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Response Function Theory for Many-Body Systems Away from Equilibrium: Conditions of Ultrafast-Time and Ultrasmall-Space Experimental Resolution

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Abstract A response function theory and scattering theory applicable to the study of physical properties of systems driven arbitrarily far removed from equilibrium, specialized for dealing with ultrafast processes, and in conditions of space resolution (including the nanometric scale) are presented. The derivation is done in the framework of a Gibbs-style nonequilibrium statistical ensemble formalism. The observable properties are shown to be connected with time- and space-dependent correlation functions out of equilibrium. A generalized fluctuation-dissipation theorem, which relates these correlation functions with generalized susceptibilities, is derived. The method of nonequilibrium-thermodynamic Green functions, which proves useful for calculations, is also presented. Two illustrative applications of the formalism, which study optical responses in ultrafast laser spectroscopy and Raman scattering of electrons in III-N semiconductors (of “blue diodes”) driven away from equilibrium by electric fields of moderate to high intensities, are described.

Keywords Semiconductors · Response function · Scattering theory · Ultrafast processes

1 Introduction

The renowned Ryogo Kubo once stated that “statistical mechanics has been considered a theoretical endeavor. However, statistical mechanics exists for the sake of the real world, not for fictions. Further progress can only be hoped by closed cooperation with experiment” [1]. This is nowadays particularly relevant because the notable development of all modern technology, fundamental for the progress and well being of the world society, poses a great deal of stress in the realm of basic physics, more precisely on thermostatics. Thus, on the one hand, we face situations in electronics and optoelectronics involving physical-chemical systems far removed from equilibrium, where ultrafast (pico- and femtosecond scale) and nonlinear processes are present. Further, we need to be aware of the rapid unfolding of nano-technologies and use of low-dimensional systems (e.g., nanometric quantum wells and quantum dots in semiconductors heterostructures) [2]. Altogether, this demands access to a statistical mechanics capable of efficiently dealing with such requirements. On the other hand, one needs to face the study of soft matter and fluids with complex structures (usually of the average self-affine fractal-like type) [3]. This is relevant for technological improvement in industries like, for example, those of polymers, petroleum, cosmetics, food, electronics, and photonics (conducting polymers and glasses), in medical engineering, etc. Moreover, in both types of the above-mentioned situations, there often appear difficulties of description and objectivity (existence of so-called hidden constraints), which impair the proper application of the conventional ensemble approach used in the general, logically and physically sound, and well-established Boltzmann-Gibbs statistics. An attempt to partially overcome such difficulties calls for unconventional approaches [4–7].

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As already pointed out, a central objective of any nonequilibrium statistical theory is to provide an understanding of the physics underlying relaxation phenomena that can be evidenced in experiments. The statistical theory must therefore be coupled with a response function theory. This is the subject of this paper. Specifically, we deal with the nonequilibrium statistical ensemble formalism (NESEF for short) [8–13].

Nowadays, two approaches appear to be the most favorable to deal with systems within an ample scope of nonequilibrium conditions. On the one hand, we have numerical simulation methods [14], also referred to as computational physics. In particular, to this branch belongs the nonequilibrium molecular-dynamics (NMD) [15], a computational method created for modeling physical systems at the microscopic level that proves adequate to study the molecular behavior of several physical processes. On the other hand, we have the kinetic theory based on the far-reaching generalization of Gibbs' ensemble formalism, NESEF [12, 13, 16]. NESEF is a powerful formalism that provides an elegant, practical, and physically clear picture for describing irreversible processes. It is adequate to deal with a large class of experimental situations, as for example, semiconductors far from equilibrium, and offers good agreement with other theoretical work and with experimental results [17–35].

Early work in computational physics laid the foundations of modern Monte Carlo simulations—the name that highlights the importance of random numbers in the procedure. After the initial groundwork in the early 1970s, computer simulation developed rapidly, in pace with the rapid development of computer hardware. Computer-simulation techniques have benefited from the introduction of substantially improved methods to measure transport coefficients, the development of stochastic dynamics methods, and other advances. How do the more sophisticated versions of computational modeling compare with the kinetic equation approaches (such as those based on NESEF, and it can be noticed that here, computers play an incidental, calculational part)?

Apparently, they are approximately equivalent (in the sense of similar numerical results and in good comparison with experimental results) when dealing with many-body systems not displaying higher-order correlations and variances, a situation that may arise in analyses of liquids presenting hydrodynamics and nonlinear instabilities. In the case of semiconductors well described by single elementary excitations (phonons, Landau-Bloch band electrons, excitons, magnons, polaritons, etc.), both approaches seem to produce comparable optical and transport properties. As an example, consider the mobility in n -doped polar semiconductors [34, 35]: in several cases, involving GaN and GaAs under intermediate to high electric fields, very good

agreement was found between the two procedures and with the available experimental results. Although one particular case showed no agreement, the results from the kinetic theory curiously came closer to experiment than those from the Monte Carlo calculations. We conjecture that the presence of certain “hidden constants” leads to this state of affairs.

The present structure of the NESEF formalism consists of an extension and generalization of earlier pioneering approaches, among which we can pinpoint the works of Kirkwood [36], Green [37], Mori-Oppenheim-Ross [38], Mori [39], and Zwanzig [40]. NESEF has been approached from different points of view: some are based on heuristic arguments, others on projection-operator techniques, the former following Kirkwood and Green, the latter following Zwanzig and Mori.

The formalism has been systematized and largely improved by the Russian School of Statistical Physics, which can be considered to have been started by the renowned Nicolai Nicolaievich Bogoliubov (e.g., see Ref. [41]). We may also recall the ideas of Nicolai Sergeievich Krylov [42] and more recently mainly through the relevant contributions of Dimitrii Zubarev [8, 9], Sergei Peletminskii [43], and others. We have presented in Refs. [12, 13] a systematization, as well as generalizations and conceptual discussions, of the matter.

These distinct approaches to NESEF can be brought together under a unique variational principle. This was originally done by Zubarev and Kalashnikov [44] and later reconsidered in Refs. [9, 12, 13]. It consists of maximizing, in the context of information theory, the Gibbs statistical entropy, that is, the average of the negative logarithm of the statistical distribution function [45, 46], which in communication theory is the Shannon informational entropy [47, 48], subject to certain constraints and including spatial nonlocality, retro-effects, and irreversibility at the macroscopic level.

Concerning response function theory, the usual approach to calculating linear responses to mechanical perturbations (e.g., Refs. [49–54]) relies on expansions in terms of equilibrium correlation functions. The initial condition is defined by the equilibrium with a thermal reservoir, and the evolution of the system then studied as if it were isolated from all external influences except the driving field. Let us here consider a mechanical perturbation applied to a system that is already far from equilibrium, in which system irreversible processes are unfolding that can be described by evolution equations for a basic set of macrovariables in the nonequilibrium-thermodynamic space of states. Since NESEF provides a seemingly powerful method to describe the macrostate of this system, it is appealing to derive a response function theory based on correlation functions in the unperturbed nonequilibrium state of the system. Schemes of this type have been proposed [52–54], and we

next systematize and extend this treatment to allow the treatment of experiments involving time resolution (including the ultrafast time scale of pico- and femtoseconds) and space resolution (including those in the burgeoning fields of nanoscience and nanotechnology).

We will show the connection between the observable properties and out-of-equilibrium correlation functions; derive a generalized fluctuation-dissipation theorem, relating correlation functions and generalized susceptibilities; and present a method useful to calculate nonequilibrium-thermodynamic Green functions. This is done in Sections 2, 3, and 4. In Section 5, we present a scattering theory, under the same conditions, namely including time and space resolution, for far-from equilibrium systems. The connection between the scattering theory and response function theory follows from application of the nonequilibrium fluctuation-dissipation theorem.

Finally, in Section 6, we present a couple of illustrations showing the theory at work in the study of two kind of experiments, namely optical responses in ultrafast laser spectroscopy of polar semiconductors and Raman scattering of electrons in doped III-N semiconductors (“blue diodes”) in the presence of electric fields with moderate to high intensities. In the latter case, the nonequilibrium fluctuation-dissipation theorem connects the Raman spectrum with nonlinear transport properties (nonlinear and time-dependent conductivity and diffusion coefficient, and a generalized—nonlinear and time-dependent—Einstein-relation).

2 Response Function Theory for Far-from-Equilibrium Systems

We consider an open many-body system out of equilibrium in contact with a set of reservoirs and under the action of pumping sources. We are essentially presenting the most general experiment one can think of, namely a sample (the open system of interest, which comprises very many degrees of freedom) subject to given experimental conditions, as diagrammatically described by Fig. 1.

The sample in Fig. 1 is constituted of a number of subsystems, σ_j , (or better to say, subdegrees of freedom; for example, in a solid-state matter, those associated with electrons, lattice vibrations, excitons, impurity states, collective excitations as plasmons, magnons, etc., hybrid excitations as polarons, polaritons, plasmaritons, and so on). They interact among themselves via interaction potentials responsible for energy and momentum exchange at certain rates τ_{ij} . Pumping sources act on different subsystems of the sample—via particular types of fields, electric, magnetic, electromagnetic, etc.—well characterized when the experiment is set up. The energy in excess of equilibrium received by the system is relaxed to the external reservoirs τ_{jR} . Finally,

the experiment is carried out: an external probing source, represented in the figure by $P(t)$, is coupled to one or more sample subsystems, and a certain response, say $R(t)$, is detected by a measuring apparatus (e.g., an ammeter, a spectrometer, etc.).

The pumping sources exert their influence on the open system through the fields they generate, say the magnetic, electric, or electromagnetic fields generated, for example, by a laser. In scattering experiments, the agent is the interaction potential with the particles of an incoming beam.

Let the Hamiltonian describing the system under the action of the pumping-source fields that drive it away from equilibrium plus the interactions with the reservoirs and fields be \hat{H}_σ . The total Hamiltonian is, then,

$$\hat{H}(t) = \hat{H}_\sigma + \hat{V}(t), \quad (1)$$

where $\hat{V}(t)$ describes the coupling to the external perturbing apparatus. For the latter, we adopt the form

$$\hat{V}(t) = - \int d^3r' \mathcal{F}(\mathbf{r}', t) \hat{A}(\mathbf{r}'). \quad (2)$$

Here, \mathcal{F} is the perturbing force, $\mathcal{F} = -\delta\hat{V}/\delta\hat{A}(\mathbf{r}')$, where δ is a functional derivative, and $\hat{A}(\mathbf{r}')$ is the system observable to which the perturbation is coupled. We recall that the system is in contact with ideal reservoirs.

We take the statistical operator to be the product of the one of the system $\varrho_\varepsilon(t)$ by the stationary canonical distribution of the reservoirs ϱ_R , denoted by the form $\mathcal{R}_\varepsilon(t) = \varrho_\varepsilon(t) \times \varrho_R$ [12, 13] (see Appendix). Moreover, $\hat{H}_\sigma = \hat{H}_0 + \hat{H}_1 + \hat{W} = \hat{H}_0 + \hat{H}'$, with the definition $\hat{H}' \equiv \hat{H}_1 + \hat{W}$, where H_1 accounts for all the interactions within the system and W for the interaction with the surroundings. The Hamiltonian \hat{H}_0 describes the free elementary excitations.

The Schrödinger equation then reads

$$i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle = \hat{H}(t) |\psi(t)\rangle. \quad (3)$$

Given the initial condition $|\psi(t_i)\rangle$ at time t_i when the perturbation is switched on, the formal solution of (3) is

$$|\psi(t)\rangle = U(t, t_i) |\psi(t_i)\rangle, \quad (4)$$

where U is the evolution operator satisfying that

$$i\hbar \frac{\partial}{\partial t} U(t, t_i) = \hat{H}(t) U(t, t_i), \quad (5)$$

where $U(t_i, t_i) = \hat{1}$ (the unit operator), which we recall, is unitary, that is $U^\dagger U = \hat{1}$.

We now introduce the interaction representation, defined by the expression

$$U(t, t_i) = U_\sigma(t, t_i) U'(t, t_i), \quad (6)$$

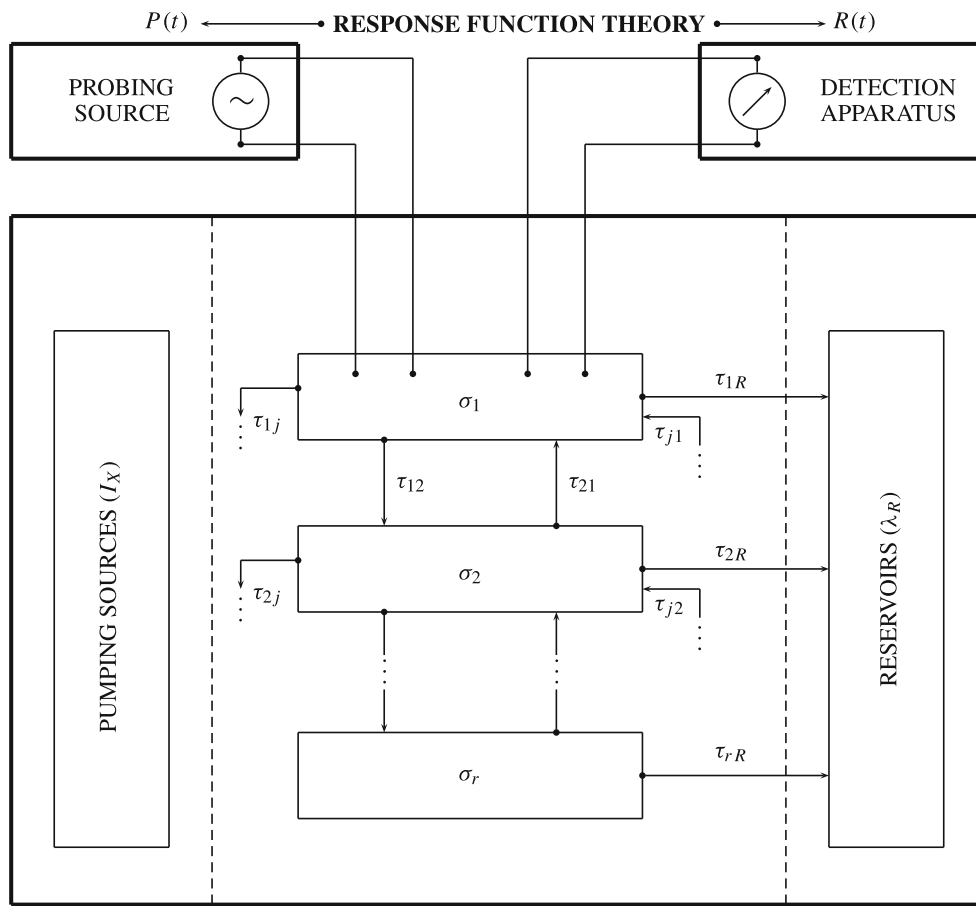


Fig. 1 Diagrammatic description of a typical pump-probe experiment in an open dissipative system

where

$$U_{\sigma}(t, t_i) = e^{(t-t_i)\hat{H}_{\sigma}/i\hbar}, \quad (7)$$

which is the evolution operator in the absence of the perturbation potential \hat{V} ; we are therefore separating the internal dynamics of the system from the dynamical effects of the perturbation, for which U' accounts. When we substitute the right-hand side of (6) for U in (5), it follows from (7) that U' satisfies the equation

$$i\hbar \frac{\partial}{\partial t} U'(t, t_i) = \tilde{V}(t) U'(t, t_i), \quad (8)$$

with $U'(t_i, t_i) = \hat{1}$, and

$$\tilde{V}(t) = U_{\sigma}^{\dagger}(t, t_i) \hat{V}(t) U_{\sigma}(t, t_i). \quad (9)$$

Equation (8) can be transformed into an equivalent integral equation, namely

$$U'(t, t_i) = \hat{1} + \frac{1}{i\hbar} \int_{t_i}^t dt' \tilde{V}(t') U'(t', t_i), \quad (10)$$

which admits the iterated solution

$$\begin{aligned} U'(t, t_i) &= \hat{1} + \frac{1}{i\hbar} \int_{t_i}^t dt' \tilde{V}(t') \\ &+ \frac{1}{(i\hbar)^2} \int_{t_i}^t dt' \int_{t_i}^{t'} dt'' \tilde{V}(t') \tilde{V}(t'') + \dots \\ &= \hat{1} + \sum_{n=1}^{\infty} \frac{1}{(i\hbar)^n} \int_{t_i}^t dt_1 \dots \\ &\times \int_{t_i}^{t_{n-1}} dt_n \tilde{V}(t_1) \dots \tilde{V}(t_n). \end{aligned} \quad (11)$$

The quantum mechanical expected value at time t of the observable $\hat{A}(\mathbf{r})$, to which the external field is coupled is then

$$\begin{aligned} a(\mathbf{r}, t) &= \langle \psi(t) | \hat{A}(\mathbf{r}) | \psi(t) \rangle \\ &= \langle \psi(t_i) | U^{\dagger}(t, t_i) U_{\sigma}^{\dagger}(t, t_i) \\ &\times \hat{A}(\mathbf{r}) U_{\sigma}(t, t_i) U'(t, t_i) | \psi(t_i) \rangle \\ &= \langle \psi(t_i) | U'^{\dagger}(t, t_i) \tilde{A}(\mathbf{r}, t) U'(t, t_i) | \psi(t_i) \rangle, \end{aligned} \quad (12)$$

where

$$\tilde{A}(\mathbf{r}, t) = U_{\sigma}^{\dagger}(t, t_i) \hat{A}(\mathbf{r}) U_{\sigma}(t, t_i). \quad (13)$$

According to (11), we have that

$$a(\mathbf{r}, t) = \langle \psi(t_i) | \left(\hat{1} - \frac{1}{i\hbar} \int_{t_i}^t dt' \tilde{\mathcal{V}}(t') + \dots \right) \times \tilde{A}(\mathbf{r}, t) \left(\hat{1} + \frac{1}{i\hbar} \int_{t_i}^t dt' \tilde{\mathcal{V}}(t') + \dots \right) | \psi(t_i) \rangle, \quad (14)$$

where we have used that $\tilde{\mathcal{V}}$ is Hermitian.

Let the system be far from equilibrium at the initial time t_i , when perturbation $\hat{\mathcal{V}}(t)$ is applied, and let the perturbation be weak. We can then truncate the expansion in (14) to first order in $\tilde{\mathcal{V}}$, that is, consider from now on a *linear response theory*, to obtain that

$$a(\mathbf{r}, t) = a(\mathbf{r}, t_i) + \frac{1}{i\hbar} \int_{t_i}^t dt' \langle \psi(t_i) | [\tilde{A}(\mathbf{r}, t), \tilde{\mathcal{V}}(t')] | \psi(t_i) \rangle, \quad (15)$$

where

$$a(\mathbf{r}, t_i) = \langle \psi(t_i) | \hat{A}(\mathbf{r}) | \psi(t_i) \rangle \quad (16)$$

is the expectation value for the observable at the time t_i , prior to the application of the perturbation.

From (2), we have that

$$\Delta a(\mathbf{r}, t) = -\frac{1}{i\hbar} \int_{t_i}^t dt' \int d^3r' \langle \psi(t_i) | [\tilde{A}(\mathbf{r}, t), \tilde{A}(\mathbf{r}', t')] \times \mathcal{F}(\mathbf{r}', t') | \psi(t_i) \rangle, \quad (17)$$

where $\Delta a(\mathbf{r}, t) = a(\mathbf{r}, t) - a(\mathbf{r}, t_i)$ is the departure of the observable \hat{A} from its value at the initial time under the action of the perturbing potential.

Introducing the statistical operator for the pure (quantum mechanical) state, namely

$$\mathcal{P}(t_i) = |\psi(t_i)\rangle \langle \psi(t_i)|, \quad (18)$$

which, we recall, is a projection operator over the vector state $|\psi(t_i)\rangle$, we can rewrite (17) in the form

$$\Delta a(\mathbf{r}, t) = -\frac{1}{i\hbar} \int_{-\infty}^t dt' \int d^3r' \text{Tr} \{ [\tilde{A}(\mathbf{r}, t), \tilde{A}(\mathbf{r}', t')] \mathcal{P}(t_i) \} \times \mathcal{F}(\mathbf{r}', t'), \quad (19)$$

where we have let $t_i \rightarrow -\infty$ and adiabatically applied the perturbation.

