# The chemical potential of radiation

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**Abstract.** In a thermodynamic treatment electromagnetic radiation of any kind is described. The difference between thermal and non-thermal radiation is accounted for by introducing the chemical potential of photons. Instead of an effective temperature all kinds of radiation have the real temperature of the emitting material. As a result Planck's law for thermal radiation is extended to radiation of any kind. The concept of the chemical potential of radiation is discussed in detail in conjunction with light-emitting diodes, two-level systems, and lasers. It allows the calculation of absorption coefficients, of emission spectra of luminescent materials, and of radiative recombination lifetimes of electrons and holes in semiconductors. Theoretical emission spectra are compared with experimental data on GaAs light-emitting diodes and excellent agreement is obtained.

## 1. Introduction

Electromagnetic radiation consists of photons which do not interact with each other. Their properties are therefore entirely determined by the interaction with matter, emitters and absorbers. The state of the emitter is reflected in the spectrum of the emitted photons. This makes spectroscopy such a powerful tool for the investigation of materials. On the other side, this dependence on the radiation-emitting material makes it difficult to recognise radiation as a thermodynamic phase. The thermodynamic treatment of radiation by Kirchhoff (1860), Wien (1896), Rayleigh (1900), and Planck (1906) culminated in Planck's famous radiation formula for black-body radiation.

Radiation emitted by black bodies is called thermal radiation, because both its intensity and its spectrum are a function of the emitter's temperature only. In contrast, non-thermal radiation is mostly recognised by its high intensity, which is far too large for the temperature of the body which emits it to be thermal radiation. It is also called luminescence and is emitted e.g. by glow discharges, luminescent diodes and lasers. For luminescent radiation the actual temperature of the emitting body seems to be of little importance. In the literature (Landsberg and Evans 1968, Landsberg and Tonge 1980, and references therein), non-thermal radiation is treated thermodynamically like black-body radiation. Instead of the real temperature, an effective temperature is used which is the temperature of black-body radiation having the same intensity in a given photon energy range. Effective temperatures therefore do not exist in any part of a system emitting non-thermal radiation. In this context the inversion of the occupation of two-level systems and the resulting emission as from masers and lasers are often described by negative absolute temperatures (Kittel 1958). A detailed account of the

thermodynamics of radiation in terms of effective temperatures was recently given by Landsberg and Tonge (1980).

In this paper a thermodynamic treatment both for thermal and non-thermal radiation is presented, in which the temperature of the radiation is the actual temperature of the emitting system. The difference between thermal and non-thermal radiation is accounted for by the chemical potential of the radiation. In contrast to effective temperatures this quantity is experimentally accessible.

## 2. Thermal radiation

Since the work of Kirchhoff (1860), Wien (1896), and in particular Planck (1906) thermal radiation is well accounted for. For the special case of black-body radiation, contained in a cavity with absorbing walls of temperature $T$, Planck has derived a radiation formula. The energy density per photon energy interval is

$$e(\hbar\omega) = \frac{(\hbar\omega)^3}{\pi^2\hbar^3c^3}[\exp(\hbar\omega/kT) - 1]^{-1}. \tag{1}$$

The radiation emitted through a small hole of the cavity into a hemisphere is black-body radiation and its intensity $I(\hbar\omega)$ per photon energy interval is

$$I_{\text{black}}(\hbar\omega) = \tfrac{1}{4}e(\hbar\omega)c \tag{2}$$

where $c$ is the velocity of light. The factor $\tfrac{1}{4}$ stems from the integration of $\cos\theta$ over a hemisphere, since photons travelling at an angle $\theta$ to the normal of the emitting hole contribute only with a factor $\cos\theta$ to the photon current. This relation is called Lambert's law.

With Kirchhoff's law the validity of this expression may be extended to the emission of thermal radiation from non-black bodies. Considering the equilibrium with a black body Kirchhoff finds that the intensity $I(\hbar\omega)$ of thermal radiation emitted by a body with absorptivity $a(\hbar\omega) < 1$ is related to the black-body intensity in (2) by

$$I(\hbar\omega) = a(\hbar\omega)\, I_{\text{black}}(\hbar\omega). \tag{3}$$

For later reference we also give the entropy $\sigma$ per photon of energy $\hbar\omega$ of thermal radiation contained in an absorbing cavity (this radiation is always black). According to Planck it is

$$\sigma = \frac{\hbar\omega}{T} - k[\exp(\hbar\omega/kT) - 1]\ln[1 - \exp(-\hbar\omega/kT)]. \tag{4}$$

