Statistics and thermodynamics of luminescent radiation

Wenyue Hsu

Physics Department, Harvard University, Cambridge, Massachusetts 02138

Richard Barakat

Division of Applied Science, Harvard University, Cambridge, Massachusetts 02138

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We have investigated luminescent radiation produced by semiconductor lasers. By using the grand canonical ensemble for the radiation field produced by the recombination of electron-hole pairs, the power spectrum and thermodynamic functions (i.e., total energy, entropy, and radiation pressure) are derived in the context of quantum statistics. The correlation function of the luminescent radiation field is also calculated and compared with blackbody radiation. Numerical calculations are performed to study the effect of the band gap and chemical potential of the luminescent material on the correlation function and various thermodynamic functions; for example, we consider the deviation of the total-energy density from the predictions of the Stefan-Boltzman law. The stimulated emission case is discussed with the introduction of negative temperature. Finally, the probability distribution and fluctuations of the photon numbers in the radiation field are discussed.

I. INTRODUCTION

The radiation from a luminescent material is not governed by thermal equilibrium,[1] and the power spectrum is not that of a blackbody radiation. Radiation fields produced by the recombination of electron-hole pairs arise in semiconductor lasers[2–4] lead to luminescent radiation. Since the radiation and absorption processes are types of chemical reactions, equilibrium implies that the photons of the radiation field are associated with some nonvanishing chemical potential μ. See Refs. 5 and 6 and recent references therein for more phenomenological aspects on luminescent radiation.

The purpose of this paper is to give a quantum-mechanical calculation of power spectral density, temporal covariance, and thermodynamic functions such as the total energy density, entropy, and radiation pressure of the luminescent radiation field. Emphasis is given to the difference between luminescent radiation and blackbody radiation as regards the above quantities. When the stimulated emission regime is reached, the system of electron-hole pairs is similar to the interacting nuclear spin system where population inversion is achieved. Such a system has been studied by Ramsey[7] many years ago by introducing the concept of negative temperatures. We shall show that to describe the stimulated emission in the context of the quantum statistical treatment, it is natural and consistent to introduce a negative temperature for the system of electron-hole pairs and the radiation field. Additionally we consider the fluctuations and Bose-Einstein distribution of the field modes.

II. POWER SPECTRUM AND TEMPORAL COVARIANCE FUNCTIONS

The balance between the luminescent radiation fields and the electron-hole pairs acts as a constraint on the ensembles of the radiation fields. With the electron-hole pair distribution predetermined by the temperature of the material, the radiation fields can be treated as a system of photons with nonvanishing chemical potential μ, which is determined by the density of electron-hole pairs in the material. When the equilibrium between the photons and the electron-hole pairs is reached, their chemical potentials are equal: $\mu = \mu_{cv}$, where the chemical potential of the electron-hole pairs is given by the difference between the chemical potential of the electrons in the conduction band μ_c and that of the electrons in the valence band μ_v, i.e., $\mu_{cv} = \mu_c - \mu_v$. The minimum energy of each photon is given by the band gap E_g. Without worrying about the exact dynamics in the luminescent radiation, we employ the grand canonical ensemble with a consequent parameter μ, the chemical potential, to describe the luminescent fields approximately. The state of the photons can be represented by the density operator ρ, which is given by minimizing the entropy $S = -\text{Tr}[\rho \ln \rho]$, subject to the constraint that the total number of photons is fixed by the number of electron-hole pairs. It can be shown that for a grand canonical ensemble[8]

$$\rho = \frac{\exp(-\beta H)}{\text{Tr}[\exp(-\beta H)]} , \tag{2.1}$$

where

$$\beta \equiv \frac{1}{k_B T} , \tag{2.2}$$

with k_B the Boltzman constant and T the absolute temperature. H is the Hamiltonian,

$$H = \sum_k (h\nu_k - \mu)a_k^+ a_k , \tag{2.3}$$

where h is the Planck's constant, ν_k is the frequency of the kth mode of the electromagnetic field, and a_k and a_k^+

are the corresponding annihilation and creation operators of the mode. Since we are performing quantum-mechanical calculations, the electromagnetic fields must be separated into positive and negative components; thus the frequency v can only take non-negative values. Finally μ is the chemical potential, given by the equilibrium between the electron-hole pairs and the photons of the luminescent radiation field. Note that for the system to have a ground state, the Hamiltonian in Eq. (2.3) must be positive semidefinite, so $h v_k \geq \mu$. In fact, the excitation energy of an electron-hole pair must be greater than the band gap E_g of the material; we have then $h v \geq E_g > \mu$.

