

On Nonequilibrium Many-Body Systems IV: Response Function Theory

R. LUZZI, A.R. VASCONCELLOS, A.C. ALGARTE

Instituto de Física Gleb Wataghin, Universidade Estadual de Campinas, Caixa Postal 6165, Campinas, 13081, SP, Brasil

and

A.J. SAMPAIO

Departamento de Física, Universidade Federal do Ceará, 60000, Fortaleza, CE, Brasil

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Abstract A response function theory for many-body systems arbitrarily away from equilibrium is presented. It is based on the nonequilibrium statistical operator method fully described in a previous article [Rev. Brasil.Fis.15, 106 (1985)]. We present a formal theory for evaluation of transition probabilities and the average values of dynamical quantities in far-from-equilibrium many-body systems under the action of external perturbations. We also derive a nonequilibrium thermodynamic Green's functions algorithm appropriate for the calculation of response functions and scattering cross sections in terms of a generalized fluctuation-dissipation theorem for far-from-equilibrium systems.

1. INTRODUCTION

The theoretical approach to the dynamic of relaxation phenomena and determination of transport coefficients has been based for a long time on the use of Boltzmann equations. Nevertheless, difficulties arise when scattering is not rare, and when the experimental conditions lead the system to far-from-equilibrium conditions. The the usual transport theory approach, based on perturbational methods starting from an equilibrium initial condition, becomes inadequate. These kinds of situations involve strong irreversible processes, begin from an arbitrary nonequilibrium state, are not always describable in terms of well defined energy interactions, and are often nonlinear, nonlocal and non-markoffian. A viable theory should incorporate these features from the outset and nowadays there exist several approaches to this question, which have been classified by Zwanzig. (Cf.1¹). Among them the nonequilibrium statistical operator method (NSOM) described in I, deserves particular interest, which applies to hamiltonian systems with very

many degrees of freedom. It is a prescription admitting in principle all many-body problems under a large class of initial conditions, and whose foundations are simple enough to be readily tested. In I we derived a method based on a variational principle which allows one to obtain a family of NSO's, and to retrieve as particular cases those of Green-Mori and Zubarev. Further, the formalism permits one to derive nonlinear generalized transport equations that describe the dynamics of relaxation processes taking place in the system; this topic was considered in 3.²

Noting that the ultimate goal of the theory is to provide a comprehension of the underlying physics related to the relaxation phenomena that can be evidenced in experiments, it needs to be coupled with a response function theory; this is the subject of the present article.

The usual theory to calculate linear and nonlinear responses to mechanical perturbations is based on expansions in terms of equilibrium correlation functions (of increasing order)³. As initial condition one takes that of equilibrium with a thermal reservoir, and next the evolution of the system is studied as if it were isolated from all external influences apart from the source field. But in any experiment the system receiving energy from the external sources releases it to its surroundings at a certain pace: although at the initial moment the system was in equilibrium with a thermostat, this equilibrium is disturbed by the mechanical perturbations. Therefore, such response function theory has its own region of applicability: it is when thermal perturbations which arises in the system as a result of the action of the external stimuli can be neglected, and also when there are no feedback mechanisms. Beyond the domain of validity of such treatment of the response function two typical situations can be distinguished. One of them is when a mechanical perturbation is superimposed on an already far-from-equilibrium system. The second one is when a strong mechanical perturbation acts on a system initially in equilibrium. In this case a strong departure from equilibrium follows, and there are large interference effects between the mechanical and the accompanying thermal perturbations.

In the first case, in the absence of the external perturbation irreversible processes develop in the system which are describable in terms of evolution equations for a basic set of nonequilibrium thermodynamic variables, or macrovariables for short (cf. 1 and 3). Since the NSO formalism provides a seemingly powerful method to obtain a description of the macroscopic state of such systems, it is reasonable to proceed, within its framework, to derive a response function theory based on correlation functions in the unperturbed *nonequilibrium* state of the system. We have proposed an scheme of this type,⁴ which we describe in detail in this article in subsection 2a and in the first part of section 3, adding new results and extensions.

