

## **On Nonequilibrium Many-Body Systems II: Ultrafast Relaxation Phenomena in Semiconductors**

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**Abstract** We describe the application of the nonequilibrium statistical operator (NSO) method to the study of the irreversible thermodynamics and optical responses of semiconductors probed by ultrafast laser spectroscopy.

### **1. INTRODUCTION**

Presently two important new problems in the physics of semiconductors can be recognized: they are the questions related to the behaviour of semiconductors (a) on very short spatial and temporal scales (sub-micrometer and sub-picosecond), and, (b) on the presence of large electric fields or intense electromagnetic radiation. Under these conditions the familiar concepts of semiconductor physics are no longer applicable and improvements in theory and experimentation are necessary. The potential payoff of these kind of studies is high not only for their relevance to the understanding and development of semiconductor devices, but also for their bearing upon other areas of physics, chemistry, and biology.

In the first case, ultrasmall electronic research requires to deal with size-related effects in transport and optoelectronic properties. The new problems that arise are those related to the physical, chemical, and metallurgical properties in these highly constrained geometrical structures in simple or layered semiconductor systems. Further, besides the interest in the reduction of size and weight, high operational speeds are sought. Hence, the study of transport and other

properties on smaller and smaller time-scales become quite relevant and, for this purpose, ultrafast laser spectroscopy (UFLS) is a powerful tool. Finally, functioning of semiconductor devices often occur in far-from-equilibrium conditions. This is case (b), the object of discussion in the present article, which belongs to the subject of nonequilibrium statistical mechanics and thermodynamics, a discipline whose general aspects have been discussed in a previous article<sup>1</sup>.

The studies of the physical properties of condensed matter systems is based on experiments whose interpretation depends on a response function theory<sup>2</sup>. For systems slightly deviated from equilibrium exact closed expressions for the response functions to external stimuli and transport coefficients can be obtained in the form of correlation functions in equilibrium. This is Kubo's transport theory and the linear and nonlinear response function theories around equilibrium<sup>3</sup>. For systems strongly departed from equilibrium theory is not so well developed as it is for systems near equilibrium. Pump-probe experiments in optics is an instance where far-from-equilibrium situations arise. This area of research has shown rapid and notable improvements as a result of technical advances which allow to produce high levels of photoexcitation in matter and to obtain ultra-fast time-resolved spectra. These experiments are providing a better understanding of nonequilibrium processes in physical, chemical, and biological systems<sup>4</sup>.

Ultrafast time-resolved laser spectroscopy is a technique sufficiently refined today to be used with confidence for the investigation of very rapid microscopic mechanisms in the biological and physical realms. Picosecond and femtosecond laser spectroscopy constitute an extremely useful experimental tool to probe nonlinear irreversible processes in matter, allowing for the study of the statistical thermodynamic evolution of many-particle systems in the trillionth of second time-scale. Clearly, this call for a parallel development of theories appropriate for the treatment of many-body systems far from equilibrium. Such theories should make it possible to determine the detailed time-evolution of the irreversible processes that take place in the system while it is probed. This is a quite attractive and actual problem connected with the nonequilibrium nonlinear statistical mechanics and thermo-

dynamics of dynamic processes<sup>5</sup>. Also, studies in ultrafast laser spectroscopy seem to appropriately fit with Kubo's statement that "statistical mechanics of nonlinear nonequilibrium phenomena is just in its infancy [and] further progress can only be hoped by close cooperation with experiment"<sup>16</sup>.

An scheme to deal with response functions in far-from-equilibrium systems can be built on the basis of the nonequilibrium statistical operator (NSO) method described in a previous article<sup>1</sup>, heretofore referred to as I. In next section we briefly outline that scheme, which rests on the calculation of correlation functions of dynamical operators with averages taken over the nonequilibrium statistical ensemble. The calculations can also be performed in terms of appropriate nonequilibrium thermodynamic Green functions. However, because the system is strongly departed from equilibrium the calculation is not closed at this level: the equation for the response function is coupled to the set of nonlinear transport equations which describe the evolution of the macroscopic state of the system. The time-resolved response function theory we obtain allows to interpret experimental data and derive information on the nonequilibrium macroscopic state of the system on the time scale limited by the time-resolution of the detection equipment in a given experiment. We also describe the application of the theoretical technique to the study of ultrafast relaxation processes in highly photoexcited semiconductors probed by ultrafast laser spectroscopy, and we summarize some results.

## 2. ULTRAFAST RELAXATION KINETICS IN SEMICONDUCTORS

For systems slightly deviated from equilibrium exact closed expressions for their response function to mechanical perturbations can be obtained in the form of correlation functions in equilibrium<sup>2</sup>. A practical way to calculate them is the double-time thermodynamic Green function formalism of Bogoliubov and Tyablikov, described in an already classic paper by Zubarev<sup>7</sup>. The actual calculation may be difficult for the case of interacting many-body systems but it is formally closed at this level. However, measurements can be performed on systems strongly

departed from equilibrium, when the responses of the system depend on their instantaneous and local nonequilibrium state. This is the case of highly excited semiconductors when spectra obtained by means of ultrafast laser spectroscopy (UFLS) depend on the characteristics of the nonequilibrium distributions of elementary excitations during the lapse of instrumental time resolution.

Hence, the usual response function theory needs be replaced by another capable to incorporate these features. A natural generalization rests on the use of the usual scattering theory in conjunction with the nonequilibrium statistical operator method described in I.

The calculation is not difficult<sup>8</sup>, and for an scattering event, involving the energy transfer  $\hbar\omega$ , the rate of transition probability at time  $t$  is given by

$$w(\omega|t) = \frac{1}{\hbar^2} \int_{-\infty}^t dt' e^{-i\omega(t'-t)} \text{Tr}\{R^\dagger(t'-t)R(0)\rho_\varepsilon(t)\} + \text{c.c.}, \quad (1)$$

where we have assumed adiabatic application of the perturbation in the remote past and Zubarev's NSO has been used (Cf. I). Near equilibrium conditions, when  $\rho_\varepsilon(t)$  can be taken as the canonical distribution, eq. (1) goes over the well known results for the temperature-dependent rate of transition probability<sup>9</sup>.  $R(t)$  is the scattering operator defined by

$$R(t) = \bar{V}(t) \left[ 1 + \frac{1}{i\hbar} \int_{-\infty}^t dt' R(t') e^{-i\omega t'} \right], \quad (2)$$

where the interaction potential between the system and the probe is  $\bar{V}(t) \exp(-i\omega t)$ , and all operators are given in the Heisenberg representation of the unperturbed system.

