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On Nonequilibrium Many-Body Systems III: Nonlinear Transport Theory

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Abstract A nonlinear transport theory for many-body systems arbitrarily away from equilibrium, based on the nonequilibrium statistical operator (NSO) method, is presented. Nonlinear transport equations for a basis set of dynamical quantities are derived using two equivalent treatments that may be considered far reaching generalizations of the Hilbert--Chapman-Enskog method and Mori's generalized Langevin equations method. The first case is considered in some detail and the general characteristics of the theory are discussed.

1. INTRODUCTION

Transport phenomena in matter have been treated for a long time within the framework of Boltzmann transporttheorywhich constitutes oneof the landmarks in the field of statistical mechanics, where it provides deep conceptual ideas and a method for the mathematical handling of the problem. In the area of solid state theory it yielded a vast number of results, however requiring to be used in conjunction with a quasi-particle (elementary excitations) picture[1]. As it is well known, in solid state systems, after the Born-Oppenheimer approximation is applied lattice vibrations can be described in terms of a phonon gas plus anharmonic interactions[1], and the conduction and valence bands electrons are treated on the basis of Landau's Fermi liquid theory[2]. In Landau's theory the system of strongly interacting electrons is replaced by a systern of new and more complex entities, the quasi-particles, using a transformation which connects both representations[3]. Landau's theory was extended by Silin[4] to encompass Coulomb effects produced by electron charge density variations, and later on it was generalized to deal with magnetic systems[5] and with excitations rapidly varying in space[6]. Boltzmann-like equations for the diagonal and nondiagonal elements of the quasi-particle density matrix are obtained from these approaches[4,5,7,8].

The original Boltzmann transport equation is derived using several restrictions on the characteristics of the scattering processes,

driving forces, and relaxation effects; all three are supposedtobeweak in order to make it possible to use linear approximations and long life -time quasi-particle states. Extensions of the method require the incorporation of the possibility to deal with dense systems, strong scattering, high intensity external fields, non-local scattering processes, strong relaxation effects, and quantal effects of driving fields. These questions have been addressed by many authors, and recently a largeconcentration of efforts have been directed towards the aim of deriving elaborate quantum transport theories. An important result was the derivation of the fluctuation-dissipation theorem[9], which shows that, for systems slightly deviated from thermodynamic equi ibrium, exact closed -form expressions for the response functions and transport coefficients can be obtained in the form of correlation functions in equilibrium.

An alternative derivation of the fluctuation-dissipation theorem can be obtained using the double-time thermodynamic Green function algorithm devised by Bogoliubov and Tyablikov, and described in an already classic paper by Zubarev[10]. This Green function algorithm is very useful to carry out calculations of response functions and transport coefficients. The actual calculations may be difficult forthecase of interacting many-body systems, but they are formally closed at this level. The method allows one to obtain linear and nonlinear responses to mechanical perturbations, but it has its own region of applicability expressed by the condition that the thermal perturbations arising alongside the mechanical action can be neglected. Threfore a completely different situation appears when one needs to deal with systems far from equilibrium. Systems strongly departed from equilibrium present a much higher level of complexity than systems that can be treated within the framework of the fluctuation-dissipation approach. This is so because of the fact that transport coefficients become dependent on the instantaneous macroscopic state of the system, and nonlinear transport effects take place during the irreversible evolution of the system.

Nonlinear transport phenomena in far from equilibrium systens is a subject of importance in many areas besides the physics of condensed matter, like physico-chemistry, biology, engineering, and others, and consequently is receiving nowadays a great deal of attention. The

origin of nonlinear transport theory is connected with the handling of higher order approximations of the solutions of Boltzmann equation via the Hilbert-Chapman-Enskog method[11]. At present several methods based on different approaches are used to derive nonlinear transport equations[12]. Some of them are built upon the generalization of ideas originated in the theory of the Brownian motion[13], and others on the extension of the Gibbs ensemble algorithm to nonequilibrium situations complemented with projection techniques[14-19]. The transport equations obtained following the latter approach are considered a far-reaching generalization of the Hilbert-Chapman-Enskog point of view[12b].

We discuss in the present article the derivation of nonlinear transport equations within the framework of the nonequilibrium statistical operator method, referred to as NSO in what follows[14-19]. The theoretical aspects involved in the treatment of many-body systems strongly departed from equilibrium were discussed in a previous article published in this journal[19], from now on referred to as I. The application of the method to the study of the irreversible thermodynamics and optical responses of semiconductors probed by ultrafast laser spectroscopy is done in reference 20. In this article, a sequence of I, we present. in section 2 the details of how to obtain the set of nonlinear transport equations which describe the irreversible processes that develop in nonequilibrium many-body systems whose evolution is described using the NSO method. The characteristics of these equations and a practical method of calculation are fully described. The results of section 2 are applied to the study of mobility and diffusion of carriers in a highly excited plasma in polar semiconductors, to be presented in a future article.

2. NONLINEAR GENERALIZED TRANSPORT EOUATIONS

At present there exist several methods to describe macroscopic processes that occur in systems with a large number of degrees of freedom[12,21]. One of them, the NSO, is a statistical rnethod based ori the use of distribution functions derived by the ensemble method initiated by Gibbs for systerns in equilibrium. For nonequilibrium systems an ensemble is built as a set of replicas of the physical system distributed with a given a priori probability over all the microscopic states satisfying

the constraints and initial especifications[14-19]. In this method the evolution of the system is described by generalized transport equations which are the equations of motion for dynamical variables averaged over the nonequilibrium ensemble.

The problem of the determination of the time-dependence of averages of dynamical quantities over the nonequilibrium ensemble can be tackled in either of two ways, (a) following the treatment proposed by Kubo, Mori, Tomita and others in which an appropriate initial distribution is defined and one looks for the dynamic equation of the quantity itself (the generalized Langevin equation method)[20], or (b) one looks for solutions for the time-dependence of the distribution function (Green-Zwanzig's approach). The nonequilibrium statistical operator method belongs to case (b) and it seems to offer a formalism in the theory of irreversible processes adequate to deal with a large class of experimental situations. It provides a macroscopic description for systems away from thermal equilibrium whose evolution, for not too short time scales, is described by a statistical operator which includes non-linear, non-local and retardation (memory) effects.