To examine the macroscopic state, we next average (19) over the nonequilibrium ensemble of pure states, compatible with the macroscopic conditions under which the sample is prepared. If as usual we call $\mathcal{P}_n(t_i)$ the statistical operator for the pure state in, say, the n -th replica, and p_n the probability of such replica in the corresponding Gibbs ensemble, the statistical average over the ensemble of mixed states of the system and over the states of the

reservoir (which is coupled to the system by the interaction \hat{W}) is

$$\begin{aligned} \Delta \langle \hat{A}(\mathbf{r}) | t \rangle &= -\frac{1}{i\hbar} \int_{-\infty}^t dt' \int d^3r' \sum_n p_n \text{Tr} \\ &\times \left\{ [\tilde{A}(\mathbf{r}, t), \tilde{A}(\mathbf{r}', t')] \mathcal{P}_n(t_i) \times \mathcal{Q}_R \right\} \mathcal{F}(\mathbf{r}', t') \\ &= -\frac{1}{i\hbar} \int_{-\infty}^t dt' \int d^3r' \text{Tr} \\ &\times \{ [\tilde{A}(\mathbf{r}, t), \tilde{A}(\mathbf{r}', t')] \mathcal{Q}_\varepsilon(t_i) \mathcal{Q}_R \} \mathcal{F}(\mathbf{r}', t'), \quad (20) \end{aligned}$$

with

$$\mathcal{Q}_\varepsilon(t_i) = \sum_n p_n \mathcal{P}_n(t_i) = \sum_n p_n |\psi_n(t_i)\rangle \langle \psi_n(t_i)|, \quad (21)$$

On the left-hand side of (20), we have introduced the notation

$$\Delta \langle \hat{A}(\mathbf{r}) | t \rangle = \text{Tr} \{ \hat{A}(\mathbf{r}) \mathcal{R}_\varepsilon(t) \} - \text{Tr} \{ \hat{A}(\mathbf{r}) \mathcal{R}_\varepsilon(t_i) \}, \quad (22)$$

where, we recall, $\mathcal{R}_\varepsilon(t) = \mathcal{Q}_\varepsilon(t) \times \mathcal{Q}_R$.

Equation (20) can be rewritten in the form

$$\begin{aligned} \Delta \langle \hat{A}(\mathbf{r}) | t \rangle &= -\frac{1}{i\hbar} \int_{-\infty}^t dt' \int d^3r' \text{Tr} \\ &\times \left\{ [\tilde{A}(\mathbf{r}, t), \tilde{A}(\mathbf{r}', t' - t)] \mathcal{R}_\varepsilon(t) \right\} \mathcal{F}(\mathbf{r}', t') \quad (23) \end{aligned}$$

since

$$\begin{aligned} \text{Tr} \{ [U_\sigma^\dagger(t, t_i) \hat{A}(\mathbf{r}) U_\sigma(t, t_i), U_\sigma^\dagger(t', t_i) \hat{A}(\mathbf{r}') U_\sigma(t', t_i)] \mathcal{R}_\varepsilon(t_i) \} \\ = \text{Tr} \{ \tilde{A}(\mathbf{r}, t), \tilde{A}(\mathbf{r}', t' - t) \mathcal{R}_\varepsilon(t) \}, \quad (24) \end{aligned}$$

where we have used the invariance of the trace operation by cyclical permutations and the group properties of operators U .

Under nonequilibrium conditions, the system is not invariant under time translations, since a statistical operator describing the irreversible evolution of the macroscopic state is time dependent; the operator $A(t' - t)$ in (24) shows time-translational invariance, because the time dependence stems from the microdynamical evolution governed by Hamiltonian \hat{H}_σ . Moreover, introducing the definitions

$$\chi''(\mathbf{r}, \mathbf{r}'; t' - t | t) = \frac{1}{2\hbar} \text{Tr} \{ [\hat{A}(\mathbf{r}), \tilde{A}(\mathbf{r}', t' - t)] \mathcal{R}_\varepsilon(t) \}, \quad (25)$$

$$\chi(\mathbf{r}, \mathbf{r}'; t - t' | t) = 2i \Theta(t - t') \chi''(\mathbf{r}, \mathbf{r}'; t' - t | t), \quad (26)$$

where Θ denotes Heaviside's step function, we see that (20) reduces to the expression

$$\Delta \langle \hat{A}(\mathbf{r}) | t \rangle = \int_{-\infty}^{\infty} dt' \int d^3r' \chi(\mathbf{r}, \mathbf{r}'; t - t' | t) \mathcal{F}(\mathbf{r}', t'). \quad (27)$$

Taking advantage of the integral representation of Heaviside's step function, namely

$$\Theta(\tau) = \lim_{s \rightarrow +0} i \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \frac{e^{-i\omega\tau}}{(\omega + is)}, \quad (28)$$

we find, after a few manipulation, that the Fourier transform in time $\tau = t - t'$ of the nonequilibrium generalized susceptibility of (26) is given by the equality

$$\chi(\mathbf{r}, \mathbf{r}'; \omega|t) = \int_{-\infty}^{\infty} \frac{d\omega'}{\pi} \frac{\chi''(\mathbf{r}, \mathbf{r}'; \omega'|t)}{(\omega' - \omega - is)}, \quad (29)$$

where $s \rightarrow +0$, and $\chi''(\mathbf{r}, \mathbf{r}'; \omega'|t)$ is the Fourier transform at frequency ω of the τ -dependent χ'' of (25), namely

$$\chi''(\mathbf{r}, \mathbf{r}'; \omega|t) = \int_{-\infty}^{\infty} d\tau \chi''(\mathbf{r}, \mathbf{r}'; -\tau|t) e^{i\omega\tau}. \quad (30)$$

Using the identities

$$\lim_{s \rightarrow +0} \frac{1}{x \pm is} = \mathcal{P} \left\{ \frac{1}{x} \mp i\pi\delta(x) \right\}, \quad (31)$$

which are the so-called advanced and retarded Heisenberg delta functions, where \mathcal{P} stands for the principal value, (29) takes the form

$$\begin{aligned} \chi(\mathbf{r}, \mathbf{r}'; \omega|t) &= \text{Re}\{\chi(\mathbf{r}, \mathbf{r}'; \omega|t)\} + i\text{Im}\{\chi(\mathbf{r}, \mathbf{r}'; \omega|t)\} \\ &= \mathcal{P} \left\{ \int_{-\infty}^{\infty} \frac{d\omega'}{\pi} \frac{\chi''(\mathbf{r}, \mathbf{r}'; \omega'|t)}{(\omega' - \omega)} \right. \\ &\quad \left. + i\chi''(\mathbf{r}, \mathbf{r}'; \omega|t) \right\}, \end{aligned} \quad (32)$$

where Re and Im stand for the real and imaginary parts, respectively.

We then have that

$$\text{Im}\{\chi(\mathbf{r}, \mathbf{r}'; \omega|t)\} = \chi''(\mathbf{r}, \mathbf{r}'; \omega|t), \quad (33)$$

$$\text{Re}\{\chi(\mathbf{r}, \mathbf{r}'; \omega|t)\} = \text{pv} \left\{ \int_{-\infty}^{\infty} \frac{d\omega'}{\pi} \frac{\text{Im}\chi(\mathbf{r}, \mathbf{r}'; \omega'|t)}{(\omega' - \omega)} \right\}, \quad (34)$$

after recalling that $\chi''(\mathbf{r}, \mathbf{r}'; \omega|t)$ is a real quantity [see (51), below].

Equation (34) is one of the so-called *generalized Kramer-Krönig relations*. The second such generalized relation,

$$\text{Im}\{\chi(\mathbf{r}, \mathbf{r}'; \omega|t)\} = -\mathcal{P} \left\{ \int_{-\infty}^{\infty} \frac{d\omega'}{\pi} \frac{\text{Re}\chi(\mathbf{r}, \mathbf{r}'; \omega'|t)}{(\omega' - \omega)} \right\}, \quad (35)$$

can be obtained from (34) and the operational relation

$$\mathcal{P} \int_{-\infty}^{\infty} \frac{d\omega''}{\pi} (\omega - \omega'')^{-1} (\omega'' - \omega')^{-1} = -\pi\delta(\omega - \omega'). \quad (36)$$

We recall that Kramer-Krönig relations are consequences of the principle of causality, related to behavior of the susceptibility in the complex plane. More specifically, once extended to the complex $z = \omega + iy$ plane, $\chi(\mathbf{r}, \mathbf{r}'; z|t)$, has poles in the lower half plane, but is regular in the upper half plane. Furthermore, $\text{Re}\{\chi\}$ is an even function of ω , while $\text{Im}\{\chi\}$ is an odd function. Therefore, as one would expect, $\chi(\mathbf{r}, \mathbf{r}'; \omega|t)$ shares the properties of the equilibrium susceptibility, which will be discussed in connection with (52), below.

Moreover, $\text{Im}\{\chi(\mathbf{r}, \mathbf{r}'; \omega|t)\}$ is related to the power absorbed by the system. To show this, we first notice that the time-dependent external force applied on the system, a real quantity, can be Fourier analyzed to yield a linear superposition of Fourier components, namely

$$\mathcal{F}(\mathbf{r}', t') = \int d\omega \frac{1}{2} \mathcal{F}(\mathbf{r}', \omega) (e^{i\omega t'} + e^{-i\omega t'}). \quad (37)$$

Consider, then, the average over time t' (and then τ) of the power absorbed by the system in a time interval Δt (typically the experimental resolution time), which is given by the expression

$$\begin{aligned} W(t) &= \frac{1}{\Delta t} \int_t^{t+\Delta t} dt' \frac{dE(t')}{dt'} \\ &= \frac{1}{\Delta t} \int_t^{t+\Delta t} dt' \frac{d}{dt'} \text{Tr}\{\hat{H}(t') \mathcal{R}_\varepsilon(t')\} \\ &= \frac{1}{\Delta t} \int_t^{t+\Delta t} dt' \text{Tr} \left\{ \frac{\partial \hat{H}(t')}{\partial t'} \mathcal{R}_\varepsilon(t') + \hat{H}(t') \frac{\partial}{\partial t'} \mathcal{R}_\varepsilon(t') \right\}. \end{aligned} \quad (38)$$

But since

$$\text{Tr} \left\{ \hat{H}(t') \frac{\partial}{\partial t'} \mathcal{R}_\varepsilon(t') \right\} = \frac{1}{i\hbar} \text{Tr} \left\{ [\hat{H}(t'), \hat{H}(t')] \mathcal{R}_\varepsilon(t') \right\} = 0, \quad (39)$$

where we have used that \mathcal{R}_ε satisfies Liouville equation, we see that

$$\begin{aligned} W(t) &= \frac{1}{\Delta t} \int_t^{t+\Delta t} dt' \text{Tr} \left\{ \frac{\partial \hat{H}(t')}{\partial t'} \mathcal{R}_\varepsilon(t') \right\} \\ &= \frac{1}{\Delta t} \int_t^{t+\Delta t} dt' \text{Tr} \left\{ \frac{\partial \hat{V}(t')}{\partial t'} \mathcal{R}_\varepsilon(t') \right\} \\ &= -\frac{1}{\Delta t} \int_t^{t+\Delta t} dt' \int d^3r' \text{Tr}\{\hat{A}(\mathbf{r}') \mathcal{R}_\varepsilon(t')\} \frac{\partial \mathcal{F}(\mathbf{r}', t')}{\partial t'}, \end{aligned} \quad (40)$$

with \hat{V} given by (2).

Account taken that

$$\begin{aligned} Tr\{\hat{A}(\mathbf{r}')\mathcal{R}_\varepsilon(t)\} &= Tr\{\hat{A}(\mathbf{r}')U(t', t_i)\mathcal{R}_\varepsilon(t_i)U^\dagger(t', t_i)\} \\ &= Tr\{U^\dagger(t', t_i)\hat{A}(\mathbf{r}')U(t', t_i)\mathcal{R}_\varepsilon(t_i)\} \\ &= Tr\{U'^\dagger(t', t_i)\tilde{A}(\mathbf{r}', t')U'(t', t_i)\mathcal{R}_\varepsilon(t_i)\}, \end{aligned} \quad (41)$$

where we have used (6) and (13), with the help of (11) to first order, i.e., within linear response, and of (20), we find that

$$\begin{aligned} W(t) &= \frac{1}{i\hbar\Delta t} \int_t^{t+\Delta t} dt' \int d^3r' \int_{-\infty}^{t'} dt'' \int d^3r'' \\ &\quad Tr\{\tilde{A}(\mathbf{r}', t'), \tilde{A}(\mathbf{r}'', t'')\mathcal{R}_\varepsilon(t_i)\}\mathcal{F}(\mathbf{r}'', t'')\frac{\partial\mathcal{F}(\mathbf{r}', t')}{\partial t'} \\ &= -\frac{1}{\Delta t} \int_t^{t+\Delta t} dt' \int d^3r' \Delta A(\mathbf{r}', t')\frac{\partial\mathcal{F}(\mathbf{r}', t')}{\partial t'}, \end{aligned} \quad (42)$$

with ΔA defined by (20).

In view of (27), we can write (42) in the alternative form

$$\begin{aligned} W(t) &= -\frac{1}{\Delta t} \int_t^{t+\Delta t} dt' \int d^3r' \int d^3r'' \int_{-\infty}^{\infty} d\tau \chi \\ &\quad \times (\mathbf{r}', \mathbf{r}''; \tau|t')\mathcal{F}(\mathbf{r}'', \tau+t')\frac{\partial\mathcal{F}(\mathbf{r}', t')}{\partial t'}, \end{aligned} \quad (43)$$

where $\tau = t'' - t'$

From (37) and the definition of the Fourier transform of χ , it follows that

$$\begin{aligned} W(t) &= -\frac{1}{\Delta t} \int_t^{t+\Delta t} dt' \int d^3r' \int d^3r'' \int d\omega i\omega\mathcal{F}(\mathbf{r}'', \omega) \\ &\quad \times \mathcal{F}(\mathbf{r}', \omega) \left\{ \chi^*(\mathbf{r}', \mathbf{r}''; \omega|t')(e^{2i\omega t'} - 1) \right. \\ &\quad \left. - \chi(\mathbf{r}', \mathbf{r}''; \omega|t')(e^{-2i\omega t'} - 1) \right\}. \end{aligned} \quad (44)$$

Consider now a particular situation without ultrafast relaxation, so that $\mathcal{R}_\varepsilon(t')$ varies weakly in the interval Δt and is therefore approximately equal to $\mathcal{R}_\varepsilon(t)$. If Δt is large in comparison with $2\pi/\omega$, the exponentials on the right-hand side of (44) cancel on average, and from (23), it follows that

$$W(t) = \frac{1}{2} \int d^3r' \int d^3r'' \int d\omega \mathcal{F}(\mathbf{r}', \omega)\mathcal{F}(\mathbf{r}'', \omega)\alpha(\mathbf{r}', \mathbf{r}''; \omega|t), \quad (45)$$

where

$$\alpha(\mathbf{r}', \mathbf{r}''; \omega|t) = \omega\chi''(\mathbf{r}', \mathbf{r}''; \omega|t) \quad (46)$$

can be identified with an absorption coefficient at frequency ω associated to the perturbing force at the macroscopic (nonequilibrium thermodynamic) state of the system at time t .

Evidently, and this is a fundamental point to be stressed, the generalized susceptibility depends on ϱ_ε , it is a

functional of the time- (and eventually of the space-) dependent variables that characterized the nonequilibrium-thermodynamic state of the system, then the calculus of responses needs be coupled with the one of the equations of evolution for the basic variables, as given by the non-linear quantum kinetic theory that the formalism provides [8–13, 16].

To close this section, let us add a few considerations. First, if the system has translational invariance (or near *translational invariance* as in the case of regular crystalline matter), χ'' and χ depend only on the difference $\mathbf{r} - \mathbf{r}'$, not on \mathbf{r} and \mathbf{r}' individually. We can then introduce the spatial Fourier transform, namely

$$\chi''(\mathbf{k}, \omega|t) = \int d^3b \chi''(\mathbf{b}, \omega|t)e^{-i\mathbf{k}\cdot\mathbf{b}}, \quad (47)$$

where $\mathbf{b} = \mathbf{r} - \mathbf{r}'$. Moreover,

$$[\chi''(\mathbf{r}, \mathbf{r}'; -\tau|t)]^* = -\chi''(\mathbf{r}, \mathbf{r}'; -\tau|t), \quad (48)$$

because χ'' is expressed as a commutator of hermitian operators and is therefore purely imaginary.

Similarly, it follows that

$$\chi''(\mathbf{r}, \mathbf{r}'; -\tau|t) = -\chi''(\mathbf{r}, \mathbf{r}'; \tau|t), \quad (49)$$

which implies that

$$\chi''(\mathbf{k}, \omega|t) = -\chi''(-\mathbf{k}, -\omega|t). \quad (50)$$

On the other hand, on the basis of (32) and (50), we have that

$$\begin{aligned} \text{im}\{\chi(\mathbf{k}, \omega|t)\} &= \frac{1}{2i} (\chi(\mathbf{k}, \omega|t) - \chi^*(\mathbf{k}, \omega|t)) \\ &= \frac{1}{2i} \int_{-\infty}^{\infty} \frac{d\omega'}{\pi} \int d^3b \int d\tau \chi''(\mathbf{b}, -\tau|t) \\ &\quad \times \left(\frac{e^{-i(\mathbf{k}\cdot\mathbf{b}-\omega'\tau)}}{\omega' - \omega - is} + \frac{e^{i(\mathbf{k}\cdot\mathbf{b}-\omega'\tau)}}{\omega' - \omega + is} \right) \\ &= \frac{1}{2i} \int_{-\infty}^{\infty} \frac{d\omega'}{\pi} \int d^3b \int d\tau e^{-i(\mathbf{k}\cdot\mathbf{b}-\omega\tau)} \\ &\quad \times \left(\frac{\chi''(\mathbf{b}, -\tau|t)}{\omega' - \omega - is} + \frac{\chi''(-\mathbf{b}, \tau|t)}{\omega' - \omega + is} \right) \\ &= \chi''(\mathbf{k}, \omega|t), \end{aligned} \quad (51)$$

which is therefore real, and so is $\chi''(\mathbf{r}, \mathbf{r}'; \omega|t)$.

Moreover, if the system is initially prepared in equilibrium with the reservoirs, characterized by a distribution ϱ_{eq} (which commutes with \hat{h}), we recover the usual expression [49]

$$\chi(\mathbf{r}, \mathbf{r}'; t - t')_{\text{eq}} = \theta(t - t') \frac{i}{\hbar} \text{tr} \{ [\hat{a}(\mathbf{r}), \tilde{a}(\mathbf{r}', t' - t)] \varrho_{\text{eq}} \}. \quad (52)$$

where, as usual, because the equilibrium has been established, the interaction between system and reservoir can be neglected.

Second, as pointed out in the introduction, the remarkable recent series of instrumentation developments, which are necessary for the study of the systems in far-from-equilibrium conditions resulting from the advanced technology search for miniaturized devices with ultrafast responses, require the mechanical-statistical analysis in short time intervals (as described above) and in nanometric spatial regions. This is also contained in the theoretical treatment described above. In fact, if the system properties, which evolve in time, are measured in a small region around position \mathbf{r} , the expected value is given in (27), which we can alternatively write as

$$\delta\langle\hat{a}(\mathbf{r})|t\rangle = \frac{1}{2\hbar} \int_{-\infty}^{\infty} dt' \text{tr} \left\{ [\hat{a}(\mathbf{r}, t), \hat{V}(t', t' - t)] \nabla_{\varepsilon}(t) \right\},$$

with [cf. (2)]

$$\hat{V}(t', t' - t) = - \int d^3r' \{ (\mathbf{r}', t') \hat{a}(\mathbf{r}', t' - t),$$

Finally, as already seen, this NESEF-based approach to response function theory involves the calculation of averages in terms of the nonequilibrium statistical operator, a quite difficult task. First, we recall that we have taken the system in contact with external reservoirs. The latter are very much larger than the system and, for all practical purposes, remain in a stationary equilibrium state throughout the experiments, and that $\nabla_{\varepsilon}(t) = \varrho_{\varepsilon}(t) \times \varrho_r$, where ϱ_r is the stationary equilibrium statistical operator of the reservoir(s), and $\varrho_{\varepsilon}(t)$ the nonequilibrium statistical operator of the system.

