

## Coupled electron-hole plasma-phonon system in far-from-equilibrium semiconductors

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Zubarev's nonequilibrium statistical thermodynamic method is applied to the study of the time evolution of a coupled carrier-LO-phonon system in polar direct-gap semiconductors. The carrier system is composed of a photoexcited electron-hole plasma, strongly departed from thermal equilibrium, generated by a pulse of laser light. The macroscopic description is done in terms of time-dependent quasitemperatures for the carriers and for the different phonon modes. These quasitemperatures can be determined by means of ultrafast optical spectroscopy; a calculation of the expected time-resolved Raman spectrum with numerical applications for the case of GaAs is presented.

### I. INTRODUCTION

Continuous development of experimental techniques in the area of optical spectroscopy, and in particular that of ultrafast time-resolved spectroscopy, will certainly provide a better understanding of nonequilibrium processes in physics, chemistry, and biology. This technique has been made possible by the availability of mode-locked lasers and allows us to investigate on the picosecond time scale the interaction of radiation with molecules, atoms, and solids.<sup>1</sup> Clearly, this also calls for improvements in theoretical techniques going beyond the usual response-function theory (linear and nonlinear), which should allow for the study of far-from-equilibrium many-body systems and give account of the time evolution of irreversible processes. A formalism to deal with these kinds of situations is given elsewhere.<sup>2</sup>

In the present paper we address ourselves to a study of the thermal relaxation of a coupled electron-phonon system. We determine the time-dependent distribution functions of electrons and longitudinal-optical (LO) phonons in a polar semiconductor, once the electron system has been initially strongly disturbed from thermal equilibrium by means of optical pumping.

Currently there exist several methods to study nonequilibrium systems.<sup>3</sup> One of them is the statistical approach based on the use of distribution functions derived by the ensemble method which was initiated by Gibbs for systems in equilibrium. Extensions of the method for nonequilibrium systems have been proposed, in which an ensemble is built as a set of replicas of the physical system distributed with a given *a priori* probability over all the microscopic states, satisfying the constraints and initial specifications. Zubarev's nonequilibrium statistical-operator method<sup>4</sup> belongs to this case, and it seems to offer a close-off formalism in the theory of irreversible processes

adequate enough to deal with a large class of experimental situations. It provides a macroscopic description for systems away from thermal equilibrium whose evolution is described by a statistical operator in which nonlinear, nonlocal, and retardation (memory) effects are incorporated into it from the onset, and permits us to obtain in a natural way descriptions of transport phenomena and thermal-relaxation processes. However, the method is not applicable for a too short time scale in the sense established by Bogoliubov,<sup>5</sup> who argues that a contracted macroscopic description of nonequilibrium statistical systems, in terms of a reduced set of macroscopic variables, should be possible if there exists a characteristic relaxation time of microprocesses much smaller than the characteristic times of variation of the macrovariables (secularity).

It should be noted that the method is not restricted to situations when the system only slightly deviates from equilibrium, but it can account for the treatment of systems far from thermal equilibrium. Further it is completely consistent with nonequilibrium nonlinear thermodynamics.<sup>6</sup>

Zubarev's method has been extensively applied to the study of a number of nonequilibrium statistical problems.<sup>7</sup> A simplified version of it, consisting of ascribing different temperatures to the various subsystems of a highly excited semiconductor, the so-called hot-excitation model, has been applied to the study of their optical responses. The hot-electron model has been amply used in the area of high-field transport in semiconductors since the pioneering work of Fröhlich,<sup>8</sup> and later on in the discussion of experiments in laser optics spectroscopy, beginning with the concept of hot excitons at weak to moderate excitation densities as reviewed by Permogorov,<sup>9</sup> and afterwards extended to the case of solid-state plasma in doped or photo-injected semiconductors at high-excitation densities, as reviewed else-

where.<sup>10</sup> The participation of nonequilibrium distributions of carriers and optical phonons, as well as many-body effects in this "hot" high-density solid-state plasma, are apparent in the behavior and shape of optical spectra. Work has been directed toward showing the possibility, for some class of experiments, of describing the state of the carriers solely by an effective temperature,<sup>11</sup> a concept that has been applied rather more casually to the nonequilibrium distribution of LO phonons produced when hot carriers cascade down the band-energy states.<sup>12</sup> Carrier effective temperatures can be measured in Raman-Doppler scattering experiments,<sup>13</sup> while optical-phonon temperatures can be determined from the ratio of Stokes to anti-Stokes intensities in the Raman spectrum. This question has originated some controversy<sup>14,15</sup> which we try to elucidate here.

In the next section we briefly summarize Zubarev's method and we specify it for the problem under consideration. Section III presents the solution of the generalized transport equations with numerical results and its discussion. The time-resolved Raman-Doppler spectra of highly photoexcited carriers is also calculated.

## II. ZUBAREV'S GENERALIZED TRANSPORT EQUATIONS

Zubarev's method is based on Bogoliubov's assertion that if there exists a relaxation time for microinformation  $\tau_\mu$ , after which the system loses the memory of the detailed initial distribution, for  $t \gg \tau_\mu$  a randomization should occur, and a reduced number of variables are enough to describe, in a macroscopic way, the state of the system.<sup>5</sup> The contraction of the initial distribution is connected with the separation from the total Hamiltonian of strong interactions with certain symmetries,<sup>16</sup> which are those related to the fast-relaxing processes.