Apart from the detailed relations in (1) and (4), thermal radiation is best characterised by a vanishing chemical potential $\mu_\gamma$ of its photons, which is thought to be a consequence of the non-conservation of photon number $N_\gamma$. According to Gibbs, energy changes d$E$ in a system are related to changes of extensive variables. For photons in a cavity it is

$$\mathrm{d}E = T\,\mathrm{d}S - p\,\mathrm{d}V + \mu_\gamma\,\mathrm{d}N_\gamma \tag{5}$$

where $S$ is entropy, $V$ volume, $T$ temperature and $p$ pressure. The equilibria of the system are characterised by a minimum of the energy $E$. For the chemical equilibrium at constant $S$ and $V$ this yields $\mu_\gamma\,\mathrm{d}N_\gamma = 0$. Due to the non-conservation of photon number it could be d$N_\gamma \neq 0$, and therefore in equilibrium it must be $\mu_\gamma = 0$. It is common

belief that a vanishing chemical potential is a general property of photons and is true also for luminescent radiation (Bebb and Williams 1972). The above argument, however, is not a strong argument. Since photons do not interact with each other, they cannot achieve equilibrium by themselves. As will be discussed later, other particles which interact with photons have to be included into the system and into equation (5) describing it. The result will be that a non-zero chemical potential of photons may occur. In any case, the chemical potential, as the Gibbs free energy per particle, has to be smaller than the smallest energy per particle in the system, otherwise the entropy could become negative.

## 3. Non-thermal radiation

The emission of radiation reflects the properties of the emitting material. Luminescent radiation may be calculated in a microscopic way quantum-mechanically, if the state in which the emitter is is known in detail. There are many cases, however, like the luminescent diode, where the existence of internal equilibria permits a more general, less microscopic treatment, and we will concentrate on these cases in the following.

Thermal radiation can be emitted by any material. Its spectrum may contain photons with any energy $\hbar\omega > 0$. In contrast, the spectrum of non-thermal radiation is characterised by some threshold photon energy $\hbar\omega_0$, with photons of smaller energy missing.

The threshold photon energy $\hbar\omega_0$ is a consequence of a gap $\Delta\varepsilon_g$ in the distribution of states as a function of energy which is characteristic for luminescent materials, like semiconductors, insulators and isolated molecules. Since the photons of luminescent radiation have energies $\hbar\omega \geq \hbar\omega_0 = \Delta\varepsilon_g$ the argument that their chemical potential $\mu_\gamma$ must be smaller than $\hbar\omega_0$ does not exclude $\mu_\gamma > 0$ in luminescence.

As a typical luminescent material we consider a semiconductor, for which $\Delta\varepsilon_g$ is the gap between valence and conduction bands as shown in figure 1. Whether a semiconductor at a given temperature emits thermal radiation or luminescent radiation is determined by the concentrations of electrons in the conduction band and of holes in the valence band, which depend not only on the temperature but also on their chemical potentials.

## 4. Electronic transitions in semiconductors

We consider the equilibrium between photons and electrons in a cavity with perfectly reflecting walls filled with homogeneous semiconducting material. The concentration $n_0(\varepsilon)$ of occupied states with energy $\varepsilon$ per energy interval in the conduction band follows from Fermi statistics

$$n_0(\varepsilon) = D(\varepsilon) f(\varepsilon) = D(\varepsilon) \{\exp[(\varepsilon - \eta_c)/kT] + 1\}^{-1}. \tag{6}$$

The concentration $n_u$ of unoccupied states per energy in the valence band is likewise

$$n_u(\varepsilon) = D(\varepsilon) [1 - f(\varepsilon)] = D(\varepsilon) \{1 - \{\exp[(\varepsilon - \eta_v)/kT] + 1\}^{-1}\} \tag{7}$$

$D(\varepsilon)$ is the density of states, and $\eta_c$ and $\eta_v$ are the electron chemical potentials governing the occupation of states with electrons in the conduction band and in the valence band respectively, as shown in figure 1. $\eta_c$ and $\eta_v$ are also known in semiconductor physics as quasi-Fermi energies. The electrochemical potential $\eta$ is related to the chemical potential
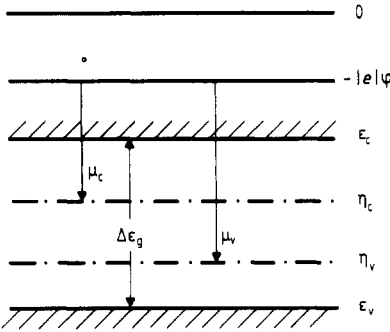
**Figure 1.** Energy diagram for electrons in a semiconductor. Electrons in the conduction band ($\varepsilon_e \geq \varepsilon_c$) have electrochemical potential (quasi-Fermi energy) $\eta_c = \mu_c - e\varphi$. Electrons in the valence band ($\varepsilon_e \leq \varepsilon_v$) have $\eta_v = \mu_v - e\varphi$. $\mu_c$ and $\mu_v$ are the respective chemical potentials.

