Optical properties of semiconductors via pump-probe experiments: statistical-thermodynamical approach, hot plasma and coherent phonon states

2000 J. Phys.: Condens. Matter 12 5325

(http://iopscience.iop.org/0953-8984/12/24/321)

J. Phys.: Condens. Matter **12** (2000) 5325–5342. Printed in the UK PII: S0953-8984(00)07032-6

Optical properties of semiconductors via pump–probe experiments: statistical–thermodynamical approach, hot plasma and coherent phonon states

Áurea R Vasconcellos†, Roberto Luzzi† and Justino R Madureira†‡

† Instituto de Física 'Gleb Wataghin', Universidade Estadual de Campinas, Unicamp 13083-970 Campinas, São Paulo, Brazil

‡ FB Physik, Universität Rostock, D-18051 Rostock, Germany

Received 17 August 1999, in final form 7 March 2000

Abstract. We present an analysis of the nonequilibrium thermodynamics and, mainly, a response function theory for the study of optical properties in ultrafast-spectroscopy pump–probe experiments. These experiments give rise to the formation of a photoinjected plasma in semiconductors in far-from-equilibrium conditions. The dissipative processes that evolve in this medium greatly influence optical and transport properties. The theory is centred on the application to the study of the phenomenon of modulated changes in the time-resolved reflectivity spectrum. In particular, we show that this phenomenon consists in the coupled effect of coherent-LO-phonon and carrier-charge-density motions, which are driven through the action of the coherent photons of the laser electromagnetic radiation. In the given conditions the modulation effect decays in time and has associated a frequency close to the zone-centre upper LO phonon–optical plasma hybrid mode, as experimentally observed.

1. Introduction

Pump–probe experiments in the field of ultrafast laser spectroscopy, devoted to the study of the nonequilibrium photoinjected plasma in semiconductors, have been extensively used in recent decades, and have been accompanied by a number of theoretical analyses [1]. It needs to be stressed that in this type of experiment the system is, as a general rule, driven far away from equilibrium. Hence, while the measurements are performed with, say, femto- or pico-second time resolution, the macroscopic (thermodynamic) state of the system is rapidly evolving from the initial state of preparation in far-from-equilibrium conditions (produced by the action of the pumping source). Consequently, while the experiment is carried on (resorting to the probing instrumentation) ultrafast relaxation (dissipative) processes develop in the system having relaxation times of the order of picoseconds to tens or hundreds of picoseconds. This implies the quite relevant point that to determine the response function of the system (a time-dependent one because it depends on the macroscopic nonequilibrium state of the system while the time-resolved measurement is performed), it is necessary to also determine the time evolution of such a, we stress, nonequilibrium time-dependent thermodynamic state of the system. This implies the fact that a theoretical formalism powerful enough to deal with these situations is necessary. One that properly provides a complete unified and powerful theory, apparently able to cover a large section of experimental situations, is a far-reaching generalization of the Gibbs–Boltzmann approach in the form of a nonequilibrium statistical ensemble formalism.

0953-8984/00/245325+18$30.00

This is the so-called nonequilibrium statistical operator method (NESOM; see for example [2–8]). The formalism has been applied to the study of ultrafast relaxation phenomena in the photoinjected plasma in semiconductors, either in the case of transport properties or as well for optical properties [9, 10].

We present in this paper an analysis in depth of this particular time-resolved optical response of the highly excited plasma in semiconductors (hereafter HEPS for short) within the framework of the above formalism. HEPS provides an excellent testing ground for concepts and methods in the field of statistical thermodynamics and mechanics of many-body systems arbitrarily away from equilibrium (some applications in semiconductor physics are listed in [10]).

The NESOM-based response function theory [8] is applied to the study of ultrafast optical properties in the photoinjected plasma in semiconductors. We obtain the frequency- and wavenumber-dependent dielectric function in arbitrary nonequilibrium conditions, a quantity which contains all the information related to the optical properties of the system (as known, it provides the absorption coefficient, the reflectivity coefficient, the Raman scattering cross section etc). Moreover, we explicitly apply the results to the study of a particular type of experiment, namely the time-resolved reflectivity changes in GaAs and other materials [11, 12] where signal changes in the reflectivity, $\Delta R/R$, of the order of 10^{-7} are detected, and a distinct oscillation of the signal in real time is observed. Such a phenomenon has been attributed to the generation of coherent lattice vibrations, and several theoretical approaches have been reported so far [13–16]. A clear description, on phenomenological bases, which captures the essential physics of the problem, is reported in [14]. A microscopic approach is attempted by the authors of [15], which we show fails to provide a proper description and arrives at faulty conclusions.

2. Reflectivity in pump–probe experiments

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 on the metallic side of the Mott transition (that is, they are itinerant carriers, and we recall that this requires concentrations of these photoinjected quasi-particles of the order of 10^{16} cm^{-3} and up), which compose a two-component Fermi fluid, moving in the lattice background. It constitutes a highly nonequilibrated system where the photoexcited carriers rapidly redistribute their energy in excess of equilibrium via, mainly, the strong long-range Coulomb interaction in a pico- to subpicosecond scale, followed by the transfer of energy to the phonon field (predominantly to the optical phonons, and preferentially to the LO phonons via Fröhlich interaction), and finally to the external thermal reservoir. Along the process the carrier density diminishes in recombination processes (nanosecond time scale) and through diffusion out of the active volume of the sample (ten picosecond time scale). Detailed descriptions of the processes are given elsewhere [10, 18].

This follows as a consequence of the action of the pumping laser light, with the macroscopic nonequilibrium thermodynamic state of the HEPS to be treated, as already noticed in the introduction, within the scope of the statistical thermodynamics based on NESOM. On the other hand, a probe interacting weakly with the HEPS is used to obtain an optical response, the reflectivity of the incoming laser photons with frequency ω and wavevector $\boldsymbol{Q}$ in the case under consideration. From the theoretical point of view, such measurement is to be analysed in terms of the all important and inevitable use of correlation functions in response function theory [19]. In the present case of a pump–probe experiment we need to resort to a theory of such a type but properly adjusted to deal with a system whose macroscopic state

is in nonequilibrium conditions and evolving in time as a result of the pumping dissipative processes that are developing while the sample is probed. Therefore, the response function theory for nonequilibrium systems needs to be coupled to the kinetic theory that describes the evolution of the nonequilibrium state of the system [5–8, 17]. Moreover, as in the case of an initial preparation in equilibrium conditions, the correlation functions that the theory introduces can be alternatively calculated in terms of an appropriate theory of nonequilibrium thermodynamic Green functions [8, 20]. We resort here to such a theory for the study of the optical properties in HEPS, and, in particular, we consider the case of reflectivity.

The reflectivity $R(\omega, \boldsymbol{Q} \mid t)$, where t is the time at which a measurement is performed in this time-resolved spectroscopy experiments, is related to the index of refraction $\eta(\omega, \boldsymbol{Q} \mid t) + \mathrm{i}\kappa(\omega, \boldsymbol{Q} \mid t)$ through the well known expression

$$R(\omega, \boldsymbol{Q} \mid t) = \frac{|\eta(\omega, \boldsymbol{Q} \mid t) - 1|^2 + |\kappa(\omega, \boldsymbol{Q} \mid t)|^2}{|\eta(\omega, \boldsymbol{Q} \mid t) + 1|^2 + |\kappa(\omega, \boldsymbol{Q} \mid t)|^2} \tag{1}$$

and the refraction index is related to the time-evolving *frequency- and wavenumber-dependent* dielectric function by

$$\varepsilon(\omega, \boldsymbol{Q} \mid t) = \varepsilon'(\omega, \boldsymbol{Q} \mid t) + \mathrm{i}\varepsilon''(\omega, \boldsymbol{Q} \mid t) = [\eta(\omega, \boldsymbol{Q} \mid t) + \mathrm{i}\kappa(\omega, \boldsymbol{Q} \mid t)]^2. \tag{2}$$

We stress that the explicit dependence on time is of course the result of the fact that the macroscopic state of the non-equilibrated plasma is evolving in time as the experiment is performed.

Therefore it is our task to calculate this dielectric function in the nonequilibrium state of the HEPS. First, we note that according to Maxwell equations in material media [21] (that is, Maxwell equations now averaged over the nonequilibrium statistical ensemble) we have that

$$\varepsilon^{-1}(\omega, \boldsymbol{Q} \mid t) - 1 = \frac{\tilde{n}(\omega, \boldsymbol{Q} \mid t)}{r(\omega, \boldsymbol{Q})} \tag{3}$$

where $r(\omega, \boldsymbol{Q})$ is the amplitude of a probe charge density with frequency ω and wavevector $\boldsymbol{Q}$, and $\tilde{n}(\omega, \boldsymbol{Q} \mid t)$ the induced polarization charge density of carriers and lattice, at time t, in the media. The latter can be calculated resorting to the response function theory for systems far from equilibrium [8, 22] (the case is quite similar to the calculation of the time-resolved Raman scattering cross section [23, 24]), and obtained in terms of the nonequilibrium thermodynamic Green functions [8, 22].

But, the expression we obtain is, as already noticed, dependent on the evolving nonequilibrium macroscopic state of the system, a fact embedded in the expressions for the time-dependent distribution functions of the carriers and phonon states. Therefore, they are to be derived within the *NESOM-based kinetic theory*, and the first and fundamental step is the choice of the set of variables deemed appropriate for the description of the macroscopic state of the system. The case of HEPS has been discussed elsewhere [10, 18] and we simply notice that a first set of variables needs to be the one composed of the carriers' density and energy, and the phonon population functions, which in NESOM have a set of associated Lagrange parameters that can be interpreted as a reciprocal quasitemperature and quasichemical potentials of carriers, and a reciprocal quasitemperature of phonons per mode [10, 18, 25]. But in the situation we are considering 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 oscillation in the reflectivity) and the latter because of the LO-phonon–plasma coupling (clearly present in Raman scattering experiments [23, 24]). Consequently the chosen basic set of dynamical quantities is

$$\{\hat{H}_c, \hat{N}_e, \hat{N}_h, \hat{n}^e_{\boldsymbol{kp}}, \hat{n}^h_{\boldsymbol{kp}}, \hat{\nu}_{\boldsymbol{q}}, a_{\boldsymbol{q}}, a^\dagger_{\boldsymbol{q}}, H_B\} \tag{4}$$

where

$$\hat{H}_c = \sum_{\boldsymbol{k}} [\varepsilon^e_{\boldsymbol{k}} c^\dagger_{\boldsymbol{k}} c_{\boldsymbol{k}} + \varepsilon^h_{\boldsymbol{k}} h^\dagger_{-\boldsymbol{k}} h_{-\boldsymbol{k}}] \tag{5}$$

