(0)}(\vec{r},\vec{p},\vec{r}\,',\vec{p}\,';t) + J_2^{(1)}(\vec{r},\vec{p},\vec{r}\,',\vec{p}\,';t) + \mathcal{J}_2(\vec{r},\vec{p},\vec{r}\,',\vec{p}\,';t) \ , \tag{48c}$$

where $\mathcal{J}$ are the collision integrals of Eq. (39b), $J_0^{(0)} = 0$, and

$$J_0^{(1)}(t) = -\int d^3r d^3p d^3r' d^3p' \frac{1}{m}\vec{p}\cdot\nabla V(|\vec{r}-\vec{r}\,'|)f_2(\vec{r},\vec{p},\vec{r}\,',\vec{p}\,';t) \tag{49a}$$

$$J_1^{(0)}(\vec{r},\vec{p};t) = -\frac{1}{m}\vec{p}\cdot\nabla f_1(\vec{r},\vec{p};t) \ , \tag{49b}$$

$$J_1^{(1)}(\vec{r},\vec{p};t) = \int d^3r' d^3p' \nabla[v(\vec{r},t) + V(|\vec{r}-\vec{r}\,'|)] \cdot \nabla_{\vec{p}} f_2(\vec{r},\vec{p},\vec{r}\,',\vec{p}\,';t) \,, \tag{49c}$$

$$J_2^{(0)}(\vec{r},\vec{p},\vec{r}\,',\vec{p}\,';t) = -\frac{1}{m}[\vec{p}\cdot\nabla + \vec{p}\,'\cdot\nabla'] f_2(\vec{r},\vec{p},\vec{r}\,',\vec{p}\,';t) \,, \tag{49d}$$

$$J_2^{(1)}(\vec{r},\vec{p},\vec{r}\,',\vec{p}\,';t) = -\nabla[v(\vec{r},t) + V(|\vec{r}-\vec{r}\,'|)] \cdot (\nabla_{\vec{p}} + \nabla_{\vec{p}\,'}) f_2(\vec{r},\vec{p},\vec{r}\,',\vec{p}\,';t)$$

$$+ \int d^3r_1 d^3p_1 \{\nabla[v(\vec{r},t) + V(|\vec{r}-\vec{r}_1|)] \cdot \nabla_{\vec{p}} + \nabla'[v(\vec{r},t) + V(|\vec{r}-\vec{r}_1\,'|)] \cdot \nabla_{\vec{p}}\} f_3(\vec{r},\vec{p},\vec{r}\,',\vec{p}\,',\vec{r}_1,\vec{p}_1;t) \,, \tag{49e}$$

where f_3 is the average value of the three-particle distribution function, i.e. the average value of the three-particle density rnatrix $n_3(\vec{r},\vec{p},\vec{r}\,',\vec{p}\,',\vec{r}_1,\vec{p}_1)$.

We concentrate next our attention on the equation of evolution for the variable $f_1(\vec{r},\vec{p};t)$, which in explicit form can written as

$$\left[\frac{\partial}{\partial t} + \frac{1}{m}\vec{p}\cdot\nabla + \vec{F}(\vec{r},t)\cdot\nabla_{\vec{p}}\right] f_1(\vec{r},\vec{p};t) = \int d^3r' d^3p' \nabla V(|\vec{r}-\vec{r}\,'|) \cdot \nabla_{\vec{p}} f_2(\vec{r},\vec{p},\vec{r}\,',\vec{p}\,';t) + \mathcal{J}_1(\vec{r},\vec{p};t) \,, \tag{50}$$

where $\vec{F} = -\nabla v(\vec{r},t)$ is the externa1 force imposed on the system. It is coupled to the equation for f_2 which is explicitly given by

$$\begin{aligned}
&\left\{\frac{\partial}{\partial t} + \frac{1}{m}[\vec{p}\cdot\nabla + \vec{p}\,'\cdot\nabla'] - \vec{F}(\vec{r},t)\cdot\nabla_{\vec{p}} - \vec{F}(\vec{r}\,',t)\cdot\nabla_{\vec{p}\,'}\right. \\
&\left. -[\nabla v(|\vec{r}-\vec{r}\,'|)\cdot\nabla_{\vec{p}} + \nabla' V(|\vec{r}-\vec{r}\,'|)\cdot\nabla_{\vec{p}\,'}]\right\} f_2(\vec{r},\vec{p},\vec{r}\,',\vec{p}\,';t) \\
&= \int d^3r_1 d^3p_1 \{\nabla[v(\vec{r},t) + V(|\vec{r}-\vec{r}_1|)]\cdot\nabla_{\vec{p}} \\
&+\nabla'[v(\vec{r}\,',t) + V(|\vec{r}\,'-\vec{r}_1|)]\cdot\nabla_{\vec{p}\,'}\} f_3(\vec{r},\vec{p},\vec{r}\,',\vec{p}\,'\vec{r}_1,\vec{p}_1;t) \\
&+\mathcal{J}_2(\vec{r},\vec{p},\vec{r}\,',\vec{p}\,';t) \,.
\end{aligned} \tag{51}$$

where f_3 is the three-particle distribution function.

