POLAR SEMICONDUCTORS UNDER CONTINUOUS PHOTOEXCITATION

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The nonequilibrium thermodynamic state of a highly excited plasma in direct-gap polar semiconductors under conditions of continuous laser illumination is studied using the nonequilibrium statistical operator method. We obtain the set of coupled nonlinear generalized transport equations for the basic set of thermodynamic variables chosen for the description of the macroscopic state of the system. These equations are solved for the specific case of GaAs, to describe the transient regime and to obtain the steady-state values of the macrovariables in terms of the laser power. The rates of energy pumping and of energy transfer through the different relaxation channels are also given. Finally, we comment on the stability of the uniform steady-state solution.

1. Introduction

Semiconductor systems can be strongly departed from equilibrium by the action of high fields or intense laser illumination. The latter produces high levels of nonthermal carriers (electron–hole pairs) in intrinsic semiconductors, which move in the (also nonthermal) lattice background giving rise to the so-called nonequilibrium plasma in semiconductors, a particular case of solid state plasma [1]. This is an attractive subject for study because of the related technological interest for application in devices and the fact that highly excited plasma in semiconductors (HEPS) offer an excellent testing ground for theoretical ideas in the area of far-from-equilibrium systems. A large amount of experimental and theoretical research has been done on HEPS. On the experimental side a particularly useful technique is the ultrafast laser spectroscopy which allows for the analysis of relaxation processes and nonlinear transport in the picosecond and even femtosecond scales [2]. On the theoretical side, efforts have been devoted to improve ways to study the macroscopic state of nonequilibrium systems with very many degrees of freedom. Several methods and approaches in nonequilibrium statistical mechanics have been developed in an effort to provide satisfactory answers to the most relevant questions in the field of irreversible processes in complex systems [3]. They are required to improve upon the limitations in the domain of validity of the usual linear and nonlinear response function theory, no longer applicable to situations involving large thermal perturbations and feedback mechanisms, as is the case for HEPS.

From the existing theoretical approaches to the question of the dynamics of relaxation processes in far-from-equilibrium many-body systems, the nonequilibrium statistical operator (NSO) method seems to offer a very effective technique to deal with a large class of physical problems. It leads to the construction of a nonlinear transport theory considered to be a far-reaching generalization of the Chapman–Enskog method in the kinetic theory of gases. The advantages of the NSO method reside in the possibility to describe a large class of experimental situations where the system can be arbitrarily away from equilibrium, and with nonlinear, nonlocal, and retardation (memory) effects incorporated from the outset. We have used the NSO method in Zubarev’s form [4] and adapted for the treatment of open systems [5] to discuss ultrafast optical responses [6] and ultrafast transient transport [7] in HEPS.

The same theoretical approach is used to study the transient evolution and the ensuing stationary condition of the macroscopic state of direct-gap polar semiconductors under continuous laser illumination.
tion, and the results are reported in section 3. This kind of situation may arise in quantum generators and semiconductor devices, and, particularly, in experiments involving laser-induced damage and annealing [8]. In the next section the NSO method is briefly reviewed and from it we derive the set of coupled nonlinear transport equations for the set of relevant thermodynamic variables that describe the macroscopic state of the HEPS. These are the quasi-temperatures of carriers and of the various phonon branches, and the concentration of carriers. Their evolution in time is derived according to the NSO method from the transport equations for the energy densities of the phonons and of the excited carrier systems. They are solved numerically for the case of GaAs at room temperature under constant laser illumination with powers up to 500 kW cm\(^{-2}\). At the steady state the quasi-temperatures of the elementary excitations become very nearly equal to the bath temperature. On the other hand, carrier concentration at the steady-state increases with the laser power up to, roughly, 10\(^{19}\) cm\(^{-3}\) for 500 kW cm\(^{-2}\). The stationary values of the effective temperatures follow in a few tens of picoseconds after application of the laser light, while the carrier concentration shows a transient time of nanoseconds.

The evolution equations for the variables that describe the macroscopic state of the HEPS under consideration are highly nonlinear, and thus the steady-state may display multiple solutions [9]. The uniform steady-state (space and time constancy of quasi-temperatures and carrier density) is the so-called thermodynamic branch of solutions [10], i.e. the one that emerges continuously from the equilibrium state with increasing photoexcitation. The detailed analysis of the stability of this solution is under way; preliminary results [11] show that beyond a certain threshold of the laser power (roughly \(\approx 10\) kW cm\(^{-2}\)) a branching point of the solutions occurs and the uniform state becomes unstable against the formation of a carrier superlattice. This is a striking case of a dissipative structure [10], which may stabilize in the open carrier system while it remains in a far-from-equilibrium macroscopic state subject to nonlinear kinetic laws like eq. (11) in the following section. Semiconductor laser filamentation could be a manifestation of this instability in the inverted populations of electrons and holes in a uniform spatial distribution [12]. Formation of spatial ordering in the HEPS may also be a mechanism for athermal recrystallization in ion-implanted semiconductors, as discussed in the last section.