2.A - The Nonequilibrium Statistical Operator Method: Fundamentals

The NSO method is based on Bogoliubov's assertion that if exists a relaxation time for microinformation, τ_μ, after which the system loses the memory of the detailed initial distribution (Cf. I), for $t >> t_\mu$ a randomization (damping of microinformation) should occur, and a reduced number of variables (e.g. a few reduced density matrices of a many-body system) are enough to describe the state of the system in a macroscopic way[22]. The initial distribution, i.e. the one that describes the evolution of the system immediately after it has been strongly departed from equilibrium, depends on the coordinates of all the degrees of freedom of the system and its subsequent contraction is connected with the separation from the total hamiltonian of strong interactions with certain symmetries, which are those related to the fast relaxing processes[23].

Hence, for not too short times, i.e. $t >> \tau_\mu$, correlations with lifetimes smaller than τ_μ can be ignored and the state of the sys-

tem can be described by a reduced set of macroscopic variables (or macrovariables for short), say $Q_1(t)$, $Q_2(t)$,..., $Q_n(t)$, which are the average values of the dynamical quantities P_1, ..., P_n over the non-equilibrium ensemble. Further one defines the set of intensive variables $F_1(t),...,F_n(t)$ thermodynamically conjugate to the macrovariables Q, in a sense to be made more precise later on (see also I). The P_j's may be chosen as densities of dynamical quantities and therefore the extensive, $Q_j(\vec{r},t)$, and intensive, $F_j(\vec{r},t)$, state variables become a function of position as well as of time.

In I we devised an approach for the construction of nonequilibrium statistical operators which describe the irreversible evolution of many-body systems from an initial macroscopic state defined by a coarse-grained statistical operator ρ_{cg}, which is a functional of the basis set of quantities P and parameters F_j. The logarithm of the coarse-grained statistical operator, log ρ_{cg}, is the projection of the logarithm of the complete NSO over the subspace defined by the quantities P_j[19]. Next, from the family of possible NSO's defined by our method we single out the one due to Zubarev[17] which is given by

$$\rho_\varepsilon(t) = \exp\{\varepsilon \int_{-\infty}^{0} dt' \, e^{\varepsilon t'} \log \rho_{cg}(t+t',t')\} , \qquad (1)$$

where $\varepsilon(>0)$ goes to zero after the trace operation in the calculation of averages has been performed (cf. I). In equation (1) the first term in the argument of ρ_{cg} stands for the time dependence of parameters $F_j(t)$, whereas the second denotes the evolution of the quantities P_j under the action of the Hamiltonian H.

The coarse-grained statistical distribution representing the effect of idealized reservoirs fixing the initial condition for the system after the randomization process has occurred is given, as shown in I, by

$$\rho_{cg}(t,0) = \exp\{-\phi(t) - \sum_{j=1}^{n} F_j(t)P_j\} . \qquad (2)$$

Here $\phi(t)$, which ensures the normalization of the coarse-grained statistical operator is a functional of the thermodynamic variables $F_j(t)$, and plays the role of a Massieu-Planck function in nonequilibrium stat-

istical thermodynamics (cf. Appendix 1 in I).

Equation (1) defines the operation of selecting the subgroup of retarded solutions corresponding to the initial value problem of Liouville's equation. This is guaranteed by the presence of an infinitesimal source which breaks the time-reversal symmetry of Liouville's equation, i.e.

$$\frac{\partial \log \rho_\varepsilon}{\partial t} + \frac{1}{i\hbar}\left[\log \rho_\varepsilon, H\right] = -\left(\log \rho_\varepsilon - \log \rho_{cg}\right) \tag{3}$$

Hence, irreversibility is associated with this symmetry breaking and the average of a physical quantity A over the ensemble defined by distribution (1) is a quasi-average in Bogoliubov's sense[24]

$$\langle A \mid t\rangle = \lim_{\varepsilon \to +0} \mathrm{Tr}\{A\, \rho_\varepsilon(t)\} \tag{4}$$

Invariance under time-reversal transformations is not satisfied for these quasi-averages because of the removal of the corresponding degeneracy in Liouville's equation[19].

Except for the normalization condition, the parameters F_j are still undetermined. An additional condition is inposed on distribution ρ_{cg} in the form

$$Q_j(\vec{r},t) = \langle P_j(\vec{r}) \mid t\rangle = \langle P_j(\vec{r}) \mid t\rangle_{cg} \equiv \mathrm{Tr}\{P_j(\vec{r})\rho_{cg}(t)\}\ , \tag{5}$$

$j = 1,2,\ldots,n$, which leads to the relation

$$-\frac{\delta \phi(t)}{\delta F_j(\vec{r},t)} = \langle P_j(\vec{r}) \mid t\rangle_{cg} = \langle P_j(\vec{r}) \mid t\rangle = Q_j(\vec{r},t)\ , \tag{6}$$

a generalization of the concept of thermodynamic parameters to the non-equilibrium state. The non-equilibrium thermodynamic parameters F_j are said to be thermodynamically conjugate to the macrovariables Q_j in the sense established by eq. (6). This definition of the thermodynamic parameters has been used, for different non-equilibrium distributions, by

several authors[14-19,25]. It should be noted that there exists the question connected with the measurement of these parameters in the non-equilibrium state. If one of the quantities P is the hamiltonian, the conjugate parameter F plays the role of an inverse temperature; in an equilibrium measurement a properly calibrated thermometer will always yield the correct value of the thermodynamic temperature. This is no longer true in a nonequilibrium situation. However, there is no difficulty in principle since one can measure the quantity Q_j and then invert eq. (6) to obtain the conjugate nonequilibrium thermodynamic parameter F_j. Alternatively one may devise a way to determine the values of the F_j through indirect measurernents, for example the ultrafast laser spectroscopy experiments described in reference 20.

The NSO formalism provides a statistico-mechanical foundation for nonequilibrium thermodynamics once a thermodynamic function of state is defined. This is done introducing a coarse-grained entropy in the form

$$\tilde{S}(t) = - \langle \log \rho_{cg}(t,0) | t \rangle \quad , \tag{7}$$

i.e. generalizing the statistical entropy for equilibrium but in the auxiliary fields $F_j(r,t)$ and with instant averages as given by eqs.(5). Using this definition it can be proved that Zubarev's statistical method is compatible with Generalized Thermodynamics[26]. Using eq. (7) we can write the reciproca1 of eq. (6),

$$F_j(\vec{r},t) = \delta\tilde{S}(t)/\delta Q_j(\vec{r},t) \quad , \tag{8}$$

which defines the intensive state variables F as the differential coefficients of the coarse-grained entropy. In our following analysiswe drop the dependence of the state variables on position.