To calculate the correlation function in eq. (1) one may resort to the use of nonequilibrium thermodynamic retarded Green functions<sup>8</sup>,

$$G_\eta(\tau; t) = -i\theta(-\tau) \text{Tr}\{[A(\tau), B]_\eta \rho_\varepsilon(t)\}, \quad (3)$$

where  $\theta$  is Heaviside's step function and  $\eta = +$  or  $-$  stands for anticommutator or commutator of operators  $A$  and  $B$  respectively.

Using the Fourier transform in  $\tau$  of the Green functions, eq.(1) can be rewritten as

$$\omega(\omega|t) = -\frac{2\pi}{A^2} \text{Im}\{G_+(\omega+is|t) + G_-(\omega+is|t)\}, \quad (4)$$

where ( $s \rightarrow +0$ )

$$G_\eta(\omega+is|t) = \int_{-\infty}^{\infty} \frac{d\tau}{2\tau} (-i)\theta(-\tau) \text{Tr}\{[\mathcal{R}^\dagger(\tau), \mathcal{R}]_\eta \rho_\epsilon(t)\} e^{-i(\omega+is)\tau}; \quad (5)$$

eq. (4) is a form of the fluctuation-dissipation theorem in the framework of the NSO-method for systems not necessarily near equilibrium. The equation of motion for the Green function  $G$  is

$$\hbar\omega \ll \mathcal{R}^\dagger; \mathcal{R} | \omega+is \gg_\eta = -\frac{\hbar}{2\pi} \text{Tr}\{[\mathcal{R}^\dagger, \mathcal{R}]_\eta \rho_\epsilon(t)\} + \ll [\mathcal{R}^\dagger, \mathcal{H}]; \mathcal{R} | \omega+is; t \gg_\eta; \quad (6)$$

where we have introduced the notation

$$G_\eta(\omega+is|t) \approx \ll A; B | \omega+is; t \gg_\eta. \quad (7)$$

Differently to the case of experiments performed near equilibrium, the equation of motion for the Green function is not closed in itself but it is coupled to the set of nonlinear transport equations which describe the nonequilibrium macroscopic state of the system, i.e. eqs. (39) in I,

$$\frac{d}{dt} Q_j(t) = \sum_{k=0}^{\infty} J_j^{(k)}(t). \quad (8)$$

Here  $Q_1(t), Q_2(t), \dots, Q_n(t)$  are the set of  $n$  variables which describe the macroscopic state of the system on the time-scale determined by the experimental conditions. On the right hand side of eq. (8) we have the series expansion in collision operators of increasing order in the interaction strengths described in I.

Alternatively it is possible to write equations of evolution for the set of intensive variables  $F_j(t), j=1,2,\dots,n$ , thermodynamically conjugated to the  $Q$ 's in the sense of eqs. (36) in I:

$$\begin{aligned} \frac{d}{dt} Q_j(t) &= - \frac{d}{dt} \frac{\partial \phi(t)}{\partial F_j(t)} = - \sum_{\ell=1}^n \frac{\partial^2 \phi(t)}{\partial F_j(t) \partial F_{\ell}(t)} \frac{d}{dt} F_{\ell}(t) = \\ &= - \sum_{\ell=1}^n C_{j\ell}(t) \frac{d}{dt} F_{\ell}(t) \quad , \end{aligned} \tag{9}$$

where

$$C_{j\ell}(t) = (P_j; P_{\ell} | t) = \text{Tr} \{ P_j \bar{P}_{\ell} \rho_{cg}(t) \} \quad ,$$

with  $\Delta P = P - \text{Tr} \{ P \rho_{cg}(t) \}$  ;

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

and  $\rho_{cg}$  is the coarse-grained statistical operator (eq. (12) in I),  $S$  is the coarse-grained entropy operator (eq. (13) in I), and  $P_j$  are the set of dynamical quantities whose average values over the nonequilibrium ensemble are the macrovariables  $Q_j(t)$  (eq. (3) in I). Thus, using eqs. (8) and (9) we find

$$\frac{d}{dt} F_j(t) = - \sum_{\ell=1}^n \sum_{k=0}^{\infty} C_{j\ell}^{-1}(t) J_{\ell}^{(k)}(t) \tag{10}$$

The advantage of writing equations for the intensive nonequilibrium variables  $F_j(t)$  is that the NSO and  $\rho_{cg}$  depend explicitly on them and only implicitly on macrovariables  $Q_j(t)$  through the nonequilibrium equations of state [eqs. (36) in I].

Let us now consider explicitly the case of highly excited plasmas in semiconductors (HEPS). Plasma in a semiconductor is the fluid of conduction electrons and/or holes generated by illumination or doping, moving in the positive background of the lattice. There are quite interesting physical systems, among other reasons, because of the flexibility in the choice of a number of parameters such as Fermi energy, plasma frequency, energy dispersion relations, cyclotron frequency, different types of carriers and effective masses, etc.<sup>10</sup>. In this plasma in solid state the presence of the lattice introduce notable differences in comparison with a gaseous plasma. Typically it produces a background

dielectric constant of the order of 10, and exciton effective masses one tenth the value of the free electron mass. Thus, the characteristics units for length and energy, the Bohr radius and the Rydberg, becomes the excitonic radius,  $r_x$ , and excitonic Rydberg,  $Ry_x$ , which are roughly 100 times larger and a hundredth time smaller than the corresponding atomic units respectively. Hence, metallic densities, i.e. intercarrier spacing,  $r_s$ , measured in units of  $r_x$ , in the range 1 to 5 arises at quite accessible laboratory conditions for concentrations of roughly  $10^{18}$  carriers per  $cm^3$ <sup>11</sup>.