2. NONEQUILIBRIUM CORRELATION FUNCTIONS

In paper I we discussed a formalism to describe the macroscopic state of a nonequilibrium system: a method to generate a nonequilibrium statistical operator $\rho_w(t)$ that should correspond to given specifications of its macrostate was proposed, and the difficulties inherent to the method, namely, existence of a contracted description, irreversibility, definition of initial conditions, and construction of a nonlinear transport theory, were discussed. The connections with projection operator techniques were pointed out, and in article III we devised a nonlinear transport theory within the framework of the NSOM. Following the method let us assume that a suitable macroscopic description of a system arbitrarily away from equilibrium, to be submitted to a mechanical perturbation, is provided by a basis set of macrovariables $Q_1(t), \dots, Q_n(t)$, which are the averages $Q_a(t) = \text{Tr}\{P_a \rho_w(t)\}$ of a set of dynamical quantities P_1, \dots, P_n . The question of completeness of the basis set of variables is discussed in articles I and III, and particular applications are given in refs. 5 and 6. The NSO $\rho_w(t)$ is a functional of the set of dynamical quantities P_j and the thermodynamically conjugated set of intensive variables $F_j(t)$, $j = 1, 2, \dots, n$; it describes the evolution of the system from a given initial macroscopic state defined by a coarse-grained distribution $\rho_{cg}(t_0)$ and is given by (Cf. I)

$$\rho_w(t) = \exp \left\{ \int_{t_0}^t dt' \omega(t, t'; t_0) \log \rho_{cg}(t+t'; t') \right\} \quad (1)$$

where

$$\rho_{cg}(t_1, t_2) = \exp\{-\phi(t_1) - \sum_{j=1}^n F_j(t_1)P_j\} ,$$

with

$$\phi(t) = \text{Tr}\{- \sum_{j=1}^n F_j(t)P_j\} .$$

We recall that t_0 is an initial time taken in such a way as to ensure that the system has lost the memory of the details of the microscopic motion in the first stages of evolution, $t_0 > \tau_\mu$, after the system has been driven away from equilibrium (cf. I). Then for $t > \tau_\mu$ it is assumed that a randomization of the microscopic state of the system has occurred and the set of n variables Q_j allows for a description of the macroscopic state of the system. The dimension of the contracted description depends on the scale of time τ_μ , and therefore it is possible to define different stages of evolution of the system with decreasing values of n . This has been discussed in articles I and III, and can be seen at work in papers II and V. The coarse-grained statistical operator $P_{cg}(t_0, 0)$ defines an initial condition for the system after the randomization process has taken place, from which the system evolves under the action of its Hamiltonian and the restrictions imposed by the function w . This function fixes the initial condition, produces irreversible evolution of the macroscopic state of the system, and makes the method fully compatible with generalized irreversible thermodynamics, once the nonequilibrium average value of the negative of the logarithm of the coarse-grained statistical operator is identified with the entropy function of generalized irreversible thermodynamics (cf. I). Finally we recall that the evolution of the macroscopic state of the system is described by the set of generalized nonlinear transport equations described and discussed in article III.

Next, we study two questions: (a) a formal theory for evaluation of transition probabilities and (b) the calculation of response functions, both in far-from-equilibrium systems.

2a. Formal Theory of Scattering for Nonequilibrium Systems

Consider the coupling of a system with an external probe. Let H_S and H_P be the Hamiltonians of the system and of the external probe respectively, and V the interaction energy. Then, given the total wavefunction at time t_0 , the solution of Schrödinger's equation at time t is

$$|\psi(t)\rangle = U(t, t_0) |\psi(t_0)\rangle \tag{2}$$

where U is the evolution operator satisfying the equation

$$i\hbar \partial U / \partial t = H U \quad ; \quad U(t_0, t_0) = 1 \tag{3}$$

and $H = H_0 + V$ ($H_0 = H_S + H_P$) is the total Hamiltonian. Following well known procedures in scattering theory, the time dependence associated with the unperturbed energy operator is first removed by introducing the operator U' such that

$$U(t, t_0) = U_0(t, t_0) U'(t, t_0) \tag{4}$$

where

$$U_0(t, t_0) = \exp\{(1/i\hbar)(t-t_0)H_0\} \tag{5}$$

and then

$$i\hbar \partial U' / \partial t = \tilde{V}(t) U'(t, t_0) \quad , \quad U'(t_0, t_0) = 1 \tag{6}$$

with

$$\tilde{A}(t) = U_0^\dagger(t, t_0) A U_0(t, t_0) \tag{7}$$

The iterative method allows us to obtain the solution of eq.(6) in the form

$$U'(t, t_0) = 1 + \sum_{n=1}^{\infty} \left(\frac{1}{i\hbar}\right)^n \int_{t_0}^t dt_1 \dots \int_{t_0}^{t_1} dt_{n-1} \tilde{V}(t_1) \dots \tilde{V}(t_n) \tag{8}$$

