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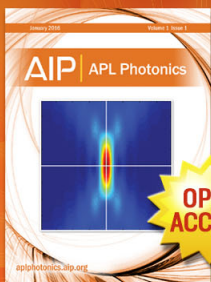J. Chem. Phys. **115**, 8481 (2001); 10.1063/1.1410381

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Thermodynamic variables in the context of a nonequilibrium statistical ensemble approach

Roberto Luzzi and Áurea R. Vasconcellos
Instituto de Física ''Gleb Wataghin,'' Universidade Estadual de Campinas, Unicamp, 13083-970
Campinas, São Paulo, Brazil

David Jou and José Casas-Vázquez
Departamento de Fisica, Universidad Autónoma de Barcelona, 08193-Bellaterra, Catalonia, Spain

We consider the question of the definition of thermodynamic-like variables in the context of a statistical thermodynamics, which is a large generalization of Gibbs statistical thermostatics and linear and local-equilibrium classical irreversible thermodynamics. It is based on a nonequilibrium ensemble approach known as the nonequilibrium statistical operator method. Some of these quasithermodynamic variables are characteristic of the nonequilibrium state and go to zero in the limit of local or global equilibrium, but others go over the thermodynamic variables that are present in such a limit. We consider in particular temperature-like variables for the different subsystems of the sample. For illustration we apply the theory to the study of optical properties of highly photoexcited plasma in semiconductors, following a good agreement between theory and experimental data. It is shown that high-resolution spectroscopy provides an excellent experimental testing ground for corroboration of the theoretical concepts, and a quite appropriate way for characterizing and measuring nonequilibrium thermodynamic-like variables. © *1997 American Institute of Physics.* [S0021-9606(97)51642-4]

I. INTRODUCTION

The science of thermodynamics admits approaches that belong to several levels of description, and among them, a relevant one is considered to be the statistical level.[1] Statistical thermodynamics (or Gibbsian thermodynamics), however well established in the case of thermostatics and classical (linear) irreversible thermodynamics, at present is not completely satisfactorily established for systems arbitrarily away from equilibrium. One quite promising approach is the so-called informational irreversible thermodynamics (IST, sometimes also dubbed as information-theoretic thermodynamics, briefly and partially described in Ref. 2; see also Ref. 3). IST was initiated with the pioneering work of Hobson[4] sometime after the publication of Jaynes' seminal papers on the foundations of statistical mechanics based on information theory.[5] Nowadays, as described in Refs. 2 and 3, IST acquires a closed form in the framework of the nonequilibrium statistical operator method (NESOM), and, particularly, within Zubarev's approach to NESOM.[6–10]

All the existing approaches to irreversible thermodynamics face the quite difficult problem of a proper definition of the macroscopic state space, appropriate for the description of many-body systems arbitrarily away from equilibrium. The situation is also present in IST, but in this approach the basic variables (those that compose the nonequilibrium thermodynamic space state) are given in terms of the average over the NESOM nonequilibrium ensemble of well defined mechanical quantities, and a condition is present to ensure the closure of the kinetic equations which describe the evolution of the macroscopic state of the system. Moreover, in terms of these basic variables—let us call them the *thermodynamic macroscopic variables*—the Lagrange multipliers,

which are introduced by the variational method to this Boltzmann–Gibbsian approach, are completely defined. It ought to be stressed that these Lagrange multipliers compose a set of *nonequilibrium thermodynamic intensive variables* which provide an alternative, and completely equivalent, description of the nonequilibrium state of the system. Of course, if desirable, and this is often the case, a mixed representation using part specific and part intensive variables can be introduced.

We consider next this question of the definition of a proper nonequilibrium thermodynamic phase space in a particular study of a thermohydrodynamics of many-body systems of carriers and lattice vibrations in the highly excited photoinjected plasma in semiconductors. We concentrate our attention on a particular Lagrange multiplier, which is a nonequilibrium thermodynamic intensive variable playing the role of a nonequilibrium temperature-like quantity, which we call *quasitemperature*. This concept of nonequilibrium temperature has been used on a phenomenological basis in different contexts by several authors, apparently beginning with Lev D. Landau more than half a century ago. The most common cases are nonequilibrium temperatures for electron or nuclear spins,[11] molecules,[12] plasma,[13] electrons excited in strong electric fields,[14] electrons in superconductors,[15] photoexcited carriers,[16] photoexcited phonons,[17] and nuclear reactions.[18] Difficulties arising in its definition in the kinetic theory of dense gases were pointed out some time ago by L. Garcia-Colin and M. S. Green.[19] Recently, the question was raised, on sound basis, in the framework of extended irreversible thermodynamics.[20] The presentation is organized as follows: in Sec. II, after a very brief review of the statistical method, we show a way to define nonequilibrium

temperature-like variables (*quasitemperatures*) in the framework of the theory. We discuss the all important problem of their dependence on the basic set of nonequilibrium thermodynamic variables—with particular attention to the fluxes. In Sec. III we particularize the results to the case of photoexcited semiconductors in electric fields, which produce fluxes of mass and of heat. In Sec. IV the measurement in optical experiments of the quasitemperature of carriers and phonon modes (i.e., the case of individual quasiparticles that arise in the standard theory of solid state physics) is described. We consider first the cases of (1) carriers, in flux-free conditions, and then in the presence of an electric field that generates irreversible fluxes, and (2) for polar phonons. This is consistently done in the framework of the statistical-mechanical method, coupling the response function theory that the method provides[9] with the nonlinear kinetic equations that describe the irreversible evolution of the system. In the last section we summarize and discuss the results.

II. THEORETICAL BACKGROUND: MaxEnt-NESOM AND QUASITHERMODYNAMIC VARIABLES

For the sake of completeness, we first recall the basic tenets of the statistical-mechanical approach to be used, namely, the so-called nonequilibrium statistical operator method (NESOM for short). It constitutes an ensemble algorithm theory for nonequilibrium systems, which largely generalizes Boltzmann's and Gibbs' seminal ideas, has precursors in Kirkwood,[21] Green,[22] Zwanzig,[23] Mori,[24] and others, and has been extended and perfected by the Russian School of Statistics, deriving, mainly, from the work of N. N. Bogoliubov (see, for example, Refs. 25 and 26). *First*, according to *Bogoliubov's principle of correlation weakening* and accompanying hierarchy of relaxation times (Ref. 26, and see also Refs. 27 and 28), the Hamiltonian of the system is separated out into two contributions, namely,

$$H = H_0 + H', \tag{1}$$

where H_0 contains the kinetic energies of the free subsystems and part of the interactions, namely, those strong enough to produce relaxation of correlations in times smaller than the characteristic time of the experiment (typically the instrumental resolution time). The other part, H', contains the other part of the interactions, that is, those producing long relaxation times. A *second* fundamental step consists of the choice of the basic dynamical variables that should provide the macroscopic description of the system dynamics. This is provided by a *closure condition, termed Zubarev–Peletminskii symmetry condition*, namely, the set $\{\hat{P}_j\}$, $j = 1,2,...$, of basic dynamical variables is composed of the quantities $\hat{P}_j$ satisfying the relationship

$$\frac{1}{i\hbar}[\hat{P}_j, H_0] = \sum_k \alpha_{jk}\hat{P}_k, \tag{2}$$

where the α's are *c*-numbers. *Third*, the NESOM statistical operator, the NESO $\varrho(t)$, is a superoperator depending on these quantities, and as noticed, we resort to Zubarev's method in its variational approach.[6–10] In terms of Zubarev's

NESO, the basic set of macrovariables $\{Q_j(t)\}$, $j=1,2,...$, is introduced, given by the average over the NESOM-nonequilibrium ensemble of the basic dynamical quantities $\hat{P}_j$, that is,

$$Q_j(t) = \text{Tr}\{\hat{P}_j \varrho(t)\}. \tag{3}$$

In this way, that is, in terms of these specific variables, the nonequilibrium thermodynamic space state in IST is introduced. The NESO $\varrho(t)$ does satisfy the *Liouville equation*, whose solutions, as known, constitute an algebraic group composed of two subsets: one is composed of the retarded solutions (evolving towards the future), and the other is the one of advanced solutions (returning from the future to the past), and thus time reversibility is verified. To ensure irreversibility in the behavior of macroscopically dissipative systems, while evolving from an initial condition, the *ad hoc* nonmechanical hypothesis (a generalized *Stosszahlansatz*) of neglecting the subset of advanced solutions is introduced. This is accomplished in a practical way introducing Bogoliubov's concept of quasiaverages.[26] In Zubarev's approach to NESOM this is done by adding an infinitesimal source (that goes to zero at the end of the calculation of quasiaverages) to the Liouville equation.[6,9] (It is a generalization of Kirkwood's time-smoothing procedure,[21] it implies in random Poissonian transitions with lifetime ε^{-1}, and is a particular form of Prigogine dynamic condition for dissipativity,[29] and has a close connection with a similar procedure in formal scattering theory as described by Gell-Mann and Goldberger.[30] Let us call Zubarev's NESO $\varrho_\varepsilon(t)$, which is given by

$$\varrho_\varepsilon(t) = \exp\left\{\ln \bar{\varrho}(t,0) - \int_{-\infty}^{t} dt' e^{\varepsilon(t'-t)} \right.$$
$$\left. \times \frac{d}{dt'} \ln \bar{\varrho}(t',t'-t)\right\}, \tag{4}$$

where $\bar{\varrho}$ is an auxiliary—but of large practical relevance in the theory—operator, given by the Gibbsian-like distribution

$$\bar{\varrho}(t,0) = \exp\left\{-\phi(t) - \sum_j F_j(t)\hat{P}_j\right\}, \tag{5a}$$

and

$$\bar{\varrho}(t',t'-t) = \exp\left\{-\frac{1}{i\hbar}(t'-t)H\right\}\bar{\varrho}(t',0)$$
$$\times \exp\left\{-\frac{1}{i\hbar}(t'-t)H\right\}, \tag{5b}$$

where $\phi(t)$ (which ensures the normalization of $\bar{\varrho}$ and in IST plays the role of the logarithm of a nonequilibrium partition function) and the nonequilibrium thermodynamic intensive variables $F_j(t)$ are the Lagrange multipliers that the method introduces.