In fig. 1 we depict the situation to be expected in a typical pump-probe experiment. It describes a sample consisting of a direct-gap polar semiconductor where a concentration  $n$  of electron-hole pairs is generated by a pulse of intense laser light. Direct absorption of one photon occurs if  $\hbar\omega_L > E_G$ , where  $\omega_L$  is the laser frequency and  $E_G$  the semiconductor energy gap. Excitation by means of nonlinear effects such as two-photon absorption or second harmonic generation, ( $\hbar\omega_L < E_G$  but  $2\hbar\omega_L > E_G$ ) allows for bulk excitation with a good degree of homogeneity. The sample is illuminated by a second laser (probe) of weak intensity, so as to avoid noticeable modification of the nonequilibrium state of the system produced by the intense pulse from the pumping laser, and an optical response is recorded. Measurements of luminescence do not require a laser probe.

On absorption of the pumping laser light electrons make transitions from the valence band to the conduction band. These carriers (electrons and holes) with a concentration  $n$  are initially narrowly distributed around the energy levels centered on, say,  $\epsilon^e$  in the conduction band and  $\epsilon^h$  in the valence band, with  $\epsilon^e - \epsilon^h \approx \hbar\omega_L$  (or  $2\hbar\omega_L$ ). Next they are rapidly redistributed in energy space due to the strong long-range Coulomb interaction among them<sup>12</sup>.

The subsequent state of this double Fermi liquid depends on the values of the concentration  $n$  and its instantaneous effective temperature  $T_c(\mathbf{t})$ . The latter is a measure of the kinetic energy of the carriers, i.e. at each time  $\mathbf{t}$  the difference between the excess energy per pair received from the laser pump and the energy lost in relaxation processes. Let us assume that the conditions are such that a fluid of electrons and holes

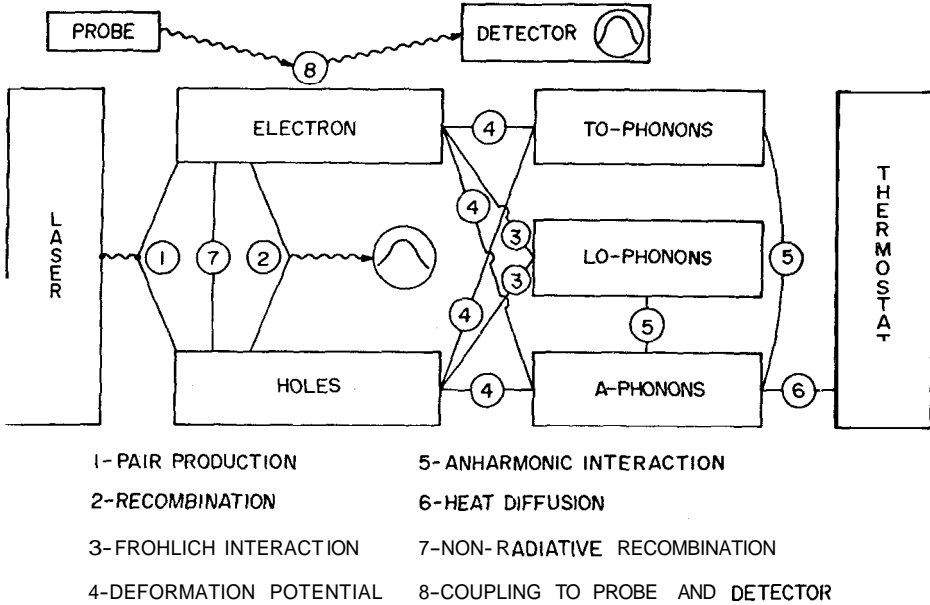


Fig.1 - Schematic description of a pump-probe optical experiment performed on a semiconductor sample. The different channels involving energy transfer are indicated.

is formed instead of the exciton gas, i.e. that the system is on the metallic side of Mott transition ( $n > n_M(T_c^*)$ ). This occurs typically for values of  $n$  of the order of  $10^{16} \text{ cm}^{-3}$  and larger<sup>13</sup>.

A HEPS has been created and to describe its macroscopic state it is a prerequisite to define a basis set of macrovariables. We have discussed this question in I and we choose a set of variables to which we have a direct or indirect access in the measurement procedure restricted by the experimental set up. In figure 1 the main energy relaxation channels between the sample subsystems and between these and external reservoirs (thermostat and pumping laser) are indicated. Since the recorded spectra is averaged over the finite volume observed by the spectrograph there is no experimental access to the local hydrodynamic properties of the HEPS. Thus, inspection of figure 1 suggests that to



describe the nonequilibrium thermodynamic state of the HEPS an appropriate set of macrovariables is

$Q_1$ : The energy of carriers,  $E_c(t) = \text{Tr}\{H_c \rho_c(t)\}$ ,

$Q_2$ : The energy of LO phonons,  $E_{LO}(t) = \text{Tr}\{H_{LO} \rho_c(t)\}$ ,

$Q_3$ : The energy of TO phonons,  $E_{TO}(t) = \text{Tr}\{H_{TO} \rho_c(t)\}$ ,

$Q_4$ : The energy of A (acoustic) phonons,  $E_A(t) = \text{Tr}\{H_A \rho_c(t)\}$ ,

$Q_5$ : The concentration of electrons,  $n(t) = \text{Tr}\{N_e \rho_c(t)\}$ ,

$Q_6$ : The concentration of holes,  $n(t) = \text{Tr}\{N_h \rho_c(t)\}$ .

The different dynamical quantities whose average over the nonequilibrium ensemble define variables Q are

$P_1$  : The carriers hamiltonian,  $H_c$ ,

$P_2$  : The LO-phonons hamiltonian,  $H_{LO}$ ,

$P_3$  : The TO-phonons hamiltonian,  $H_{TO}$ ,

$P_4$  : The A-phonons hamiltonian,  $H_A$ ,

$P_5$  : The number operator for electrons,  $N_e$ ,

$P_6$  : The number operator for holes,  $N_h$ .

Finally the set of intensive variables thermodynamically conjugated to the macrovariables above in the sense of eqs. (27) in i is

$F_1$  : The reciprocal effective temperature of carriers,  $\beta_c(t) = 1/kT_c^*(t)$ ,

$F_2$  : The reciprocal effective temperature of LO phonons,  $\beta_{LO}(t) = 1/k T_{LO}^*(t)$ ,

$F_3$  : The reciprocal effective temperature of TO phonons,  $\beta_{TO}(t) = 1/k T_{TO}^*(t)$ ,

$F_4$  : The reciprocal effective temperature of A phonons,  $\beta_A(t) = 1/k T_A^*(t)$ ,

$F_5$  : The quasi-chemical potential of electrons,  $-\beta_c(t)\mu_e(t)$ ,

$F_6$  : The quasi-chemical potential of holes,  $-\beta_c(t)\mu_h(t)$ .