2.B - The Generalized Transport Equations

Next we consider the time evolution of the nonequilibrium system, i.e. we proceed to derive the equations of motion for the non-equilibrium thermodynamic variables, or generalized transport equations. By time-differentiation of both sides of equation (5) we obtain

$$\frac{d}{dt}\, Q_j(t) = \frac{d}{dt} \langle P_j | t\rangle_{cg} = \frac{d}{dt} \langle P_j | t\rangle = \langle \dot{P}_j | t\rangle = \frac{1}{i\hbar} \langle [P_j, H] | t\rangle \ . \qquad (9)$$

Alternatively it is possible to write equations of evolution for the intensive state variables F_j using the fact that

$$\frac{d}{dt}\, Q_j(t) = \sum_{\ell=1}^{n} \frac{\delta Q_j(t)}{\delta F_\ell(t)} \frac{d}{dt} F_\ell(t) = - \sum_{\ell=1}^{n} C_{j\ell}(t) \dot{F}_\ell(t) \quad , \qquad (10)$$

where

$$- \frac{\delta Q_j}{\delta F_\ell} = C_{j\ell}(t) = - \frac{\delta Q_\ell}{\delta F_j} = C_{\ell j}(t) \quad .$$

$C(t)$ is the correlation matrix,

$$C_{ij}(t) \equiv (P_i; P_j | t) = \mathrm{Tr} \langle P_i \, \Delta\tilde{P}_j \, \rho_{cg}(t) \} \ ,$$

$i, j = 1, 2, \ldots, n$, and where

$$\Delta P = P - \langle P | t\rangle = P - Q(t) \ ,$$

$$\tilde{A} = \int_0^1 du \, e^{-uS(t,0)} \, A \, e^{uS(t,\,0)}$$

is a generalized Kubo-transform of operator A, and

$$S(t,0) = - \log \rho_{cg}(t,0) = \phi(t) + \sum_{j=1}^{n} F_j(t) P_j \qquad (11)$$

is the coarse-grained entropy operator (cf. 1).

Defining a n-dimensional space of vectors $\vec{Q}(t) \equiv (Q_1, Q_2, \ldots, Q_n)$, and the space composed by the thermodynamically conjugate vectors $\vec{F}(t) \equiv (F_1, F_2, \ldots, F_n)$, we can write in compact form

$$\frac{d}{dt} \vec{Q}(t) = \vec{f}(t) \quad , \qquad (12a)$$

and

$$\frac{d}{dt} \vec{F}(t) = -\hat{C}^{-1}(t) \vec{f}(t) \quad , \qquad (12b)$$

where

$$\dot{\vec{F}}(t) \equiv (\langle \dot{P}_1 | t \rangle, \ldots, \langle \dot{P}_n | t \rangle) \quad ,$$

is a vector of *generalized* forces $\langle P|t\rangle$. It should be noted that, whenever convenient, one can write the equations of evolution (12) in a mixed representation involving part of variables Q, and part of variables F, say $Q_1, Q_2, \ldots, Q_s$ $(s<n)$ and $F_{s+1}, \ldots, F_n$.

We recall (cf. 1) that Zubarev's NSO (2) can be rewritten in the form

$$\rho_\varepsilon(t) = \rho_{cg}(t,0) + \rho'(t) \quad , \tag{13}$$

where

$$\rho'(t) = D_\varepsilon(t) \quad \rho_{cg}(t,0) \quad , \tag{14}$$

$$D_\varepsilon(t) = \int_0^1 du \; Y(\zeta_\varepsilon|u) e^{-uS(t,0)} \zeta_\varepsilon(t) e^{uS(t,0)} \quad , \tag{15a}$$

$$\zeta_\varepsilon(t) = \int_{-\infty}^0 dt' \; e^{\varepsilon t'} \; \Delta\dot{S}(t+t',t') \quad , \tag{15b}$$

$$\Delta\dot{S}(t_1,t_2) = \sum_{j=1}^n (\dot{F}_j(t_1)\Delta P_j(t_2) + F_j(t_1)\Delta\dot{P}_j(t_2)) \quad , \tag{15c}$$

$$Y(\zeta_\varepsilon|u) = 1 + \int_0^u dx \; Y(\zeta_\varepsilon|x) \; e^{-xS(t,0)} \; \zeta_\varepsilon(t,0) \; e^{xS(t,0)} \tag{15d}$$

Operator $\rho' = \rho_\varepsilon - \rho_{cg}$, given by eq. (14), describes the relaxation processes that develop in the media; note that there is no dissipation in the coarse-grained ensemble, $\langle \dot{S}|t\rangle_{cg} = 0$, and then $\Delta\dot{S} = \dot{S}$.

Using eqs. (13) to (15) we can write the generalized transport equations in the form

$$\frac{d}{dt}\ Q_j(t) = \langle \dot{P}_j | t \rangle_{cg} + \sum_{\ell} \int_{-\infty}^{0} dt'\ e^{\varepsilon t'} \langle \dot{P}_j ; \dot{P}_\ell(t') | t \rangle F_\ell(t+t') +$$

$$+ \sum_{\ell} \int_{-\infty}^{0} dt'\ e^{\varepsilon t'}\ \{\dot{P}_j ; P_\ell(t') | t\} \dot{F}_\ell(t+t')$$

$$= \langle \dot{P}_j | t \rangle_{cg} + \{\dot{P}_j ; \zeta_\varepsilon(t) | t\} \quad , \tag{16}$$

where

$$\{A ; B(t') | t\} = \int_0^1 du\ \langle A\ Y(\zeta_\varepsilon | u) e^{-uS(t,0)} \Delta B(t') e^{uS(t,0)} | t \rangle_{cg} \tag{17}$$

is a generalized correiation function of quantities A and B. Putting $Y=1$ we obtain the generalized transport equations in the so called quasi--linear approximation in the NSO-theory of relaxation processes[27]. Further, using the fact that

$$\sum_{\ell} \mathrm{Tr}\ \{F_\ell(t) [H, P_\ell]\ \rho_{cg}\} = \mathrm{Tr}\{[H,S]\rho_{cg}\} = \mathrm{Tr}\{H[S, \rho_{cg}]\} = 0 \quad ,$$

after deriving with respect to F_j we obtain

$$\langle \dot{P}_j | t \rangle_{cg} + \sum_{\ell} F_\ell \frac{\delta}{\delta F_j} \langle \dot{P}_\ell | t \rangle_{cg} = 0 \quad ,$$

and therefore the first term on the r.h.s. of eq. (16) becomes

$$\langle \dot{P}_j | t \rangle_{cg} = \sum_{\ell} F_\ell(t) \langle \dot{P}_\ell\ \Delta\tilde{P}_j | t \rangle_{cg} = \sum_{R} \{\dot{P}_\ell ; P_i | t\}_{Y=1}\ F_\ell(t)$$