$$\hat{N}_e = \sum_{\boldsymbol{k}} c^\dagger_{\boldsymbol{k}} c_{\boldsymbol{k}} \qquad \hat{N}_e = \sum_{\boldsymbol{k}} h^\dagger_{-\boldsymbol{k}} h_{-\boldsymbol{k}} \tag{6}$$

$$\hat{n}^e_{\boldsymbol{kp}} = c^\dagger_{\boldsymbol{k+p}} c_{\boldsymbol{k}} \qquad \hat{n}^h_{\boldsymbol{kp}} = h_{-\boldsymbol{k}-\boldsymbol{p}} h^\dagger_{\boldsymbol{k}} \tag{7}$$

$$\hat{\nu}_{\boldsymbol{q}} = a^\dagger_{\boldsymbol{q}} a_{\boldsymbol{q}} \tag{8}$$

where $c(c^\dagger)$, $h(h^\dagger)$ and $a(a^\dagger)$ are as usual annihilation (creation) operators in electron, hole and LO-phonon states respectively ($\boldsymbol{k}$, $\boldsymbol{p}$, $\boldsymbol{q}$ run over the Brillouin zone). Moreover, the effective mass approximation is used and Coulomb interaction is dealt with in the random phase approximation, and then $\varepsilon^e_{\boldsymbol{k}} = E_G + \hbar^2|\boldsymbol{k}|^2/2m_e$ and $\varepsilon^h_{\boldsymbol{k}} = \hbar^2|\boldsymbol{k}|^2/2m_h$. Finally, H_B is the Hamiltonian of the lattice vibrations different from the LO one. We write for the NESOM Lagrange multipliers associated with the quantities of equation (4)

$$\{\beta_c(t), -\beta_c(t)\mu_e(t), -\beta_c(t)\mu_h(t), F^e_{\boldsymbol{kp}}(t), F^h_{\boldsymbol{kp}}(t), \hbar\omega_{\boldsymbol{q}}\beta_{\boldsymbol{q}}(t), \varphi_{\boldsymbol{q}}(t), \varphi^*_{\boldsymbol{q}}(t), \beta_0\} \tag{9}$$

where μ_e and μ_h are the quasichemical potentials for electrons and for holes respectively; we write $\beta_c(t) = 1/k_B T^*_c(t)$ introducing the carriers' quasitemperature T^*_c; $\beta_{\boldsymbol{q}}(t) = 1/k_B T^*_{\boldsymbol{q}}(t)$ introducing the LO-phonon quasitemperature per mode ($\omega_{\boldsymbol{q}}$ is the dispersion relation) [10, 26, 27], $\beta_0 = 1/k_B T_0$ with T_0 the temperature of the thermal reservoir. We indicate the corresponding macrovariables, that is, those which define the nonequilibrium thermodynamic Gibbs space as

$$\{E_c(t), n(t), n(t), n^e_{\boldsymbol{kp}}(t), n^h_{\boldsymbol{kp}}(t), \nu_{\boldsymbol{q}}(t), \langle a_{\boldsymbol{q}} \mid t\rangle, \langle a^\dagger_{\boldsymbol{q}} \mid t\rangle = \langle a_{\boldsymbol{q}} \mid t\rangle^*, E_B\} \tag{10}$$

which are the statistical average of the quantities of equation (4), that is

$$E_c(t) = \mathrm{Tr}\{\hat{H}_c \rho_\varepsilon(t)\} \tag{11}$$

$$n(t) = \mathrm{Tr}\{\hat{N}_{e(h)} \rho_\varepsilon(t)\} \tag{12}$$

etc, where $\rho_\varepsilon(t)$ is the nonequilibrium statistical operator (Zubarev's approach is used throughout) [1–7], 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 1 for simplicity. The statistical operator $\rho_\varepsilon(t)$ is determined by the auxiliary operator $\bar{\rho}(t, 0)$ (sometimes called the 'coarse-grained part' of $\rho_\varepsilon(t)$) [5–8], which in the present case is given by

$$\begin{aligned}\bar{\rho}(t,0) = \exp\Bigg\{ & -\phi(t) - \beta_c(t)[\hat{H}_c - \mu_e(t)\hat{N}_e - \mu_h(t)\hat{N}_h] \\ & - \sum_{\boldsymbol{kp}} [F^e_{\boldsymbol{kp}}(t)\hat{n}^e_{\boldsymbol{kp}}(t) + F^h_{\boldsymbol{kp}}(t)\hat{n}^h_{\boldsymbol{kp}}(t)] \\ & - \sum_{\boldsymbol{q}} [\beta_{\boldsymbol{q}}(t)\hbar\omega_{\boldsymbol{q}}\hat{\nu}_{\boldsymbol{q}} + \varphi_{\boldsymbol{q}}(t)a_{\boldsymbol{q}} + \varphi^*_{\boldsymbol{q}}(t)a^\dagger_{\boldsymbol{q}}] - \beta_0 H_B \Bigg\}\end{aligned} \tag{13}$$

where $\phi(t)$ ensures its normalization, playing the role of a kind of logarithm of a nonequilibrium partition function.

The next step is to derive the equations of evolution for the basic variables that characterize the nonequilibrium macroscopic state of the system, and from them the evolution of the Lagrange multipliers (or intensive nonequilibrium thermodynamic variables). We resort to the generalized nonlinear quantum kinetic theory that the NESOM provides [4–8, 17] in the so-called second-order approximation in relaxation theory [17]. This is an approximation

which retains only two-body collisions but with memory being neglected, consisting in the Markovian limit of the theory [28]. A relevant point needs to be discussed here, namely the validity of the Markovian approximation for dealing with experiments with ultrafast resolution. This question is closely related to the choice of the basic set of basic variables: as noticed by Zwanzig [29], to use a Markovian approximation for description of relaxation processes in shorter and shorter times requires an ever expanding set of basic variables. The present case of the photoinjected plasma in semiconductors was discussed in [10] and [18]. For resolution times in the tens of femtoseconds it is necessary to introduce a complete description in terms of single particles, that is introducing the complete set of Dirac–Landau–Wigner dynamical operators. However when dealing with times involving hundreds of femtoseconds, as in the case we are considering here, the internal thermalization of the carriers has occurred and the diagonal terms of Dirac–Landau–Wigner single particle matrices (statistical averages of the corresponding dynamical operators), which are the populations, can be expressed in a reduced description involving the carriers' quasitemperature and quasichemical potentials as we have done here. The good agreement of the theory and experiment, here and in other applications, appears to validate the argument.

Let us first consider the equations of evolution for the basic homogeneous variables $E_c(t)$ and $n(t)$, namely [10]

$$\frac{\mathrm{d}}{\mathrm{d}t}E_c(t) = E'_{cL}(t) + E'_{cR}(t) + E'_{cph}(t) + E'_{cD}(t) + \mathcal{N}_c(t) \tag{14}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}n(t) = n'_L(t) + n'_R(t) + n'_D(t) + \mathcal{N}_n(t) \tag{15}$$

where

$$E'_{cL}(t) = \frac{2\pi}{\hbar}\theta(t_L - t)\sum_{\boldsymbol{k}}|G_L|^2(\varepsilon^e_{\boldsymbol{k}} + \varepsilon^h_{\boldsymbol{k}})\nu_L[1 - \bar{f}^h_{\boldsymbol{k}}(t) - \bar{f}^e_{\boldsymbol{k}}(t)]\delta(\varepsilon^e_{\boldsymbol{k}} + \varepsilon^h_{\boldsymbol{k}} - \hbar\omega_L) \tag{16}$$

$$n'_L(t) = \frac{2\pi}{\hbar}\theta(t_L - t)\sum_{\boldsymbol{k}}|G_L|^2\nu_L[1 - \bar{f}^h_{\boldsymbol{k}}(t) - \bar{f}^e_{\boldsymbol{k}}(t)]\delta(\varepsilon^e_{\boldsymbol{k}} + \varepsilon^h_{\boldsymbol{k}} - \hbar\omega_L) \tag{17}$$

are source terms implying in pumping effects from the laser; G_L is the matrix element of the carrier–laser field interaction for interband transitions, ω_L the photon frequency, θ is the Heaviside step function with t_L being the duration of the pumping laser pulse and ν_L is the number of photons per unit volume in the laser beam, and we recall that the dipolar approximation is used as usual (that is the photon wavenumber is taken as zero implying the so-called vertical transitions);

$$E'_{cR}(t) = -\frac{2\pi}{\hbar}\sum_{\boldsymbol{kp}}|G_R(\boldsymbol{p})|^2(\varepsilon^e_{\boldsymbol{k}} + \varepsilon^h_{\boldsymbol{k}})\bar{f}^e_{\boldsymbol{k}}(t)\bar{f}^h_{\boldsymbol{k}-\boldsymbol{p}}(t)\delta(\varepsilon^e_{\boldsymbol{k}} + \varepsilon^h_{\boldsymbol{k}-\boldsymbol{p}} - \hbar\omega_{R\boldsymbol{p}}) \tag{18}$$

$$n'_R(t) = -\frac{2\pi}{\hbar}\sum_{\boldsymbol{kp}}|G_R(\boldsymbol{p})|^2\bar{f}^e_{\boldsymbol{k}}(t)\bar{f}^h_{\boldsymbol{k}-\boldsymbol{p}}(t)\delta(\varepsilon^e_{\boldsymbol{k}} + \varepsilon^h_{\boldsymbol{k}-\boldsymbol{p}} - \hbar\omega_{R\boldsymbol{p}}) \tag{19}$$

are relaxation terms associated with recombination effects, $G_R(\boldsymbol{p})$ is the matrix element of the carrier–radiation-recombination field interaction, $\omega_{R\boldsymbol{p}}$ the corresponding photon frequencies, and we recall that we are keeping only spontaneous recombination contributions with $\boldsymbol{p}$ being the wavevector of the photon in the luminescent radiation;

$$\begin{aligned}E'_{cph}(t) = \frac{2\pi}{\hbar}\sum_{\boldsymbol{kq}a}|C_a(\boldsymbol{q})|^2\varepsilon^a_{\boldsymbol{k}}\{&[(\nu_{\boldsymbol{q}}(t)+1)\bar{f}^a_{\boldsymbol{k}+\boldsymbol{q}}(t)(1-\bar{f}^a_{\boldsymbol{k}}(t)) - \nu_{\boldsymbol{q}}(t)(1-\bar{f}^a_{\boldsymbol{k}+\boldsymbol{q}}(t))\bar{f}^a_{\boldsymbol{k}}(t)]\\ &\times\delta(\varepsilon^a_{\boldsymbol{k}+\boldsymbol{q}} - \varepsilon^a_{\boldsymbol{k}} - \hbar\omega_{\boldsymbol{q}}) - [(\nu_{\boldsymbol{q}}(t)+1)\bar{f}^a_{\boldsymbol{k}}(t)(1-\bar{f}^a_{\boldsymbol{k}+\boldsymbol{q}}(t))\\ &-\nu_{\boldsymbol{q}}(t)\bar{f}^a_{\boldsymbol{k}+\boldsymbol{q}}(t)(1-\bar{f}^a_{\boldsymbol{k}}(t))]\delta(\varepsilon^a_{\boldsymbol{k}+\boldsymbol{q}} - \varepsilon^a_{\boldsymbol{k}} + \hbar\omega_{\boldsymbol{q}})\}\end{aligned} \tag{20}$$