Concentration  $n(t)$  and quasi-chemical potentials are connected, once the internal thermalization of carriers has occurred, by the relations

$$n(t) = n_e^0(t) F_{1/2}[\beta_c(t) \mu_e(t)] = n_h^0(t) F_{1/2}[\beta_c(t) \mu_h(t)] , \quad (11)$$

where

$$n_\alpha^0(t) = 2 [2\pi m_\alpha kT_c^*(t) / \hbar^2]^{3/2} , \quad (12)$$

and  $F$  are Fermi functions of index half<sup>14</sup>;  $\alpha$  is  $e$  or  $h$ .

We recall that eq. (11) remains valid as long as the instrumental resolution time is larger than the relaxation time of carriers towards a state of internal thermalization, which is typically a fraction of picosecond<sup>12</sup>.

The semiconducting sample is an open system in contact with the external reservoirs composed of the laser and the thermal bath. We assume that they are ideal reservoirs, i.e. their macroscopic states do not change as a result of the interactions with the sample. The laser is characterized by the intensity and frequency of the radiation field and the thermal bath by a constant temperature  $T_0$ . Then, we write

$$\rho_{C, cg}(t) = \rho_{R, cg}(0) \times \rho_{cg}(t) , \quad (13)$$

where  $\rho_{C, cg}$  is the coarse-grained statistical operator of the closed system of sample and reservoirs,  $\rho_{R, cg}(0)$  is the steady-state statistical distribution of the reservoirs, and  $\rho_{cg}(t)$  the coarse-grained statistical operator of the open system under experimentation. According to the formalism of I, and for the set of macrovariables we have chosen for the description of the macrostate of the HESP,  $\rho_{cg}(t)$  is given by

$$\rho_{cg}(t) = \exp\{-\phi(t) - \beta_c(t) [H_c - \mu_e(t) N_e - \mu_h(t) N_h] - \beta_{L0}(t) H_{L0} - \beta_{T0}(t) H_{T0} - \beta_A(t) H_A\} \quad (14)$$

The nonequilibrium thermodynamic evolution of the HEPS can now be obtained by solving the nonlinear transport equations (8) for the macrovariables or the corresponding equations (9) for the thermodynamic Lagrange parameters. We solve them, in the quasi-linear relaxation approximation (Cf. I), for situations encountered in several experiments reported in the literature<sup>15</sup>. In the quasi-linear relaxation approximation the scattering operators are cast in the form of instantaneous Boltzmann-like collision terms. They have the form that would be obtained using Born-approximation in perturbation theory but with the equilibrium distributions replaced by those characterized by the thermodynamic parameters F already listed<sup>16</sup>. The approximate nonlinear transport equations:

$$\frac{d}{dt} E_c(t) = \frac{d}{dt} [E_{c,L}(t) + E_{c,R}(t) + E_{c,LO}(t) + E_{c,TO}(t) + E_{c,A}(t)] \quad (15)$$

where the different terms on the right hand side are the contributions to the rate of variation of the carrier energy due to interactions with the laser source, radiative recombination, and interactions with longitudinal-optical (LO), transverse-optical (TO), and acoustic (A) phonon fields, respectively. The five terms are

$$\frac{d}{dt} E_{c,L}(t) = \frac{2\pi}{\hbar} \sum_{\vec{k}, \vec{q}} |U^L(\vec{k}, \vec{q})|^2 \hbar \Omega_L [1 - f_{\vec{k}}^e(t) - f_{\vec{k}}^h(t)] \delta(\epsilon_k^e + \epsilon_k^h - \hbar \Omega_L) \quad (16a)$$

$$\frac{d}{dt} E_{c,R}(t) = - \frac{2\pi}{\hbar} \sum_{\vec{k}, \vec{q}} |U^R(\vec{k}, \vec{q})|^2 (\epsilon_k^e + \epsilon_k^h) f_{\vec{k}}^e(t) f_{\vec{k}}^h(t) \delta(\epsilon_k^e + \epsilon_k^h - \hbar c q) \quad (16b)$$

$$\begin{aligned} \frac{d}{dt} E_{c,Y}(t) = & \frac{2\pi}{\hbar} \sum_{\alpha} \sum_{\vec{k}, \vec{q}} |U^Y(\vec{k}, \vec{q})|^2 (\epsilon_{k+q}^{\alpha} - \epsilon_k^{\alpha}) \{v_{\vec{q}}^Y(t) f_{\vec{k}}^{\alpha}(t) [1 - f_{\vec{k}+\vec{q}}^{\alpha}(t)] - \\ & - [1 + v_{\vec{q}}^Y(t)] [1 - f_{\vec{k}}^{\alpha}(t)] f_{\vec{k}+\vec{q}}^{\alpha}(t)\} \delta(\epsilon_{k+q}^{\alpha} - \epsilon_k^{\alpha} - \hbar \omega_q^Y) \end{aligned} \quad (16c)$$

In above equations  $\alpha = e$  or  $h$ ,  $Y = LO, TO$ , or  $A$ ,

$$f_{\vec{k}}^{\alpha}(t) = \{ \exp \{ \beta_e(t) [\epsilon_k^{\alpha} - \mu_{\alpha}(t)] \} + 1 \}^{-1}, \quad (17a)$$

$$v_{\vec{q}}^Y(t) = \{ \exp [ \beta_Y(t) \hbar \omega_q^Y ] - 1 \}^{-1}, \quad (17b)$$

and the matrix elements are

$$|U^R(\vec{k}, \vec{q})|^2 = \frac{4\pi e^2 \hbar E_G}{V \epsilon_{\infty} c q} \left( \frac{1}{m_e} + \frac{1}{m_h} \right) \quad (18a)$$

$$|U_{\alpha}^{LO}(\vec{k}, \vec{q})|^2 = \frac{2\pi e^2 \hbar \omega_{LO}}{V q^2 \epsilon^2(q, t)} \left( \frac{1}{\epsilon_{\infty}} - \frac{1}{\epsilon_0} \right) \quad (18b)$$

where we have used the RPA dielectric function

$$\epsilon(\vec{q}, t) = 1 + |q_0^2(t)/q^2|, \quad (19)$$

$$q_0^2(t) = \frac{4\pi e^2}{\epsilon_0 V} \sum_{\alpha, \vec{k}} \left| \frac{\partial f_{\vec{k}}^{\alpha}(t)}{\partial \epsilon_k^{\alpha}} \right|$$