$\mu$ and the electrical potential $\varphi$ by $\eta = \mu + q\varphi$, where $q$ is the charge of the particle of interest. As will be seen we are interested only in local processes involving both occupied and unoccupied states. Thus only the difference $\eta_c - \eta_v = \mu_c - \mu_v$ is important.

In assigning a single chemical potential $\mu_c$ and a single temperature $T$ to all the occupied states in the conduction band, we take advantage of two equilibria:

(i) the chemical equilibrium with regard to the exchange of electrons between states of different energy in the conduction band, which establishes a uniform chemical potential $\mu_c$ for the conduction band; and

(ii) the thermal equilibrium regarding the exchange of entropy between the electrons and the lattice which establishes a uniform temperature $T$ equal to the lattice temperature. The same equilibria exist separately for the states in the valence band.

Transitions between occupied states in the conduction band and unoccupied states in the valence band are comparatively rare and chemical equilibrium with regard to the exchange of electrons between states of the conduction band and of the valence band does not always exist. it is therefore not necessarily $\mu_c = \mu_v$.

Occupied states in the conduction band and unoccupied states in the valence band are generated in pairs by transitions from the valence band to the conduction band. They disappear in pairs through recombinative transitions. For the moment we assume that these transitions are entirely radiative. This means that generating transitions are accompanied by the absorption of photons with $\hbar\omega \geq \Delta\varepsilon_g$ and recombinative transitions by the emission of such photons. In the cavity the equilibrium with the photons is characterised by the balance between absorption and emission processes.

The absorption rate per volume and per photon energy interval $r_a(\hbar\omega)$ is proportional to the density of photons $n_\gamma(\hbar\omega)$ and to the density of all pairs of occupied valence band states and unoccupied conduction band states, which differ in energy by $\hbar\omega$ (Stern 1963)

$$r_a(\hbar\omega) = n_\gamma(\hbar\omega) \int_0^\infty M(\varepsilon, \hbar\omega) \, n_0(\varepsilon) \, n_u(\varepsilon + \hbar\omega) \, \mathrm{d}\varepsilon \tag{8}$$

$M$ contains the matrix element which may depend on $\varepsilon$ and $\hbar\omega$.

In a stimulated emission process a photon triggers the transition from the conduction band to the valence band. The stimulated emission rate per volume and per energy (=rate of stimulated recombination) is

$$r_{st}(\hbar\omega) = n_\gamma(\hbar\omega) \int_0^\infty M(\varepsilon, \hbar\omega) \, n_u(\varepsilon) \, n_0(\varepsilon + \hbar\omega) \, \mathrm{d}\varepsilon. \tag{9}$$

The rate of spontaneous emission processes per volume and per energy $r_{sp}(\hbar\omega)$ is proportional to the density of the same semiconductor states that give rise to stimulated emission and it is proportional to the density of states per energy for photons $D_\gamma(\hbar\omega)$

$$r_{sp}(\hbar\omega) = D_\gamma(\hbar\omega) \int_0^\infty M(\varepsilon, \hbar\omega) \, n_u(\varepsilon) \, n_u(\varepsilon + \hbar\omega) \, d\varepsilon. \tag{10}$$

The density of states for photons in a cavity with refractive index $\kappa$ is

$$D_\gamma(\hbar\omega) = \frac{\kappa^3(\hbar\omega)^2}{\pi^2\hbar^3c^3}. \tag{11}$$

From the balance

$$r_{sp}(\hbar\omega) + r_{st}(\hbar\omega) - r_a(\hbar\omega) = 0 \tag{12}$$

the density of photons $n_\gamma(\hbar\omega)$ is

$$n_\gamma(\hbar\omega) = \frac{\kappa^3(\hbar\omega)^2}{\pi^2\hbar^3c^3}$$

$$\times \frac{\int_0^\infty M(\varepsilon, \hbar\omega) \, n_u(\varepsilon) \, n_0(\varepsilon + \hbar\omega) \, d\varepsilon}{\int_0^\infty M(\varepsilon, \hbar\omega) \, n_u(\varepsilon) \, n_0(\varepsilon + \hbar\omega) \, [n_0(\varepsilon) \, n_u(\varepsilon + \hbar\omega)/n_u(\varepsilon) \, n_0(\varepsilon + \hbar\omega) - 1] \, d\varepsilon}. \tag{13}$$