Eqs. (50) and (51), together with the equation of evolution for the kinetic energy $U_0(t)$ comprise the complete set of equations of motion for the chosen basic variables in NSOM. We mention that if the basic chosen set of variables is truncated by neglecting n_2, Eq. (50), once the collision integral is neglected, becomes an equation of the form of Vlasov-Landau implying a mean field approximation, since then $f_2(\vec{r},\vec{p},\vec{r}\,',\vec{p}\,';t) = f_1(\vec{r},\vec{p},t) f_1(\vec{r}\,',\vec{p}\,';t)$ [32].

We proceed with the analysis of Eq. (50) introducing several approximations:

1. In Eq. (51) it is neglected the second member, i.e. the collision integral and the term involving ternary interactions;

2. It is taken a weak explicit time dependence of f_2, i.e. $\partial f_2/\partial t \simeq 0$, on account of the fact that neglecting ternary interactions during the binary encounter, two molecules moved unaffected by the rest of the gas, and the relevant time variation should then extend over the duration of a two-body collision.

Hence, after using these approximations Eq. (51) becomes

$$\frac{1}{m}(\vec{p}\cdot\nabla+\vec{p}\,'\cdot\nabla')f_2(\vec{r},\vec{p},\vec{r}\,',\vec{p}\,';t) = \{\nabla[v(\vec{r}-t)+V(|\vec{r}-\vec{r}'|)]\cdot\nabla_{\vec{p}}+ +\nabla'[v(\vec{r}-t)+V(|\vec{r}-\vec{r}\,'|)]\cdot\nabla_{\vec{p}\,'}\}f_2(\vec{r},\vec{p},\vec{r}\,',\vec{p}\,';t)\ , \tag{52}$$

and then, replacing this result in Eq. (50) we obtain that

$$\left\{\frac{\partial}{\partial t}+\frac{1}{m}\vec{p}\cdot\nabla+\vec{F}(\vec{r},t)\cdot\nabla_{\vec{p}}\right]f_1(\vec{r},\vec{p};t)=\int d^3r'd^3p'\frac{1}{m}[\vec{p}\cdot\nabla+\vec{p}\,'\cdot\nabla']f_2(\vec{r},\vec{p},\vec{r}\,',\vec{p}\,';t)\ , \tag{53}$$

which is still coupled to f_2. This latter quantity is the average value of n_2 with $\bar{\rho}$ of Eq. (46), where the auxiliary NSOM $\bar{\rho}$ is composed of terms involving single particles and terms involving two correlated particles. Next we calculate f_2 as composed of a part without correlations plus a part involving them, resorting to the use of Heims-Jaynes perturbation expansion for averages[33] to obtain

$$f_2(\vec{r},\vec{p},\vec{r}\,',\vec{p}\,';t)=f_1^0(\vec{r}\,',\vec{p}\,';t)+\Lambda_2(\vec{r},\vec{p},\vec{r}\,',\vec{p}\,';t) \tag{54}$$

where

$$\Lambda_2(\vec{r},\vec{p},\vec{r}\,',\vec{p}\,';t)=\sum_{n=1}^{\infty}<Q_n\Delta n_2|t>^{(0)}\ , \tag{55a}$$

$$Q_n=S_n-\sum_{k=1}^{n-1}<Q_k|t>^{(0)}S_{n-k}\ , \tag{55b}$$

$$S_n=\frac{1}{n!}\left[\int d^3rd^3pd^3r'd^3p'\varphi_2(\vec{r},\vec{p},\vec{r}\,',\vec{p}\,';t)n_2(\Gamma|\vec{r},\vec{p},\vec{r}\,',\vec{p}\,';t)\right]^n\ . \tag{55c}$$

$$\Delta n_2=n_2-<n_2|t>^{(0)}\ . \tag{55d}$$

Same procedure is used to express f_1 as

$$f_1(\vec{r},\vec{p};t)=f_1^0(\vec{r},\vec{p};t)+\Lambda_1(\vec{r},\vec{p};t)\ , \tag{56}$$

where

$$\Lambda_1(\vec{r},\vec{p};t)=\sum_{n=1}^{\infty}<Q_n\Delta n_1|t>^0\ , \tag{57}$$

with $\Delta n_1=n_1-<n_1|t>^0$, and

$$<\ldots|t>^{(0)}=\int d\Gamma\ldots\bar{\rho}_0(\Gamma|t,0) \tag{58}$$

with

$$\bar{\rho}_0(\Gamma|t,0)=\{\exp-\phi_0(t)-\beta(t)H_0+\int d^3rd^3p\varphi_1(\vec{r},\vec{p};t)n_1(\Gamma|\vec{r},\vec{p})\}\ . \tag{59}$$

with ϕ_0 ensuring its normalization of $\bar{\rho}_0$. Moreover

$$f_1^0(\vec{r},\vec{p};t)=\int d\Gamma\bar{\rho}_0(\Gamma|t,0)n_1(\Gamma|\vec{r},\vec{p})\ , \tag{60}$$

is the one-particle density function in the uncorrelated state described by $\bar{\rho}_0$.