The time dependence of the dielectric function is a result of its dependence on the instantaneous macroscopic state of the system.  $E_G$  is the forbidden energy gap,  $\epsilon_0$  and  $\epsilon_{\infty}$  the static and high frequency dielectric constants,  $\omega_{LO}$  the dispersionless frequency of LO phonons, and  $V$  the active volume of the sample.  $\epsilon_k^e = E_G + (\hbar^2 k^2 / 2m_e)$ ,  $\epsilon_k^h = \hbar^2 k^2 / 2m_h$  are the energy dispersion relations for electrons and holes with effective masses  $m_e$  and  $m_h$  respectively.

Moreover,

$$|U^{T0}(\vec{k}, \vec{q})|^2 = \frac{E_{T0, \alpha} \hbar}{2\rho V \omega_{T0}},$$

$$|U_{\alpha}^A(\vec{k}, \vec{q})|^2 = \frac{E_{A, \alpha}^2 \hbar q}{2\rho V s},$$

where  $\rho$  is the density of the material,  $s$  the speed of sound, a Debye model was used to describe the A phonons (then  $\omega_q^A = sq$ ),  $\omega_{T0}$  is the dispersionless frequency of T0 phonons, and  $E_{\gamma, \alpha}$  the strengths of

the deformation potential interactions.

The rate of carriers energy variation due to interaction with a laser source of frequency  $\omega_L$  and flux intensity  $I_L(t)$ , eq. (16a), is written in the form

$$\frac{d}{dt} E_{c,L}(t) = \begin{cases} \alpha_1(\omega_L) I_L(t) [1 - f^e(t) - f^h(t)] & (20a) \\ \alpha_2(\omega_L) I_L^2(t) [1 - f^e(t) - f^h(t)] & (20b) \end{cases}$$

where  $\alpha_1$  and  $\alpha_2$  are the absorption coefficients of one and two photons respectively;  $\Omega_L$  in eq. (16a) is  $\omega_L$  or  $2\omega_L$  for the two cases (20a) and (20b), and  $U^L$  is the corresponding matrix element. In the calculations we use the experimental values of the absorption coefficients. Finally,  $f^e$  and  $f^h$  are Fermi distributions with energies  $\epsilon^{e,h} = (m_x/m_{e,h})(\hbar\omega_L - E_G)$  where  $m_x^{-1} = m_e^{-1} + m_h^{-1}$ , and for temperature  $T_c^*(t)$  and chemical potentials  $\mu_e(t)$  and  $\mu_h(t)$ .

We also have

$$\frac{d}{dt} E_{LO}(t) = - \frac{d}{dt} E_{c,LO}(t) + \frac{d}{dt} E_{LO,A}(t) , \quad (21)$$

where

$$\frac{d}{dt} E_{LO,A}(t) = \sum_q \hbar\omega_{LO} \frac{v_{\vec{q}}^{LO}(t) - v_{\vec{q}}^{LO}(t, T_A^*)}{\tau_{LO,A}} , \quad (22)$$

is the rate of energy transfer of LO to A phonons due to anharmonic processes:  $\tau$  is a phenomenological relaxation time, and  $v_{\vec{q}}^{LO}(t, T_A^*) = \{ \exp[\beta_A(t) \hbar\omega_{\vec{q}}^{LO}] - 1 \}^{-1}$ .

For the rate of variation of energy of TO and A phonons we find

$$\frac{d}{dt} E_{TO}(t) = - \frac{d}{dt} E_{c,TO}(t) + \frac{d}{dt} E_{TO,A}(t) , \quad (23)$$

$$\frac{d}{dt} E_{TO,A}(t) = \sum_q \hbar\omega_{TO} \frac{v_{\vec{q}}^{TO}(t) - v_{\vec{q}}^{TO}(t, T_A^*)}{\tau_{TO,A}} , \quad (24)$$

$$\frac{d}{dt} E_A(t) = - \frac{d}{dt} E_{c,A}(t) - \frac{d}{dt} E_{L0,A}(t) - \frac{d}{dt} E_{T0,A}(t) + \frac{d}{dt} E_{A,B}(t) , \quad (25)$$

$$\frac{d}{dt} E_{A,B}(t) = - \sum_{\vec{q}} \bar{n}_{sq} \frac{v_{\vec{q}}^A(t) - v_{\vec{q}}^A(T_0)}{\tau_{A,B}} \quad (26)$$

where  $B$  refers to the thermal bath at temperature  $T_0$ . Eq.(26) accounts for heat diffusion from the A-phonon system to the thermal bath, and we have introduced in it a phenomenological relaxation time for heat diffusion which depends on the diffusion coefficient and the dimensions of the surface of the active volume of the sample, and it should be estimated for each case when performing specific numerical calculations. The other phenomenological relaxation times,  $\tau_{L0A}$  and  $\tau_{T0A}$ , can be evaluated from line-widths of Raman lines.