where a in the sum denotes contribution from electrons ($a = e$) as well as from holes ($a = h$). $E'_{cph}(t)$ is the rate of relaxation of the carriers' energy towards the lattice, and $C(\boldsymbol{q})$ the matrix element of Fröhlich interaction given by

$$C_a(\boldsymbol{q}) = -\mathrm{i}\frac{\sqrt{2\pi}}{|\boldsymbol{q}|}e(\varepsilon_\infty^{-1} - \varepsilon_0^{-1})^{1/2}(\hbar\omega_{\boldsymbol{q}}^{TO})^{1/2} \tag{21}$$

where $\omega_{\boldsymbol{q}}^{TO}$ is the frequency of TO phonons and ε_0 and ε_∞ are the static and optical dielectric constants;

$$E'_{cD}(t) = -\frac{E_c(t)}{\tau_{cD}(t)} \tag{22}$$

$$n'_D(t) = -\frac{n(t)}{\tau_{nD}(t)} \tag{23}$$

are terms of diffusion (out of the active volume of the sample, once we consider uniform illumination in a half-spherical region and take into account Fick's and Fourier's laws for matter and heat diffusion), where τ_{cD} and τ_{nD} are ambipolar diffusion times, and finally

$$\begin{aligned}\mathcal{N}_c(t) = {} & \frac{1}{\hbar}\theta(t_L - t)\sum_{\boldsymbol{kQ}}|G_L|^2(\varepsilon_{\boldsymbol{k}}^e + \varepsilon_{\boldsymbol{k}}^h)n_{\boldsymbol{kQ}}^e(t)n_{\boldsymbol{k}-\boldsymbol{k}_L,\boldsymbol{Q}}^{h*}(t)\left\{\pi\delta(\hbar\Omega_{cL}(\boldsymbol{k},\boldsymbol{Q})) + \frac{1}{\mathrm{i}\hbar\Omega_{cL}(\boldsymbol{k},\boldsymbol{Q})}\right\} \\ & + \sum_{\boldsymbol{kQp}}|G_R(\boldsymbol{p})|^2(\varepsilon_{\boldsymbol{k}}^e + \varepsilon_{\boldsymbol{k}}^h)n_{\boldsymbol{kQ}}^e(t)n_{\boldsymbol{k}-\boldsymbol{p},\boldsymbol{Q}}^{h*}(t) \\ & \times\left\{\pi\delta(\hbar\Omega_{cR}(\boldsymbol{k},\boldsymbol{Q},\boldsymbol{p})) + \frac{1}{\mathrm{i}\hbar\Omega_{cR}(\boldsymbol{k},\boldsymbol{Q},\boldsymbol{p})}\right\} \\ & + \sum_{\boldsymbol{kqQ}a}|C(\boldsymbol{q})|^2(\varepsilon_{\boldsymbol{k}+\boldsymbol{Q}}^a - \varepsilon_{\boldsymbol{k}}^a)n_{\boldsymbol{k}+\boldsymbol{q},\boldsymbol{Q}}^a(t)n_{\boldsymbol{kQ}}^{a*}(t) \\ & \times\left\{\pi\delta(\hbar\Omega_{cph}(\boldsymbol{k},\boldsymbol{Q},\boldsymbol{q})) + \frac{1}{\mathrm{i}\hbar\Omega_{cph}(\boldsymbol{k},\boldsymbol{Q},\boldsymbol{q})}\right\} + \mathrm{CC}\end{aligned} \tag{24}$$

and

$$\begin{aligned}\mathcal{N}_n(t) = {} & \frac{1}{\hbar}\theta(t_L - t)\sum_{\boldsymbol{kQ}}|G_L|^2 n_{\boldsymbol{kQ}}^e(t)n_{\boldsymbol{k}-\boldsymbol{k}_L,\boldsymbol{Q}}^{h*}(t)\left\{\pi\delta(\hbar\Omega_{cL}(\boldsymbol{k},\boldsymbol{Q})) + \frac{1}{\mathrm{i}\hbar\Omega_{cL}(\boldsymbol{k},\boldsymbol{Q})}\right\} \\ & + \sum_{\boldsymbol{kQp}}|G_R(\boldsymbol{p})|^2 n_{\boldsymbol{kQ}}^e(t)n_{\boldsymbol{k}-\boldsymbol{p},\boldsymbol{Q}}^{h*}(t)\left\{\pi\delta(\hbar\Omega_{cR}(\boldsymbol{k},\boldsymbol{Q},\boldsymbol{p})) + \frac{1}{\mathrm{i}\hbar\Omega_{cR}(\boldsymbol{k},\boldsymbol{Q},\boldsymbol{p})}\right\} + \mathrm{CC}\end{aligned} \tag{25}$$

where

$$\hbar\Omega_{cL}(\boldsymbol{k},\boldsymbol{Q}) = \varepsilon_{\boldsymbol{k}+\boldsymbol{Q}}^e + \varepsilon_{\boldsymbol{k}+\boldsymbol{Q}-\boldsymbol{k}_L}^h - \hbar\omega_L \tag{26a}$$

$$\hbar\Omega_{cR}(\boldsymbol{k},\boldsymbol{Q},\boldsymbol{p}) = \varepsilon_{\boldsymbol{k}+\boldsymbol{Q}}^e + \varepsilon_{\boldsymbol{k}+\boldsymbol{Q}-\boldsymbol{p}}^h - \hbar\omega_{R\boldsymbol{p}} \tag{26b}$$

$$\hbar\Omega_{cph}(\boldsymbol{k},\boldsymbol{Q},\boldsymbol{q}) = \varepsilon_{\boldsymbol{k}+\boldsymbol{Q}+\boldsymbol{q}}^a - \varepsilon_{\boldsymbol{k}+\boldsymbol{Q}}^a - \hbar\omega_{\boldsymbol{q}}. \tag{26c}$$

It can be noticed that the collision operators of equations (16) to (20) can be identified with the golden rule of quantum mechanics averaged over the nonequilibrium ensemble at each time t. In these equations are present the populations

$$\nu_{\boldsymbol{q}} = \mathrm{Tr}\{\hat{\nu}_{\boldsymbol{q}}\bar{\rho}(t,0)\} = [\exp\{\beta_{\boldsymbol{q}}(t)\hbar\omega_{\boldsymbol{q}}\} - 1]^{-1} - |\langle a_{\boldsymbol{q}} \mid t\rangle|^2 \tag{27a}$$

$$\bar{f}_{\boldsymbol{k}}^e(t) = \mathrm{Tr}\{c_{\boldsymbol{k}}^\dagger c_{\boldsymbol{k}}\bar{\rho}(t,0)\} \qquad \bar{f}_{\boldsymbol{k}}^h(t) = \mathrm{Tr}\{h_{-\boldsymbol{k}}^\dagger h_{-\boldsymbol{k}}\bar{\rho}(t,0)\} \tag{27b}$$

with $\bar{\rho}$ being the auxiliary operator of equation (13). The terms $\mathcal{N}$ are additional contributions associated with the plasma wave oscillations; other contributions have cancelled out, including

those containing the amplitudes of the coherent phonons. Furthermore, we call attention to the fact the contributions in equations (16) and (17) can be rewritten as

$$E'_{cL}(t) = \alpha(\omega_L) I_L \qquad n'_L(t) = \alpha(\omega_L) I_L / \hbar\omega_L \tag{28}$$

where α is the one-photon absorption coefficient at the frequency ω_L of the laser photons, and I_L is the power intensity of the laser beam.

The equation of evolution for the phonon populations is

$$\frac{\mathrm{d}}{\mathrm{d}t} \nu_{\boldsymbol{q}}(t) = J^{(1)}_{\boldsymbol{q}}(t) + J^{(2)}_{\boldsymbol{q}}(t) \tag{29}$$

where

$$J^{(1)}_{\boldsymbol{q}}(t) = -\frac{1}{\mathrm{i}\hbar} \sum_{ka} (C_a(\boldsymbol{q}) n^a_{k\boldsymbol{q}} \langle a_{\boldsymbol{q}} \mid t\rangle - C^*_a(\boldsymbol{q}) n^{a*}_{k\boldsymbol{q}} \langle a_{\boldsymbol{q}} \mid t\rangle^*) \tag{30}$$

and

$$J^{(2)}_{\boldsymbol{q}}(t) = \frac{2\pi}{\hbar} \sum_{ka} |C_a(\boldsymbol{q})|^2 [(\nu_{\boldsymbol{q}}(t) + 1) \bar{f}^a_{k+q}(t)(1 - \bar{f}^a_k(t)) - \nu_{\boldsymbol{q}}(t)(1 - \bar{f}^a_{k+q}(t)) \bar{f}^a_k(t)] \times \delta(\varepsilon^a_{k+q} - \varepsilon^a_k - \hbar\omega_q). \tag{31}$$

In equation (31) $J^{(2)}_{\boldsymbol{q}}(t)$ is the collision operator in the Markovian approach to the NESOM kinetic theory, which in this particular case corresponds to the golden rule averaged over the nonequilibrium ensemble. It can be noticed that, different to the case of equations (14) and (15), the right-hand side of equation (31) does not contain the plasma or phonon amplitudes explicitly—they are implicitly contained in the populations as we will see below.

On the basis of equations (14), (15) and (29) we can derive equations of evolution for the Lagrange multipliers $\beta_c(t)$, $\mu_{e(h)}(t)$ and $\beta_{\boldsymbol{q}}(t)$. But for that purpose we need to notice first the important information that the experimental data tell us, namely, that the modulation effect produced by the phonons is very small (one part in 10^7), and also very small are the amplitudes of the carrier charge density (plasma oscillations). Hence, from now on we keep only linear terms in $\langle a_{\boldsymbol{q}} \mid t\rangle$ and $n^a_{k\boldsymbol{q}}(t)$ (or $\varphi_{\boldsymbol{q}}(t)$ and $F^a_{k\boldsymbol{q}}(t)$): since in the equations of evolution for the energy, $E_c(t)$, and density, $n(t)$, and the phonon populations, $\nu_{\boldsymbol{q}}(t)$, the contributions in the above amplitudes are quadratic (as shown by equation (27*a*)) they are neglected. Hence, we do have a closed system of equations to derive the evolution of the carriers' quasitemperature, the carriers' quasichemical potential, and the hot phonons' quasitemperature per mode (in this case there occurs the so-called hot phonon temperature overshoot phenomenon [25, 30]). The time evolution of the reflectivity is, of course, governed by the evolution of these quantities.