Neglecting the correlations A in Eqs. (54) and (56) implies to express f_2 as factorized in terms of a product of two f_1^0 corresponding to different positions and momenta; such approximation can be considered as the introduction of Boltzmann's Stosszahlansatz, or assumption of molecular chaos. In fact, after these approximations are introduced. Eq. (53) becomes

$$\left[\frac{\partial}{\partial t}+\frac{1}{m}\vec{p}\cdot\nabla+\vec{F}(\vec{r},t)\cdot\nabla_{\vec{p}}\right]f_1^0(\vec{r},\vec{p};t)=\int d^3r'd^3p'\frac{1}{m}\left[\vec{p}\cdot\nabla+\vec{p}\,'\cdot\nabla'\right]f_1^0(\vec{r}\,',\vec{p}\,';t) \tag{61}$$

It ought to be mentioned that Eq. (61) also follows from the BBGKY hierarchy in the uncorrelated particle limit[5,34], and from Kirkwood's time-smoothing approach[24] in the same lirnit.

Next, following the procedures described in the extensive literature on the subject (E.g. [5,34]), Eq. (61) can be brought under the usual form of Boltzmann equation. We recall that the upper naught iridex in f_1^0 indicates the fact that it corresponds to the one-particle distribution function in the uncorrelated limit with assumption of molecular chaos.

Thus, we have shown that the celebrated Boltzmann transport equation is contained as a particular case of the generalized transport theory derived from the MaxEnt-NSOM. In continuation we proceed in following section to discuss the effect of the approximations that were introduced, through the analysis of the resulting nonequilibrium thermodynamic properties of the system, in particular the entropy production that can be defined in MaxEnt-NSOM and Boltzmann approaches, a function of relevance to characterize the irreversible evolution of the system.

As a final word we stress that Boltzmann equation (61) had its origin in Eq. (48b); the latter may then be considered a large generalization of Boltzmann approach, containing in the collision integral $\mathcal{J}_1$ the effects of the interaction potentials in all powers in their strengths. The practical handling of these collision integral~i,e. its form as given by Eq. (42), will be reported in a forthcoming article[32].

V. Entropy production and a generalized $\mathcal{H}$-theorem

The MaxEnt-NSOM provides mechano-statistical foundations to phenomenological irreversible thermodynamics[13,21]. This is done through the definition of a *MaxEnt-entropy* function

$$\bar{S}(t)=-\int d\Gamma\rho_w(\Gamma|t)\ln\bar{\rho}(t,0)\ , \tag{62}$$

in units of Boltzmann constant k, and to be put in correspondence with those defined in phenomenological thermodynamic theories. This definition and the use of the coarse-graining condition of Eq. (18) leads to the relations

$$F_j(\vec{r},t)=\delta\bar{S}(t)/\delta Q_j(\vec{r},t)\ , \tag{63a}$$

$$Q_j(\vec{r},t)=\delta\phi(t)/\delta F_j(\vec{r},t)\ , \tag{63b}$$

formally similar to that obtained in equilibrium. These are nonequilibrium equations of state in the sense that they relate extensive and intensive therrnodynamic variables. We have used the nomenclature of section II and δ stands for functional derivative. Further, using the expression for $\bar{\rho}$ and the coarse-graining condition of Eqs. (18) the MaxEnt-entropy function acquires the form

$$\bar{S}(t)=\phi(t)+\sum_{j=1}^{n}\int d^3rF_j(\vec{r},t)Q_j(\vec{r},t)\ , \tag{64}$$

what defines ϕ as a Massieu-Planck-like functional in nonequilibrium conditions.

Taking into account Eqs.(64) and (63), the *MaxEnt-entropy* production is given by

$$\bar{\sigma}(t) = \frac{d}{dt}\bar{S}(t) = \sum_{j=1}^{n}\int d^3r F_j(\vec{r},t)\frac{\partial}{\partial t}Q_j(\vec{r},t)\ . \quad (65)$$

In Eq. (65) the time evolution of the basic macrovariables is obtained through the use of the generalized transport equations (38). However it should be noticed that

$$\sum_{j=1}^{n}\int d^3r F_j(\vec{r},t)J_j^{(0)}(\vec{r},t) = \sum_{j=1}^{n}\int d^3r F_j(\vec{r},t)\int d\Gamma\{P_j(\Gamma|\vec{r}),H_0(\Gamma)\}\bar{\rho}(\Gamma|t,0) =$$
$$\int d\Gamma\{\ln\bar{\rho}(\Gamma|t,0) = \int d\Gamma\{\bar{\rho}(\Gamma|t,0),\ln\bar{\rho}(\Gamma|t,0)\}H_0(\Gamma) = 0\ , \quad (66)$$

and similarly for the term involving $J_j^{(1)}$. Hence,

$$\bar{\sigma}(t) = \sum_{j=1}^{n}\int d^3r F_j(\vec{r},t)\mathcal{J}_j(\vec{r},t)\ , \quad (67)$$

or,

$$\bar{\sigma}(t) = \sum_{k=1}^{\infty}\int_{t_0}^{t} dt' W(t,t')(\hat{\sigma}(\Gamma|t,0);\hat{\sigma}(\Gamma|t',t'-t|t)^{(k)} \quad (68)$$

after using Eq. (40) and introducing the super-correlation functions defined in Eq. (41).