The rate of change of the carriers density is

$$\frac{d}{dt} n(t) = \frac{d}{dt} n(t)]_R + \frac{1}{\hbar\omega_L} \frac{d}{dt} E_{c,L}(t) \quad (27)$$

where

$$\frac{d}{dt} n_R(t)]_R = - \frac{2\pi}{\hbar} \sum_{\vec{k},\vec{q}} |U^R(\vec{k},\vec{q})|^2 f_{\vec{k}}^e(t) f_{\vec{k}}^h(t) \delta(\epsilon_{\vec{k}}^e + \epsilon_{\vec{k}}^h - \hbar\omega_L) \quad (28)$$

To obtain the intensive nonequilibrium thermodynamic parameters  $F_i$ , eqs. (15), (21), (23), (25) and (27) must be complemented with eq. (11), and

$$\frac{d}{dt} E_c(t) = -(H_c; H_e | t) \dot{\beta}_c + (H_c; N_e | t) (\mu_e \dot{\beta}_c) + (H_c; N_h | t) (\mu_h \dot{\beta}_c) , \quad (29a)$$

$$\frac{d}{dt} E_{L0}(t) = -(H_{L0}; H_{T0} | t) \dot{\beta}_{T0} , \quad (29b)$$

$$\frac{d}{dt} E_{T0}(t) = -(H_{T0}; H_{T0} | t) \dot{\beta}_{T0} , \quad (29c)$$

$$\frac{d}{dt} E_A(t) = - (H_A; H_A | t) \dot{\beta}_A \quad (29d)$$

$$\frac{d}{dt} n(t) = - (N_\alpha; H_c | t) \dot{\beta}_c + (N_\alpha; N_\alpha | t) (v_\alpha \dot{\beta}_c) , \quad (29e)$$

where we have introduced the correlation matrix  $C(t)$  with elements

$$(H_c; H_c | t) = \sum_{\alpha, \vec{k}} (\epsilon_\alpha^\alpha)^2 f_{\vec{k}}^\alpha(t) [1 - f_{\vec{k}}^\alpha(t)] \quad (30a)$$

$$(H_{LO}; H_{LO} | t) = \sum_{\vec{q}} \hbar^2 \omega_{LO}^2 v_{\vec{q}}^{LO}(t) [1 - v_{\vec{q}}^{LO}(t)] \quad (30b)$$

$$(H_{TO}; H_{TO} | t) = \sum_{\vec{q}} \hbar^2 \omega_{TO}^2 v_{\vec{q}}^{TO}(t) [1 - v_{\vec{q}}^{TO}(t)] \quad (30c)$$

$$(H_A; H_A | t) = \sum_{\vec{q}} (\hbar s q)^2 v_{\vec{q}}^A(t) [1 - v_{\vec{q}}^A(t)] \quad (30d)$$

$$(N_\alpha; N_\alpha | t) = \sum_{\vec{k}} f_{\vec{k}}^\alpha(t) [1 - f_{\vec{k}}^\alpha(t)] \quad (30e)$$

$$(H_c; N_\alpha | t) = (N_\alpha; H_c | t) = \sum_{\vec{k}} \epsilon_\alpha^\alpha f_{\vec{k}}^\alpha(t) [1 - f_{\vec{k}}^\alpha(t)] \quad (30f)$$

and all cross correlation functions other than (30f) are null.

We apply next these results to the case of GaAs samples receiving a laser pulse with a gaussian time-profile of length  $t_L$ , peak flux intensity  $I_L$  and frequency  $\omega_L$ . The system of equations for the five thermodynamic variables,  $\beta_c$ ,  $\beta_{LO}$ ,  $\beta_{TO}$ ,  $\beta_A$ , and  $n$ , given by eqs. (29) together with equations (15), (21), (23), (25), and (27) are solved computationally. This can be done once initial conditions are defined. First we choose an initial time,  $t = t_0$ , taken such that the laser illumination has produced a concentration of carriers of roughly  $5 \times 10^{15}$  pairs per cubic centimeter, thus ensuring that the system is on the metallic side of Mott transition. The initial value of the effective temperature of A phonons is taken equal to the bath temperature since transference

of energy from the overheated carriers and optical phonons begins to be relevant in the scale of tens of picosecond to nanosecond. To present no experiment has been performed giving the initial values of the effective temperatures in the early stages of the relaxation processes. Therefore we have proceeded making a rough estimative of the number of optical phonons  $f_{L0}$  and  $f_{T0}$  produced by collision with carriers up to the initial time  $t_0$ . Next  $T_c^*(t_0)$  is defined by

$$3k T_c^*(t_0) = [\hbar \Omega_L - E_G] - f_{L0} \hbar \omega_{L0} - f_{T0} \hbar \omega_{T0} ,$$

where on the left side we wrote the average classic thermal energy per electron-hole pair, and on the right side we wrote the difference between the energy pumped by the laser and the energy lost to the optical-phonon system.  $T_{L0, T0}^*(t_0)$  follow from the relation

$$v_{L0, T0}(T_{L0, T0}^*(t_0)) - v_{L0, T0}^{equil}(t_0) = f_{L0, T0} n(t_0) v_{cell} ,$$

which is the number of  $L0$  or  $T0$  phonons in excess of equilibrium at  $t=t_0$ . The value of  $n(t_0)$  is given by

$$(\hbar \omega_L)^{-1} \alpha_1 (\omega_L) \bar{I}_L \quad (\text{or } (\hbar \omega_L)^{-1} \alpha_2 (\omega_L) \bar{I}_L^2 ,$$

where  $\bar{I}_L$  is the integrated flux intensity of the Gaussian pulse up to  $t_0$ .

The values of the parameters and of the initial conditions used in the calculation for two different cases, are given in table 1.

The two cases roughly correspond to the experimental conditions of the experiments of references (15 a and b) respectively. In figures 2 and 3 we show the evolution of the effective temperatures of carriers, and  $L0$  and  $T0$  phonons. Figures 4 and 5 show the evolution of the quasi-chemical potentials for electrons and for holes. The zero in the scale of time indicates the time at which the pulse intensity is  $e^{-1}$  the peak value.

Inspection of these curves and of the values of the rates of relaxation energies between subsystems (not shown here) lead us to summarize the behaviour of highly photoexcited semiconductors as follows:



Table 1 - Initial Conditions and Parameters Used in the Numerical Calculations

	Case 1	Case 2
$n(0)$	$5 \times 10^{16} \text{ cm}^{-3}$	$5.5 \times 10^{16} \text{ cm}^{-3}$
$T_c(0)$	$9608^0 \text{ K}$	$406^0 \text{ K}$
$T_{LO}(0)$	$300^0 \text{ K}$	$30^0 \text{ K}$
$T_{TO}(0)$	$300^0 \text{ K}$	$26^0 \text{ K}$
$T_A(0) = T$	$300^0 \text{ K}$	$10^0 \text{ K}$
$t_L$	1 ps	.5 ps
$I_L$	$4.6 \times 10^{15} \text{ eV cm}^{-2} \text{ ps}^{-1}$	$1.9 \times 10^{15} \text{ eV cm}^{-2} \text{ ps}^{-1}$
$\omega_L$	$6.1 \times 10^{15} \text{ s}^{-1}$	$2.5 \times 10^{15} \text{ s}^{-1}$
$\alpha_1(\omega_L)$	$9.8 \times 10^3 \text{ cm}^{-1}$	$5.3 \times 10^3 \text{ cm}^{-1}$
$\tau_{LO}$	30 ps	60 ps
$\tau_{TO}$	30 ps	60 ps
$\tau_{A,B}$	$4.6 \times 10^5 \text{ ps}$	46 ps