Considering a scattering event involving a transition of the external probe between states p' to p , with energy transfer $\hbar\omega = \hbar\omega_p - \hbar\omega_{p'}$, the

transition probability at time t from state $|\psi(t_0)\rangle = |p'\rangle|\phi(t_0)\rangle$ is

$$P(t) = \sum_n |\langle n|\langle p| U'(t, t_0) |p'\rangle|\phi(t_0)\rangle|^2, \quad (9)$$

where $|n\rangle$ and $|p\rangle$, E_n and $\hbar\omega_p$ are the eigenfunctions and eigenenergies of the system and probe Hamiltonians, i.e.

$$H_s |n\rangle = E_n |n\rangle, \quad H_p |p\rangle = \hbar\omega_p |p\rangle.$$

Replacing eq.(8) in eq.(9) we find

$$P(t) = \frac{1}{\hbar^2} \int_{t_0}^t dt' \int_{t_0}^t dt'' \langle \phi(t_0) | R^\dagger(t'') R(t') | \phi(t_0) \rangle e^{-i\omega(t''-t')}, \quad (10)$$

with R defined by the integral equation

$$R(t) = \bar{W}(t) \left[1 + \frac{1}{i\hbar} \int_{t_0}^t dt' e^{i\omega t'} R(t') \right], \quad (11)$$

where we have introduced

$$\langle p | \bar{V}(p) | p' \rangle = \bar{W}(t) \cdot e^{i\omega t} = e^{i\omega t} U_s^\dagger(t, t_0) W U_s(t, t_0), \quad (12)$$

and

$$U_s(t, t_0) = \exp \left[\frac{1}{i\hbar} (t-t_0) H_s \right].$$

Since

$$U_s^\dagger(t', t_0) \phi(t') = \phi(t_0),$$

and using that

$$U_s(t, t_0) U_s^\dagger(t', t_0) = U_s(t, t'),$$

eq.(10) be rewritten as

$$P(t) = \frac{1}{R^2} \int_{t_0}^t dt' \int_{t_0}^t dt'' \langle \phi(t') | Q^\dagger(t''-t') Q(0) | \phi(t') \rangle e^{-i\omega(t''-t')}. \quad (13)$$

Finally, taking the average of eq.(13) over the nonequilibrium ensemble characterized by $\rho_w(t)$ we obtain

$$[\bar{P}(t)]_{AV} = \frac{1}{\hbar^2} \int_{t_0}^t dt' \int_{t_0}^{t'} dt'' \text{Tr}\{R^\dagger(t''-t')R(0)\rho_w(t'')\}e^{-i\omega(t''-t')} , \quad (14)$$

and the rate of transition probability at time t becomes

$$\Omega(\omega|t) = \frac{d}{dt} [\bar{P}(t)]_{AV} = \frac{1}{\hbar^2} \int_{t_0}^t dt' e^{-i\omega(t'-t)} \text{Tr}\{R^\dagger(t'-t)R(0)\rho_w(t')\} + \text{c.c.} \quad (15)$$

Near equilibrium, for a perturbation adiabatically applied at $t_0 = -\infty$ and to lowest order in V , eq. (15) becomes

$$\Omega(\omega) = \frac{1}{\hbar^2} \int_{-\infty}^{\infty} d\tau e^{-i\omega\tau} \text{Tr}\{W^\dagger(\tau)W(0)\rho^{\text{equil.}}\} ,$$

which reproduces well-known results for the temperature-dependent rate of transition probability⁷.

Further, assuming adiabatic application of the perturbation beginning at $t_0 = -\infty$ and after the variable transformation $\tau = t'-t$ is performed eq. (15) becomes

$$\Omega(\omega|t) = \frac{1}{\hbar^2} \int_{-\infty}^0 d\tau e^{-i(\omega+is)\tau} \text{Tr}\{R_{\square}^\dagger(\tau)R(0)\rho_w(t)\} + \text{c.c.} , \quad (16)$$

with $s \rightarrow +0$.