It should be noticed that $\bar{\sigma}$ is the average of tlie NSOM quantity in phase space $\hat{\sigma}(\Gamma|t,0)$ of Eq. (41b), namely

$$\bar{\sigma}(t) = \int d\Gamma\hat{\sigma}(\Gamma|t,0)[\rho(t,0)+\rho'_w(t)] =$$
$$= \int d\Gamma\hat{\sigma}(\Gamma|t,0)\rho'_w(\Gamma|t)\ , \quad (69)$$

i.e., as already stated in section II there is no dissipation associated to tlie auxiliary (coarse-grained) distribution $\bar{\rho}$. Eq. (69) in conjunction with Eq. (17) allowed us to write Eq. (68). The latter tells us that tlie MaxEnt entropy production function is composed of an infinite series of ever increasing correlations of the MaxEnt-entropy production quantity in phase space, $\hat{\sigma}(\Gamma|t,0)$, allowing for a classification of the dissipative processes in the different orders of correlations of the entropy production quantity.

Looking at the form of tlie scattering integral $\mathcal{J}$ given by Eq. (39b), it is clear that dissipative-entropy-producing effects are described by the contribution ρ'_w to the total statistical distribution in Eq. (16), namely those dissipative effects governed by the interactions in H'.

In phenomenological nonequilibrium thermodynamic theories[35] it is assumed that (for the isolated system or for the interna1 production of entropy) $\sigma(t) \geq 0$, and also for its local expression

$$\bar{\sigma}(\vec{r},t) = \sum_{j=1}^{n} F_j(\vec{r},t)\frac{d}{dt}Q_j(\vec{r},t) \quad (70)$$

At present we are not able to verify this property for the MaxEnt-entropy production (global or local). We can see that it has an extremely complicated expression [Cf. Eq. (68)], but we can prove a *weak principle of* non-negative local informational entropy production, namely that

$$\int_{t_0}^{t} d^3r\int_{t_0}^{t} dt'\bar{\sigma}(\vec{r},t') \geq 0 \quad (71)$$

as demonstrated in the Appendix A.

Let us now look for the case of section IV, when

$$\bar{S}(t) = \phi(t) + \beta(t)U_0(t) - \int d^3r d^3p \varphi_1(\vec{r},\vec{p};t) f_1(\vec{r},\vec{p};t) - \\ - \int d^3r d^3p d^3r' d^3p' \varphi_2(\vec{r},\vec{p},\vec{r}\,',\vec{p}\,';t) f_2(\vec{r},\vec{p},\vec{r}\,',\vec{p}\,';t) \tag{72}$$

and

$$\sigma(t) = \beta(t) + \dot{U}_0(t) - \int d^3r d^3p \varphi_1(\vec{r},\vec{p};t) \dot{f}_1(\vec{r},\vec{p};t) - \\ - \int d^3r d^3p d^3r' d^3p' \varphi_2(\vec{r},\vec{p},\vec{r}\,',\vec{p}\,';t) \dot{f}_2(\vec{r},\vec{p},\vec{r}\,',\vec{p}\,';t) \tag{73}$$

where the upper dots stand for time derivative. Furthermore

$$\sigma(t) = \beta(t)\mathcal{J}_0(t) - \int d^3r d^3p \varphi_1(\vec{r},\vec{p};t) \mathcal{J}_1(\vec{r},\vec{p};t) \\ - \int d^3r d^3p d^3r' d^3p' \varphi_2(\vec{r},\vec{p},\vec{r}\,',\vec{p}\,';t) \mathcal{J}_2(\vec{r},\vec{p},\vec{r}\,',\vec{p}\,';t) \tag{74}$$

since, as shown, the terms $J^{(0)}$ and $J^{(1)}$ do not contribute to entropy production.

Now, resorting to the use of Heims-Jaynes perturbation expansion for averages[33], we can calculate $U_0(t)$, and $f_1(\vec{r},\vec{p},t)$ as composed of a part without correlations plus a part involving them. Consequently Eq. (72) can be written as

$$\bar{S}(t) = \bar{S}^0(t) + \Delta\bar{S}(t) \tag{75a}$$

where

$$\bar{S}^0(t) = \phi^0(t) + \beta^0(t)U_0^0(t) - \int d^3r d^3p \varphi_1^0(\vec{r},\vec{p};t) f_1^0(\vec{r},\vec{p};t), \ , \tag{75b}$$

and $\Delta\bar{S}(t)$ contains the contributions due to two, three, etc., particle correlations. In last equation upper naught indexes stand for the correlationless values. In these conditions the correlationless part of the auxiliary distribution is factorizable, i.e.

