ELSEVIER

Physica A 300 (2001) 403–416

PHYSICA A

www.elsevier.com/locate/physa

Thermodynamics of nonequilibrium radiation. (II) Irreversible evolution and experimental setup

A.R. Vasconcellos[a], J. Fort[b,*], D. Jou[c,d], R. Luzzi[a]

[a] *Instituto de Física "Gleb Wataghin", Universidade Estadual de Campinas, Unicamp, 13083-970 Campinas, Sao Paulo, Brazil*

[b] *Departament de Física, Escola Politècnica Superior, Universitat de Girona, Avda. Lluis Santalo s/n, 17071 Girona, Catalonia, Spain*

[c] *Departament de Física, Universitat Autònoma de Barcelona, E-08193 Bellaterra, Catalonia, Spain*

[d] *Institut d'Estudis Catalans, Carme 47, 08001 Barcelona, Catalonia, Spain*

Received 22 January 2001

Abstract

Giving continuation to the study of the thermodynamics of nonequilibrium radiation presented in the preceding article [Physica A 300 (2001) 386], we derive the evolution in time of its macroscopic nonequilibrium state. The case of a semiconductor sample and the coupling of radiation and transverse optical phonons is explicitly considered. Excitation of the latter drives the radiation field out of equilibrium. Under constant excitation, a steady state sets in which is analyzed. It is shown that the quasitemperature per mode of the radiation field, which has been defined in the preceding paper, can be determined in optical experiments such as Raman scattering.

Keywords: Nonequilibrium radiation; Informational Statistical Thermodynamics; Radiation Nonequilibrium Temperature

1. Introduction

The thermodynamics of nonequilibrium radiation is further analyzed by extending the general theory presented in the preceding article [1], heretofore referred to as Paper I. Continuing to resort to the MaxEnt-NESOM-based informational statistical thermodynamics [2–5], we derive the equations of evolution of the basic

* Corresponding author. Fax: +34-972-41-80-98.
E-mail address: joaquim.fort@udg.es (J. Fort).

0378-4371/01/$ - see front matter
PII: S0378-4371(01)00347-8

macrovariables, and indirectly of the intensive nonequilibrium thermodynamic variables, which are the Lagrange multipliers in MaxEnt-NESOM [6–8].

In Section 2 we consider from the outset a particular case, namely a semiconductor where we pay attention to the radiation which is in interaction with the transverse optical vibrations (TO phonons). This interaction shall be responsible to drive the radiation field (initially in equilibrium with the TO phonons) out of equilibrium when the TO phonons are excited by an external source. We derive the equations of evolution for the populations of photons and TO phonons in the framework of the nonlinear quantum kinetic theory that is founded on the MaxEnt-NESOM [6–10]. The macroscopic (nonequilibrium thermodynamic) state of both systems can be completely and equivalently characterized by the MaxEnt-NESOM Lagrange multipliers associated with the populations, which can be redefined in terms of nonequilibrium temperatures (quasitemperatures) per mode for photons [1] and phonons [11,12].

The photons of the black-body radiation and the TO phonons, due to the bilinear coupling of their transverse electric fields (radiation field and transverse polarization field, respectively), form particular hybrid excitations called polaritons (see, for example, Ref. [13]), the so-called upper- and lower-branch polaritons. They can be studied via optical experiments, for example the Raman scattering (see, for example, Chapter 1 in Ref. [13]). In Section 3 we propose the experimental determination of the quasitemperature of the nonequilibrium radiation by means of the analysis of the Raman spectrum of scattering by polaritons.

2. System and its equations of evolution

Let us consider an inverted-band polar semiconductor (e.g. GaAs, CdS, III-nitrides, etc.), under the action of infrared-laser radiation which drives the TO phonons away from equilibrium, and also in contact with a thermal reservoir at temperature T_0. We take the system Hamiltonian

$$\hat{H} = \hat{H}_0 + \hat{H}' \,, \tag{1}$$

where

$$\hat{H}_0 = \hat{H}_{ph} + \hat{H}_{TO} + \hat{H}_S \,, \tag{2}$$

$$\hat{H}' = \hat{H}'_{ph-TO} + \hat{H}'_{ph-S} + \hat{H}'_{TO-S} + \hat{H}'_{TOf} + \hat{H}'_{res} \,, \tag{3}$$

with

$$\hat{H}_{ph} = \sum_{\vec{k}} \hbar\Omega_{\vec{k}} \left(a^{\dagger}_{\vec{k}} a_{\vec{k}} + \frac{1}{2} \right) \,, \tag{4}$$

$$\hat{H}_{TO} = \sum_{\vec{q}} \hbar\omega_{\vec{q}} \left(b^{\dagger}_{\vec{q}} b_{\vec{q}} + \frac{1}{2} \right) \tag{5}$$

for the Hamiltonians of the free subsystems of photons and TO phonons, and $\hat{H}_S$ is the Hamiltonian of the other subsystems in the sample (electrons in Bloch bands, lattice

vibrations other than the TO ones, etc.) whose detail is not needed here. The wavevector $\vec{q}$ runs over the Brillouin zone, $\Omega_{\vec{k}}$ and $\omega_{\vec{q}}$ are the photons and TO phonons energy dispersion relations, and $a_{\vec{k}}\left(a^{\dagger}_{\vec{k}}\right)$, $b_{\vec{q}}\left(b^{\dagger}_{\vec{q}}\right)$, the corresponding annihilation (creation) operators. H' contains all of the interactions, where that between TO phonons and the radiation field is given by