With the distribution functions for $n_0$ and $n_u$ in equations (6) and (7) the expression in square brackets in the denominator of (13) is

$$\frac{n_0(\varepsilon) \, n_u(\varepsilon + \hbar\omega)}{n_u(\varepsilon) \, n_0(\varepsilon + \hbar\omega)} - 1 = \exp\left(\frac{\hbar\omega - (\mu_c - \mu_v)}{kT}\right) - 1. \tag{14}$$

Since this expression does not depend on the variable $\varepsilon$ equation (13) is simplified considerably

$$n_\gamma(\hbar\omega) = \frac{\kappa^3(\hbar\omega)^2}{\pi^2\hbar^3c^3} \left[\exp\left(\frac{\hbar\omega - (\mu_c - \mu_v)}{kT}\right) - 1\right]^{-1}. \tag{15}$$

This relation was derived under the condition of equilibrium between the excitations of a semiconductor characterised by their chemical potential $\mu_c - \mu_v$ and the photons. In this equilibrium the chemical potential of photons is therefore

$$\mu_\gamma = \mu_c - \mu_v.$$

This yields the radiation formula

$$n_\gamma(\hbar\omega, \mu_\gamma) = \frac{\kappa^3(\hbar\omega)^2}{\pi^2\hbar^3c^3} \left[\exp\left(\frac{\hbar\omega - \mu_\gamma}{kT}\right) - 1\right]^{-1}. \tag{16}$$

Equation (16) gives the density of photons in equilibrium with an electronic system in which each of the two sets of states involved in optical transitions is described by a single chemical potential ($\mu_c$ and $\mu_v$). It is of general validity, since all details of the states, like their density or transition probabilities, drop out in its derivation. The general radiation formula (16) describes all kinds of radiation, thermal and non-thermal. It contains Planck's formula for thermal black-body radiation as a special case, in which the two sets of states have the same chemical potential and $\mu_\gamma = \mu_c - \mu_v = 0$.

## 5. Generalisation of Kirchhoff's law for non-thermal radiation

By regarding the equilibrium between a black and a non-black body of equal temperature, Kirchhoff (1860) related the photon emission of the non-black body to its absorptivity. This relation has been extended to the non-equilibrium case, where a non-black body emits thermal radiation into an environment of different temperature by Weinstein (1960), Bauer (1969), and Baltes (1976). Here we will show that Kirchhoff's relation can even be extended to the case where a non-black body emits non-thermal radiation into an environment of different temperature and different chemical potential $\mu_\gamma$ of its photons.

We consider a slab of material in vacuum with no photons incident from the outside as shown in figure 2.
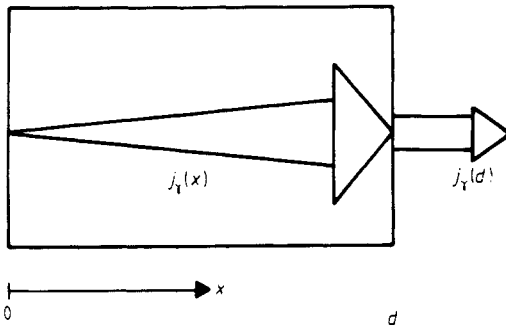


**Figure 2.** In a material with no incident photons the photon current $j_\gamma$ increases in $x$-direction and is partly reflected before emission.

The continuity equation in steady state for the photon current $j_\gamma$, flowing through the slab towards the right surface in the $x$-direction is

$$\text{div } j_\gamma = \tfrac{1}{4} r_{sp} - (r_a - r_{st}). \tag{17}$$

According to Lambert's law only $\tfrac{1}{4}$ of all photons generated spontaneously and homogeneously contribute to the current in the $x$-direction, whereas the net absorption rate, the difference between the actual absorption rate $r_a$ and the stimulated emission rate $r_{st}$, is proportional to all photons $N_\gamma$ in the photon current $j_\gamma = N_\gamma c/\kappa$. The net absorption rate can also be expressed by the absorption coefficient $\alpha(\hbar\omega)$ as

$$r_a - r_{st} = \alpha(\hbar\omega)j_\gamma = \alpha(\hbar\omega)N_\gamma c/\kappa \tag{18}$$

which yields

$$\text{div } j_\gamma = \tfrac{1}{4} r_{sp} - \alpha j_\gamma. \tag{19}$$

With no photons incident from the left the spatial dependence of the photon current in the $x$-direction is

$$j_\gamma(x) = j_\gamma(\infty)\,(1 - e^{-\alpha x}) \tag{20}$$

where

$$j_\gamma(\infty) = r_{sp}/(4\alpha) \tag{21}$$

is the photon current at $x = \infty$ of an infinitely thick slab, where $\text{div } j_\gamma = 0$.