Hence, for not-too-short times, i.e.,  $t \gg \tau_\mu$ , one can ignore correlations with lifetimes smaller than  $\tau_\mu$ , and the state of the system can be described by a reduced set of macroscopic variables (or macrovariables for short), for example,  $Q_1(t), \dots, Q_s(t)$ , which are the average values of the dynamical quantities  $P_1, \dots, P_s$  over the nonequilibrium ensemble. Next an auxiliary distribution is defined, the so-called quasiequilibrium statistical operator (QESO)  $\rho_q(t, 0)$ , as an idealized initial condition for the system after the randomization process and from which it evolves. This means that at all (subsequent) times the NESO is a functional of  $\rho_q$  satisfying the Liouville-von Neumann equation.

The QESO is chosen so as to make extremal Gibbs entropy

$$S(t) = -\text{Tr}[\rho_q(t, 0) \ln \rho_q(t, 0)]$$

for given average values of the quantities  $P$ , i.e.,

$$\rho_q(t, 0) = \exp\left(-\phi(t) - \sum_{m=1}^s F_m(t) P_m\right), \quad (1)$$

where  $\phi(t)$  is defined by the normalization condition  $\text{Tr}[\rho_q(t, 0)] = 1$ , and the set of parameters  $F_1(t), \dots, F_s(t)$  are Lagrange multipliers.

The NESO corresponding to the initial-value problem (initial time is taken as  $t_0 \rightarrow -\infty$ ) given by  $\rho_q$  is written as

$$\rho(t) = \exp\left(\epsilon \int_{-\infty}^0 dt' e^{\epsilon t'} \ln \rho_q(t+t', t')\right), \quad (2)$$

with  $\epsilon$  going to  $+0$  after the trace operation has been performed in the calculation of averages. In Eqs. (1) and (2) the first term in the argument of  $\rho_q$  stands for the time dependence on the parameters  $F$ , whereas the second denotes the evolution of the quantities  $P$  under the action of the system Hamiltonian  $H$ .

The NESO satisfies the Liouville equation with infinitesimal sources:

$$\frac{\partial \ln \rho}{\partial t} + \frac{1}{i\hbar} [\ln \rho, H] = -\epsilon (\ln \rho - \ln \rho_q). \quad (3)$$

Equation (2) defines the operation of projecting the QESO of Eq. (1) over the subspace of the retarded solutions of the initial-value problem of the Liouville equation. These are the solutions that correspond to an increase in entropy, thus satisfying the second law of thermodynamics. This is ensured by the presence of the infinitesimal source in Eq. (3), which also fixes the initial condition, breaking the time-reversal symmetry of the Liouville equation. Irreversibility is then associated with this symmetry breaking, and the average of any physical quantity over the ensemble defined by distribution (2) is a quasiaverage in Bogoliubov's sense.<sup>17</sup>

Except for the normalization condition, the parameters  $F_m(t)$  are still open. An additional condition is imposed on distribution  $\rho$  in the form

$$Q_m(t) \equiv \langle P_m | t \rangle = \langle P_m | t \rangle_q, \quad (4)$$

where

$$\begin{aligned} \langle P_m | t \rangle &= \text{Tr}[P_m \rho(t)], \\ \langle P_m | t \rangle_q &= \text{Tr}[P_m \rho_q(t, 0)]. \end{aligned}$$

Equation (4) guarantees the conservation of normalization and leads to the definition

$$\frac{\partial \phi(t)}{\partial F_m(t)} = -\langle P_m | t \rangle_q = -\langle P_m | t \rangle \equiv -Q_m(t), \quad (5)$$

which is the generalization of the concept of

thermodynamic parameters to the nonequilibrium state. The nonequilibrium thermodynamic parameters  $F_m(t)$  are said to be thermodynamically conjugated to the macrovariables  $Q_m(t)$  in the sense established by Eq. (5).<sup>18,19</sup> The definition for the entropy  $S(t)$ , already given, makes possible the connection with generalized thermodynamics,<sup>6</sup> and provides the reciprocal relation of Eq. (5),  $F_m(t) = \delta S(t) / \delta Q_m(t)$ .

Now conditions are set so as to close the formalism by providing a way to determine the time evolution of the macroscopic state of the nonequilibrium system. This is done by introducing Zubarev's generalized transport equations (GTEq), that is to say, the equations of motion for the nonequilibrium thermodynamic variables. By time differentiation of both sides of Eq. (5) one obtains

$$\frac{dQ_m(t)}{dt} = \frac{d}{dt} \langle P_m | t \rangle = \langle \dot{P}_m | t \rangle = \left\langle \frac{1}{i\hbar} [P_m, H] | t \right\rangle. \quad (6)$$

Alternatively one can write kinetic equations for the thermodynamic parameters using the fact that

$$\frac{dQ_m(t)}{dt} = \sum_n \frac{\delta Q_m(t)}{\delta F_n(t)} \frac{dF_n(t)}{dt} = - \sum_n M_{mn}(t) \dot{F}_n(t), \quad (7)$$

where

$$M_{mn}(t) = \frac{\delta^2 \phi(t)}{\delta Q_m \delta Q_n} \equiv \{P_m, P_n | t\} = \langle \Delta P_m \Delta \tilde{P}_n | t \rangle_q, \quad (8)$$

with

$$\Delta P = P - \langle P | t \rangle_q,$$

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

and

$$S(t,0) = \phi(t) + \sum_m F_m(t) P_m.$$

Here  $M$  is the correlation matrix over the quasi-equilibrium ensemble,  $\tilde{A}$  is a generalized Kubo transform of operator  $A$ , and  $S$  is the entropy operator  $S(t,0) = -\ln \rho_q(t,0)$ .