2. Theoretical background

2.1. The nonequilibrium statistical operator method

The NSO method is based on the construction of an ensemble of replicas of the system distributed over all microscopic states in accordance with the initial specifications and constraints imposed on the system by the experimental conditions. To the representative ensemble one associates a distribution function (statistical operator for the quantal case) \(\rho(t)\), and the average over the ensemble of a dynamical quantity \(A\):

\[
\langle A|t\rangle = \text{Tr}\{A\rho(t)\},
\]

is placed in correspondence with the result of a measurement, \(a(t)\) of \(A\), performed on the actual physical system. The NSO, \(\rho(t)\), is a functional of a reduced set of dynamical quantities \(P_1, \cdots, P_n\), where \(n\) is much smaller than the number of degrees of freedom of the physical system. The average values of the \(P_j (j = 1, 2, \cdots, n)\) over the nonequilibrium ensemble, \(Q_j(t) = \text{Tr}\{P_j\rho(t)\}\), are the set of nonequilibrium thermodynamic variables, or macrovariables for short, that describe the macroscopic state of the system. It ought to be stressed that this contracted macroscopic description is based on
Bogoliubov’s assertion that such contraction is possible on time scales larger than a certain time for microinformation, $\tau_w$, which characterizes the lifetime for correlations that can then be ignored [13]. Thus, the contraction process is dependent on the separation from the total Hamiltonian of strong interactions with certain symmetries, i.e. those related to the fast relaxing processes [14]. To present there seems to be no wholly satisfactory theory to generate a unique selection of the basic set of variables; the modelling of a concrete problem amounts to a judicious choice of the variables and the form of their evolution equations [15].

Different forms of NSOs have been constructed by several authors using either heuristic approaches [16–19], or projection operator techniques [20–22]. All of these results can be put under a unified description [23] using Jaynes’ maximum entropy formalism [24]. This is done maximizing Gibbs (statistical) entropy:

$$S_G(t) = -\text{Tr}\{\rho(t) \ln \rho(t)\} ,$$

with $\rho(t)$ normalized at all times, i.e. $\text{Tr}\{\rho(t')\} = 1$, and subjected to the constraints $Q_j(t') = \text{Tr}\{P_j \rho(t')\}$, $t_0 \leq t' \leq t$, for a given basis of dynamical quantities $P_j$, $j = 1, 2, \cdots, n$, to be used for the contracted description of the macroscopic state of the system after the initial time $t_0$. We obtain the NSO

$$\rho_w(t) = \exp \left\{ \int_{t_0}^{t} dt' \, w(t, t'; t_0) \ln \tilde{\rho}(t', t' - t) \right\} ,$$

where

$$\tilde{\rho}(t_1, t_2) = \exp \left\{ -\phi(t_1) - \sum_{j=1}^{n} F_j(t_1) P_j(t_2) \right\}$$

is called the coarse-grained statistical operator. For simplicity we neglect the possible spatial dependence of $P, Q$, and $F$, and operators $P$ are given in the Heisenberg representation. In eq. (3), $\phi$ ensures the normalization of $\tilde{\rho}$, and the $F_j(t)$, $j = 1, 2, \cdots, n$, are the Lagrange multipliers defined by the relations

$$Q_j(t) = \text{Tr}\{P_j \rho_w(t)\} = \text{Tr}\{P_j \tilde{\rho}(t)\} .$$

Finally, $w(t, t'; t_0)$ is an auxiliary function which allows, firstly, to make possible to identify the $F_j(t)$ with the intensive variables conjugated to $Q_j(t)$ in the sense of Generalized Thermodynamics [10], and, secondly, to include irreversible evolution of the macroscopic state of the system from an initial condition fixed by $\rho_w(t_0) = \tilde{\rho}(t_0)$. The normalization of the coarse-grained statistical operator, together with eq. (4) implies in the normalization of the NSO. Zubarev’s NSO [4] is retrieved as a particular case of the general method of construction we have just summarized by the choice $w(t, t'; t_0) = \exp\{\varepsilon(t' - t)\}$, $t_0 \to -\infty$, and $\varepsilon(>0)$ is an infinitesimal real number which goes to zero after the trace operation in the calculation of averages have been performed.

The NSO of eq. (2) can be separated in two parts

$$\rho_w(t) = \tilde{\rho}(t) + \rho'(t) ,$$

where $\tilde{\rho}(t)$ is a non-dissipative term (which defines the instantaneous mean values of the operators $P_j$,
as given by eq. (4)), and \( \rho' \) carries the information on the microscopic dynamics relevant to the description of the irreversible evolution of the system.

Connection with irreversible thermodynamics is made through the definition of the coarse-grained entropy

\[
\mathcal{S}(t) = -\text{Tr}\{\rho_w(t) \ln \rho(t)\} = -\text{Tr}\{\tilde{\rho}(t) \ln \tilde{\rho}(t)\},
\]

where the last equality is a result of eq. (4). This function is next identified with the phenomenological entropy of generalized thermodynamics [10], having the property that the rate of entropy production is given by

\[
\sigma(t) = \frac{d}{dt} \mathcal{S}(t) = \sum_{j=1}^{n} F_j(t) \frac{d}{dt} Q_j(t),
\]

where

\[
F_j(t) = \frac{\delta \mathcal{S}(t)}{\delta Q_j(t)}
\]

defines each \( F_j \) as thermodynamically conjugated to \( Q_j \).