In a slab of finite thickness $d$, the part $R'j_\gamma(d)$ of the photon current incident from a hemisphere onto the right surface from the inside is reflected back into the slab. The part $(1 - R')j_\gamma(d)$ is transmitted through the surface. The transmission $(1 - R')$ of the surface for radiation incident from the inside of a medium with refractive index $\kappa$ is an unusual quantity. It is related to the more familiar transmission $(1 - R)$ of the surface for radiation incident from the outside, where $\kappa = 1$, by (Drude 1959, Stern 1963)

$$(1 - R') = (1/\kappa^2)(1 - R). \tag{22}$$

With this relation and allowing for multiple reflection between the two surfaces of the slab, a distance $d$ apart, the photon current emitted through the right surface is

$$j_\gamma(d) = a(\hbar\omega) r_{sp}/(4\alpha\kappa^2). \tag{23}$$

$a(\hbar\omega)$ is the absorptivity of the slab and is

$$a(\hbar\omega) = [1 - R(\hbar\omega)][1 - \exp(-\alpha(\hbar\omega)d)][1 - R(\hbar\omega)\exp(-\alpha(\hbar\omega)d)]^{-1}. \tag{24}$$

The absorption coefficient $\alpha$ as a material property is related to the transition probabilities and the occupation of the electronic states of the material. By comparison of (18) with (8) and (9) using (6) and (7) this relation is (Stern 1963)

$$\alpha(\hbar\omega) = (\kappa/c) \int_0^\infty M(\varepsilon, \hbar\omega) D(\varepsilon) D(\varepsilon + \hbar\omega)[f(\varepsilon) - f(\varepsilon + \hbar\omega)] \, d\varepsilon. \tag{25}$$

With (25) also the spontaneous emission rate $r_{sp}$ in (10) can be expressed in terms of the absorption coefficient $\alpha$ by (Bebb and Williams 1972)

$$r_{sp}(\hbar\omega) = \alpha(\hbar\omega) \frac{\kappa^2(\hbar\omega)^2}{\pi^2\hbar^3c^2} \left[\exp\left(\frac{\hbar\omega - (\mu_c - \mu_v)}{kT}\right) - 1\right]^{-1}. \tag{26}$$

With (26) the generalised Kirchhoff law is obtained for thermal and non-thermal photon currents emitted by a non-black emitter

$$j_\gamma(\hbar\omega) = a(\hbar\omega) \frac{(\hbar\omega)^2}{4\pi^2\hbar^3c^2} \left[\exp\left(\frac{\hbar\omega - (\mu_c - \mu_v)}{kT}\right) - 1\right]^{-1}. \tag{27}$$

This relation could be interpreted as describing a photon current in equilibrium with the excitations of the emitter, i.e. with $\mu_\gamma = \mu_c - \mu_v$, but modified for an absorptivity $a(\hbar\omega) < 1$. A more detailed interpretation of this generalised Kirchhoff law has to distinguish between two cases.

(i) If the penetration depth of the photons $1/\alpha$ is much smaller than the thickness of the material opposite to the direction of photon emission, then $\operatorname{div} j_\gamma = 0$ at the emitting surface and absorption and emission rates are balanced. Since this is the condition for equilibrium between the excitations of the emitter and the photons, the chemical potential of the emitted photons is $\mu_\gamma = \mu_c - \mu_v$, identical to the equilibrium in the cavity. In general, chemical equilibrium with $\mu_\gamma = \mu_c - \mu_v$ exists for a given photon momentum $\hbar k$, if opposite to $k$, i.e. to the direction of emission, the transmissivity of the emitter is zero and $a(\hbar\omega) = 1 - R(\hbar\omega)$. It is irrelevant for this equilibrium whether the emitted photon current is balanced by an incident photon current or not, since the incident photons with their opposite momentum are not involved in the equilibrium of the emitted photons.

(ii) If the penetration depth of the photons is not much smaller than the thickness of

the emitter in a direction opposite to the emission current, and there are no photons incident from the outside, then $\operatorname{div} j_\gamma > 0$ at the emitting surface. Although this is a non-equilibrium situation, the photon emission current is still given by (27). The non-equilibrium is taken care of by the value of the absorptivity $a(\hbar\omega)$ rather than by the proper value of the chemical potential of the emitted photons which in this case is $\mu_\gamma < \mu_c - \mu_v$, since $\operatorname{div} j_\gamma > 0$. In general, in this non-equilibrium case, photons with different energies have different chemical potentials. We note that this problem exists for 'thermal' emitters with $\mu_c - \mu_v = 0$, too. If their transmissivity is non-zero, then the emitted radiation has $\mu_\gamma < 0$ and is 'non-thermal' according to the definition that radiation with $\mu_\gamma \neq 0$ is non-thermal radiation.