We can moreover write the expression [8–13]

$$\varrho_{\varepsilon}(t) = \bar{\varrho}(t) + \varrho'_{\varepsilon}(t), \quad (53)$$

that is, the sum of the “instantaneously frozen” auxiliary statistical operator $\bar{\varrho}$ and the contribution ϱ'_{ε} , which accounts for the relaxation processes in the media. Therefore, we can write (25) in the form

$$\chi''(\mathbf{r}, \mathbf{r}'; t' - t|t) = \bar{\chi}''(\mathbf{r}, \mathbf{r}'; t' - t|t) + \chi''_{\varepsilon}(\mathbf{r}, \mathbf{r}'; t' - t|t), \quad (54)$$

where in $\bar{\chi}''$ the averaging is over the auxiliary ensemble, characterized by $\bar{\varrho}$, and χ''_{ε} is the averaging in terms of the contribution ϱ'_{ε} . Using the expression for ϱ'_{ε} , given in terms of $\bar{\varrho}$ [12, 13], it can be shown that it is expressed in a born-perturbation-like series in powers of \hat{h}' , the internal interactions in the system. Therefore, whereas the weak-coupling limit can be used, we can retain only $\bar{\chi}$ to a good degree of approximation. In the NESEF-based kinetic equations this limit renders the equation markovian in character [16]. We stress again that the response function theory for systems away from equilibrium is always coupled with the kinetic equations that describe the evolution of the nonequilibrium-thermodynamic state of the system.

Next, we will see another important property of the nonequilibrium generalized susceptibility, namely a fluctuation-dissipation theorem under far-from-equilibrium conditions.

3 Fluctuation-Dissipation Theorem Under Far-from-Equilibrium Conditions

The fluctuation-dissipation theorem (FDT)—originally a relation between the equilibrium fluctuations in a system and the dissipative response induced by external forces—provided major impetus for the development of discussions of irreversible processes. A classical particular form seems to have been proved by Nyquist [55] for the relationship between the thermal noise and the impedance of a resistor. Derivations from phenomenological points of view followed, along with stochastic approaches, and finally, the discussion was drawn into the domain of statistical mechanics [56–58].

The results, which cover the immediate neighborhood of equilibrium, were very well established. For systems out of equilibrium (particularly those far from equilibrium), the situation is less clearly delineated. A few methods are available for steady-state conditions in a stochastic approach [59] and for transient regimes in particular ensembles [60]. We address here the derivation of a FDT for far-from-equilibrium systems, in the framework of the nonequilibrium ensemble NESEF formalism, which is a generalization to arbitrary nonequilibrium conditions of the formalism developed by Kubo [57, 58] in the case of equilibrium systems.

A fluctuation-dissipation theorem for systems arbitrarily away from equilibrium in the NESEF follows from the comparison of two expressions: one is a correlation function of two quantities, and the other a dynamic response of the system to an external deterministic perturbation, that is, the generalized susceptibility of Section 3.

Let us first recall the equilibrium case [57, 58]. Consider the quantities \hat{A} and \hat{B} : their correlation function over the canonical ensemble in equilibrium is given by the equality

$$\begin{aligned} S_{AB}(\mathbf{r}, \mathbf{r}', t - t') &= \text{Tr} \{ \Delta \hat{A}(\mathbf{r}, t) \Delta \hat{B}(\mathbf{r}', t') \varrho_c \} \\ &= \text{Tr} \{ \Delta \hat{A}(\mathbf{r}, t - t') \Delta \hat{B}(\mathbf{r}') \varrho_c \}, \end{aligned} \quad (55)$$

where $\Delta \hat{A} = \hat{A} - \text{Tr} \{ \hat{A} \varrho_c \}$, and the generalized susceptibility is

$$\begin{aligned} \chi''_{AB}(\mathbf{r}, \mathbf{r}'; t - t') &= \frac{1}{2\hbar} \text{Tr} \{ [\hat{A}(\mathbf{r}, t), \hat{B}(\mathbf{r}', t')] \varrho_c \} \\ &= \frac{1}{2\hbar} \text{Tr} \{ [\hat{A}(\mathbf{r}, t - t'), \hat{B}(\mathbf{r}')] \varrho_c \}, \end{aligned} \quad (56)$$

which is a generalization of the one in (25), with

$$\hat{A}(\mathbf{r}, t) = e^{-\frac{1}{i\hbar}t\hat{H}}\hat{A}e^{\frac{1}{i\hbar}t\hat{H}}, \quad (57)$$

where \hat{H} is the system Hamiltonian (in the absence of any external perturbation), that is, the operators are given in Heisenberg representation, and

$$\varrho_c = \frac{e^{-\frac{\hat{H}}{k_B T}}}{Z(T, N, V)} \quad (58)$$

is the equilibrium canonical distribution in equilibrium.

Using the operational relationship

$$\begin{aligned} e^{-\beta\hat{H}}e^{-\frac{1}{i\hbar}t\hat{H}}\hat{A}(\mathbf{r})e^{\frac{1}{i\hbar}t\hat{H}} &= e^{-\frac{1}{i\hbar}(t+i\beta\hbar)\hat{H}}\hat{A}(\mathbf{r}) \\ &\quad \times e^{\frac{1}{i\hbar}(t+i\beta\hbar)\hat{H}}e^{-\beta\hat{H}} \\ &\equiv \hat{A}(\mathbf{r}, t+i\beta\hbar)e^{-\beta\hat{H}}, \end{aligned} \quad (59)$$

we have that

$$\text{Tr}\{\varrho_c\hat{A}(\mathbf{r}, t)\hat{B}(\mathbf{r}', t')\} = \text{Tr}\{\varrho_c\hat{B}(\mathbf{r}', t')\hat{A}(\mathbf{r}, t+i\hbar\beta)\}. \quad (60)$$

Furthermore, let us introduce the time Fourier transform of the correlation function, namely

$$S_{AB}(\mathbf{r}, \mathbf{r}'; t-t') = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \tilde{S}_{AB}(\mathbf{r}, \mathbf{r}'; \omega) e^{i\omega(t-t')}, \quad (61)$$

and consider

$$\begin{aligned} \tilde{S}_{AB}(\mathbf{r}', \mathbf{r}; -\omega) &= \int_{-\infty}^{\infty} d\tau \text{Tr}\{\Delta\hat{B}(\mathbf{r}')\Delta\hat{A}(\mathbf{r}, \tau)\varrho_c\}e^{-i\omega\tau} \\ &= \int_{-\infty}^{\infty} d\tau \text{Tr}\{\varrho_c\Delta\hat{B}(\mathbf{r}') \\ &\quad \times \Delta\hat{A}(\mathbf{r}, \tau+i\beta\hbar)\}, \end{aligned} \quad (62)$$

where we have used (59), and $\tau = t-t'$. Introducing $\tau = \tau' + i\beta\hbar$, it results that

$$\tilde{S}_{AB}(\mathbf{r}', \mathbf{r}, -\omega) = \tilde{S}_{BA}(\mathbf{r}, \mathbf{r}'; \omega)e^{-\beta\hbar\omega}. \quad (63)$$

On the other hand,

$$\begin{aligned} \chi''_{AB}(\mathbf{r}, \mathbf{r}'; \omega) &= \int_{-\infty}^{\infty} d\tau e^{i\omega\tau} \frac{1}{2\hbar} \text{Tr}\{[\hat{A}(\mathbf{r}, \tau), \hat{B}(\mathbf{r}')] \varrho_c\} \\ &= \int_{-\infty}^{\infty} d\tau e^{i\omega\tau} \frac{1}{2\hbar} \text{Tr}\{[\Delta\hat{A}(\mathbf{r}, \tau), \Delta\hat{B}(\mathbf{r}')] \varrho_c\} \\ &= \frac{1}{2\hbar} \{\tilde{S}_{AB}(\mathbf{r}, \mathbf{r}'; \omega) - \tilde{S}_{BA}(\mathbf{r}', \mathbf{r}; -\omega)\}, \end{aligned} \quad (64)$$

where we were allowed to substitute ΔA for A and ΔB for B because the extra terms cancel out in the commutation.

From (63), it then follows that

$$\tilde{S}_{AB}(\mathbf{r}, \mathbf{r}'; \omega) = 2\hbar[1 - e^{-\beta\hbar\omega}]^{-1} \chi''_{AB}(\mathbf{r}, \mathbf{r}'; \omega), \quad (65)$$

which is the traditional form of the fluctuation-dissipation theorem.

In the linear regime around equilibrium, the dependence on the space coordinates is usually of the form $\mathbf{r} - \mathbf{r}'$. The spatial Fourier transform of (65) therefore yields the result

$$\tilde{S}_{AB}(\mathbf{k}, \omega) = 2\hbar[1 - e^{-\beta\hbar\omega}]^{-1} \chi''_{AB}(\mathbf{k}, \omega), \quad (66)$$

where χ'' is the imaginary part of the generalized susceptibility identified in Section 3 [cf. (33)].

Let us now consider a system away from equilibrium. To this end, we define

$$S_{AB}(\mathbf{r}, t; \mathbf{r}', t'|t_i) = \text{Tr}\{\Delta\hat{A}(\mathbf{r}, t)\Delta\hat{B}(\mathbf{r}', t')\varrho_\varepsilon(t_i)\}, \quad (67)$$

$$\chi''_{AB}(\mathbf{r}, t; \mathbf{r}', t'|t_i) = \frac{1}{2\hbar} \text{Tr}\{[\hat{A}(\mathbf{r}, t), \hat{B}(\mathbf{r}', t')]\varrho_\varepsilon(t_i)\}, \quad (68)$$

where $\varrho_\varepsilon(t_i)$ is the distribution characterizing the preparation, in nonequilibrium conditions, of the system at time t_i when the experiment begins, and $\Delta\hat{A}(\mathbf{r}, t) = \hat{A}(\mathbf{r}, t) - \text{Tr}\{\hat{A}(\mathbf{r}, t)\varrho_\varepsilon(t_i)\} = \hat{A}(\mathbf{r}, t) - \text{Tr}\{\hat{A}(\mathbf{r})\varrho_\varepsilon(t)\}$, after using that

$$\hat{A}(\mathbf{r}, t) = U^\dagger(t)\hat{A}(\mathbf{r})U(t), \quad (69)$$

$$\varrho_\varepsilon(t) = U(t)\varrho_\varepsilon(t_i)U^\dagger(t), \quad (70)$$

$$U(t) = e^{-\frac{1}{i\hbar}(t-t_i)\hat{H}}. \quad (71)$$

For ϱ_ε , we write that

$$\varrho_\varepsilon(t) = \exp\{-\hat{S}_\varepsilon(t)\}, \quad (72)$$

where

$$\hat{S}_\varepsilon(t) = \hat{S}(t, 0) + \hat{\zeta}_\varepsilon(t), \quad (73)$$

with

$$\hat{\zeta}_\varepsilon(t) = - \int_{-\infty}^t dt' e^{\varepsilon(t'-t)} \frac{d}{dt'} \hat{S}(t', t'-t). \quad (74)$$

In the spirit of our treatment of the equilibrium case, we first write the expressions

$$\begin{aligned} \text{Tr}\{\Delta\hat{B}(\mathbf{r}, t)\Delta\hat{A}(\mathbf{r}', t')\varrho_\varepsilon(t_i)\} &= \text{Tr}\{U^\dagger(t)\Delta\hat{B}(\mathbf{r}', t)U(t) \\ &\quad \times U^\dagger(t)\Delta\hat{A}(\mathbf{r})U(t)\varrho_\varepsilon(t_i)\} \\ &= \text{Tr}\{\Delta\hat{B}(\mathbf{r}', t)\Delta\hat{A}(\mathbf{r})\varrho_\varepsilon(t)\}. \end{aligned} \quad (75)$$

Moreover,

$$\begin{aligned} \text{Tr}\{\hat{A}(\mathbf{r}, t)\hat{B}(\mathbf{r}', t')\varrho_\varepsilon(t_i)\} &= \text{Tr}\{\hat{B}(\mathbf{r}', t')\varrho_\varepsilon(t_i)\hat{A}(\mathbf{r}, t)\} \\ &= \text{Tr}\left\{e^{-\hat{S}_\varepsilon(t_i)}e^{\hat{S}_\varepsilon(t_i)}U^\dagger(t')\hat{B}(\mathbf{r}')U(t')\right. \\ &\quad \times e^{-\hat{S}_\varepsilon(t_i)}U^\dagger(t)\hat{A}(\mathbf{r})U(t)\left.\right\} \\ &= \text{Tr}\left\{e^{-\hat{S}_\varepsilon(t_i)}U^\dagger(t)U(t)e^{\hat{S}_\varepsilon(t_i)}U^\dagger(t)U(t)U^\dagger(t')\right. \\ &\quad \times \hat{B}(\mathbf{r}')U^\dagger(t')U^\dagger(t)U(t)e^{-\hat{S}_\varepsilon(t_i)}U^\dagger(t)\hat{A}(\mathbf{r})U(t)\left.\right\} \\ &= \text{Tr}\left\{\left(U(t)e^{-\hat{S}_\varepsilon(t_i)}U^\dagger(t)\right)\left(U(t)e^{\hat{S}_\varepsilon(t_i)}U^\dagger(t)\right)\right. \\ &\quad \times \left(U(t)U^\dagger(t')\hat{B}(\mathbf{r}')U(t')U^\dagger(t)\right)\left(U(t)e^{-\hat{S}_\varepsilon(t_i)}U^\dagger(t)\right)\hat{A}(\mathbf{r})\left.\right\} \\ &= \text{Tr}\{e^{-\hat{S}_\varepsilon(t)}e^{\hat{S}_\varepsilon(t)}\hat{B}(\mathbf{r}', t'-t)e^{-\hat{S}_\varepsilon(t)}\hat{A}(\mathbf{r})\} \\ &= \text{Tr}\{\hat{B}_\varepsilon(\mathbf{r}', t'-t|\hat{A}(\mathbf{r})\varrho_\varepsilon(t)\}, \end{aligned} \quad (76)$$

where

$$\hat{B}_\varepsilon(\mathbf{r}', -\tau|t) = e^{\hat{S}_\varepsilon(t)}U(\tau)\hat{B}(\mathbf{r}')U^\dagger(\tau)e^{-\hat{S}_\varepsilon(t)}, \quad (77)$$

with $\tau = t - t'$, and we recall that $U(-\tau) = U^\dagger(\tau)$.

Consider now the susceptibility. We then have that

$$\begin{aligned} \chi''_{AB}(\mathbf{r}, t; \mathbf{r}', t'|t_i) &= \frac{1}{2\hbar}\text{Tr}\{[\hat{A}(\mathbf{r}, t), \hat{B}(\mathbf{r}', t')]\varrho_\varepsilon(t_i)\} \\ &= \frac{1}{2\hbar}\text{Tr}\{[\Delta\hat{A}(\mathbf{r}, t), \Delta\hat{B}(\mathbf{r}', t')]\varrho_\varepsilon(t_i)\} \\ &= \frac{1}{2\hbar}\text{Tr}\left\{\left(\Delta\hat{A}(\mathbf{r}, t)\Delta\hat{B}(\mathbf{r}', t')\right.\right. \\ &\quad \left.\left.- \Delta\hat{B}(\mathbf{r}', t')\Delta\hat{A}(\mathbf{r}, t)\right)\varrho_\varepsilon(t_i)\right\} \\ &= \frac{1}{2\hbar}\text{Tr}\left\{\left(\Delta\hat{B}_\varepsilon(\mathbf{r}', -\tau|t)\Delta\hat{A}(\mathbf{r})\right.\right. \\ &\quad \left.\left.- \Delta\hat{B}(\mathbf{r}', -\tau)\Delta\hat{A}(\mathbf{r})\right)\varrho_\varepsilon(t)\right\} \end{aligned} \quad (78)$$

where we have used (76).

The distribution ϱ_ε in the last expression can be given as given at the time t when a measurement is performed. Equation (78) can now be written in the form

$$\chi''_{AB}(\mathbf{r}, \mathbf{r}'; t' - t|t) = \frac{1}{2\hbar}[S_{BA}^\varepsilon(\mathbf{r}', \mathbf{r}; t' - t|t) - S_{BA}(\mathbf{r}', \mathbf{r}; t' - t|t)], \quad (79)$$

after defining

$$S_{BA}^\varepsilon(\mathbf{r}', \mathbf{r}; t' - t|t) = \text{Tr}\{\Delta\hat{B}_\varepsilon(\mathbf{r}', -\tau)\Delta\hat{A}(\mathbf{r})\varrho_\varepsilon(t)\}, \quad (80)$$

$$S_{BA}(\mathbf{r}', \mathbf{r}; t' - t|t) = \text{Tr}\{\Delta\hat{B}(\mathbf{r}', -\tau)\Delta\hat{A}(\mathbf{r})\varrho_\varepsilon(t)\}. \quad (81)$$

The nonequilibrium distribution admits a separation in two parts. One of them is the so-called relevant part, $\bar{\varrho}$. The other is a contribution, ϱ'_ε , which accounts for relaxation processes which are governed by \hat{H}' in (1). We therefore separate the fluctuation-dissipation relation of (64) in a

“relevant” part (the one depending on $\bar{\varrho}$ and \hat{H}_0 alone) and the remainder. That “relevant” part is then

$$\begin{aligned} \bar{\chi}''_{AB}(\mathbf{r}, \mathbf{r}', -\tau|t) &= \frac{1}{2\hbar}\text{Tr}\left\{\left(e^{\hat{S}(t,0)}\Delta\hat{B}(\mathbf{r}', -\tau)_0e^{-\hat{S}(t,0)}\right.\right. \\ &\quad \left.\left.\Delta\hat{A}(\mathbf{r}) - \Delta\hat{B}(\mathbf{r}', \tau)_0\Delta\hat{A}(\mathbf{r})\right)\right. \\ &\quad \left.\times \bar{\varrho}(t, 0)\right\}, \end{aligned} \quad (82)$$

where

$$\Delta\hat{B}(\mathbf{r}, -\tau)_0 = e^{\frac{1}{i\hbar}\tau\hat{H}_0}\hat{B}(\mathbf{r})e^{-\frac{1}{i\hbar}\tau\hat{H}_0}. \quad (83)$$

Fourier transforming in τ and in the space coordinates—we assume dependence on $\mathbf{r} - \mathbf{r}'$, that is, that the system is translationally invariant—we convert (79) into the form

$$\chi''_{AB}(\mathbf{k}, \omega|t) = \frac{1}{2\hbar}[S_{BA}^\varepsilon(\mathbf{k}, \omega|t) - S_{BA}(\mathbf{k}, \omega|t)], \quad (84)$$

which constitutes a fluctuation-dissipation relation for systems arbitrarily far from equilibrium. In particular, as expected, we recover (66) when the canonical distribution ϱ_c is substituted for $\varrho_\varepsilon(t)$.

On the other hand, in the case of space- and time-resolved experiments in systems with no translational invariance, we have the following result for the response in a region $\Delta\mathbf{r}$ (the experimental space resolution on, say, the micro- or nanometric scale) around the position \mathbf{r} :

$$\begin{aligned} \chi''_{AB\ell}(\mathbf{r}; t' - t|t) &= \int d^3r' \chi''_{AB}(\mathbf{r}, \mathbf{r}'; t' - t|t) \\ &= \frac{1}{2\hbar}[S_{BA\ell}^\varepsilon(\mathbf{r}; t' - t|t) \\ &\quad - S_{BA\ell}(\mathbf{r}; t' - t|t)], \end{aligned} \quad (85)$$

where ℓ stands for “local,” with the last two correlations over the nonequilibrium ensemble corresponding to the integration over \mathbf{r}' of those on the right of (79).

As an illustration, we consider a free-fermion gas, for which

$$\hat{H}_0 = \sum_{\mathbf{k}} \epsilon_{\mathbf{k}} c_{\mathbf{k}}^\dagger c_{\mathbf{k}}, \quad (86)$$

where $c_{\mathbf{k}} \left(c_{\mathbf{k}}^\dagger\right)$ annihilates (creates) a fermion in state \mathbf{k} (we omit the spin index), and $\epsilon_{\mathbf{k}}$ is the energy-dispersion relation.