$$\hat{H}'_{ph-TO} = \sum_{\vec{q}} W_{\vec{q}}\left(a_{\vec{q}} - a^{\dagger}_{-\vec{q}}\right)\left(b_{\vec{q}} - b^{\dagger}_{-\vec{q}}\right) + \sum_{\vec{k}\,\vec{q}} V_{\vec{k}\,\vec{q}}\left(a_{\vec{k}} - a^{\dagger}_{-\vec{k}}\right)\left(b_{\vec{q}} - b^{\dagger}_{-\vec{q}}\right)\left(b_{-\vec{k}-\vec{q}} - b^{\dagger}_{\vec{k}+\vec{q}}\right), \tag{6}$$

where $W_{\vec{q}}$ and $V_{\vec{k}\,\vec{q}}$ are the matrix elements; this radiation–TO phonons interaction is composed of two terms: the first one is the interaction of the radiation electric field with the dipolar polarization of TO phonons, and the second one is that with the quadrupolar polarization. We recall that the $\vec{q}$-wavevector amplitude of the electric field of the radiation is (for example Ref. [14])

$$\varepsilon\left(\vec{q}\right) = \mathrm{i}\sqrt{2\pi\hbar\Omega_{\vec{q}}}\left(a_{\vec{q}} - a^{\dagger}_{-\vec{q}}\right) \tag{7}$$

and the $\vec{q}$-mode TO-polarization is

$$P_{TO}\left(\vec{q}\right) = -\,\mathrm{i}\,e^{*}\sqrt{\frac{\hbar}{2\Omega_{\vec{q}}}}\left(b_{\vec{q}} - b^{\dagger}_{-\vec{q}}\right), \tag{8}$$

where e^{*} is the Szigetti effective charge [15]. The other contributions in Eq. (3) are, respectively, the interaction of the radiation with the degrees of freedom of the system other than the TO phonons, the interaction of the TO phonons with the exciting source, and finally the interactions with the thermal reservoir (the latter is responsible to drive the system to final equilibrium at temperature T_0 after switching off the pumping source). We do not need these terms here in explicit form.

We take as the MaxEnt-NESOM basic sets of variables for the two subsystems of interest

$$\left\{\hat{N}_{\vec{k}}, \hat{v}_{\vec{q}}\right\}, \quad \left\{F_{\vec{k}}(t), \varphi_{\vec{q}}(t)\right\}, \quad \left\{N_{\vec{k}}(t), v_{\vec{q}}(t)\right\}, \tag{9}$$

which are the operators for the number of photons in state $\vec{k}$ and of TO phonons in state (mode) $\vec{q}$, the corresponding Lagrange multipliers, and finally the macrovariables (defining the nonequilibrium thermodynamic space of states) consisting of the distribution functions of photons and TO phonons.

Furthermore, we recall that the Lagrange multipliers (i.e., the intensive nonequilibrium thermodynamic variables in IST) can be redefined in terms of quasitemperatures per mode for photons [1] and for TO phonons [11,12] by introducing

$$F_{\vec{k}}(t) = \frac{\hbar\Omega_{\vec{k}}}{k_B T^{*}_{\vec{k}}(t)}, \quad \varphi_{\vec{q}}(t) = \frac{\hbar\omega_{\vec{q}}}{k_B T^{*}_{\vec{q}\,TO}(t)}. \tag{10}$$

The MaxEnt-NESOM nonequilibrium statistical operator is the one of Eq. (2) in paper I but where now the informational-statistical entropy operator is

$$\hat{S}(t,0) = \phi(t) + \sum_{\vec{k}} F_{\vec{k}}(t)\hat{N}_{\vec{k}} + \sum_{\vec{q}} \varphi_{\vec{q}}(t)\hat{v}_{\vec{q}} + \hat{\zeta}(t,0)\,, \tag{11}$$

where, we recall, $\hat{\zeta}$ contains the contributions from all of the subsystems other than the radiation and TO phonons (for our purposes, we can consider them as characterized by a distribution in equilibrium with the thermal reservoir at temperature T_0).

After a straightforward calculation, one finds that

$$N_{\vec{k}}(t) = Tr\left\{\hat{N}_{\vec{k}}\rho_\varepsilon(t)\right\} = Tr\left\{\hat{N}_{\vec{k}}\bar{\rho}(t,0)\right\} = \left[\exp\{F_{\vec{k}}(t)\} - 1\right]^{-1}\,, \tag{12}$$

$$v_{\vec{q}}(t) = Tr\left\{\hat{v}_{\vec{q}}\rho_\varepsilon(t)\right\} = Tr\left\{\hat{v}_{\vec{q}}\bar{\rho}(t,0)\right\} = \left[\exp\left\{\varphi_{\vec{q}}(t)\right\} - 1\right]^{-1}\,, \tag{13}$$

recalling that the average value with the statistical operator and the one calculated with the auxiliary one $\bar{\rho}$ of Eq. (6) in paper I coincide only for the basic variables, as are the two above. With the interpretation given by Eq. (10), the populations of Eqs. (12) and (13) take the form of Planck-like distributions with an effective temperature (quasitemperature) for each mode.