$$\bar{\rho}^0(t,0) = \prod_{j=1}^{\mathcal{N}} \exp\left\{-\phi_{(j)}^0 - \beta^0(t)\frac{p_j^2}{2m} + \int d^3r d^3p \varphi_1^0(\vec{r},\vec{p};t) n_1^j(\vec{r},\vec{p})\right\} \ , \tag{76}$$

where $\phi_{(j)}^0$ normalizes each factor and

$$n_1^j(\vec{r},\vec{p}) = \delta(\vec{r} - \vec{r}_j)\delta(\vec{p} - \vec{p}_j) \tag{77}$$

Also, we find for the uncorrelated one-particle distribution function the simple expression

$$f_1^0(\vec{r},\vec{p};t) = \exp\left\{-\phi_1^0(t) - \beta^0(t)\frac{p^2}{2m} + \varphi_1^0(\vec{r},\vec{p};t)\right\} \ , \tag{78}$$

and then the entropy of Eq. (75b) can be written, in this and *only* approximation, as

$$\bar{S}^0(t) = -\mathcal{N}\int d^3r d^3p \tilde{f}_1^0(r,p;t) \ln \tilde{f}_1^0(\vec{r},\vec{p};t) \tag{79}$$

where we wrote $\tilde{f}_1^0 = f_1^0/\mathcal{N}$, and then

$$\sigma^0(\mathrm{t}) = -\frac{d}{dt}\mathcal{H}(t) = \int d^3r d^3p [1 + \ln \tilde{f}_1^0(\vec{r},\vec{p};t)]\frac{\partial}{\partial t}\tilde{f}_1^0(\vec{r},\vec{p};t) \tag{80}$$

Here 3-1 is Boltzmann's 'H-function and, as well known $-d\mathcal{H}/dt[\sigma^0$ of Eq. (80)] is definite positive if for the time evolution of f_1^0 Boltzmann equation is used (viz. Eq. (53) accompanied of Eq. (54) followed by the Stosszahlanzatz of putting $\Lambda_1 = \Lambda_2 = 0$). This is the celebrated $\mathcal{H}$ theorem. The equality holds in the case when detailed balance is satisfied, that is, when the rates of direct and inverse collisions are equal.

'H is minus the expression of Eq. (79) and it is a decreasing function of time, but $-k\mathcal{H}(t) = k\bar{S}^0(t)$ cannot be identified with the entropy of the macroscopic state of an arbitrarily nonequilibrated thermodynamic system, and Eq. (79) is not related to the positive production of thermodynamic entropy. It must also be kept in mind that in ordinary thermodynamic theory the second law refers only to the difference of the values of the entropy between two equilibrium states of any arbitrary isolated system when goes through a transition between two such states, but says nothing on how the entropy production evolves in between: this is what implies Eq. (71) for the MaxEnt-entropy production.

Boltzmann equation was derived within the frame of MaxEnt-NSOM from the terms $J^{(0)}$ and $J^{(1)}$ (neglecting the collision integrals $\mathcal{J}$) but involving several approximations. But in NSOM, neglecting $\mathcal{J}$ leads to a nondissipative evolution of the system: implies neglecting ρ'_w which, as shown, is responsible for dissipation. Evidently the apparent contradiction is explained by the forced introduction of the Stosszahlanzatz. In fact, we have that $\bar{\sigma}$ of Eq. (74) is null if we neglect the collision integrals; call this σ_0 and then

$$\sigma_0(t) = \beta(t)\dot{U}_0^{(01)}(t) - \int d^3r d^3p \varphi_1(\vec{r},\vec{p};t)\dot{f}_1^{(01)}(\vec{r},\vec{p};t) \times \int d^3r d^3p d^3r' d^3p' \varphi_2(\vec{r},\vec{p},\vec{r}\,'\vec{p}\,';t)\dot{f}_2^{(01)}(\vec{r},\vec{p},\vec{r}\,',\vec{p}\,';t) = 0 , \quad (81)$$

where upper index (01) stands for the contributions to the time derivative from the terms $J^{(0)} + J^{(1)}$ of Eqs. (49) in each case.

But, if we once again separate the auxiliary distribution in one for the individual single particles and a part containing the correlations, after using Heims-Jaynys scheme we obtain for $\bar{S}$ the Boltzmann expression of Eq. (75) - as already done - and

$$\sigma_0(t) = \sigma^0(t) + \Delta\sigma_0(t) = 0 \quad (82)$$

where σ^0 is that of Eq. (80) and $\Delta\sigma_0$ contains the contributions due to two, three, etc., particle correlations. Because of the $\mathcal{H}$-theorem $\sigma^0 \geq 0$ and then $\Delta\sigma_0$ is negatlve (or null in equilibrium), compensating σ^0.

To compare Boltzmann approach and the complete one in MaxEnt- NSOM we can analize the production of entropy in both cases, that is to say, to compare σ^0 with a of Eq . (74), with the collision integrals in the latter in an approximation that neglects correlations.

