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Response Function Theory for Far-from-Equilibrium Statistical Systems

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A formalism to determine the response function of a sample in conditions far from thermal equilibrium is presented. It consists in a generalization of scattering theory coupled to the statistical theory of irreversible processes, the nonequilibrium statistical operator method, developed by Zubarev. The scattering cross section is expressed in terms of double-time correlation functions, which are related to appropriate nonequilibrium thermodynamic Green's functions. The latter are also used to treat generalized transport equations, and, as an illustration, the method is applied to the study of the time-resolved Raman spectroscopy of a photoexcited semiconductor plasma.

KEY WORDS: Response function; nonequilibrium thermodynamic Green's functions; nonequilibrium statistical operator; generalized Langevin equations; photoexcited semiconductor plasma.

1. INTRODUCTION

Kubo(1) has pointed out that "statistical mechanics of non-linear non-equilibrium phenomena is just in its infancy," and that "further progress can only be hoped by close cooperation with experiments." In the description of physical measurements correlation functions play an important and inevitable role.(2) For systems deviating slightly from thermodynamic equilibrium, exact closed expressions for the response functions of the systems can be obtained in the form of correlation functions at equilibrium (the fluctuation-dissipation theorem in the linear approximation in external forces).(3) The response theory of equilibrium system is intimately related to the Green's function formalism of Bogoliubov and Tyablikov, as described in the already classic paper by Zubarev(4a) (see also Refs. 4b and 13). The actual calculation may be difficult for the case of interacting many-body systems, but it is formally closed at this level.

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However, measurements may be performed on systems which can depart strongly from equilibrium. One may ask if, in these conditions, it is also possible to construct a closed macroscopic description of the system which can be adequate for a class of physical experiments. The response of highly excited systems to external perturbations involves the participation of nonequilibrium distributions of elementary excitations, and to provide a formalism to evaluate the response function for such cases is the object of the present study.

Clearly, to deal with this question we should need to resort to some treatment of nonequilibrium statistical thermodynamics in order to describe the macroscopic state of the sample. There exists several methods to describe macroscopic processes that occur in nonequilibrium systems with a large number of degrees of freedom. Among them is the statistical approach based on the use of distribution functions derived by the ensemble method initiated by Gibbs for systems in equilibrium. Zubarev's method(5) belongs to this kind of approach, and it seems offer a closed-off 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 is described by a statistical operator which includes nonlinear, nonlocal, and retardation effects. It should be stressed that the method is not restricted to situations when the system deviates only slightly from equilibrium (the linear domain), but it can treat systems far from thermal equilibrium. Further, the method permits the recovery of the results of nonequilibrium nonlinear thermodynamics.(6) The formalism developed by Zubarev consists in obtaining nonequilibrium statistical operators through a generalization of the Gibbsian method, using dynamical conservation laws. It is based on Bogoliubov's idea that a contracted description of nonequilibrium statistics may be possible if the system, in its approach to equilibrium, can be characterized by a hierarchy of relaxation times of quite different orders of magnitude.(7) Zubarev's method has been extensively applied to the study of a number of nonequilibrium statistical problems,[2] and it is briefly reviewed in Section 3.

In Section 2, to obtain the response function of nonequilibrium statistical systems (NESS) to external perturbations, e.g., scattering cross sections, emission spectra, etc., we evaluate the rate of transition probabilities, governed by the interaction potential, using Landau's density matrix approach.(9) An ensemble average of the density matrix of the nonequilibrium system is introduced using the hypothesis that there exists a macroscopic contracted description of the state of the system in terms of a small number of macroscopic variables, the mean values of a certain restricted set of physical

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[2] See the references in Zubarev(5) and, for more recent work, Refs. 8.

quantities, whose time dependence reflects the evolution of the nonequilibrium statistical system. Similar to the equilibrium case, the transition probability can be written in terms of time correlation functions, with averages over the nonequilibrium statistical ensemble. The formalism is closed with the choice of Zubarev's distribution function to specify the ensemble average.

The calculation of correlation functions of the nonequilibrium many-body system could be handled through the introduction of appropriate Green's functions, which are defined in Section 4 as a natural generalization of the thermodynamic double-time Green's functions of Ref. 4. However, in contrast to the equilibrium case, the equations for the Green's functions are not closed in themselves, but they are coupled to the set of dynamic equations for the macroscopic variables on which the NESS depends. We relate the response function of a NESS to the nonequilibrium thermodynamic Green's functions (NET GF), i.e., the generalization of the fluctuation-dissipation theorem. Further, we establish the connection of the generalized transport equations of the Zubarev method (the dynamic equations for the macroscopic variables) and the NET GF. An application to the study of the evolution of a coupled system of phonons and a highly excited semiconductor plasma, the latter being probed by means of time-resolved Raman spectroscopy, is presented in Section 4.

2. FORMAL THEORY OF SCATTERING FOR NESS

In this section we consider the response of a nonequilibrium statistical system to an external perturbation.

Consider a NESS whose coordinates are designated by q, interacting with other systems (the set of which we call the thermal bath, of coordinates Q), and coupled to an external probe (coordinates x).

We write for the total Hamiltonian

$$H(q, Q, x) = H_\sigma(q) + H_B(Q) + W(q, Q) + H_p(x) + V(q, x) \tag{1}$$

where H_σ is the system Hamiltonian, H_B is the thermal bath Hamiltonian, W is the interaction energy between the system and the bath, H_p is the external probe Hamiltonian, and V is the interaction energy between the system and the external probe. Furthermore, we introduce the notation $|\mu\rangle$ and $|p\rangle$ for the eigenfunctions of the system and thermal bath and external probe, respectively, and $H_p|p\rangle = h\omega_p|p\rangle$ and $(H_\sigma + H_B + W)|\mu\rangle = E_\mu|\mu\rangle$.