The thermodynamic treatment of radiation as presented in this paper relies on the chemical and thermal equilibrium among the electrons in the conduction band and among the electrons in the valence band. If these equilibria exist, the emission of luminescent radiation is an equilibrium problem as much as the emission of thermal radiation. If these equilibria do not exist, which may occur if the lifetime of the excitations of an emitter is very short, a thermodynamic treatment is inappropriate (Fowler and Dexter 1962).

## 6. Chemical reactions of electrons and holes with photons and phonons

Unoccupied states in the valence band make up the free hole gas and occupied states in the conduction band constitute the free electron gas. On the energy scale of figure 1, where electron energies increase 'upwards', hole energies increase 'downwards'. If the energy of an electron in a given state is $\varepsilon_e$, the energy of a hole in this state would be

$$\varepsilon_h = -\varepsilon_e \tag{28}$$

counted from the same (arbitrary) zero line. This applies also to the chemical potential of holes $\mu_h$ which is related to that of the electrons in states in the valence band $\mu_v$ by

$$\mu_h = -\mu_v. \tag{29}$$

This notation has been introduced by Tauc (1962). With the chemical potential for free electrons $\mu_e$ equal to the chemical potential for the conduction band $\mu_c$, the difference of quasi-Fermi levels is equal to the chemical potential $\mu_{eh}$ of electron–hole pairs

$$\mu_c - \mu_v = \mu_e + \mu_h = \mu_{eh}. \tag{30}$$

In figure 3 four different kinds of processes are shown in which electrons and holes participate. With process 1, the thermalisation of electrons in the conduction band and of holes in the valence band is achieved by reactions with a phonon $\Gamma$

$$e \rightleftarrows e' + \Gamma \tag{31}$$
$$h \rightleftarrows h' + \Gamma.$$

In process 2 the same thermalisation of electrons in the conduction band and of holes in the valence band is accomplished by intraband transitions in reactions with photons $\gamma$

$$e \rightleftarrows e' + \gamma \tag{32}$$
$$h \rightleftarrows h' + \gamma.$$

Process 3, the radiative generation or recombination of electron–hole pairs via interband transitions is a reaction with photons $\gamma$ which are either absorbed or emitted. The spontaneous reaction is

$$e + h \rightleftarrows \gamma \tag{33a}$$

and the stimulated reaction is

$$e + h + \gamma \rightleftarrows 2\gamma. \tag{33b}$$

Process 4, the non-radiative generation or recombination of electron–hole pairs, is
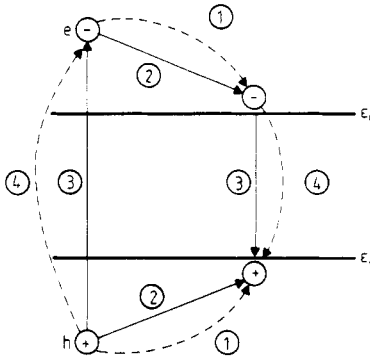


**Figure 3.** Reactions of electron–hole pairs with photons (full curves) and phonons (broken curves) are classified as non-radiative (1) and radiative (2) thermalisation and radiative (3) and non-radiative (4) generation and recombination.

a reaction with many phonons $\nu\Gamma$, since the phonon energy is usually much smaller than the energy of an electron–hole pair.

$$e + h \rightleftarrows \nu\Gamma. \tag{34}$$

Each of the above reactions has its own equilibrium, in which at constant entropy $S$ and volume $V$ the energy $E$ has a minimum as a function of the exchange of particles participating in the reaction.

For process 3, the generation or recombination reaction of electron–hole pairs with photons, it is therefore according to (5)

$$dE = \mu_e \, dN_e + \mu_h \, dN_h + \mu_\gamma \, dN_\gamma = 0. \tag{35}$$

From the reaction equations (33a, b) follows the relation between the particle numbers for spontaneous and stimulated reactions

$$dN_e = dN_h = -dN_\gamma \tag{36}$$

which express the conservation of the number of electron–hole pairs and photons. With (35) and (36) the equilibrium condition for the reaction of electron–hole pairs with photons is

$$\mu_e + \mu_h = \mu_\gamma. \tag{37}$$

This relation is the justification for introducing the chemical potential of photons $\mu_\gamma$ into the radiation formula (16).

Equilibrium of process 1 in the thermalisation reactions with phonons (31) exists in analogy to (37) if

$$\mu_e = \mu_{e'} + \mu_\Gamma$$

and                                                                                    (38)

$$\mu_h = \mu_{h'} + \mu_\Gamma.$$

Since the energy per phonon is very small, it is always $\mu_\Gamma \approx 0$.