These results call the attention to the question of irreversibility and its characterization: as noted by Jaynes, to obtain an expression that increases with the nonequilibrium evolution of the system does not necessarily implies positive entropy production in a proper thormodynamic sense. In fact the notion of entropy and entropy production in nonequilibrium states of arbitrar systems is not well established. In phenomenological irreversible thermodynamics it is constructed on intuitive basis, and local in space and instantaneous in time non-negative entropy production is imposed[35]. In statistical mechanics both functions need be defined and justified that they are proper definitions for arbitrarily away-from-equilibrium thermodynamic states.

Here we have introduced the MaxEnt-entropy, i.e. an expression depending on the basic macrovariables that in MaxEnt-NSOM describes the nonequilibrium state of the system: it is given by Eq. (62), what implies

the statistical average over the nonequilibrium state of the system of the logarithm of the coarse-grained auxiliary distribution $\bar{\rho}$, the one that provides the instantaneous values of tlie basic macrovariahles but is relaxation free. This coarse-graining is introduced by tlie conditions of Eqs. (18) and performed through the projection operation defined by Eq. (33a). We also stres~ that, as shown in the Appendix A, the condition of Eqs. (18) is used to demonstratc the wealt principle of MaxEnt-entropy production of Eq. (71).

This result is an alternative expression of the one derived by del Rio and Garcia-Colin[36] for tlie time behavior of, what they call, Shannon-Jaynes entropy where the inequality $\Delta\bar{S} \geq 0$ ($\Delta\bar{S}$ in Eq. (A3) in tlie Appendix A) is interpreted as characterizing tlie fact tliat every time that tlie system is observed, information is lost. Again we stress that this is not a definite proof of the second law as instantaneously valid, since it is not clear the connection of tlie MaxEnt-entropy (in other nomenclature tlie informational Shannon-Jaynes entropy) and thermodynamic entropy in Clausius sense. As mentioned before, the MaxEnt-NSOM provides mechano-statistical forrnclations to phenornenological irreversible thermodynamics[21] except for this point.

VI. Concluding remarks

Witliin tlie context of classical mechanics we have shown that a mechano-statistical formulation tliat is a generalization of Gibbs and Boltzrnann ideas, narnely the Nonequilibrium Statistical Operator Method, is derived (and tlie different approaches unified) using a variational principle. The formalism is based on Jaynes' Predictive Statistical Mechanics and tlie variational procedure MaxEnt (Principle of maximization of the informational-statistical entropy, including memory effects and ad lioc hypotheses to ensure irreversible beliavior in the evolution of the macroscopic state of tlie system from an initial condition).

The MaxEnt-NSOM provides tlie basis for tlie construction of a nonequilibrium nonlinear transport theory of large scope, as described in Section III. As already remarlted, the collision operators involved are of unmanageable proportions, but a practical metliod can be devised that allows for an expression for the collision operators in the form of a series of simpler ones organized in ever increasing powers in the strength of the interactions responsible for the dissipative processes that develop in the media[32]. Such MaxEnt-NSOM transport eyuations can be considered far reaching generalizations of Hilbert-Chapman-Enskog's and Mori's methods. In Appendix B we show how Mori's equations can be retrievecl from the method.

This generalized MaxEnt-NSOM transport theory is applied, as described in section IV, to the study of tlie evolution of a system of particles interacting through central forces and in nonequilibriiim conditions. For its macroscopic description we introduce as basic variables the one-particle and two-particle dynamical distribution functions. The equations of evolution for their statistical average values, i.e. the one-particle and two-particle distribution functions, are derived. They are a set of coupled equations that also depend on the three-particle distribution function. Neglecting tliree-particle collisions, talting into account that - under this circumstance - the two-particle distribution varies slowly in time (foi times larger than tlie time of a binary collision), and finally neglecting two-particle correlations we recover the well known Boltzmann equation. Hence, we prove that Boltzmann equation is contained In the MaxEnt-NSOM in the lowest approximation in tlie interactions (very dilute fluicl) and under the approximations just stated, which involve tlie Stosszahlansatz condition.

The generalized transport theory, that follows from the MaxEnt-NSOM in the context of Jaynes' Predictive Statistical Mechanics, can then be considerecl - for classical systems - a far-reaching generalization of Boltzmann transport theory. In principle, it allows to go over the study of transport phenomena in systems arbitrarily away from equilibrium and even dense fluids with highly correlated component particles.