We consider the nonequilibrium generalized grand-canonical ensemble [12, 13], for which the basic variables in the nonequilibrium statistical operator are the energy and particle densities and fluxes (currents), and all the other tensorial fluxes of higher orders, $r = 2, 3, \dots$, with r also being the tensor rank. Further, we restrict the analysis to the homogeneous condition, i.e., for densities and fluxes

independent of the space coordinates. Then, in reciprocal space, the informational entropy operator takes the form

$$\hat{S}(t, 0) = \sum_{\mathbf{k}} \left\{ F_h(t) \epsilon_{\mathbf{k}} + F_n(t) + \sum_{r \geq 1} [F_h^{[r]}(t) \otimes u^{[r]}(\mathbf{k}) \epsilon_{\mathbf{k}} + F_n^{[r]}(t) \otimes u^{[r]}(\mathbf{k})] \right\} c_{\mathbf{k}}^{\dagger} c_{\mathbf{k}}. \quad (87)$$

In (87), the F 's are the nonequilibrium-thermodynamic variables associated with the energy, the number of particles, and the energy and particle fluxes of order r ($r = 1, 2, \dots$); $u^{[r]}(\mathbf{k})$ is the tensorial product of r by the generating velocity $\mathbf{u}(\mathbf{k}) = \hbar^{-1} \nabla_{\mathbf{k}} \epsilon_{\mathbf{k}}$, that is, the group velocity of the fermion in state \mathbf{k} ; the symbol \otimes denotes a fully contracted product of tensors.

Equation (87) can be written in the compact form

$$\hat{S}(t, 0) = \sum_{\mathbf{k}} \varphi_{\mathbf{k}}(t) c_{\mathbf{k}}^{\dagger} c_{\mathbf{k}}, \quad (88)$$

where φ is the term between curly brackets in (87).

We hence have that the “relevant” part of the correlation in (80) is

$$\begin{aligned} S_{BA}^{\varepsilon}(\mathbf{r}', \mathbf{r}; -\tau|t)^{\text{rel}} &= \text{Tr} \left\{ e^{\hat{S}(t,0)} e^{-\frac{1}{i\hbar} \tau \hat{H}_0} \hat{B}(\mathbf{r}') e^{\frac{1}{i\hbar} \tau \hat{H}_0} \right. \\ &\quad \left. \times e^{-\hat{S}(t,0)} \hat{A}(\mathbf{r}) \bar{\varrho}(t, 0) \right\} \\ &= \text{Tr} \left\{ e^{\frac{1}{i\hbar} \sum_{\mathbf{k}} \tau_{\mathbf{k}} \epsilon_{\mathbf{k}} c_{\mathbf{k}}^{\dagger} c_{\mathbf{k}}} \hat{B}(\mathbf{r}') \right. \\ &\quad \left. \times e^{-\frac{1}{i\hbar} \sum_{\mathbf{k}} \tau_{\mathbf{k}} \epsilon_{\mathbf{k}} c_{\mathbf{k}}^{\dagger} c_{\mathbf{k}}} \hat{A}(\mathbf{r}) \bar{\varrho}(t, 0) \right\} \end{aligned} \quad (89)$$

where we have defined the quantity

$$\tau_{\mathbf{k}} = \tau - i\hbar(\varphi_{\mathbf{k}}(t)/\epsilon_{\mathbf{k}}), \quad (90)$$

which has the dimension of time.

To further simplify matters, we truncate the basic set of macrovariables, retaining only the energy \hat{H}_0 , the number of particles N , and the flux of matter \mathbf{I}_n , which, multiplied by the mass of the fermions, becomes the linear momentum, \mathbf{P} . We call the associated nonequilibrium-thermodynamic variables $F_h = \beta^*(t)$, $F_n = -\beta^*(t)\mu^*(t)$, and $\mathbf{F}_n(t) = -\beta^*(t)m^*\mathbf{v}(t)$, introducing the reciprocal $\beta^*(t) = 1/k_B T^*(t)$ of a quasi-temperature, a quasi-chemical potential $\mu^*(t)$, and a drift velocity $\mathbf{v}(t)$ [12, 13, 61–64]. We are using a kind of nonequilibrium canonical distribution with an additional term stemming from the current with drift velocity $\mathbf{v}(t)$. Moreover, for \hat{A} and \hat{B} , we will choose the nondiagonal elements of Dirac-Landau-Wigner single-particle density matrix in second quantization form, namely

$$\hat{A} \equiv \hat{n}_{\mathbf{k}\mathbf{Q}} = c_{\mathbf{k}-\frac{1}{2}\mathbf{Q}}^{\dagger} c_{\mathbf{k}+\frac{1}{2}\mathbf{Q}}, \quad (91)$$

$$\hat{B} \equiv \hat{n}_{\mathbf{k}\mathbf{Q}} = c_{\mathbf{k}+\frac{1}{2}\mathbf{Q}}^{\dagger} c_{\mathbf{k}-\frac{1}{2}\mathbf{Q}}, \quad (92)$$

which will appear later in our calculation of inelastic scattering cross sections.

The relevant part of the corresponding correlation is hence

$$S_{nn^{\dagger}}(\mathbf{k}, \mathbf{Q}, -\tau|t)^{\text{rel}} = \text{Tr} \{ \tilde{U}(\tau|t) \hat{n}_{\mathbf{k}\mathbf{Q}} \tilde{U}^{\dagger}(\tau|t) \hat{n}_{\mathbf{k}\mathbf{Q}}^{\dagger} \bar{\varrho}(t, 0) \}, \quad (93)$$

where

$$\begin{aligned} \tilde{U}(\tau|t) &= \exp \left\{ \frac{1}{i\hbar} \sum_{\mathbf{k}} [\epsilon_{\mathbf{k}}(\tau - i\hbar\beta^*(t)) - i\hbar\beta^*(t)\mu^*(t) \right. \\ &\quad \left. + i\hbar\beta^*(t)\mathbf{v}(t) \cdot \hbar\mathbf{k}] c_{\mathbf{k}}^{\dagger} c_{\mathbf{k}} \right\}, \end{aligned} \quad (94)$$

and we have that

$$\begin{aligned} \tilde{U}(\tau|t) n_{\mathbf{k}\mathbf{Q}} \tilde{U}^{\dagger}(\tau|t) &= \exp \left\{ \frac{1}{i\hbar} (-\tau + i\hbar\beta^*(t)) \right. \\ &\quad \times \left(\epsilon_{\mathbf{k}+\frac{1}{2}\mathbf{Q}} - \epsilon_{\mathbf{k}-\frac{1}{2}\mathbf{Q}} \right) \\ &\quad \left. + i\hbar\beta^*(t)\mathbf{v}(t) \cdot \mathbf{Q} \right\} n_{\mathbf{k}\mathbf{Q}} \\ &= e^{\beta^*(t)\mathbf{v}(t) \cdot \mathbf{Q}} n_{\mathbf{k}\mathbf{Q}} (-\tau + i\hbar\beta^*(t)). \end{aligned} \quad (95)$$

Hence,

$$\begin{aligned} S_{nn^{\dagger}}(\mathbf{k}, \mathbf{Q}; -\tau|t)^{\text{rel}} &= e^{\hbar\beta(t)\mathbf{v}(t) \cdot \mathbf{Q}} \text{Tr} \\ &\quad \times \{ n_{\mathbf{k}\mathbf{Q}} (-\tau + i\hbar\beta^*(t)) n_{\mathbf{k}\mathbf{Q}}^{\dagger} \bar{\varrho}(t, 0) \}, \end{aligned} \quad (96)$$

and using (82), after some algebra, we find that

$$\begin{aligned} S_{nn^{\dagger}}(\mathbf{k}, \mathbf{Q}; -\tau|t)^{\text{rel}} &= 2\hbar [1 - e^{-\beta(\hbar\omega - \mathbf{v}(t) \cdot \mathbf{Q})}]^{-1} \\ &\quad \times \chi_{nn^{\dagger}}(\mathbf{k}, \mathbf{Q}; \omega|t)^{\text{rel}}. \end{aligned} \quad (97)$$

For $\mathbf{v} = 0$ and in the equilibrium case, we recover the well-known result (66).

4 Nonequilibrium-Thermodynamic Green Functions

As explained in the previous sections, to obtain response functions, we must compute nonequilibrium correlation functions. This difficult mathematical task can be simplified by the introduction of appropriate nonequilibrium-thermodynamic Green functions [65–67]. The approach is an extension of the equilibrium-thermodynamic Green function formalism of Tyablikov and Bogoliubov [68].

We define the retarded and advanced nonequilibrium-thermodynamic Green functions of two operators \hat{A} and \hat{B} in the Heisenberg representation by the expressions

$$\begin{aligned} \langle \langle \hat{A}(\mathbf{r}, \tau); \hat{B}(\mathbf{r}')|t \rangle \rangle_{\eta}^{(r)} &= \frac{1}{i\hbar} \Theta(\tau) \text{Tr} \left\{ [\hat{A}(\mathbf{r}, \tau), \hat{B}(\mathbf{r}')]_{\eta} \right. \\ &\quad \left. \times \mathcal{R}_{\varepsilon}(t) \right\}, \end{aligned} \quad (98a)$$

$$\langle\langle\hat{A}(\mathbf{r}, \tau); \hat{B}(\mathbf{r}')|t\rangle\rangle_{\eta}^{(a)} = -\frac{1}{i\hbar}\Theta(-\tau) \\ \times \text{Tr} \left\{ [\hat{A}(\mathbf{r}, \tau), \hat{B}(\mathbf{r}')]_{\eta} \mathcal{R}_{\varepsilon}(t) \right\}, \quad (98b)$$

where $\tau = t' - t$ and $\eta = +$ or $\eta = -$ stand for the anticommutator or commutator of the operators \hat{A} and \hat{B} .

These Green functions satisfy the equations of motion

$$i\hbar \frac{\partial}{\partial \tau} \langle\langle\hat{A}(\mathbf{r}, \tau); \hat{B}(\mathbf{r}')|t\rangle\rangle_{\eta}^{(r,a)} \\ = \delta(\tau) \text{Tr} \left\{ [\hat{A}(\mathbf{r}), \hat{B}(\mathbf{r}')]_{\eta} \mathcal{R}_{\varepsilon}(t) \right\} \\ + \langle\langle[\hat{A}(\mathbf{r}, \tau), H]; \hat{B}(\mathbf{r}')|t\rangle\rangle_{\eta}^{r,a}. \quad (99)$$

In (99) and henceforth, $[\hat{A}(\mathbf{r}), \hat{B}(\mathbf{r}')]_{\eta}$ without subscript denotes the commutator of the operators A and B . Introducing the Fourier transform

$$\langle\langle\hat{A}(\mathbf{r}); \hat{B}(\mathbf{r}')|\omega; t\rangle\rangle_{\eta} = \int_{-\infty}^{\infty} d\tau e^{i\omega\tau} \langle\langle\hat{A}(\mathbf{r}, \tau); \hat{B}(\mathbf{r}')|t\rangle\rangle_{\eta}, \quad (100)$$

Equation (99) becomes

$$\hbar\omega \langle\langle\hat{A}(\mathbf{r}); \hat{B}(\mathbf{r}')|\omega; t\rangle\rangle_{\eta} = \frac{1}{2\pi} \text{Tr} \left\{ [\hat{A}(\mathbf{r}), \hat{B}(\mathbf{r}')]_{\eta} \mathcal{R}_{\varepsilon}(t) \right\} \\ + \langle\langle[\hat{A}(\mathbf{r}), H]; \hat{B}(\mathbf{r}')|\omega; t\rangle\rangle_{\eta} \quad (101)$$

4.1 Green Functions and the Fluctuation-Dissipation Theorem

We next connect these Green functions with correlation functions. Consider the nonequilibrium correlation functions

$$F_{AB}(\mathbf{r}, \mathbf{r}'; \tau; t) = \text{Tr} \left\{ \hat{A}(\mathbf{r}, \tau) \hat{B}(\mathbf{r}') \mathcal{R}_{\varepsilon}(t) \right\}, \quad (102a)$$

$$F_{BA}(\mathbf{r}, \mathbf{r}'; \tau; t) = \text{Tr} \left\{ \hat{B}(\mathbf{r}') \hat{A}(\mathbf{r}, \tau) \mathcal{R}_{\varepsilon}(t) \right\}, \quad (102b)$$

and let $|n\rangle$ and E_n be the eigenstates and eigenvalues of the Hamiltonian \hat{H} .

Defining the nonequilibrium spectral density functions

$$J_{AB}(\mathbf{r}, \mathbf{r}'; \omega|t) = 2\pi \sum_{lmn} \langle n | \hat{A}(\mathbf{r}') | m \rangle \langle m | \hat{B}(\mathbf{r}') | l \rangle \\ \times \langle l | \mathcal{R}_{\varepsilon}(t) | n \rangle \delta(\hbar\omega - E_m + E_n) \quad (103a)$$

$$K_{BA}(\mathbf{r}, \mathbf{r}'; \omega|t) = 2\pi \sum_{lmn} \langle n | \hat{B}(\mathbf{r}') | m \rangle \langle m | \hat{A}(\mathbf{r}') | l \rangle \\ \times \langle l | \mathcal{R}_{\varepsilon}(t) | n \rangle \delta(\hbar\omega - E_l + E_m) \quad (103b)$$

we obtain the relations

$$F_{AB}(\mathbf{r}, \mathbf{r}'; \tau; t) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} J_{AB}(\mathbf{r}, \mathbf{r}'; \omega|t) e^{-i\omega\tau}, \quad (104a)$$

$$\tilde{F}_{BA}(\mathbf{r}, \mathbf{r}'; \tau; t) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} K_{BA}(\mathbf{r}, \mathbf{r}'; \omega|t) e^{-i\omega\tau}, \quad (104b)$$

and

$$\langle\langle\hat{A}(\mathbf{r}'); \hat{B}(\mathbf{r}')|\omega \pm is; t\rangle\rangle_{+} + \langle\langle\hat{A}(\mathbf{r}'); \hat{B}(\mathbf{r}')|\omega \pm is; t\rangle\rangle_{-} \\ = \frac{1}{\hbar} \int_{-\infty}^{\infty} \frac{d\omega'}{\pi} \frac{J_{AB}(\mathbf{r}, \mathbf{r}'; \omega'|t)}{(\omega - \omega' \pm is)}, \quad (105a)$$

$$\langle\langle\hat{A}(\mathbf{r}'); \hat{B}(\mathbf{r}')|\omega \pm is; t\rangle\rangle_{-} - \langle\langle\hat{A}(\mathbf{r}'); \hat{B}(\mathbf{r}')|\omega \pm is; t\rangle\rangle_{+} \\ = \frac{1}{\hbar} \int_{-\infty}^{\infty} \frac{d\omega'}{\pi} \frac{K_{BA}(\mathbf{r}, \mathbf{r}'; \omega'|t)}{(\omega - \omega' \pm is)}, \quad (105b)$$

with $s \rightarrow +0$. The $+$ ($-$) sign multiplying is on the right-hand side corresponds to the retarded (advanced) Green function, and we have used the relation

$$\int_{-\infty}^{\infty} d\tau \Theta(\pm\tau) e^{i(\omega - \omega')\tau} = \pm \frac{i}{\omega - \omega' \pm is}. \quad (106)$$

Equations 105a and 105b may be regarded as particular generalizations of the fluctuation-dissipation theorem for systems arbitrarily away from equilibrium. Near equilibrium, replacing ϱ_{ε} by the canonical Gibbs distribution, we recover the well-known result

$$\langle\langle\hat{A}(\mathbf{r}'); \hat{B}(\mathbf{r}')|\omega + is\rangle\rangle_{\eta}^{\text{equil.}} - \langle\langle\hat{A}(\mathbf{r}'); \hat{B}(\mathbf{r}')|\omega - is\rangle\rangle_{\eta}^{\text{equil.}} \\ = \frac{(1 - \eta e^{-\beta\hbar\omega})}{i\hbar} J_{AB}^{\text{equil.}}(\omega) \quad (107)$$

where $\beta = 1/(k_B T)$.

We recall that the nonequilibrium-thermodynamic Green functions in (98a) and (98b) depend on the macroscopic state of the system, and therefore their *equations of motion*, (99) or (101), must be solved along with the generalized nonlinear transport equations for the basic set of nonequilibrium-thermodynamic variables [16]. Finally, if we write $\mathcal{V} = \lambda e^{i\omega t} \hat{B}(\mathbf{r}')$ for the interaction energy, where λ is a coupling-strength constant, it follows that

$$\langle\hat{A}(\mathbf{r})|t\rangle - \langle\hat{A}(\mathbf{r})|t\rangle^0 \\ = -\frac{\lambda}{i\hbar} \int_{-\infty}^0 d\tau e^{-i\omega\tau} \text{Tr} \{ [\hat{A}(\mathbf{r}), \tilde{B}(\mathbf{r}', \tau)] \mathcal{R}_{\varepsilon}(t) \} + \text{c.c.} \\ = -\frac{\lambda}{i\hbar} \int_{-\infty}^{\infty} d\tau \Theta(\tau) [\tilde{F}_{\tilde{A}\tilde{B}}(\mathbf{r}, \mathbf{r}'; \tau; t) - F_{\tilde{B}\tilde{A}}(\mathbf{r}, \mathbf{r}'; \tau; t)] \\ \times e^{i\omega\tau} + \text{c.c.} \\ = \frac{\lambda}{\hbar} \int_{-\infty}^{\infty} \frac{d\omega'}{2\pi} \frac{K_{\tilde{A}\tilde{B}}(\mathbf{r}, \mathbf{r}'; \omega'|t) - J_{\tilde{B}\tilde{A}}(\mathbf{r}, \mathbf{r}'; \omega'|t)}{\omega - \omega' + is} + \text{c.c.} \\ = 2\lambda \text{Re} \{ \langle\langle\tilde{B}(\mathbf{r}'); \tilde{A}(\mathbf{r})|\omega + is; t\rangle\rangle_{-} \}, \quad (108)$$

where Re indicates the real part, and we have used the definition (98a) of the advanced Green function. Hence, the linear response function to an external harmonic perturbation is given by an advanced nonequilibrium-thermodynamic Green function dependent on the macroscopic state of the system characterized by the nonequilibrium-thermodynamic macrovariables $F_j(t)$ [or equivalently $Q_j(t)$], as described in the Appendix.

To close this section we note that, since the nonequilibrium-thermodynamic Green functions in (98a) and (98b) are defined as nonequilibrium averages of dynamical quantities, recalling the separation of ϱ_ε in a secular and a nonsecular (dissipative) parts, we can write that

$$\langle\langle \hat{A}(\mathbf{r}'); \hat{B}(\mathbf{r}') | \omega; t \rangle\rangle = \langle\langle \hat{A}(\mathbf{r}'); \hat{B}(\mathbf{r}') | \omega; t \rangle\rangle^{\text{sec.}} + \langle\langle \hat{A}(\mathbf{r}'); \hat{B}(\mathbf{r}') | \omega; t \rangle\rangle', \quad (109)$$

where

$$\begin{aligned} \langle\langle \hat{A}(\mathbf{r}'); \hat{B}(\mathbf{r}') | \omega; t \rangle\rangle^{\text{sec.}} \\ = \pm \frac{1}{i\hbar} \int_{-\infty}^{\infty} d\tau e^{i\omega\tau} \Theta(\pm\tau) \text{Tr}\{\hat{A}(\mathbf{r}', \tau), \hat{B}(\mathbf{r}')\}_\eta \bar{\mathcal{R}}(t, 0) \end{aligned} \quad (110a)$$

and

$$\begin{aligned} \langle\langle \hat{A}(\mathbf{r}'); \hat{B}(\mathbf{r}') | \omega; t \rangle\rangle' \\ = \pm \frac{1}{i\hbar} \int_{-\infty}^{\infty} d\tau e^{i\omega\tau} \Theta(\pm\tau) \{[\hat{A}(\mathbf{r}', \tau), \hat{B}(\mathbf{r}')]\}_\eta; \mathcal{R}'_\varepsilon(t) | t \}. \end{aligned} \quad (110b)$$

In general, the last term in (101) couples the Green-function equation with higher-order Green functions, which obey analogous equations, and therefore we obtain a hierarchy of coupled equations. To solve this hierarchy, one usually resorts to a truncation procedure, such as some kind of random phase approximation. For these nonequilibrium-thermodynamic Green functions, a second type of expansion and truncation, is also present, one that is associated with the irreversible processes encompassed in the contribution $\mathcal{R}'_\varepsilon(t)$ to the statistical operator in (110b). Care should be taken that the truncations in the two procedures be consistent, i.e., that terms of the same order are kept in the interaction strengths. We recall that the Markovian approximation in the NESEF-based kinetic theory [16, 69] requires that we keep terms containing the interaction-energy operators up to the second order only. The formalism of this section has been applied to time-resolved Raman spectroscopy, as described by Refs. [70, 71].