With the density operator given in Eq. (2.1), the total energy density u of the radiation field is given by

$$u = \frac{1}{V} \text{Tr} \left[\sum_k h v_k a_k^+ a_k \rho \right] , \tag{2.4}$$

where V is the total volume. From the identity

$$\text{Tr}[\exp(-x a_k^+ a_k)] = [1 - \exp(-x)]^{-1} \quad (x > 0) \tag{2.5}$$

we obtain the density operator for the radiation field in Eq. (2.1) by taking $x = \beta(h v_j - \mu)$,

$$\rho = \prod_k \left[[1 - e^{-\beta(h v_k - \mu)}] \exp[-\beta(h v_k - \mu) a_k^+ a_k) \right] , \tag{2.6}$$

where the explicit form of the Hamiltonian Eq. (2.3) has been used. The total energy density can then be evaluated by using the identity that for $x > 0$,

$$\text{Tr}[a_k^+ a_k \exp(-x a_k^+ a_k)] = \exp(-x)[1 - \exp(-x)]^{-2} , \tag{2.7}$$

thus

$$\text{Tr}[a_j^+ a_j \rho] = \{\exp[\beta(h v_j - \mu)] - 1\}^{-1} ; \tag{2.8}$$

from Eq. (2.4) we have then

$$u = \frac{1}{V} \text{Tr} \left[\sum_k h v_k \{\exp[\beta(h v_k - \mu)] - 1\}^{-1} \right] . \tag{2.9}$$

In Eqs. (2.6) and (2.9) the index k represents the available modes of the field, thus the frequency must be higher than $v_g = E_g / h$, i.e., $v_k \geq v_g$, for only these modes contribute to the luminescent radiation fields.

The chemical potential μ plays an important role here. For $\mu > 0$, which is the usual case, there is no net absorption of the photons, while for $\mu < 0$, the system of photons would tend to go into lower occupation number states to have a lower energy that corresponds to the case when the luminescent material absorbs energy from the radiation field to excite the electron-hole pairs. We will discuss the system for both cases.

Summation over all modes in the cavity (assumed large) leads to

$$u = \int_0^\infty \Phi(v) dv . \tag{2.10}$$

Here $\Phi(v)$ is the power spectral density of the luminescent radiation field,

$$\Phi(v) = \left[\frac{8\pi v^2}{c^3} \right] \{(h v)[e^{\beta(h v - \mu)} - 1]^{-1}\} \quad (v_g \leq v < \infty)$$

$$\Phi(v) = 0 \quad (v < v_g) \tag{2.11}$$

where $v_g = E_g / h$ is the lowest frequency of the radiation field. In deriving Eq. (2.11) we have restricted ourselves to free space and have thus neglected the effect of the index of refraction. The first factor on the right-hand side is the number of cavity resonances per unit volume and frequency, assuming that wavelengths are small compared to the average diameter of the cavity $V^{1/3}$ and bandwidths dv/c are large compared to $(2V^{1/3})^{-1}$. More precisely the expression is valid for

$$\frac{V^{1/3} v}{c} \gg 1 \quad \text{and} \quad \frac{2 V^{1/3} dv}{c} \gg 1 . \tag{2.12}$$

This asymptotic mode counting expression was first derived by Rayleigh and later by Weyl for general cavities.[9] We consider only this situation, as the inclusion of finite volume effects leads to the rise of many additional features. When E_g and μ are zero, Eq. (2.11) reduces to the power spectrum of blackbody radiation:

$$\Phi(v) = \frac{8\pi h v^3}{c^3} [\exp(\beta h v) - 1]^{-1} \quad (0 \leq v < \infty) ,$$

$$\Phi(v) = 0 \quad (v < 0) . \tag{2.13}$$

By the Wiener-Khintchine theorem, the temporal covariance function $C(\Delta t)$ is given by the Fourier transform of the power spectrum

$$C(\Delta t) = \int_0^\infty \Phi(v) e^{-2\pi i v \Delta t} dv . \tag{2.14}$$

More explicitly,

$$C(\Delta t) = \frac{8\pi h}{c^3} \int_{v_g}^\infty v^3 \{\exp[\beta(h v - \mu)] - 1\}^{-1} e^{-2\pi i v \Delta t} dv , \tag{2.15}$$
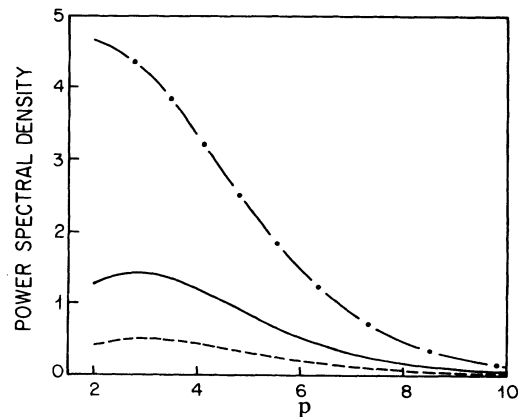

FIG. 1. Power spectral density of luminescent radiation as a function of the normalized frequency photon energy p, in Eq. (2.17), for $p_g = 2$: — — —, $\alpha = -1.0$; ——, $\alpha = 0$; —·—·—·, $\alpha = 1.0$.
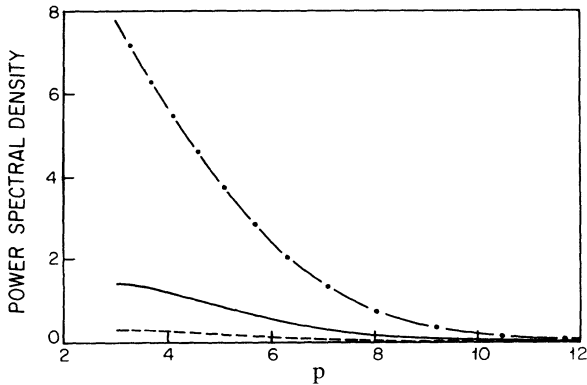
FIG. 2. Power spectral density of luminescent radiation as a function of the normalized photon energy p for $p_g = 3$: – – –, $\alpha = -1.5$; ——, $\alpha = 0$; –·–·–·, $\alpha = 1.5$. See Eq. (2.17).