Sometimes a "mixed representation" involving equations for some macrovariables and some parameters may be used, as we do in our study of the coupled electron-phonon system in the next section. It should be noted that in the linear regime near the equilibrium state one retrieves Mori projection formalism,<sup>20</sup> and in the same asymptotic limit the response-function theory<sup>2</sup> based on Zubarev's method replicates Kubo results<sup>21</sup> for transport coefficients. Further, GTEq (Ref. 6) (or those for the thermodynamic parameters, or

those in a mixed representation) are highly nonlinear integrodifferential equations. This is an important fact, since one is then dealing with dynamical systems with feedback mechanisms, which may present stationary solutions corresponding to small perturbations increasing up to a stable final macroscopic fluctuation, irrespective of the initial conditions.<sup>22,23</sup> This is in accord with the results of generalized thermodynamics,<sup>6</sup> which studies these so-called dissipative structures.<sup>23</sup>

Concerning the choice of the set of state variables  $Q$ , it is dictated in principle by the fact that they must be sufficient for the description of the macroscopic state of the system on the time scale of interest. A detailed study of the question of completeness of the basis of macrovariables is given by Kalashnikov.<sup>24</sup>

We are now in a condition to attack the proposed problem of the evolution of a nonequilibrium coupled electron-phonon system, which provides an illustration of the application of Zubarev's method.

### III. PHOTOEXCITED PRODUCTION OF LO PHONONS

The coupled electron-phonon system has been treated by many authors either in connection with the question of the approach to equilibrium or in the study of conductivity or other transport problems. Usually it has dealt with the linearized version of the Boltzmann transport equations method, which basically requires detailed calculations of collision times for phonons and for electrons.<sup>25</sup> More elaborate approaches, like those of Kubo,<sup>21</sup> Mori,<sup>20</sup> and the thermodynamic Green-function method of Bogoliubov and Tyablikov,<sup>26</sup> have been used to provide a more rigorous and in-depth treatment of the problem.

Recently, studies of optical properties of semiconductors under high-excitation densities provided measurements of the effective temperature of hot carriers,<sup>11</sup> and determination of the distribution functions  $\nu_q$  of hot phonons generated by the photoexcited carriers.<sup>12</sup>

We proceed next to develop a study of the time evolution of such a system when an initial high concentration of photoexcited electrons has been created by means of a pulse of laser light. Owing to Coulomb interaction, the electron system should be brought into internal thermalization in a fraction of a picosecond.<sup>27,28</sup> Further we consider the case of strong-to-intermediate polar semiconductors when Fröhlich interaction predominates over the deformation-potential interaction. Assuming that cross relaxation between carriers and LO phonons occurs more rapidly than final thermalization with the thermal bath

and recombination of the photoexcited pairs, we restrict our analysis to a time interval when the carriers and LO phonons can be considered as practically isolated from the thermal bath and the carrier concentration remains almost constant. Under these conditions one can choose (as a complete set of macrovariables to describe the state of the system) the electron energy  $H_E$  and the LO phonon number operator  $b_{\vec{q}}^\dagger b_{\vec{q}} = \eta_{\vec{q}}$ .

The total Hamiltonian is taken as

$$H = H_E + H_{LO} + H_F, \quad (9)$$

where

$$H_E = \sum_{\vec{k}, n} \epsilon(\vec{k}n) C_{\vec{k}n}^\dagger C_{\vec{k}n} \quad (10a)$$

is the effective Hamiltonian for a two-parabolic inverted-band semiconductor and  $C_{\vec{k}n}^\dagger$  creates an electron of momentum  $\vec{k}$  in band  $n$  (conduction and valence).

Coulomb interaction is not explicitly considered, only indirectly called forth to ensure the very rapid thermalization of carriers at all times. The LO-phonon Hamiltonian is

$$H_{LO} = \sum_{\vec{q}} \hbar\omega_0 (b_{\vec{q}}^\dagger b_{\vec{q}} + \frac{1}{2}), \quad (10b)$$

i.e., we consider a longitudinal mode of constant frequency  $\omega_0$  throughout the Brillouin zone whose interaction with the carriers is given by the Fröhlich Hamiltonian

$$H_F = \sum_{\vec{k}, \vec{k}', n, n'} V(\vec{q}; \vec{k}n, \vec{k}'n') b_{\vec{q}} C_{\vec{k}n}^\dagger C_{\vec{k}'n'} + \text{H.c.} \quad (10c)$$

The matrix element  $V$  is given by

$$V(\vec{q}; \vec{k}n, \vec{k}'n') = -i\delta_{nn'} 2\omega_0 (\alpha_n \pi / V)^{1/2} (1/2m\omega_0)^{1/4},$$

where  $\alpha_n$  is the so-called Fröhlich coupling constant, and interband transitions have been neglected. This is the bare Fröhlich interaction, i.e., not corrected by the screening effects of the carrier polarization.<sup>25</sup>

According to our previous analysis, the QESO for the initial condition of the system, after the randomization process has set in, is

$$\rho_{\vec{q}}(t, 0) = \exp\left(-\phi(t) - \beta(t)H_E - \sum_{\vec{q}} F_{\vec{q}}(t)\eta_{\vec{q}}\right). \quad (11)$$

The nonequilibrium thermodynamic parameters are the reciprocal carrier temperature  $\beta(t)$  and the set of  $F_{\vec{q}}$  conjugated to the phonon-number operator in each  $\vec{q}$  mode.