A nonlinear transport theory follows from the NSO formalism through the construction of the generalized transport equations (equations of evolution for macrovariables \( Q_j \))

\[
\frac{d}{dt} Q_j(t) = \frac{1}{\hbar} \text{Tr}\{[P_j, H] \rho_w(t)\},
\]

where \( H \) is the total Hamiltonian. Alternatively, eq. (9) can be transformed into a set of coupled equations for the intensive thermodynamic variables \( F_j(t) \) using the relation

\[
\frac{d}{dt} F_j(t) = \sum_{k=1}^{n} \frac{\delta F_j(t)}{\delta Q_k(t)} \frac{d}{dt} Q_k(t) = -\sum_{k=1}^{n} C_{jk}^{-1}(t) \frac{d}{dt} Q_k(t),
\]

where \( C_{jk}^{-1}(t) = -\frac{\delta^2 \mathcal{S}(t)}{\delta Q_j(t) \delta Q_k(t)} \) is the inverse of the correlation matrix of quantities \( P_j \) in the coarse-grained ensemble,

\[
C_{jk}(t) = \frac{\delta^2 \mathcal{S}(t)}{\delta F_j(t) \delta F_k(t)} = (P_j; P_k|t).
\]

The use of this thermodynamically equivalent representation is convenient from a practical point of view since the right-hand side of eqs. (9) is explicitly dependent on the \( F_j(t) \), and only implicitly dependent on the \( Q_j(t) \) through eq. (8).

Using the separation of the NSO given by eq. (5), and assuming that the total Hamiltonian \( H \) can be split into two parts \( H_0 + H' \), such that for the set of operators \( P_j \) it is satisfied that \([P_j, H_0] = \Sigma_k a_{jk} P_k\), where \( a_{jk} \) are real coefficients, the right-hand side of eq. (9) can be written in the form of a series of collision operators of an ever increasing order in the interaction strengths [25]. Each of these collision operators involve correlation functions in the coarse-grained statistical ensemble, and, for the particular case of Zubarev's method, we have [4, 25, 26]

\[
\sum_{k} C_{jk} \frac{d}{dt} F_k(t) = -\sum_{j=0}^{\infty} J^{(j)}_j(t),
\]
\[ J_{j}^{(0)}(t) = \frac{1}{i\hbar} \text{Tr}\{[P_j, H_0]\tilde{\rho}(t)\}, \]  
\[ J_{j}^{(1)}(t) = \frac{1}{i\hbar} \text{Tr}\{[P_j, H']\tilde{\rho}(t)\}, \]  
\[ J_{j}^{(2)}(t) = \left(\frac{1}{i\hbar}\right)^2 \int_{-\infty}^{0} dt' e^{it'} \text{Tr}\{[H'(t'), [H', P_j]]\tilde{\rho}(t)\} + \frac{1}{i\hbar} \sum_{k=1}^{n} \int_{-\infty}^{0} dt' e^{it'} \text{Tr}\{[H'(t'), P_k]\tilde{\rho}(t)\} \frac{\partial J_{j}^{(1)}(t)}{\partial Q_k(t)}. \]  

The set of nonlinear transport equations (12) are of first order in the time derivative, and therefore its solution requires to provide initial conditions, i.e. the values \(Q_j(t_0)\), or \(F_j(t_0)\), and (also boundary conditions if space dependence is considered). Thus we see a posteriori that the NSO constructed using the MEF with information gathered on the time interval \((t_0, t)\), can be obtained with only the knowledge of the values of the basic set of variables at a unique time \(t_0\). The subsequent values for \(t > t_0\) are consistently given by the formalism through the nonlinear transport theory it provides. Next we apply the results summarized in this subsection to the case of HEPS under continuous illumination.

### 2.2. Transient and steady states in HEPS

Consider an intrinsic direct-gap polar semiconductor under illumination from a continuous laser source, with electron–hole pairs created in the processes of absorption of one photon. The excess energy optically pumped into the electron system is mainly transferred to the lattice via relaxation processes mediated by the deformation potential and the Fröhlich interactions. The number of pairs varies in recombination processes, and anharmonic effects redistribute the excess energy among the different phonon modes. The highly excited photogenerated carrier system is brought into internal equilibrium in a fraction of a picosecond due to the Coulomb interaction, acquiring a distribution in energy space characterized by a quasi-temperature, \(T_c(t)\), and by quasi-chemical potentials \(\mu_e(t)\) and \(\mu_h(t)\), which are dependent on \(T_c\) and the carrier concentration \(n(t)\) [6, 28, 29]. Next, in moderate to strong polar semiconductors mutual thermalization of carriers and longitudinal-optical (LO) and transverse-optical (TO) photons sets in very rapidly (picosecond time scale), being followed by energy relaxation to the acoustic (A) phonons via the anharmonic interaction in, typically, a tens of ps time scale. The carrier concentration varies as a consequence of the interaction with the laser photon field, which builds it up in absorption processes, while recombination processes reduce it. We consider only radiative spontaneous recombination, neglecting induced recombination, non-radiative recombination, self-absorption, and the Auger effect, as well as diffusion from the volume of laser light focalization. Furthermore, we assume a constant laser light intensity throughout the focused spot. The sample is in contact with a thermal bath at temperature \(T_0\), and \(I_L\) indicates the laser power flux, and \(\omega_L\) the laser photon frequency.