The time evolution of the carriers' quasitemperature and concentration, as well as that of the hot phonons' quasitemperature per mode, have been calculated in NESOM for the case of several experiments obtaining a very good agreement between theory and experimental data [10]. We notice the relevant fact that the kinetics of evolution is strongly influenced by the experimental protocol: in particular, very short exciting pulses are followed by a very rapid variation in the evolution of the quasitemperature, while long exciting pulses imply a slower evolution with the presence of a near plateau experimentally detected in several experiments. Moreover, the relevance of ambipolar diffusion effects in the ten picosecond time scale and the hot phonon temperature overshoot phenomenon are evidenced [25, 30]. In figure 1 we show the expected evolution (after solving equations (14) and (15)) of the carriers' quasitemperature in the conditions of the experiment of Cho *et al* [11]. It can be noticed that the quasitemperature $T^*_c(t)$ rapidly decreases from its initial value of nearly 5800 K to roughly 800 K two picoseconds after the end of the exciting laser pulse.

After having taken account of the equations for the homogeneous variables, we consider the equations of evolution for the phonon amplitudes and carriers' charge-density amplitude, which are

$$\frac{\partial}{\partial t}\langle a_{\boldsymbol{q}} \mid t\rangle + \mathrm{i}\omega_{\boldsymbol{q}}\langle a_{\boldsymbol{q}} \mid t\rangle = \frac{1}{\hbar}C_a(\boldsymbol{q})n(\boldsymbol{q} \mid t) - \frac{1}{\tau_{\boldsymbol{q}}}\langle a_{\boldsymbol{q}} \mid t\rangle \tag{32}$$

and

$$\frac{\partial}{\partial t}n^a_{\boldsymbol{kq}}(t) - \mathrm{i}\omega^a_{\boldsymbol{kq}}n^a_{\boldsymbol{kq}}(t) = -\frac{\mathrm{i}}{\hbar}[\bar{f}^a_{\boldsymbol{k}+\boldsymbol{q}}(t) - \bar{f}^a_{\boldsymbol{k}}(t)]\{2V(\boldsymbol{q})n(\boldsymbol{q} \mid t) - C_a(\boldsymbol{q})[\langle a_{\boldsymbol{q}} \mid t\rangle - \langle a^{\dagger}_{-\boldsymbol{q}} \mid t\rangle]$$
$$-\delta_{\boldsymbol{q},\boldsymbol{Q}}\theta(t_L - t)\Lambda^a_L(\boldsymbol{k},\boldsymbol{Q})[\langle b_{\boldsymbol{Q}} \mid t\rangle - \langle b^{\dagger}_{-\boldsymbol{Q}} \mid t\rangle]\} - \frac{1}{\tau^a_{\boldsymbol{kq}}(t)}n^a_{\boldsymbol{kq}}(t) \tag{33}$$

where $\boldsymbol{Q}$ is the wavevector of the photons in the laser beam; the last term on the right-hand side of equation (32) accounts for the delay of the phonon amplitude through relaxation to the thermal bath; similarly, the last term on the right-hand side of equation (33) accounts for the decay of the variable involving Landau damping and relaxation to the lattice (the detailed structure of the two relaxation times in both equations is not necessary to be made explicit for the purpose of this communication). The second term on the left of equation (32) arises out of the term $J^{(0)}$ in the kinetic equations, while the first term on the right of equation (32) comes from $J^{(1)}$ and the carrier–phonon interaction [5, 8, 17]. In equation (33) the second term on the left is also originated in $J^{(0)}$, while the first three terms on the right are of the type $J^{(1)}$, arising out of Coulomb interaction with matrix element $V(\boldsymbol{Q})$; Fröhlich interaction with matrix element $C_a(\boldsymbol{q})$; the interaction for intraband transitions (with matrix element $\Lambda^a_L(\boldsymbol{k},\boldsymbol{Q})$) of each type of carrier with the laser electromagnetic field, and this term—arising out of $J^{(1)}$—accounts for the force exerted by the electric field of the laser, as shown below. Moreover, $\hbar\omega^a_{\boldsymbol{kq}} = \varepsilon^a_{\boldsymbol{k}+\boldsymbol{q}} - \varepsilon^a_{\boldsymbol{k}}$; b ($b^{\dagger}$) are annihilation (creation) operator for photons in the laser radiation field and

$$n(\boldsymbol{q} \mid t) = \sum_{\boldsymbol{k}}(n^e_{\boldsymbol{kq}}(t) + n^h_{\boldsymbol{kq}}(t)) \tag{34}$$

is (in units of $-e$) the carrier charge density Fourier amplitude (in the motion of the collective plasma wave).

We can notice that according to equation (32) the phonon amplitudes are enhanced by the presence of the source term on the right which is directly proportional to the carrier charge density amplitude. But, of fundamental relevance is the fact that in the equation of evolution, equation (33), the third term between curly brackets on the right, resulting from the coupling of the carriers with the electric field of the pumping laser radiation, is null except for the particular case when $\boldsymbol{q}$ is the photon wavevector $\boldsymbol{Q}$. We recall, first, that in this case the averaged amplitudes of the photon field, $\langle b_{\boldsymbol{Q}} \mid t\rangle$, are not null because of the property of coherence of the laser photons, and, second, they are related to the electrical field $E(\boldsymbol{Q}, t)$ in the laser beam by the expression [31]

$$E(\boldsymbol{Q}, t) = (2\pi\hbar\omega_{LQ})^{1/2}\mathrm{i}(\langle b_{\boldsymbol{Q}} \mid t\rangle - \langle b^{\dagger}_{-\boldsymbol{Q}} \mid t\rangle) \tag{35}$$

and we recall that the volume is taken equal to 1.

These are quite relevant results for the interpretation of the phenomenon. In summary, the amplitudes of the coherent phonons, $\langle a_{\boldsymbol{q}} \mid t\rangle$, according to equation (32) are pumped by the amplitudes (at the same wavevector $\boldsymbol{q}$) of the charge oscillations, $n(\boldsymbol{q} \mid t)$. But according to equation (33), the latter are in general very small (plasma oscillations with strong Landau damping), except the one with wavevector $\boldsymbol{Q}$ (the one of the laser radiation field) which is strongly pumped because of the coupling with the coherent photons in the laser electric field

of equation (35). Therefore, the coherent phonon amplitude for wavevector $\boldsymbol{Q}$, i.e. $\langle a_{\boldsymbol{Q}} \mid t\rangle$, acquire large values, while the others are practically negligible.

For given initial conditions at, say, $t = 0$, equation (33) can be rewritten in the form of an integral equation via the method of the *matriçant* [32], namely

$$n^a_{\boldsymbol{kq}}(t) = \Phi^a_{\boldsymbol{kq}}(t)n^a_{\boldsymbol{kq}}(0) + \Phi^a_{\boldsymbol{kq}}(t)\int_0^t \mathrm{d}t'[\Phi^a_{\boldsymbol{kq}}(t')]^{-1}\zeta^a_{\boldsymbol{kq}}(t') \tag{36}$$

$$\Phi^a_{\boldsymbol{kq}}(t) = \exp\left\{\int_0^t \mathrm{d}t'\left(\mathrm{i}\omega^a_{\boldsymbol{kq}} - \frac{1}{\tau^a_{\boldsymbol{kq}}(t')}\right)\right\} \tag{37}$$

$$\hbar\zeta^a_{\boldsymbol{kq}}(t) = [\tilde{f}^a_{\boldsymbol{k+q}}(t) - \tilde{f}^a_{\boldsymbol{k}}(t)]\Big\{-2\,\mathrm{i}V(\boldsymbol{q})n(\boldsymbol{q}\mid t) + \mathrm{i}C_a(\boldsymbol{q})[\langle a_{\boldsymbol{q}}\mid t\rangle - \langle a^{\dagger}_{-\boldsymbol{q}}\mid t\rangle]$$
$$+\delta_{q,Q}\left(\frac{V}{2\pi\hbar\omega}\right)^{1/2}\theta(t_L - t)\Lambda^a_L(\boldsymbol{k},\boldsymbol{Q})E(\boldsymbol{Q},t)\Big\} \tag{38}$$

and where the populations with a tilde over f are those of equation (27) after in the coarse-grained distribution $\bar{\rho}$ of equation (13) the inhomogeneous terms are neglected (i.e. taking φ_q and $F_{\boldsymbol{kq}}$ as null); this is done, as already noticed, because those terms give contributions quadratic in the weak inhomogeneities. From a direct calculation we obtain that

$$\tilde{f}^a_{\boldsymbol{k}}(t) = [1 + \exp\{\beta_c(t)(\varepsilon^a_{\boldsymbol{k}} - \mu_a(t))\}]^{-1}. \tag{39}$$

In equation (36) the first term on the right-hand side is simply the individual quasiparticle damped oscillation at the Bohr frequency $\hbar\omega_{\boldsymbol{kq}} = \varepsilon_{\boldsymbol{k+q}} - \varepsilon_{\boldsymbol{k}}$, and the second term has the contributions associated with quantity ζ, namely, (1) collective plasma oscillation, (2) coupling to the phonon field and (3) the coupling with the source arising out of the interaction with the radiation field of the laser (the coherent photons). On the other hand, we can similarly rewrite equation (32) as

$$\langle a_{\boldsymbol{q}}\mid t\rangle = \Psi_q(t)\langle a_{\boldsymbol{q}}\mid 0\rangle + \Psi_q(t)\int_0^t \mathrm{d}t'[\Psi_q(t')]^{-1}\sum_a \frac{1}{\hbar}C_a(\boldsymbol{q})n^a(\boldsymbol{q}\mid t') \tag{40}$$

where

$$\Psi_q(t) = \exp\left\{-\int_0^t \mathrm{d}t'\left(\mathrm{i}\omega_q + \frac{1}{\tau_q(t')}\right)\right\}. \tag{41}$$

In this equation (40) the first term on the right-hand side is the simple oscillation of the amplitude with frequency ω_q and decay time τ_q, while the second is the one associated with the coupling with the carrier's plasma oscillation.