The GTEq for this problem are

$$\frac{d}{dt} \langle H_E | t \rangle_{\vec{q}} = \left\langle \frac{1}{i\hbar} [H_E, H] | t \right\rangle, \quad (12a)$$

$$\frac{d}{dt} \nu(\vec{q} | t) = \left\langle \frac{1}{i\hbar} [b_{\vec{q}}^\dagger b_{\vec{q}}, H] | t \right\rangle, \quad (12b)$$

where  $\nu(\vec{q} | t) = \langle \eta_{\vec{q}} | t \rangle_{\vec{q}}$  is the LO-phonon distribution function. These equations need to be supplemented by initial conditions.

Reverting to an electron-hole representation for the electrons in the inverted parabolic band semiconductor, we write

$$\langle H_E | 0 \rangle_{\vec{q}} = n_x (\hbar\omega_1 - E_G), \quad (13a)$$

where  $n_x$  is the number of electron-hole pairs produced by the pulse,  $\hbar\omega_1$  the one- (or two-) photon energy necessary to produce one photoexcited pair, and  $E_G$  the gap energy. The initial condition for the phonon distribution is chosen as

$$\nu(\vec{q} | 0) = \nu^0(\vec{q}) = [\exp(\beta_0 \hbar\omega_0) - 1]^{-1}, \quad (13b)$$

i.e., the number of LO phonons in equilibrium with the thermal bath at temperature  $\beta_0^{-1}$ .

Recalling the fact that the carriers are rapidly brought into thermal equilibrium among themselves, in the usual experimental conditions<sup>11</sup> they form a nondegenerate plasma with a Maxwellian-type distribution,

$$f(\vec{k}j | t) = A_j(t) \exp[-\beta(t)\epsilon(\vec{k}j)], \quad j = e, h \quad (14)$$

where

$$A_j(t) = [4\pi^3 n_x / (2\pi m_j)^{3/2}] \beta^{3/2}(t).$$

The energy equipartition relation  $\langle H_E | t \rangle = 3n_x \beta^{-1}(t)$  holds during the time interval in which Eq. (14) remains valid. This prompts us to redefine Eq. (12a) as

$$-3n_x \beta^{-2}(t) \dot{\beta}(t) = \frac{d}{dt} \langle H_E | t \rangle, \quad (15)$$

with the initial reciprocal temperature given by  $\beta(0) = 3(\hbar\omega_1 - E_G)^{-1}$ .

To evaluate the rhs of Eqs. (12) one needs to calculate the average over Zubarev's nonequilibrium ensemble after the commutations have been performed. To proceed further, recalling definition (2) we obtain, using QESO (11),

$$\begin{aligned} \rho(t) &= \exp\left(-S(t, 0) + \int_{-\infty}^0 dt' e^{t't} \Delta \dot{S}(t+t', t')\right) \\ &= \exp[-S(t, 0) + \xi(t, 0)], \end{aligned} \quad (16)$$

where

$$S(t, 0) = \phi(t) + \beta(t)H_E + \sum_{\vec{q}} F_{\vec{q}} \eta_{\vec{q}},$$

part integration has been performed, and  $\dot{S} = dS/dt'$ . Using the operator relation

$$\begin{aligned} e^{-A+B} &= Y(B | 1) e^{-A}, \\ Y(B | x) &= 1 + \int_0^x du Y(B | u) e^{-uA} B e^{uA} \end{aligned}$$

one can write

$$\rho(t) = \rho_q(t, 0) + D(t, 0)\rho_q(t, 0), \quad (17)$$

with

$$D(t, 0) = \int_0^1 du Y(\xi | u) e^{-uS} \zeta(t, 0) e^{uS} \zeta(t, 0). \quad (18)$$

With these results we obtain

$$\langle \dot{H}_E | t \rangle = \langle H_E | t \rangle_q + \langle \dot{H}_E D(t, 0) | t \rangle_q, \quad (19a)$$

$$\langle \dot{\eta}_q | t \rangle = \langle \dot{\eta}_q | t \rangle_q + \langle \dot{\eta}_q D(t, 0) | t \rangle_q. \quad (19b)$$

But, because  $H_E$  and  $\eta$  commute with  $\rho_q$ ,  $\langle \dot{H}_E | t \rangle_q = \langle \dot{\eta}_q | t \rangle_q = 0$ . Next we consider the linear relaxation approximation, i.e., setting  $Y = 1$  in Eq. (18), and then

$$\langle \dot{H}_E | t \rangle \simeq \int_{-\infty}^0 dt' e^{tt'} [\langle \dot{H}_E, \dot{H}_E(t') | t \rangle \beta(t+t') + \langle \dot{H}_E, H_E(t') | t \rangle \dot{\beta}(t+t')], \quad (20a)$$

$$\langle \dot{\eta}_q | t \rangle \simeq \sum_{q'} \int_{-\infty}^0 dt e^{tt'} [\langle \dot{\eta}_q, \dot{\eta}_q(t') | t \rangle F_{q'}(t+t') + \langle \dot{\eta}_q, \eta_q(t') | t \rangle \dot{F}_{q'}(t+t')]. \quad (20b)$$