where $v_g > \mu/h$. In the case of absorption, we have a negative chemical potential $(\mu < 0)$; when absorption is absent, $\mu \geq 0$. Note that by definition the variance of the radiation field $C(0)$ is equal to u, the total-energy density of the radiation field.

At this point it is convenient to employ normalized variables and parameters. Let

$$p = \beta h v, \quad \alpha = \beta \mu, \quad p_g = \beta h v_g, \quad \tau = 2\pi \Delta t / (\beta h) . \quad (2.16)$$

In the normalized version,

$$\Phi(p) = \frac{8\pi}{c^3 h^3 \beta^4} p^3 [\exp(p - \alpha) - 1]^{-1} \quad (p \geq p_g) ,$$

$$\Phi(p) = 0 \quad (p < p_g) , \quad (2.17)$$

$$C(\tau) = \frac{8\pi}{c^2 h^3 \beta^4} \int_{p_g}^{\infty} p^3 [\exp(p - \alpha) - 1]^{-1} e^{-i\tau p} dp , \quad (2.18)$$

with $\alpha < 0$ for absorption and $\alpha > 0$ for no absorption. In Figs. 1 and 2 we plot the spectral density of the luminescent radiation field in the normalized version, with parameters properly chosen to be close to experimental situations.[2] The overall temperature-dependent factor has been neglected in the figures.

III. BEHAVIOR OF TOTAL-ENERGY DENSITY AND THE TEMPORAL COVARIANCE FUNCTION

The temperature dependence of the total-energy density now is not given by the T^4 power law of the blackbody radiation. From Eq. (2.18) we write the total-energy density as

$$u \equiv C(0) = \frac{8\pi}{c^3 h^3 \beta^4} \int_{p_g}^{\infty} p^3 [\exp(p - \alpha) - 1]^{-1} dp , \quad (3.1)$$

and understand that in the case of no absorption $p_g > \alpha > 0$, while $\alpha < 0$ when there is absorption. Equation (3.1) is a generalization of the Stefan-Boltzman law with the effect of the band gap and chemical potential in-

cluded. In the limit of $\alpha = p_g = 0$, the case of blackbody radiation, the above integral is evaluated as $\pi^4/15$ and reduces to the Stefan-Boltzman law for blackbody radiation,[8,10]

$$u = 8\pi^5 / (15 c^3 h^3 \beta^4) . \quad (3.2)$$

The integral in Eq. (3.1) depends on the temperature, because of the explicit temperature dependence of the parameters α and p_g in Eq. (2.16).

In Fig. 3, we show the result from direct numerical calculation of the above integral, as a function of temperature, for a set of parameters chosen to be close to the experimental situation. We plot the ratio of the luminescent energy density and blackbody radiation energy density, as a function of the temperature. As the temperature increases, the ratio approaches unity. The high-temperature behavior can be explained as follows. For very high temperature, the thermal energy dominates; the effect of the band gap and the chemical potential is minimal, and so is the difference between the two kinds of radiation. On the other hand, it is important to take the effect of the band gap and chemical potential into account at the low-temperature limit. The ratio is zero in the zero-temperature limit, and rises according to the power law of $p_g^3 \exp[\alpha - p_g]$ as the temperature increases. In the case for no absorption, i.e., $\alpha > 0$, the ratio goes up quickly, exceeds unity, and then reaches its maximum; when the temperature is increased further, the ratio decreases in magnitude and eventually approaches unity. For the case of absorption, the ratio is never greater than 1 and there is no maximum. In this situation, the luminescent field has a lower energy density than the blackbody radiation field at the same temperature because of the absorption of the radiation by the material.

We have obtained formal solutions of the temporal covariance function, in terms of generalized Langevin functions, but they are extremely unwieldy for numerical evaluation. We chose to do the numerics by direct quadrature.

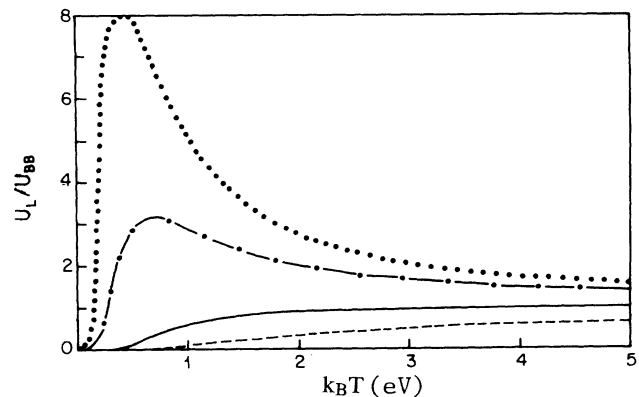We first notice that the temporal covariance function is