2.1. The equations of evolution

The equations of evolution are

$$\frac{\mathrm{d}}{\mathrm{d}t}Q(t) = Tr\left\{\frac{1}{\mathrm{i}\hbar}[\hat{P},\hat{H}]\rho_\varepsilon(t)\right\} = J^{(0)}(t) + J^{(1)}(t) + \Im(t)\,, \tag{14}$$

where Q and $\hat{P}$ stand for the populations of Eqs. (12) and (13), and the operators $\hat{N}_{\vec{k}}$ and $\hat{v}_{\vec{q}}$, respectively. Eq. (14) is the Heisenberg equation of motion for $\hat{P}$ averaged over the nonequilibrium ensemble which, as indicated, can be rewritten in terms of

$$J^{(0)}(t) = Tr\left\{\frac{1}{\mathrm{i}\hbar}[\hat{P},\hat{H}_0]\bar{\rho}(t,0)\right\}\,, \tag{15}$$

$$J^{(1)}(t) = Tr\left\{\frac{1}{\mathrm{i}\hbar}[\hat{P},\hat{H}']\bar{\rho}(t,0)\right\}\,, \tag{16}$$

$$\Im(t) = Tr\left\{\frac{1}{\mathrm{i}\hbar}[\hat{P},\hat{H}']\rho'_\varepsilon(t)\right\}\,, \tag{17}$$

where $\hat{H}_0$ and $\hat{H}'$ are those of Eqs. (2) and (3), and the expression $\rho_\varepsilon(t) = \bar{\rho}(t,0) + \rho'_\varepsilon(t)$ has been used, separating out the relaxation-free ("instantaneously frozen") part $\bar{\rho}$ and the one accounting for the dissipative and pumping processes and irreversible evolution of the system, i.e., ρ'_ε [6–10].

In the present case $J^{(0)}$ and $J^{(1)}$ are null, and the collision operator, which admits an expansion in an infinite series of partial collision operators in the MaxEnt-NESOM-based

kinetic theory [9], is taken in the so-called second-order approximation in relaxation theory (which is the Markovian form of the equations of evolution, valid in the weak coupling situation we are considering [16]). Hence,

$$\Im(t) \simeq J^{(2)}(t) = \left(\frac{1}{\mathrm{i}\hbar}\right)^2 \int_{-\infty}^{t} \mathrm{d}t' \mathrm{e}^{\varepsilon(t'-t)} G(t',t)\,, \tag{18}$$

where

$$G(t',t) = Tr\{[H'(t'-t)_0,\ [\hat{H}', \hat{P}]]\ \tilde{\rho}(t,0)\}\,, \tag{19}$$

a double commutation operation, with subindex nought indicating evolution in interaction representation (i.e., under the action of $\hat{H}_0$ alone).

Performing the calculations we obtain that

$$\frac{\mathrm{d}}{\mathrm{d}t} N_{\vec{k}}(t) = \sum_{\vec{q}} J_{\vec{k}\,\vec{q}}(t) - \frac{1}{\tau_{r\,\vec{k}}} \left[N_{\vec{k}}(t) - N^{eq}_{\vec{k}}\right]\,, \tag{20}$$

$$\frac{\mathrm{d}}{\mathrm{d}t} v_{\vec{q}}(t) = I_{\vec{q}} - \sum_{\vec{k}} J_{\vec{k}\,\vec{q}}(t) - \frac{1}{\tau_{TO\,\vec{q}}} \left[v_{\vec{q}}(t) - v^{eq}_{\vec{q}}\right]\,, \tag{21}$$

where

$$\begin{aligned} J_{\vec{k}\,\vec{q}}(t) = & -\frac{2\pi}{\hbar^2} |W_{\vec{k}}|^2 \left[N_{\vec{k}}(t) - v_{\vec{q}}(t)\right]\ \delta\left(\Omega_{\vec{k}} - \omega_{\vec{q}}\right)\ \delta_{\vec{k}\,\vec{q}} \\ & - \frac{2\pi}{\hbar^2} \left|V_{\vec{k}\,\vec{q}}\right|^2\ \delta\left(\Omega_{\vec{k}} - \omega_{\vec{q}} - \omega_{\vec{k}-\vec{q}}\right) \\ & \times \left\{N_{\vec{k}}(t)\left[1 + v_{\vec{q}}\right]\left[1 + v_{\vec{k}-\vec{q}}\right] - \left[1 + N_{\vec{k}}(t)\right] v_{\vec{q}}(t) v_{\vec{k}-\vec{q}}(t)\right\} \\ & - \frac{2\pi}{\hbar^2} \left|V_{\vec{k}\,\vec{q}}\right|^2\ \delta\left(\Omega_{\vec{k}} + \omega_{\vec{q}} - \omega_{\vec{k}+\vec{q}}\right) \\ & \times \left\{N_{\vec{k}}(t) v_{\vec{q}}(t)\left[1 + v_{\vec{k}+\vec{q}}(t)\right] - \left[1 + N_{\vec{k}}(t)\right]\left[1 + v_{\vec{q}}(t)\right] v_{\vec{k}+\vec{q}}(t)\right\}\,. \end{aligned} \tag{22}$$

In Eqs. (20) and (21) the last term on the right-hand side has been written in a phenomenological way, by introducing the relaxation times $\tau_{r\,\vec{k}}$ and $\tau_{TO\,\vec{q}}$, to account for the relaxation to equilibrium as a result of the interactions with the other subsystems of the sample via the processes corresponding to the terms in Eq. (3) which is different from $\hat{H}'_{ph-TO}$ of Eq. (6), the latter being responsible for the term containing $J_{\vec{k}\,\vec{q}}$ in Eq. (22). The superscript *eq* indicates the distribution in equilibrium at temperature T_0, and $I_{\vec{q}}$ the rate of production of TO phonons in mode $\vec{q}$ generated by the action of the external exciting source.

Finally, we notice that the scattering operator in the Markovian limit in Eqs. (20), (21) can be recognized—in this particular case—as the result of applying the golden rule of quantum mechanics averaged over the MaxEnt-NESOM nonequilibrium ensemble.