After this analysis of the nonequilibrium (dissipative) state of the system, let us return to the calculation of the reflectivity, in which expression, as given by equation (1), we introduce the relation of the index of refraction with the complex dielectric function (cf equation (2)), and the latter is written in terms of the Green functions of [8]. Next, we separate out from the expression thus obtained for the reflectivity the part that involves the influence of the coherent photons, which we call $\delta R(t)$, from the rest to be called $R^0(t)$, as described in appendix A, to obtain that

$$\frac{\delta R(\omega,\boldsymbol{Q}\mid t)}{R^0(\omega,\boldsymbol{Q}\mid t)} = A(\omega,\boldsymbol{Q}\mid t)\sum_a \delta L_a(\omega,\boldsymbol{Q}\mid t) \tag{42}$$

where A is a coefficient given in equation (A14), and, according to equation (A13),

$$\delta L_a(\omega,\boldsymbol{Q}\mid t) = \sum_{\boldsymbol{kq}} K_a(\omega,\boldsymbol{Q};\boldsymbol{k},\boldsymbol{q}\mid t)n^a_{\boldsymbol{kq}}(t)\langle a_{\boldsymbol{q}}\mid t\rangle + \mathrm{cc} \tag{43}$$

with K_a described in appendix A.

Inspection of equations (42) and (43) tells us that the reflectivity is modulated in time by the term of equation (43), that is, the effect of the plasma–phonon coupling, while the remaining time dependence—contained in the coefficient A—is the one associated with the time evolution of the carriers' quasitemperature and concentration. The modulating effect in equation (42) is evidenced by equations (36) and (40). Finally, we recall the quite important fact that the product of $\langle a_{\boldsymbol{q}} \mid t\rangle$ and $n^a_{k\boldsymbol{q}}(t)$ in equation (43) is very small except for the particular wavevector $\boldsymbol{q} = \boldsymbol{Q}$, that is, the wavevector of the laser radiation field, and then

$$\delta L_a(\omega, \boldsymbol{Q} \mid t) \simeq \sum_{\boldsymbol{k}} K_a(\omega, \boldsymbol{Q}; \boldsymbol{k}, \boldsymbol{Q} \mid t) n^a_{k\boldsymbol{Q}}(t) \langle a_{\boldsymbol{Q}} \mid t\rangle + \text{cc}. \tag{44}$$

Consequently, the reflectivity is modulated by both the phonon and the carrier-density amplitudes, with both coupled together via the dominant Fröhlich interaction. Therefore we must expect a modulation consisting of six contributions: two arise from the coupling of LO phonons, with frequency $\omega_{\boldsymbol{Q}}$, and quasi-particle excitations (electrons and holes) oscillating with Bohr's frequency $\hbar\omega^a_{k\boldsymbol{Q}} = \varepsilon^a_{k+\boldsymbol{Q}} - \varepsilon^a_k \simeq \boldsymbol{Q}\cdot\boldsymbol{k}/2m_a$ in the effective mass approximation. Two others are the hybrid optical plasma–LO phonon excitations, with the dispersion relation [33, 34]

$$\omega^2_{\pm}(\boldsymbol{Q}) = \tfrac{1}{2}[\omega^2_{\boldsymbol{Q}} + \omega^2_{pl}(\boldsymbol{Q})] \pm [\tfrac{1}{4}(\omega^2_{\boldsymbol{Q}} + \omega^2_{pl}(\boldsymbol{Q}))^2 - \omega^2_{\boldsymbol{Q}}\omega^2_{pl}(\boldsymbol{Q})]^2 \tag{45}$$

where $\omega_{pl}(\boldsymbol{Q})$ is the optical plasmon dispersion relation

$$\omega_{pl}(\boldsymbol{Q}) = \omega_{pl} + \tfrac{3}{2}v^2_{th}|\boldsymbol{Q}|^2 \tag{46}$$

in the semiclassical limit, $\omega^2_{pl} = 4\pi ne^2/\varepsilon_0 m_x$, m_x is the excitonic mass ($m_x^{-1} = m_e^{-1} + m_h^{-1}$) and v_{th} is the thermal velocity given by $m_x v^2_{th} = k_B T^*_c$. Finally, the other two are the hybrid acoustical plasma–LO phonon excitations, similar to that of equation (45), but where the acoustical plasma dispersion relation $\omega_{pl,A}(\boldsymbol{Q}) = s_A|\boldsymbol{Q}|$ now enters, with s_A being the group velocity of these plasma waves.

We proceed in the next section to an analysis of this result for the particular case of the experiment of Cho *et al* in [11].

3. Comparison with experiment

To compare with the experimental results reported in [11], we introduce in equation (44) the results of equations (36) and (40), to obtain

$$\begin{aligned}\delta L_a(\omega, \boldsymbol{Q} \mid t) = \sum_{\boldsymbol{k}} K_a(\omega, \boldsymbol{Q}; \boldsymbol{k}, \boldsymbol{Q}) \Phi^a_{k\boldsymbol{Q}}(t) \left\{ n^a_{k\boldsymbol{Q}}(0) + \int_0^t \mathrm{d}t' [\Phi^a_{k\boldsymbol{Q}}(t')]^{-1} \xi^a_{k\boldsymbol{Q}}(t') \right\} \Psi_{\boldsymbol{Q}}(t) \\ \times \left\{ \langle a_{\boldsymbol{Q}} \mid 0\rangle + \int_0^t \mathrm{d}t' [\Psi_{\boldsymbol{Q}}(t')]^{-1} \sum_a \frac{1}{\hbar} C_a(\boldsymbol{Q}) n^a_{k\boldsymbol{Q}}(t') \right\}\end{aligned} \tag{47}$$

which demonstrates the existence of a multiple modulation of the reflectivity coefficient. As already noticed this is a combination of all six possible coupled LO phonon and carriers' oscillations, and then the modulation of the reflectivity coefficient is of the form

$$\begin{aligned}\frac{\delta R(t)}{R^0(t)} \simeq \sum_{ka} \mathcal{B}(\boldsymbol{k}, \boldsymbol{Q} \mid t) \exp\{-\mathrm{i}(\omega_{\boldsymbol{Q}} + \omega^a_{k\boldsymbol{Q}})t - (\gamma_{\boldsymbol{Q}}(t) + \gamma_{k\boldsymbol{Q}}(t))\} + \text{cc} \\ + \mathcal{O}_+(\boldsymbol{Q} \mid t) \exp\{-\mathrm{i}\omega_+(\boldsymbol{Q})t - \gamma_+(\boldsymbol{Q} \mid t)\} + \text{cc} + \mathcal{O}_-(\boldsymbol{Q} \mid t) \\ \times \exp\{-\mathrm{i}\omega_-(\boldsymbol{Q})t - \gamma_-(\boldsymbol{Q} \mid t)\} + \text{cc} + \mathcal{A}_+(\boldsymbol{Q} \mid t) \\ \times \exp\{-\mathrm{i}\omega_{A+}(\boldsymbol{Q})t - \gamma_{A+}(\boldsymbol{Q} \mid t)\} + \text{cc} + \mathcal{A}_-(\boldsymbol{Q} \mid t) \\ \times \exp\{-\mathrm{i}\omega_{A-}(\boldsymbol{Q})t - \gamma_{A-}(\boldsymbol{Q} \mid t)\} + \text{cc}\end{aligned} \tag{48}$$

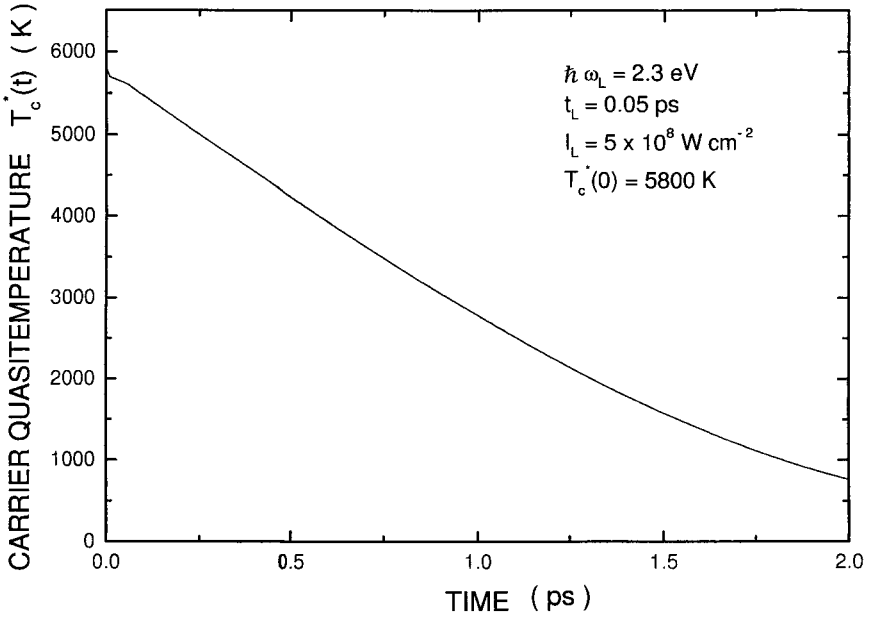

Figure 1. Calculated evolution of the carriers' quasitemperature in the conditions of the experiment by Cho *et al* in [11].

where $\mathcal{B}$, $\mathcal{O}$ and $\mathcal{A}$ are amplitudes whose detailed expressions are not necessary to make explicit for our purposes here, but we recall that their dependence on time (and then that of $R^0(t)$ and $\delta R(t)$) arises out of the evolution in time of the carriers' quasitemperature and of the concentration. However, in the subpicosecond scale used in the measurements the carriers' concentration is nearly constant, but the quasitemperature, which has an initial value of roughly 5800 K because of the very short and intense exciting pulse, has during the measurement of the modulation phenomenon a rapid decrease, and in the given interval during which the measurements are performed, it roughly varies in the interval between 4900 K and 800 K, as shown in figure 1. Quantities $\gamma(t)$, given by

$$\gamma_{kQ}(t) = \int_0^t \mathrm{d}t' \tau_{kQ}^{-1}(t') \tag{49}$$

etc, can be approximated on average by the usual form $t/\tau(t)$ giving rise to six instantaneous relaxation times, one for each type of excitation.

In the conditions of the experiment of [11] we have that, first, τ_{A+} and τ_{A-} are very small as a result of the fact that the acoustic plasma oscillations are embedded in the quasiparticle continuum and very rapidly die down. Moreover, in the given conditions ($n \simeq 6.5 \times 10^{17}$ cm^{-3} and for the expected carrier quasitemperature) coupling to optical plasma waves is much more intense than to single quasiparticles, a result of the fact that $\Lambda_{DH}^2 |\boldsymbol{Q}|^2$ is much smaller than one, where Λ_{DH} is the Debye–Hückel screening length [35].