We have defined the correlation functions

$$[A, B(t') | t] = \text{Tr}[A e^{-uS} B(t') e^{uS} \rho_q(t, 0)],$$

and use was made of the fact that the cross correlations  $\langle \dot{H}_E, \dot{\eta} \rangle$  and  $\langle \dot{\eta}, \dot{H}_E \rangle$  vanish. Up to second order in the interaction energy,  $H_E$ , the Heisenberg operators in the correlation functions, are to be taken as evolving under the action of the free Hamiltonian. Within these approximations one obtains

$$\begin{aligned} \dot{\beta}(t) = & -\frac{2\pi}{3n_x} \beta^2(t) \left( \sum_{\vec{k}\vec{q}} |V_j(q)|^2 \epsilon(\vec{k}j) [\nu_q(t) + 1] f_{\vec{k}+\vec{q}j} (1 - f_{\vec{k}j}) - \nu_q f_{\vec{k}} (1 - f_{\vec{k}+\vec{q}j}) \right) \delta(\epsilon_{\vec{k}+\vec{q}j} - \epsilon_{\vec{k}j} - \hbar\omega_0) \\ & - \sum_{\vec{k}\vec{q}j} |V_j(q)|^2 \epsilon_{\vec{k}j} [\nu_q(t) + 1] f_{\vec{k}j} (1 - f_{\vec{k}-\vec{q}j}) - \nu_q f_{\vec{k}-\vec{q}j} (1 - f_{\vec{k}j}) \delta(\epsilon_{\vec{k}-\vec{q}j} - \epsilon_{\vec{k}j} + \hbar\omega_0) \end{aligned} \quad (21a)$$

and

$$\dot{\nu}(\vec{q} | t) = 2\pi \sum_{\vec{k}j} |V_j(q)|^2 f_{\vec{k}j} e^{-\beta\omega_0} \left( 1 - \frac{\nu_q}{\nu_0} \right) \delta(\epsilon_{\vec{k}+\vec{q}j} - \epsilon_{\vec{k}j} - \hbar\omega_0), \quad (21b)$$

where it has been defined  $\nu_0 = [\exp[\beta(t)\omega_0] - 1]^{-1}$ .

Introducing the following definitions and scaling,

$$x = \beta(t)\hbar\omega_0, \quad \theta = 2\pi\alpha_e\omega_0 [1 + (m_h/m_e)^{1/2}]^{-1}t, \quad \lambda_e = \left( \frac{2m_e\omega_0}{\hbar} \right)^{-1/2},$$

$$y = \lambda_e q, \quad n^* = n_x [1 + (m_h/m_e)^{1/2}]^{-1}, \quad y_{\pm}(z) = z \pm (z^2 + 1)^{1/2},$$

$$f(y) = \frac{1}{4} (y + y^{-1})^2, \quad y' = (m_e/m_h)y,$$

after performing the integrations  $\vec{K}$  and  $\vec{q}$  we are left with the expressions

$$\frac{dx(\theta)}{d\theta} = \frac{x^{7/8}}{3\pi^{3/2}} e^{-x} \int_0^{\infty} dz e^{-xz^2} z \int_{y_-}^{y_+} \frac{dy}{y} \left( 1 - \frac{\nu(y|\theta)}{\nu_0(\theta)} \right), \quad (22a)$$

$$\frac{d\nu(\vec{q}|\theta)}{d\theta} = \frac{\pi^{1/2} n^* \lambda_e^3}{y^3} x^{1/2} [e^{-xf(y)} + (m_h/m_e) e^{-xf(y')}] \left( 1 - \frac{\nu(y|\theta)}{\nu_0(\theta)} \right). \quad (22b)$$

Clearly, Eqs. (22) have a steady-state solution,  $\dot{\beta} = 0$ ,  $\dot{\nu} = 0$ , when  $\nu(\vec{q} | t) = \nu_0(t)$  for all  $\vec{q}$ . This is the condition of equilibrium of the two subsystems, wherever the composed system remains isolated.

The initial conditions have already been stated. Finally the reciprocal temperature  $\beta(\vec{q}, t)$  of LO phonons in mode  $\vec{q}$  is defined in the sense of non-equilibrium thermodynamics by

$$\nu(q | t) = -\delta\phi / \delta x(\vec{q} | t) = [\exp x(\vec{q} | t) - 1]^{-1}, \quad (23)$$

where

$$x(\vec{q} | t) = \beta(\vec{q} | t)\hbar\omega_0 \equiv F_q(t).$$

Next we evaluate Eqs. (22) using for the effective masses and phonon frequency those values corresponding to GaAs.

#### IV. APPLICATION AND CONCLUSIONS

For the case of a pure sample of GaAs with an initial concentration of photoexcited carriers  $n = 3 \times 10^{17} \text{ cm}^{-3}$ , Fig. 1 shows the evolution of the reciprocal temperatures of carriers and a few

LO-phonon modes. Figure 2 gives the rate of LO-phonon generation versus  $x(t)$ . It should be kept in mind that the origin of time in Fig. 1 is defined by the condition of internal thermalization of the carriers, typically a fraction of a picosecond after the application of the laser pulse.<sup>27,28</sup> Therefore, Fig. 2, however extrapolated to the origin, has only significance for values of  $x(t)$  larger than  $x(0) = \hbar\omega_0 3(\hbar\omega_1 - E_G)^{-1}$ , which is the initial condition for the carrier temperature. That value for the phonons is  $x(\vec{q} | 0) = \hbar\omega_0/k_B T_0$ , with  $T_0$  the temperature of a liquid-helium bath.