FIG. 3. Total-energy density of luminescent radiation, Eq. (3.1), as a function of the thermal energy $k_B T$ (eV), for $E_g = 3$ eV: – – –, $\mu = -2.0$; ——, $\mu = 0$; –·–·–·, $\mu = 1.5$; ····, $\mu = 2.0$ (eV).
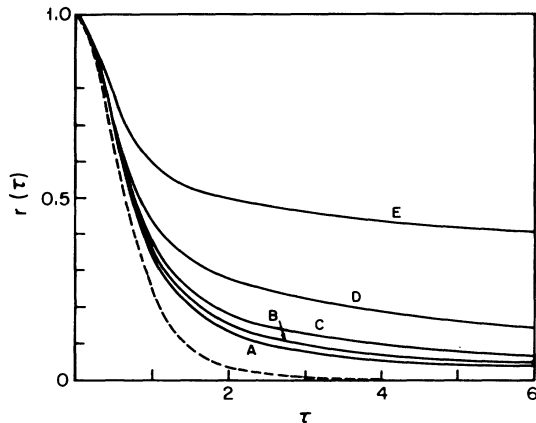
FIG. 4. Temporal correlation function of luminescent radiation, Eq. (2.18), when $p_g = 2$: A, $\alpha = 0$; B, $\alpha = 1.0$; C, $\alpha = 1.5$; D, $\alpha = 1.90$; E, $\alpha = 1.99$. The dashed line represents blackbody radiation.

temperature dependent. This can be seen directly from Eq. (2.18). In addition to the explicit factor of T^4, the integrand and the lower limit of the integral in the expression for $C(\tau)$ are dependent on the temperature, according to the normalized units that we have employed in Eq. (2.16). Only in the limit of $\alpha = p_g = 0$, which corresponds to the case of blackbody radiation, do the temporal covariance functions depend on the normalized time τ only (besides the explicit T^4 factor). We thus have drawn the correlation function (the normalized amplitude of the temporal covariance function) of the blackbody radiation fields as a reference to both Figs. 4 and 5, where we present the result from numerical calculation of the correlation functions for the luminescent radiation fields, in terms of the normalized time. With changing temperature, one only needs to rescale the time axis to find the correlation functions of blackbody radiation at different temperatures. This universal feature of the correlation function for the blackbody radiation does not seem to ap-
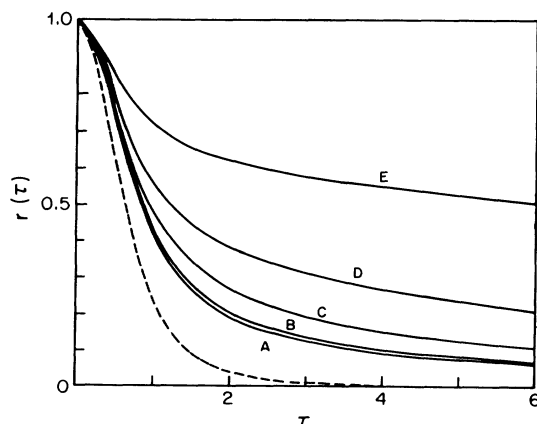

FIG. 5. Temporal correlation function of luminescent radiation, Eq. (2.18), when $p_g = 3$: A, $\alpha = 0$; B, $\alpha = 1.0$; C, $\alpha = 2.5$; D, $\alpha = 2.90$, E, $\alpha = 2.99$. The dashed line represents blackbody radiation.

pear for the luminescent radiation, where the effect of the band gap and the chemical potential must be taken into account. The normalized parameters in Figs. 4 and 5 are so chosen that they are close to the experimental situations. By normalized parameters, we are referring to Eq. (2.16), and thus the band gap, chemical potential, and the time are all measured in proper units relative to the temperature. When the temperature is changed, one must rescale not only the time, but also the band gap and chemical potential in order to find the corresponding correlation function. Here we are particularly interested in knowing how the correlation length of the radiation is affected by the band gap and the chemical potential. Since we are only concerned with the relative amplitude of the temporal covariance function, only the moduli of the correlation functions are calculated. Two sets of parameters are used. The T^4 factor in the covariance functions is immaterial as far as the correlation is concerned; however it plays an important role in the thermodynamic functions, which will be further discussed in Sec. IV.

The moduli of the temporal correlation functions for the case of absorption were also calculated, but they differ little from the case when the chemical potential is zero while the band gap is the same. This is merely due to the fact that the correlation function is normalized so that its value at a vanishing time interval is 1. The exact amplitudes of the covariance functions are dependent on the chemical potential. In fact we can see this directly from the long-time limit of $C(\tau)$.