Using Eq. (4) it is possible to show that the NESO is composed of two terms

$$\varrho_\varepsilon(t) = \bar{\varrho}(t,0) + \varrho'_\varepsilon(t), \tag{6}$$

with relevant physical meanings: The first one on the right of this Eq. (6), i.e., $\bar{\varrho}(t,0)$, provides for the instantaneous values of the basic dynamical variables, but does not describe the dissipative processes, which is done by $\varrho'_\varepsilon(t)$.[6–10] Furthermore, as noticed, the Lagrange multipliers, or nonequilibrium thermodynamic intensive variables, are completely defined by Eq. (3). A *fourth*, and last, step is the construction of a NESOM-based nonlinear, nonlocal in space, memory dependent, quantum *kinetic theory*. This follows straightforwardly, in principle, by noting that the equations of evolution for the basic specific variables are simply the average over the nonequilibrium ensemble of the quantum mechanical Heisenberg equation of motion, that is,

$$\frac{\partial}{\partial t} Q_j(\mathbf{r},t) = \mathrm{Tr}\left\{\frac{1}{i\hbar}[\hat{P}_j(\mathbf{r}),H]\varrho_\varepsilon(t)\right\}, \tag{7}$$

where we have introduced a dependence on the space variable. It has, in general, a formidable structure of unmanageable proportions. However, using the separation of the Hamiltonian of Eq. (1), that of the NESO ϱ as given by Eq. (6), and the closure condition of Eq. (2), Eq. (7) can be written in the form of a far-reaching generalization of Mori–Langevin equations (as shown in Refs. 31 and 32; see also Refs. 6, 7, and 33), namely,

$$\frac{\partial}{\partial t} Q_j(\mathbf{r},t) = J_j^{(0)}(\mathbf{r},t) + \mathscr{J}_j(\mathbf{r},t), \tag{8}$$

where $J^{(0)}$ is, in Mori's nomenclature,[24] a precession term (as shown below it is given by the divergence of the flux of quantity Q), plus a supercollision operator which can be written as the superposition of an infinite series of collision integrals, and can be interpreted as involving two, three, four, and so on, particle collisions.[31,32]

Let us consider now the NESOM-based construction of a statistical thermodynamics, the so-called informational statistical thermodynamics. In IST, a relevant state function is the NESOM entropy (or informational entropy, or IST entropy, or quasientropy, extensively discussed in Ref. 34), given by

$$\bar{S}(t) = -\mathrm{Tr}\{\varrho_\varepsilon(t)\ln \bar{\varrho}(t,0)\}$$
$$= \phi(t) + \sum_{j=1}^{n} \int d^3r F_j(\mathbf{r},t) Q_j(\mathbf{r},t). \tag{9}$$

The NESOM-entropy production function is

$$\bar{\sigma}(t) = d\bar{S}/dt = \sum_{j=1}^{n} \int d^3r F_j(\mathbf{r},t) \frac{\partial}{\partial t} Q_j(\mathbf{r},t), \tag{10}$$

which can be associated with a generalized $\mathscr{H}$-theorem,[34,35] and the differential of the NESOM entropy at space position $\mathbf{r}$ and time t satisfies the Pfaffian form (generalized Gibbs' relation)

$$d\bar{s}(\mathbf{r},t) = \sum_{j=1}^{n} F_j(\mathbf{r},t) dQ_j(\mathbf{r},t). \tag{11}$$

Moreover, we recall that the equations of irreversible evolution for the basic variables follow consistently from the method [cf. Eq. (7)]: for the space-dependent variables $Q_j(\mathbf{r},t)$, these equations take a general form of the type

$$\frac{\partial}{\partial t} Q_j(\mathbf{r},t) = -\mathrm{div}\,\mathbf{I}_j(\mathbf{r},t) + \xi_j(\mathbf{r},t), \tag{12}$$

where $\mathbf{I}_j$ is interpreted as the flux of quantity Q_j,[36,37] and ξ_j accounts for sources and/or sinks of such a quantity. Making use of is Eq. (12), we can write a continuity equation for the NESOM entropy density, namely,

$$\frac{\partial}{\partial t} \bar{s}(\mathbf{r},t) + \mathrm{div}\,\mathbf{I}_s(\mathbf{r},t) = \sigma_s(\mathbf{r},t). \tag{13}$$

In this Eq. (13), $\mathbf{I}_s$ is the flux of NESOM entropy given by

$$\mathbf{I}_s(\mathbf{r},t) = \sum_{j=1}^{n} F_j(\mathbf{r},t) \mathbf{I}_j(\mathbf{r},t), \tag{14}$$

where σ_s, which accounts for the presence of sources and/or sinks, takes the form

$$\bar{\sigma}_s(\mathbf{r},t) = \sum_{j=1}^{n} \{\mathbf{I}_j(\mathbf{r},t)\cdot\nabla F_j(\mathbf{r},t) + F_j(\mathbf{r},t)\xi_j(\mathbf{r},t)\}, \tag{15}$$

and represents the space and time-dependent entropy-production density in the formalism.

We consider next the differential coefficients of the NESOM entropy. We recall that in equilibrium conditions the differential coefficients of the thermodynamic entropy play an important role: they constitute the set of equations of state which relate extensive and intensive variables. Take a system composed of s subsystems. Let $\varepsilon_{\diagup}(\mathbf{r},t)$ be the energy densities and $n_{\diagup}(\mathbf{r},t)$ the number densities in each $\diagup (=1,2,...,s)$ subsystem, which are taken as basic specific variables in NESOM. We call $\beta_{\diagup}(\mathbf{r},t)$ and $\varphi_{\diagup}(\mathbf{r},t)$ their associated intensive variables [Lagrange multipliers F in Eq. (5) that the formalism introduces]. But, as shown elsewhere,[3,37] the closure condition of Eq. (2) requires the introduction of the fluxes of these quantities[6,36,37] as basic variables, and with them all the other higher order fluxes (of tensorial rank $r \geq 2$). Consequently, the NESO depends on all the densities and their fluxes, and Eq. (11) tells us that the Lagrange multipliers associated with them depend, each one, on all these basic variables, namely, the densities $\varepsilon_{\diagup}(\mathbf{r},t)$, $n_{\diagup}(\mathbf{r},t)$, their vectorial fluxes $\mathbf{I}_{\varepsilon\diagup}(\mathbf{r},t)$, $\mathbf{I}_{n\diagup}(\mathbf{r},t)$, and the tensorial fluxes $\Psi_\varepsilon^{(r)}(\mathbf{r},t)$, $\Psi_n^{(r)}(\mathbf{r},t)$ (with $r \geq 2$).

But, the Lagrange multipliers in NESOM are the differential coefficients of the entropy in IST [cf. Eq. (11)], i.e., as already noted, they are in this sense nonequilibrium thermodynamic variables conjugated to the basic ones. Taking only the case of the densities, we have that

$$\beta_{\diagup}(\mathbf{r},t) = \delta\bar{S}(t)/\delta\varepsilon_{\diagup}(\mathbf{r},t), \tag{16a}$$

$$\varphi_{\diagup}(\mathbf{r},t) = \delta\bar{S}(t)/\delta n_{\diagup}(\mathbf{r},t), \tag{16b}$$

where δ stands for the functional derivative.[38] The IST entropy of Eq. (9) goes over the corresponding one of local equilibrium in classical irreversible thermodynamics, when

all Lagrange multipliers β_ℓ become an identical β for all subsystems and are the reciprocal of the local equilibrium temperature, while the φ_ℓ become equal to $-\beta\mu_\ell$, where the μ_ℓ are the local chemical potentials for the different chemical species in the material. All the other Lagrange multipliers, that is those associated with the fluxes, are null in such a limit. Of course, when the complete equilibrium is achieved, they go over the corresponding values in equilibrium, and Gibbs' grand-canonical distribution is recovered. Consequently, in NESOM we can introduce the space and time-dependent nonequilibrium temperature-like variables $\Theta_\ell(\mathbf{r},t)$, which we shall call *quasitemperature* for each system $\ell = 1$ to s, namely

$$\beta_\ell(\mathbf{r},t) = \delta\bar{S}(t)/\delta\varepsilon_\ell(\mathbf{r},t) \equiv \Theta_\ell^{-1}(\mathbf{r},t), \tag{17}$$

where then Θ depends on all the set of variables $\{\varepsilon_k, n_k, \mathbf{I}_{\varepsilon k}, \mathbf{I}_{nk}, \Psi_{\varepsilon k}^{(r)}, \Psi_{nk}^{(r)}\}$, with the Boltzmann constant taken as a unit.

We stress that Eq. (17) is the formal definition of the so-called quasitemperature in IST, a very convenient one because of the analogy with local equilibrium and equilibrium theories, which are recovered in the appropriate asymptotic limit. But we recall that it is a Lagrange multiplier that the method introduces from the outset, and then it is explicitly defined by the average value of the energy operator over the nonequilibrium ensemble. Therefore, its evolution in time, and then its local and instantaneous value, follow from the solution of the generalized transport equations, namely Eq. (12), for the densities and all their fluxes. Moreover, we can obtain (the extensive details are omitted for the sake of brevity) an expression of the form

$$\Theta_\ell(\mathbf{r},t) = \beta_\ell^{-1}(\mathbf{r},t) = T_\ell^*(\varepsilon_k, n_k)$$
$$- \Delta\Theta_\ell\{\varepsilon_k, n_k, I_{\varepsilon k}, I_{\ell k}, ...\}, \tag{18}$$

$\ell = 1, 2, ..., s$, where T^* is the expression for the quasitemperature in a flux-free description and $\Delta\Theta$ is the modification that the inclusion of the fluxes produce. The point is illustrated in Appendix A.

We emphasize that in Eq. (18) all the expressions are given in NESOM at the microscopic (mechano-statistical) level, and with $\Delta\Theta$ vanishing in the absence of fluxes. Clearly, Eq. (18) tells us that if Θ is a measurable quantity, it is affected by the presence of fluxes (in particular the heat flux, which is a combination of all the fluxes of quantities Q_j). Here we will pursue these results further, considering *accessible experiments that provide the characterization and, particularly, measurements of the quasitemperatures*, obtaining a corroboration of the concepts thus introduced through a good agreement of theory and experimental data.