The intensive nonequilibrium thermodynamic variables (the MaxEnt-NESOM Lagrange multipliers) satisfy equations of evolution which are derived from those in Eqs. (20), (21), once we take into account Eqs. (12) and (13), whose left-hand sides become

$$\frac{\mathrm{d}}{\mathrm{d}t}N_{\vec{k}}(t) = -N_{\vec{k}}(t)[1+N_{\vec{k}}(t)]\frac{\mathrm{d}}{\mathrm{d}t}F_{\vec{k}}(t)\,, \tag{23}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}v_{\vec{q}}(t) = -v_{\vec{q}}(t)\left[1+v_{\vec{q}}(t)\right]\frac{\mathrm{d}}{\mathrm{d}t}\varphi_{\vec{q}}(t) \tag{24}$$

and here and on the right-hand side we use Eqs. (12) and (13) for expressing the populations in terms of the Lagrange multipliers alone.

2.2. The polariton states

Due to the bilinear term in Eq. (6), accounting for the coupling of the radiation field with the dipolar field of the TO phonons, photons and TO phonons form hybrid excitations known as polaritons [13]. The diagonalization of this part of the Hamiltonian, together with H_{ph} and H_{TO} follows from the rotation-like transformation to new operators of upper- and lower-branch polaritons, namely

$$\alpha_{\vec{q}+} = \cos\theta_{\vec{q}}a_{\vec{q}} + \sin\theta_{\vec{q}}b_{\vec{q}}\,, \tag{25}$$

$$\alpha_{\vec{q}-} = -\sin\theta_{\vec{q}}a_{\vec{q}} + \cos\theta_{\vec{q}}b_{\vec{q}}\,, \tag{26}$$

with angle $\theta_{\vec{q}}$ given by

$$\theta_{\vec{q}} = \frac{1}{2}\tan^{-1}\frac{|W_{\vec{q}}|}{|\hbar\Omega_{\vec{q}} - \hbar\omega_{\vec{q}}|}\,, \tag{27}$$

where, we recall, $\vec{q}$ runs over the Brillouin zone. Their eigenfrequencies are given by

$$\omega^2_{\vec{q}\pm} = \frac{1}{2}\left(\Omega^2_{\vec{q}} + \omega^2_{\vec{q}}\right) \pm \sqrt{\frac{1}{4}\left(\Omega^2_{\vec{q}} + \omega^2_{\vec{q}}\right)^2 - \frac{1}{\hbar^2}|W_{\vec{q}}|^2}\,. \tag{28}$$

At the crossover point $\vec{q}_{co}$ (degeneracy) where $\Omega_{\vec{q}} = \omega_{\vec{q}}$, the angle $\theta_{\vec{q}}$ is $\pi/4$ and the hybrid excitation is 50% radiation vibration and 50% mechanical (and also dipolar) vibration. For decreasing values of q below the crossover q_{co}, the lower-branch polariton is predominantly purely radiation in character, while for increasing values of q above the crossover q_{co}, it becomes predominantly a TO vibration. Fig. 1 illustrates the frequency dispersion relation of Eq. (28) for the case of GaP.

We also notice that the populations are related by the expressions:

$$\eta_{\vec{q}-}(t) = \cos^2\theta_{\vec{q}}N_{\vec{q}}(t) + \sin^2\theta_{\vec{q}}v_{\vec{q}}(t)\,, \tag{29}$$

$$\eta_{\vec{q}+}(t) = \sin^2\theta_{\vec{q}}N_{\vec{q}}(t) + \cos^2\theta_{\vec{q}}v_{\vec{q}}(t)\,, \tag{30}$$

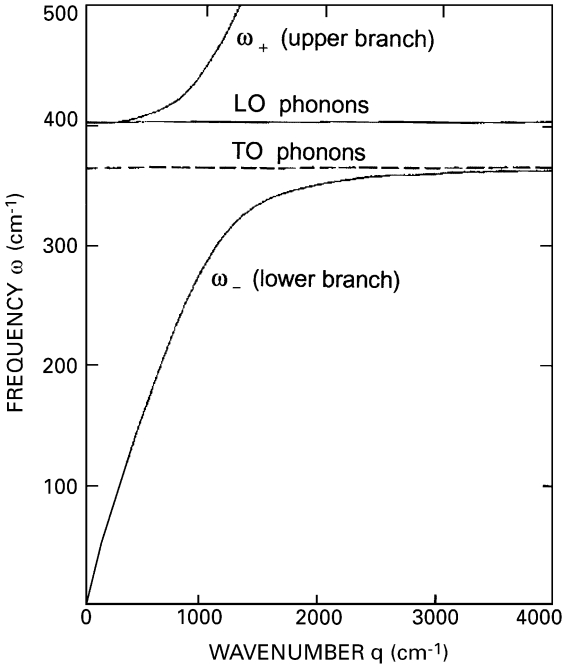

Fig. 1. Upper (ω_+) and lower (ω_-) branches of the polariton frequency dispersion relation in GaP. The horizontal lines correspond to near dispersionless LO phonons (full horizontal line) and to the nonhybridized relation for the TO phonons (dashed line) [adapted from Ref. [13]].

where, as noticed, $\theta_{\vec{q}} \to 0$ for $\vec{q} \to 0$ ($q \ll q_{co}$) and $\theta_{\vec{q}} \to \pi/2$ for high values of q ($q \gg q_{co}$),

$$\eta_{\vec{q}\mp}(t) = Tr\left\{\alpha^{\dagger}_{\vec{q}\mp}\alpha_{\vec{q}\mp}\bar{\rho}(t,0)\right\} \tag{31}$$

and, evidently, their equations of evolution are the corresponding linear combinations of those of the photon populations, Eq. (20), and TO-phonon populations, Eq. (21), but after neglecting the first term on the right-hand side of Eq. (22), i.e., the one responsible for the formation of the polariton.

From the above analysis we can see that in an experiment testing the region of low values of q ($q < q_{co}$) the lower-branch polariton would be mainly described by the radiation field, while the upper-band polariton would be almost a purely lattice vibration. For higher values of q ($q > q_{co}$) these features become inverted.