1. There occurs a very rapid decrease of the carriers effective temperature until it nearly equals the effective temperature of the optical phonons.
2. At intermediate to high reservoir temperatures ( $T_0 \gtrsim 77^0 \text{ K}$ ) the effective temperature of the optical phonons increases only slightly above  $T_0$ . At low temperatures ( $T_0 \lesssim 20^0 \text{ K}$ )  $T_{LO}$  and  $T_{TO}$  increase rapidly from the equilibrium value  $T_0$ .
3. After roughly five picoseconds the LO-phonons, TO-phonons and carriers systems are nearly mutually thermalized. From then on the three subsystems proceed to final thermal equilibrium with the thermal bath

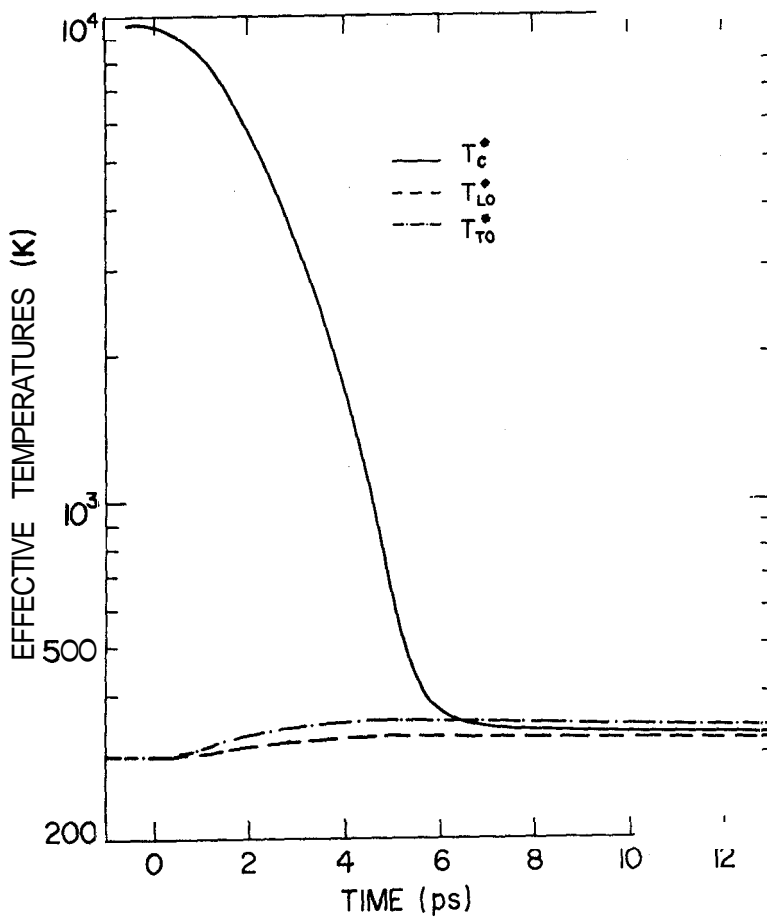


Fig.2 - Time-evolution of the effective temperatures of carriers,  $T_c^*$ , LO phonons,  $T_{LO}^*$ , and TO phonons,  $T_{TO}^*$ , calculated in the conditions of the experiment of reference (15a).

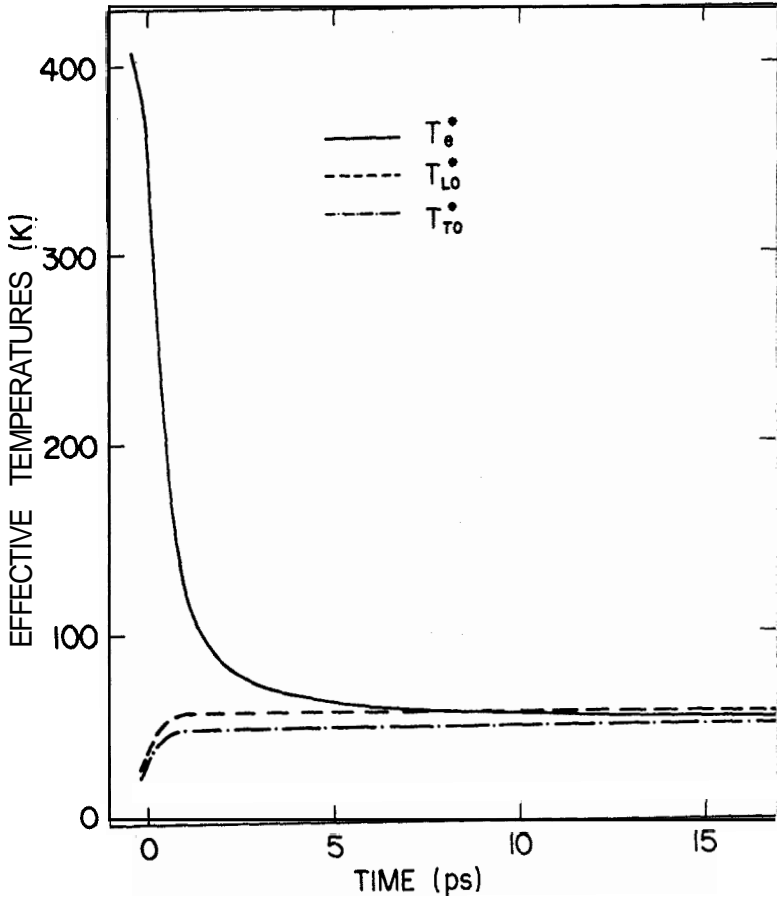


Fig.3 - Time-evolution of the effective temperature of carriers,  $T_e^*$ , L0 phonons,  $T_{L0}^*$ , and T0 phonons,  $T_{T0}^*$ , calculated in the conditions of the experiment of reference (15b).