5 Scattering Theory for Far-from-Equilibrium Systems

In a scattering experiment, a beam of particles (e.g., photons, ions, electrons, or neutrons) with energy ε_0 and momentum $\hbar\mathbf{k}_0$ impinging upon a sample, with subsystems of which they interact (e.g., atoms, molecules, electrons, phonons). The interaction scatters the particles, a process involving transference of energy ΔE and momentum $\hbar\mathbf{q}$ to an excitation created or annihilated in the system; Fig. 2 schematically depicts the experiment.

Letting ε_1 and $\hbar\mathbf{k}_1$ be the energy and momentum of the scattered particle, the conservation of energy and momentum require that

$$\Delta E = \varepsilon_0 - \varepsilon_1, \quad (111)$$

$$\hbar\mathbf{q} = \hbar\mathbf{k}_0 - \hbar\mathbf{k}_1, \quad (112)$$

or

$$q^2 = k_0^2 + k_1^2 - 2k_0k_1 \cos \theta \quad (113)$$

after the scalar product of (112) with itself. Here, θ is the scattering angle, indicated in Fig. 2.

We now discuss the general theory. The scattering can be characterized by the *differential scattering cross section*, $d^2\sigma(\Delta E, \mathbf{q})$, defined as the ratio between the number $\delta\dot{N}$ of scattered particles collected by a detector within an element of solid angle $d\Omega(\theta, \varphi)$ in direction (θ, φ) per unit time and the flux Φ_0 of incident particles, that is, the number of particles entering the sample per unit time and unit area. The flux is given by the expression

$$\Phi_0 = n v_0, \quad (114)$$

where n is the density of incident particles and v_0 their mean velocity (e.g., the velocity of light in the case of photons or

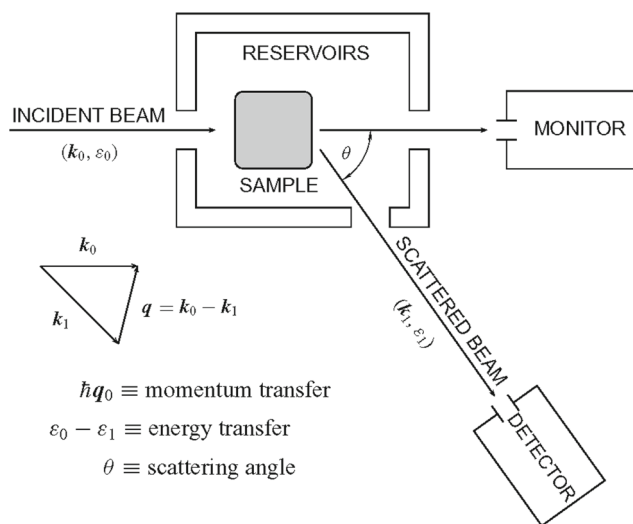


Fig. 2 Scattering experiment

the thermal velocity in the case of thermalized neutrons). On the other hand, we have that

$$\delta \dot{N} = nV \sum_{\mathbf{p}'_1 \in d\Omega} w_{\mathbf{p}_0 \rightarrow \mathbf{p}'_1}(\Delta E), \quad (115)$$

where w is the probability per unit time that an incident particle with momentum \mathbf{p}_0 transitions to a state of momentum \mathbf{p}'_1 in a direction contained in the solid angle $d\Omega(\theta, \varphi)$, the axis of which we denote \mathbf{p}_1 (or $\hbar\mathbf{k}_1$), ΔE is the energy transfer in the scattering event, nV is the number of particles, and V is the active sample volume, i.e., the volume of the region involved in the process, for example, the laser-beam focalization region, for photon scattering.

Since $d\Omega$, which is fixed by the size of the detector window, is small, we can take all the contributions in the sum over \mathbf{p}_1 to be the same, equal to $w_{\mathbf{p}_0 \rightarrow \mathbf{p}_1}(\Delta E)$, to a good approximation.

Hence,

$$d^2\sigma(\Delta E, \mathbf{q}) = \frac{\delta \dot{N}}{\Phi_0} = \frac{V}{v_0} w_{\mathbf{p}_0 \rightarrow \mathbf{p}_1}(\Delta E) b(\mathbf{p}_1, d\Omega), \quad (116)$$

where

$$b(\mathbf{p}, d\Omega) = \sum_{\mathbf{p}'_1 \in d\Omega} 1 \simeq \frac{V}{(2\pi\hbar)^3} p_1^2 dp_1 d\Omega \quad (117)$$

is the number of states of the particles in the scattered beam entering the detector, $\mathbf{p} = \hbar\mathbf{k}$, and the sum is over the plane-wave state of wavevector \mathbf{k} .

To calculate the differential cross section, we therefore have to evaluate the transition probability w per unit time. For that purpose, let us consider a system with Hamiltonian \hat{H}_σ ; call \hat{H}_P the Hamiltonian of the particles in the experiment, and \hat{V} the interaction potential between the system and the particles, that is

$$\hat{H} = \hat{H}_\sigma + \hat{H}_P + \hat{V}. \quad (118)$$

We introduce the variables $|\mu\rangle$ and $|\mathbf{p}\rangle$ to denote the eigenfunctions of the system and the particles in the probe, i.e.,

$$\hat{H}_\sigma |\mu\rangle = E_\mu |\mu\rangle, \quad (119)$$

$$\hat{H}_P |\mathbf{p}\rangle = \hbar\omega_{\mathbf{p}} |\mathbf{p}\rangle, \quad (120)$$

where the states $|\mathbf{p}\rangle$ are plane waves for the free particle with momentum \mathbf{p} in the incident and scattered beams. Moreover, let

$$|\psi(t_i)\rangle = |\Phi(t_i)\rangle |\mathbf{p}_0(t_i)\rangle \quad (121)$$

be the wavefunction at the initial time t_i , that is, the state in which the system was prepared.

As discussed in previous sections, it is convenient to work in the interaction representation. The wavefunction of the system and probe at time t is then

$$|\psi(t)\rangle = U_0(t, t_i) U'(t, t_i) |\psi(t_i)\rangle \quad (122)$$

[cf. (5)–(8)], with

$$i\hbar \frac{\partial}{\partial t} U'(t, t_i) = \tilde{V}(t) U'(t, t_i), \quad (123)$$

where $\tilde{V}(t)$ is the potential in the interaction representation, i.e., evolving with $\hat{H}_0 = \hat{H}_\sigma + \hat{H}_P$, [cf. (9) and (10)].

The evolution operator U_0 is given by the expression

$$U_0(t, t_i) = U_\sigma(t, t_i) U_P(t, t_i) = e^{\frac{1}{i\hbar}(t-t_i)\hat{H}_\sigma} e^{\frac{1}{i\hbar}(t-t_i)\hat{H}_P}, \quad (124)$$

and we recall that the iterated solution of (10) is given by (11).

If we define the function

$$|\tilde{\psi}(t)\rangle = U_0^\dagger(t, t_i) |\psi(t)\rangle = U'(t, t_i) |\psi(t_i)\rangle, \quad (125)$$

we can easily verify that it satisfies the equation

$$i\hbar \frac{\partial}{\partial t} |\tilde{\psi}(t)\rangle = \tilde{V}(t) |\tilde{\psi}(t)\rangle, \quad (126)$$

with $|\tilde{\psi}(t_i)\rangle = |\psi(t_i)\rangle$, which can be rewritten as

$$|\tilde{\psi}(t)\rangle = |\psi(t_i)\rangle + \frac{1}{i\hbar} \int_{t_i}^t dt' \tilde{V}(t') |\tilde{\psi}(t')\rangle, \quad (127)$$

and then has the iterated solution

$$|\tilde{\psi}(t)\rangle = \left[\sum_{n=0}^{\infty} \frac{1}{(i\hbar)^n} \int_{t_i}^t dt_1 \cdots \times \int_{t_i}^{t_{n-1}} dt_n \tilde{V}(t_1) \cdots \tilde{V}(t_n) \right] |\psi(t_i)\rangle, \quad (128)$$

and for algebraic convenience, we notice that we can write that

$$\tilde{V}(t) |\tilde{\psi}(t)\rangle = \tilde{\mathcal{E}}(t) |\psi(t_i)\rangle, \quad (129)$$

with $\tilde{\mathcal{E}}$, called the scattering operator, satisfying the integral equation

$$\tilde{\mathcal{E}}(t) = \tilde{V}(t) \left[1 + \frac{1}{i\hbar} \int_{t_i}^t dt' \tilde{\mathcal{E}}(t') \right]. \quad (130)$$

The right-hand side of (128) determines the effect of the perturbation \mathcal{V} to all orders over the initial nonperturbed wavefunction, equivalent to the first-order effect upon the interaction-representation function $|\tilde{\psi}(t)\rangle$.

Let us now fix the scattering channel, i.e., we consider, as required by (115), the scattering event with probe particles making transitions between states of momentum $|\mathbf{p}_0\rangle$ and $|\mathbf{p}_1\rangle$. According to the general theory of quantum

mechanics, the probability for this event at time t is given by the expression

$$P_{\mathbf{p}_0 \rightarrow \mathbf{p}_1}(t) = \sum_{\mu} |\langle \mathbf{p}_1, \mu | \psi(t) \rangle|^2, \quad (131)$$

where the summation over all states $|\mu\rangle$ of the system will be a posteriori restricted by the selection rule involving conservation of energy and momentum in the scattering events.

We can rewrite (131) in the form

$$\begin{aligned} P_{\mathbf{p}_0 \rightarrow \mathbf{p}_1}(t) &= \sum_{\mu} |\langle \mathbf{p}_1, \mu | U_0(t, t_i) U'(t, t_i) | \psi(t_i) \rangle|^2 \\ &= \sum_{\mu} |\langle \mathbf{p}_1, \mu | U_0(t, t_i) | \tilde{\psi}(t) \rangle|^2, \end{aligned} \quad (132)$$

where we have used (125). On the other hand,

$$\langle \mathbf{p}, \mu | U_0(t, t_i) = \langle \mathbf{p}, \mu | e^{-(t-t_i)(E_{\mu} + \hbar \omega_{\mathbf{p}})/i\hbar}, \quad (133)$$

so that the exponential on the right-hand side becomes a unitary factor in (132), and we have that

$$\begin{aligned} P_{\mathbf{p}_0 \rightarrow \mathbf{p}_1}(t) &= \sum_{\mu} |\langle \mathbf{p}_1, \mu | \psi(t) \rangle|^2 \\ &= \sum_{\mu} |\langle \mathbf{p}_1, \mu | [1 + \frac{1}{i\hbar} \int_{t_i}^t dt' \tilde{\mathcal{E}}(t')] | \psi(t_i) \rangle|^2 \\ &= \sum_{\mu} |\langle \mathbf{p}_1, \mu | \frac{1}{i\hbar} \int_{t_i}^t dt' \tilde{\mathcal{E}}(t') | \Phi(t_i), \mathbf{p}_0 \rangle|^2, \end{aligned} \quad (134)$$

where we have used (127) and (129), together with (121), and the fact that the plane wave states $|\mathbf{p}_0\rangle$ and $|\mathbf{p}_1\rangle$ are normalized and orthogonal to each other.

Introducing

$$\tilde{\mathcal{E}}_{\mathbf{q}}(t) = \langle \mathbf{p}_1 | \tilde{\mathcal{E}}(t) | \mathbf{p}_0 \rangle = \int d^3r \frac{e^{\frac{1}{i\hbar} \mathbf{p}_1 \cdot \mathbf{r}}}{\sqrt{V}} \tilde{\mathcal{E}}(t) \frac{e^{-\frac{1}{i\hbar} \mathbf{p}_0 \cdot \mathbf{r}}}{\sqrt{V}}, \quad (135)$$

with, we recall, $\hbar \mathbf{q} = \mathbf{p}_0 - \mathbf{p}_1$, and using that the squared modulus can be written as the product of the complex number times its complex conjugate, we can write the expression

$$\begin{aligned} P_{\mathbf{p}_0 \rightarrow \mathbf{p}_1}(t) &= \frac{1}{\hbar^2} \sum_{\mu} \langle \phi(t_i) | \int_{-\infty}^t dt'' \tilde{\mathcal{E}}_{\mathbf{q}}^{\dagger}(t'') | \mu \rangle \langle \mu | \\ &\quad \times \int_{-\infty}^t dt' \tilde{\mathcal{E}}_{\mathbf{q}}(t') | \Phi(t_i) \rangle \\ &= \frac{1}{\hbar^2} \int_{-\infty}^t dt' \int_{-\infty}^t dt'' \text{Tr} \left\{ \tilde{\mathcal{E}}_{\mathbf{q}}^{\dagger}(t'') \tilde{\mathcal{E}}_{\mathbf{q}}(t') \right. \\ &\quad \times \mathcal{P}_0(t_i) \left. \right\}, \end{aligned} \quad (136)$$

with $\mathcal{P}_0(t_i)$ being the projection operator (statistical operator for the pure state $|\Phi(t_i)\rangle$ in (121), and we have considered adiabatic application of the perturbation in $t_i \rightarrow -\infty$), implying in that the initial ultrafast transient is ignored.

So far, we have a purely quantum-mechanical calculation, and we have an expression depending on the initial preparation of the system as characterized by the statistical operator for the pure state given above. We next have to statistically average over the mixed state, which amounts to averaging over the corresponding Gibbs ensemble of all possible initial pure states compatible with the thermodynamic condition under which the system was prepared at time t_i , that is, we have that

$$\langle P_{\mathbf{p}_0 \rightarrow \mathbf{p}_1}(t) \rangle = \frac{1}{\hbar^2} \int_{-\infty}^t dt' \int_{-\infty}^t dt'' \times \text{Tr} \left\{ \tilde{\mathcal{E}}_{\mathbf{q}}^{\dagger}(t'') \tilde{\mathcal{E}}_{\mathbf{q}}(t') \varrho_{\varepsilon}(t_i) \times \varrho_{\mathbf{R}} \right\}, \quad (137)$$

where $\varrho_{\varepsilon}(t_i) \times \varrho_{\mathbf{R}} = \mathcal{R}_{\varepsilon}(t_i)$ is the corresponding statistical operator, where ϱ_{ε} is the operator for the system in interaction with the thermal bath and $\varrho_{\mathbf{R}}$, for the thermal bath. The latter which has been assumed to constantly remain in equilibrium at temperature T_0 .

The rate of transition probability w , in (116), is then

$$\begin{aligned} w_{\mathbf{p}_0 \rightarrow \mathbf{p}_1}(\Delta E|t) &= \frac{d}{dt} \langle P_{\mathbf{p}_0 \rightarrow \mathbf{p}_1}(t) \rangle \\ &= \frac{1}{\hbar^2} \int_{-\infty}^t dt' \text{Tr} \{ \tilde{\mathcal{E}}_{\mathbf{q}}^{\dagger}(t) \tilde{\mathcal{E}}_{\mathbf{q}}(t') \varrho_{\varepsilon}(t_i) \varrho_{\mathbf{R}} \} \\ &\quad + \frac{1}{\hbar^2} \int_{-\infty}^t dt' \text{Tr} \{ \tilde{\mathcal{E}}_{\mathbf{q}}^{\dagger}(t') \tilde{\mathcal{E}}_{\mathbf{q}}(t) \varrho_{\varepsilon}(t_i) \varrho_{\mathbf{R}} \}. \end{aligned} \quad (138)$$

Using that

$$\begin{aligned} \text{Tr} \{ U_0^{\dagger}(t, t_i) \tilde{\mathcal{E}}_{\mathbf{q}}^{\dagger} U(t, t_i) U_0^{\dagger}(t', t_i) \tilde{\mathcal{E}}_{\mathbf{q}} U_0(t', t_i) \mathcal{R}_{\varepsilon}(t_i) \} \\ = \text{Tr} \{ \tilde{\mathcal{E}}_{\mathbf{q}}^{\dagger} \tilde{\mathcal{E}}_{\mathbf{q}}(t' - t) \varrho_{\varepsilon}(t) \times \varrho_{\mathbf{R}} \}, \end{aligned} \quad (139)$$

and that

$$\begin{aligned} \tilde{\mathcal{E}}_{\mathbf{q}}(t' - t) &= \langle \mathbf{p}_1 | U_P^{\dagger}(t' - t) U_{\sigma}^{\dagger}(t' - t) \tilde{\mathcal{E}}_{\mathbf{q}} U_{\sigma}(t' - t) \\ &\quad \times U_P(t' - t) | \mathbf{p}_0 \rangle \\ &= e^{-\frac{1}{i\hbar}(t'-t)\hbar(\omega_{\mathbf{p}_0} - \omega_{\mathbf{p}_1})} \tilde{\mathcal{E}}_{\mathbf{q}}(t' - t)_{\sigma}, \end{aligned} \quad (140)$$

where $\tilde{\mathcal{E}}_{\mathbf{q}}(t' - t)_{\sigma} = U_{\sigma}^{\dagger}(t' - t, t_i) \tilde{\mathcal{E}}_{\mathbf{q}} U_{\sigma}(t' - t, t_i)$, we can write the expression

$$\begin{aligned} w_{\mathbf{p}_0 \rightarrow \mathbf{p}_1}(\Delta E|t) &\equiv w(\mathbf{q}, \omega|t) \\ &= \frac{1}{\hbar^2} \int_{-\infty}^t dt' e^{i\omega(t'-t)} \\ &\quad \times \text{Tr} \{ \tilde{\mathcal{E}}_{\mathbf{q}}^{\dagger} \tilde{\mathcal{E}}_{\mathbf{q}}(t' - t)_{\sigma} \varrho_{\varepsilon}(t) \varrho_{\mathbf{R}} \} + \text{c.c.}, \end{aligned} \quad (141)$$

where $\omega = \omega_{\mathbf{p}_0} - \omega_{\mathbf{p}_1}$, and the statistical operator is given at measurement time t .

In equilibrium case, i.e., if we substitute the canonical distribution ϱ_c for $\varrho_\varepsilon(t)$, and take into account that ϱ_c and \hat{H}_σ commute, we find that

$$w(\mathbf{q}, \omega)_{\text{eq}} = \frac{1}{\hbar^2} \int_{-\infty}^{\infty} d\tau' e^{-i\omega\tau'} \text{Tr}\{\tilde{\mathcal{E}}_{\mathbf{q}}^\dagger(\tau')_\sigma \tilde{\mathcal{E}}_{\mathbf{q}}\varrho_c\}, \quad (142)$$

which is the known temperature-dependent rate of transition probability (see for example Ref. [72]).

In conclusion, the differential cross section is then given by the expression

$$\begin{aligned} \frac{d^2\sigma(\mathbf{q}, \omega|t)}{d\omega d\Omega} &= \frac{V^2}{(2\pi\hbar)^3} \frac{g(\omega)}{v_0} \frac{1}{\hbar^2} \left[\int_{-\infty}^t dt' e^{i\omega(t'-t)} \right. \\ &\quad \times \text{Tr}\{\tilde{\mathcal{E}}_{\mathbf{q}}^\dagger \tilde{\mathcal{E}}_{\mathbf{q}}(t'-t)_\sigma \mathcal{R}_\varepsilon(t)\} \\ &\quad + \int_{-\infty}^t dt' e^{-i\omega(t'-t)} \\ &\quad \times \text{Tr}\{\tilde{\mathcal{E}}_{\mathbf{q}}^\dagger(t'-t)_\sigma \tilde{\mathcal{E}}_{\mathbf{q}}\varrho_\varepsilon(t) \times \varrho_{\mathbf{R}}\} \Big], \quad (143) \end{aligned}$$

where we have defined

$$p^2 dp = g(\omega) d\omega, \quad (144)$$

and expression that introduces the density of states $g(\omega)$, which can be easily determined since the dispersion relation $\omega_{\mathbf{p}}$ is known.

Since the two terms within the square brackets are complex conjugate to each other, the right-hand side of (143) is real, as expected.

Unlike the equilibrium case, under nonequilibrium sample preparation, the equation for the scattering cross section is not closed in itself; instead, it is coupled to the set of kinetic equations describing the evolution of the out-of-equilibrium system, i.e., the equations determining the statistical operator $\mathcal{R}_\varepsilon(t)$. The same issue arises in the response function formalism of the previous sections.