To find the long-time asymptotic behavior of $C(\tau)$, we employ the following formula of Erdelyi[11] for an N times differentiable function:

$$\int_a^b \Phi(p)e^{-i\tau p}dp \sim \sum_{n=0}^{N-1} i^{n-1}\Phi^{(n)}(b)(-\tau)^{-(n+1)}e^{-i\tau b}$$
$$- \sum_{n=0}^{N-1} i^{n-1}\Phi^{(n)}(a)(-\tau)^{-(n+1)}e^{-i\tau a} .$$

$$(3.3)$$

Calculations yield

$$|C(\tau)| \sim \Phi(p_g)\tau^{-1} + \cdots$$

$$= \left[\frac{8\pi p_g^3}{c^3 h^3 \beta^4} \right][e^{p_g-\alpha}-1]^{-1}\tau^{-1} + \cdots . \quad (3.4)$$

Note that the difference between the case of absorption and no absorption is in the sign of the parameter α. For comparison, the covariance function of blackbody radiation in the long-time limit easily follows from Eq. (3.3) and is

$$|C(\tau)| \sim \Phi^{(2)}(0, \alpha=0)\tau^{-3} = \left[\frac{16\pi}{c^3 h^3 \beta^4} \right]\tau^{-3} . \quad (3.5)$$

The long-time behavior of the temporal covariance is predominantly governed by the excitation of modes with low frequencies. In the case of luminescent radiation, the nonvanishing band gap of the material cuts off the available mode frequencies from below, and leads to the $1/\tau$ long-time behavior Eq. (3.4). In the case of blackbody ra-

diation, the power spectrum Eq. (2.13) and its first derivative vanish as the frequency approaches zero. Since there is no limit on the mode frequencies, the long-time behavior of the temporal covariance function, which is determined by the nonvanishing second derivative of the power spectrum at zero frequency, decreases in magnitude as $1/\tau^3$ for blackbody radiation.

IV. THERMODYNAMIC FUNCTIONS

Just as in the study of blackbody radiation, one can determine the thermodynamic functions for the luminescent radiation field in the context of quantum statistics. We will only calculate the entropy and radiation pressure, although other state functions can be determined in like fashion.

The von Neumann entropy[8] defined by

$$S = -k_B \mathrm{Tr}(\rho \ln \rho) \tag{4.1}$$

can be calculated by using Eq. (2.6) and the identities on trace Eqs. (2.5) and (2.7). We obtain

$$S = k_B \beta \sum_k (h\nu_k - \mu)[\exp(\beta h\nu_k - \beta\mu) - 1]^{-1}$$
$$- k_B \sum_k \ln[1 - \exp(\beta\mu - \beta h\nu_k)] , \tag{4.2}$$

subject to the constraint $\nu_k \geq \nu_g$. In the large volume limit, we can convert the summation over modes k into an integral over frequency; the final result is

$$S = \frac{8\pi k_B V}{c^3 h^3 \beta^3} \int_{p_g}^{\infty} p^2 \{(p-\alpha)[\exp(p-\alpha)-1]^{-1}$$
$$- \ln[1 - \exp(\alpha - p)]\} dp . \tag{4.3}$$

Here V is the total volume, $p_g > \alpha > 0$ when there is no absorption, and $\alpha < 0$ when there is absorption. The blackbody radiation limit is obviously seen when we take the limit of $p_g = \alpha = 0$, and notice that the above integral has a value of $4\pi^4/45$. The temperature dependence of the integral in Eq. (4.3) indicates the difference between the luminescent radiation and the blackbody radiation. The numerical result is shown in Fig. 6 where we plot the ratio of the luminescent radiation entropy over the blackbody radiation entropy. It shows a similar temperature dependence of the ratio for the total energy density in Fig. 3. The high-temperature limit for the ratio approaches unity, since both p_g and α approach zero in this limit, and consequently there is no difference between the luminescent radiation and the blackbody radiation. In the low-temperature limit, from Eq. (4.3) we have

$$S \sim \frac{p_g^2(p_g - \alpha)}{\beta^3} \exp[-(p_g - \alpha)] \quad (T \to 0) . \tag{4.4}$$

Here we have used the fact that when the temperature approaches zero, we can make the approximation for the integrand in Eq. (4.3) that $\exp[p - \alpha] \gg 1 \gg \exp[\alpha - p]$.

The radiation pressure P can be calculated from the relation[8]
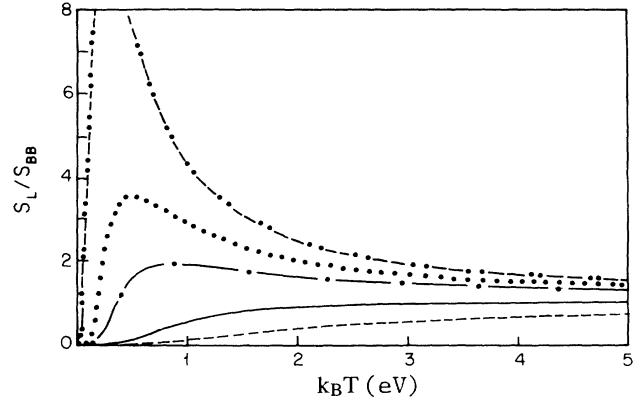
$$PV = TS + \mu N - uV . \tag{4.5}$$

FIG. 6. Entropy of luminescent radiation S as a function of thermal energy $k_B T$ (eV) for $E_g = 3$ eV: — — —, $\mu = -2.0$; ———, $\mu = 0$; —·—·—·, $\mu = 1.5$; ····, $\mu = 2.0$; —···—··, $\mu = 2.5$ (eV). See Eq. (4.3).