2.C - The Linear Regime Around Equilibrium: Mori's Equations

Consider next the particular case of a system slightly deviated from equilibrium. Let $\mathcal{A}_j$ and F_j^0 be the values of the state variables in equilibrium, and we write

$$\Delta Q_j(t) = Q_j(t) - Q_j^0$$
$$\Delta F_j(t) = F_j(t) - F_j^0$$

for the deviations of Q and F from their equilibrium values. The coarse-grained statistical operator is for this case

$$\rho_{cg}(t) = \exp\{-\phi^0 - \beta H - \delta\phi(t) - \sum_{j=1}^{n} \Delta F_j(t) P_j\} ,$$

where the exponent is composed of the contribution corresponding to the equilibrium canonical distribution and the deviation from equilibrium. Mori's equations are the equations of evolution for the deviations in the linear regime (i.e. in the domain of Onsager's theory) meaning that eq. (10) is now

$$\Delta Q_j(t) = - \sum_{\ell} (P_j : P_\ell)^0 \Delta F_j(t) ,$$

where

$$(P_j ; P_\ell)^0 = C_{j\ell,0} = \int_0^1 du \, \langle P_j \, \Delta P_\ell(i\hbar\beta u) \rangle_0$$

is the scalar product defined by Mori[13,28], with

$$P(i\hbar\beta u) = \exp\{\beta u H\} P \exp\{-\beta u H\} ,$$

and $\langle \ldots \rangle$ stands for average value over the equilibrium (canonical) ensemble; as usual $\beta = 1/kT$. Further,

$$\langle \dot{P}_j | t \rangle_{cg} = \mathrm{Tr}\{\dot{P}_j \, \rho_{cg}(t)\} = \sum_m \int_0^1 du \langle \dot{P}_j \, \Delta P_m(i\hbar\beta u) \rangle_0 \, \Delta F_m(t) =$$

$$= \sum_{mk} \int_0^1 du \, \langle \dot{P}_j \, \Delta P_m(i\hbar\beta u) \rangle_0 \, C^{-1}_{mk,0} \, \Delta Q_k(t) , \qquad (18a)$$

the second term on the right hand side of eq. (16) becomes

$$\sum_{m,k} \int_{-\infty}^{0} dt' \, e^{\varepsilon t'} \int_0^1 du \, \langle \dot{P}_j \, \Delta \dot{P}_m(t' + i\hbar\beta u) \rangle_0 \, C^{-1}_{mk,0} \, \Delta Q_k(t+t') , \qquad (18b)$$

and the last term in eq. (16) is now

$$\sum_{m,k} \int_{-\infty}^{0} dt' \, e^{\varepsilon t'} \int_0^1 du \, \langle \dot{P}_j \, \Delta P_m(t' + i\hbar\beta u) \rangle_0 \, C^{-1}_{mk,0} \, \frac{d}{dt} \Delta Q_k(t+t') . \qquad (18c)$$

Replacing the right hand side of eqs. (16) by the sum of the three terms given by eqs. (18), we obtain an integral 'equation for $Q_j(t)$. Using the iterative method we replace the time derivative of AQ in eq. (18c) by (18a); however, we neglect (18b) since it leads to a term of third order in the interaction strengths. Thus, using these results, in the linear regime near equilibrium eqs. (16) become Mori's equations

$$\frac{d}{dt}\,\Delta Q_j(t) = i \sum_k \Omega_{jk}\,\Delta Q_k(t) - \sum_k \int_{-\infty}^{\infty} dt'\; \gamma_{jk}(t'-t)\Delta Q_k(t') \qquad (19)$$

where

$$\Omega_{jk} = -i \sum_m \int_0^1 du\; \langle \dot{P}_j\; \Delta P_m(i\hbar\beta u)\rangle_0\; C^{-1}_{mk,0} \quad , \qquad (20a)$$

is in Mori's terrninology the precession matrix, and

$$\gamma_{jk}(\tau) = \theta(-\tau)\; e^{\varepsilon\tau} \sum_m \int_0^1 du\; \langle \dot{P}_j\; \Delta\dot{P}_m(\tau+i\hbar\beta u)\rangle_0\; C^{-1}_{mk,0}$$

$$+\; \theta(-\tau)\; e^{\varepsilon\tau} \sum_{mk} \int_0^1 du\; \langle \dot{P}_j\; \Delta P_m(\tau+i\hbar\beta u)\rangle_0\; C^{-1}_{mk,0}$$

$$\times \sum_{rs} \int_0^1 \langle \dot{P}_k\; \Delta P_r(i\hbar\beta u)\rangle_0\; C^{-1}_{rs,0} \qquad (20b)$$

is the memory function matrix. θ is Heaviside's step function.

In a compact forrn,

$$\frac{d}{dt}\,\Delta\vec{Q}(t) = i\,\hat{\Omega}\,\Delta\vec{Q}(t) - \int_{-\infty}^{\infty} dt'\;\hat{\gamma}(t-t')\;\Delta\vec{Q}(t') \quad , \qquad (21)$$

with

$$\hat{\Omega} = -i(\vec{\dot{P}};\vec{P})_0\;\hat{C}_0^{-1} \quad , \qquad (22a)$$

$$\hat{\gamma}(\tau) = \theta(-\tau)\; e^{\varepsilon\tau}(\vec{\dot{P}};\vec{\dot{P}}(\tau))_0\; C_0^{-1} + \theta(-\tau)e^{\varepsilon\tau}(\vec{P};\vec{\dot{P}}(\tau))_0\;\hat{C}_0^{-1}(\vec{P};\vec{P})^{*}_0\; C_0^{-1}. \qquad (22b)$$

Mori's equations (21) are the average values over the equilibrium ensemble of the generalized Langevin equations[13], and, by analogy,

one may consider the generalized transport equations (16) as the averages over the nonequilibrium ensembleof the generalized Cangevin equations for quantities P_j. Oefinition (5) ensures the cancellation of the rapidly varying forces, making the state variables $Q_j(t)$ secular, i.e. of smooth time variation compared with time variations on a microscopic scale.