We take the system Hamiltonian to be composed of (a) the electron energy operator (Bloch bands Hamiltonian plus Coulomb interaction; the electrons are treated as Landau’s quasi-particles in the random phase approximation (RPA), and the effective mass approximation in the electron–hole representation is used), (b) the Hamiltonians of the phonon and photon free fields and (c) the
interaction energy operators between these different subsystems. They are well-known and therefore we do not write them down here \[30,31\].

Next, to apply the statistical procedure of section 2.1 to the nonequilibrium system being considered, we need to define the basic set of macrovariables. First we consider the semiconductor sample as an open system interacting with the laser source and the thermal bath, both taken as ideal reservoirs, i.e. it is assumed that they remain in near-stationary conditions (characterized by \(I_L \) and \(T_0 \)) sustaining negligible modifications as a consequence of the coupling with the semiconductor. The total NSO is then the product of the constant statistical operator for the external sources and reservoirs with the NSO of the time-evolving open system \[5\]. We take the latter to be dependent on the set of dynamical quantities composed of the Hamiltonian of the carriers, \(H_c \), the Hamiltonian of the optical phonons, \(H_{LO} \) and \(H_{TO} \), the Hamiltonian of the acoustic phonons, \(H_A \), and the number operators for electrons, \(N_e \), and for holes, \(N_h \), i.e. \(\{P\} = \{H_c, H_{LO}, H_{TO}, H_A, N_e, N_h\} \). We introduce for the set of intensive variables \(\{F(t)\} = \{\beta_c(t), \beta_{LO}(t), \beta_{TO}(t), \beta_A(t), -\beta_c(t)\mu_e(t), -\beta_c(t)\mu_h(t)\} \), defining the inverse of quasi-temperatures of carriers, \(T_c^*(t) \), of phonons, \(T_{LO}^*(t), T_{TO}^*(t), T_A^*(t) \), and the quasi-chemical potentials for electrons and holes, \(\mu_e(t) \) and \(\mu_h(t) \). The associated extensive nonequilibrium thermodynamical variables are then \(\{Q(t)\} = \{E_c(t), E_{LO}(t), E_{TO}(t), E_A(t), n(t), n(t)\} \), i.e. the energies of the carriers and phonons subsystems and the carrier concentration (the same for electrons and holes since they are produced and annihilated in pairs). The coarse-grained statistical operator for the semiconductor system with the above selection of macrovariables, according to eq. (3), is

\[
\tilde{\rho}(t) = \exp\{-\phi(t) - \beta_c(t)H_c - \beta_{LO}(t)H_{LO} - \beta_{TO}(t)H_{TO} - \beta_A(t)H_A \\
+ \beta_c(t)\mu_e(t)N_e + \beta_c(t)\mu_h(t)N_h\}.
\]

(14)

The total Hamiltonian is separated into \(H_0\), containing the Hamiltonians of the free subsystems of carriers and phonons, plus \(H'\), composed of all the interactions between the subsystems and the interaction of the carriers with the laser and recombination radiation fields. Heat diffusion effects from the volume of laser focalization will be included in a phenomenological way in the transport equations. The basic set of dynamical quantities commute between themselves, and also with \(H_0\). Hence, the corresponding collision operators \(J^{(0)}\) and \(J^{(1)}\) of eqs. (13a) and (13b) are, for the present case, null. Next we solve the six generalized transport equations in the quasi-linear approximation, i.e. retaining only \(J^{(2)}\), which then reduces to the calculation of the first term on the right-hand side of eq. (13c). In the quasi-linear approximation the scattering operators are cast in the form of instantaneous Boltzmann-like collision terms. They have the form that would be obtained using the Born approximation in the perturbation theory but with the equilibrium distributions replaced by those characterized by the thermodynamic parameters \(F\) already listed.