The term μN in this relation is due to the fact that we are using the grand canonical ensemble, and the chemical potential of the luminescent radiation field is not equal to zero. We can write the radiation pressure in Eq. (4.5) as

$$P = -\frac{8\pi}{c^3 h^3 \beta^4} \int_{p_g}^{\infty} p^2 \ln[1 - \exp(\alpha - p)] dp . \tag{4.6}$$

One can easily verify that in the limit of $p_g = \alpha = 0$, the above expression becomes the equation of state for blackbody radiation, i.e., $P = u/3$, see Refs. 4 and 6. The deviation from blackbody radiation is due to the additional temperature dependence of the integral in the above equation. In Fig. 7 we show the comparison between the blackbody radiation pressure and the luminescent radiation pressure by plotting the ratio of the luminescent radiation pressure over the blackbody radiation pressure. One can see that the ratio approaches unity in the high-temperature limit, for when the temperature is very high, both p_g and α can be approximated as zero, and Eq. (4.6)
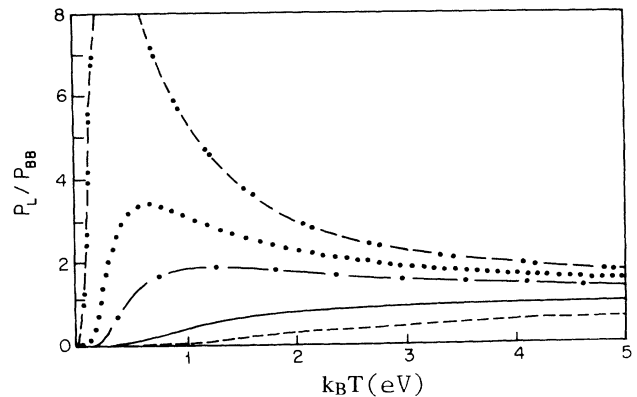

FIG. 7. Luminescent radiation pressure P as a function of thermal energy $k_B T$ (eV) for $E_g = 3$ eV: — — —, $\mu = -2.0$; ———, $\mu = 0$; —·—·—·, $\mu = 1.5$; ····, $\mu = 2.0$; —···—··, $\mu = 2.5$ (eV). See Eq. (4.6).

reduces to the blackbody radiation pressure. In the low-temperature limit, we have according to Eq. (4.6)

$$P \sim \frac{p_g^2}{\beta^4} \exp[-(p_g - \alpha)] \quad (T \to 0) . \tag{4.7}$$

V. STIMULATED EMISSION CALCULATIONS

The above treatment is restricted to the case for spontaneous emission region, i.e., the chemical potential of the electron-hole pairs is less than the band gap of the material, so that the following inequality holds: $h\nu \geq E_g > \mu$. However, one may achieve the opposite so that $\mu > E_g$. This corresponds to the stimulated emission regime[4] where the radiation fields are constantly amplified through the medium. Semiconductor lasers usually operate under such a condition. Our treatment, presented in previous sections, can be extended to this stimulated emission regime by introducing a negative temperature for the system of radiation fields.

It is seen that when the frequency of the radiation fields is limited by $E_g \leq h\nu < \mu$, the Hamiltonian defined in Eq. (2.3) is negative semidefinite. For the density operator ρ in Eq. (2.1) to be meaningful, the temperature T must be negative. We can use the same formalism in Secs. II–VI for the stimulated emission case, provided that we associate the system of radiation fields with a negative temperature, and that the frequency of radiation fields is limited by $E_g/h \leq \nu < \mu/h$.

For most semiconductor laser operations, the mode structure is determined by the properties of the cavity and environment of the device itself. We will omit the effects due to complicated mode structures, and study a single mode of the radiation field first. The total contribution to the luminescent radiation results from the superposition of various frequency components of the radiation field.

We now proceed with the density operator for the single mode of the radiation field:

$$\rho = \{1 - \exp[\beta(\mu - h\nu)]\} \exp[\beta(\mu - h\nu)a^+a]$$

$$(E_g/h \leq \nu < \mu/h) \tag{5.1}$$

where $\beta = 1/(k_B T) < 0$ and a and a^+ are the annihilation and creation operators of the field mode, respectively. With the above-defined density operator, we can calculate the expectation values of the thermodynamic functions. Thus the luminescent energy in a mode is found to be, analogous to Eq. (2.9),

$$U(\nu) = h\nu \{\exp[\beta(h\nu - \mu)] - 1\}^{-1} . \tag{5.2}$$

The contribution to the entropy is given by, via Eq. (4.2),

$$\frac{S(\nu)}{k_B} = \beta(h\nu - \mu)\{\exp[\beta(h\nu - \mu)] - 1\}^{-1}$$

$$-\ln\{1 - \exp[\beta(\mu - h\nu)]\} . \tag{5.3}$$

The average number of photons in a mode is

$$N(\nu) = \{\exp[\beta(h\nu - \mu)] - 1\}^{-1} . \tag{5.4}$$

If we denote the number of modes per unit volume per unit frequency by $g(\nu)$, then the total energy density u due to the stimulated emission is given by

$$u = \int_{E_g/h}^{\mu/h} g(\nu)U(\nu)d\nu , \tag{5.5}$$

which is the ratio of U/V, with V the total volume and U the total energy of the stimulated emission. The entropy and total number of photons, being extensive quantities, can be calculated in the same way. Explicitly, we have for the total entropy S and the number of photons N in the stimulated emission field,

$$S = V \int_{E_g/h}^{\mu/h} g(\nu)S(\nu)d\nu , \tag{5.6}$$

$$N = V \int_{E_g/h}^{\mu/h} g(\nu)N(\nu)d\nu . \tag{5.7}$$

The pressure P can then be calculated from Eq. (4.5).