Inspection of eq. (16) show us that the rate of transition probability involves the calculation of a time-dependent nonequilibrium correlation of operators. Recalling that [eq. (25) ff. in I]

$$\rho_w(t) = \rho_{cg}(t) + \rho^1(t) = [1 + D_w(t)] \rho_{cg}(t) ,$$

with D defined by eq. (26d) in I, it follows that $\Omega(t)$ is composed of two parts: one involving only the average over the coarse-grained (relaxation free) ensemble, plus terms that couple the mechanical effects with the thermal effects that develop in the nonequilibrium system. Hence, using the results of article I, we can write

$$\Omega(\omega|t) = \bar{\Omega}(\omega|t) + \Omega^1(\omega|t) , \quad (17)$$

where

$$\Omega(\omega|t) = \frac{1}{\hbar^2} \int_{-\infty}^0 d\tau e^{-i(\omega+i\delta)\tau} \langle R^\dagger(\tau)R(0) | t \rangle_{cg} + \text{c.c.} \quad , \quad (18a)$$

$$\Omega'(\omega|t) = \frac{1}{\hbar^2} \int_{-\infty}^0 d\tau e^{-i(\omega+i\delta)\tau} \langle R^\dagger(\tau)R(0)D_\omega(t) | t \rangle_{cg} + \text{c.c.} \quad , \quad (18b)$$

with

$$\langle \dots | t \rangle_{cg} = \text{Tr} \{ \dots \rho_{cg}(t) \} \quad , \quad (18c)$$

and eq. (18b) admits a series expansion of increasing order in the statistical-entropy production operator of which $D_\omega(t)$ is a functional (Cf I and III and see eq. (44) in section 3 below). Further, it must be kept in mind that the calculation of eq. (16) depends on the set of variable $F_j(t)$ which are obtained by solving the generalized nonlinear transport equations which govern their evolution [eqs. (9) and (10) in I].

2b. Response Function Theory

Let A be an operator associated with a certain dynamical quantity of a system coupled to an external perturbation through an energy interaction $V(t)$. The average value of this quantity A at time t is

$$a(t) = \langle \psi(t) | A | \psi(t) \rangle = \langle \psi(t_0) | U^\dagger(t, t_0) A U(t, t_0) | \psi(t_0) \rangle \quad , \quad (19)$$

and using the results of subsection 2a

$$\begin{aligned} a(t) &= \langle \psi(t_0) | U^{\dagger\dagger}(t, t_0) U_0^\dagger(t, t_0) A U_0(t, t_0) U^{\dagger}(t, t_0) | \psi(t_0) \rangle = \\ &= \langle \psi(t_0) | U^{\dagger\dagger}(t, t_0) \tilde{A}(t-t_0) U^{\dagger}(t, t_0) | \psi(t_0) \rangle \quad , \quad (20) \end{aligned}$$

Taking the average value of eq. (20) over the nonequilibrium ensemble we get

$$\overline{[A|t]} = \overline{[a(t)]}_{AV} = \text{Tr} \{ U^{\dagger\dagger}(t, t_0) \tilde{A}(t) U^{\dagger}(t, t_0) \rho_w(t_0) \} \quad . \quad (21)$$

But because of eq.(8), in the linear approximation in the interaction strength, i.e.

$$U^i(t, t_0) \approx 1 + \frac{1}{i\hbar} \int_{t_0}^t dt' \tilde{V}(t') \quad , \quad (22)$$

it follows that

$$[A|t] = \langle A|t \rangle + \frac{1}{i\hbar} \int_{t_0}^t dt' \text{Tr}\{[\tilde{A}(t), \tilde{V}(t')] \rho_w(t_0)\} \quad , \quad (23)$$

where

$$\langle A|t \rangle = \text{Tr}\{A \rho_w(t)\} \quad .$$

Using the properties of operator U_0 , eq.(23) can be rewritten as

$$[A|t] - \langle A|t \rangle = \frac{1}{i\hbar} \int_{t_0}^t dt' \text{Tr}\{[\tilde{A}(0), \tilde{V}(t'-t)] \rho_w(t)\} \quad . \quad (24)$$

Assuming adiabatic application of the perturbation in the remote past ($s \rightarrow +\infty$) we find that

$$\begin{aligned} [A|t] - \langle A|t \rangle &= \frac{1}{i\hbar} \int_{-\infty}^0 d\tau e^{s\tau} \text{Tr}\{[\tilde{A}(0), \tilde{V}(\tau)] \rho_w(t)\} \\ &= \frac{1}{i\hbar} \int_{-\infty}^0 d\tau e^{s\tau} \langle [\tilde{A}(0), \tilde{V}(\tau)] |t \rangle \quad . \end{aligned} \quad (25)$$