The same can be argued about the thermalisation reaction with photons in process 2. These small-energy photons react directly with phonons and have the same chemical potential as the phonons. They belong to thermal black-body radiation which is always present. Since photons do not react with each other, the small-energy photons are not necessarily in equilibrium with the high-energy photons participating in interband transitions in process 3. In summary, thermalisation reactions do not alter the chemical potential of electrons or holes.

Parallel to radiative generation and recombination reactions with photons in process 3 occur non-radiative reactions with phonons in process 4. Their equilibrium condition is

$$\mu_e + \mu_h = \nu\mu_\Gamma \approx 0. \tag{39}$$

One reason for $\mu_\gamma = 0$ in thermal black-body radiation was that there is no conservation of the number of photons. This is not a very strong argument, since the photon number is not the only extensive variable of the photon system. Others are momentum and spin. Their conservation requires reaction partners to carry them off. The photon number is therefore always restricted by reaction equations like (33) and (36) and from this argument $\mu_\gamma$ could have any value. In non-radiative transitions the final reaction partners are phonons and it is the coupling to this system and the equilibrium with it which result in $\mu_\gamma = \mu_\Gamma = 0$ for thermal radiation. Consequently if this coupling is weak it is possible that $\mu_\gamma \neq 0$.

Phonon and photon generation and recombination reactions occur always in parallel and compete with each other. Whereas the phonon equilibrium requires $\mu_e + \mu_h = 0$, the photon equilibrium can exist at any value $\mu_e + \mu_h \leq \Delta\varepsilon_g$, the band gap of the semiconductor and the smallest photon energy, with which the electron–hole system can interact. A chemical potential $\mu_\gamma \neq 0$ of the emitted photons therefore coincides with a deviation from equilibrium of the phonon reaction. How large this deviation is is determined by the resistance of the phonon and the photon reactions to generation or recombination currents imposed externally on the electron–hole–phonon–photon system. The processes with the smaller resistance dominate and determine the chemical potential of the electron–hole system. In small band-gap materials and in materials with many impurity levels the resistance of the phonon reaction is small. On the other hand, the resistance of the interband phonon reaction is large in large band-gap materials with little impurities which may therefore be good luminescent materials.

## 7. Light-emitting diodes

Figure 4 shows the energy diagram of a p–n junction biased in the forward direction. Holes and electrons are injected into the junction with the electrical current and recombine in phonon and in photon reactions. The radiative recombination processes lead to the emission of luminescent radiation. Since the electrical current feeds both the non-
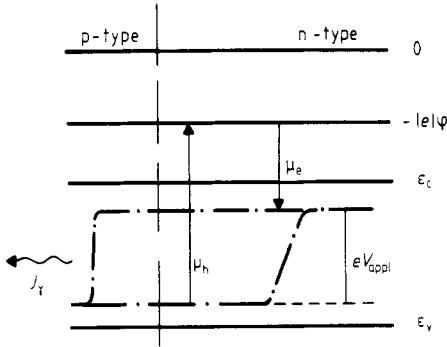
**Figure 4.** Energy diagram of ideal light-emitting diode. The chemical potential of electron–hole pairs $\mu_e + \mu_h = eV_{appl}$ is constant over light-emitting region.

radiative and the radiative reactions, there is no clear relation between electrical current and photon current emitted. However, as was discussed before, there is a clear relation between photon current and chemical potential of the electron–hole pairs, as expressed by the generalised Kirchhoff law in (27). The light-emitting diode is ideal to check this relation, because in a good p–n junction, where the voltage drop outside the junction can be neglected, the chemical potential $\mu_{eh}$ of electron–hole pairs is given by the applied voltage $V$ as indicated in figure 4.

$$eV = \mu_e + \mu_h = \mu_\gamma. \tag{40}$$

From (27) the emission intensity from a light-emitting diode with applied voltage $V$ then is

$$I(\hbar\omega) = \frac{a(\hbar\omega)}{4\pi^2\hbar^3c^2} \frac{(\hbar\omega)^3}{\exp[(\hbar\omega - eV)/kT] - 1}. \tag{41}$$

This expression contains two parameters which effect the emission spectrum differently. Whereas $\mu_\gamma$ affects mainly the intensity, the temperature $T$ of the electron–hole gas affects the intensity and determines the shape of the spectrum. Equation (41) does not contain a free parameter. The temperature $T$ is that of the electron–hole gas, which is equal to the lattice temperature, and the chemical potential $\mu_\gamma$ is equal to that of the electron–hole pairs, which is determined by the voltage across the p–n junction. The prediction of equation (41) may therefore be checked experimentally provided a diode can be fabricated in which the junction extends right to the emitting surface with a constant value of the carrier concentration or of their chemical potential. If the recombination rate at the surface were larger than in the interior, part of the radiation which is emitted close to the surface would have a chemical potential much smaller than the applied voltage, resulting in a complicated spectrum of the emitted radiation. This complication is often said to arise from self-absorption or re-absorption (Bebb and Williams 1972). It is, however, not absorptivity by itself which is harmful, it is the absorption in a region with a different chemical potential of electron–hole pairs, which deteriorates the emission spectrum.