We notice that the negative temperature for the system of photons is consistent with our understanding of the physical situation of the electron-hole pairs in the stimulated emission regime. When the condition $\mu > h\nu > E_g$ is satisfied, the system of electron-hole pairs is analogous to a system of inverted two-level atoms with energy level $h\nu$. Since this "inversion" is determined by the occupation of the electronic states in the valence and conduction bands, which in turn is determined by the lattice temperature as well as properties of the material, we can find a relation between the effective negative temperature of the electron-hole pairs, or that of the photons. Denote the lattice temperature of the semiconducting material by T_{lat}, the Fermi statistics of the electron gives that the occupation of the conduction band is proportional to

$$f_c(\varepsilon) = \{\exp[(\varepsilon - \eta_c)/k_B T_{lat}] + 1\}^{-1} , \tag{5.8}$$

where ε is the energy of the electronic state and η_c is the chemical potential for conduction electrons. Similarly, the occupation for the valence band is proportional to

$$f_v(\varepsilon) = \{\exp[(\varepsilon - \eta_v)/k_B T_{lat}] + 1\}^{-1} , \tag{5.9}$$

with η_v the chemical potential for the valence electrons. When the transition at an energy $h\nu$ between the valence band and conduction band is considered, the electron-hole pairs can be just treated as two-level atoms. The population on the excited state is proportional to $f_c(\varepsilon + h\nu)[1 - f_v(\varepsilon)]$; on the ground state it is proportional to $[1 - f_c(\varepsilon + h\nu)]f_v(\varepsilon)$. Hence the ratio of the populations on the excited state N_e to that on the ground state N_g is given by

$$\frac{N_e}{N_g} = \frac{f_c(\varepsilon + h\nu)[1 - f_v(\varepsilon)]}{f_v(\varepsilon)[1 - f_c(\varepsilon + h\nu)]} . \tag{5.10}$$

Here ε refers to the valence electron energy. For the effective two-level system, the left-hand side of the above equation is equal to $\exp[-h\nu/(k_B T)]$. When Eqs. (5.8) and (5.9) are applied, we obtain then the effective temperature of the two-level system

$$T = \frac{h\nu}{h\nu - \mu} T_{lat} . \tag{5.11}$$

Here we have used $\mu = \eta_c - \eta_v$ to denote the chemical potential of the electron-hole pair.

It is clear from the above equation that when $h\nu < \mu$, we have $T < 0$. Thus the temperature for the stimulated emission field is negative. Also we notice that according to the above equation, when $\mu = 0$, the condition for thermal equilibrium between the radiation field and the material, the temperature of the radiation field is the same as that of the material: $T = T_{lat}$. This equality also holds for $h\nu \gg \mu$. In general, the temperature for non-thermal radiation field is different from the lattice temperature. Strictly speaking, the inverted two-level system (i.e., electron-hole pairs) and the radiation field generated by the recombinations of the electron-hole pairs are not a closed system, as there are many possible dynamic processes involved. In other words, there is constantly an energy flow between the above system and external world. To describe such a system in thermodynamic terms, one is assuming that the equilibrium established inside the system itself, i.e., the equilibrium between the electron-hole pairs and the radiation fields generated from their recombination, is reached in a much shorter time than other time scales, such as the external pumping rate and the thermal relaxation time of the lattice, so that effectively one can treat the electron-hole pairs and the luminescent radiation as an isolated system. Only then, one can assign a meaningful temperature, as well as other thermodynamic quantities, to the radiation field and the effective two-level system.

VI. FLUCTUATIONS AND PHOTON COUNTING RATES

There are other properties that can demonstrate the difference between luminescent and blackbody radiation. An example is the photon statistics of radiation fields.[12] We now calculate the fluctuation in the photon numbers of the luminescent radiation field.