Taking into account the separation of ρ in the form $\rho_{cg} + \rho^i$, eq.(25) can be rewritten in the form

$$[A|t] = [A|t]_{cg} + [A|t]^i \quad , \quad (26)$$

where

$$[A|t]_{cg} = \langle A|t \rangle_{cg} + \frac{1}{i\hbar} \int_{-\infty}^0 d\tau e^{s\tau} \langle [\tilde{A}(0), \tilde{V}(\tau)] |t \rangle_{cg} \quad , \quad (27a)$$

$$[A|t]^i = \langle A^i_w(t) |t \rangle_{cg} + \frac{1}{i\hbar} \int_{-\infty}^0 d\tau e^{s\tau} \langle [\tilde{A}(0), \tilde{V}(\tau)] D_w(t) |t \rangle_{cg} \quad (27b)$$

and, similarly to the case of eq. (18b) $[A|t]$ admits a series expansion in terms of increasing order in the statistical-entropy production operator on which $D_w(t)$ depends (see eqs. (26d) and (26e) in I and eq. (44) in the next section).

Therefore, according to sections 2a, b the calculation of transition probabilities and of response functions involve calculations of nonequilibrium correlation functions. This is in general a difficult mathematical task, which can be more easily performed using the formalism of nonequilibrium thermodynamic Green functions described in the next section.

3. NONEQUILIBRIUM THERMODYNAMIC GREEN'S FUNCTIONS

We describe in this section a Green's function formalism for nonequilibrium statistical systems, which is a natural generalization of the equilibrium thermodynamic Green's function formalism.⁸ Let A and B be two operators in the Heisenberg representation. We define the retarded Green's function

$$\langle\langle A(\tau); B|t \rangle\rangle_{\eta} = -i\theta(-\tau)\text{Tr}\{[\bar{A}(\tau), \bar{B}]_{\eta} \rho_w(t)\} \quad , \quad (28)$$

where $\eta = +$ or $-$ stands for anticommutator or commutator of operators A and B , and θ is Heaviside's step function. This Green's functions satisfy the equation of motion

$$i\hbar \frac{\partial}{\partial \tau} \langle\langle A(\tau); B|t \rangle\rangle_{\eta} = -\hbar\delta(\tau) \langle[A, B]_{\eta}|t\rangle + \langle\langle [A(\tau); H]; B|t \rangle\rangle_{\eta} \quad . \quad (29)$$

In eq. (29) and in what follows, $[A, B]$ without subscript is the commutator of quantities A and B .

Introducing a Fourier transform of the Green's function (28) in the form

$$\langle\langle A; B|\omega; t \rangle\rangle_{\eta} = \int_{-\infty}^{\infty} \frac{d\tau}{2\pi} e^{-i\omega\tau} \langle\langle A(\tau); B|t \rangle\rangle_{\eta} \quad , \quad (30)$$

eq. (29) becomes

$$-\hbar\omega \langle\langle A; B|\omega; t \rangle\rangle_{\eta} = -\frac{\hbar}{2\pi} \langle[A, B]_{\eta}|t\rangle + \langle\langle [A, H]; B|\omega; t \rangle\rangle_{\eta} \quad (31)$$

We also define the nonequilibrium correlation functions

$$F_{AB}(\tau; t) = \langle A(\tau)B | t \rangle = \text{Tr} \{ A(\tau)B \rho_w(t) \} \quad , \quad (32a)$$

$$\tilde{F}_{BA}(\tau; t) = \langle B A(\tau) | t \rangle = \text{Tr} \{ B A(\tau) \rho_w(t) \} \quad , \quad (32b)$$

and using a complete set of eigenfunctions of H , $|n\rangle$, with eigenenergies E_n , we find

$$F_{AB}(\tau; t) = \sum_{\ell mn} \langle n|A|m\rangle \langle m|B|\ell\rangle \langle \ell | \rho_w(t) | n \rangle e^{(1/i\hbar)(E_m - E_n)\tau} \quad (33a)$$

$$\tilde{F}_{BA}(\tau; t) = \sum_{\ell mn} \langle n|B|m\rangle \langle m|A|\ell\rangle \langle \ell | \rho_w(t) | n \rangle e^{(1/i\hbar)(E_\ell - E_m)\tau} \quad (33b)$$