III. QUASITEMPERATURES IN A PARTICULAR ILLUSTRATIVE EXAMPLE

Let us consider the system composed of carriers (electrons and holes) and lattice vibrations (phonons) in a highly photoexcited plasma in semiconductors (HEPS).[39,40] We consider the system alternatively without and with the presence of a constant electric field, and in both cases in a homogeneous condition. Following NESOM, for the description of the macroscopic (nonequilibrium thermodynamic) state of the system, we take as basic variables: (a) for the carriers, $\hat{H}_c$, the particle numbers, $\hat{N}_e$ and $\hat{N}_h$ (e for electrons, h for holes), the linear momenta, $\hat{\mathbf{p}}_e$ and $\hat{\mathbf{p}}_h$ (which divided by the mass are the fluxes of matter), the energy fluxes, $\hat{\mathbf{I}}_e$ and $\hat{\mathbf{I}}_h$, and all the other higher rank tensorial fluxes, $\hat{\varphi}_e^{(r)}$ and $\hat{\varphi}_h^{(r)}$, for mass motion, and $\hat{\psi}_e^{(r)}$ and $\hat{\psi}_h^{(r)}$, for thermal motion ($r = 2, 3, ...$),[37] and, (b) the phonon populations $\hat{\nu}_\mathbf{q}$, in mode $\mathbf{q}$ of branch γ. Explicitly,

$$\hat{H}_c = \sum_{\mathbf{k}a} \epsilon_{\mathbf{k}a} C_{\mathbf{k}a}^\dagger C_{\mathbf{k}a}, \tag{19a}$$

$$\hat{N}_a = \sum_{\mathbf{k}} C_{\mathbf{k}a}^\dagger C_{\mathbf{k}a}, \tag{19b}$$

$$\hat{\mathbf{P}}_a = \sum_{\mathbf{k}} \hbar\mathbf{k} C_{\mathbf{k}a}^\dagger C_{\mathbf{k}a}, \tag{19c}$$

$$\hat{\mathbf{I}}_a = \sum_{\mathbf{k}} \epsilon_{\mathbf{k}a}(\hbar\mathbf{k}/m_a) C_{\mathbf{k}a}^\dagger C_{\mathbf{k}a}, \tag{19d}$$

$$\hat{\varphi}_a^{(2)} = \sum_{\mathbf{k}} [\hbar\mathbf{k}(\hbar\mathbf{k}/m_a)] C_{\mathbf{k}a}^\dagger C_{\mathbf{k}a}, \tag{19e}$$

$$\hat{\psi}_a^{(2)} = \sum_{\mathbf{k}} \epsilon_{\mathbf{k}a}\left[\frac{\hbar\mathbf{k}}{m_a}\frac{\hbar\mathbf{k}}{m_a}\right] C_{\mathbf{k}a}^\dagger C_{\mathbf{k}a}, \tag{19f}$$

where [**AB**] stands for tensorial product of vectors.

It should be noticed that we are treating the carriers in Landau's single quasiparticle approximation (i.e., Coulomb interaction is dealt with in the random phase approximation).[41] Further, we introduced the effective mass approximation,[42] i.e., $\epsilon_{\mathbf{k}a} = \hbar^2 k^2/2m_a$ ($a = e$ for electrons and $a = h$ for holes), $C(C^\dagger)$ are annihilation (creation) operators in band states $\mathbf{k}a$. Furthermore,

$$\hat{\nu}_{\mathbf{q}\gamma} = b_{\mathbf{q}\gamma}^\dagger b_{\mathbf{q}\gamma}, \tag{20}$$

with $b(b^\dagger)$ being annihilation (creation) operators in phonon states $\mathbf{q}\gamma$. Vectors $\mathbf{k}$ and $\mathbf{q}$ run over the Brillouin zone.

We call the corresponding NESOM macrovariables [i.e., the average value over the nonequilibrium ensemble of the dynamical quantities of Eqs. (19)] $E_c(t)$, $N_a(t)$, $\mathbf{P}_a(t)$, $\mathbf{I}_a(t)$, $\varphi_a^{(r)}(t)$, $\psi_a^{(r)}(t)$, and $\nu_{\mathbf{q}\gamma}(t)$, respectively. The associated NESOM intensive variables (Lagrange multipliers of Sec. II) are indicated, respectively, by $\beta_c(t)$; $-\beta_c(t)\mu_a(t)$; $-\beta_c(t)\mathbf{v}_a(t)$; $-\beta_c(t)\boldsymbol{\alpha}_a(t)$; $-\beta_c(t)u_a^{(r)}(t)$; $-\beta_c(t)U_a^{(r)}(t)$; and $F_{\mathbf{q}\gamma}(t)$. Moreover, in Eq. (1) we have in this case

$$\hat{H}_0 = \hat{H}_c + \sum_{\mathbf{q}\gamma} \hbar\omega_{\mathbf{q}\gamma}\left(b_{\mathbf{q}\gamma}^\dagger b_{\mathbf{q}\gamma} + \frac{1}{2}\right), \tag{21}$$

where $\omega_{\mathbf{q}\gamma}$ are the frequency dispersion relations for the different types of phonons. (γ, in general, is A for acoustic phonons, LO for longitudinal, and TO for transverse optical phonons).[40] Also, the Zubarev–Peletminskii condition, Eq. (2), is satisfied, with all coefficients α being null in this case.

The partial Hamiltonian operator H' in Eq. (1) is composed now of the carrier–phonon interaction, carrier–radiation interaction, and the interaction of the carriers with an applied electric field, of intensity $\mathscr{E}$, in the cases when the latter is switched on.

Finally, according to the NESOM,[6–10] the auxiliary NSO is then given by

$$
\begin{aligned}
\bar{\varrho}(t,0)=\exp\bigg\{ & -\phi(t)-\beta_c(t)[\hat{H}_c-\mu_e(t)\hat{N}_e-\mu_h(t)\hat{N}_h] \\
& +\beta_c(t)\mathbf{v}_e(t)\cdot\hat{P}_e+\beta_c(t)\mathbf{v}_h(t)\cdot\hat{P}_h+\beta_c(t)\boldsymbol{\alpha}_e(t) \\
& \cdot\hat{\mathbf{I}}_e+\beta_c(t)\boldsymbol{\alpha}_h(t)\cdot\hat{\mathbf{I}}_H+\beta_C(T)\underline{u}_e^{(2)}(t)\otimes\underline{\hat{\varphi}}^{(2)} \\
& +\beta_c(t)\underline{u}_h^{(2)}(t)\otimes\underline{\hat{\varphi}}_h^{(2)}+\beta_c(t)\underline{U}_e^{(2)}(t)\otimes\underline{\hat{\psi}}_e^{(2)} \\
& +\beta_c(t)\underline{U}_h^{(2)}(t)\otimes\underline{\hat{\psi}}_h^{(2)}+\ldots+\sum_{\mathbf{q}\gamma}F_{\mathbf{q}\gamma}(t)\hat{v}_{\mathbf{q}\gamma}\bigg\},
\end{aligned}
$$

$$(22)$$

where a dot stands as usual for the scalar product of vectors, and we wrote $\otimes$ for fully contracted tensorial product.

As noted in Sec. II, there is no wholly satisfactory way to choose the basic variables, which needs to be done in a case by case approach. For the given choice we have introduced, we took into account the well known fact that in HEPS the carrier system is brought into internal thermalization very rapidly (subpicosecond time scale)[39,40,43] by the action of the long range and strong Coulomb interaction; hence the choice of $\hat{H}_c$ and $\hat{N}_a$, with, then, β_c and μ_a playing the role of a carrier's reciprocal quasitemperature [cf. Eq. (17)] and of quasichemical potentials, respectively. When an electric field is present, it produces a current, i.e., mass motion, and then it is required to introduce the linear momentum, with $\mathbf{v}_a$ playing the role of a drift velocity. Also, Joule and electrothermal effects, which are required to introduce the energy flux, should be present. Once the fluxes of matter and energy are introduced, it is natural for the method to incorporate all the other higher order fluxes.[36,37] The choice of the phonon populations is a result of the theoretical and experimental verification that the different modes are differently photoexcited.[44]

We introduce a simplifying assumption, viz. that of neglecting higher order, $r \geq 2$, fluxes, which are shown *a posteriori* to have negligible influence. In other words, we introduce a truncation procedure, retaining only the variables E_c, N_a, $\mathbf{P}_a$, $\mathbf{I}_a$, $\nu_{\mathbf{q}\gamma}$. Under these conditions, a straightforward calculation tells us that

$$
\begin{aligned}
\mathrm{Tr}\{C_{\mathbf{k}a}^{\dagger}C_{\mathbf{k}a}\bar{\varrho}(t,0)\}&=f_{\mathbf{k}a}(t) \\
&=[1+\exp\{\beta_c(t)[\epsilon_{\mathbf{k}a}-\mu_a(t) \\
&\quad-\mathbf{v}_a(t)\cdot\hbar\mathbf{k}-\epsilon_{\mathbf{k}a}\boldsymbol{\alpha}_a(t)\cdot\hbar\mathbf{k}/m_a]\}]^{-1},
\end{aligned}
$$

$$(23a)$$

and

$$
\mathrm{Tr}\{b_{\mathbf{q}\gamma}^{\dagger}b_{\mathbf{q}\gamma}\bar{\varrho}(t,0)\}=\nu_{\mathbf{q}\gamma}(t)=[\exp\{F_{\mathbf{q}\gamma}(t)\}-1]^{-1}.
$$

$$(23b)$$

Clearly, the average values of the quantities of Eqs. (19) depend on these two distribution functions, which have a form reminiscent of a shifted Fermi–Dirac and a Planck distribution function, respectively, given at each time t, i.e., evolving along with the dissipative processes that develop in the media.