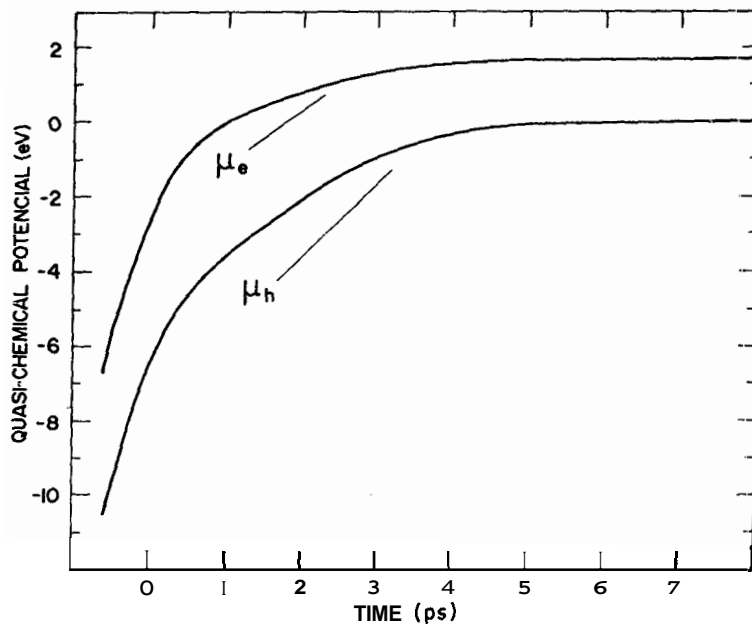


Fig.4 - Time-evolution of the quasi-chemical potentials in case 1.

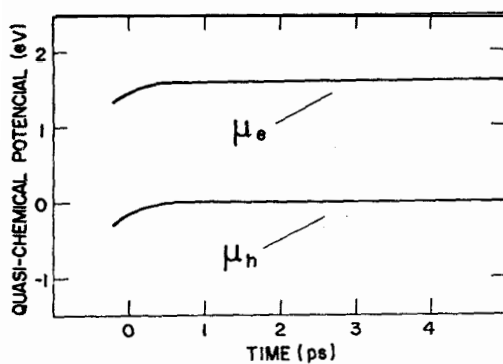


Fig.5 - Time-evolution of the quasi-chemical potentials in Case 2.

at a much slower pace, governed by the mechanism described in 5 below together with heat diffusion.

4. The rate of energy relaxation of carriers to the optical-phonon system is, during and immediately after the application of the laser pulse, roughly a factor 100 larger than the rate of relaxation to A phonons,

5. The rate of energy transfer from optical phonons to A phonons via anharmonic interaction is roughly one order of magnitude greater than the one resulting from collisions of carriers and A phonons. Thus, this mechanism is the relevant one to lead the system towards final equilibrium in a nanosecond time scale.

6. The acoustic-phonons effective temperature remains practically equal to the thermal bath temperature. The A phonons are slightly heated in case 1 when the excitation of the laser light is high (providing an excess of 2.5 eV per electron-hole pair).

7. The curves for the quasi-chemical potentials show the expected behaviour: they begin with values characteristic of a classical system and then, as  $T_C^*$  decreases tend to the expected quantum values for given n.

8. The long near plateaux in the graph of  $T_C^*$  vs  $t$  experimentally observed can then be ascribed to the interplay of the effects described in 3 and 5.

These conclusions apply to any polar direct-gap semiconductors under excitations of picosecond duration and energy transfer of the order of up to a few joules per cubic centimeter. Optical saturation does not allow to pump larger amounts of energy to obtain carrier concentrations above roughly  $10^{20}$  carriers/cm<sup>3</sup>. This situation is altered in the case of indirect-gap semiconductors, e.g. Si, Ge, when carrier concentration of  $10^{21}$  cm<sup>-3</sup> and up can result. Then laser-annealing processes are possible and an intense heating of the whole lattice occurs<sup>17</sup>. This may also be the case in polar direct-gap semiconductors under continuous illumination or under the action of long pulses (nanosecond duration). In such conditions the steady-state effective temperature of A phonons increases smoothly with increasing laser power, but a pronounced enhancement is expected near a critical value of the intensity of the laser radiation leading the system to melting conditions<sup>18</sup>.

It is worth mentioning that it has been suggested the possibility that a kind of condensation phenomena may take place before melting<sup>19</sup>. Such transformation of the excess energy into an *ordered structure* may occur in far-from-equilibrium conditions governed by nonlinear transport equations like eqs. (29). A few theoretical examples of these kind in semiconductor physics are found in the literature: formation of superlattice<sup>20a</sup>, Bose-like condensation of LO phonons<sup>20b</sup>, Bose-like condensation of excitons<sup>20c</sup>, and spatial ordering in HEPs<sup>20d</sup>. At this point the method of I makes contact with Prigogine's concept of dissipative structures in far-from-equilibrium systems<sup>21</sup>.

In conclusion we may say that techniques of ultrafast laser light spectroscopy in conjunction with statistical mechanics methods, which yield nonlinear transport equations for the description of the kinetic and relaxation processes in nonequilibrium physical systems, provide a powerful tool for the study of picosecond responses in semiconductor systems.

*The situation at present calls for additional concerted experimental and theoretical work to obtain a more general and comprehensive picture of the behaviour of semiconductor systems during ultra-short time intervals.* For that purpose it would be of interest to have measurements of optical and transport properties of semiconductors under a variety of experimental situations.

Finally we comment that UFLS with a companion theoretical nonlinear nonequilibrium statistical thermodynamics can apply to a wide range of problems in Physics, Chemistry and Biology. The kind of studies we have described here are quite worthwhile to pursue because they provide a manageable problem with easily repetitive experimental conditions and, thus, can be used to test techniques and procedures useful for the study of dynamical systems at a more complex level, e.g. biological systems.

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#### Resumo

É descrita a aplicação do método do operador estatístico de não-equilíbrio ao estudo da termodinâmica irreversível e as respostas ópticas de semicondutores polares de gap direto em experimentos de espectroscopia laser ultra-rápida.