In section V we dealt with the thermodynamic implications of the results of section IV, mainly tlie discussion of $\mathcal{H}$-theorems. This of course involves the old question of how to define entropy in nonequilibrium conditions ancl the meaning of a local in space and instantaneous in time second law. In MaxEnt-NSOM an entropy and cntropy production can be de-

fined in terms of the chosen set (in general truncated) of basic variables, and a very close identification with those of existing phenomenological irreversible thermodynamics can be obtained, what provides statistical mechanical foundations for the latter. We showecl that Boltzmann's $\mathcal{H}$-theorem is contained in MaxEnt-NSOM only **as** a result of the approximations introduced and, clearly, is not a manifestation of the second law. Also, in MaxEnt-NSOM it is not possible, on the one hand, to make any acceptable correlation of the MaxEnt-entropy and MaxEnt-entropy production with identifiable truly thermodynamic corresponding state functions. At most, as already noticed, this can be done with those of existing phenomenological irreversible thermodynamic theories, being also possible to prove - at the statistical-mechanical level- Prigogine's principle of minimum entropy production in the linear regime, Glansdorff-Prigogine universal criterion of evolution, and Glansdorff-Prigogine(in)stability conditions in the steady state of far-from-equilibrium systems. In section V (see also Appendix A) we have demonstrated what we called a weak piinciple of nonnegative entropy production, which can also be interpreted as a generalized $\mathcal{H}$-theorem (in Jancel's sense[37]) and **as** an expression that the MaxEnt-NSOM entropy cannot decrease in time. This result is equivalent to that of reference 36, whose authors interpret the resulting inequality as the fact that, in MaxEnt, sequence of observations performed on a macroscopic system undergoing irreversible processes always results in a loss of information in Jaynes-Shannon's sense.

As a final word, following Zwanzig[1] we remark that, seemingly, the MaxEnt-NSOM - a formalism based on Jaynes' Predictive Statistical Mechanics - possesses a remarkable compactness and has by far a most appealing structure, being a veiy effective method for dealing with nonlinear and nonlocal in space and time (namely, including spacial correlations and memory effects) transport processes in far-from-equilibrium many-body systems. In this paper we showed, in particular, how Boltzmann's transport theory is contained in it as an asymptotic result under very restrictive approximations imposed upon the MaxEnt-NSOM transport equations.

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Appendix A: A generalized $\mathcal{H}$-theorem in MaxEnt-NSDM

Taking into account the definition of the MaxEnt-entropy of Eq. (62) it follows that

$$\bar{S}(t) - \bar{S}(t_0) = \int d\Gamma[\rho_w(\Gamma|t) \ln \bar{\rho}(\Gamma|t,0) - \rho_w(\Gamma|t_0) \ln \bar{\rho}(\Gamma|t_0,0)] \qquad (A.1)$$

But, because of the initial condition of Eq. (15) we have that $\ln \bar{\rho}(\Gamma|t_0,0) = \ln \rho_w(\Gamma|t_0)$, and, further, since the quantity $\rho_w(\Gamma|t) \ln \rho_w(\Gamma|t)$ is conserved (constant in time), we can write

$$\bar{S}(t) - \bar{S}(t_0) = -\int d\Gamma \rho_w(\Gamma|t)[\ln \bar{\rho}(\Gamma|t,0) - [\ln \bar{\rho}(\Gamma|t)] = -\int d\Gamma \rho_w(\Gamma|t)[\mathcal{P}_w(t) - 1] \ln \rho_w(\Gamma|t) \ , \qquad (A.2)$$

where $\mathcal{P}_w$ is the time-dependent projection operator of Eq. (31). Hence,

$$\bar{S}(t) - \bar{S}(t_0) = \bar{S}(t) - S_G(t) \ , \qquad (A.3)$$

where $S_G(t)$ is the Gibbs'statistical entropy of Eq. (3).

Recalling that the coarse-graining condition of Eq. (18) ensures (besides the definition of the Lagrange multipliers F_j in accord with phenomenological irre-

versible thermodynamics) the normalization of both ρ_w and $\bar{\rho}$, we can express Eq. (A.2) as

$$\Delta\bar{S}(t) \equiv \bar{S}(t) - \bar{S}(t_0) = -\int d\Gamma[\rho_w(\Gamma|t)\ln\bar{\rho}(\Gamma|t,0) - \rho_w(\Gamma|t)\ln\rho_w(\Gamma|t) + \rho_w(\Gamma|t) - \bar{\rho}(\Gamma|t,0)] \tag{A.4}$$

Next we note that **AS** cancels for $\rho_w = \bar{\rho}$, and that its variation is given by

$$\delta\Delta\bar{S}(t) = \int d\Gamma\delta\rho_w(\Gamma|t)\ln\frac{\rho_w(\Gamma|t)}{\bar{\rho}(\Gamma|t,0)} = \int d\Gamma\delta\rho_w(\Gamma|t)\ln\left[1+\frac{\rho'_w(\Gamma|t)}{\bar{\rho}(\Gamma|t,0)}\right] , \tag{A.5}$$

where we used the separation of the total distribution as $\rho_w = \bar{\rho} + \rho'_w$ as given by Eq. (16).

The variation in Eq. (A.5) is null for $\rho_w = \bar{\rho}$, or in other words, for $\rho'_w = 0$. Hence, A S is a minimum for $\rho_w = \bar{\rho}$, when it is zero, and positive otherwise, i.e. $\Delta S(t) \geq$ O.. This is for the MaxEnt-NSOM the equivalent of Jancel's generalized $\mathcal{H}$-theorem[37].