Omitting the details of the calculations we only write down the final form of the nonlinear transport equations, beginning with that for the carrier energy:

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

(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 the longitudinal-optical (LO), transverse-optical (TO), and acoustic (A) phonon fields, respectively. The five terms are

\[
\frac{d}{dt} E_{c,t}(t) = \frac{2\pi}{\hbar} \sum_k |U_k(k, q)|^2 \hbar \Omega_L [1 - f_k^c(t) - f_k^h(t)] \delta(\epsilon_k^c + \epsilon_k^h - \hbar \Omega_L),
\]

(16a)
\[ \frac{d}{dt} E_{c,R}(t) = -\frac{2\pi}{h} \sum_{k,q} |U^R(k, q)|^2 (\varepsilon_k^e + \varepsilon_k^h) f_k^e(t) f_k^h(t) \delta \left( \varepsilon_k^e + \varepsilon_k^h - \frac{hcq}{\varepsilon_m^{1/2}} \right), \]  
(16b)

\[ \frac{d}{dt} E_{c,\gamma}(t) = \frac{2\pi}{h} \sum_{k,q} |U_{\alpha}^{\gamma}(k, q)|^2 (\varepsilon_k^{\alpha} - \varepsilon_q^{\alpha})(\nu_q^\gamma(t) f_k^{\alpha}(t)[1 - f_{k+q}^{\alpha}(t)] 
- [1 + \nu_q^\gamma(t)][1 - f_k^{\alpha}(t)] f_{k+q}^{\alpha}(t)) \delta(\varepsilon_k^{\alpha} - \varepsilon_k - \hbar\omega_q^\gamma). \]  
(16c)

In the above equations, \( \alpha = e \) or \( h \), \( \gamma = \text{LO, TO, or A} \),

\[ f_k^{\alpha}(t) = \{\exp\{\beta_\alpha(t)[\varepsilon_k^{\alpha} - \mu_\alpha(t)]\} + 1\}^{-1}, \]  
(17a)

\[ \nu_q^\gamma(t) = \{\exp[\beta_\gamma(t)\hbar\omega_q^\gamma] - 1\}^{-1}, \]  
(17b)

and the matrix elements are

\[ |U^R(k, q)|^2 = \frac{4\pi e^2 \hbar E_G}{V\varepsilon_m c q} \left( \frac{1}{m_e} + \frac{1}{m_h} \right), \]  
(18a)

\[ |U_{\alpha}^{\text{LO}}(k, q)|^2 = \frac{2\pi e^2 \hbar \omega_{\text{LO}}}{Vq^2 \varepsilon_m(q, t)} \left( \frac{1}{\varepsilon_m} - \frac{1}{\varepsilon_0^e} \right), \]  
(18b)

where we have used the RPA dielectric function

\[ \varepsilon(q, t) = 1 + \frac{q_0^2(t)}{q^2}, \]

\[ q_0^2(t) = \frac{4\pi e^2}{\varepsilon_0^e} \sum_{\alpha,k} \left| \frac{\partial f_k^{\alpha}(t)}{\partial \varepsilon_k^{\alpha}} \right|. \]

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, \( \varepsilon_0^e \) and \( \varepsilon_m \) the static and high-frequency dielectric constants, \( \omega_{\text{LO}} \) the dispersionless frequency of the LO phonons, and \( V \) the active volume of the sample. \( E_k^e = E_G + (\hbar^2 k^2/2m_e) \), \( E_k^h = \hbar^2 k^2/2m_h \) are the energy dispersion relations for the electrons and the holes with effective masses \( m_e \) and \( m_h \), respectively. Moreover,

\[ |U_{\alpha}^{\text{TO}}(k, q)|^2 = \frac{E_{\alpha,\omega}^{2,\text{TO}}}{2gV\omega_{\text{TO}}}, \]  
(19a)

\[ |U_{\alpha}^{\text{A}}(k, q)|^2 = \frac{E_{\alpha,\omega}^{2,\text{A}}}{2gVs}, \]  
(19b)

where \( g \) is the density of the material, \( s \) the speed of sound, a Debye model was used to describe the A phonons (then \( \omega_{\text{A}}^\alpha = sq \)), \( \omega_{\text{TO}} \) is the dispersionless frequency of the TO phonons, and \( E_{\omega,\alpha} \) the strengths of the deformation potential interactions.

The rate of carrier 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

\[ \frac{d}{dt} E_{c,\omega}(t) = \frac{\hbar \Omega_L - E_G}{\hbar \Omega_L} \left[ \alpha_1(\omega_L) I_L(t)[1 - f^e(t) - f^h(t)], \right. \]  
(20a)

\[ \left. \alpha_2(\omega_L) I_L^2(t)[1 - f^e(t) - f^h(t)]. \right] \]  
(20b)
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 $2\omega_L$, respectively, for the two cases (20a) and (20b), and $U^k$ is the corresponding matrix element.

To perform numerical calculations we use the experimental values of the absorption coefficients. Finally, $f^e$ and $f^h$ are the Fermi distributions with energies $\varepsilon^e,h = \left( m_x/m_{e,h}\right)\left(\hbar \Omega_L - E_g\right)$, where $m^{-1}_e = m^{-1}_x + m^{-1}_h$, and for temperature $T_e(t)$ and chemical potentials $\mu_e(t)$ and $\mu_h(t)$.

We also have

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

(21)

where

$$\frac{d}{dt} E_{LO,A}(t) = -\sum_q \hbar \omega_{LO} \frac{v^L_{q}(t) - v^L_{q}(t, T_s^A)}{\tau_{LO,A}}$$

(22)

is the rate of energy transfer of LO phonons to A phonons due to anharmonic processes; $\tau$ is a phenomenological relaxation time, and $v^{LO}(t, T_s^A) = \left[\exp[\beta^A(t)\hbar \omega_{LO}] - 1\right]^{-1}$.