In Eq. (2.8) we used the identity Eq. (2.7) to calculate the averaged photon number in the jth mode of the radiation field,

$$\langle a_j^+ a_j \rangle = \{\exp[\beta(h\nu_j - \mu)] - 1\}^{-1},\quad (6.1)$$

which reduces to

$$\langle a_j^+ a_j \rangle = [\exp(\beta h\nu_j) - 1]^{-1}\quad (6.2)$$

for blackbody radiation. Similarly, by using the identity

$$\mathrm{Tr}[(a_k^+ a_k)^2 \exp(-x a_k^+ a_k)]$$

$$= \exp[-x][1 - \exp(-x)]^{-2}$$

$$+ 2\exp(-2x)[1 - \exp(-x)]^{-3} \quad (x > 0)\quad (6.3)$$

we obtain

$$\langle (a_j^+ a_j)^2 \rangle = \{\exp[\beta(h\nu_j - \mu) - 1]\}^{-1}$$

$$+ 2\{\exp[\beta(h\nu_j - \mu) - 1]\}^{-2},\quad (6.4)$$

where the explicit form of the density operator in Eq. (2.6) has been used in evaluating the above expectation value and x is taken to be $\beta(h\nu_j - \mu)$. Equation (6.4) can

also be rewritten as, by using Eq. (6.2),

$$\langle (a_j^+ a_j)^2 \rangle = \langle a_j^+ a_j \rangle + 2(\langle a_j^+ a_j \rangle)^2,\quad (6.5)$$

so that the variance of the occupation number in the jth mode is obtained as

$$\langle (a_j^+ a_j - \langle a_j^+ a_j \rangle)^2 \rangle = \langle a_j^+ a_j \rangle + (\langle a_j^+ a_j \rangle)^2.\quad (6.6)$$

This form of the variance in the occupation number is true for both luminescent and blackbody radiation fields. The corresponding expectation values of the occupation number are given by Eqs. (6.1) and (6.2). Thus the variance of occupation number N_j in the jth mode of the field is, for the luminescent radiation,

$$\mathrm{var}(N_j) = \exp[\beta(h\nu_j - \mu)]\{\exp[\beta(h\nu_j - \mu)] - 1\}^{-2},$$

$$(6.7\mathrm{a})$$

whereas for blackbody radiation,

$$\mathrm{var}(N_j) = \exp(\beta h\nu_j)[\exp(\beta h\nu_j) - 1]^{-2}.\quad (6.7\mathrm{b})$$

Note that for the luminescent radiation, the frequency must be above the frequency limit ν_g due to the restriction of the band gap of the material.[13] The fluctuations in the occupation numbers of the modes in the system are explicitly dependent on the band gap and the chemical potential. The photon statistics of the luminescent radiation field will then also depend on the two parameters of the luminescent material. For blackbody radiation, the only parameter that depends on the experimental situation is the temperature.

The photon counting rate of the radiation field is directly related to the occupation number distribution, which can be derived by taking the diagonal matrix element of the density operator.[12] We obtain the probability of having m photons in the jth mode of the radiation field

$$P_j(m) = \langle m | \rho_j | m \rangle.\quad (6.8)$$

For luminescent radiation, ρ_j is the density operator of the jth mode of the luminescent radiation field obtained from the total density operator for the field Eq. (2.6),

$$\rho_j = [1 - e^{-\beta(h\nu_j - \mu)}]\exp[-\beta(h\nu_j - \mu)a_j^+ a_j].\quad (6.9)$$

Thus we have

$$P_j(m) = \{1 - \exp[-\beta(h\nu_j - \mu)]\}\exp[-\beta(h\nu_j - \mu)m].$$

$$(6.10)$$

For the blackbody radiation, the density operator can be obtained as the limiting case of Eq. (6.9) for $\mu = \nu_g = 0$. Hence the probability of having m photons in the jth mode is

$$P_j(m) = [1 - \exp(-\beta h\nu_j)]\exp(-\beta h\nu_j m).\quad (6.11)$$

We can write the probability distribution for the two radiation fields in the same form, in terms of the averaged occupation number in the field mode, given by Eqs. (6.1) and (6.2), as

$$P_j(m) = \frac{(\langle a_j^+ a_j \rangle)^m}{(1 + \langle a_j^+ a_j \rangle)^{m+1}} , \qquad (6.12)$$

which is a Bose-Einstein distribution in $\langle a_j^+ a_j \rangle$. In fact, one can show directly that given a density operator in the form of Eq. (2.6), the variance in the occupation number M of a field mode is related to the mean by

$$\mathrm{var}(M) = \langle M \rangle^2 + \langle M \rangle , \qquad (6.13)$$

where M represents the number operator of the corresponding mode $M = a^+ a$. Of course, for the luminescent radiation $\langle a_j^+ a_j \rangle$, as well as $P_j(m)$, depends upon the chemical potential.

VII. CONCLUSION

We have studied the statistical and thermodynamic properties of the luminescent radiation field generated by the recombination of electron-hole pairs. It is possible to describe the radiation field in thermodynamic terms when the equilibrium between the electron-hole pairs and radiation fields can be reached in a short time relative to other processes. We then find the effective temperature of the radiation field is related to the lattice temperature, which determines the excitation of the electron-hole pairs.

Thermodynamic functions are calculated based on statistical mechanics in the context of the grand canonical ensemble. They in general depend on the band gap as well as the chemical potential of the electron-hole pair. Coherence properties of the radiation field is also calculated and compared to that of blackbody radiation.

Properties of the radiation field can be obtained from the photon counting rates. For this purpose, we have calculated the statistics of the luminescent radiation fields. By comparing the statistics with that of blackbody radiations, one can further examine the difference between luminescent radiation and thermal radiation.

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