Taking into account that $\bar{\sigma}$ is the MaxEnt-entropy production [Cf. Eqs. (65) and (70)] we can write the inequality $\Delta S(t) \geq 0$ **as**

$$\int_{t_0}^{t} dt'\bar{\sigma}(t') = \int_{t_0}^{t} dt' \int d^3r\bar{\sigma}(\vec{r},t') \geq 0 . \tag{A.6}$$

which is a weak principle of non-negative entropy production. As a final word we stres that the inequality in Eq. (A.6) is, as shown by Eq. (A.5), a consequence of the presence of the term ρ'_w, then accounts for the irreversible behavior of the system. [Also Cf. Eq. (69)].

Appendix B: Mori's equations in NSOM

Let us consider Eq. **(38)** for the case of a system slightly deviated from equilibrium. Given the variables $\{P_j\}$, $\{Q_j(t)\}$, and $\{F_j(t)\}$, and the auxiliary NSD

$$\bar{\rho}(\Gamma|t,0) = \exp\left\{-\phi_0 - \beta H(\Gamma) - \delta\phi - \sum_{j=1}^{n}\Delta F_j(t)P_j(\Gamma)\right\} , \tag{B.1}$$

where the exponent is composed of the contribution corresponding to the equilibrium canonical distribution plus a deviation from equilibrium; $\phi_0 + \delta\phi$ ensures the normalization with $\phi_0 = \beta F$, F being the free energy, $\beta = 1/kT$, and H is the total Hamiltonian of the system. Further we introduce

$$\Delta F_j(t) = F_j(t) - F_j^0 , \tag{B.2a}$$

$$\Delta Q_j(t) = Q_j(t) - Q_j^0 , \tag{B.2b}$$

where index naught indicates equilibrium values.

Both deviations from equilibrium in Eqs.(B.2) are connected by the relation

$$\Delta Q_j(t) = \sum_k \frac{\delta}{\delta\Delta F_k(t)}\int d\Gamma P_k(\Gamma)\bar{\rho}(\Gamma|t,0)\Delta F_k(t) \simeq -\sum_k C_{jk,0}\Delta F_k(t) , \tag{B.3}$$

where

$$C_{jk,0} = \int d\Gamma P_j(\Gamma)\Delta P_k(\Gamma)\rho_0(\Gamma) , \qquad (B.4a)$$

$$\rho_0(\Gamma) = \exp\{-\phi_0 - \beta H\} , \qquad (B.4b)$$

and the approximate sign in Eq. (B.3) means that it has been taken a linear approximation in A F, and we have defined A P = P− < P $>_0$, where < ... $>_0$ is the statistical average over the canonical equilibrium ensemble.

Hence, using Eq. (38) but taking only contribution to the collision operator in Eq. (40), we find that

$$\frac{d}{dt}\Delta Q_j(t) = -\sum_{k,m}\int d\Gamma \dot{P}_j(\Gamma)\Delta P_k(\Gamma)\rho_0(\Gamma)C^{-1}_{km,0}\Delta Q_m(t) + \sum_{\mathrm{km}}\int_{t_0}^{t} dt' W(t,t') \int d\Gamma \dot{P}_j(\Gamma)$$

$$\times\Delta\dot{P}_k(\Gamma|t'-t)\rho_0(\Gamma)C^{-1}_{km,0}\Delta Q_m(t') - \sum_{km}\int_{t_0}^{t} dt' W(t,t')\int d\Gamma \dot{P}_j(\Gamma)$$

$$\Delta P_k(\Gamma|t'-t)C^{-1}_{km,0}\frac{d}{dt'}\Delta Q_m(t') . \qquad (B.5)$$

In the linear regime around equilibrium, Eq. (B.5) can be rearranged in first order in AQ introducing in the last time derivative the first two terms, in an iterative process of solution, to obtain

$$\frac{d}{dt}\Delta Q_j(t) = i\sum_k \Omega_{jk}\Delta Q_k(t) - \sum_k\int_{t_0}^{t} dt' W(t,t')\gamma_{jk}(t'-t)\Delta Q_k(t') , \qquad (B.6)$$

where

$$\Omega_{jk} = -i\sum_{\mathrm{m}}\int d\Gamma \dot{P}_j(\Gamma)\Delta P_m(\Gamma)\rho_0(\Gamma)C^{-1}_{mk,0} \qquad (B.7a)$$

is, in Mori's terminology, the precession matrix, and

$$\gamma_{jk}(t'-t) = \sum_m\int d\Gamma[\dot{P}_j(\Gamma)\Delta\dot{P}_m(\Gamma;t'-t)\rho_0(\Gamma)C^{-1}_{mk,0} +$$

$$+\sum_{mrs}\int d\Gamma \dot{P}_j(\Gamma)\Delta P_m(\Gamma;t'-t)\rho_0(\Gamma)C^{-1}_{mr,0}\int d\Gamma \dot{P}_r\Delta P_s(\Gamma;t'-t)\rho_0(\Gamma)C^{-1}_{sk,0}] , \qquad (B.7b)$$

is the memory matrix. Except for the weight function W, Eqs. (B.6) are Mori equations which are average values over the canonical equilibriurn distribution of generalieed Langevin equation[4].

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