It should be noted that we have neglected the energy exchange between the subsystems during the interval of internal thermalization of the carriers (subpicosecond scale), a restriction inherent to the method since it cannot account for the description of the system at too-short times, i.e., previous to the secularization of the macrovariables. Consequently the effective temperatures of the LO-phonon modes are underestimated, mainly for the shell in reciprocal space in the range of  $\vec{q}$  vectors more favorable for the production of excess phonons in the early stages of the relaxation process.<sup>12,15</sup> Figures 1 and 2 present the result of our calculations in a time interval which runs over a few decades of picosecond, to be consistent with the approximation introduced in disregarding the rate of pair recombination and energy relaxation in the lattice (thermal bath).

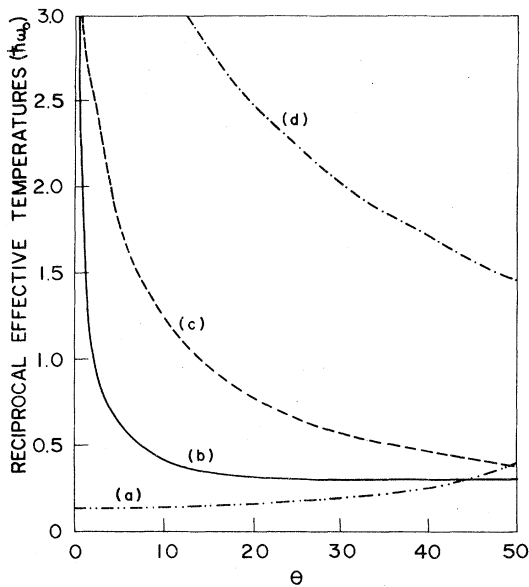


FIG. 1. Reciprocal quasitemperatures (in units of  $\hbar\omega_0$ ) for (a) electrons and LO phonons of wave vectors, (b) 0.1, (c) 0.5, and (d) 1.0 (wave vectors in units of  $\lambda = 39 \text{ \AA}$ ) as a function of the reduced time  $\theta = 1.15t$  ( $t$  in picoseconds).

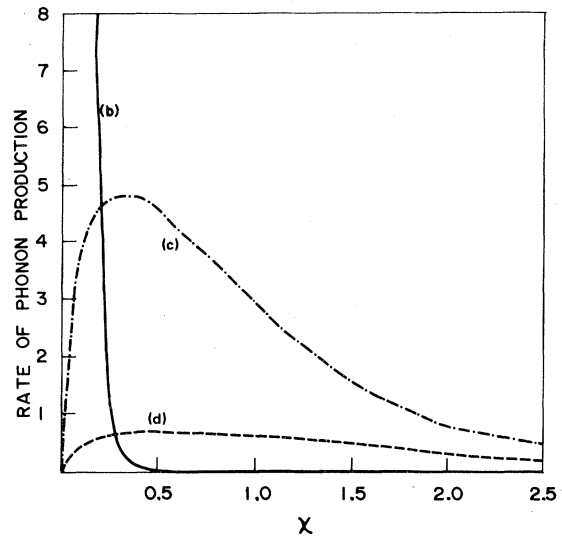


FIG. 2. The rate of LO-phonon production  $\partial\nu(\vec{q}, \theta)/\partial\theta$  as a function of the electron quasitemperature  $x = \beta\hbar\omega_0$ . Indexes are the same as in caption to Fig. 1.

Inspection of Eq. (22b) tells us that the LO-phonon generation rate will approximately follow a third-power law of the phonon wavelength<sup>14</sup> only in conditions when the carrier temperature remains almost constant and the number of phonons is not too large [ $\nu(\vec{q} | t)/\nu_0(t) \ll 1$ ]. Further, because of the very rapid internal thermalization of the photoexcited electron-hole plasma, the rate of production of LO phonons is much larger, the smaller the wave number. Thus, long-wavelength phonons are the warmer ones prior to final thermalization; this seems to be in agreement with the experimental results of Ref. 12. This removes the inconsistency observed when the experimental results were compared with a theoretical model that considered the decay of the energetic carriers through LO-phonon production while cascading down from the narrow energy strip to which they were excited by photon absorption.<sup>12,15</sup> Such a model overlooked the role of electron-electron collisions.

As already pointed out, the quasitemperatures of carriers and LO phonons are defined in the sense of nonequilibrium statistical thermodynamics as  $\beta(\vec{q} | t) = \delta S(t)/\delta\langle H_B | t \rangle$  and  $\beta(\vec{q} | t) = \delta S(t)/\hbar\omega_0 \delta\nu(\vec{q} | t)$ , where  $S$  is the nonequilibrium entropy  $S(t) = -\text{Tr}[\rho \ln \rho_q(t, 0)]$ . One may ask how to measure these quasitemperatures. Several methods can be devised and here we just consider the time-resolved Raman spectroscopy.