Given the total wave function at time t_0, $\Psi(t_0)$, the solution of Schrödinger equation at time t is

$$\Psi(t) = U(t, t_0)\Psi(t_0) \tag{2}$$

with U satisfying the equation

$$i\hbar\, \partial U(t, t_0)/\partial t = HU(t, t_0), \qquad U(t_0, t_0) = 1 \tag{3}$$

Following well-known procedures in scattering theory,$^{(10)}$ the time dependence associated with the unperturbed energy operator is first removed by introducing the operator U' defined by

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

where

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

with

$$H_0 = H - V \tag{6}$$

U' satisfies the equation

$$i\hbar\, \partial U'(t, t_0)/\partial t = \tilde{V}(t)U'(t, t_0) \tag{7}$$

where

$$\tilde{V}(t) = U_0{}^{+}(t, t_0)VU_0(t, t_0) \tag{8}$$

Equation (7) possesses the iterated solution

$$U'(t, t_0) = \sum_{n=0}^{\infty} \left(\frac{1}{i\hbar}\right)^n \int_{t_0}^{t} dt_1 \cdots \int_{t_0}^{t_{n-1}} dt_n\, \tilde{V}(t_1) \cdots \tilde{V}(t_n) \tag{9}$$

Fixing the scattering channel $p' \to p$, we obtain the transition probability at time t from state $\Psi(t_0)$:

$$P_{p' \to p}(t) = \sum_{\mu} |\langle \mu | U'_{pp'}(t, t_0) | \psi(t_o) \rangle|^2 \tag{10}$$

where $\psi = \langle p' | \Psi \rangle$ and $U'_{pp'} = \langle p | U' | p' \rangle$. For simplicity we henceforth drop the indexes p and p'.

Equation (10) can be written alternatively

$$P_\omega(t) = \frac{1}{\hbar^2} \int_{t_0}^{t} dt' \int_{t_0}^{t} dt'' \,\{\exp[-i\omega(t'' - t')]\} \langle \psi(t_0) | \tilde{\mathscr{R}}^{+}(t'')\tilde{\mathscr{R}}(t') | \psi(t_o) \rangle \tag{11}$$

where $\omega = \omega_p - \omega_{p'}$ is the energy transfer in the scattering event, $\tilde{V} = \langle p | \tilde{V} | p' \rangle$, and the scattering operator $\mathscr{R}$ is defined by

$$\tilde{\mathscr{R}}(t) = \tilde{V}(t)\left[1 + \frac{1}{i\hbar} \int_{t_0}^{t} dt'\, \tilde{\mathscr{R}}(t')\right] \tag{12}$$

Using Eq. (2), we can write Eq. (11) as

$$\begin{aligned} P_\omega(t) = \frac{1}{\hbar^2} \int_{t_0}^{t} dt' \int_{t_0}^{t} dt'' \int dq \int dQ\, \{[U_0{}^{+}(q, Q; t'', t')\mathscr{R}^{+}(0) \\ \times U_0(q, Q; t'', t')\mathscr{R}(0)\rho(qQ, q'Q'; t')]\, e^{-i\omega(t''-t')}\}_{q=q';\, Q=Q'} \end{aligned} \tag{13}$$

where we have defined the density matrix[9]

$$\rho(qQ, q'Q'; t') = \psi(q, Q; t')\psi^*(q', Q'; t') \tag{14}$$

At this point we define a nonequilibrium ensemble average, introducing the hypothesis that there exists a contracted description of the macroscopic state of the NESS in terms of a small number of macrovariables, in a way to be made more precise in next section. Further, however, the transition probability of Eq. (13) contains the interaction potential to all orders, i.e., it is not confined to a purely linear response; we are restricting the conditions of applicability of our treatment to situations when the interaction with the probe produces thermal perturbations that can be neglected in comparison with those already present in the highly excited prepared sample.

Taking the ensemble average in Eq. (13) and introducing the NESS $\rho(t)$ defined by

$$\langle \rho(qQ, q'Q'; t)\rangle_{\text{av}} = \langle qQ|\rho(t)|q'Q'\rangle \tag{15}$$

it follows that

$$\langle P_\omega(t)\rangle_{\text{av}} = \frac{1}{\hbar^2}\int_{t_0}^{t} dt' \int_{t_0}^{t} dt''\, e^{-i\omega(t''-t')}\,\mathrm{Sp}\{\mathscr{R}^+(t''-t')\mathscr{R}(0)\rho(t')\} \tag{16}$$

where Sp stands for the trace of the operator within the curly bracket. The operators are now given in the Heisenberg representation of the unperturbed system.

Finally, the rate of transition probability for the scattering process at time t is given by

$$w(t|\omega) = \frac{d}{dt}\langle P_\omega(t)\rangle_{\text{av}} = \frac{1}{\hbar^2}\int_{t_0}^{t} dt'\, e^{-i\omega(t'-t)}\,\mathrm{Sp}\{\mathscr{R}^+(t'-t)\mathscr{R}(0)\rho(t)\} + \text{c.c.} \tag{17}$$

For equilibrium systems where $\rho(t) = Z^{-1}e^{-\beta H}$, Eq. (17) reproduces well-known results for the temperature-dependent rate of transition probability.[4b,11]

Next we specify the nonequilibrium statistical operator $\rho(t)$.

3. THE NONEQUILIBRIUM STATISTICAL DISTRIBUTION

Zubarev's method is based on Bogoliubov's assertion that if there exists a relaxation time for microinformation τ_μ after which the system loses the memory of the detailed initial distribution for $t \gg \tau_\mu$, a randomization should occur, and a reduced number of variables is enough to describe in a macroscopic way the state of the system.(7) The contraction of the initial distribution, the latter dependent on all degrees of freedom, is connected with the separation from the total Hamiltonian of strong interactions with certain symmetries.(12) These are related to the rapidly relaxing processes.

Hence, for not too short times, i.e., $t \gg \tau_\mu$, correlations with lifetimes smaller than τ_μ can be ignored and the state of the system may be described by a reduced set of macroscopic variables (or macrovariables for short), say $Q_1(t),..., Q_s(t)$, which are the average values over the nonequilibrium ensemble of a set of dynamical quantities $P_1,..., P_s$. Next an auxiliary statistical operator is defined, sometimes referred to as the quasi-equilibrium statistical distribution (QESD), $\rho_q(t, 0)$, as an idealized initial condition for the system after the randomization process has occurred, and from which the system evolves under dynamical laws governed by its Hamiltonian H. This means that at all times the NESS, which must satisfy Liouville–von Neumann equation, is a functional of ρ_q.