2.D - NSO Generalized Transport Equations from Projection Operator Techniques

We show next how the generalized transport equations (16) can be obtained in an alternative form using the projection techniques described in I.

First, we recall the definition of the projection operator $P(t)$ of eq. (30) in I

$$P(t)A(\tau) = \sum_{j,m=1}^{n} \tilde{C}^{-1}_{jm}(t)\ \{P_m; A(\tau)|t\}P_j \tag{23}$$

where

$$\tilde{C}_{jm}(t) = \{P_j; P_m|t\}\ . \tag{24}$$

This projection operator, specialized for the case of Zubarev's method, can be used to write Liouville's equation with sources, eq. (2), in the form of a Liouville's equation with a modified Liouvillian

$$\frac{\partial}{\partial t} \log \rho_\varepsilon(t) + i\Lambda \log \rho_\varepsilon(t) = 0 \tag{25}$$

where

$$i\Lambda = iL + \varepsilon[1-P(t)]\ . \tag{26}$$

The time-reversal symmetry of Liouville's equation is broken and irreversibility is thus introduced in the theory (cf. eq. (5) in I).

We now return to eqs. (16), which in the quasi-linear approximation ($Y = 1$ in eq. (15a)) are

$$\frac{d}{dt} Q_j(t) = \langle \dot{P}_j | t \rangle_{cg} +$$

$$+ \sum_{\ell} \int_{-\infty}^{\infty} dt' \, \theta(t-t') e^{\varepsilon(t'-t)} (\dot{P}_j ; \dot{P}_\ell(t'-t) | t) F_\ell(t')$$

$$- \sum_{\ell k m} \int_{-\infty}^{\infty} dt' \, \theta(t-t') e^{\varepsilon(t'-t)} (\dot{P}_j ; P_\ell(t'-t) | t) \, C^{-1}_{\ell k}(t')$$

$$\times (P_k ; \dot{P}_m | t') F_m(t') \tag{27}$$

where

$$(A;B|t) = \{A;B|t\}_{Y=1} ,$$

we have used eq. (10) in the inverted form

$$\frac{d}{dt'} F_\ell(t') = - \sum_k C^{-1}_{\ell k}(t') \frac{d}{dt} Q_k(t') \tag{28}$$

and, consistent with the quasi-linear approximation, we put

$$\frac{d}{dt'} Q_k(t') \simeq \langle \dot{P}_k | t' \rangle_{cg} = \sum_m (\dot{P}_k ; P_m | t') F_m(t') \, . \tag{29}$$

Noting that

$$e^{i(t'-t)L} P(t') \dot{P}_m = \sum_{\ell, m} P_\ell(t'-t) C^{-1}_{\ell k}(t') (P_k ; \dot{P}_m | t') \, , \tag{30}$$

we find

$$\frac{d}{dt} Q_j(t) = \langle \dot{P}_j | t \rangle_{cg} + \sum_m \int_{-\infty}^{\infty} dt' \, K_{jm}(t,t') F_m(t') \tag{31}$$

where

$$K_{j\ell}(t,t') = \theta(t'-t) e^{i\varepsilon(t'-t)} (\dot{P}_j ; e^{i(t'-t)L} [1 - P(t')] P_m | t) \, . \tag{32a}$$

The evolution equations (31) are akin to those derived by Robertson when the quasi-linear approximation is used. However, it should

regime and far-from-equilibrium conditions. Further, the generalized transport equations (16) can be written in a form that contain on the right hand side a series expansion in collision operators, involving only the calculation of averages over the coarse-grained ensemble, as shown next, thus providing a quite practical way for calculations.

2.E - The Generalized Transport Equations in Terms of Collision Operators

Let us assume that the hamiltonian of the system can be writtem in the form

$$H = \sum_{\alpha} H_{\alpha} + V = (\sum_{\alpha} H_{\alpha} + V^{sec}) + V' \equiv H_0 + V' \tag{33}$$

where $\sum_{\alpha} H_{\alpha}$ is the sum of the hamiltonians of the free sub-systems ofthe whole system, V is the interaction energy operator between them, and the separation $V = V^{sec} + V'$ has the symmetry property

$$[P_j, H_0] = \sum_{m=1}^{n} i\hbar\alpha_{jm} P_m \quad , \quad j = 1,2,\ldots,n \quad , \tag{34}$$

where the a_{jm} are real coefficients. Then

$$\frac{d}{dt} Q_j(t) = -i \sum_{m} \alpha_{jm} Q_m + \frac{1}{i\hbar} \langle [P_j, V'] | t \rangle_{cg} + \sum_{\ell=2}^{\infty} \eta_j^{(\ell)}(t) \tag{35}$$

where

$$\sum_{\ell=2}^{\infty} \eta_j^{(\ell)}(t) = \langle \dot{P}_j \, D_{\varepsilon}(t) | t \rangle_{cg} = \{\dot{P}_j; \zeta(t) | t\} =$$

$$= \int_0^1 du \, \langle \dot{P}_j \, Y(\zeta|u) \tilde{\zeta}_u(t) | t \rangle_{cg} \quad ,$$

but because of eq. (34) and taking into account eq. (5), it follows tl

$$\{\dot{P}_j; \zeta_{\varepsilon}(t) | t\} = \frac{1}{i\hbar} \{[P_j, H_0 + V']; \zeta_{\varepsilon}(t) | t\} = \{\dot{P}'_j; \zeta_{\varepsilon}(t) | t\}$$

- we wrote

be noted two differences: (a) the initial time is taken in the remote past instead of $t_0=0$ of Rpbertson's theory, and (b) we have introduced the weight function W defined in article I, which in Zubarev's method is exp $\{\varepsilon(t'-t)\}$, which fixes the initial condition and provides irreversible behavior for the macroscopic evolution of the system. Near equilibrium, when $\langle\ldots\rangle_{cg}$ is replaced by an average over the canonical ensemble, and the projector P becomes time-independent we recover Mori's equations (21) in the framework of the projection operator formalism[13], but in the quasi-linear approximation.