Let us consider the subsystem of carriers with energy $E_c(t)$, and the phonon subsystems composed of the superposition [cf. Eq. (21)] of single independent subsystems corresponding to each state $\mathbf{q}\gamma$, with energy per mode $\mathbf{q}$ in branch γ given by $\hbar\omega_{\mathbf{q}\gamma}\nu_{q\gamma}(t)$ (the zero point energy is just a constant of no relevance). Following Eq. (16a), we introduce the carrier quasitemperature $\Theta_c(t)$ [cf. Eq. (17)],

$$
\beta_c(t)=\delta\bar{S}(t)/\delta E_c(t)=1/k_B\Theta_c(t) \tag{24}
$$

(where we have explicitly introduced the Boltzmann constant k_B) and the phonon quasitemperatures per mode $\Theta_{\mathbf{q}\gamma}(t)$,

$$
\beta_{\mathbf{q}\gamma}(t)=\delta\bar{S}(t)/\delta\hbar\omega_{\mathbf{q}\gamma}\nu_{q\gamma}(t)=F_{\mathbf{q}\gamma}(t)/\hbar\omega_{\mathbf{q}\gamma}
$$
$$
=1/k_B\Theta_{\mathbf{q}\gamma}(t), \tag{25}
$$

where $\bar{S}(t)$ is the NESOM entropy for the given description of the HEPS, i.e., the one given by Eq. (9) but with $\bar{\varrho}$ of Eq. (22) after taking $\mathbf{u}_{e,h}^{(2)}$, $\mathbf{U}_{e,h}^{(2)}$, etc., null, in the truncated description we are using. Furthermore, the other Lagrange multipliers are given by

$$
\beta_c(t)\mu_a(t)=-\delta\bar{S}(t)/\delta N_a(t), \tag{26a}
$$

$$
\beta_c(t)\mathbf{v}_a(t)=-\delta\bar{S}(t)/\delta\mathbf{P}_a(t), \tag{26b}
$$

$$
\beta_c(t)\boldsymbol{\alpha}_a(t)=-\delta\bar{S}(t)/\delta\mathbf{I}_a(t), \tag{26c}
$$

which define the quasichemical potentials, μ_a, the drift velocities, $\mathbf{v}_a$, and the quantities $\boldsymbol{\alpha}_a$ interpreted as drift velocities associated with the energy fluxes.

Next we look for the equivalent of Eq. (18), i.e., a way to put into explicit evidence the dependence of the quasitemperatures on the fluxes $\mathbf{P}$ and $\mathbf{I}$ (of matter and of energy, respectively). In the limit of a weak contribution $\boldsymbol{\alpha}\cdot\mathbf{I}$, we obtain up to second order in α that

$$
E_c(t)=\widetilde{E}_c(t)+\sum_a[A_a(t)\mathbf{v}_a(t)\cdot\boldsymbol{\alpha}_a(t)+A_a'(t)\alpha_a^2(t)],
$$

$$(27a)$$

$$
N_a(t)=\widetilde{N}_a(t)+B_a(t)\mathbf{v}_a(t)\cdot\boldsymbol{\alpha}_a(t)+B_a'(t)\alpha_a^2(t), \tag{27b}
$$

$$
\mathbf{P}_a(t)=C_{1a}(t)\mathbf{v}_a(t)+C_{2a}(t)\boldsymbol{\alpha}_a(t)+\mathbf{C}_{2a}'(t)\alpha_a^2(t), \tag{27c}
$$

$$
\mathbf{I}_a(t)=D_{1a}(t)\mathbf{v}_a(t)+D_{2a}(t)\boldsymbol{\alpha}_a(t)+\mathbf{D}_a'(t), \tag{27d}
$$

where the coefficients on the right are given in Appendix B.

Equations (27a) and (27b) for E_c and N_a are composed of α-independent contributions, indicated by the variables with an upper wavy line, plus terms involving the Lagrange parameters $\mathbf{v}$ and $\boldsymbol{\alpha}$. Using Eqs. (27c) and (27b) we can express the latter in terms of $\mathbf{P}$ and $\mathbf{I}$, namely,

$$
\mathbf{v}_a(t)=L_{1a}(t)\mathbf{P}_a(t)+L_{2a}(t)\mathbf{I}_a(t), \tag{28a}
$$

$$
\boldsymbol{\alpha}_a(t)=M_{1a}(t)\mathbf{P}_a(t)+M_{2a}(t)\mathbf{I}_a(t), \tag{28b}
$$

where the kinetic coefficients L and M are given in Appendix C. Moreover, these two fluxes are related to the flux of heat through the expression

$$\mathbf{I}_a = k_B \Theta_c \mathbf{I}_s = \sum_a \left[\mathbf{I}_a - (\mu_a/m_a) \mathbf{P} \right], \quad (29)$$

where $\mathbf{I}_s$ is the flux of NESOM entropy in this case [cf. Eq. (14)].

We proceed now to compare, for this particular case, the description as given by the statistical distribution of Eq. (22), and the one based on only the energy and concentration, that is, neglecting all the fluxes. The latter case has then associated the NSO given by

$$\bar{\varrho}_0(t) = \exp\left\{ -\phi_0 - \beta_{co}(t)[\hat{H}_c - \mu_{eo}(t)\hat{N}_e - \mu_{ho}(t)\hat{N}_h] \right.$$
$$\left. + \sum_{\mathbf{q}\gamma} F_{\mathbf{q}\gamma}(t) \nu_{\mathbf{q}\gamma} \right\}. \quad (30)$$

We introduce the corresponding carriers' quasitemperature in this flux-free representation, that is

$$k_B T^*(t) = 1/\beta_{co}(t), \quad (31)$$

and a straightforward calculation (see last part of Appendix B) tells us that

$$E_0(t) = \frac{3}{2} \sum_a N_a(t) k_B T^*(t), \quad (32)$$

which has the form of an equipartition of carriers' energy at the quasitemperature $T_c^*(t)$. Furthermore, the quasichemical potential is given by the relation

$$n_a(t) = (2\pi m_a k_B T^*/4\pi^2\hbar^2)^{3/2} \exp\{\beta_c[\mu_a + \tfrac{1}{2} m_a v_a^2]\}. \quad (33)$$

Combining Eq. (27a), together with Eq. (B1) in Appendix B, and Eq. (32), it follows in the considered nondegenerate-like limit, that

$$\Theta_c(t) = T_c^*(t) - \Delta\Theta_c(t), \quad (34)$$

where

$$k_B \Delta\Theta = \sum_a \left\{ \frac{1}{3} m_a v_a^2 + \left[\frac{2}{3} A_a - B_a k_B \Theta(1+\chi_a) \right] \mathbf{v}_a \cdot \boldsymbol{\alpha}_a \right.$$
$$\left. + \left[\frac{2}{3} A_a' - B_a' k_B \Theta(1+\chi_a) \right] \alpha^2 \right\}, \quad (35)$$

and the coefficients A, B, A', B', and χ are given in Appendix D.

Consider now the case when there is no flux of matter (implying that thermalstriction effects, in this case thermoelectric effects, are neglected). Setting $v=0$ in Eq. (35), and using that, then,

$$\mathbf{I}_a(t) = (35/8m_a)N_a(T) k_B T_c^*(t) \boldsymbol{\alpha}_a(t), \quad (36)$$

we find

$$\Theta_c(t) = T_c^*(t) - \frac{2}{5} \sum_a [m_a/k_B^3 T_c^{*2}] |\mathbf{I}_a(t)/N_a(t)|^2, \quad (37)$$

which, once we identified $\mathbf{I}$ with the heat flux, we fully recover the result derived in the context of phenomenological extended irreversible thermodynamics,[20] however, in the present case, for the two fluid system of electrons and holes.

We have obtained an expression for the (nonequilibrium) quasitemperature Θ_c, in this case defined by Eq. (24), which takes the form predicted by the general theory, viz. Eq. (18): It is composed of the contribution T_c^* derived from the generalized NESOM entropy depending only on energy and density, plus the corrections due to the presence of the fluxes of matter and energy.

IV. EXPERIMENTAL BACKGROUND: CHARACTERIZATION AND MEASUREMENT OF QUASITEMPERATURES

We address next the all important question of the characterization and measurement of quasitemperatures. As it is well known, theory and experiment are related through response function theory.[45,46] We resort here to the use of a response function theory for arbitrary far-from-equilibrium systems built within the scope of NESOM[9,47] for the discussion of experiments which can provide the sought after characterization and measurement of quasitemperatures. We consider the use of optical spectroscopy, a precise and powerful experimental technique with high-resolution power. Moreover, two types of experiments will be considered, namely, those in time-resolved and time-integrated optical spectroscopy. The first provides resolution in ultrashort time scales (femtoseconds), thus allowing following the rapid dissipative processes taking place in the HEPS, while the second provides information encompassing larger time intervals, typically in the nanosecond range. We consider, next, several situations.

A. The carrier quasitemperature for null v and α (i.e., absence of an electric field)

In this case $\Delta\Theta$ in Eq. (37) is null and the carrier quasitemperature is a T_c^* at null **v**. This is in the nonequilibrium condition resulting from the pumping of the electromagnetic energy provided by the laser beam that generates the HEPS. This quasitemperature can be determined in experiments performing measurements of optical properties of HEPS, particularly Raman scattering and luminescence. In both cases, the calculation of the spectra is consistently performed in the framework of a response function theory based on NESOM.[9,47]

Let us consider first Raman scattering. The corresponding differential cross section is:[48]

$$d^2\sigma(\omega,\mathbf{q}|t) = \begin{cases} \mathscr{A}_{CD}(1-e^{-\beta(t)\hbar\omega})^{-1} \mathscr{T}\varepsilon^{-1}(\mathbf{q},\omega|t) \\ \mathscr{A}_{SD}(1-e^{-\beta(t)\hbar\omega})^{-1} \mathscr{T}\mu^{-1}(\mathbf{q},\omega|t), \end{cases} \quad (38)$$

where $\mathscr{A}$ are amplitude coefficients, $\mathscr{T}$ stands for imaginary part, and where the upper expression corresponds to scattering by charge-density fluctuations and the lower one by spin-

density fluctuations. Moreover, $\hbar\omega$ is the energy transfer and $\hbar\mathbf{q}$ the momentum transfer in the scattering event; ε is the frequency and wave number dependent dielectric function, and μ the magnetic permeability. They are given, in the random phase approximation,[41] by[39,49]

$$\varepsilon(\mathbf{q},\omega|t)=1-(8\pi e^2/\epsilon_0 Vq^2)\sum_{\mathbf{k}a} F_a(\mathbf{k},\mathbf{q};\omega|t), \quad (39)$$

$$\mu(\mathbf{q},\omega|t)=1+\sum_{\mathbf{k}a} (U_a/N_a)F_a(\mathbf{k},\mathbf{q};\omega|t), \quad (40)$$

where ϵ_0 is the background dielectric constant, V is the volume of the sample, U the exchange energy integral, and

$$F_a(\mathbf{k},\mathbf{q};\omega|t)=\frac{f_{\mathbf{k}+\mathbf{q},a}(t)-f_{\mathbf{k}a}(t)}{\hbar\omega-\epsilon_{\mathbf{k}a}+\epsilon_{\mathbf{k}-\mathbf{q},a}+is}, \quad (41a)$$

with $s\rightarrow +0$, we recall that $\epsilon_{\mathbf{k},a}=\hbar^2k^2/2m_a^*$, and the distribution function f is now given by

$$f_{\mathbf{k}a}(t)=[1+\exp\{\beta_c(t)[\epsilon_{\mathbf{k}a}-\mu_a(t)]\}]^{-1}. \quad (41b)$$