Introducing the nonequilibrium spectral density functions

$$J_{AB}(\omega|t) = \hbar \sum_{\ell mn} \langle n|A|m\rangle \langle m|B|\ell\rangle \langle \ell | \rho_w(t) | n \rangle \delta(\hbar\omega - E_n + E_m) \quad , \quad (34a)$$

and

$$K_{BA}(\omega|t) = \hbar \sum_{\ell mn} \langle n|B|m\rangle \langle m|A|\ell\rangle \langle \ell | \rho_w(t) | n \rangle \delta(\hbar\omega - E_m + E_\ell) \quad , \quad (34b)$$

we obtain that

$$F_{AB}(\tau; t) = \int_{-\infty}^{\infty} d\omega J_{AB}(\omega|t) e^{i\omega\tau} \quad , \quad (35a)$$

$$\tilde{F}_{BA}(\tau; t) = \int_{-\infty}^{\infty} d\omega K_{BA}(\omega|t) e^{i\omega\tau} \quad , \quad (35b)$$

and

$$\langle\langle A; B | \omega; t \rangle\rangle_+ + \langle\langle A; B | \omega; t \rangle\rangle_- = \int_{-\infty}^{\infty} \frac{d\omega'}{\pi} \frac{J_{AB}(\omega'|t)}{\omega - \omega' + i\epsilon} \quad , \quad (36a)$$

$$\langle\langle A;B|\omega;t\rangle\rangle_+ - \langle\langle A;B|\omega;t\rangle\rangle_- = \int_{-\infty}^{\infty} \frac{d\omega'}{\pi} \frac{K_{BA}(\omega'|t)}{\omega - \omega' + is} \quad (36b)$$

with $s \rightarrow +0$.

Eqs. (36) are a generalization of the fluctuation-dissipation theorem to systems arbitrarily away from equilibrium. Near equilibrium conditions, where $\rho_w(t)$ is replaced by the canonical distribution, one recovers the well known result^e

$$\begin{aligned} \langle\langle A;B|\omega+is\rangle\rangle_{\eta} + \eta \langle\langle A;B|\omega-is\rangle\rangle_{\eta} &= -\frac{1}{2} (1 + \eta e^{-\beta\hbar\omega}) J_{AB}^{\text{eq}}(\omega) = \\ &= -\frac{1}{2} (\eta + e^{-\beta\hbar\omega}) K_{BA}^{\text{eq}}(\omega) \quad , \quad (37) \end{aligned}$$

where $\beta = 1/kT$, and it should be noted that our $K_{BA}^{\text{eq}}(\omega)$ is Zubarev's $J_{BA}^{\text{eq}}(-\omega)$.⁸

We are now in conditions to rewrite the expressions for the rate of transition probability and the response functions of section 2 in terms of nonequilibrium thermodynamics Green's Functions. First, using eqs. (32a), (35a) and eq. (16) becomes

$$\begin{aligned} \Omega(t) &= \frac{1}{\hbar^2} \int_{-\infty}^{\infty} d\tau e^{-i(\omega+is)\tau} F_{R^{\dagger}R}(\tau;t) + \text{C.C.} \\ &= \frac{1}{\hbar^2} \int_{-\infty}^{\infty} d\tau \int_{-\infty}^{\infty} d\omega' e^{-i(\omega-\omega'+is)\tau} J_{R^{\dagger}R}(\omega'|t) + \text{C.C.} \\ &= \frac{i}{\hbar^2} \int_{-\infty}^{\infty} d\omega' \frac{J_{R^{\dagger}R}(\omega'|t)}{\omega - \omega' + is} + \text{C.C.} \quad , \quad (38) \end{aligned}$$

Finally, because of eq. (36a) we find

$$\Omega(\omega|t) = -\frac{2\pi}{\hbar^2} \text{Im}[\langle\langle R^{\dagger};R|\omega+is;t\rangle\rangle_+ + \langle\langle R^{\dagger};R|\omega+is;t\rangle\rangle_-] \quad , \quad (39)$$

i.e. the rate of transition probability, in any order in the interaction strength and any order in the rate of statistical-entropy production, is given by the imaginary part of the sum of the retarded non-equilibrium thermodynamic Green functions of the scattering operator taken with commutator and anticommutator. We recall that the Green's functions of eq. (39) depend on the macroscopic state of the system through variables $F_j(t)$, and therefore the equation for the Green's functions must be solved in conjunction with the generalized nonlinear transport equations for the set $\{F_j(t)\}$ (Cf.3).