Further, because of eqs. (5) it results that

$$\langle \Omega D_\varepsilon(t) | t \rangle_{cg} = \{\Omega ; \zeta_\varepsilon(t) | t\} = 0$$

where R is any linear combination of quantities P_j. Thus, in eq.(16) we can rewrite the last term as

$$\{\dot{P}_j ; \zeta_\varepsilon(t) | t\} = \{\dot{P}_j ; [1-P(t)]\zeta_\varepsilon(t) | t\} ,$$

and then

$$K_{jl}(t,t') = \theta(t'-t) e^{i\varepsilon(t'-t)} (\dot{P}_j ; [1-P(t)] e^{i(t'-t)L} [1-P(t')] \dot{P}_m | t) \cdot \quad (32b)$$

The presence of the operator $1-P$ in the kinetic coefficients $K_{ij}(t,t')$ projects the $\dot{P}$ on the orthogonal space to the one defined by the basis set of P's, i.e. in Mori's language, K is a correlation matrix of the rapidly fluctuating generalized forces. Inspection of eq. (16) tells us that this is achieved in the NSO method through the difference between the correlation matrix of the total generalized forces minus the projection of the generalized forces over the space of variables P; we will return to this point later on. Finally it should be mentioned that beyond the quasi-linear approximation the kinetic rnatrix K contains time-ordered projection operators in the exponential, which renders the mathematical handling for actual calculations a quite difficult task[29]. These partial results make it possible to advance the conjecture that eqs. (16), derived in the framework of the NSO method, represent a far-reaching generalization of Mori's approach extended to the nonlinear

regime and far-from-equilibrium conditions. Further, the generalized transport equations (16) can be written in a form that contain on the right hand side a series expansion in collision operators, involving only the calculation of averages over the coarse-grained ensemble, as shown next, thus providing a quite practical way for calculations.

2.E - The Generalized Transport Equations in Terms of Collision Operators

Let us assume that the hamiltonian of the system can be written in the form

$$H = \sum_{\alpha} H_{\alpha} + V = (\sum_{\alpha} H_{\alpha} + V^{sec}) + V' \equiv H_0 + V' \tag{33}$$

where $\sum_{\alpha} H_{\alpha}$ is the sum of the hamiltonians of the free sub-systems of the whole system, V is the interaction energy operator between them, and the separation $V = V^{sec} + V'$ has the symmetry property

$$[P_j, H_0] = \sum_{m=1}^{n} \hbar\alpha_{jm} P_m \quad , \quad j = 1,2,\ldots,n \quad , \tag{34}$$

where the a_{jm} are real coefficients. Then

$$\frac{d}{dt} Q_j(t) = -i \sum_m \alpha_{jm} Q_m + \frac{1}{i\hbar} \langle [P_j, V'] | t \rangle_{cg} + \sum_{\ell=2}^{\infty} \eta_j^{(\ell)}(t) \tag{35}$$

where

$$\sum_{\ell=2}^{\infty} \eta_j^{(\ell)}(t) = \langle \dot{P}_j \, D_{\varepsilon}(t) | t \rangle_{cg} = \{\dot{P}_j; \zeta(t) | t\} =$$

$$= \int_0^1 du \, \langle \dot{P}_j \, Y(\zeta|u) \tilde{\zeta}_u(t) | t \rangle_{cg} \quad ,$$

but because of eq. (34) and taking into account eq. (5), it follows that

$$\{\dot{P}_j; \zeta_{\varepsilon}(t) | t\} = \frac{1}{i\hbar} \{[P_j, H_0 + V']; \zeta_{\varepsilon}(t) | t\} = \{\dot{P}'_j; \zeta_{\varepsilon}(t) | t\}$$

where we wro'te

$$\dot{P}'_j = \frac{1}{i\hbar}\,[P_j, V]\ .$$

Further, formally solving eq. (15d) by the iterative process we obtain,

$$\begin{aligned}\sum_{\ell=2}^{\infty} \eta_j^{(\ell)}(t) &= \int_0^1 du\ \langle \dot{P}'_j\ \tilde{\zeta}_u(t)\ |t\rangle_{cg} \\ &+ \int_0^1 du \int_0^u dx\ \ \langle \dot{P}'_j\ \tilde{\zeta}_u(t)\ \tilde{\zeta}_x(t)\,|t\rangle_{cg} \\ &+ \ \ldots\ + \\ &+ \int_0^1 du \int_0^u dx_1 \ \ldots\ \int_0^{x_{n-1}} dx_n\ \langle \dot{P}'_j\ \tilde{\zeta}_u(t)\tilde{\zeta}_{x_1}(t)\ldots\tilde{\zeta}_{x_n}(t)\,|t\rangle_{cg} \\ &+ \ \ldots \end{aligned} \tag{36}$$

with

$$\begin{aligned}\tilde{\zeta}_x(t) &= e^{-xS(t,0)}\ \zeta(t)\ e^{xS(t,0)} \\ &= \int_{-\infty}^{0} dt'\ e^{\varepsilon t'}\ e^{-xS(t,0)}\ \Delta\dot{S}(t+t',t')e^{xS(t,0)} \\ &= \int_{-\infty}^{0} dt'\ e^{\varepsilon t'}\ e^{-xS(t,0)}\ \Big(\sum_m \dot{F}_m(t+t')\Delta P_m(t') \\ &+ \sum_m F_m(t+t')\dot{P}_m(t')\Big)e^{xS(t,0)}\ .\end{aligned} \tag{37}$$