The QESD is chosen so as to make extremal the information entropy $-\ln \rho_q$ for given average values of the quantities P_m, thus yielding the generalized canonical-like distribution

$$\rho_q(t, 0) + \exp\left[-\phi(t) - \sum_m F_m(t) P_m \right], \qquad m = 1, 2,..., s \tag{18}$$

where $\phi(t)$ is given by the normalization condition $\mathrm{Sp}\{\rho_q(t, 0)\} = 1$, and the set of Lagrange multipliers $F_1(t),..., F_s(t)$ are parameters thermodynamically conjugate to the macrovariables Q in a sense to be defined later. Let us observe that the quantities P_m can be taken as densities of dynamical quantities, and therefore the state variables $Q_m(\mathbf{r}, t)$ and thermodynamic parameters (now thermodynamic fields) $F_m(\mathbf{r}, t)$ are functions of position.

Next the NESS corresponding to the initial value $(t_0 \to -\infty)$ ρ_q is defined as

$$\rho_\epsilon(t) = \exp\left[\epsilon \int_{-\infty}^{0} dt'\, e^{\epsilon t'} \ln \rho_q(t + t', t') \right] \equiv \exp[\mathscr{P}_\epsilon \ln \rho_q(t, 0)] \tag{19}$$

with ϵ going to $+0$ after the trace operation has been performed in the calculation of averages, and where the first term in the argument of ρ_q stands for the time dependence of the thermodynamic parameters F, whereas the second denotes the evolution of the parameters P under the action of the system Hamiltonian H (the Heisenberg representation), and the last identity defines the projection operator $\mathscr{P}_\epsilon$ (see Appendix). This statistical operator satisfies the Liouville equation with infinitesimal sources

$$\frac{\partial \ln \rho_\epsilon}{\partial t} + \frac{1}{i\hbar} [\ln \rho_\epsilon, H] = -\epsilon(\ln \rho_\epsilon - \ln \rho_q) \tag{20}$$

We observe at this point that the NESS of Eq. (19) is completely equivalent to the one that can be defined as $\rho_\epsilon' = \mathscr{P}_\epsilon \rho_q$.(5)

Equation (19) defines the operation of projecting the QESD over the subspace of the retarded solutions of the initial value problem of the Liouville equation. These are the solutions that correspond to an increase in entropy, thus satisfying the second law of thermodynamics.(5) This is ensured by the presence of the infinitesimal source in Eq. (20), which also fixes the initial condition, breaking the time-reversal symmetry of the Liouville–von Neumann equation. Irreversibility is then associated with this symmetry-breaking, and the average of any physical quantity over the ensemble defined by distribution (19) is a quasiaverage in Bogoliubov's sense.(13) In this way invariance under time-reversal transformations is not satisfied for these quasiaverages because of the removal of the corresponding degeneracy in the Liouville equation.

Except for the normalization condition, the parameters F are still open. To uniquely define them, an additional condition is imposed on the distribution ρ_ϵ in the form

$$Q_m(\mathbf{r}, t) = \mathrm{Sp}\{P_m(\mathbf{r})\rho_\epsilon(t)\} \equiv \langle P_m(\mathbf{r})|t\rangle = \langle P_m(\mathbf{r})|t\rangle_q \equiv \mathrm{Sp}\{P_m(\mathbf{r})\rho_q(t, 0)\} \quad (21)$$

which guarantees the conservation of normalization in Eq. (19), and leads to the definition

$$Q_m(\mathbf{r}, t) \equiv \langle P_m(\mathbf{r})|t\rangle = \langle P_m|t\rangle_q = -\delta\phi(t)/\delta F_m(\mathbf{r}, t) \quad (22)$$

Equation (22) is the generalization of the concept of thermodynamic parameters(14) to the nonequilibrium state; the nonequilibrium thermodynamic parameters (fields) F_m are said to be thermodynamically conjugate to the macrovariables Q_m in the sense established by Eq. (22), and a similar definition has been used, for different nonequilibrium distributions, by several authors(15–18) (see also Appendix).

To make contact with thermodynamics a time-dependent entropy for systems away from equilibrium needs to be defined, and this is done by generalizing the Gibbs entropy for equilibrium using the auxiliary fields $F_m(\mathbf{r}, t)$ and the instant averages of Eq. (21), i.e.,

$$\mathscr{S}(t) = -\langle \ln \rho_q(t, 0)|t\rangle = -\langle \ln \rho_q(t, 0)|t\rangle_q \quad (23)$$

Using this definition, it can be proved(5) that Zubarev's statistical method is compatible with generalized thermodynamics,(6) and furthermore it provides us with the reciprocal of Eq. (22):

$$F_m(\mathbf{r}, t) = \delta\mathscr{S}(t)/\delta Q_m(\mathbf{r}, t), \qquad m = 1, 2, \ldots, s \quad (24)$$

Next we consider the time evolution of the NESS, i.e., besides the thermodynamic equalities (22), one needs to write the generalized transport equations (GTEq), i.e., the equations of motion for the nonequilibrium thermodynamic variables. By time differentiation of both sides of Eq. (21) one obtains

$$\frac{dQ_m(t)}{dt} = \frac{d}{dt}\langle P_m|t\rangle_q = \frac{d}{dt}\langle P_m|t\rangle = \langle \dot{P}_m|t\rangle = \left\langle \frac{1}{i\hbar}[P_m, H]|t\right\rangle \tag{25}$$

Further,

$$\frac{dQ_m}{dt} = \sum_n \frac{\delta Q_m}{\delta F_n}\frac{dF_n}{dt} = -\sum_n M_{mn}(t)\dot{F}_n(t) \tag{26}$$

where

$$M_{mn}(t) = \delta^2\phi(t)/\delta F_m\,\delta F_n \equiv (P_m, P_n|t) = \langle \Delta P_m\,\Delta P_n|t\rangle_q \tag{27}$$

with

$$\Delta P = P - \langle P|t\rangle_q, \qquad \Delta P = \int_0^1 du\, e^{-uS(t,0)}\,\Delta P\, e^{uS(t,0)}$$

and

$$S(t,0) = -\ln \rho_q(t,0) = \phi(t) + \sum_m F_m(t)P_m$$

Here, M is a correlation matrix, $\tilde{A}$ is a generalized Kubo-like transform of the operator A,(16) and S is the entropy operator.

Equation (26) allows us to introduce kinetic equations for thermodynamic parameters F as

$$\frac{dF_m(t)}{dt} = -\sum_n M_{mn}^{-1}(t)\langle \dot{P}_n|t\rangle \tag{28}$$

where

$$M_{mn}^{-1}(t) = -\delta^2 S(t)/\delta Q_m(t)\,\delta Q_n(t) \tag{29}$$

is the inverse correlation matrix. The equations of evolution could be written, if convenient, in a mixed representation involving a part of quantities Q and a part of parameters F, e.g., as in the application described in Section 4.