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

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

(23)

$$\frac{d}{dt} E_{TO,A}(t) = -\sum_q \hbar \omega_{TO} \frac{v^T_{q}(t) - v^T_{q}(t, T_s^A)}{\tau_{TO,A}},$$

(24)

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

(25)

$$\frac{d}{dt} E_{A,B}(t) = -\sum_q \hbar s q \frac{v^T_{q}(t) - v^A_{q}(t, T_0)}{\tau_{A,B}},$$

(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 [30], and it should be estimated for each case when performing specific numerical calculations. The other phenomenological relaxation times, $\tau_{LO,A}$ and $\tau_{TO,A}$, can be evaluated from linewidths of the Raman lines.

The rate of change of the carrier density is

$$\frac{d}{dt} n(t) = \left[ \frac{d}{dt} n(t) \right]_R + \left( \hbar \Omega_L - E_g \right)^{-1} \frac{d}{dt} E_{c,L}(t),$$

(27)

where

$$\frac{d}{dt} n(t) \big|_R = -\frac{2\pi}{\hbar} \sum_{k,q} |U^R(k, q)|^2 f^e_k(t) f^a_{q,k}(t) \delta \left( \varepsilon^e_k + \varepsilon^h_q - \frac{\hbar c q}{\epsilon_{\infty}^{1/2}} \right).$$

(28)

To obtain the intensive nonequilibrium thermodynamic parameters $F_j$, eqs. (15), (21), (23), (25) and (27) must be complemented with eq. (10), or better with their reversed form.
\[ \frac{d}{dt} E_c(t) = -(H_c; H_c) \beta_c + \sum_\alpha (H_c; N_\alpha | t)(\mu_\alpha \beta_c + \mu_\alpha \beta_c), \]  
(29a)  
\[ \frac{d}{dt} E_{LO}(t) = -(H_{LO}; H_{LO}| t) \beta_{LO}, \]  
(29b)  
\[ \frac{d}{dt} E_{TO}(t) = -(H_{TO}; H_{TO}| t) \beta_{TO}, \]  
(29c)  
\[ \frac{d}{dt} E_A(t) = -(H_A; H_A | t) \beta_A, \]  
(29d)  
\[ \frac{d}{dt} n(t) = -(N^\alpha; H_c | t) \beta_c + (N^\alpha; N^\alpha | t)(\mu_\alpha \beta_c + \mu_\alpha \beta_c), \]  
(29e)

where we have introduced the correlation matrix \( C(t) \) with elements
\[ (H_e; H_e | t) = \sum_{\alpha, \kappa} (\epsilon_\alpha^2)^2 f_\alpha(t)[1 - f_\kappa(t)], \]  
(30a)  
\[ (H_{LO}; H_{LO}| t) = \sum_q \hbar^2 \omega_{LO}^2 \nu_L^{\alpha}(t)[1 + \nu_L^{\alpha}(t)], \]  
(30b)  
\[ (H_{TO}; H_{TO}| t) = \sum_q \hbar^2 \omega_{TO}^2 \nu_T^{\alpha}(t)[1 + \nu_T^{\alpha}(t)], \]  
(30c)  
\[ (H_A; H_A | t) = \sum_q (\hbar s)^2 \nu_A^{\alpha}(t)[1 + \nu_A^{\alpha}(t)], \]  
(30d)  
\[ (N^\alpha; N^\alpha | t) = \sum_q f_\alpha(t)[1 - f_\kappa(t)], \]  
(30e)  
\[ (H_e; N_e | t) = (N_e; H_e | t) = \sum_k \epsilon_\kappa^2 f_\kappa(t)[1 - f_\kappa(t)]. \]  
(30f)

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

Finally, the concentration of carriers is related to the quasi-chemical potentials by [34]
\[ n(t) = n_{e0}(t) F_{1/2}[\beta_c(t)(\mu_c(t) - E_c)] = n_{h0}(t) F_{1/2}[\beta_c(t)\mu_h(t)]. \]  
(31)

where
\[ n_{e,h0}(t) = 2[2\pi m_{e,h} k T_e(t) / \hbar^2]^{3/2}, \]
and \( F_{1/2} \) are the Fermi functions of index half.

We proceed next to obtain numerical solutions for the case of gallium arsenide samples.

### 3. Uniform electron–hole fluid in GaAs

A GaAs sample is assumed to be in contact with a thermal bath at room temperature \( (T_0 = 300 \text{ K}) \), and illuminated by a constant laser light with power flux \( I_L \) (to be varied) and photon energy \( \hbar \omega_L = 2.4 \text{ eV} \). The one-photon absorption coefficient is \( \sim 1 \times 10^4 \text{ cm}^{-1} \); this calculated value is in good agreement with the experimental data [33]. The parametric relaxation time used in the calculations is
\( \tau_{AN} \sim 10 \text{ ps} \) [32]. We assume that the acoustic phonons remain constantly at room temperature; [35] all other parameters, such as effective masses, dielectric constant, interaction strengths, etc. are obtained from the current literature [36].