Finally, in the given conditions the lifetime of the upper hybrid (optical plasmon–LO phonon) mode L_+ is much larger than the one of the lower hybrid mode L_-. This is a result of the fact that the L_+ mode at the given density n is predominantly of the longitudinal-optical vibration type, and then its lifetime is of the order of picoseconds while the L_- mode is predominantly a plasma oscillation, with lifetime of the order of femtoseconds [24, 34]. Consequently, the modulation of the reflectivity coefficient occurs in terms of

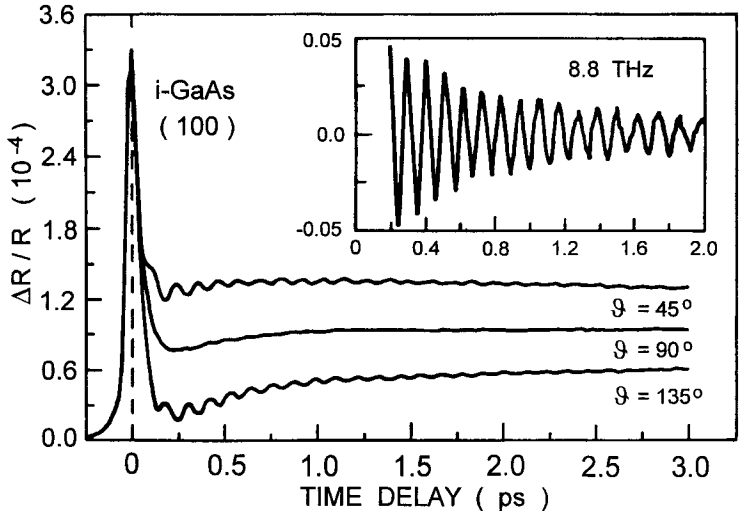

Figure 2. Reproduction of the time-resolved reflectivity changes in GaAs, as reported by Cho *et al* in [11].

the frequency $\omega_+(\boldsymbol{Q})$ which is 8.85 THz for a concentration of photoinjected carriers of roughly 6.5×10^{17} cm^{-3}, in coincidence within the experimental error with the observed one of 8.8 ± 0.15 THz. The observed modulation, see figure 2, has a decay time of roughly 0.79 ± 0.03 ps. It can be noticed that the expected value of τ_+ should nearly coincide with the one of the LO phonon near the zone centre, that is, of the order of five to ten picoseconds [36, 37]. This is roughly five times the observed one, and the explanation for this very rapid apparent decay resides in the effect of the variation in time of the carriers' quasitemperature during the interval when the measurement is performed, as shown in appendix B. In figure 3, leaving as an adjustable parameter only the amplitude—which we fix, fitting the maximum value with that of one experimental point, is shown the calculated modulation effect which is compared with the experimental result (we have only placed the positions of maxima and minima of the amplitude taken from the experimental data).

In that way this demonstrates the reason for the presence of the observed modulating phenomenon in the reflectivity spectra, occurring with the frequency of the near zone centre LO phonon (more precisely the one of the upper L_+ hybrid mode) with wavevector $\boldsymbol{Q}$, the one 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 then an open parameter in the theory to be fixed by the experimental data.

4. Conclusion

In summary, we have presented an analysis of the optical properties of the photoinjected plasma in semiconductors, a far-from-equilibrium dissipative system. The optical response of such a system needs then to be dealt with in the framework of a theory which can account for the time evolution of the nonequilibrium macroscopic state of the system while it is probed in pump–probe experiments. We have derived such a theory within the scope of a nonequilibrium statistical ensemble formalism, namely, the nonequilibrium statistical operator method and Zubarev's approach was used. The frequency- and wavenumber-dependent

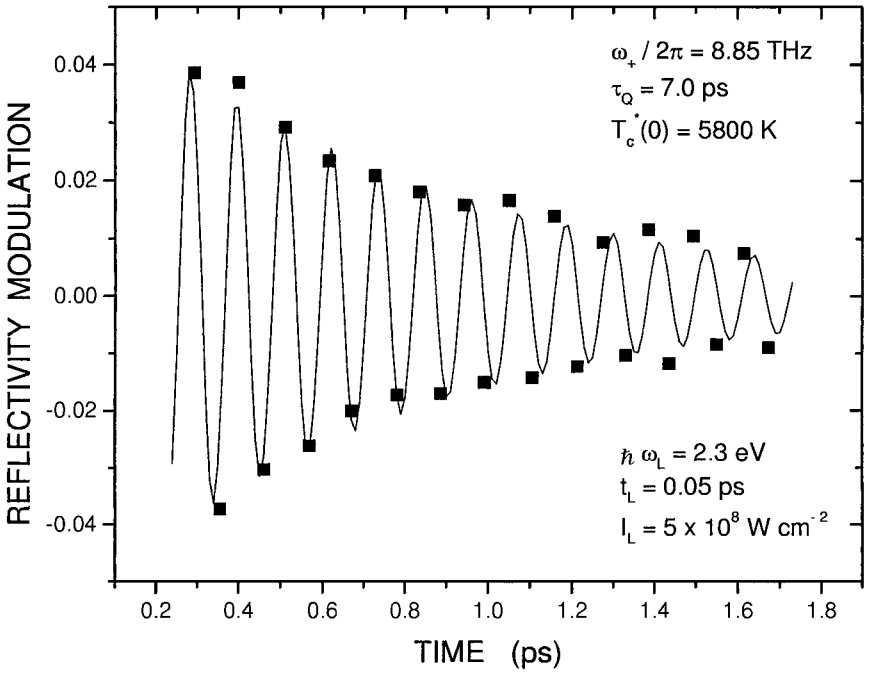

Figure 3. The theoretically evaluated modulation of the time-resolved reflectivity in the conditions of [11], compared with the experimental data. For simplicity we have drawn only the positions of the maxima and minima of the figure in the inset of figure 2.

dielectric function, which also depends on time in these time-resolved experiments as the nonequilibrium dissipative state of the system is evolving, was calculated. We recall that this quantity provides for all the optical properties, like absorption and reflectivity coefficients, Raman-scattering cross section etc, and we have specifically used these results to analyse the reflectivity, more precisely, a detailed study of an interesting phenomenon recently observed, consisting in the presence of a distinct oscillation of the signal in real time.

Such a phenomenon was attributed to the generation of coherent lattice vibrations, and a clear description on phenomenological bases given in [14] captures the essential physics of the problem. We have presented here a derivation at the microscopic mechanical–statistical level—within the theory referred to above—showing the origin of the phenomenon, which in fact arises out of the coupling of coherent phonon optical lattice vibrations with the carriers' charge density waves, the latter amplified by the coupling of the carriers with the pumping-laser electromagnetic radiation (at the wavenumber of the corresponding photons). Moreover, as shown, of all the possible contributions to the phenomenon, the leading one is that resulting from the oscillation of the so-called upper-branch hybrid mode of longitudinal optical phonons and the optical plasmons.

We notice that an earlier attempt of Kuznetzov and Stanton [5] presents a partial analysis however arriving at faulty results. The conclusion of those authors that the *strictly zone-centre phonons* are the ones associated with the phenomenon cannot be sustained on physical grounds. On the one hand any sample in a laboratory is finite in size, and then vibrations with an infinite wavelength cannot be excited (the smallest wavenumber contributing to the lattice vibrations should be of the order of π/L, where L is the shortest dimension of the sample). Moreover, even if we disregard this point (considering the idealized thermodynamic limit, thus ignoring

boundary conditions), the strictly zero-wavenumber mode has null density of states and null group velocity (corresponding to a van Hove singularity), with this zone-centre mode being a type of Goldstone mode (which is associated with a symmetry-breaking process): its excitation, in this case, would correspond to production of a finite uniform-in-space polarization (for these optical modes associated with the collective movement in the relative coordinate of the ions; in the case of the acoustical modes—associated with the collective movement in the centre of mass coordinate of the ion pairs in a cell—it corresponds to a shift of the centre of mass of the whole sample) [38]. To circumvent this point the argument was raised that it would follow a Bose–Einstein condensation, which admits no justification. We call the attention to the fact that, for the authors of [15] it is fundamental that the excited mode is the one with *strictly zero wavenumber*, for the amplitude of the modulation to depend on the population of the electron states. Again, some misrepresentation occurs here: the theory is based on the coupling of the vibrational displacement (and polarization charge) with the plasma wave amplitude (carrier charge density wave). The latter is expressed in terms of the carriers' single particle Dirac–Landau–Wigner density matrices, and their limits of infinite wavelength are not the carriers' distribution functions. The latter describe the population in single particle states and do not represent any charge density amplitude [39]. In contrast, as shown in the previous sections the amplitude of the modulation is governed by the carriers' charge density amplitude coupled to the strong pumping electromagnetic laser coherent field.

Acknowledgments

We acknowledge financial support of our research group provided in different opportunities by the São Paulo State Research Foundation (FAPESP); the National Research Council (CNPq); the Ministry of Planning (Finep); Unicamp Foundation (FAEP); IMB—Brasil; USA National Science Foundation (USA–Latin-America Cooperation Project, NSF, Washington, USA) and the John Simon Guggenheim Memorial Foundation (New York, USA). One of the authors (JRM) is a FAPESP post-doctoral fellow, and the other two (ARV, RL) are CNPq research fellows.