For systems deviating slightly from thermal equilibrium and in the linear approximation the results of the memory function method of Mori(16) are retrieved.(19) The GTEq (25) may be considered the average over the nonequilibrium ensemble of generalized Langevin equations, with definition (21) ensuring the cancellation of the rapidly varying random forces, i.e., producing the secularization of the state variables.

In summary, for systems governed by Hamiltonian dynamics, Zubarev's statistical method provides a way to describe the evolution and behavior of far-from-equilibrium systems through appropriate generalized transport equations. Their solutions are uniquely determined for given initial conditions, but since they are nonlinear equations, a branching point of solutions(20) is apt to appear at a certain threshold in the intensities of the external sources that drive the system away from equilibrium. Beyond the instability an ordered pattern stabilizes, which has been termed a *dissipative structure*, and may be one of various spatiotemporal self-organizations.(21) The stability depends on the signature of the excess entropy production function for all fluctuations compatible with the equations of evolution, the Glansdorff–Prigogine stability criterion.(6)

Closing this section, we observe that the set of dynamical quantities P_m is defined by the microscopic structure of the system itself, i.e., by the explicit form of its Hamiltonian.(12) Thus, the choice of the set of macroscopic variables is not universal, but it depends completely on a concrete problem. The modeling of a concrete problem amounts to a judicious choice of the variables and the form of the kinetic equations. The question of the completeness of the set of macrovariables has been discussed by Kalashnikov.(22)

4. A GREEN'S FUNCTION FORMALISM FOR NONEQUILIBRIUM STATISTICAL SYSTEMS

As we have seen, either for the determination of response functions of the NESS or the study of its evolution, time-dependent correlation functions need to be calculated. A practical way to accomplish this consists in connecting them with appropriate thermodynamic Green's functions, and for this purpose in this section we briefly present a Green's function formalism to be used for the study of nonequilibrium statistical systems described by the nonequilibrium statistical operator of Section 3, which is a natural generalization of the equilibrium case described in Ref. 4.

Consider two operators $A(t)$ and $B(t)$ in the Heisenberg representation. Using the nonequilibrium statistical operator of Eq. (19), we define a retarded Green's function

$$G_\eta(t, \tau) = -i\theta(-\tau)\,\mathrm{Sp}\{[A(\tau), B]_\eta \rho_\epsilon(t)\} \tag{30}$$

Here $\eta = +$ stands for the anticommutator and $\eta = -$ for the commutator of quantities A and B.

We also define the nonequilibrium correlation functions

$$F_{AB}(t, \tau) = \mathrm{Sp}\{A(\tau)B\rho_\epsilon(t)\} = \langle A(\tau)B|t\rangle \tag{31}$$

and

$$\tilde{F}_{BA}(t, \tau) = \mathrm{Sp}\{BA(\tau)\rho_\epsilon(t)\} = \langle BA(\tau)|t\rangle \tag{32}$$

Let $|n\rangle$ be a complete set of eigenfunctions of H, the NESS Hamiltonian. Then

$$\begin{aligned} F_{AB}(t,\tau) &= \sum_{lmn} \langle n|A|m\rangle\langle m|B|l\rangle\langle l|\rho_\epsilon(t)|n\rangle e^{(1/i\hbar)\tau(E_m - E_n)} \\ &= \int_{-\infty}^{\infty} d\omega\, J_{AB}(t|\omega)e^{i\omega\tau} \end{aligned} \tag{33}$$

The last equality defines the nonequilibrium spectral density

$$J_{AB}(t|\omega) = \sum_{lmn} \hbar\langle n|A|m\rangle\langle m|B|l\rangle\langle l|\rho_\epsilon(t)|n\rangle\; \delta(\hbar\omega - E_n + E_m) \tag{34}$$

Similarly we obtain

$$\begin{aligned} \tilde{F}_{BA}(t, \tau) &= \sum_{lmn} \langle n|B|m\rangle\langle m|A|l\rangle\langle l|\rho_\epsilon(t)|n\rangle e^{(1/i\hbar)\tau(E_l - E_m)} \\ &= \int_{-\infty}^{\infty} d\omega\, K_{BA}(t|\omega)e^{i\omega\tau} \end{aligned} \tag{35}$$

where

$$K_{BA}(t|\omega) = \sum_{lmn} \hbar\langle n|B|m\rangle\langle m|A|l\rangle\langle l|\rho_\epsilon(t)|n\rangle\; \delta(\hbar\omega - E_m + E_l) \tag{36}$$

The spectral densities J and K satisfy the relationship

$$K^*_{A^+B^+}(-\omega) = J_{AB}(\omega) \tag{37}$$

Defining the Fourier transform

$$G_\eta(t|\omega) = \int_{-\infty}^{\infty} \frac{d\tau}{2\pi}\, G_\eta(t, \tau)e^{-i\omega\tau} \tag{38}$$

and using Eqs. (33), (35), and (30), one obtains

$$G_+(t|\omega) + G_-(t|\omega) = \int_{-\infty}^{\infty} \frac{d\omega'}{\pi}\, \frac{J_{AB}(t|\omega')}{\omega - \omega' + is} \tag{39}$$

$$G_+(t|\omega) - G_-(t|\omega) = \int_{-\infty}^{\infty} \frac{d\omega'}{\pi}\, \frac{K_{BA}(t|\omega')}{\omega - \omega' + is} \tag{40}$$

with $s \rightarrow +0$.

Furthermore, the equations of motion for the retarded Green's functions and its Fourier transforms are

$$i\hbar \frac{\partial G_\eta(t, \tau)}{\partial \tau} = -\hbar\delta(\tau)\langle[A, B]_\eta|t\rangle + \langle\langle[A(\tau), H]; B|t\rangle\rangle_\eta \tag{41}$$

and

$$-\hbar\omega G_\eta(t|\omega) = -\frac{\hbar}{2\pi}\langle[A, B]_\eta|t\rangle + \langle\langle[A, H]; B|t, \omega\rangle\rangle \tag{42}$$

where we have introduced the notations

$$\langle\langle A(\tau); B|t\rangle\rangle_\eta = G_\eta(t, \tau) \tag{43}$$

$$\langle\langle A; B|t, \omega\rangle\rangle_\eta = G_\eta(t|\omega) \tag{44}$$

Because of the equivalence of the NESS obtained by taking the quasi-invariant part of either the auxiliary operator ρ_q or the entropy operator $\ln \rho_q$, as done here,(5,23) these Green's functions should coincide with those defined and studied by Kalashnikov.(24) However, one difference must be stressed, which consists in the presence of an additional damping-like factor $e^{\varepsilon\tau}$ in front of the retarded Green's function defined in Ref. 24. However, our final result will recover a factor $e^{s\tau}$, with $s \to +0$, whose origin will be the adiabatic turning on of the perturbation and not the adiabatic decoupling of the system and reservoir of the Kalashnikov theory.