We obtain the evolution in time of the six thermodynamical variables, i.e. the solutions of the system of coupled integrodifferential equations obtained in the last section, which show that, as expected, a steady state appears after a transient time. The values of the variables in the steady state are reconfirmed solving the stationary equations \( dQ_j/dt = J_j^{(2)} = 0 \), \( j = 1 \) to 6. The solution of the kinetic equations requires to give initial conditions; for this purpose the initial time \( t_0 \) is taken as the delay time after application of the laser light such that the carrier concentration is roughly \( 10^{14} \) to \( 10^{15} \text{ cm}^{-3} \) \( (n(t_0) = \alpha I_L t_0 / \hbar \omega_L) \). Since the excitation energy is \( \hbar \omega_L - E_G = 0.88 \text{ eV} \), giving an effective carrier temperature of roughly \( 3000 \text{ K} \), at those concentrations the excited pairs should form a double Fermi liquid on the metallic side of the Mott transition, being nearly in internal equilibrium, and then be susceptible to the theoretical treatment of section 2.

For laser powers in the range 5 to 500 kW cm\(^{-2}\) we take \( t_0 = 0.5 \text{ ps} \); up to this delay time and with the thermal bath temperature at 300 K only a small fraction of optical phonons in excess of equilibrium is present at \( t_0 \). Thus, we take 300 K for the initial quasi-temperature of phonons, and \( \sim 3000 \text{ K} \) for that of carriers \( (3kT^*_{\text{c}}(t_0) = \hbar \omega_L - E_G) \). It should be noticed that the solution of the kinetic equations is weakly dependent on the initial conditions when the results are analyzed in a larger than picosecond time scale, as we do here. Finally, given \( T^*_{\text{c}}(t_0) \) and \( n(t_0) \), the initial values of the quasi-chemical potentials follow from eq. (31). Next, we solved computationally the system of coupled differential equations for laser powers of up to 500 kW/cm\(^{-2}\).

The effective temperatures of carriers and optical phonons after rapid equalization, that takes place in a few ps as already demonstrated in earlier studies of ultrafast laser spectroscopy [6], decrease to nearly room temperature in a lapse of time of the order of 20 to 40 ps after the initial application of the laser illumination for \( I_L \) in the range 10 to 500 kW cm\(^{-2}\) (see fig. 1). On the other hand, the carrier concentration grows in time attaining a stationary value after transient times of orders of magnitude larger than those for \( T^*_{\text{c}} \). Fig. 2 shows the evolution of \( n(t) \) for three values of the laser power, and fig.

![Time evolution of the quasi-temperature of carriers for three different values of laser power.](image)
3 the transient times for laser power up to 0.5 MW cm$^{-2}$; these transient times are defined as the lapse of time between the switching on of the laser light and the moment when $n$ differs by 10% of its stationary value.

Fig. 4 provides the values of the carriers concentration in the steady state, $n_0$, for laser powers up to 50 kW cm$^{-2}$. At low laser powers, $I_L \lesssim 10$ kW cm$^{-2}$ producing values of $n_0$ smaller than $10^{18}$ cm$^{-3}$, a very near dependence of $n$ on the square root of $I_L$ is observed, roughly given by $n_0 \approx 5 \times 10^{17} I_L^{1/2}$ cm$^{-3}$; this is a result that in eq. (28) the carrier population functions of eq. (17a) approximate the classic Maxwell distribution. Carriers concentrations larger than $10^{18}$ cm$^{-3}$ follow for laser power $I_L \gtrsim 10$ kW cm$^{-2}$. Stretching out the calculations well beyond this point, a value $n_0 = 10^{19}$ cm$^{-3}$ is obtained.

Fig. 3. The transient time for carriers concentration to attain the steady-state value.
Fig. 4. Concentration of the photo-injected electron-hole pairs in the steady state.

Fig. 5. The rates of energy pumping (full line), of energy loss in recombination processes (dashed line), and of energy transfer from carriers to optical phonons (dot-dashed line) and to acoustical phonons (double dot-dashed line). (Note the different scale factors indicated in the upper left corner.)
Fig. 6. The recombination times in the steady state for increasing values of laser power.

for $I_L = 200 \text{ kW cm}^{-2}$, and for $I_L = 500 \text{ kW cm}^{-2}$ we get $n^0 = 2 \times 10^{19} \text{ cm}^{-3}$. The parabolic dependence between $n^0$ and $I_L$ obtained for $I_L \leq 10 \text{ cm}^{-2}$ is no longer satisfied and in the range $50 \leq I_L \leq 500 \text{ kW cm}^{-2}$ we find the approximate relationship $n^0 \approx 0.8 (1 + 0.9 I_L^{1/2}) \times 10^{18} \text{ cm}^{-3}$.