As pointed out in Section 4, we can write $\mathcal{R}_\varepsilon(t) = \varrho_\varepsilon(t) \times \varrho_{\mathbf{R}}$ and take advantage of the separation $\varrho_\varepsilon(t) = \bar{\varrho}(t) + \varrho'_\varepsilon(t)$ to obtain that

$$d^2\sigma(\mathbf{q}, \omega|t) = d^2\bar{\sigma}(\mathbf{q}, \omega|t) + d^2\bar{\sigma}'(\mathbf{q}, \omega|t), \quad (145)$$

that is, the sum of a contribution $d^2\bar{\sigma}$, in which the trace is taken with $\bar{\varrho}$, and another $d^2\bar{\sigma}'$, with the trace taken with ϱ'_ε .

Let now the scattering be time and space resolved. The detector in Fig. 2 collects the scattered particles arriving from a volume element $\Delta V(\mathbf{r})$ around a position \mathbf{r} in the sample. For simplicity, we consider first-order scattering, which in practice amounts to substituting the leading contribution $\hat{\mathcal{V}}$ on the right-hand side of (130) for the scattering operator Ξ on the right-hand side of (142). For $\hat{\mathcal{V}}$, we write the expression

$$\hat{\mathcal{V}} = \sum_{\mu=1}^{N'} \sum_{j=1}^N v(\mathbf{R}_\mu - \mathbf{r}_j), \quad (146)$$

where \mathbf{r}_j is the position of the j -th particle in the system and \mathbf{R}_μ , the position of the μ -th particle in the incident beam. Therefore, we have that

$$\hat{\mathcal{V}}_{\mathbf{q}} = \langle \mathbf{p}_0 | \hat{\mathcal{V}} | \mathbf{p}_1 \rangle = n_b v(\mathbf{q}) \sum_{j=1}^N e^{i\mathbf{q} \cdot \mathbf{r}_j}, \quad (147)$$

where we have introduced the Fourier amplitude

$$v(\mathbf{q}) = \int d^3b v(b) e^{i\mathbf{q} \cdot \mathbf{b}}, \quad (148)$$

with $\mathbf{b} = \mathbf{r} - \mathbf{r}_j$, and we recall that $\hbar\mathbf{q} = \mathbf{p}_0 - \mathbf{p}_1$, and n_b is the particle density in the beam.

Retaining in (143) only the contribution in first order in \mathcal{V} only, we have that

$$\frac{d^2\sigma(\mathbf{q}, \omega|t)}{d\omega d\Omega} = \frac{V^2}{(2\pi\hbar)^3} \frac{g(\omega)}{\hbar^2 v_0} n_b^2 |v(\mathbf{q})|^2 S_{nn}(\mathbf{q}, \omega|t), \quad (149)$$

where

$$\begin{aligned} S_{nn}(\mathbf{q}, \omega|t) &= \sum_{j,l} \int_{-\infty}^t dt' e^{i\omega(t'-t)} \text{Tr}\{e^{-i\mathbf{q} \cdot [\mathbf{r}_j(t'-t) - \mathbf{r}_l]} \\ &\quad \times \varrho_\varepsilon(t) \times \varrho_{\mathbf{R}}\} + \text{c.c.}, \quad (150) \end{aligned}$$

We now introduce the density operator

$$\hat{n}(\mathbf{r}, \tau) = \sum_j \delta(\mathbf{r} - \mathbf{r}_j(\tau)) \quad (151)$$

and then we can rewrite the correlation function of (150) as follows:

$$\begin{aligned} S_{nn}(\mathbf{q}, \omega|t) &= \int d^3r \int d^3r' \int_{-\infty}^t dt' e^{i\omega(t'-t)} \\ &\quad \times e^{-i\mathbf{q} \cdot (\mathbf{r} - \mathbf{r}')} \text{Tr}\{\hat{n}^\dagger(\mathbf{r}, t' - t) \hat{n}(\mathbf{r}') \varrho_\varepsilon(t) \\ &\quad \times \varrho_{\mathbf{R}}\} + \text{c.c.}, \quad (152) \end{aligned}$$

where the space integrations run over the active volume of the sample (region of concentration of the particle beam), or in the case of a space-resolved experiment over $\Delta V(\mathbf{r})$ and then we do have the time- and space-resolved spectrum

$$\begin{aligned} \frac{d^2\sigma(\mathbf{r}; \mathbf{q}, \omega|t)}{d\omega d\Omega} &= \Delta V(\mathbf{r}) \int d^3r' \int_{-\infty}^t dt' e^{i\omega(t'-t)} \\ &\quad \times e^{-i\mathbf{q} \cdot (\mathbf{r} - \mathbf{r}')} \text{Tr}\{\hat{n}^\dagger(\mathbf{r}, t' - t) \hat{n}(\mathbf{r}') \varrho_\varepsilon(t) \\ &\quad \times \varrho_{\mathbf{R}}\} + \text{c.c.}, \quad (153) \end{aligned}$$

In a photoluminescence experiment, one that involves the recombination of photoexcited electrons and holes, the potential has the form

$$\mathcal{V} = \sum_j \mathbf{A}(\mathbf{r}_j, t) \cdot \mathbf{p}_j, \quad (154)$$

and then, in the dipolar approximation, which neglects the photon momentum, the luminescence spectrum is given by the equality

$$P_L(\mathbf{r}; \omega|t) \sim \sum_{\mathbf{k}} \bar{f}_{\mathbf{k}}^e(\mathbf{r}, t) \bar{f}_{\mathbf{k}}^h(\mathbf{r}, t) \delta(\hbar k^2/2m_x + E_G - \hbar\omega), \quad (155)$$

In arbitrary units, where we have introduced a local approximation and used the effective mass approximation for electrons (e) and holes (h), $m_x^{-1} = m_e^{-1} + m_h^{-1}$ is the excitonic mass, E_G is the energy gap, and $\bar{f}_{\mathbf{k}}^{e(h)}(\mathbf{r}, t)$ is the electron (hole) population in the state \mathbf{k} , at the position \mathbf{r} , and at the time t , which is given by the expression

$$\bar{f}_{\mathbf{k}}^{e(h)}(\mathbf{r}, t) = \frac{1}{1 + \exp\{\beta^*(\mathbf{r}, t)[\hbar^2 k^2/2m_{e(h)}^* - \mu_{e(h)}^*(\mathbf{r}, t)]\}}, \quad (156)$$

where $\beta^*(\mathbf{r}, t)$ is the reciprocal of the nonequilibrium-temperature field, and $\mu_{e(h)}^*(\mathbf{r}, t)$ the quasi-chemical potential.

6 Illustrative Examples

6.1 Experiments in Ultrafast Laser Spectroscopy

Pump-probe experiments in ultrafast laser spectroscopy, an area devoted to the study of the nonequilibrium photoexcited plasma in semiconductors, have been extensively used in recent decades and accompanied by a number of theoretical analysis [73–89]. In a typical experiment the system is driven far from equilibrium. Consequently, its theoretical description falls into the realm of the thermodynamics of irreversible processes in far-from-equilibrium systems, and the accompanying kinetic and statistical theories. A particularly appropriate approach is the NESEF, described in the Appendix, on the basis of which the previous section presented a detailed derivation of a response function theory to study ultrafast optical properties in photoexcited plasmas in semiconductors. In particular, one needs the frequency- and wave number-dependent dielectric function in arbitrary nonequilibrium conditions, which contains all the information on the optical properties of the system, such as the absorption coefficient, reflectivity coefficient, or the Raman scattering cross section. This is described below. Moreover, we apply the results to a particular type of experiment, namely the time-resolved reflectivity changes in GaAs and other materials [74, 75, 75, 76] where relative changes $\Delta R/R$ in the reflectivity of the order of 10^{-7} are detected, distinct oscillations in real time being observed. Figure 3

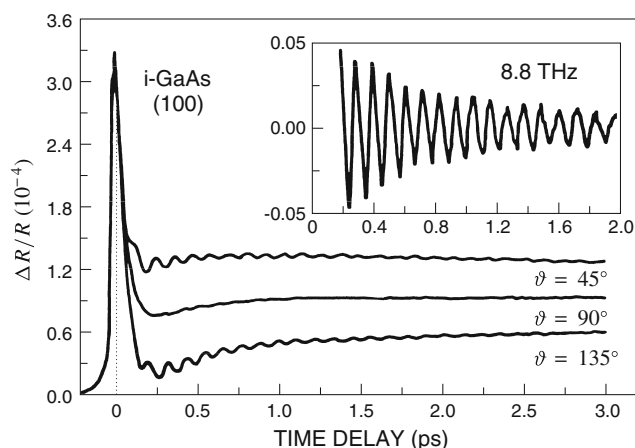


Fig. 3 Time-resolved reflectivity changes in GaAs. Reproduced from Ref. [73]

reproduces time-resolved reflectivity spectra; the upper-right inset shows the part corresponding to the observed oscillation, as reported by Cho et al. [73].

The phenomenon has been attributed to the generation of coherent lattice vibrations, and several theoretical approaches have been reported [76–78]. Reference [77] has presented a clear phenomenological description capturing the essential physics of the problem, and Ref. [79], an analysis based on the NESEF, which discusses the different physical aspects of the problem. The oscillatory effect is shown to stem from the displacive excitation of the polar lattice vibrations, due to the coupling between the carrier charge density and polar modes. Its decay is mainly governed by the cooling of the carriers. The experiment and all the pertaining NESEF-based calculations are described next.

Let us consider a direct-gap polar semiconductor in a pump-probe experiment. We recall that the exciting intense laser pulse produces the so-called highly excited plasma in semiconductors, namely electron-hole pairs in the metallic side of the Mott transition. In other words, the photoexcited quasi-particles are itinerant carriers with minimum concentration of the order of 10^{16} cm^{-3} . They form a two-component Fermi fluid, moving in the lattice background. This is a system highly out of equilibrium, in which the photoexcited carriers rapidly redistribute their excess energy, relative to the equilibrium state, chiefly via the strong long-range Coulomb interaction (pico- to subpico-second scale), followed by the transfer of energy to the phonon field (predominantly to the optical phonons, preferentially to the LO phonons via the Fröhlich interaction), and finally via acoustic phonons to the external thermal reservoir. Along the process, the carrier density diminishes, due to recombination (nanosecond time scale) and through ambipolar diffusion out of the active sample volume (tenfold picosecond time scale).

A probe interacting weakly with the HEPS generates an optical response, namely the reflectivity of the incoming laser photons with frequency ω and wave vector \mathbf{Q} . From the theoretical point of view, as already noticed, the measurement is described by correlation functions in response function theory. The usual application in normal probe experiments on a system initially in equilibrium had a long history of success. A practical, elegant treatment employed the double-time (equilibrium) thermodynamic Green functions method [67, 68]. To describe a pump-probe experiment, we have to apply an analogous theory to a system whose macroscopic state is out of equilibrium and evolves in time as a result of dissipative processes that develop while the sample is probed. More specifically, we apply the theory discussed in the previous section and recall that the response function theory for nonequilibrium systems needs be coupled to the kinetic theory that describes the evolution of the nonequilibrium state of the system. Here, we follow this approach to study the reflectivity experiments of Ref. [73].

The reflectivity $R(\omega, \mathbf{Q}|t)$, which is time-dependent because it changes as the macrostate of the out-of-equilibrium system evolves, is related to the index of refraction $\eta(\omega, \mathbf{Q}|t) + i\kappa(\omega, \mathbf{Q}|t)$ through the well-known expression

$$R(\omega, \mathbf{Q}|t) = \frac{[\eta(\omega, \mathbf{Q}|t) - 1]^2 + [\kappa(\omega, \mathbf{Q}|t)]^2}{[\eta(\omega, \mathbf{Q}|t) + 1]^2 + [\kappa(\omega, \mathbf{Q}|t)]^2}, \quad (157)$$

and the refraction index is related to the time-dependent frequency- and wave vector-dependent dielectric function by the equation

$$\epsilon(\omega, \mathbf{Q}|t) = \epsilon'(\omega, \mathbf{Q}|t) + i\epsilon''(\omega, \mathbf{Q}|t) \\ = [\eta(\omega, \mathbf{Q}|t) + i\kappa(\omega, \mathbf{Q}|t)]^2, \quad (158)$$

where t denotes the measurement time; and η and ϵ' , and κ and ϵ'' are the real and imaginary parts of the refraction index and of the dielectric function, respectively.

The dielectric function depends on the frequency and the wave vector of the radiation, and its time dependence reflects the evolution of the nonequilibrium plasma during the experiment. It is our task, therefore to calculate this dielectric function in the nonequilibrium state of the system. From Maxwell's equations in material media, that is, Maxwell's equations averaged over the nonequilibrium statistical ensemble, we have that

$$\epsilon^{-1}(\omega, \mathbf{Q}|t) - 1 = \frac{n(\omega, \mathbf{Q}|t)}{r(\omega, \mathbf{Q})}, \quad (159)$$

where $r(\omega, \mathbf{Q})$ is the amplitude of a probe charge density with frequency ω and wave vector \mathbf{Q} , and $n(\omega, \mathbf{Q}|t)$ is the induced polarization-charge density of the carriers and lattice in the media. As we have shown the latter can be

calculated by response function theory for systems that are far from equilibrium, a problem quite similar to the calculation of the time-resolved Raman scattering cross section [70], and related to the nonequilibrium-thermodynamic Green functions, as we now proceed to describe.

The formalism in Section 4, 98a and 98b, yields the following expression for $\epsilon(\omega, \mathbf{Q}|t)$:

$$\epsilon^{-1}(\omega, \mathbf{Q}) - 1 = V(\mathbf{Q}) [G_{cc}(\omega, \mathbf{Q}) + G_{ci}(\omega, \mathbf{Q}) \\ + G_{ic}(\omega, \mathbf{Q}) + G_{ii}(\omega, \mathbf{Q})], \quad (160)$$

where the Green functions are given by the equations

$$G_{cc}(\omega, \mathbf{Q}) = \langle \hat{n}_c(\mathbf{Q}); \hat{n}_c^\dagger(\mathbf{Q}) | \omega; t \rangle, \quad (161)$$

$$G_{ci}(\omega, \mathbf{Q}) = \langle \hat{n}_c(\mathbf{Q}); \hat{n}_i^\dagger(\mathbf{Q}) | \omega; t \rangle, \quad (162)$$

$$G_{ic}(\omega, \mathbf{Q}) = \langle \hat{n}_i(\mathbf{Q}); \hat{n}_c^\dagger(\mathbf{Q}) | \omega; t \rangle, \quad (163)$$

$$G_{ii}(\omega, \mathbf{Q}) = \langle \hat{n}_i(\mathbf{Q}); \hat{n}_i^\dagger(\mathbf{Q}) | \omega; t \rangle, \quad (164)$$

where $V(\mathbf{Q}) = 4\pi ne^2/V\epsilon_0 Q^2$ is the matrix element of the Coulomb potential in plane-wave states and $\hat{n}_c(\mathbf{Q})$, and $\hat{n}_i(\mathbf{Q})$, refer to the \mathbf{Q} -wavevector Fourier transform of the operators for the carrier charge densities and the polarization charge of longitudinal optical phonons, respectively. The time-dependent distribution functions for the carrier and phonon states make the results dependent on the evolving nonequilibrium macroscopic state. They have to be derived, therefore, within the kinetic theory in the NESEF. The first fundamental step is to choose the set of variables deemed appropriate for the description of the macroscopic state of the system. A first set of variables has to comprise the carrier densities and energies and the phonon population functions, along with the set of associated nonequilibrium-thermodynamics variables that, as we have seen, can be interpreted as a reciprocal carrier quasi-temperatures and quasi-chemical potentials, and reciprocal phonon quasi-temperatures, one for each mode [64, 80–83]. In the case under study, we need to add, on the basis of the information provided by the experiment, the amplitudes of the LO-lattice vibrations and the carrier charge density: the former because it is clearly present in the experimental data (the reflectivity oscillations) and the latter because of the LO-phonon-plasma coupling, clearly present in Raman scattering experiments [84, 85]). Consequently, the chosen basic set of dynamical quantities is

$$\{\hat{H}_c, \hat{N}_e, \hat{N}_h, \hat{n}_{\mathbf{k}\mathbf{p}}^e, \hat{n}_{\mathbf{k}\mathbf{p}}^h, \hat{v}_{\mathbf{q}}, a_{\mathbf{q}}, a_{\mathbf{q}}^\dagger, H_B\}, \quad (165)$$

where

$$\hat{H}_c = \sum_{\mathbf{k}} \left[\varepsilon_{\mathbf{k}}^e c_{\mathbf{k}}^\dagger c_{\mathbf{k}} + \varepsilon_{\mathbf{k}}^h h_{-\mathbf{k}}^\dagger h_{-\mathbf{k}} \right], \quad (166)$$

$$\hat{v}_{\mathbf{q}} = a_{\mathbf{q}}^\dagger a_{\mathbf{q}}, \quad (167)$$

$$\hat{N}_e = \sum_{\mathbf{k}} c_{\mathbf{k}}^\dagger c_{\mathbf{k}}, \quad \hat{N}_h = \sum_{\mathbf{k}} h_{-\mathbf{k}}^\dagger h_{-\mathbf{k}}, \quad (168)$$

$$\hat{n}_{\mathbf{k}\mathbf{p}}^e = c_{\mathbf{k}+\mathbf{p}}^\dagger c_{\mathbf{k}}, \quad \hat{n}_{\mathbf{k}\mathbf{p}}^h = h_{-\mathbf{k}-\mathbf{p}}^\dagger h_{-\mathbf{k}}, \quad (169)$$

where c (c^\dagger), h (h^\dagger), and a (a^\dagger) annihilate (create) electron, hole, and LO-phonon states, respectively, and \mathbf{k} , \mathbf{p} , \mathbf{q} run over the Brillouin zone. We use the effective mass approximation and deal with the Coulomb interaction in the random phase approximation, so that $\varepsilon_{\mathbf{k}}^e = E_G + \hbar^2 |\mathbf{k}|^2 / 2m_e^*$ and $\varepsilon_{\mathbf{k}}^h = \hbar^2 |\mathbf{k}|^2 / 2m_h^*$. Finally, \hat{H}_B is the Hamiltonian of the lattice vibrations other than the LO mode.

For the NESEF-nonequilibrium-thermodynamic variables associated with the quantities in (165), we have that

$$\{\beta_c^*(t), -\beta_c^*(t)\mu_e^*(t), -\beta_c^*(t)\mu_h^*(t), F_{\mathbf{k}\mathbf{p}}^e(t), F_{\mathbf{k}\mathbf{p}}^h(t), \hbar\omega_{\mathbf{q}}\beta_{\mathbf{q}}^*(t), \varphi_{\mathbf{q}}(t), \varphi_{\mathbf{q}}^*(t), \beta_0\}, \quad (170)$$

respectively, where μ_e^* and μ_h^* are the quasi-chemical potentials for electrons and for holes; we write $\beta_c^*(t) = 1/k_B T_c^*(t)$, which defines the carrier quasi-temperature T_c^* ; $\beta_{\mathbf{q}}^*(t) = 1/k_B T_{\mathbf{q}}^*(t)$, which defines the LO-phonon quasi-temperature for each mode ($\omega_{\mathbf{q}}$ is the dispersion relation); and $\beta_0 = 1/k_B T_0$ where T_0 is the thermal reservoir temperature. We indicate the corresponding macrovariables, that is, those defining the nonequilibrium-thermodynamic Gibbs space as

$$\{E_c(t), n(t), n(t), n_{\mathbf{k}\mathbf{p}}^e(t), n_{\mathbf{k}\mathbf{p}}^h(t), v_{\mathbf{q}}(t), \langle a_{\mathbf{q}} | t \rangle, \langle a_{\mathbf{q}}^\dagger | t \rangle = \langle a_{\mathbf{q}} | t \rangle^*, E_B\}, \quad (171)$$

which are the statistical average of the quantities of (165), that is

$$E_c(t) = \text{Tr} \left\{ \hat{H}_c \varrho_\epsilon(t) \times \varrho_R \right\}, \quad (172)$$

$$n(t) = \text{Tr} \left\{ \hat{N}_{e(h)} \varrho_\epsilon(t) \times \varrho_R \right\}, \quad (173)$$

and so on, where ϱ_R is the stationary statistical distribution of the reservoir and $n(t)$ is the carrier density, which is equal for electrons and for holes since they are produced in pairs, in the intrinsic semiconductor. The volume of the active region of the sample (where the laser beam is focused) is taken equal to be unitary, for simplicity.