Using the Green's function formalism just introduced, we can write the rate of transition probability given by Eq. (17)

$$\begin{aligned} w(t|\omega) &= \frac{1}{\hbar^2}\int_{-\infty}^{0} d\tau \int_{-\infty}^{\infty} d\omega'\, e^{-i(\omega-\omega'+is)\tau} J_{R^+R}(t|\omega') + \text{c.c.} \\ &= \frac{i}{\hbar^2}\int_{-\infty}^{\infty} d\omega' \frac{J_{R^+R}(t|\omega')}{\omega - \omega' + is} + \text{c.c.} \\ &= -\frac{2\pi}{\hbar^2}\operatorname{Im}\{G_+(t|\omega + is) + G_-(t|\omega + is)\} \end{aligned} \tag{45}$$

where adiabatic application of the perturbation at time $t_0 \to -\infty$ has been assumed, and where $G_\eta(t|\omega) = \langle\langle \mathscr{R}^+; \mathscr{R}|t, \omega\rangle\rangle_\eta$.

For systems in equilibrium conditions described by the canonical ensemble, one retrieves the result(11)

$$w(\omega) = (2\pi/\hbar)(1 + \eta e^{-\beta\omega}) \operatorname{Im} G_\eta(\omega + is) \tag{46}$$

where β^{-1} is the reservoir temperature. Further, in situations when the parameters F_m vary slowly in time during intervals of time characteristic of the measurement that is being performed, the NESS is in a quasi-steady state and, in a first approximation, one can take the F_m as constants, thus bypassing the solution of the complicated equation (28) and using them as phenomenological parameters. Under such restrictions the NESS becomes

$$\ln \rho_\epsilon = \phi + \sum_m F_m P_m - \sum_m F_n \int_{-\infty}^{0} dt' \, e^{\epsilon t'} \dot{P}_m(t') \tag{47}$$

and the corresponding auxiliary distribution is

$$\rho_{\mathrm{hx}} = Z_{\mathrm{hx}}^{-1} \exp\left(-\sum_m F_m P_m\right), \qquad Z_{\mathrm{hx}} = \mathrm{Sp}\left\{\exp\left(-\sum_m F_m P_m\right)\right\} \tag{48}$$

We call ρ_{hx} the distribution for hot excitations. In the state described by this distribution there are no dissipative processes, which are carried by the last term in Eq. (47). If relaxation processes can be neglected, e.g., if the rates of entropy flux between the subsystems involve relaxation times much larger than the characteristic time of the measurement being performed, then the hot excitation distribution describes the uniform quasi-steady state of the system. It corresponds to an equilibrium distribution constructed on the basis of (nearly) integrals of motion P_m with thermodynamically conjugate parameters F_m. In most cases of interest the P_m are the Hamiltonians and particle numbers of each subsystem $\{H_i, N_i\}$, and then the F_m are the inverse quasi-temperatures and quasi-chemical potentials $\{\beta_i, -\beta_i\mu_i\}$. The concepts of quasi-temperature and quasi-chemical potential for different internal degrees of freedom in quasiequilibrium have been applied to different experimental situations.[3] The generalization of the results of equilibrium statistics to the "hot" NESS is not difficult. In particular one can easily obtain the equivalent of the fluctuation-dissipation theorem as

$$\begin{aligned} \langle A_i A_j \rangle_\omega &= \frac{1}{2\pi} \int d\tau \, e^{-\omega\tau} \langle A_i A_j(\tau) \rangle_{\mathrm{hx}} \\ &= \frac{1}{2\pi} d\tau \, e^{-i\omega\tau} \langle A_i(\tau) A_i(i\beta_i) \rangle_{\mathrm{hx}} = \langle A_j A_i \rangle_{-\omega} \, e^{\beta_i \omega} \end{aligned} \tag{49}$$

and

$$\mathrm{Im}\langle\langle A_i; A_j | \omega \rangle\rangle_\eta^{(\mathrm{hx})} = (1 + \eta e^{-\beta_i \omega}) \langle A_i A_j \rangle_\omega \tag{50}$$

where A_i is an operator that depends only on the coordinates of the ith subsystem. This result was used to study interference effects in Raman scattering in photoexcited semiconductors.$^{(26)}$

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[3] For example, to electron and nuclear spins,$^{(25a,25b)}$ molecules,$^{(25c)}$ plasmas,$^{(25d,25e)}$ electrons excited in strong electric fields,$^{(25f)}$ and photoexcited electrons$^{(25g)}$; also Ref. 25h.

The hot excitation model has been applied to the study of optical properties of solid state plasmas in doped or photoinjected semiconductors under high excitations. A review of this subject is given elsewhere.(27)

The calculation of the transition probability rate of Eq. (45) does not simply reduce to the determination of the appropriate Green's functions, as is the case for samples initially in equilibrium, once the equation for the nonequilibrium thermodynamic Green's functions are not closed but coupled to the highly nonlinear kinetic equations (28), i.e., those describing the evolution of the NESS during the time it is probed. Such evolution is equivalently governed by the GTEq (25), which are equations of motion for correlation functions and therefore also admit a treatment using the Green's function formalism that opened this section. In fact, consider $P_m = AB$ (for most practical cases $B = A^+$) and then

$$\frac{dQ_m(t)}{dt} = \frac{d}{dt}\langle P_m|t\rangle = i\sum_\eta \int_{\to\infty}^{\infty} d\omega \, \frac{d}{dt}\langle\langle A;B|t,\omega\rangle\rangle_\eta \tag{51}$$

where we have used the relation

$$\sum_\eta \int_{-\infty}^{\infty} d\omega \, G_\eta(t|\omega+\zeta) = -i\int_{-\infty}^{\infty} d\omega \, J_{AB}(t|\omega) = -iF_{AB}(t,0) \tag{52}$$

The next section presents, as an example of the application of the method, a study of time-resolved laser-light scattering (Raman) spectroscopy.