Consider the nondegenerate-like limit, that is, when the exponential in Eq. (41b) is much larger than 1, which is the usual experimental situation; in that case one finds that

$$\sum_{\mathbf{k}} F_a(\mathbf{k};\mathbf{q};\omega|t)=\beta_c(t)n_a(t)-(2\sqrt{\pi})\beta_c(t)n_a(t)I(\xi_a)$$

$$+\sqrt{2\pi}n_a\beta_c(t)\xi_a(t)e^{-\xi_a^2(t)}, \quad (42)$$

where n_a is the density of carriers of type a (e or h),

$$I(\xi_a)=\int_0^\infty dx\,x\,\exp\{-x^2\xi_a^2\}\,\ln\left|\frac{x+1}{x-1}\right|, \quad (43a)$$

and

$$\xi_a^2(t)=m_a\omega^2/2q^2k_BT_c^*(t). \quad (43b)$$

Thus, Eq. (38) becomes

$$d^2\sigma(\omega|t)=\begin{cases} d^2\sigma^0(\omega|t)_{CD}/|\varepsilon(\mathbf{q},\omega|t)|^2 \\ d^2\sigma^0(\omega|t)_{SD}/|\mu(\mathbf{q},\omega|t)|^2, \end{cases} \quad (44)$$

where $d^2\sigma^0$ stands for the cross sections for scattering by charge-density fluctuations (CD) and spin-density fluctuations (SD) of single independent carriers, i.e., the sum of two terms that have the form $2\pi Na\beta_c\xi_a\exp\{-\xi_a^2\}$, and the denominators introduce the corrections due to polarization effects arising out of Coulomb interaction. But $[1-\exp\{-\beta_c\hbar\omega\}]^{-1}$ in Eq. (38) is approximately $k_BT_c^*/\hbar\omega$, and then

$$d^2\sigma_a^0\sim\exp\{-\omega^2m_a/2q^2k_BT_c^*(t)\}, \quad (45)$$

which provides the main ω-dependent contribution to the scattering cross section, since the denominators in Eq. (44) have only influence for $\omega\lesssim q\bar{v}_a$, where $\bar{v}$ is the thermal velocity $k_BT_c^*=m_a\bar{v}_a^2/2$. Hence, outside this low frequency range, the *logarithm of the scattering cross section versus* ω^2 is very nearly a straight line, *whose slope is inversely proportional to* T_c^*. Since, as a general rule, m_h is one order of magnitude larger than m_e, one may expect two clearly dif-
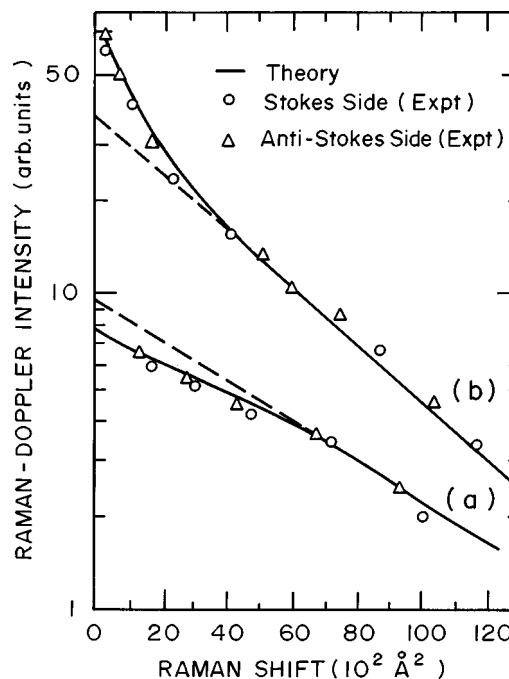

FIG. 1. Inelastic light scattering by single photoexcited carriers in *n*-GaAs. (a) sample with concentration 2×10^{15} cm^{-3}; (b) sample with 1.7×10^{17} cm^{-3}. Broken lines are the extrapolated Maxwell-like profile at quasitemperature T^*. Carrier quasitemperatures are (a) 560 and (b) 400 K. (After Ref. 49. Experimental points are from Ref. 50).

ferentiated slopes, one at low frequencies due to scattering by holes and a second at not too low frequencies due to scattering by electrons. Figure 1 shows the case of a *n*-type GaAs sample, where the doping concentration of electrons is much larger than the photoinjected concentration of pairs. Hence, scattering by electrons predominates, and there is only one discernible straight line that determinates T_c^*:[49,50] (a) is the case of scattering by charge-density fluctuations and (b) by spin-density fluctuations. The expected deviations from the Maxwellian profile [cf. Eq. (45)] is a result of, as already mentioned, correlation and exchange effects: respectively, a depletion in case (a) and an enhancement in case (b) in the region $\omega\lesssim q\bar{v}_e$. Experimental data are from Ref. 50. This is a time-integrated experiment, that is, T_c^* is a time average value taken along the interval of the collection of data. The values of the quasitemperature in each case are indicated in the figure, and the thermal bath temperature is 300 K.

Consider now the case of photoluminescence, another kind of experiment sensitive to the nonequilibrium distribution of carriers and, hence, dependent on Θ. The luminescence spectrum calculated in MaxEnt-NESOM is given by[51]

$$I(\omega|t)=\mathscr{A}_L(\omega|t)$$

$$\times\sum_{\mathbf{k}} f_{\mathbf{k}e}(t)f_{\mathbf{k}h}(t)\delta(\hbar\omega-E_G-\epsilon_{\mathbf{k}e}-\epsilon_{\mathbf{k}h}), \quad (46)$$

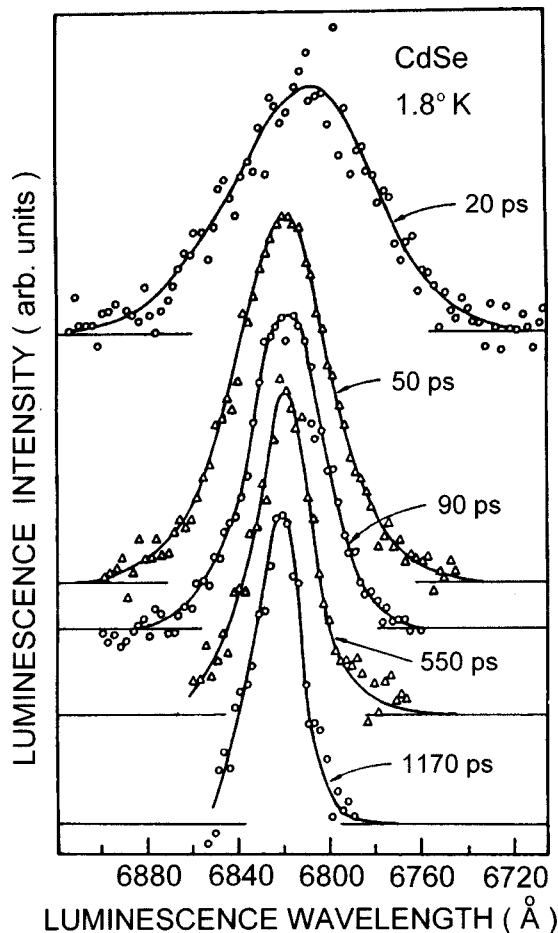where $\mathscr{A}$ is an amplitude coefficient and E_G the energy gap.

FIG. 2. Photoluminescence spectra of CdSe platelets under high levels of excitation, obtained at the indicated delay time after pulse excitation. (After Ref. 52.)
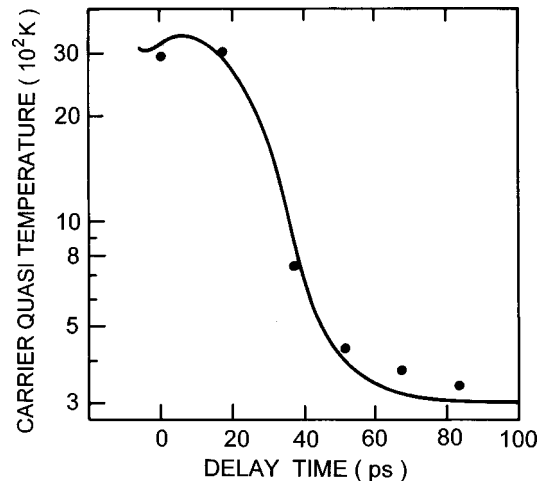

FIG. 3. Evolution of the carrier quasitemperature in highly excited GaAs. The MaxEnt-NESOM calculation (full line) is from Ref. 53, and experimental data (dots) are from Ref. 54.

When in Eq. (46) we introduce the distributions f of Eq. (41) in the nondegenerate-like limit and use the energy-conserving delta function, we obtain

$$I(\omega|t) = g(\omega|t)\exp\{-(\hbar\omega - E_G)/k_B T_c^*(t)\}, \qquad (47)$$

meaning that the high frequency side of the spectrum decays exponentially, with the exponent being inversely proportional to the (nonequilibrium) quasitemperature. In that frequency region, $g(\omega)$ is an almost constant absorption coefficient, and then *the logarithm of $I(\omega)$ is a near straight line* (as experimentally verified), whose slope is $\hbar/k_B T_c^*$, that is,

$$k_B T_c^*(t) = -\hbar[d\ln I(\omega|t)/d\omega]^{-1}, \qquad (48)$$

gives a measure of T_c^*. Time-resolved measurements of luminescence are shown in Fig. 2.[52] In this case the slope at the high frequency side keeps increasing in time, which is an indication of the fact that the carrier system relaxes its excess energy to the lattice and, hence, the quasitemperature decreases in time. This provides a quite clear illustration as to how the time evolution of the excited macrostate of the system proceeds towards equilibrium as dissipative processes develop in the medium. This is explicitly shown in Fig. 3,[53] where experimental data[54] compare very well with the cal-

culation. In that way we collect information on the evolution of the relaxation processes in the system, with the experiment providing a quite appropriate *measuring technique allowing* the following of the time evolution of the carrier quasitemperature in the picosecond time scale.