2.3. The steady state

Under conditions of continuous constant excitation, after a rapid transient has elapsed, a steady state sets in, then $dN_{\vec{k}}(t)/dt = 0$ and $dv_{\vec{q}}(t)/dt = 0$ in Eqs. (20) and (21), and we proceed to its analysis. For that purpose, and in order to simplify matters, we are going to restrict the conditions imposed on the system by assuming the same

intensity of the pumping source acting on each TO-phonon mode, i.e., $I_{\vec{q}} = I$ for all $\vec{q}$ in Eq. (20). On the basis of this, and also of the energy redistribution among the modes due to the interaction with the other subsystems in the sample, we can safely assume that the TO phonons have achieved internal thermal equilibrium (however, in nonequilibrium conditions), i.e., that the quasitemperature is the same for all modes, $T^*_{\vec{q}} = T^*_{TO}$ in this steady state, and then

$$v^{ss}_{\vec{q}} = (\exp[\hbar\omega_{\vec{q}}/k_B T^*_{TO}] - 1)^{-1} . \tag{32}$$

With this result in mind, we can rearrange Eqs. (20), (21) to obtain—after we take as zero the time derivatives and perform some algebra—compact and interesting expressions of the form

$$\frac{\bar{N}^{TO}_{\vec{k}} - N^{ss}_{\vec{k}}}{\tau_{\vec{k}}} - \frac{N^{ss}_{\vec{k}} - N^{eq}_{\vec{k}}}{\tau_{r\vec{k}}} = 0 , \tag{33}$$

$$I - \frac{\bar{N}^{TO}_{\vec{q}} - N^{ss}_{\vec{q}}}{\tau_{\vec{q}}} - \frac{v^{ss}_{\vec{q}} - v^{eq}_{\vec{q}}}{\tau_{TO\vec{q}}} = 0 , \tag{34}$$

where

$$\frac{1}{\tau_{\vec{k}}} = \frac{2\pi}{\hbar^2}\frac{1}{\bar{N}^{TO}_{\vec{k}}}\sum_{\vec{q}} \left|V_{\vec{k}\vec{q}}\right|^2 v^{ss}_{\vec{q}} v^{ss}_{\vec{k}+\vec{q}} \tag{35}$$

$$\times\left[\delta\left(\Omega_{\vec{k}} + \vec{\omega}_{\vec{q}} - \omega_{\vec{k}+\vec{q}}\right)\exp\left\{\beta_{TO}\hbar\omega_{\vec{q}}\right\} + \delta\left(\Omega_{\vec{k}} - \vec{\omega}_{\vec{q}} - \omega_{\vec{k}+\vec{q}}\right)\right], \tag{36}$$

the same for $\tau_{\vec{q}}$ through the exchange $\vec{k} \leftrightarrow \vec{q}$, and we have defined

$$\bar{N}^{TO}_{\vec{k}} \equiv \left(\exp\left[\beta^{ss}_{TO}\hbar\Omega_{\vec{k}}\right] - 1\right)^{-1} , \tag{37}$$

that is, what would be the population of the photons at the quasitemperature of the TO phonons, since $\beta^{ss}_{TO} = 1/k_B T^*_{TO}$ (case of mutual thermalization).

From Eq. (33) we obtain that

$$N^{ss}_{\vec{k}} = \frac{\overline{\tau_{\vec{k}}}}{\tau_{\vec{k}}}\bar{N}_{\vec{k}} + \frac{\overline{\tau_{\vec{k}}}}{\tau_{r\vec{k}}}N^{eq}_{\vec{k}} , \tag{38}$$

where

$$\frac{1}{\overline{\tau_{\vec{k}}}} = \frac{1}{\tau_{\vec{k}}} + \frac{1}{\tau_{r\vec{k}}} \tag{39}$$

and from Eq. (34) and using Eq. (37) it follows that

$$v^{ss}_{\vec{q}} = I\tau_{TO\vec{q}} + v^{eq}_{\vec{q}} + \frac{\tau_{TO\vec{q}}}{\tau_{\vec{q}}}\left[\left(\frac{\overline{\tau_{\vec{q}}}}{\tau_{\vec{q}}} - 1\right)\bar{N}^{TO}_{\vec{q}} + \frac{\overline{\tau_{\vec{q}}}}{\tau_{r\vec{k}}}N^{eq}_{\vec{k}}\right] \simeq I\tau_{TO\vec{q}} , \tag{40}$$

the approximate value being valid for sufficiently high values of I, noticing that for typical semiconductors at room temperature $v_{\vec{q}}^{eq} < 1$, and under the assumption that $\tau_{r\vec{k}} \gg \tau_{\vec{q}}$ $\left(\text{then } \overline{\tau_{\vec{q}}} \simeq \tau_{\vec{q}}\right)$, what is consistent with I $\left(\text{and then } v_{\vec{q}}^{ss}\right)$ being large.