5. TIME-RESOLVED RAMAN SPECTROSCOPY IN PHOTOEXCITED SEMICONDUCTORS

Important developments have recently occurred in the area of fast time-resolved spectroscopy, making it possible to investigate, on the picosecond time scale, the interaction of laser radiation with atoms, molecules, and condensed matter.(28) Certainly this is a very useful measurement technique, which can provide an access to the detailed study of nonequilibrium processes in physics, chemistry, and biology.

Here we apply the formalism developed in previous sections to the determination of the time-resolved Raman spectra of photoexcited electrons, at high excitation densities, and coupled to the system of longitudinal optical phonons in n-doped direct-gap polar semiconductors. The carrier system, which we assume initially departs strongly from thermal equilibrium due to a pulse of laser light, should be brought into a uniform internal thermalization within a fraction of a picosecond because of the Coulomb interactions(28,29) and from then on the conditions for the application of Zubarev's method are established. Further, we restrict the problem to situations when the carrier-phonon energy relaxation time is much shorter than the relaxation times to the thermal bath, and the concentration of photoexcited pairs much smaller than the concentration of impurities.

Under these conditions one can choose as a complete set of macrovariables the carrier energy H_E and the LO-phonon number operator $\eta_{\mathbf{K}} = b_{\mathbf{K}}{}^{+} b_{\mathbf{K}}$. The quasiequilibrium statistical operator is then taken as

$$\rho_q(t, 0) = \exp\left[-\phi(t) - \beta(t) H_E - \sum_{\mathbf{K}} F_{\mathbf{K}}(t) \eta_{\mathbf{K}} \right] \tag{53}$$

where the nonequilibrium thermodynamic parameters are $\beta(t)$ and $F_{\mathbf{K}}(t)$, with the LO-phonon wave vector **K** defined over the whole Brillouin zone. The usual model of a parabolic conduction band semiconductor, dispersionless LO phonons, and a bare Frohlich interaction between both systems is used.

The differential time-resolved Raman scattering cross section for an event with energy transfer $\omega = \omega_L - \omega_S$, where ω_L is the laser photon frequency and ω_S the scattered photon frequency, and momentum transfer $\mathbf{q} = \mathbf{K}_L - \mathbf{K}_S$, is given by

$$\frac{d^2\sigma(t/\omega)}{d\Omega\, d\omega} = \frac{V^2 \omega_S{}^2}{4\pi^2 C^4} \operatorname{Im} \sum_{\eta} \langle\langle R^+ ; R | t, \omega \rangle\rangle_\eta \tag{54}$$

Here, V is the scattering volume and the scattering operator is

$$R = \frac{e^2}{mc^2} \frac{2\pi\hbar c^2}{V\epsilon_\infty \omega_L} \frac{2\lambda}{m} P_{vc}^2 \frac{E_G{}^2 + \omega_L{}^2}{E_G{}^2 - \omega_L{}^2} \sum_{\mathbf{k}} \langle \uparrow | \boldsymbol{\sigma} \cdot (\mathbf{e}_L \times \mathbf{e}_S) | \downarrow \rangle C_{k\uparrow}^{+} C_{k\downarrow} + \text{H.C.} \tag{55}$$

where $\mathbf{e}_{L,S}$ are the polarization unit vectors of the incident and scattered electric fields, P_{vc} is the matrix element of the momentum operator between center-zone conduction and valence band states, E_G is the energy gap, λ is the spin–orbit coupling constant, and the dipole approximation for the electron–radiation interaction has been used. This is the contribution to the scattering due to spin density fluctuations, whose observation can be separated from the contribution from charge density fluctuations by appropriate choice of the scattering geometry, since they have Raman tensors with different symmetry. The latter, however much more intense, is not considered because plasmon effects strongly mask the quasiparticle band, the one more appropriate for the purposes of this illustration.

For the sake of brevity, we omit the lengthy but straightforward calculation of the Green's functions of Eq. (54); suffice to say that the random phase approximation is used to deal with the Coulomb interaction between conduction band electrons, and that the lifetime of the carrier states is neglected. The final result is

$$\frac{d^2\sigma}{d\omega\, d\Omega} = \left(\frac{d^2\sigma}{d\omega\, d\Omega} \right)_0 |\mu^{-1}(\mathbf{q}, \omega | t)|^2 \tag{56}$$

where

$$(d^2\sigma/d\omega\, d\Omega)_0 = |V|^2(n/qV_{\text{th}})e^{-\xi^2}$$

is the scattering cross section for the bare electrons, with V the p-independent matrix of the scattering potential; $\xi(t) = \omega/qV_{\text{th}}(t)$, and $V_{\text{th}}(t) = [2/m^*\beta(t)]^{1/2}$ is the average thermal velocity, with m^* the effective mass of electrons.

Equation (56) shows that the scattering cross section for the independent carriers is corrected by a factor $|\mu|^{-2}$ due to correlation effects, μ being the RPA magnetic permeability

$$\mu(\mathbf{q}, \omega|t) = 1 - \beta n[1 - \xi(t)D(\xi)] + i2\pi^{1/2}\beta(t)U\xi(t)e^{-\xi^2} \tag{57}$$

where $D(\xi)$ is the Dawson integral$^{(30)}$ and U is the almost $\mathbf{p}$-independent exchange integral.$^{(31)}$ In deriving Eq. (57) we have used the Maxwell distribution

$$f(\mathbf{p}|t) = [4\pi^3 N/(2\pi m^*)^{3/2}]\beta^{3/2}(t)\exp[-\beta(t)\epsilon(\mathbf{p})] \tag{58}$$

for the occupation number of electron states, since at the usual excitations the carrier fluid is nondegenerate during the time interval we are considering. Here $\epsilon(\mathbf{p}) = \hbar^2 p^2/2m^*$.