For the LO phonons within the range of  $\vec{q}$  values accessible with a Raman probe, this is done by means of the measurements of the ratio of the intensities of the Stokes  $I_S$  to anti-Stokes  $I_{AS}$  bands

since

$$\hbar\omega_0\beta(\tilde{q}|t) = \ln(1 + I_S/I_{AS})^{-1}. \quad (24)$$

The usual (time-integrated) experiments provide a value resulting from the integration of the scattered intensity over the time resolution  $\Delta t$  of the spectrometer. It has been observed that for a 90° experimental geometry in measurements conducted at room temperature no noticeable departure of phonons from their equilibrium values was detected, but variations in the Raman-band line-width followed variations of the exciting laser power.<sup>15</sup> Our calculation permits us to estimate roughly that in these experiments the phonons in excess of equilibrium should be small compared to the number present at room temperature for the region in  $\tilde{q}$  space accessible to the Raman probe, but that as a consequence of the warmer long-wavelength LO-phonon contribution to intra-branch scattering, and mainly because of their interaction with the hot carriers, the Raman band-width should vary with excitation density, thus confirming the findings of Castro *et al.*<sup>15</sup> Determination of the carrier quasitemperature becomes more difficult due to many-body effects.

According to the response-function theory for far-from-equilibrium systems,<sup>2</sup> the differential time-resolved scattering cross section for an event with energy transfer  $\omega = \omega_L - \omega_S$ , where  $\omega_L$  is the laser-photon frequency and  $\omega_S$  the scattered-phonon frequency, and momentum transfer  $\tilde{q} = \tilde{k}_L - \tilde{k}_S$  is given by

$$\frac{d^2\sigma(t|\omega)}{d\Omega d\omega} = \frac{v^2\omega_s^2}{4\pi^2c^4} \text{Im} \sum_{\eta} \langle\langle V^{\dagger}; V|t, \omega \rangle\rangle_{\eta}. \quad (25)$$

Here  $v$  is the scattering volume,  $V$  is the scattering operator in the dipole approximation

$$V_1 = (e^2/mc^2)(\tilde{\epsilon}_L \cdot \tilde{\epsilon}_S)[2\pi\hbar c^2/v\epsilon_{\infty}(\omega_L\omega_S)^{1/2}], \quad (26a)$$

for scattering by charge-density fluctuations, and

$$V_2 = (e^2/mc^2)[2\pi\hbar c^2/v\epsilon_{\infty}(\omega_L\omega_S)^{1/2}](2\lambda/m) \times P_{vc}^2 \frac{E_G^2 + \omega_L^2}{(E_G^2 - \omega_L^2)^2} \sum_{\alpha} \langle\bar{\alpha}|\tilde{\sigma} \cdot (\tilde{\epsilon}_L \times \tilde{\epsilon}_S)|\alpha\rangle \quad (26b)$$

for scattering by spin-density fluctuations. Also  $\tilde{\epsilon}_{L,S}$  are the polarization vectors of the incident and scattered electric fields,  $\lambda$  is the spin-orbit coupling constant,  $P_{vc}$  is the matrix element of the electron momentum between conduction- and valence-band states at the zone center,  $\epsilon_{\infty}$  is the high-frequency dielectric constant,  $E_G$  is the energy gap, and  $\sigma$  are the Pauli matrices. Note the different symmetry of the Raman tensors for both

cases; index  $\alpha$  runs over the spin states, band split-off effect has been neglected, and we have taken  $\omega_S = \omega_L$  in the energy denominators.

Furthermore  $\langle\langle \dots |t, \omega \rangle\rangle_{\eta}$  stands for the Fourier transform of the nonequilibrium thermodynamic double-time Green function,

$$\langle\langle A; B|t, \tau \rangle\rangle = -i\theta(-\tau) \text{Tr}\{[A(\tau), B]_{\eta}\rho(t)\}, \quad (27)$$

where a statistical average is taken over Zubarev's nonequilibrium ensemble and  $\eta = +1$  or  $-1$  for anti-commutator or commutator of operators  $A$  and  $B$ , respectively. The equation of motion for the Green function is

$$\begin{aligned} -\hbar\omega \langle\langle A; B|t, \omega \rangle\rangle_{\eta} \\ = -\frac{\hbar}{2\pi} \langle[A, B]|t\rangle + \langle\langle[A, H]; B|t, \omega \rangle\rangle_{\eta}. \end{aligned} \quad (28)$$

The Green functions of Eq. (28) are evaluated using the random-phase approximation to deal with the Coulomb interaction between carriers, to obtain for the Raman cross section for scattering by charge-density fluctuations (cdf),

$$\left(\frac{d^2\sigma(t|\omega)}{d\omega d\Omega}\right)_{\text{cdf}} = \left(\frac{d^2\sigma(t|\omega)}{d\Omega d\omega}\right)_{\text{cdf}}^0 |\epsilon^{-1}(\tilde{q}, \omega|t)|^2, \quad (29)$$

where

$$\left(\frac{d^2\sigma}{d\Omega}\right)_{\text{cdf}}^0 = |V_1|^2 \sum_j \left(\frac{n_j}{qv_{\text{th}}^j}\right) e^{-t_j^2} \quad (30)$$

is the scattering cross section for the individual (bare) carriers,  $\xi_j(t) = \omega/qv_{\text{th}}^j(t)$ ,  $v_{\text{th}}^j(t) = [2/m_j^* \beta(t)]^{1/2}$  is the average thermal velocity, and  $j = e$  or  $h$  for electrons or holes.

The factor  $|\epsilon|^{-2}$  is due to direct Coulomb correlation effects,  $\epsilon$  being the RPA dielectric function

$$\begin{aligned} \epsilon(\tilde{q}, \omega|t) = 1 - 2 \sum_j \left(\frac{\omega_{Pj}}{qv_{\text{th}}^j}\right)^2 [-1 + 2\xi_j D(\xi_j)] \\ + i2\sqrt{\pi} \sum_j \left(\frac{\omega_{Pj}}{qv_{\text{th}}^j}\right)^2 \xi_j e^{-\xi_j^2}, \end{aligned} \quad (31)$$

where  $D(\xi)$  is the Dawson integral,<sup>29</sup> and  $\omega_{Pj}^2 = 4\pi n_j e^2/\epsilon_0 m_j^*$  is the plasma frequency.