We notice now that to take the same quasitemperature for all the modes is equivalent to use from the outset a contracted description that takes as macrovariable for the TO phonons their energy, i.e.,

$$E_{TO}(t) = \sum_{\vec{q}} \hbar\omega_{\vec{q}} v_{\vec{q}}(t) \,, \tag{41}$$

with an associated Lagrange multiplier $\beta(t) = 1/k_B T_{TO}^*(t)$ (this is a manifestation of the contraction of description in Bogoliubov's sense [17,18]). Hence, multiplying Eq. (39) by $\hbar\omega_{\vec{q}}$ and summing over $\vec{q}$, the equation for the energy in the steady state is

$$E_{TO}^{ss} \simeq I \sum_{\vec{q}} \hbar\omega_{\vec{q}} \tau_{TO\,\vec{q}} \equiv E_0 \,. \tag{42}$$

An Einstein model of dispersionless phonons, i.e., $\omega_{\vec{q}} = \omega_0$ independent of $\vec{q}$, is a good one for optical phonons, mainly in the case of small values of q to be analyzed in the following section. Then,

$$E_{TO}^{ss} = N\hbar\omega_0 v_0^{ss} \simeq E_0 \,, \tag{43}$$

where

$$v_0^{ss} = (\exp[\hbar\omega_0/k_B T_{TO}^*] - 1)^{-1} \tag{44}$$

and N is the number of modes. From Eqs. (41)–(43) we obtain, if $\hbar\omega_0/\bar{E}_0 \ll 1$, that

$$\frac{1}{k_B T_{TO}^*} \simeq \frac{1}{\hbar\omega_0} \ln\left[\frac{\hbar\omega_0}{\bar{E}_0} + 1\right] \simeq \frac{1}{\bar{E}_0} \,, \tag{45}$$

where $\bar{E}_0 = E_0/N$ is the energy pumped by the external source per mode. Moreover, using Eq. (40) for the dispersionless phonons,

$$\bar{E}_0 = \frac{E_0}{N} = I\hbar\omega_0\tau_{TO} \,, \tag{46}$$

with

$$\tau_{TO} = \frac{1}{N} \sum_{\vec{q}} \tau_{TO\,\vec{q}} \,. \tag{47}$$

Finally, we have a value for the TO phonons quasitemperature, namely

$$T_{TO}^* = I\tau_{TO}\theta_E \,, \tag{48}$$

where θ_E is the Einstein temperature, defined by $k_B\theta_E = \hbar\omega_0$, which in typical semiconductors is of the order of 400–500 K, and the relaxation time τ_{TO} is in the tenfold picosecond scale. Therefore, we can estimate that for the TO-phonon quasitemperature to be, say, twice the Einstein temperature (order of 1000 K), an effectively absorbed

power of roughly 1.5×10^{-9} W per mode would be necessary. Let us consider the case of GaAs and the set of modes of low wavevectors (say $q < 10^5$ cm^{-1}), those involved in the Raman scattering of light to be considered later on: since the number of these modes is roughly 3×10^3 per cm^3, then the total effective power would need to be of the order of 50 kW per cm^3 of the sample.

One way to transfer energy to the TO phonons is by illumination with infrared light; another way, of an indirect type, is the excitation of the electron system (creation of the so-called "hot carriers") through the action of strong laser pulses or intense electric fields. The highly excited electrons relax the energy received from the pumping source to the, mainly, optical phonons heating them up.

Finally, under the condition that $\tau_{r\vec{k}} \gg \tau_{\vec{k}}$ $\left(\text{and then } \overline{\tau_{\vec{k}}} \simeq \tau_{\vec{k}}\right)$, Eq. (37) tells us that

$$N^{ss}_{\vec{k}} \simeq \bar{N}_{\vec{k}} = \left(\exp\left[\hbar\Omega_{\vec{k}}/k_B T^*_{TO}\right] - 1\right)^{-1} , \tag{49}$$

implying a mutual thermalization; however, in nonequilibrium conditions, of the radiation field in the steady state with the TO-phonon system, their macroscopic state being characterized by a common quasitemperature T^*_{TO}. Hence, the nonequilibrium temperature is the same for all modes (equivalent to the case of the truncated description of Section IIIa in paper I). This is a consequence of the restrictions we have imposed on the way to characterize the macroscopic steady state of nonequilibrium radiation in interaction with transverse optical lattice vibrations.

3. Experimental characterization

Raman scattering by the excited steady-state lower-branch polaritons is possible, and the resulting spectrum can be used to "measure" the quasitemperature of these excitations. We recall the results of Section 2.1, according to which at low values of wavenumber ($q < q_{co}$, in a near forward-scattering experiment), the excitation is predominantly of the radiation character and we can determine the quasitemperature of the photons. On the other hand, for higher values of wavenumber ($q > q_{co}$, in a mean forward scattering experiment), the excitation is predominantly of a TO-vibrational character and we can determine the quasitemperature of the TO phonons.

The Raman cross section can be expressed as the frequency and wavenumber-dependent density–density correlation function of the quasiparticles involved in the collision process (in this case the lower-branch polaritons interacting with the laser radiation). Through the fluctuation–dissipation theorem, such a correlation can be related to the dielectric function $\varepsilon(\vec{q}, \omega)$ of the system, namely, the differential cross section is

$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\omega\,\mathrm{d}\Omega} = \frac{C}{1 - \exp[-\beta\hbar\omega]} \operatorname{Im} \varepsilon^{-1}\left(\vec{q}, \omega\right) , \tag{50}$$

where C is a constant, $\hbar\omega = \hbar\omega_L - \hbar\omega_S$ is the energy transfer and $\hbar\vec{q} = \hbar\vec{k}_L - \hbar\vec{k}_S$ the momentum transfer in the scattering event: $\vec{k}_L$, ω_L, $\vec{k}_S$ and ω_S are the wave-vector and frequency of the laser light (incident photons) and of the scattered photons ($\vec{k}_L$ and ω_L are fixed by the lasing machine, ω_S is measured by the detection apparatus, and $\vec{k}_S$ is determined by the experimental geometry which fixes the scattering angle) [19]. Moreover, $\beta^{-1} = k_B T^*_{\vec{q}}$ is the reciprocal of the quasitemperature of the polariton in mode $\vec{q}$.