But

$$\dot{P}_m = -i \sum_{j=1}^{n} \alpha_{jm} P_j + \frac{1}{i\hbar}\,[P_m, V]\ ,$$

and then

$$\bar{\zeta}_x(t) = \int_{-\infty}^{0} dt' \; e^{\varepsilon t'} e^{-xS(t,0)} \left[\sum_m \Delta P_m(t') \frac{d}{dt'} F_m(t+t')\right] e^{xS(t,0)}$$

$$+ \int_{-\infty}^{0} dt' \; e^{\varepsilon t'} e^{-xS(t,0)} \left[-i \sum_{jm} F_m(t+t') \alpha_{mj} P_j(t')\right] e^{xS(t,0)}$$

$$+ \int_{-\infty}^{0} dt' \; e^{\varepsilon t'} e^{xS(t,0)} \sum_m F_m(t+t') e^{-xS(t,0)} \frac{1}{i\hbar} \left[P_m(t'), V'\right] e^{xS(t,0)} \tag{38}$$

Replacing eq. (38) in (36), and the latter in eq. (35), we can see that the quantities with increasing index R contribute with terms involving from one to ℓ times the interaction energy operator V'. Thus they can be rearranged in a series of collision operators of increasing powers in the interaction strengths. Note that this implies to incorporating the entropy production operator, contained in 5, in ever increasing contributions into correlation functions calculated over the coarse-grained ensemble. For the case $\alpha_{ij} = 0$ we obtain

$$\frac{d}{dt} Q_j(t) = \frac{1}{i\hbar} \langle [P_j, V'] | t \rangle_{cg} + \sum_m \int_{-\infty}^{0} dt' e^{\varepsilon t'} \dot{F}_m(t+t') (\dot{P}'_j; P_m(t') | t)$$

$$+ \sum_m \int_{-\infty}^{0} dt' \; e^{\varepsilon t'} \; F_m(t+t') (\dot{P}'_j; \dot{P}'_m(t') | t) + \ldots \tag{39}$$

where

$$(A;B|t) = \{A;B|t\}_{Y=1} = \int_0^1 du \, \langle A \, \Delta B_u(t') | t \rangle_{cg} \; , \tag{40}$$

and

$$\Delta B_u = e^{-uS(t,0)} \; \Delta B \; e^{uS(t,0)}$$

Keeping only the terms written in eq. (39), i.e. taking $Y = 1$ in the correlation functions defined by eq. (17), corresponds to the so called quasi-linear approximation in the NSO-theory of relaxation pro-

cesses. Up to this second order in the interaction strengths we canmake in eq. (39) the approximation

$$\sum_m F_m(t+t')\dot{P}'_m(t') \simeq \sum_m F_m(t)\dot{P}'_m \ ,$$

and using the fact that

$$\sum_m e^{-uS}\,[F_m(t)P_m, V'(t')]e^{uS} = \frac{d}{du}\, e^{-uS}\, V'(t')e^{uS} \ ,$$

we obtain

$$\sum_m \int_{-\infty}^{0} dt'\, e^{\varepsilon t'}\, F_m(t+t')(\dot{P}'_j;\dot{P}'_m(t')\,|t)$$

$$= -\frac{1}{\hbar^2}\int_{-\infty}^{0} dt'\, e^{\varepsilon t'} < [V'(t'),[V',P_m]]\,|\,t>_{cg} \ . \qquad (41)$$

Furthermre, recalling that $[P_j,H_0] = 0$ it follows that

$$(\dot{P}_j;P_m(t')\,|t) \simeq -\frac{1}{i\hbar}\,\delta<[P_j,V']\,|t>_{cg} = \delta F_m(t) \ , \qquad (42)$$

and

$$\frac{d}{dt'}F_m(t+t') \simeq \frac{d}{dt}F_m(t) = -\sum_k C^{r}_{km}(t)\,\frac{d}{dt}Q_k(t)$$

$$= -\sum_k C^{-1}_{km}(t)\,\frac{1}{i\hbar}<[P_k,V']\,|t>_{cg} \ . \qquad (43)$$

Hence, up to second order in the interaction strengths

$$\sum_m \int_{-\infty}^{0} dt' \; e^{\varepsilon t'} \frac{d}{dt'} F_m(t+t')(\dot{P}_j; P_m(t') \,|\, t)$$

$$= -\frac{1}{\hbar} \sum_{km} \int_{-\infty}^{0} dt' \; e^{\varepsilon t'} \langle [P_k, V'(t')] \,|\, t \rangle_{cg} \; C^{-1}_{km}(t) \; \frac{\delta \langle [P_j, V'] \,|\, t \rangle_{cg}}{\delta F_m(t)}$$

$$= -\frac{1}{\hbar^2} \sum_{k} \int_{-\infty}^{0} dt' \; e^{\varepsilon t'} \langle [P_k, V'(t')] \; \frac{\delta \langle [P_j, V'] \,|\, t \rangle_{cg}}{\delta Q_k(t)} \; . \qquad (44)$$

Replacing eqs. (44) and (43) into eq. (39) we obtain the non-linear transport equations for the quantities P_m in the quasi-linearapproximation in the NSO-theory for relaxation effects: these are the equations given in article I. In the quasilinear approximation ρ' ofeq. (14) depends only on the first power of the coarse-grained entropy production operator $\dot{S}$; it will be shown in a future article that in the quasi-linear approximation the production of entropy (of generalized thermodynamics) can be written in the form of a self-correiation of the coarse-grained entropy production operator, defined in the coarse-grained ensemble, and that the fluctuations of the macrovariables Q follows a Gaussian distribution.

3. CONCLUDING REMARKS

The generalized transport equations (12a), or the equations for the thermodynamic parameters F, eqs. (12b), or those in a mixed representation, contain non-local (dependence on position $\vec{r}$ has not been shown explicitly in our previous treatment), and memory effects, and, fundamentally, they are highly nonlinear integrodifferential equations. This is a quite important fact since one is then dealing with autonomous dynamical systems (non-autonomous if the hamiltonian contains a time--dependent potential energy) with feedback mechanisms. Such systems may present stable solutions corresponding to small perturbations increasing up to a stable final macroscopic fluctuation irrespective of the initial conditions, in accord with the results of Generalized Thermo-

dynamics[26]. For a long time unstable transitions leading to different kinds of flow patterns in Hydrodynamics have been known, and widely studied. Similar situations appears in physico-chemical systems, like chemical or biochemical reaction networks, and clearly the most striking feature is the high level of complexity and organization in biological organisms. These steady states can occur in open systems since for isolated systems the second law of thermodynamics precludes ordered structures[30]. Further, some physical systems comprising devices like lasers, tunnel diodes, Gunn oscillators etc, can also be included as having similar kind of transitions to ordered steady states.