Next, we have to derive the equation of evolution for the basic variables characterizing the nonequilibrium macroscopic state of the system and, from them, the evolution of

the nonequilibrium-thermodynamic variables. This is done according to the generalized NESEF-based nonlinear quantum transport theory [12, 16], in the second-order approximation in relaxation theory. The second-order approximation retains only two-body collisions. Since memory and vertex corrections are neglected, this is the Markovian limit of the theory. It is sometimes referred to as the quasi-linear approximation in relaxation theory [65, 66], a name we avoid because the word “linear”, which refers to the lowest order in dissipation, is misleading, given that the equations are highly nonlinear.

The NESEF-auxiliary (“instantaneously frozen”) statistical operator is in the present case given, in terms of the variables of (165), and the nonequilibrium-thermodynamic variables in (170), by the expression

$$\bar{\varrho}(t, 0) = \exp \left\{ -\phi(t) - \beta_c^*(t) [\hat{H}_c - \mu_e^*(t) \hat{N}_e - \mu_h^*(t) \hat{N}_h] - \sum_{\mathbf{k}\mathbf{p}} [F_{\mathbf{k}\mathbf{p}}^e(t) \hat{n}_{\mathbf{k}\mathbf{p}}^e(t) + F_{\mathbf{k}\mathbf{p}}^h(t) \hat{n}_{\mathbf{k}\mathbf{p}}^h(t)] - \sum_{\mathbf{q}} [\beta_{\mathbf{q}}^*(t) \hbar\omega_{\mathbf{q}} \hat{v}_{\mathbf{q}} + \varphi_{\mathbf{q}}(t) a_{\mathbf{q}} + \varphi_{\mathbf{q}}^*(t) a_{\mathbf{q}}^\dagger] - \beta_0 H_B \right\}, \quad (174)$$

where $\phi(t)$ ensures the normalization of $\bar{\varrho}(t, 0)$.

Using this statistical operator, the Green functions that define the dielectric function [cf. (160)] can be calculated. This is an arduous task, which calls for the evaluation of the occupation functions

$$f_{\mathbf{k}}(t) = \text{Tr} \{ c_{\mathbf{k}}^\dagger c_{\mathbf{k}} \bar{\varrho}_\epsilon(t) \}, \quad (175)$$

which depend on the variables of (170).

The time evolution of the resulting (nonequilibrium) carrier quasi-temperature T_c^* is shown in Fig. 4.

Figure 5, in which the only adjustable parameter is the amplitude—to fix which we fit the first maximum—shows

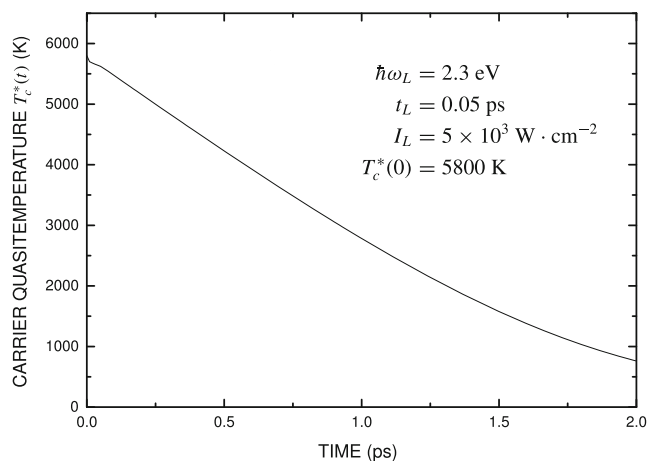


Fig. 4 Evolution of the carrier quasi-temperature, calculated under the conditions of the experiment in Fig. 3

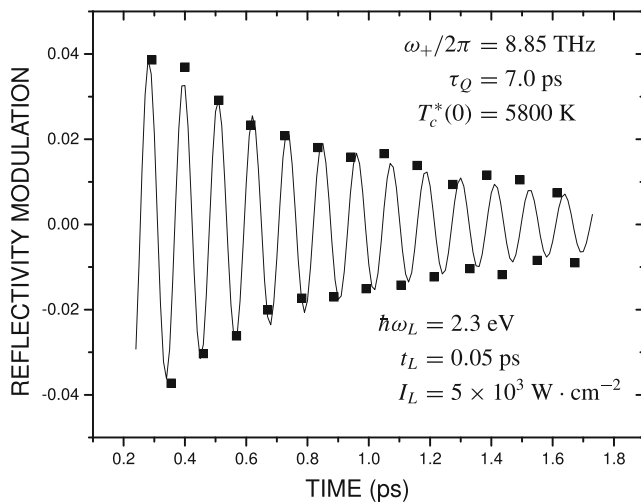


Fig. 5 Theoretically evaluated modulation of the time-resolved reflectivity under the conditions of Ref. [73], compared with the experimental data. For simplicity we have drawn only the positions of the maxima and minima of the *inset* Fig. 3

the calculated modulation effect, which is compared with the experimental result. For clarity, we only show the the higher and lower amplitudes from the experimental data, indicated by the full squares.

This explains the observed modulation of the reflectivity spectra, which occurs with the frequency of the near zone center LO-phonon, (or more precisely the one of the upper L_+ hybrid mode [85]) with wave vector \mathbf{Q} , the wave vector of the photon in the laser-radiation field. The amplitude of the modulation is determined by the amplitude of the laser-radiation-driven carrier charge density, which is coupled to the optical vibration, and by an open parameter in the theory, to be fixed by the experimental observation. This example provides a good illustration of the full use of the NESEF, with application to a quite interesting experiment, in which the observed modulation signal is 7 orders of magnitude smaller than the main signal upon which is superimposed.

6.2 Charge Transport in Doped Semiconductors

NESEF is particularly appropriate to describe the transient and steady state of semiconductors under intermediate to strong electric fields (say tens to hundreds of kV/cm), which drive the system far away from equilibrium. The problem defined by such systems has raised much technological interest because such conditions are found in the integrated circuits of electronic and optoelectronic devices.

Let us consider an n -doped direct-gap polar semiconductor, under conditions such that the extra electrons act as mobile carriers in the conduction band. We use the effective mass approximation, and hence a parabolic band; electric fields sufficiently strong to produce intervalley scattering lie

beyond the scope of our treatment. The Hamiltonian of the system then reads

$$\hat{H} = \hat{H}_0 + \hat{H}_1 + \hat{H}_{AN} + \hat{H}_{CF} + \hat{W}, \quad (176)$$

where

$$\hat{H}_0 = \sum_{\mathbf{k}} (\hbar^2 k^2 / 2m_e^*) c_{\mathbf{k}}^\dagger c_{\mathbf{k}} + \sum_{\mathbf{q}, \gamma} \hbar \omega_{\mathbf{q}, \gamma} (b_{\mathbf{q}, \gamma}^\dagger b_{\mathbf{q}, \gamma} + 1/2), \quad (177)$$

is the Hamiltonian of free electrons and phonons in branches $\gamma = \text{LO, AC}$, and

$$\hat{H}_1 = \sum_{\mathbf{k}, \mathbf{q}, \gamma, \sigma} \left[M_{\gamma}^{\sigma}(\mathbf{q}) b_{\mathbf{q}, \gamma} c_{\mathbf{k}+\mathbf{q}, \gamma}^\dagger c_{\mathbf{k}} + M_{\gamma}^{\sigma*}(\mathbf{q}) b_{\mathbf{q}, \gamma}^\dagger c_{\mathbf{k}}^\dagger c_{\mathbf{k}+\mathbf{q}, \gamma} \right], \quad (178)$$

is the Hamiltonian describing their interaction.

In (176)–(178), c and b annihilate an electron in state $|\mathbf{k}\rangle$ and a phonon in mode $|\mathbf{q}\rangle$, branch $\gamma = \text{LO}$ (longitudinal optical), AC (acoustical), respectively. TO (transverse optical) phonons, which interact weakly with the electrons, are ignored. $M_{\gamma}^{\sigma}(\mathbf{q})$ is the matrix element of the interaction between carriers and γ phonons, the superscript σ indicating the nature of the interaction (polar, deformation potential, piezoelectric). \hat{H}_{AN} stands for the anharmonic interaction in the phonon system, and

$$\hat{H}_{CF} = - \sum_i e \mathbf{E} \cdot \mathbf{r}_i, \quad (179)$$

is the interaction between the electron (with charge $-e$, at position \mathbf{r}_i) and an electric field \mathbf{E} of intensity \mathcal{E} .

The interaction of the system with an external reservoir is described by \hat{W} in (35); the reservoir is taken as ideal, a very good approximation in most cases, its macroscopic (thermodynamic) state being characterized by a canonical statistical distribution at temperature T_0 .

Consider now the nonequilibrium-thermodynamic state of the system: the electric field changes transfers energy in excess of equilibrium to the electrons. This excess is in turn transferred to the lattice and from there to the reservoir, while the flux of electrons gives rise to an electron current. Thus, we need to choose as basic the variables

$$\{E_e(t), N_e(t), \mathbf{P}_e(t), E_{\text{LO}}(t), E_{\text{AC}}(t), E_{\text{R}}\}, \quad (180)$$

that is, the carrier energy, number and linear momentum, the TO and AC phonon energies, and the energy of the reservoir, respectively; the latter being ideal, its energy is constant in time. The corresponding dynamical quantities are

$$\{\hat{H}_e, \hat{N}_e, \hat{\mathbf{P}}_e, \hat{H}_{\text{LO}}, \hat{H}_{\text{AC}}, \hat{H}_{\text{R}}\}, \quad (181)$$

i.e., the Hermitian operators for the partial Hamiltonians, the electron number, and the linear momentum.

Our choice disregards electro-thermal effects. To include them, we would have to give attention to the flux of carrier energy, or heat flux, an elaboration that would have minor influence upon the following results. Thermoelectric effects are of relevance in certain physical processes in the dynamics of modern devices. Of practical interest, for example, is the so-called thermoelectric figure of merit associated with microprocessor refrigeration and heat transport in small systems with constrained geometries. This aspect of the problem, which belongs to the area of nonequilibrium phonon dynamics, more precisely to the subject of phonon hydrodynamics associated to nonequilibrium (irreversible) thermodynamics, has been extensively studied in the framework of NESEF-kinetic theory [86].

According to the nonequilibrium statistical ensemble formalism, described in the [Appendix](#), the nonequilibrium-thermodynamic state of the system can be completely characterized by the set of nonequilibrium-thermodynamic variables conjugate to those in (181), namely

$$\{F_e(t), F_{ne}(t), \mathbf{F}_e(t), F_{LO}(t), F_{AC}(t), \beta_0\}, \quad (182)$$

respectively.

The conjugate variables are present in the auxiliary statistical operator introduced by the formalism. Here, the operator is given by the equality

$$\bar{\varrho}(t, 0) = \exp \left\{ -\phi(t) - F_{ne}(t) \hat{N}_e - F_e(t) \hat{H}_e - \mathbf{F}_e(t) \cdot \hat{\mathbf{P}}_e - F_{LO}(t) \hat{H}_{LO} - F_{AC}(t) \hat{H}_{AC} \right\} \varrho_R, \quad (183)$$

where ϱ_R is the canonical distribution of the reservoir at temperature T_0 .

The operator in (183) is not the statistical operator describing the macroscopic state of the system, which is a super-operator of this one, and $\phi(t)$, which plays the role of a logarithm of a nonequilibrium partition function, ensures the normalization of $\bar{\varrho}(t, 0)$.

The nonequilibrium-thermodynamic variables of (182) are usually redefined as

$$F_e(t) = \beta_e^*(t) = [k_B T_e^*(t)]^{-1}, \quad (184)$$

$$F_{ne}(t) = -\beta_e^*(t) \mu_e^*(t), \quad (185)$$

$$\mathbf{F}_e(t) = -\beta_e^*(t) \mathbf{v}_e(t), \quad (186)$$

$$F_{LO}(t) = \beta_{LO}^*(t) = [k_B T_{LO}^*(t)]^{-1}, \quad (187)$$

$$F_{AC}(t) = \beta_{AC}^*(t) = [k_B T_{AC}^*(t)]^{-1}, \quad (188)$$

and we recall that β_0 [in (182)] is $(k_B T_0)^{-1}$.

Equations (184)–(188) define the quasi-temperatures, $T_e^*(t)$, $T_{LO}^*(t)$, and $T_{AC}^*(t)$, of the electrons and phonons, and the quasi-chemical potential $\mu_e^*(t)$ and drift velocity $\mathbf{v}_e(t)$ of the electrons.

For the time evolution of the basic variables, we obtain the following set of equations [64, 82, 83, 86]:

$$\frac{d}{dt} E_e(t) = -\frac{e}{m_e^*} \mathbf{E} \cdot \mathbf{P}_e(t) - J_{E_e}^{(2)}(t), \quad (189)$$

$$\frac{d}{dt} \mathbf{P}_e(t) = -n V e \mathbf{E} + \mathbf{J}_{\mathbf{P}_e}^{(2)}(t) + \mathbf{J}_{\mathbf{P}_e, \text{imp}}^{(2)}(t), \quad (190)$$

$$\frac{d}{dt} E_{LO}(t) = J_{E_{LO}}^{(2)}(t) - J_{LO, AN}^{(2)}(t), \quad (191)$$

$$\frac{d}{dt} E_{AC}(t) = J_{E_{AC}}^{(2)}(t) + J_{LO, AN}^{(2)}(t) - J_{AC, \text{dif}}^{(2)}(t), \quad (192)$$

where, we recall, $E_e(t)$ and $\mathbf{P}_e(t)$ are the carrier energy and linear momentum. $E_{LO}(t)$ is the energy of the LO phonons, which interact strongly with the carriers via the Fröhlich potential in these strongly polar semiconductors. We disregard the weaker nonpolar-deformation potential interaction. $E_{AC}(t)$ is the energy of the acoustic phonons playing the role of a thermal bath. Finally, \mathbf{E} represents the constant electric field.

Let us now analyze these equations term by term. The first term on the right-hand side of (189) accounts for the rate of energy transferred from the electric field to the carriers, and the second term accounts for the transfer of the resulting excess energy of the carriers to the phonons. In (190) the first term on the right-hand side is the driving force generated by the electric field. The second term is the rate of momentum transfer due to the interaction with the phonons, and the last one is due to impurity scattering. These two terms contribute to momentum relaxation. The first terms on the right-hand sides of (191) and (192) describe the phonon energy rate of change due to interaction with the electrons. More precisely, they account for the energy gain from the hot carriers; the sum of $J_{E_{LO}}^{(2)}(t)$ and $J_{E_{AC}}^{(2)}(t)$ is the negative of the last term on the right-hand side of (189). The second term on the right-hand side of (191) accounts for the rate of transfer of energy from the optical to the acoustic phonons, via anharmonic interaction. $J_{LO, AN}^{(2)}(t)$ appears with opposite signs on the right of (191) and (192). Finally, the last term on the right-hand side of (192) accounts for heat diffusion from the AC phonons to the external reservoir. Detailed expressions for the collision operators can be found in Ref. [64]. Here, we only note that the J is positive.

The solution of the above equations allows detailed analysis of the nonequilibrium-thermodynamic state and

transport properties of these materials. Let us consider first the III-nitride compounds, which nowadays are raising particular interest because they have potential application in lasers and diodes emitting in the blue and ultraviolet region (see, for example, Refs. [87, 88]).

Let us consider the steady state, which is very rapidly established, in the time scale of 100 fs, because the strong Fröhlich interaction raises the rate of energy transfer from carriers to LO phonons so that it quickly becomes equal to the rate of energy pumped into the system by the external field, of intensity \mathcal{E} , even at high fields. The dynamics is then characterized by the time-independent quasi-temperature, T_e^* , drift velocity, \mathbf{v}_e , and quasi-chemical potential, μ_e^* , all pertaining to the electron system, and the LO-phonon quasi-temperature T_{LO}^* and the AC phonon quasi-temperature T_{AC}^* . Figure 6 shows the electric-field dependence of T_e^* ; Fig. 7 displays the electric-field dependence for the drift velocity for n -doped GaN, with $n = 10^{17} \text{ cm}^{-3}$. The quasi-chemical potential is determined by the concentration and electron quasi-temperature. The deviations of T_{LO}^* and T_{AC}^* from the equilibrium value are small and can be neglected.

We can now proceed to calculate the light scattering cross section by electrons under the electric field \mathcal{E} . Taking into account that the interaction of electrons and radiation is given by

$$V_{ER}\mathbf{Q} = G(\mathbf{Q})\hat{n}_{\mathbf{Q}} + H.c., \quad (193)$$

where $\hbar\mathbf{Q}$ is the momentum of the photon, $G(\mathbf{Q})$ is the matrix element of the interaction, and

$$\hat{n}_{\mathbf{Q}} = \sum_{\mathbf{k}} \hat{n}_{\mathbf{k}\mathbf{Q}} = \sum_{\mathbf{k}} c_{\mathbf{k}+\mathbf{Q}}^\dagger c_{\mathbf{k}}, \quad (194)$$

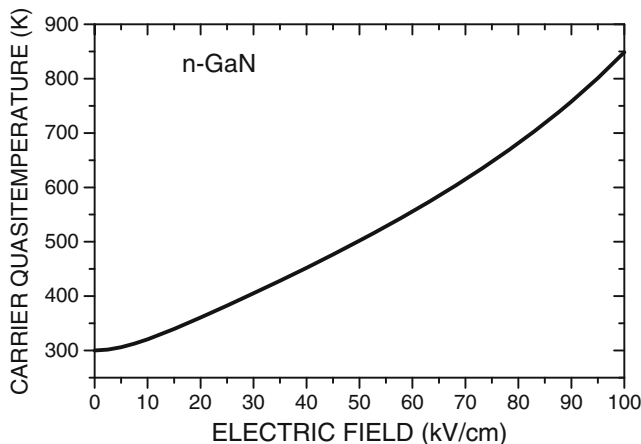


Fig. 6 Electric-field dependence of the quasi-temperature T_e^* in the steady state for n -doped GaN. We have chosen $m^* = 0.19m_0$, $\varepsilon_0 = 9.5$, carrier concentration $n = 10^{17} \text{ cm}^{-3}$, and the thermal bath temperature $T_0 = 300 \text{ K}$. After Ref. [89]

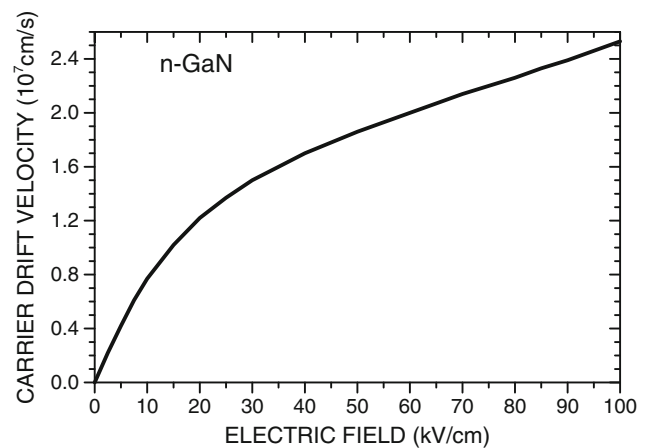


Fig. 7 Electric-field dependence of the electron drift velocity in the steady state for n -doped GaN. The experimental conditions are those in the caption of Fig. 6. After Ref. [89]

to first order in the scattering operator the cross section in (143) is given by the expression

$$\frac{d^2\sigma(\mathbf{Q}, \omega)}{d\omega d\Omega} = \frac{V^2}{(2\pi\hbar)^3} \frac{\hbar\omega^2}{c^4} |G(\mathbf{Q})|^2 \int_{-\infty}^{\infty} d\tau e^{-i\omega\tau} \times \text{Tr}\{n_{\mathbf{Q}}^\dagger n_{\mathbf{Q}} \mathcal{R}_\varepsilon\}. \quad (195)$$

We recall that the system is in steady state, and that the two integrals in (143) can be combined as above. We have used that $g(\omega) = \hbar^3\omega^2/c^3$ and $v_0 = c$.