The Raman cross section for scattering by spin-density fluctuations (sdf) is

$$\left(\frac{d^2\sigma(t|\omega)}{d\Omega d\omega}\right)_{\text{sdf}} = \left(\frac{d^2\sigma(t|\omega)}{d\Omega d\omega}\right)_{\text{sdf}}^0 |\mu^{-1}(\tilde{q}, \omega|t)|^2, \quad (32)$$

where now the scattering cross section for the bare carriers is the same as given by Eq. (30) except for the matrix element, and  $\mu$  is the RPA magnetic permeability

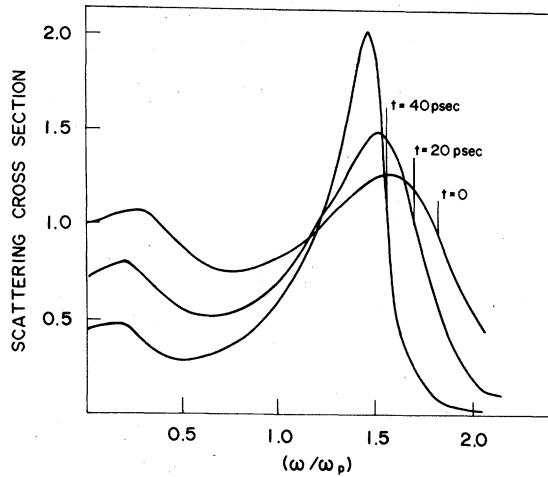


FIG. 3. Inelastic scattering of light by charge-density fluctuations in the nonequilibrium GaAs plasma at different times after completion of the exciting laser pulse. Ordinate in arbitrary units.

$$\mu(\vec{q}, \omega/t) = 1 + \sum_j \beta U_j [-1 + 2\xi_j D(\xi_j)] + i\sqrt{2\pi} \sum_j \beta U_j \xi_j e^{-\xi_j^2}, \quad (33)$$

with  $U_j$  being the exchange integrals. Figures 3 and 4 show Raman spectra for both cases. Scattering by cdf produces a spectrum with two main contributions: (a) single-particle Doppler-Raman scattering showing a deviation from the expected Maxwellian behavior at very low energy transfer due to Coulomb scattering effects, and (b) a band due to plasma scattering. The latter becomes more intense and more sharply defined with increasing time, whereas the quasiparticle band tends to fade away, because of the decreasing value of  $qv_{th}(t)$ , as expected.<sup>30</sup> Since no adjustable parameter is involved in the determination of the shape of the spectrum, fitting with the experimental data should provide the value of the quasitemperature  $\beta^{-1}(t)$ .

The spectrum due to scattering by sdf as given by Eq. (32) depends on the exchange integrals  $U_j$ , the  $s$ -wave contribution to Landau's two quasiparticle interaction functions.<sup>31</sup> To draw Fig. 4

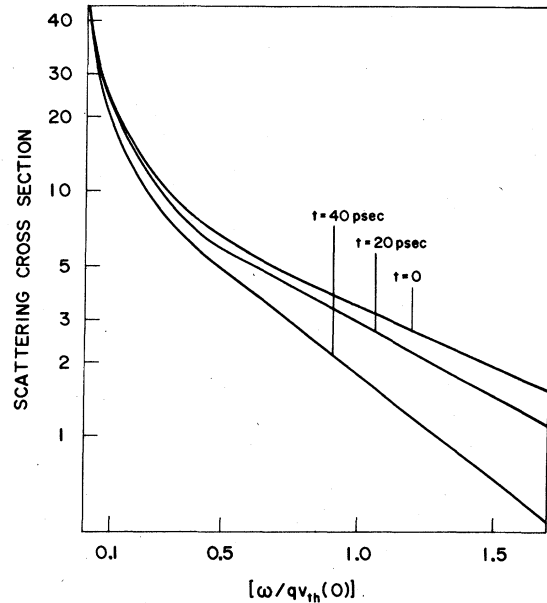


FIG. 4. Inelastic scattering of light by spin-density fluctuations in the nonequilibrium GaAs plasma at different times after completion of the exciting laser pulse. Ordinate in arbitrary units.

we have chosen  $U_e = U_h = 17$  meV, as roughly estimated from the work of Hedin.<sup>32</sup> The expected Maxwellian behavior is also upset by exchange-correlation effects contained in the Stoner-type enhancement factor  $|\mu^{-1}|^2$ . Again, fitting of experimental data should provide the values of the quasitemperature and, in this case, also of the exchange integral at each quasitemperature.

We have shown that Zubarev's nonequilibrium statistical-operator method, summarized in Sec. II, provides a quite convenient formalism to study the time evolution of far-from-equilibrium elementary excitations in semiconductors. It was exemplified in an application which analyzed a coupled photoexcited plasma and LO-phonons system, however restricted by the conditions imposed on the hierarchy of relaxation times involved. Detailed analysis of the nonequilibrium distributions of elementary excitations and optical-response functions of semiconductors under high levels of excitations are currently under way.<sup>33</sup>

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