Next we write down the GTEq for the macrovariables in order to close the problem,

$$\frac{d}{dt}\langle H_E|t\rangle_q = i\sum_{\eta}\sum_{\mathbf{p}}\sum_{\mathbf{p}'}\epsilon_{\mathbf{p}}\epsilon_{\mathbf{p}'}\frac{d}{dt}\langle\langle C_{\mathbf{p}}{}^{+}; C_{\mathbf{p}'}|t, \omega\rangle\rangle_{\eta} \tag{59a}$$

$$\frac{d}{dt}\langle b_{\mathbf{k}}{}^{+}b_{\mathbf{k}}|t\rangle_q = i\sum_{\eta}\frac{d}{dt}\langle\langle b_{\mathbf{k}}{}^{+}; b_{\mathbf{k}}|t, \omega\rangle\rangle \tag{59b}$$

But because of Eq. (60)

$$\frac{d}{dr}\langle H_E|t\rangle_q = \frac{d}{dt}\sum_{p}\epsilon_p f_k(t) = -3n\beta^{-2}(t)\frac{d\beta(t)}{dt} \tag{59a$'$}$$

and we will use the mixed representation of Eqs. (59a′) and (59b) to describe the evolution of the coupled electron–phonon system.

The Green's functions of Eqs. (59) are calculated according to the basic equation (42), which of course leads us to an infinite system of Green's functions of ever-increasing order. We proceed to decouple the system to second order in the electron–phonon interaction to obtain a set of equations formally identical to those available in the literature for systems in equilibrium,$^{(4)}$ except for the replacement of the carrier distribution functions by those of Eq. (58) and the phonon distribution function by $\nu_{\mathbf{k}}(t) = \langle b_{\mathbf{k}}{}^{+}b_{\mathbf{k}}|t\rangle_q$. Details as well as the solution of the coupled nonlinear GTEq (59) are given elsewhere.$^{(32)}$ Sufficient for the present purposes is the knowledge of the reciprocal electron temperature $\beta(t)$, which is shown in the inset of Fig. 1 for the specific case of GaAs with a concentration of carriers of $3 \times 10^{17}\ \mathrm{cm}^{-3}$. The anti-Stokes contribution to the Raman spectra at different times after application of the initial pulse excitation is shown in Fig. 1 on a logarithmic scale.

Excluding the region of low energy transfer (basically $\omega \lesssim V_{\mathrm{th}}^{(t)}q$), where many-body effects built into the magnetic response function distort the spectrum, it mainly consists of a straight line whose tangent $\omega^2/q^2 V_{\mathrm{th}}^2(t)$ gives a measure of the effective electron temperature $\beta^{-1}(t)$, and thus one has a "thermometer" to follow up the thermal evolution of the carriers.

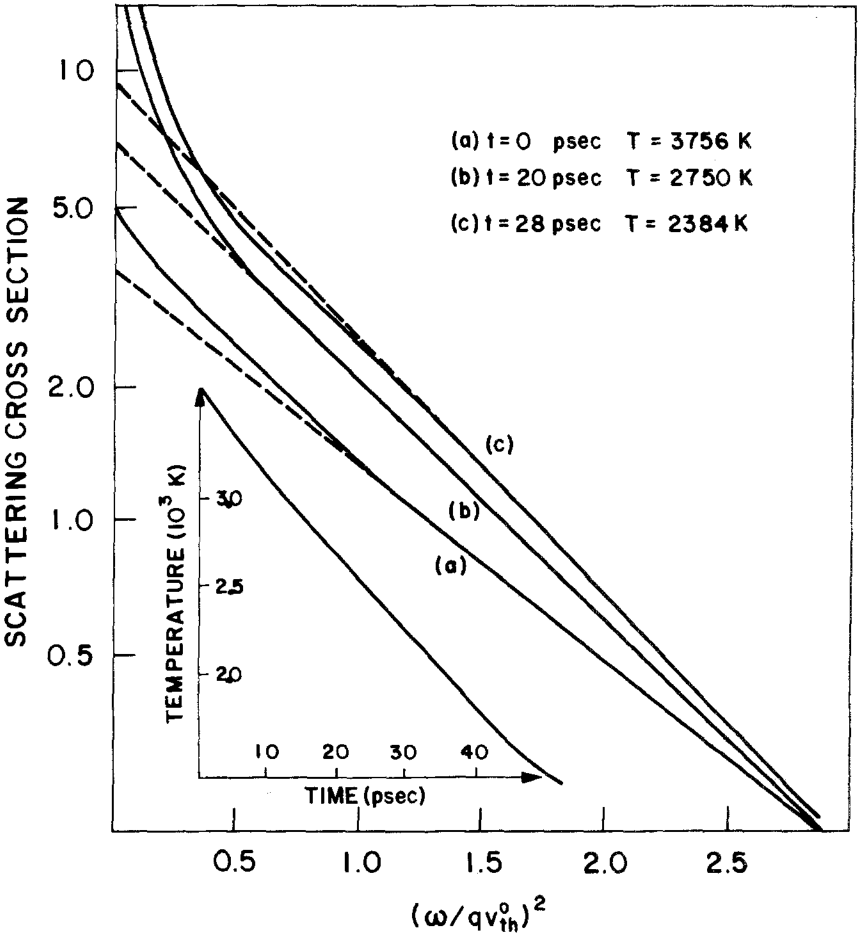

Fig. 1. Cross section for time-resolved Doppler–Raman scattering by spin density fluctuations in n-doped direct-gap polar semiconductor. The inset shows the evolution of the effective temperature of the photoexcited carriers in contact with a reservoir of optical phonons.

We believe that this simple example illustrates the fundamentals of the method; more elaborate studies of the behavior of condensed matter under high excitation conditions, and probed by means of optical experiments or magnetic resonance experiments, are presently under way.(33)

In conclusion we may say that the response of a highly excited prepared sample can be described by means of the formalism presented in this work. It mainly consists in coupling the usual scattering theory with a method to deal with nonequilibrium statistical mechanics. This has been done using Zubarev's method, which provides a contracted description of the state of the system in terms of a small number of macroscopic variables, following a Gibbsian-like approach. The present formalism provides a response function for a measurement operation involving characteristic time intervals much larger than the relaxation time for microprocesses,(7) after which a description of the macroscopic state of the system is given by the coarse-grained distribution described in Section 3. In this way, it is a generalization of the Kubo formalism(3) given the linear and nonlinear responses of the system in terms of correlation functions calculated not in equilibrium but in the nonequilibrium state defined by the distribution $\rho_\varepsilon(t)$. Thus, it describes the effect of the mechanical perturbation on a system which is evolving in an irreversible way governed by the generalized transport equations (25).