Next, going over eq. (25), assuming an interaction energy of the form $V(t) = \frac{\lambda}{2} e^{-i\omega t} B(0) + \text{C.C.}$, where λ is a coupling constant and B an hermitian operator, we find that

$$\begin{aligned} [A|t] - \langle A|t \rangle &= \frac{\lambda}{2i\hbar} \int_{-\infty}^t d\tau e^{-i(\omega+i\epsilon)\tau} \langle [A, \tilde{B}(\tau)] |t \rangle + \text{C.C.} \\ &= \frac{\lambda}{2i\hbar} \int_{-\infty}^{\infty} d\tau \theta(-\tau) e^{-i(\omega+i\epsilon)\tau} \langle [A, \tilde{B}(\tau)] |t \rangle + \text{C.C.} \\ &= \frac{\hbar}{2i\hbar} \langle \langle A; B | \omega+i\epsilon, t \rangle \rangle_- + \text{C.C.} \end{aligned} \tag{40}$$

where we used the definition of the retarded Green's function, eq. (28).

Hence, the linear response function to a harmonic perturbation is given by a retarded nonequilibrium thermodynamic Green's function dependent on the macroscopic state of the system characterized by macrovariables $F_j(t)$ (or $Q_j(t)$).

Closing this section, we note that since the nonequilibrium Green's functions of eq. (28) are defined as nonequilibrium averages of dynamical quantities, recalling that $\rho_w = \rho_{cg} + \rho^1$, and that ρ^1 admits a series expansion in terms of ever increasing order in the statistical entropy-production operator, we can write

$$\langle \langle A(\tau); B | t \rangle \rangle_{\eta} = \langle \langle A(\tau); B | t \rangle \rangle_{\eta, cg} + \langle \langle A(\tau); B | t \rangle \rangle_{\eta}^1, \tag{41}$$

where

$$\langle\langle A(\tau); B|t \rangle\rangle_{\eta, \text{cg}} = -i\theta(-\tau) \text{Tr}\{[\underline{A}(\tau), \underline{B}]_{\eta} \rho_{\text{cg}}(t)\} \quad , \quad (42)$$

$$\langle\langle A(\tau); B|t \rangle\rangle_{\eta}^{\dagger} = -i\theta(-\tau) \text{Tr}\{[\underline{A}(\tau), \underline{B}]_{\eta} D_w(t) \rho_{\text{cg}}(t)\} \quad . \quad (43)$$

Writing

$$D_w(t) = \sum_{n=1}^{\infty} D_w^{(n)}(t) \quad (44)$$

where $D_w^{(n)}(t)$ is defined in 3, we obtain a series expansion for the Green's functions in the form

$$\langle\langle A; B|w; t \rangle\rangle_{\eta} = \langle\langle A; B|w; t \rangle\rangle_{\eta, \text{cg}} + \sum_{n=1}^{\infty} \langle\langle A; B|w; t \rangle\rangle_{\eta}^{(n)} \quad , \quad (45)$$

with the terms of the series on the right hand side satisfying the equations

$$-i\hbar\omega \langle\langle A; B|w; t \rangle\rangle_{\eta, \text{cg}} = -\frac{\hbar}{2\pi} \langle [\underline{A}, \underline{B}] |t \rangle_{\text{cg}} + \langle\langle [\underline{A}, \underline{H}]; B|w; t \rangle\rangle_{\eta, \text{cg}} \quad (46)$$

$$-i\hbar\omega \langle\langle A; B|w; t \rangle\rangle_{\eta}^{(n)} = -\frac{\hbar}{2\pi} \langle [\underline{A}, \underline{B}]_{\eta} D_w^{(n)}(t) |t \rangle_{\text{cg}} + \langle\langle [\underline{A}, \underline{H}]; B|w; t \rangle\rangle_{\eta}^{(n)} \quad (47)$$

Whenever any truncation procedure process is introduced to approximately solve these equations, care should be taken to maintain terms of the same order in the interaction strengths. For example, if we start with eq. (46) where the term involving $[\underline{A}, \underline{H}]$ leads, as it is well known, to an infinite set of coupled equations of ever increasing order in the interaction strengths, a truncation procedure that closes the system in second order in the interaction strengths requires the inclusion of the Green's functions of eqs. (47) with $n = 1$ and $n = 2$, but neglecting the interactions in the Hamiltonian in eq. (47) for $n=2$.