Two bands are observed in the spectrum, with frequencies $\omega_S = \omega_L + \omega_{\vec{q}\,-}$ and $\omega_S = \omega_L - \omega_{\vec{q}\,-}$ (the so-called anti-Stokes and Stokes bands), corresponding to processes with absorption or emission, respectively, of a lower-branch polariton in the scattering event. Let us call I_{AS} and I_S the band intensities (i.e., their areas in frequency space).

It follows that, since the polaritons are boson-like particles, I_{AS} is proportional to the population of the lower-band polaritons in mode $\vec{q}$, and I_S is proportional to this population plus 1.

Hence,

$$\frac{I_S}{I_{AS}} = \frac{\eta^{ss}_{\vec{q}\,-} + 1}{\eta^{ss}_{\vec{q}\,-}} = 1 + \frac{1}{\eta^{ss}_{\vec{q}\,-}}\,, \tag{51}$$

but, we recall, for $q < q_{co}$ we have $\eta^{ss}_{\vec{q}\,-} \simeq N^{ss}_{\vec{q}}$ and for $q > q_{co}$ it holds that $\eta^{ss}_{\vec{q}\,-} \simeq v^{ss}_{\vec{q}}$. Therefore, for $q \ll q_{co}$

$$N^{ss}_{\vec{q}} \simeq \eta^{ss}_{\vec{q}\,-} = \frac{I_{AS}}{I_S - I_{AS}}\,, \tag{52}$$

but because of Eqs. (12) and (10)

$$T^*_{\vec{q}} = \frac{\hbar\Omega_{\vec{q}}}{k_B}\,\frac{1}{\ln(I_S/I_{AS})}\,, \tag{53}$$

with $\Omega_{\vec{q}} \simeq \omega_{\vec{q}\,-}$, and thus a "measurement" of the quasitemperature of the nonequilibrium radiation can be obtained from the experimental data; we can say that the Raman scattering experiment acts like a "thermometer" (of course, with systems in equilibrium what results is the value of the equilibrium temperature of the system, which is that of the reservoir).

In Fig. 2 it is shown that the frequency dispersion relation for polariton branches (full lines), and the dots indicate the values obtained from the scattering spectrum [19]. This is the case of tetragonal $BaTiO_3$ which possesses three families of optical phonons; thus the presence of the four curves of polariton states, since the radiation couples with the three TO-phonon branches. It can be noticed that the upper-branch polaritons (ω_+) do not contribute to Raman scattering, which is forbidden because the conservation of energy and momentum in the collision event is not possible. This experiment corresponds to the case of nonexcited polaritons, i.e., $I = 0$ in our equations.

In Fig. 3 we can observe Raman spectra at room temperature for different values of the scattering angle θ, corresponding to the experimental geometries which produce

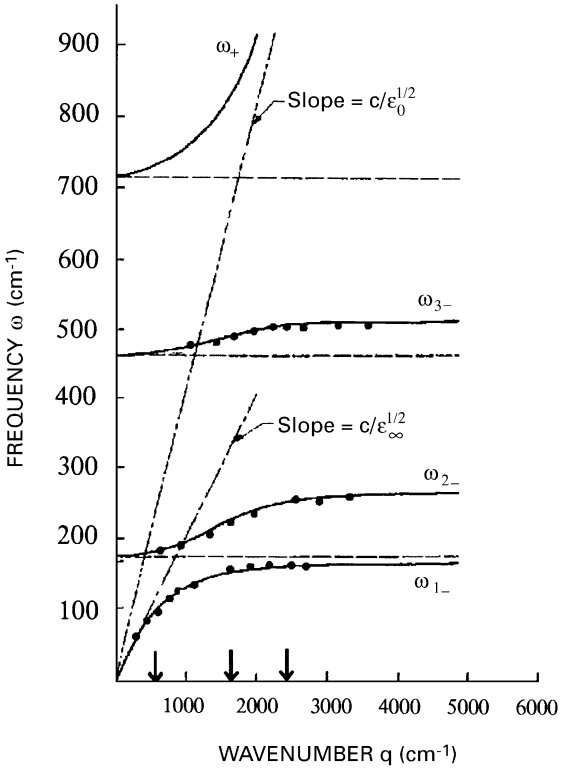

Fig. 2. Polariton frequency dispersion curves in tetragonal $BaTiO_3$, having three optical-phonon branches. Dots are from Raman scattering experiments (adapted from Ref. [19]).

the data at the wavenumbers indicated by arrows in Fig. 2. Here, only the anti-Stokes bands are shown, the Stokes ones are on the negative Raman frequency shift; as we have seen the ratio of intensities of them (the ratio of areas enclosed by the bands or, approximately, the ratio of the peak values when they can be approximated by a Lorentzian) gives information on the populations, and thus on the quasitemperatures of the polariton modes. In the case of the experiment of Ref. [19] this is simply the temperature in equilibrium (since $I = 0$).

4. Concluding remarks

The general theory for the statistical thermodynamics of nonequilibrium radiation in matter, presented in the preceding article, has been complemented with the study of the irreversible evolution in time of the nonequilibrated populations of photons. We have considered the particular case of polar semiconductors and the interaction of the black-body radiation with the transverse optical phonons. This is particularly quite an interesting system since both, photons and TO phonons, form a hybrid excitation