Finally the possibility should also be mentioned of the stabilization of spatial steady-state dissipative structures in the nonlinear thermodynamic regime in highly excited semiconductors. Convection instability (Bénard-like effect) in the hot electron gas in semiconductors has been considered by Bonch-Bruevich,(34) and in the photogenerated electron–hole plasma by Kerner and Osipov.(35) Nonlinear instabilities are also responsible for self-organized inhomogeneous steady states of currents and fields in semiconductor devices.(36) Formation of a superlattice in polar semiconductors under strong infrared light irradiation has been suggested.(37) This question of symmetry breaking at branching points of the solutions of nonlinear generalized kinetic equations [e.g., Eq. (25) or (28)] with accompanying coherent behavior(21) constitutes a quite engaging and challenging problem, which doubtless will generate mounting interest in coming years.

APPENDIX. PROJECTORS, MEMORY FUNCTION, AND ZUBAREV'S METHOD

We show here that Zubarev's method can be connected with a projection operator technique in a form that resembles an extension to nonlinear nonequilibrium conditions of the Mori formalism.(16)

Consider the set of quantities $P_1, P_2, \ldots, P_s$ chosen for the contracted description of the macroscopic state of the system. To them we add the unity operator $P_0 = 1$. The nonequilibrium thermodynamic parameters are $F_1(t), \ldots, F_s(t)$, and $F_0(t) = \phi(t)$ is the conjugate to P_0. The entropy operator is $S(t, 0) = \sum_{m=0}^{s} F_m(t) P_m$, and the QESD and Zubarev's NESS are given by Eqs. (18) and (19). The latter can be rewritten, after integration by parts, as

$$\rho_\epsilon(t) \exp[-S(t, 0) + \zeta_\epsilon(t, 0)] = \rho_q(t, 0) + \rho'(t, 0) \tag{A1}$$

where

$$\zeta_\epsilon(t, 0) = \int_{-\infty}^{0} dt'\, e^{\epsilon t'} \Delta \frac{d}{dt'} S(t + t', t') \tag{A2}$$

$$\rho'(t, 0) = D_\epsilon(t, 0) \rho_q(t, 0) \tag{A3}$$

$$D_\epsilon(t, 0) = \int_{-\infty}^{0} dt'\, e^{\epsilon t'} \int_{0}^{1} du\; Y(\zeta|u) e^{-uS} \zeta e^{uS} \tag{A4}$$

with the operator Y defined by the integral equation

$$Y(\zeta|x) = 1 + \int_{0}^{x} du\; Y(\zeta|u) e^{-uS} \zeta e^{uS} \tag{A5}$$

The NESS (A1) is composed of two additive parts, the local equilibrium distribution ρ_q and a term that accounts for the relaxation effects to all orders in the thermodynamic forces. We restrict the following analysis to the linear relaxation approximation around the quasiequilibrium state, i.e., the first-order expansion in the operator ζ, by putting $Y = 1$ in the previous equations.

Next we define a metric space of vectors P_m with the inner product

$$(P_m|P_n; t) = M_{mn}(t) = \int_{0}^{1} du\, \mathrm{Sp}\{P_m e^{-uS} P_n e^{uS} \rho_q(t, 0)\} \tag{A6}$$

which is a correlation function of the quantities P_m and P_n, and M is the correlation matrix.

Definition (A6) allow us to introduce the operator

$$\mathscr{P}(t)A = \sum_{mn} P_m M_{mn}^{-1}(t)(P_n|A; t) \tag{A7}$$

with the properties of linearity, hermiticity, and idempotency, which projects the logarithm of the Zubarev NESS (A1) over the entropy operator $S(t, 0)$. In fact

$$-\mathscr{P}(t) \ln \rho_\epsilon(t) = \sum_{mn} \mathrm{P}_m \mathrm{M}_{mn}^{-1}(\mathrm{t})(\mathrm{P}_m|[\mathrm{S}(\mathrm{t}, 0) - \zeta_\epsilon(\mathrm{t}, 0)]; t) = S(t, 0) \tag{A8}$$

where we used definition (21), which tells us that $(P_m|\zeta; t) = 0$.

Given the operator $P_m(\tau) = P_m e^{i\tau\mathscr{L}}$, where $\mathscr{L}$ is the Liouvillian operator of the system, and using the identity $\mathscr{L} = \mathscr{L}(\mathscr{P} + Q)$, where $Q = 1 - \mathscr{P}$, we can write the exact equation of motion for $P_m(\tau)$ in the alternative generalized Langevin equation form

$$i \frac{d}{d\tau} P_m(\tau) = \sum_n \Omega_{mn}(t) P_n(\tau) - i \sum_n \int d\tau' \, \Gamma_{mn}(\tau - \tau'|t) P_n|\tau') + f_m(\tau|t) \qquad \text{(A9)}$$

where

$$\Omega_{mn}(t) = i \sum_l (\dot{P}_m|P_l;\, t) M_{ln}^{-1}(t) \qquad \text{(A10a)}$$

$$\Gamma_{mn}(\tau|t) = i \sum_l (\dot{P}_m|Q e^{i\tau Q\mathscr{L}Q} Q|\dot{P}_l;\, t) M_{ln}^{-1}(t) \qquad \text{(A10b)}$$

$$f_m(\tau|t) = i\dot{P}_m Q e^{i\tau Q\mathscr{L}Q} Q \qquad \text{(A10c)}$$

Equation (A9) contains three terms on the rhs: (a) a precession term, (b) a memory term, and (c) a driving force. The latter is uncorrelated to the variables P_m, i.e., $[f_m(\tau|t)|P_m;\, t] = 0$, has null average value over the quasiequilibrium ensemble, and satisfies

$$[f_m(\tau|t)|f_n(0|t);\, t] = \Gamma_{mn}(\tau|t) \qquad \text{(A11)}$$

which is a generalization of the fluctuation-dissipation theorem connecting correlations to the memory function. The inner product of Eq. (A9) with P_n produces the equations for the correlation matrix elements; the average over the Zubarev nonequilibrium ensemble followed by the limit of τ going to zero reproduces Eq. (25); and taking the canonical equilibrium distribution for ρ_q, one fully retrieves Mori's results. This suggests that Zubarev's method may be considered as a generalization of Mori's method, providing a very practical way for dealing with nonlinear effects in far-from-equilibrium statistical systems.

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