Appendix A. The oscillation in reflectivity

Let us introduce

$$\varepsilon(\omega, \boldsymbol{Q} \mid t) = \varepsilon^0(\omega, \boldsymbol{Q} \mid t) + \delta\varepsilon(\omega, \boldsymbol{Q} \mid t) \tag{A1}$$

where ε^0 is the contribution in the absence of the coherent-phonon amplitudes, and $\delta\varepsilon$ the contribution due to the latter, which is given by

$$\delta\varepsilon(\omega, \boldsymbol{Q} \mid t) = V(\boldsymbol{Q})\delta G(\omega, \boldsymbol{Q} \mid t) = V(\boldsymbol{Q})[\delta G_{cc} + \delta G_{ci} + \delta G_{ic} + \delta G_{ii}] \tag{A2}$$

where δG is a result of the presence of the term δf in the carrier populations arising out of the coherence of the LO phonons as given by equation (C6). Then, separating the real, ε_1, and imaginary, ε_2, parts of the dielectric function ($\varepsilon = \varepsilon_1 + \mathrm{i}\varepsilon_2$ and $G = G_1 + \mathrm{i}G_2$, and we have omitted the argument $(\omega, \boldsymbol{Q} \mid t)$ in the partial contributions to δG, as we also do for several other quantities below) we find that

$$\delta\varepsilon_1 = -V(\boldsymbol{Q})[\varepsilon_1^0\delta G_1 - \varepsilon_2^0\delta G_2] \tag{A3a}$$

$$\delta\varepsilon_2 = -V(\boldsymbol{Q})[\varepsilon_1^0\delta G_2 - \varepsilon_2^0\delta G_1]. \tag{A3b}$$

Moreover, introducing

$$\eta + \mathrm{i}\kappa = \varepsilon^{1/2} \qquad \varepsilon^0 = |\varepsilon^0|\mathrm{e}^{\mathrm{i}\alpha_0} \qquad \eta = \eta^0 + \delta\eta \qquad \kappa = \kappa^0 + \delta\kappa \tag{A4}$$

etc in equations (1)–(3), together with equations (A3), after some algebra we arrive at the result that

$$\frac{\Delta R(\omega, \boldsymbol{Q} \mid t)}{R(\omega, \boldsymbol{Q} \mid t)} \simeq V(\boldsymbol{Q})[B_1(\omega, \boldsymbol{Q} \mid t)\delta G_1(\omega, \boldsymbol{Q} \mid t) + B_2(\omega, \boldsymbol{Q} \mid t)\delta G_2(\omega, \boldsymbol{Q} \mid t)] \tag{A5}$$

where

$$B_1(\omega, \boldsymbol{Q} \mid t) = b_1(\varepsilon_1^0 \cos\alpha_0 + \varepsilon_2^0 \sin\alpha_0) - b_2(\varepsilon_1^0 \sin\alpha_0 - \varepsilon_2^0 \cos\alpha_0) \tag{A6a}$$

$$B_2(\omega, \boldsymbol{Q} \mid t) = b_1(\varepsilon_1^0 \sin\alpha_0 - \varepsilon_2^0 \cos\alpha_0) + b_2(\varepsilon_1^0 \cos\alpha_0 + \varepsilon_2^0 \sin\alpha_0) \tag{A6b}$$

with

$$b_1 = \frac{\eta^0 + 1}{d^0} \qquad b_2 = \frac{\kappa^0}{d^0} \tag{A7a}$$

$$d^0 = |\varepsilon^0|^{1/2}[(\eta^0 + 1)^2 + (\kappa^0)^2] \tag{A7b}$$

and we recall that $\tan(2\alpha_0) = \varepsilon_2^0/\varepsilon_1^0$. Moreover,

$$\delta G_{1(2)}(\omega, \boldsymbol{Q} \mid t) = \delta G_{cc1(2)} + \delta G_{ci1(2)} + \delta G_{ic1(2)} + \delta G_{ii1(2)} \tag{A8}$$

where index 1 and 2 refer to the real and imaginary parts of these δG, which result in very cumbersome expressions. However, in the experimental conditions of [11] they can be greatly simplified once we take into account that $\omega_{k\boldsymbol{Q}} \ll \omega_0$, $\omega_{pl} \ll \omega_0$ (ω_0 is the dispersionless LO-phonon frequency), and $V(\boldsymbol{Q})L_a(\omega, \boldsymbol{Q} \mid t) \ll 1$, where

$$L_a(\omega, \boldsymbol{Q} \mid t) = \sum_{\boldsymbol{k}}[f_{\boldsymbol{k}}^a(t) - f_{\boldsymbol{k}+\boldsymbol{Q}}^a(t)](\hbar\omega - \hbar\omega_{k\boldsymbol{Q}})^{-1} \tag{A9a}$$

$$2\pi\delta G_{cc} \simeq -\sum_a \delta L_a \tag{A9b}$$

$$2\pi\delta G_{ci} \simeq (\Omega_{\boldsymbol{Q}}/D_{\boldsymbol{Q}}^0)^2 \sum_a \delta L_a \tag{A9c}$$

$$2\pi\delta G_{ii} \simeq 2\pi\delta G_{ci} \simeq (\Omega_{\boldsymbol{Q}}/D_{\boldsymbol{Q}}^0)^2 \sum_a \delta L_a \tag{A9d}$$

where

$$\Omega_{\boldsymbol{Q}}^2 = \omega_{\boldsymbol{Q}}^2 - (\omega_{\boldsymbol{Q}}^{TO})^2 \tag{A10}$$

$$(D_{\boldsymbol{Q}}^0) = \omega^2 - \omega_0^2 - \Omega_{\boldsymbol{Q}}^2 \tag{A11}$$

and

$$\delta L_a(\omega, \boldsymbol{Q} \mid t) = \sum_{\boldsymbol{k}} \frac{\delta f_{\boldsymbol{k}+\boldsymbol{Q}}^a(t) - \delta f_{\boldsymbol{k}}^a(t)}{\hbar(\omega - \omega_{k\boldsymbol{Q}}^a)} \tag{A12}$$

with δf given in appendix C. Using equation (C6) we obtain that

$$\delta L_a(\omega, \boldsymbol{Q} \mid t) = \sum_{\boldsymbol{kq}} K_a(\omega, \boldsymbol{Q}; \boldsymbol{k}, \boldsymbol{q} \mid t) n_{\boldsymbol{kq}}^a(t) \langle a_{\boldsymbol{q}} \mid t \rangle \tag{A13}$$

where K_a follows by comparison with equations (C6) and (C7). Finally, using equation (A13) in equations (A9) and next replacing equations (A6), (A8) and (A9) in equation (A5), we arrive at the result of equation (42), where then

$$A(\omega, \boldsymbol{Q} \mid t) = \frac{V(\boldsymbol{Q})}{2\pi}\left[1 - \left(\frac{\Omega_{\boldsymbol{Q}}}{D_{\boldsymbol{Q}}^0}\right)^2\right] B_1(\omega, \boldsymbol{Q} \mid t) \tag{A14}$$

$$\delta G_1(\omega, \boldsymbol{Q} \mid t) = V(\boldsymbol{Q}) \sum_a \delta L_a(\omega, \boldsymbol{Q} \mid t) \tag{A15}$$

and δG_2 vanishes.

Appendix B. Decay of the modulation effect

We notice that in equation (C5) the dependence on time of the coefficient $\mathcal{M}$ (cf equation (C7) *et seq*) arises basically from the population f of equation (C10). Hence, we can rewrite in equation (49)

$$\frac{\delta R(t)}{R^0(t)} \simeq \mathcal{O}_+(\boldsymbol{Q} \mid t)\exp\{-\mathrm{i}\omega_+(\boldsymbol{Q})t - \gamma_+(\boldsymbol{Q} \mid t)\} + \mathrm{cc} \tag{B1}$$

that

$$\mathcal{O}_+(\boldsymbol{Q} \mid t) = \sum_{ka} \mathcal{E}_a(\boldsymbol{k}, \boldsymbol{Q})\beta_c^{3/2}(t)\exp\left\{-\beta_c(t)\frac{\hbar^2|\boldsymbol{k}|^2}{2m_a}\right\} \tag{B2}$$

where the coefficient $\mathcal{E}$ is nearly time independent. To proceed further we take the exponential out of the summation (integration) in the sense of the mean value theorem, and, moreover, we consider only the leading contribution due to the electrons, i.e.

$$\frac{\delta R(t)}{R^0(t)} \approx M_e(\boldsymbol{Q})\beta_c^{3/2}(t)\exp\left\{-\mathrm{i}\left(\omega_{A+} - \mathrm{i}\frac{1}{\tau_+(\boldsymbol{Q} \mid t)}\right)t - \frac{\hbar^2|\bar{\boldsymbol{k}}(t)|^2}{2m_e}\beta_c(t)\right\} \tag{B3}$$

where

$$M_e(\boldsymbol{Q}) = \sum_{\boldsymbol{k}} \mathcal{E}_e(\boldsymbol{k}, \boldsymbol{Q}) \tag{B4}$$

and $|\bar{\boldsymbol{k}}(t)|$ is the value fixed, at each time t, by the mean value theorem. Moreover, we have written, as noted in the main text,

$$\gamma_+(\boldsymbol{Q} \mid t) = \frac{t}{\tau_+(\boldsymbol{Q} \mid t)} \tag{B5}$$

where τ, predominantly the decay of the LO phonon at mode $\boldsymbol{Q}$, varies around 7 ps [24, 34, 37]. We recall that $\beta_c(t) = 1/k_B T_c^*(t)$, the evolution of the carriers' quasitemperature is given in figure 1, and $n \simeq 6.5 \times 10^{17}$ cm^{-3} is practically constant in time in the given interval when the observation and measurement was performed. We obtain a good fitting of the experimental curve shown in the upper-right inset in figure 2 using values of $|\bar{\boldsymbol{k}}(t)|$ ranging, for 0.24 ps $\leqslant t \leqslant$ 1.73 ps, from $\sim 7.5 \times 10^6$ cm^{-1} to $\sim 8.2 \times 10^6$ cm^{-1} with an intermediate maximum of $\sim 9.2 \times 10^6$ cm^{-1}, and an average of roughly 8.4×10^6 cm^{-1}. The interesting point can be noticed that these are values comparable with the thermal wavenumber $k_{th}(t)$ defined by $\hbar^2 k_{th}^2(t)/2m_e = (3/2)k_B T_c^*(t)$, whose average value in the given interval is roughly 7.2×10^6 cm^{-1}. This then demonstrates that the decay of the modulation is a result of the changing of the nonequilibrium thermodynamic state, which, we recall, is characterized, while the time-resolved measurements are performed, by a nearly constant concentration of the photoinjected carriers, but with a rapidly changing carrier quasitemperature, while the phonon bath remains at nearly the reservoir temperature.