The quasitemperature T_c^* can also be determined in measurements of gain spectra. The response, calculated in MaxEnt-NESOM,[55] is given by

$$\alpha(\omega|t) = \mathscr{A}_G(t)\omega[1 + \exp\{\beta(t)(\hbar\omega - E_G)\}]$$

$$\times \sum_{\mathbf{k}} f_{\mathbf{k}e}(t) f_{\mathbf{k}h}(t)\,\delta(\hbar\omega - E_G - \epsilon_{\mathbf{k}e} - \epsilon_{\mathbf{k}h}),$$

$$(49)$$

where $\mathscr{A}_G$ is an amplitude coefficient, the distributions f are given by Eq. (41), making the gain spectrum $\alpha(\omega|t)$ dependent on the (nonequilibrium) quasitemperature $T_c^*(t)$ and the (nonequilibrium) quasichemical potential. Figure 4 shows a very good agreement between calculations consistently done in the framework of the NESOM, and an experiment providing a time-integrated spectrum, with T_c^* being 15 K while the thermal bath temperature is 2 K.[56] The quasichemical potential, $\mu = E_G + \mu_e + \mu_h$, is determined by the point where there occurs transition from absorption to gain, as indicated in the figure. In this experiment, the nondegenerate-like limit does not apply, and the calculations were performed using the distribution function of Eq. (41).

We can then state that the carriers' quasitemperature defined in NESOM-based IST [cf. Eq. (24)] is an observable quantity (one in the set that characterizes the macroscopic state of the nonequilibrium system). It can be determined by means of, say, a ''thermometer'' consisting of a reading of the slope of the logarithm of the high frequency side of the recombination spectrum, or, as shown, of that in Raman scattering experiments. Also, it follows from a best fitting pro-
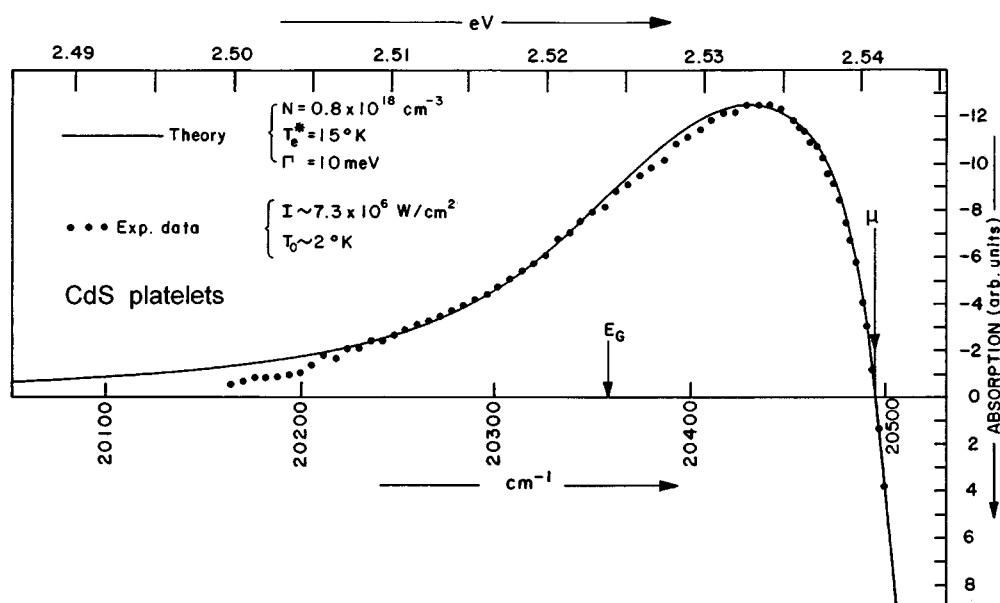
FIG. 4. Calculated (in MaxEnt-NESOM) gain spectrum (full line) and experimental data (dots) in highly photoexcited platelets of CdS. (After Ref. 56.)

cedure as in the case of gain spectra, where one can also easily determine the (nonequilibrium) quasichemical potential.

B. The carrier quasitemperature dependence on fluxes

The presence of a uniform electric field produces fluxes of matter and energy in the photoinjected carrier system, and then a flux-dependent (nonequilibrium) carrier quasitemperature Θ_c is present in the Fermi–Dirac-type distribution function $\bar{f}$ of Eq. (23a). It can also be determined using the experiments referred to in Sec. IV A.

In this case, since the fluxes are created by the presence of an electric field of intensity $\mathscr{E}$, they are dependent on this field intensity. The flux of matter is a result of the electric field producing an electric current in the charged system, and so **P** needs to be introduced in the macroscopic description of the system. Also, because of the electrothermal effect it follows heat motion, and so the energy flux **I** is to be included in the basic set of macrovariables [let us recall that the heat flux is a combination of both, cf. Eq. (29)]. Hence, Eq. (34) holds in this case, once we consider the nondegenerate-like limit in the carrier system.

Again, the determination of Θ_c follows from the photoluminescence spectra. In fact, in the non-degenerate-like regime the carrier's distribution function is

$$\bar{f}_{\mathbf{k}a} \simeq \exp\{-\beta_c[\epsilon_{\mathbf{k}a} - \mu_a - \mathbf{v}_a \cdot \hbar\mathbf{k} - \epsilon_{\mathbf{k}a}\boldsymbol{\alpha}_a \cdot \hbar\mathbf{k}/m_a]\},\tag{50}$$

and then, in Eq. (46), once $\bar{f}$ of Eq. (50) is introduced, we obtain an exponential dependence of the form

$$I(\omega) = g(\omega)\exp\{-(\hbar\omega - E_G)/k_B\Theta_c\},\tag{51}$$

in the steady state generated by the constant electric field. Hence, from the high frequency side of the spectrum, where g(ω), namely, the absorption coefficient, is weakly dependent on ω, we obtain

$$k_B\Theta_c = -\hbar[d \ln I(\omega)/d\omega]^{-1}.\tag{52}$$

Photoluminescence experiments in HEPS in the presence of an electric field are, for example, available in the case of modulation spectroscopy in semiconductor heterostructures, which are currently the object of large interest.[57]

From the experimental data from modulation spectroscopy provided by Mendez *et al.*,[58] by means of application of Eq. (51) we obtain the values of Θ_c indicated by dots in Fig. 5(a) (right ordinate), and the curve was obtained by a polynomial interpolation.

We consider now the description that excludes the flux of energy, namely, the one in terms of only the carriers' energy, numbers, and momenta (as in Ref. 59). Let us call Θ_c^0 the quasitemperature corresponding to this description, which, for weak to intermediate electric field intensities, increases monotonically with a very nearly square dependence on the electric field intensity (Ref. 59, and as shown below in an explicit calculation depicted in Fig. 5), namely,

$$\Theta_c^0 = T_c^* + D\mathscr{E}^2,\tag{53}$$

where T_0^* is the photoexcited carriers' quasitemperature at null electric field and D is field independent. Hence, it follows that

$$(T^* - T_0^*)/\mathscr{E}^2 = D\tag{54}$$

is field independent. On the other hand, if the correction $\Delta\Theta_c$ due to the presence of the energy flux is considered, we have that
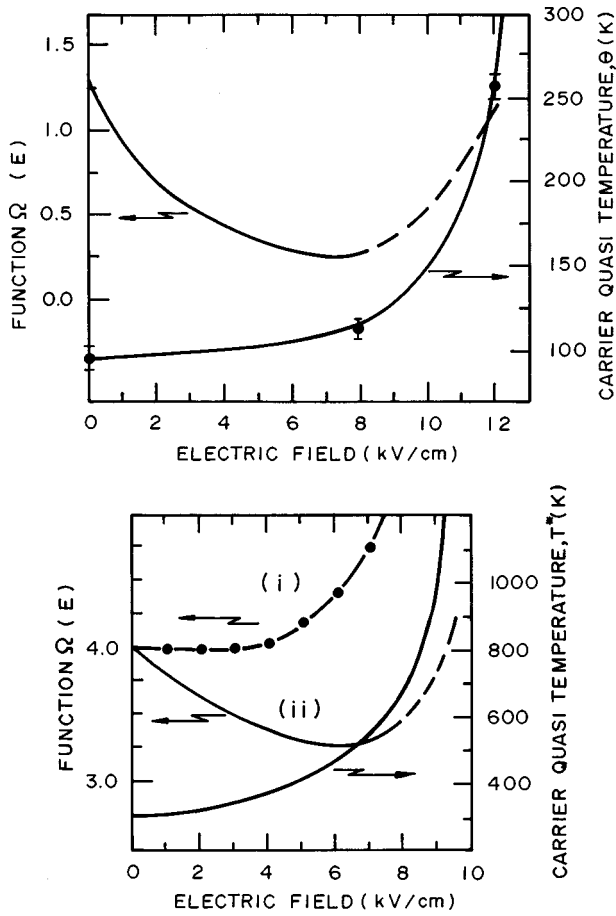
FIG. 5. Carrier quasitemperature Θ (right ordinate) obtained from (a) the photoluminescent spectra of a GaAs–GaAlAs superlattice for various field intensities, after Ref. 58 (upper figure) and (b) a MaxEnt-NESOM calculation for the case of bulk GaAs (lower figure). Also the function $\Omega(\mathscr{E})$ of Eq. (55), which points to the dependence of the nonequilibrium temperature on the energy flux: (a) in the upper figure the one derived from the experimental data, and (b) in the lower curve the one calculated according to the method, while the dot-dash line is the one in which the energy flux is disregarded.

$$\Omega(\mathscr{E})=(\Theta_c-T_c^*)/\mathscr{E}^2=\frac{\Theta_c^0-T_c^*}{\mathscr{E}^2}-\frac{\Delta_I\Theta_c}{\mathscr{E}^2}=D-\frac{\Delta\Theta_c}{\mathscr{E}^2}.$$
(55)

Consequently a field-dependent departure of this quantity Ω from a constant might be ascribed to $\Delta\Theta$, which in that way would evidence the influence of the energy flux on the nonequilibrium temperature. This is verified in the above referred experiment, as shown in Fig. 5(a) (left ordinate).