4. CONCLUDING REMARKS

We have shown that the nonequilibrium statistical operator method described in paper I provides the framework to build a response function theory for many-body systems arbitrarily away from equilibrium. The formalism provides response functions or scattering cross sections for a measurement operation which involves characteristic time intervals much longer than the relaxation time for microprocesses, τ_{μ} , i.e. for time intervals that are consistent with the contracted description of the macroscopic state of the system in terms of the basic set of dynamical quantities P_j , $j = 1, 2, \dots, n$, and the n thermodynamically conjugated variables $F_j(t)$. An accompanying nonequilibrium thermodynamic Green's functions algorithm was described in section 3.

The theory developed in this paper can be considered a natural extension of Kubo's formalism, and it provides the linear and nonlinear responses of many-body systems arbitrarily away from equilibrium in terms of correlation functions calculated in the nonequilibrium ensemble characterized by the MD $\rho_w(t)$. Thus, it describes the effect of a mechanical perturbation on a system which is evolving in an irreversible way governed by the nonlinear generalized transport equations discussed in III. In a forthcoming paper we apply the results presented here to the study of optical responses in highly excited plasma in semiconductors?

REFERENCES

1. A.C. Algarte, A.R. Vasconcellos, R. Luzzi and A.J. Sampaio, *Rev. Brasil. Fis.* 15, 106 (1985), referred to in the text as I.
2. R. Luzzi, A.R. Vasconcellos and A.C. Algarte, *Rev. Brasil. Fis.* 16, 495 (1986), referred to in the text as III.
3. E.g. P.C. Martin, *Measurements and Correlation Functions*, *The Many-Body Problem*, edited by C. de Witt and R. Balian (Gordon and Breach, New York, 1967); R. Kubo, *J. Phys. Soc. Japan* 12, 570 (1957); see also reference 8.
4. R. Luzzi and A.R. Vasconcellos, *Journ. Stat. Phys.* 23, 539 (1980).

5. A.C.Algarte, A.R.Vasconcellos, R.Luzzi and A.J.Sampaio, Rev.Brasil. Fis., 16, 42 (1986), referred to in the text as II.
6. V.N.Freire, A.R.Vasconcellos, R.Luzzi and A.J.Sampaio, Rev.Brasil. Fis., to be submitted, referred to in the text as V, and short communication in *Proceedings of the International Conference on High Speed Electronics* (Stockholm, 1986), edited by B. Källbäck and H. Beneking (Springer, Berlin-Heidelberg, 1987); also, A.C.Algarte, A. R.Vasconcellos and R.Luzzi, to be published, and short communication in *Proceedings of the 18-IUPAP International Conference on the Physics of Semiconductors* (Stockholm 1986), edited by O. Engström (World Scientific, Singapore, in press).
7. L.van Hove, Phys. Rev. 95, 249 (1964); *ibid* 95, 1374 (1964); V.L. Tyablikov, *Methods in the Quantum Theory of Magnetism* (Plenum, New York, 1974).
8. D.N.Zubarev, Uspekhi. Fiz. Nauk, 71, 71 (1960) [Soviet Phys. Uspekhi 3, 320 (1960)].
9. See also A.J.Sampaio, thesis (UNICAMP, 1983, unpublished); A.R.Vasconcellos and R.Luzzi, J.Raman Spectrosc. 10, 28 (1981); *ibid* 14, 39 (1983); A.R.Vasconcellos and R.Luzzi, Phys.Rev. B27, 3874 (1983); C. Machado, M. Sc. thesis (UNICAMP, 1985, unpublished).

Resumo

É apresentada uma teoria da função resposta apropriada para tratar sistemas de muitos corpos arbitrariamente afastados do equilíbrio, construída usando o método do operador estatístico de não-equilíbrio previamente descrito (Rev.Brasil.Fis.15, 106 (1985)). Derivamos um algoritmo de funções de Green termodinâmicas de não-equilíbrio, assim como uma generalização, dentro do arcabouço destas últimas, do teorema de flutuação-dissipação para sistemas longe do equilíbrio.