Fig. 5 shows, for different values of the laser power and in the steady-state, the rates of energy transfer along various channels of relaxation and pumping. For laser powers in the range 10 to 50 kW cm$^{-2}$, a fairly linear dependence of the rates of energy transfer from carriers to TO, LO, and A phonons, as well as for the rate of energy pumping, could be noted. The latter varies between 0.1 mJ ps$^{-1}$ cm$^{-3}$ (or 0.14 meV ps$^{-1}$ per pair) and 0.5 mJ ps$^{-1}$ cm$^{-3}$ (or 0.52 meV ps$^{-1}$ per pair) in that range. Most of that energy is transferred in recombination processes at a rate roughly 5% smaller than that of pumping. To attain the steady state, that difference is taken care of by the energy transfer to LO phonons, and, to an almost negligible degree, to the A phonons. [Note the different scaling factors for the different channels used in fig. 5.]

The rate of pair production (not shown here) is practically linear with laser power, and from the angular coefficient we obtain the one-photon absorption coefficient $\alpha_L (\omega_L) = 1 \times 10^4 \text{ cm}^{-1}$; the photoexcited carriers population inversion does not modify in the region of interest the value of the absorption coefficient experimentally determined in near equilibrium condition (the measured value is in very good agreement with that obtained by direct calculation). Evidently, in the steady state the recombination rate equals the production rate, and the recombination times, defined by $\tau_R = -n/(dn/dt)_R$, are found to vary from ~7 ns at $I_L = 10 \text{ kW cm}^{-2}$ ($n^0 = 1.7 \times 10^{18} \text{ cm}^{-3}$) to ~5 ns at $I_L = 50 \text{ kW cm}^{-2}$ ($n^0 = 5.7 \times 10^{18} \text{ cm}^{-3}$); see fig. 6. We recall that in our calculations we have neglected the induced recombination, selfabsorption, and the Auger effect, as well as assisted and nonradiative recombination effects.

4. Concluding remarks

We have studied a GaAs sample under illumination from a continuous laser source and in contact with a thermal bath at temperature $T_0 = 300 \text{ K}$. All the calculations were performed using the nonequilibrium statistical operator method in Zubarev’s form and adapted to treat open systems. The solutions of the system of transport equations for the thermodynamic variables of the system, for different laser powers $I_L$, are obtained by an iterative numerical calculation. We have varied $I_L$ from 5 kW cm$^{-2}$ to 500 kW cm$^{-2}$ and for each $I_L$ we have obtained the time evolution of the macrovariables towards the uniform stationary states, characterized by space and time constancy of effective temperatures and carrier density.
At the steady state the effective temperatures of the elementary excitations are very nearly equal to the bath temperature. On the other hand, the concentrations of carriers at the steady state increases with the laser power up to, roughly, $10^{19}$ cm$^{-3}$ for $I_L \sim 500$ KW cm$^{-2}$. The stationary values of the effective temperatures are attained in a few tens of picoseconds after application of the laser light. This is a result of the rapid relaxation of the carriers excess energy to the optical phonon system with final stationary quasi-temperatures very near the bath temperature. Differently, the concentration of carriers shows a transient time of nanoseconds that decreases with increasing laser powers. The figures presented in the last section provide a good description of the macroscopic state of the highly excited plasma in polar inverted-band semiconductors. However the numerical calculations refers to the specific case of GaAs, we expect that qualitatively and semiquantitatively those results may represent the situation to be expected in most intermediate to strong polar semiconductors.

As already noted in the Introduction, we have obtained the so-called thermodynamic branch of solutions [10] of the highly nonlinear generalized transport equations, and an instability at a possible branching point of the solutions [9] cannot (and must not) be ruled out without further analysis. We have shown, using linear stability analysis [9], that for a description of the macroscopic state of the HEPS in the Gibbs space of the six chosen macrovariables the thermodynamic branch is stable. However, this analysis must be extended to include the Gibbs spaces of enlarged dimensions. Extending the thermodynamic fluctuation theory to steady states far from equilibrium, we have been able to test the existence of instabilities of the uniform steady state in HEPS against the formation of spatial ordering. Preliminary results [11] indicate that a plasmon mode in the carriers system becomes "soft", leading to the formation of a steady-state charge density wave, i.e. a dissipative (spatially ordered) structure in Prigogine’s sense [10]. Filamentation in semiconductor lasers could be a manifestation of this instability [12, 37]. This instability is also akin to the one proposed by Van Vechten [38] in indirect nonpolar semiconductors, in the debate on thermal vs. athermal laser annealing of ion-implanted semiconductors. The controversy for that case seems to be definitely settled in favor of the thermal effect. Our results may feed the conjecture that the self-organizing effect in far-from-equilibrium conditions may eventually be possible in direct-gap polar semiconductors. To present our treatment has been based on an itinerant plane-wave model for the carrier system, and will be reported in the near future; a more elaborate study using the chemical-bond approach is under way.

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References


[26] A general form of the collision operator $J^{(i)}$ is given by J. Luczka, Phys. Lett. A69 (1979) 393; however, his result seems to have missing terms involving multiple commutators of $P_j$ com $H'$ for $i > 3$.


[36] The most relevant are listed in ref. 6b, p. 149.