Appendix C. The carrier population functions

The calculations of the reflectivity, via the dielectric function, requires us to determine the carrier occupation-number distributions, namely,

$$f_{\boldsymbol{k}}^a(t) = \mathrm{Tr}\{c_{\boldsymbol{k}}^\dagger c_{\boldsymbol{k}} \rho_\varepsilon(t)\}. \tag{C1}$$

This can be done using the fact that the expression of the nonequilibrium distribution $\rho_\varepsilon(t)$ can be written in a series of contributions [17] involving powers of the interaction potential in a kind of perturbational expansion, namely

$$\rho_\varepsilon(t) = \bar{\rho}(t, 0) + \sum_{n=1}^{\infty} \rho_\varepsilon^{(n)}(t, 0) \tag{C2}$$

where the first contribution to this series, the only one we retain below to write the distribution function of equation (C1) is

$$\rho_\varepsilon^{(1)}(t,0) = \frac{1}{\mathrm{i}\hbar}\int_{-\infty}^{t} \mathrm{d}t'\, \mathrm{e}^{\varepsilon(t'-t)}[\hat{H}'(t'-t)_0, \bar{\rho}(t', t'-t)_0] + \frac{1}{\mathrm{i}\hbar}\sum_{j=1}^{9}\int_{-\infty}^{t} \mathrm{d}t'\, \mathrm{e}^{\varepsilon(t'-t)}\frac{\delta\bar{\rho}(t', t'-t)_0}{\delta Q_j(t')}\mathrm{Tr}\{[\hat{H}', \hat{P}_j]\bar{\rho}(t', 0)\} \tag{C3}$$

where $\hat{P}_j$ and Q_j, with $j = 1, 2, \ldots$, represent the nine dynamical variables of equation (4) and the macrovariables of equation (10) respectively. The lower right index zero indicates evolution in the interaction representation. Then, in lowest order we have

$$f_{\boldsymbol{k}}^a(t) \simeq \mathrm{Tr}\{c_{\boldsymbol{k}}^\dagger c_{\boldsymbol{k}}\bar{\rho}(t,0)\} + \mathrm{Tr}\{c_{\boldsymbol{k}}^\dagger c_{\boldsymbol{k}}\rho_\varepsilon^{(1)}(t,0)\}. \tag{C4}$$

Taking into account the expression for the auxiliary coarse-grained operator given by equation (13), we find after resorting to Heims–Jaynes perturbative expansion for averages [40] that, to lowest order in the amplitudes $n_{\boldsymbol{kq}}$ and $\langle a_{\boldsymbol{q}}\rangle$, that is, only up to first order in these quantities,

$$f_{\boldsymbol{k}}^a(t) = \bar{f}_{\boldsymbol{k}}^a(t) + \delta f_{\boldsymbol{k}}^a(t) \tag{C5}$$

where $\bar{f}_{\boldsymbol{k}}$ is given in equation (27), and

$$\delta f_{\boldsymbol{k}}^a(t) = \sum_{\boldsymbol{q}} \mathcal{M}_{\boldsymbol{q}}^a(t)\langle a_{\boldsymbol{q}} \mid t\rangle + \mathrm{cc} \tag{C6}$$

where

$$\mathcal{M}_{\boldsymbol{q}}^a(t) = S_{\boldsymbol{q}}^a(t)/[\delta E(t)/\delta F_{\boldsymbol{k}}^a(t)] \tag{C7}$$

$$S_{\boldsymbol{q}}^a(t) = \frac{2}{3\hbar}C_a(\boldsymbol{q})\sum_{\boldsymbol{k}'}\frac{n_{\boldsymbol{k}'\boldsymbol{q}}^a(t)}{\omega_{\boldsymbol{k}'\boldsymbol{q}} - \omega_{\boldsymbol{q}} - \mathrm{i}\varepsilon} - \frac{2}{3\hbar}C_a^*(\boldsymbol{q})\sum_{\boldsymbol{k}'}\frac{n_{\boldsymbol{k}'\boldsymbol{q}}^{*a}(t)}{\omega_{\boldsymbol{k}'\boldsymbol{q}} - \omega_{\boldsymbol{q}} - \mathrm{i}\varepsilon} \tag{C8}$$

$$\frac{\delta E(t)}{\delta f_{\boldsymbol{k}}^a} = -\beta_c(t)[\varepsilon_{\boldsymbol{k}}^a - \tfrac{3}{2}k_B T_c^*(t)]\tilde{f}_{\boldsymbol{k}}^a(t) \tag{C9}$$

where ε tends to +0, and we have used for $\tilde{f}_{\boldsymbol{k}}^a$ of equation (39) a nondegenerate-like limit, valid in the typical experimental conditions, that is,

$$\tilde{f}_{\boldsymbol{k}}^a(t) \to \frac{8\pi^3 n(t)\hbar^3}{(2\pi m_a)^{3/2}}\beta_c^{3/2}(t)\exp\{-\beta_c(t)\varepsilon_{\boldsymbol{k}}^a\}. \tag{C10}$$

References

[1] For example see articles in Alfano R R (ed) 1984 *Semiconductors Probed by Ultrafast Laser Spectroscopy* vols 1 and 2 (New York: Academic)
also in the series Harris C B, Ippen E P, Mourou G A and Zewail A H (eds) 1989 *et seq. Ultrafast Phenomena* (Berlin: Springer)

[2] Zubarev D N 1970 *Fortschr. Phys./Prog. Phys.* **18** 125

[3] Mori H, Oppenheim I and Ross J 1962 *Studies in Statistical Mechanics I* ed J de Boer and G E Uhlenbeck (Amsterdam: North-Holland) pp 217–98

[4] Zubarev D N and Novikov M Ju 1973 *Fortschr. Phys./Prog. Phys.* **21** 703

[5] Zubarev D N 1970 *Neravnovesnaia Statisticheskaia Termodinamika* (Moscow: Nauka) (Engl. transl. 1974 *Nonequilibrium Statistical Thermodynamics* (New York: Consultants Bureau))

[6] Zubarev D N 1980 Modern methods of the statistical theory of nonequilibrium processes *Reviews of Science and Technology: Modern Problems of Mathematics* vol 15, ed R B Gamkreludze (Moscow: Izd. Nauka) (in Russian) (Engl. transl. 1981 *Sov. J. Math.* **16** 1509)

[7] Zubarev D N, Morozov V G and Röpke G 1996 *Statistical Mechanics of Nonequilibrium Phenomena: Basic Concepts, Kinetic Theory* vol 1 (Berlin: Akademie)
Zubarev D N, Morozov V G and Röpke G 1997 *Statistical Mechanics of Nonequilibrium Phenomena: Relaxation and Hydrodynamic Processes* vol 2 (Berlin: Akademie)
[8] Luzzi R and Vasconcellos A R 1990 *Fortschr. Phys./Prog. Phys.* **38** 887
Luzzi R, Vasconcellos A R and Ramos J G *A Nonequilibrium Statistical Ensemble Formalism. MaxEnt-NESOM: Basic Concepts, Construction, Application, Open Questions and Criticisms (Fundamental Theories of Physics Series)* ed A van der Merwe (Dordrecht: Kluwer) in preparation
[9] Ferry D K, Grubin H L and Giafrate G J 1984 *Semiconductors Probed by Ultrafast Laser Spectroscopy* vol 1, ed R R Alfano (New York: Academic)
Freire V N, Vasconcellos A R and Luzzi R 1988 *Phys. Rev.* B **39** 13 264
Vasconcellos A R, Algarte A C and Luzzi R 1995 *Phys. Rev.* B **52** 13 936
[10] See for example the review article, Algarte A C, Vasconcellos A R and Luzzi R 1992 *Phys. Status Solidi* b **173** 487
[11] Cho G C, Kütt W and Kurz H 1990 *Phys. Rev. Lett.* **65** 764
[12] Albrecht W, Kruse Th and Kurz H 1992 *Phys. Rev. Lett.* **69** 1451
Pfeifer T, Kütt W, Kurz H and Scholz R 1992 *Phys. Rev. Lett.* **69** 3248
Cheng T K, Brorson S D, Kazeroonian A S, Moodera J S, Dresselhaus G, Dresselhaus M S and Ippen E P 1990 *Appl. Phys. Lett.* **57** 1004
[13] Scholz R, Pfeifer P and Kurz H 1993 *Phys. Rev.* B **47** 16 229
[14] Zeiger H J, Vidal J, Cheng T K, Ippen E P, Dresselhaus G and Dresselhaus M S 1992 *Phys. Rev.* B **45** 768
[15] Kuznetsov A V and Stanton C J 1994 *Phys. Rev. Lett.* **73** 3243
[16] Mazin I I, Liechtenstein A I, Jepsen O, Anderson O K and Rodriguez C O 1994 *Phys. Rev.* B **49** 9210
[17] Lauck L, Vasconcellos A R an Luzzi R 1990 *Physica* A **168** 789
[18] Vasconcellos A R, Algarte A C and Luzzi R 1990 *Physica* A **166** 517
[19] Martin P C 1968 Measurements and correlation functions *Many-Body Physics* ed C de Witt and R Balian (New York: Gordon and Breach)
[20] Kalashnikov V P 1971 *Teor. Mat. Fiz.* **9** 94 (Engl. transl. *Theor. Math. Phys.* (USSR) **9** 1003)
Kalashnikov V P 1971 *Teor. Mat. Fiz.* **9** 406 (Engl. transl. *Theor. Math. Phys.* (USSR) **9** 1230)
[21] de Groot S R 1969 The Maxwell equations *Studies in Statistical Mechanics* vol IV, ed J de Boer and G E Uhlenbeck (Amsterdam: North-Holland)
[22] Luzzi R and Vasconcellos A R 1980 *J. Stat. Phys.* **23** 539
[23] Vasconcellos A R and Luzzi R 1983 *J. Raman Spectrosc.* **14** 39
[24] Mooradian A 1969 *Light Scattering Spectra of Solids* ed G B Wright (New York: Springer)
[25] Algarte A C, Vasconcellos A R and Luzzi R 1996 *Phys. Rev.* B **54** 11 311
[26] Luzzi R, Vasconcellos A R, Casas-Vázquez J and Jou D 1997 *J. Chem. Phys.* **107** 7383
[27] Luzzi R, Vasconcellos A R, Casas-Vázquez J and Jou D 1997 *Physica* A **234** 699
[28] Madureira J R, Vasconcellos A R, Luzzi R and Lauck L 1998 *Phys. Rev.* E **57** 3637
[29] Zwanzig R 1981 Where do we go from here? *Perspectives in Statistical Physics* ed H J Ravechè (Amsterdam: North-Holland)
[30] Kim D and Yu P Y 1990 *Phys. Rev. Lett.* **64** 946
[31] See for example Haken H 1978 *Synergetics* (Berlin: Springer)
Haken H 1970 Laser theory *Handbook der Physik XXV/C2* ed S Flügge (Berlin: Springer)
[32] Gantmacher F R 1974 *The Theory of Matrices* (New York: Chelsea) ch XIV pp 125 *et seq.*
[33] Mooradian A and McWhorter A L 1969 *Light Scattering Spectra of Solids* ed G B Wright (New York: Springer)
[34] Ferrari C A and Luzzi R 1979 *Phys. Rev.* B **19** 5284
[35] Wolff P A 1969 *Light Scattering Spectra of Solids* ed G B Wright (New York: Springer)
[36] von der Linde D, Kuhl J and Klingenberg H 1980 *Phys. Rev. Lett.* **44** 1505
[37] Chang R K, Ralston J M and Keating D E 1969 *Light Scattering Spectra of Solids* ed G B Wright (New York: Springer) pp 369–79
[38] Brout R 1965 *Phase Transitions* (New York: Benjamin) ch 1
Goldstone J 1961 *Nuovo Cimento* **19** 154
Goldstone J, Salam A and Weinberg S 1962 *Phys. Rev.* **127** 965
[39] Feynman R P 1972 *Statistical Mechanics: a Set of Lectures* (Reading, MA: Benjamin)
[40] Heims S P and Jaynes E T 1962 *Rev. Mod. Phys.* **34** 143