We reinforce this result with a theoretical analysis. To this end we consider the HEPS produced in bulk GaAs by a very short laser pulse. We choose for illustration the case of photons having an energy of 120 meV above the energy gap value; a concentration of photoinjected carriers (fixed by the pulse intensity) $n=1.4\times10^{17}$ cm^{-3}; several values of the electric field intensity are considered; and the thermal bath is taken at 300 K. We derive the equations of evolution for the macrovariables in a description in IST that includes the carriers' energy, concentration, and momentum, which are com-

putationally solved for the case of the numerical values given above and using parameters characteristic of GaAs. In Fig. 5(b) the stationary carrier quasitemperature dependence on the field intensity (right ordinate) is shown. Also, is shown (left ordinate) the function $\Omega(\mathscr{E})$ of Eq. (55) in the conditions, first, neglecting the influence of the energy flux, i.e., taking $\Delta\Theta=0$, which is indicated by the dot-dash line, and second, introducing such an effect. Inspection of this curve shows that the result already predicted in Fig. 5(a), where we used the experimental data, is recovered. For $\Delta\Theta=0$, leading to the dot-dash line in Fig. 5(b), we recover the almost constant Ω [equal to D in Eq. (55)] at low fields, followed by a monotonic increased with $\mathscr{E}$. On the other hand, $\Omega(\mathscr{E})$ monotonically decreases in the Ohmic regime (the latter roughly going up to 6 kV/cm, followed by a non-Ohmic regime) in, qualitatively, the same way as detected from the use of the experimental data.

Consequently, these results point to the fact that the experimental data appear to give an indication of the effective dependence of the quasitemperature on the energy flux. From the data of Fig. 5(a) we can estimate that the contribution due to the presence of the energy flux leads to a decrease of the otherwise flux-free quasitemperature by, roughly, the order of 5% for field intensities in the range of 4 to 6 kV/cm.

C. The phonon (nonequilibrium) quasitemperature

As previously noticed; the phonon system requires the definition of a (nonequilibrium) quasitemperature for each mode in each branch. (This applies particularly to optical phonons in polar semiconductors; the acoustic phonons, if there is a very good contact between the sample and a thermal reservoir, are expected to remain in near thermal equilibrium with the latter.) Equation (25) has introduced these $\Theta_{\mathbf{q}\gamma}(t)$, which, as shown, are closely related to the Lagrange multipliers $F_{\mathbf{q}\gamma}$ of MaxEnt-NESOM. It may be noticed that Eq. (23b) becomes a Planck-like distribution with a particular quasitemperature for each mode once we write $F_{\mathbf{q}\gamma}=\hbar\omega_{\mathbf{q}\gamma}/k_B\Theta_{\mathbf{q}\gamma}$.

This is an observable quantity when resorting again to optical spectroscopy. In the case of Raman scattering of phonons, the intensity of the lines is dependent on the phonon population of each individual mode probed in the experiment.[60] More precisely, the ratio of Stokes to anti-Stokes intensities is given by

$$I_{AS}/I_S|_{\mathbf{q}\gamma}=(\nu_{\mathbf{q}\gamma}+1)/\nu_{\mathbf{q}\gamma}=\exp\{\hbar\omega_{\mathbf{q}\gamma}/k_B\Theta_{\mathbf{q}\gamma}\},$$
(56)

which provides a way to measure $\Theta_{\mathbf{q}\gamma}$, that is, from Eq. (56),

$$k_B\Theta_{\mathbf{q}\gamma}=\hbar\omega_{\mathbf{q}\gamma}/\ln(I_{AS}/I_A).$$
(57)

Figure 6 shows the time evolution of the (nonequilibrium) quasitemperature of a LO-phonon mode, where dots are experimental points from a Raman time-resolved experiment,[61] determined through the use of Eq. (57), and the full line is the calculation in MaxEnt-NESOM.[62] Optical phonons are produced well in excess of equilibrium (in the collision processes with carriers) in a privileged off-center
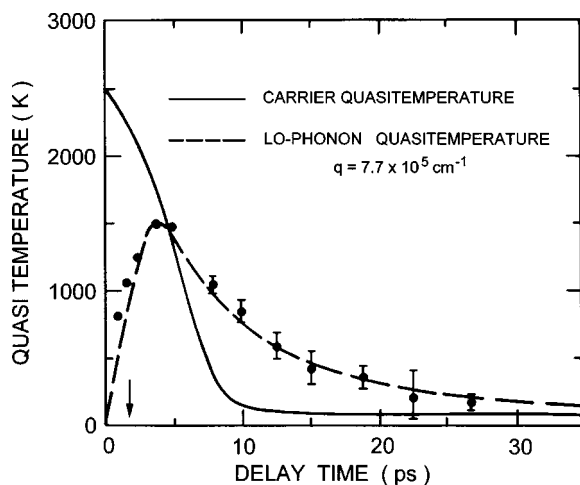
FIG. 6. Evolution of the quasitemperature of a LO phonon mode in GaAs. Full line is the calculation in MaxEnt-NESOM, from Ref. 62, and dots are from Ref. 61, with bars indicating the experimental error.

region of Brillouin zone.[40,63] It leads to the phenomenon of phonon quasitemperature overshoot, that is to say, these privileged modes attain quasitemperatures larger than those of the exciting carriers.[44] In this pump–probe experiment, mutual thermalization of carriers and phonons in all modes, i.e., all attaining the same quasitemperature, follows in delay times (after switch-off of the laser excitation) of the order of several tens of picoseconds. From then on this common (nonequilibrium) quasitemperature tends to the temperature of equilibrium with the thermal reservoir.[62]

V. CONCLUDING REMARKS

We have mentioned in the Introduction the use of phenomenological nonequilibrium temperatures.[11–18] The concept does not arise in classical irreversible thermodynamics,[64] where local equilibrium is assumed. For general situations, different concepts of nonequilibrium temperatures have been considered by several authors in several thermodynamic approaches: Meixner sets the concept of a ''dynamical temperature,''[65] Müller introduces ''coldness,''[66] Muschik postulates a ''contact temperature,''[67] Keizer introduces it in the framework of his formulation of nonequilibrium thermodynamics based on statistical considerations of molecular fluctuations,[68] and Nettleton[69] considers the concept of a kinetic temperature related to the kinetic energy per particle in a discussion within the framework of MaxEnt. Two of the present authors have proposed, within the framework of extended irreversible thermodynamics,[20] a nonequilibrium temperature stemming as the partial derivative of a nonequilibrium entropy-like function that incorporates the dissipative fluxes as variables. In a forthcoming paper,[70] a partial tentative comparison of several approaches with IST is to be reported.

In the previous sections we have introduced a nonequilibrium temperature-like variable (which we call quasitemperature) in the context of IST, which depends, in principle, on all the macrovariables, composed of the densities, fluxes,

and higher-order fluxes of matter and of energy appropriate for the description of the macroscopic state of the system. This quasitemperature is not the only thermodynamic quantity to contain contributions from irreversible fluxes; the same applies to chemical potentials, drift velocities, and all the intensive thermodynamic variables defined by the Lagrange multipliers in the construction of the NESOM in its variational formulation.

In Sec. IV we have described experiments that *evidence and measure such (nonequilibrium) quasitemperature in IST*. We have considered the case of highly excited semiconductors and pump–probe experiments providing measurements of optical properties. This is a field of extensive research because of the technological interest involved, i.e., the functioning of semiconductors in electronic devices. We have looked for experiments that can be described by means of a response function theory for far-from-equilibrium systems encompassed in NESOM,[8,47] and so introducing the (nonequilibrium) quasitemperature(s) defined within its context, that is (nonequilibrium) quasitemperatures for the different subsystems of the whole sample. In HEPS (see Ref. 40 and last of Refs. 28) in the usual experimental conditions it is possible to introduce a carrier (nonequilibrium) quasitemperature and quasichemical potentials. In experiments probing the system in the first several tens of femtoseconds after initiation of the exciting laser pulse, it is possible to introduce carrier population functions (second of Refs. 43) with a (nonequilibrium) quasitemperature for each single quasiparticle quantum mechanical state. For an initial probing time smaller than the period of a plasma wave (say, typically 10 fs in the experiments we are considering), a single-particle description is no longer possible. However, it is worth noticing that 10 fs approaches the limit of detection in ultrafast spectroscopy in the visible and near visible region set forth by Heisenberg's uncertainty principle, and then the statistical theory is almost always applicable. In the case of phonons the definition of *a (nonequilibrium) quasitemperature for each single quasiparticle quantum mechanical state* is required. Carriers and phonons attain a unique (nonequilibrium) quasitemperature (that is, mutual thermalization, but in nonequilibrium conditions) in relaxation times of, roughly, less than 100 picoseconds.

We have first considered experiments associated with measurement of optical properties in HEPS, the latter in a homogeneous condition and free of fluxes, to obtain a *measurement of the carrier quasitemperature*. This was described, first in time-integrated experiments with the data shown in Fig. 1, and, next, a determination, resorting to ultrafast spectroscopy,[71] of the time evolution of the carrier quasitemperature while dissipative processes develop in the sample, as shown in Figs. 2 and 3. This gives a description of the irreversible evolution that takes place in the system. In Fig. 4 we considered a measurement of gain spectrum, which allows the determination of the quasitemperature as well as the quasichemical potential.

In Sec. IV B, we have considered the important question of the dependence of the nonequilibrium temperature on the fluxes. Those of matter and heat are created by means of the

action of an electric field acting on the itinerant carriers. Experiments determining luminescence spectra also provide a way to measure quasitemperatures in the carrier system. The expected increase of the quasitemperature with the field intensity is verified, but in a way that seems to clearly point to the confirmation of the *dependence of the (nonequilibrium) quasitemperature on the fluxes*, as predicted by extended irreversible thermodynamics, and also in IST as described in this paper; theory and the experimental data of Ref. 58 are in a relatively good agreement. This result encourages the realization of detailed measurements for this specific purpose, together with an accompanying detailed calculation. Optical measurements, like those proposed here, have a large advantage over all other types of measurements because of their high-resolution power and the existing very advanced instrumentation.

In Sec. IV C we have considered a homogeneous and flux-free phonon system. As in the case of the carriers, theory (in the context of the NESOM), together with the experiment, allows for the definition and *determination of a (nonequilibrium) quasitemperature per phonon mode*. In this case, Raman scattering provides an appropriate measuring technique, as shown.