We can now use the generalized fluctuation-dissipation theorem of Section 3. We keep only the relevant part defined in that section, i.e., substitute $\bar{\mathcal{R}}$ for \mathcal{R}_ε in (183). In the steady state, we then find that

$$\frac{d^2\sigma(\mathbf{Q}, \omega)}{d\omega d\Omega} \sim [1 - e^{-\beta^*(\hbar\omega - \mathbf{Q}\cdot\mathbf{v}_e)}]^{-1} \text{Im}\{\epsilon^{-1}(\mathbf{Q}, \omega|\mathcal{E})\}, \quad (196)$$

In (196), $\epsilon(\mathbf{Q}, \omega|\mathcal{E})$ is the dielectric function at the wave vector \mathbf{Q} and frequency ω (i.e., the momentum and energy transfer in the scattering event, as we have seen), since we use that

$$\epsilon(\mathbf{Q}, \omega|\mathcal{E}) = 1 - \mathcal{V}(\mathbf{Q}) \sum_{\mathbf{k}} \frac{f(\mathbf{k} + \mathbf{Q}|\mathcal{E}) - f(\mathbf{k}|\mathcal{E})}{\mathcal{E}(\mathbf{k} + \mathbf{Q}) - \mathcal{E}(\mathbf{k}) - \hbar(\omega + is)}, \quad (197)$$

where $\mathcal{E}(\mathbf{k}) = \hbar^2 k^2 / 2m_e^*$, in the effective mass approximation, and s is a positive infinitesimal; we let $s \rightarrow +0$ to obtain the real and imaginary parts of $\epsilon(\mathbf{Q}, \omega) = \epsilon_1(\mathbf{Q}, \omega) + i\epsilon_2(\mathbf{Q}, \omega)$.

Equation (197) has the form of the Lindhardt (RPA) dielectric function, here written in terms of the nonequilibrium distribution functions $f(\mathbf{k}|\mathcal{E})$. The latter have the form

of a drifted Fermi-Dirac-like distribution (with the electric field-dependent quasi-temperature and quasi-chemical potential), which under usual experimental conditions is approximately equal to a drifted Maxwell-Boltzmann distribution, namely

$$f(\mathbf{k}|\mathcal{E}) = A \exp\{-\beta_e^*(\mathcal{E})[\mathcal{E}(\mathbf{k}) - \mathbf{E} \cdot \hbar\mathbf{k}]\}, \quad (198)$$

with

$$\beta_e^*(\mathcal{E}) = \frac{1}{k_B T^*(\mathcal{E})}, \quad (199)$$

$$A(\mathcal{E}) = \frac{8\pi^3 n \hbar^3 [\beta_e^*(\mathcal{E})]^{3/2}}{(2\pi m_e^*)^{3/2}}, \quad (200)$$

where we have recalled that $\mathcal{V}(\mathbf{Q}) = 4\pi e^2/(V\epsilon_0 Q^2)$ is the Fourier transform of the Coulomb potential with ϵ_0 being the static dielectric constant, and V the volume of the system. Going over to the continuum, i.e., transforming the summation in (197) into an integral and using spherical coordinates k, θ, φ , we find for the real part of the dielectric function

$$\epsilon_1(\mathbf{Q}, \omega) = 1 - \frac{\mathcal{V}(\mathbf{Q})}{4\pi^3} F(\mathbf{Q}, \omega), \quad (201)$$

where

$$F(\mathbf{Q}, \omega) = -\frac{n\pi^3 \sqrt{2^5 m_e^* \beta_e^*}}{\hbar Q} [D(y_1) + D(y_2)], \quad (202)$$

with

$$D(y) = e^{-y^2} \int_0^y e^{x^2} dx, \quad (203)$$

which is Dawson's integral, and

$$y_1 = \sqrt{\frac{\beta_e^* \hbar^2}{2m_e^*}} \left[\frac{Q}{2} + \frac{m_e^*}{\hbar Q} (\omega - \mathbf{Q} \cdot \mathbf{v}_e) \right], \quad (204)$$

$$y_2 = \sqrt{\frac{\beta_e^* \hbar^2}{2m_e^*}} \left[\frac{Q}{2} - \frac{m_e^*}{\hbar Q} (\omega - \mathbf{Q} \cdot \mathbf{v}_e) \right], \quad (205)$$

Substituting (202) in (201), we obtain that

$$\epsilon_1(\mathbf{Q}, \omega) = 1 + \sqrt{\frac{2m_e^*}{\beta_e^*}} \frac{k_{DH}^2}{\hbar Q^3} [D(y_1) + D(y_2)], \quad (206)$$

where

$$k_{DH}^2 = \frac{4\pi e^2 n}{\epsilon_0 k_B T_e^*}, \quad (207)$$

is the Debye-Huckel screening factor.

The imaginary part of the dielectric constant is given by equality

$$\epsilon_2(\mathbf{Q}, \omega) = \frac{\pi \sqrt{m_e^*} k_{DH}^2}{2\beta_e^* \hbar Q^3} [e^{-y_2^2} - e^{-y_1^2}]. \quad (208)$$

Let us consider GaN in the steady-state thermodynamic conditions indicated in Figs. 6 and 7, under an electric field $\mathcal{E} = 100$ kV/cm, in three experimental geometries, i.e., for three scattering angles θ . The scattering spectrum is composed of two contributions, namely in Fig. 8 with $Q = 1.8 \times 10^5$ cm⁻¹, scattering off individual electrons at low ω , and in Fig. 9, with $Q = 5 \times 10^4$ cm⁻¹, scattering off collective excitations (plasmons) around the plasma frequency $\omega_p^2 = 4\pi n e^2 / \epsilon_0 m_e^*$. Both Figs. 8 and 9 show a shift in the scattering bands, which depends on the scattering angle. The shift is due to the term $\mathbf{Q} \cdot \mathbf{v}_e$ in the exponent within square brackets on the right-hand side of (196), which vanishes for the experimental geometry in which the momentum transfer \mathbf{Q} is perpendicular to the drift velocity, i.e., perpendicular to the electric field ($\mathbf{v}_e = \mathcal{M}_e \mathbf{E}$, where \mathcal{M}_e is the electron mobility), and maximum when \mathbf{Q} and \mathbf{v}_e are parallel. A quite interesting consequence is a simple procedure to determine the drift velocity and therefore the mobility under the experimental conditions from the frequency shift. If we call $\Delta\omega_{\text{peak}}$ the frequency difference between the peak positions in the plasmon-scattering bands for $\theta = 0$ and $\theta = \pi/2$ (Fig. 9), then the drift velocity v_e is given by the equality

$$v_e = \frac{\Delta\omega_{\text{peak}}}{Q}, \quad (209)$$

and the mobility \mathcal{M}_e , by the equality

$$\mathcal{M}_e = \frac{v_e}{\mathcal{E}} = \frac{\Delta\omega_{\text{peak}}}{Q\mathcal{E}}. \quad (210)$$

This experimental method to measure the drift velocity/mobility is more accurate than the alternative procedures that have been used so far.

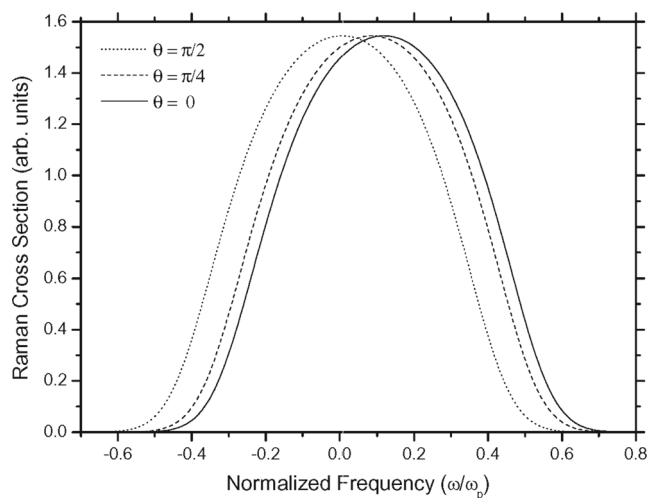


Fig. 8 Raman band due to scattering by single-particle elementary excitations. $\mathcal{E} = 100$ kV/cm, $Q = 1.8 \times 10^5$ cm⁻¹, the thermodynamic state is as described in Figs. 6 and 7 for the given \mathcal{E} . The scattering angles are $\theta = 0$ (solid line), $\theta = \pi/4$ (dashed), and $\theta = \pi/2$ (dotted). After Ref. [89]

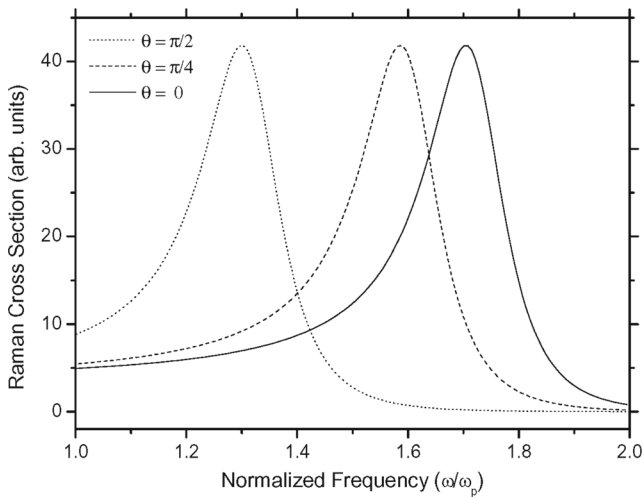


Fig. 9 Raman band due to scattering by plasma excitations. The specifications are as in the caption of Fig. 8, except that $Q = 5 \times 10^4 \text{ cm}^{-1}$. After Ref. [89]

7 Final Remarks

We have presented a response function theory, accompanied by a fluctuation dissipation theorem, and a theory of scattering adapted to deal with systems arbitrarily far removed from equilibrium, including time- and space-resolved experiments.

The theory was built within the framework of a Gibbs-style nonequilibrium statistical ensemble formalism. The general form of the generalized (space- and time-dependent) susceptibility is obtained in the form of space- and time-dependent correlation functions defined over the nonequilibrium ensemble. It is also dependent on the variables that characterized the nonequilibrium-thermodynamic state of the system. The generalized susceptibility for the corresponding experimental situation is therefore coupled to the equations of evolution of the nonequilibrium-thermodynamic variables. We have also presented a method to calculate nonequilibrium-thermodynamic Green functions, that is, the extension to arbitrary nonequilibrium conditions of the Bogoliubov-Tyblkov thermodynamic Green functions.

A fluctuation-dissipation theorem in the context of the nonequilibrium ensemble formalism was presented in Section 3, which is an extension to arbitrary nonequilibrium conditions of Kubo's theorem.

In Section 5, we have presented a theory of scattering for scattering experiments on systems that are arbitrarily far removed from equilibrium. A space- and time-dependent scattering cross section was obtained, which like the generalized susceptibility of response function theory, depends on the nonequilibrium-thermodynamic state of the system. The

scattering cross section is therefore coupled to the equations of evolution for the nonequilibrium variables.

Finally, Section 6 presented a few illustrative examples. We applied the theory to the analysis of experimental results, namely, in ultrafast laser spectroscopy and charge transport in doped polar semiconductors.

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In Memoriam: With very sad feelings, we regret to report the passing away of our dear colleague Prof. Dr. Áurea Rosas Vasconcellos, a genuine, devoted, and extremely competent teacher and researcher with fervent dedication to Theoretical Physics in the Condensed Matter area.

Appendix: The Nonequilibrium Statistical Operator

The construction of nonequilibrium statistical ensembles, that is, a nonequilibrium statistical ensemble formalism, NESEF for short [8–13], basically consisting of deriving a nonequilibrium statistical operator (probability distribution in the classical case) has been attempted along several lines. In a brief summarized way, we describe the construction of NESEF within a heuristic approach. In this context, several important points must be carefully taken into account in each case under consideration:

1. *Choice of the basic variables.* The choices for equilibrium and for nonequilibrium are different; for systems in equilibrium, it suffices to consider the constants of motion. To choose the variables for systems out of equilibrium, we must identify macroscopic processes and measurements and focus attention not only on the observables, but also on the character and expectations concerning the evolution equations for these variables [12, 13, 90]. Although all observables—along with their correlations, in certain cases—must be dealt with at the initial stage, as time elapses more and more contracted descriptions become possible as Bogoliubov's principle of correlation weakening and the accompanying hierarchy of relaxation times comes into play [91].
2. *Irreversibility* (or Eddington's arrow of time). Concerning this facet of the problem, Rudolf Peierls has stated that “In any theoretical treatment of transport problems, it is important to realize at what point the irreversibility has been incorporated. If it has not been incorporated, the treatment is wrong. A description of the situation that preserves the reversibility in time is bound to give the answer zero or infinity for any conductivity. If we do not see clearly where the irreversibility is introduced, we do not clearly understand what we are doing” [92].

3. *Historicity*. Proper treatment must incorporate the entire past dynamics of the system, or historicity effects, from a starting description of the macrostate of the sample in the experiment under study, say at t_0 , up to the time t when a measurement is performed. This is a quite important point in the case of dissipative systems, as emphasized among others by John Kirkwood, Melvin Green, Robert Zwanzig, and Hazime More [36–40]. It implies that the history of the system is not merely the series of events involving the system, but the series of transformations along time through which the system progressively comes into being at the measurement time t , through the evolution governed by the laws of mechanics [93]

Concerning the choice of the basic variables, in contrast with the equilibrium case, immediately after the open N -particle system, in contact with external sources and reservoirs, has been driven out of equilibrium, it becomes necessary to describe its state in terms of all its observables and, in certain instances, to introduce direct and cross-correlations. As time elapses, however, Bogoliubov's principle of correlation weakening allows us to introduce increasing contractions of descriptions.

On the question of irreversibility, Nicolai S. Krylov [42] considered that there always exists a physical interaction between the measured system and the external world that is constantly “jolting” the system out of its exact microstate. Thus, the instability of trajectories and the unavoidable finite interaction with the outside would guarantee the validity of a “crudely prepared” macroscopic description. In the absence of a proper way to introduce this effect, one needs to resort to the *interventionist's approach*, which is grounded on this ineluctable randomization process and leads to the asymmetric evolution of the macrostate.

The “intervention” consists of introducing in the Liouville equation for the statistical operator of the otherwise isolated system, a special source accounting for Krylov's “jolting” effect, in the following form (for the logarithm of the statistical operator):

$$\frac{\partial}{\partial t} \ln \mathcal{R}_\varepsilon(t) + \frac{1}{i\hbar} [\ln \mathcal{R}_\varepsilon(t), \hat{H}] = -\varepsilon [\ln \mathcal{R}_\varepsilon(t) - \ln \bar{\mathcal{R}}(t, 0)], \quad (211)$$

where ε (effectively the reciprocal of a relaxation time) is taken to go to $+0$ after the average values have been computed.

This mathematically inhomogeneous term, in the otherwise normal Liouville equation, implies a continuous tendency to relax the statistical operators toward a *referential distribution*, $\bar{\mathcal{R}}$, which, as discussed below, represents an instantaneous quasi-equilibrium condition.

We can regard (211) as a regular Liouville equation with an infinitesimal source, which provides Bogoliubov's symmetry breaking of time reversal and justifies disregarding the advanced solutions [8, 12, 13, 94, 95]. This is described by a Poisson distribution and the result at time t is obtained by averaging over all t' in the interval (t_0, t) , since the solution of (211) is

$$\mathcal{R}_\varepsilon(t) = \exp \left\{ -\hat{S}(t, 0) + \int_{t_0}^t dt' e^{\varepsilon(t'-t)} \frac{d}{dt'} \hat{S}(t', t' - t) \right\}, \quad (212)$$

where

$$\hat{S}(t, 0) = -\ln \bar{\mathcal{R}}(t, 0), \quad (213)$$

$$\begin{aligned} \hat{S}(t', t' - t) &= \exp \left\{ -\frac{1}{i\hbar} (t' - t) \hat{H} \right\} \hat{S}(t', 0) \\ &\times \exp \left\{ \frac{1}{i\hbar} (t' - t) \hat{H} \right\}, \end{aligned} \quad (214)$$

and the initial-time condition at time t_0 , when the formalism begins to be applied, is

$$\mathcal{R}_\varepsilon(t_0) = \bar{\mathcal{R}}(t_0, 0). \quad (215)$$

The first time variables in the arguments of both $\bar{\mathcal{R}}$ and \hat{S} refer to the evolution of the nonequilibrium-thermodynamic variables, and the second time variables, to the time evolution of the dynamical variables, both of which affect the operator.

The time t_0 , which starts the statistical description, is usually taken in the remote past ($t_0 \rightarrow -\infty$), which introduces an adiabatic switching-on of the relaxation process. In (212), the time integration in the interval (t_0, t) is weighted by the kernel $\exp\{\varepsilon(t' - t)\}$. The presence of this kernel introduces a kind of *evanescent history* as the system macrostate evolves toward the future from the boundary condition of (215) at time ($t_0 \rightarrow -\infty$), a fact evidenced in the resulting kinetic theory [8–13, 16, 38], which clearly indicates that a *fading memory* of the dynamical process has been introduced. The statistical operator can be written in the form

$$\mathcal{R}_\varepsilon(t) = \bar{\mathcal{R}}(t, 0) + \mathcal{R}'_\varepsilon(t). \quad (216)$$

involving the auxiliary probability distribution $\bar{\mathcal{R}}(t, 0)$, plus $\mathcal{R}'_\varepsilon(t)$, which contains the historicity and irreversibility effects.

In most cases, we can consider the system as composed of the system of interest, i.e., the system on which we are performing an experiment, and ideal reservoirs in contact with it. Therefore, we can write the expression

$$\bar{\mathcal{R}}(t, 0) = \bar{\varrho}(t, 0) \times \varrho_R. \quad (217)$$

and

$$\mathcal{R}_\varepsilon(t) = \varrho_\varepsilon(t) \times \varrho_R, \quad (218)$$

where $\varrho_\varepsilon(t)$ is the statistical operator of the nonequilibrium system, $\bar{\varrho}$ the auxiliary one, and ϱ_R the stationary operator for the ideal reservoirs, with $\varrho_\varepsilon(t)$ then given by the equality

$$\varrho_\varepsilon(t) = \exp \left\{ -\hat{S}(t, 0) + \int_{-\infty}^t dt' e^{\varepsilon(t'-t)} \frac{d}{dt'} \hat{S}(t', t' - t) \right\}, \quad (219)$$

with the initial value $\bar{\varrho}(t_0, 0)$ ($t_0 \rightarrow -\infty$), and where

$$\hat{S}(t, 0) = -\ln \bar{\varrho}(t, 0), \quad (220)$$

Finally, we have to provide the auxiliary statistical operator $\bar{\varrho}(t, 0)$. This operator, sometimes dubbed the *quasi-equilibrium statistical operator*, expresses an instantaneous distribution at time t describing a “frozen” equilibrium that defines the macroscopic state of the system at that moment. On the basis of this notion (or, alternatively, via the variational procedure [12, 13, 96–104]) and considering the description of the system nonequilibrium state in terms of the basic set of dynamical variables \hat{P}_j , the reference or instantaneous quasi-equilibrium statistical operator is taken as a canonical-like one given by the equality

$$\bar{\varrho}(t, 0) = \exp \left\{ -\phi(t) - \sum_j^n F_j(t) \hat{P}_j \right\}, \quad (221)$$

with $\phi(t)$ ensuring the normalization of $\bar{\varrho}$ and playing the role of a logarithm of a partition function, say, $\phi(t) = \ln \bar{Z}(t)$.

Moreover, in (221), F_j is the nonequilibrium-thermodynamic variable associated with the basic dynamical variable \hat{P}_j . The nonequilibrium-thermodynamic space of states is composed by the basic variables $\{Q_j(t)\}$, which comprise the averages of the $\{\hat{P}_j\}$ over the nonequilibrium ensemble, namely,

$$Q_j(t) = \text{Tr} \{ \hat{P}_j \varrho_\varepsilon(t) \}, \quad (222)$$

which are then functionals of the $\{F_j(t)\}$ and there follow the equations of state

$$Q_j(t) = -\frac{\delta \phi(t)}{\delta F_j(t)} = -\frac{\delta \ln \bar{Z}(t)}{\delta F_j(t)}, \quad (223)$$

where δ denotes functional derivative.

Moreover,

$$\bar{S}(t) = \text{Tr} \{ \hat{S}(t, 0) \bar{\varrho}(t, 0) \} = -\text{Tr} \{ \bar{\varrho}(t, 0) \ln \bar{\varrho}(t, 0) \}, \quad (224)$$

is the so-called informational entropy characteristic of the distribution $\bar{\varrho}$, a functional of the basic variables $\{Q_j(t)\}$, in terms of which the following alternative form of the equations of state can be written:

$$-\frac{\delta \bar{S}(t)}{\delta Q_j(t)} = F_j(t), \quad (225)$$

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