The profound analogies of general behaviourof these systems are a priori surprising as are the analogies in behaviour with purely dissipative systems around the situation of thermal and mechanical equilibrium and second order phase transitions. This diversity of situations have been brought under a comnon description through Generalized Thermodynamics[26,30], which put into evidence the common features, and in fact common origin, of these phenomena: the fundamental point is that one deals with nonlinear dynamical systems where instabilities may arise in conditions of far-from-thermal equilibrium. External sources in these open systems force the departure of the elementary excitation distributions from their equilibrium values to new ones compatible with the constraints. A decrease of the degree of order may occur because of collective effects among the elementary excitations after a certain threshold in the intensity of the external sources has been attained. Beyond the instability an ordered pattern stabilizes, which has been termed dissipative structure[30,31], and may be one of various spatio-temporal self-organizations.

Two main questions connected with this subject are (a) what is themicroscopic originof these transitions and (b) how to deal theoretically, or better to say, how to analyse these transitions rigorously. For systems governed by Hamiltonian dynamics the NSO method provides a way to describe the evolution aod behaviour of far-from-equilibrium systems through appropriate generalized transportequations. Their solutions are uniquely determined for given conditions; however, being nonlinear equations a branching point of solutions is apt to ap-

pear, with branches corresponding to different self-organized dissipative structures whose stability need be analized. For physico- chemical dynamical systems this is given by the Glansdorff-Prigogine stability criterion[26,30]. In future articles we will return to these questions: it will be shown how the NSO method could provide statistical foundations for generalized thermodynamics, and its used for the study of stability and fluctuations in far-from-equilibrium systems.

Concerning the set of state variables Q and conjugate thermodynamic parameters F we have already mentioned that they must be sufficient for the description of the macroscopic state of the system on the time scale of interest. As noted in I, one of the basic questions associated with the forrnalism resides in the 'justification' of a definite choice of macrovariables. One can distinguish two aspects of the question, i.e. when one set of operators P is replaced by another P', (a) what changes are there in the description of the evolution of the macrovariables, and (b) what are the changes in the thermodynamic functions as entropy production and the like. It can be seen that eitherthe lack or the excess of quantities P is corrected by the fact that the evolution equations for the macrovariables contain ar coefficients time-dependent correlation functions, which satisfy hierarchies of equations to be solved simultaneously with the generalized transport equations. Additional equations for the correlation functions will be necessary to correct the deficit in the original set of rnacrovariables, or a number of equations will become equivalent if there are *superfluous quantities* P[32]. Let us observe that if the number of quantities P is varied, the separation of the part V^{sec}, of the potential V, that mixes them as in eq. (21), also varies. Suppose that $\tilde{V}^{sec}$ is the part of V that now produces H_0 such that the new set $\{P'\}$ satisfies that

$$[P_s;H_0] = \sum_m i\alpha'_{sm} P'_{sm} \quad , \quad s,m = 1,2,\ldots,n' < n \quad ,$$

and

$$V = V^{sec} + V' = \tilde{V}_0 + V' + (V_{sec} - \tilde{V}^{sec}) = \tilde{V}^{sec} + V' + V'' \quad .$$

Then

$$\frac{dQ'_s}{dt} = -i \sum_m \alpha'_{sm} P'_m + \frac{1}{i\hbar} \langle [P'_s, V' + V'] | t \rangle \quad ; \qquad (45)$$

the number of dynamical equations diminishes but the number of correlation functions is increased through the term $[P', V']$.

Finally it should be noted that in eq. (16) we can write the last term as

$$\{\dot{P}_j; \zeta_\varepsilon(t) | t\} = \int_{-\infty}^{\infty} dt' \, \theta(-t') e^{\varepsilon t'} \frac{d}{dt'} \{\dot{P}_j; S(t+t', t') | t\} =$$

$$= \sum_\ell \int_{-\infty}^{\infty} dt' \, \theta(-t') e^{\varepsilon t'} \{\dot{P}_j; \dot{P}_\ell(t') + P(t') \frac{d}{dt'}\} F_\ell(t+t') =$$

$$= \int_{-\infty}^{m} dt' \, \theta(-t') e^{\varepsilon t'} \{\dot{P}_j; \hat{\sigma}(t+t', t') | t\} \quad ,$$

where

$$\hat{\sigma}(t,0) = \Delta \dot{S}(t,0)/dt \, ,$$

which shows that the collision operator in eq. (16) tgkes the form of a generalized correlation, in the sense of eq. (17), between the generalized force $\dot{P}$ and the entropy-production operator $\hat{\sigma}$, with $S(t, 0)$ defined in eq. (11). It contributes with two terms, one involving the correlation of pair of generalized forces, and another involvingthe variation of the thermodynamic parameters, dF/dt', which substracts the correlation of secular forces, i.e. the part of the total generalized forces projected over the manifold defined by the quantities P_j. Thus, in Mori's terminology, the memory function is a generalized correlation of the rapidly varying forces. This is also evident in eqs. (32), and in the quasi-linear approximation a more explicit form for both terms is given by eqs. (41) and (44). Sometimes formulae for the memory function found in the literature corresponding to calculations in the Markovian limit neglect the time derivative of $F(t+t')$, and may lead to incorrect results[32].

In conclusion, we may say that the NSO method, derivable from a unique variational principle as shown in I, allows the construction of a nonlinear transport theory which could be consider an ample generalization of Mori's approach. Further, the theory providesa practical form of calculation, which requires the obtention of correlation functions in the coarse-grained ensemble, avoiding the cumbersome task of dealing with projection operators which, for the general case of systems arbitrarily away from equilibrium, are dependent on time. We illustrate the use of the method by applying it to the study of ultrafast transient transport in highly excited semiconductors, which will be presented in a future article.

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Resumo

Baseada no método do operador estatístico de não-equilíbrio (Rev.Brasil.Fis. 15, 106 (1985)) é desenvolvida uma teoria não-linear de transporte para sistemas de muitos corpos arbitrariamente afastados do equilíbrio. É derivado o conjunto de equações de transporte não lineares para as variáveis básicas à descrição do estado macroscópico do sistema. Dois tratamentos alternativos são descritos os quais podem ser considerados como generalizações do método de Chapman-Enskog e do método de Mori. O primeiro caso é considerado com certo detalhe, e as características da teoria são discutidas.