As final words we stress the demonstrated fact of the dependence of the nonequilibrium entropy and temperature in IST on the whole set of macrovariables that describe the nonequilibrium macrostate of the system. As already noticed, there is not a wholly satisfactory way to make a selection, which depends on a case by case approach, according to the problem in hand. Consequently, the entropy in IST is different for each chosen set of basic macrovariables. In a single quasiparticle description as the one used in dealing with HEPS—and for that matter with any solid state system—one should in principle incorporate as basic variables the whole (infinite) set of fluxes of all orders. Usually a truncation procedure is required and, evidently, a criterion (involving an expansion parameter) for evaluation of such truncation needs to be produced.[3,72] This implies showing that the information lost when performing the truncation is not relevant when compared with the one that is kept. We call attention to the fact that Meixner[73] and Tisza[1] gave arguments of this kind, in the sense that it is very unlikely that a nonequilibrium state function playing the role of an entropy for quite general nonequilibrium conditions may be uniquely defined.

ACKNOWLEDGMENTS

APPENDIX A: ENERGY-FLUX DEPENDENT DESCRIPTION

Consider on the one hand the description of a gas of fermions in terms of the basic set (E,N) composed of the energy and the particle number, with Lagrange multipliers $(\beta^*, -\beta^*\mu^*)$, and, on the other, the one that includes the flux of energy, namely, in terms of $(E,N,\mathbf{I})$ with Lagrange multipliers $(\beta, -\beta\mu, -\beta\boldsymbol{\alpha})$. As noted in the main text, this implies neglecting thermostriction effects. We take for the energy levels a parabolic dispersion relation. Applying the theory described in Sec. II, we find in the first description that

$$E = \tfrac{3}{2} N k_B T^*, \tag{A1}$$

$$N = (2\pi m k_B T^*/4\pi^2\hbar^2)\exp\{\mu^*/k_B T^*\}, \tag{A2}$$

while in the second description it follows that

$$E = N_0\left[\frac{3}{2} k_B\Theta + \frac{945}{32}\frac{k_B\Theta}{m}\alpha^2\right], \tag{A3}$$

$$N = N_0\left(1 + \frac{35}{16}\frac{k_B\Theta}{m}\alpha^2\right), \tag{A4}$$

$$\mathbf{I} = \frac{35}{8}\frac{k_B^2\Theta}{m}\boldsymbol{\alpha}N_0, \tag{A5}$$

where

$$N_0 = (2\pi m k_B\Theta/4\pi^2\hbar^2)\exp\{\mu/k_B\Theta\}, \tag{A6}$$

$$\beta^* = 1/k_B T^*, \quad \beta = 1/k_B\Theta, \tag{A7}$$

N is given by unit volume, and we have kept corrections up to second order in α.

Equating Eqs. (A1) with (A3) and (A2) with (A4), and making use of Eq. (A5), after some algebra we obtain

$$\Theta = T^* - \frac{2}{5}\frac{m}{k_B^3 T^{*2}}\left|\frac{\mathbf{I}}{N}\right|^2. \tag{A8}$$

Equation (A8) recovers the results that are derived in the context of phenomenological extended irreversible thermodynamics (fourth citation in Ref. 20).

APPENDIX B: COMPLEMENT TO EQS. (27)

The several coefficients present in Eqs. (27) are

$$\widetilde{E}_c(t) = \sum_{\mathbf{k}a}\epsilon_{\mathbf{k}a}\widetilde{f}_{\mathbf{k}a}(t) \equiv \sum_a \widetilde{E}_a(t) \tag{B1}$$

$$\widetilde{N}_a(t) = \sum_{\mathbf{k}}\widetilde{f}_{\mathbf{k}a}(t), \tag{B2}$$

$$A_a(t) = \beta_c(t)\sum_{\mathbf{k}}\epsilon_{\mathbf{k}a}^2 F_a(\mathbf{k}+m_a\mathbf{v}_a(t);t), \tag{B3}$$

$$A_a'(t) = \beta_c^2(t)\sum_{\mathbf{k}}\epsilon_{\mathbf{k}a}^3(\hbar k_\alpha/m_a)^2\phi_a(\mathbf{k};t), \tag{B4}$$

$$B_a(t) = \beta_c(t) \sum_{\mathbf{k}} \epsilon_{\mathbf{k}a} F_a(\mathbf{k} + m_a \mathbf{v}_a(t); t), \tag{B5}$$

$$B'_a(t) = \beta_c^2(t) \sum_{\mathbf{k}} \epsilon_{\mathbf{k}a}^2 (\hbar k_\alpha)^2 \phi_a(\mathbf{k}; t) / m_a^2, \tag{B6}$$

$$C_{1a}(t) = m_a \widetilde{N}_a(t), \tag{B7}$$

$$C_{2a}(t) = m_a \beta_c(t) \sum_{\mathbf{k}} \epsilon_{\mathbf{k}a} (\hbar k_\alpha / m_a)^2 F_a(\mathbf{k}; t) \tag{B8}$$

$$C'_{2a}(t) = (\hbar \mathbf{k} / m_a)(\hbar k_\alpha / m_a) \phi_a(\mathbf{k}; t) \tag{B9}$$

$$D_{1a}(t) = E_a(t), \tag{B10}$$

$$D_{2a}(t) = \beta_c(t) \sum_{\mathbf{k}} \epsilon_{\mathbf{k}a}^2 (\hbar k_\alpha / m_a)^2 F_a(\mathbf{k}; t), \tag{B11}$$

$$D'_{2a}(t) = \beta_c^2(t) \sum_{\mathbf{k}} \epsilon_{\mathbf{k}a} (\hbar \mathbf{k} / m_a)(\hbar k_\alpha / m_a)^2 \phi_a(\mathbf{k}, t) \tag{B12}$$

where k_α means, in this isotropic model, the component of $\mathbf{k}$ in the direction of $\boldsymbol{\alpha}$, and

$$F_a(\mathbf{k}; t) = \widetilde{f}_{\mathbf{k}a}(t)[1 - \widetilde{f}_{\mathbf{k}a}(t)], \tag{B13a}$$

$$\phi_a(\mathbf{k}; t) = \tfrac{1}{2} F_a(\mathbf{k}; t)[1 - 2\widetilde{f}_{\mathbf{k}a}(t)] \tag{B13b}$$

and

$$\widetilde{f}_{\mathbf{k}a}(t) = [1 + \exp\{\beta_c(t)[\epsilon_{\mathbf{k}a} - \mu_\alpha(t) - \mathbf{v}_a(t) \cdot \hbar \mathbf{k}]\}]^{-1}. \tag{B14}$$

i.e., $\widetilde{f}$ of Eq. (B14) is reminiscent of a shifted instantaneous Fermi–Dirac-like distribution [note that it is that of Eq. (23a) in the absence of the term associated with the energy flux, viz. the one containing the corresponding Lagrange multiplier $\boldsymbol{\alpha}$]. Finally, the expression in each equation after the last sign is a calculation in a nondegenerate-like regime, that is, $\widetilde{f}$ of Eq. (B14) is replaced in the calculation by the one given by

$$\widetilde{f}_{\mathbf{k}a}(t) = \exp\{-\beta_c(t)[\epsilon_{\mathbf{k}a} - \mu_a(t) - \mathbf{v}_a(t) \cdot \hbar \mathbf{k}]\}. \tag{B15}$$

This Eq. (B15) implies that in Eq. (B14) the exponential is much larger than 1, which is known to be valid in the case of high levels of excitation and not too large concentrations of photoinjected carriers, as is the case in the usual experimental conditions and functioning in semiconductor electronic devices.

In the case of the description given by the distribution of Eq. (30), we obtain

$$E_c(t) = \sum_{\mathbf{k}a} \epsilon_{\mathbf{k}a} f^*_{\mathbf{k}a}(t) = \frac{3}{2} \sum_a N_a k_B T^*(t), \tag{B16}$$

the last identity following in the nondegenerate-like regime when

$$f^*_{\mathbf{k}a}(t) = \exp\{-\beta_c^*(t)[\epsilon_{\mathbf{k}a} - \mu_a^*(t)]\}, \tag{B17}$$

where

$$\beta_c^*(t) = 1/k_B T_c^*(t), \tag{B18}$$

is the reciprocal of the quasitemperature, and μ^* the quasichemical potential in this description.

APPENDIX C: COMPLEMENTS TO EQS. (28)

The kinetic coefficients in Eqs. (28) are

$$L_{1a}(t) = C_{1a}^{-1}(t) + C_{2a}(t) D_{1a}(t) C_{1a}^{-1}(t) \Delta_a^{-1}(t), \tag{C1}$$

$$L_{2a}(t) = C_{2a}(t) \Delta_a^{-1}(t), \tag{C2}$$

$$M_{1a}(t) = D_{1a}(t) \Delta_a^{-1}(t), \tag{C3}$$

$$M_{2a}(t) = C_{1a}(t) \Delta_a^{-1}(t), \tag{C4}$$

$$\Delta_2^{-1}(t) = C_{2a}(t) D_{1a}(t) - C_{1a}(t) D_{2a}(t), \tag{C5}$$

where coefficients C and D are given in Appendix B.

APPENDIX D: COEFFICIENTS *A*, *B*, *C*, AND *D* OF EQS. (27) AND (35) IN THE NONDEGENERATE LIMIT

Using Eqs. (B1) to (B2), together with Eq. (B15), we obtain

$$A_a(t) = k_B \Theta_c \widetilde{N}_a \left(\tfrac{35}{4} + 7 x_a + x_a^3 \right), \tag{D1}$$

$$B_a(t) = \widetilde{N}_a \left(\tfrac{5}{2} + x_a \right), \tag{D2}$$

$$C_{1a}(t) = \widetilde{N}_a m_a, \tag{D3}$$

$$C_{2a}(t) = k_B \Theta_c \widetilde{N}_a \left(\tfrac{5}{2} + 8 x_a + 2 x_a^2 \right), \tag{D4}$$

$$D_{1a}(t) = k_B \Theta_c \widetilde{N}_a \left(\tfrac{5}{4} + x_a \right), \tag{D5}$$

$$D_{2a}(t) = (k_B \Theta_c)^2 (\widetilde{N}_a / m_a) \left(\tfrac{35}{8} + \tfrac{185}{12} x_a + 17 x_a^2 + 2 x_a^3 \right), \tag{D6}$$

where $x_a = (1/2) m_a v_a^2 / k_B \Theta_c$.

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