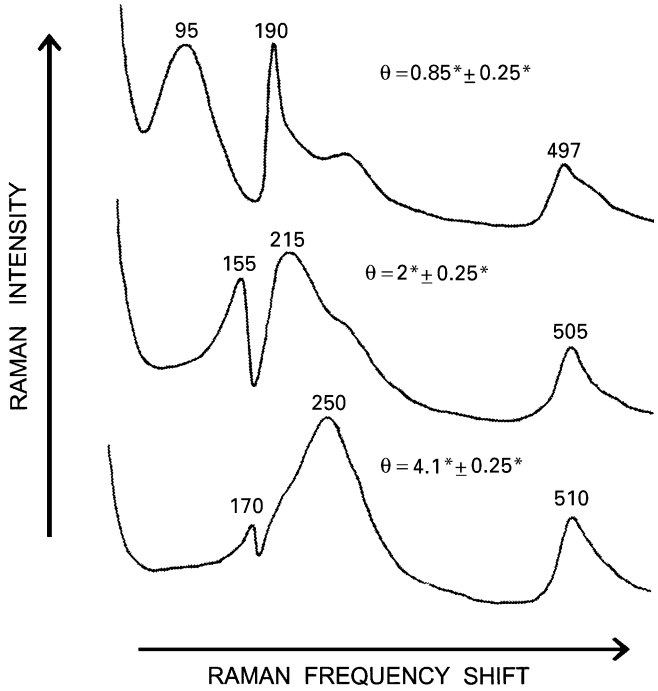

Fig. 3. Raman spectra in near forward scattering by polaritons in $BaTiO_3$ at room temperature. Here θ is the scattering angle, which fixes the wavenumbers (momentum transfer) indicated by the arrows in Fig. 2. The numbers indicated at the top of the bands are the Raman frequency shifts in cm^{-1} at the peak value (adapted from Ref. [19]).

consisting of the so-called polaritonic waves, with polaritons being the corresponding quantized pseudoparticles. Hence, the TO phonons can be excited by the action of an external pumping source, e.g. infrared radiation from a laser machine, and then to have excited (nonequilibrated) polaritons. The low-frequency polaritons are predominantly composed of electromagnetic waves and then we can have experimental information on the nonequilibrated photons.

Quite a convenient type of experiment is inelastic scattering of light, or Raman scattering by polaritons. From the relation between the intensity of Stokes and anti-Stokes bands, it is possible to determine the population of polaritons, which is practically the population of photons in the low-frequency side of the lower polariton branch, as already noticed. From these data it can be calculated [cf. Eq. (53)] the quasi-temperature for the different radiation modes, and in that way to have a "measurement" of such a quantity.

In conclusion, articles I and II attempt to provide an extensive treatment of the nonequilibrium (irreversible) thermodynamics of radiation. This has been done in terms of the seemingly promising statistical approach consisting of the MaxEnt-NESOM-based informational statistical thermodynamics.

Acknowledgements

This work has been partially supported by the State of São Paulo Research Agency (FAPESP) and the Brazilian National Research Council (CNPq) (ARV and RL), by the CICYT of the Spanish Ministry of Science and Technology under Grants nos. BFM2000-0351 (DJ and JF) and REN2000-1621 CLI (JF), and by the Direcció General de Recerca of the Generalitat de Catalunya under Grant 2000 SGR 00095 (DJ).

References

[1] A.R. Vasconcellos, R. Luzzi, J. Fort, D. Jou, Physica A 300 (2001) 386.
[2] R. Luzzi, A.R. Vasconcellos, J.G. Ramos, Fortschr. Phys./Prog. Phys. 47 (1999) 937.
[3] M.A. Tenan, A.R. Vasconcellos, R. Luzzi, Fortschr. Phys./Prog. Phys. 45 (1997) 1.
[4] A.R. Vasconcellos, R. Luzzi, L.S. García-Colín, Phys. Rev. A 43 (1991) 6622, 6633.
[5] R. Luzzi, A.R. Vasconcellos, J.G. Ramos, Statistical Foundations of Irreversible Thermodynamics, Teubner, Leipzig, 2000.
[6] R. Luzzi, A.R. Vasconcellos, Fortschr. Phys./Prog. Phys. 38 (1990) 887.
[7] J.G. Ramos, R. Luzzi, A.R. Vasconcellos, Fortschr. Phys./Prog. Phys. 43 (1995) 265.
[8] R. Luzzi, A.R. Vasconcellos, J.G. Ramos, Foundations of a Nonequilibrium Ensemble Formalism, Kluwer Academic, Dordrecht, in press. (Also URV E-print http://xxx.lanl.gov/abs/cond-mat/9909160.)
[9] L. Lauck, A.R. Vasconcellos, R. Luzzi, Physica A 168 (1990) 789.
[10] D.N. Zubarev, Nonequilibrium Statistical Thermodynamics, Consultants Bureau, New York, 1974.
[11] A.C. Algarte, A.R. Vasconcellos, R. Luzzi, Phys. Rev. B 54 (1996) 11311.
[12] D. Kim, P.Y. Yu, Phys. Rev. Lett. 64 (1990) 946.
[13] R. Loudon, in: G.B. Wright (Ed.), Light Scattering Spectra of Solids I, Springer, New York, 1969.
[14] H. Haken, Synergetics, Springer, Berlin, 1978.
[15] N.W. Ashcroft, N.D. Mermin, Solid State Physics, Holt, Reinhardt, and Winston, New York, 1976.
[16] J.R. Madureira, A.R. Vasconcellos, R. Luzzi, L. Lauck, Phys. Rev. E 57 (1998) 3637.
[17] N.N. Bogoliubov, in: J. de Boer, G.E. Uhlenbeck (Eds.), Studies in Statistical Mechanics, Vol. 1, Gordon and Breach, New York, 1967.
[18] G.E. Uhlenbeck, in: M. Kac (Ed.), Lectures in Statistical Mechanics, American Mathematical Society, Providence, RI, 1963.
[19] E. Burstein, S. Ushioda, A. Pinczuk, J.F. Scott, in: G.B. Wright (Ed.), Light Scattering Spectra of Solids I, Springer, New York, 1969.