For light-emitting diodes which have a band gap $\Delta\varepsilon_g > 1$ eV and which are far from lasing the Kirchhoff relation (41) can be approximated by

$$I(\hbar\omega) = \exp(eV/kT) \frac{a(\hbar\omega)}{4\pi^2\hbar^3c^2} \frac{(\hbar\omega)^3}{\exp(\hbar\omega/kT)}. \tag{42}$$

This approximation holds as long as $\exp[(\Delta\varepsilon_g - \mu_{eh})/kT] \gg 1$, i.e. as long as the electrons and holes are ideal gases. If this condition is met, (42) means that the spectrum of luminescent radiation is identical to the spectrum of thermal radiation, when emitted by the same system. The intensity of luminescent radiation, however, is larger by a factor $\exp(\mu_{eh}/kT) = \exp(\mu_\gamma/kT)$.

Almost ideal diodes have been prepared by Sarace *et al* (1965). Their observed luminescent intensity spectrum $I(\hbar\omega)$ is reproduced as the full curve in figure 5. In their paper Sarace *et al* (1965) fitted it to the thermal emission rate per volume ($\mu_\gamma = 0$) characterised by the absorption coefficient $\alpha(\hbar\omega)$. This inappropriate comparison of an observed emitted photon current with the theoretical photon generation rate per volume is common practice (Lasher and Stern 1964, Pankove 1971). Differences which then must occur between experiment and theory are explained by 'self-absorption'. Attempts are made to correct the observed emission for self-absorption to obtain the 'true' emission spectrum. From the preceeding paragraphs it is clear that according to the generalised Kirchhoff relation the experimental spectrum must correctly be compared with the generation rate per surface area in (51) characterised by the absorptivity $a(\hbar\omega)$. 'Self-absorption' serves to establish the equilibrium between photons and electron–hole pairs.
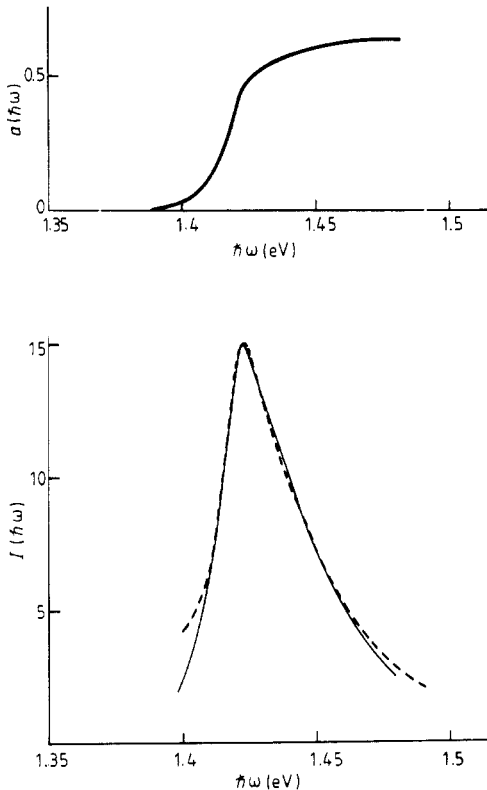


**Figure 5.** Spectrum of luminescence intensity $I(\hbar\omega)$ of GaAs light-emitting diode. Experimental curve (full curve) is according to Sarace *et al* (1965). Theoretical curve (broken curve) is calculated from equation (42) with the absorptivity $a(\hbar\omega)$ of the light-emitting region as shown in the upper part of the figure.

Using the absorption data for GaAs by Sturge (1962) corrected for the proper doping concentration according to Casey *et al* (1975) we have determined the absorptivity $a(\hbar\omega)$ from (24) and with it the theoretical emission spectrum from (42) which are both shown in figure 5. For a good fit to the experimental curve a depth of the emitting region of 3 μm had to be implied. This depth is the minority carrier diffusion length and a fit of experimental spectra could well serve to determine it. The agreement between theory and experiment in figure 5 is very good. A quantitative check of equations (41) or (42), however, is not possible, since Sarace *et al* (1965) have not measured the luminescence intensity absolutely and they only give the current, but do not specify the applied voltage.

The relation between emission intensity $I$ and applied voltage $V$ as predicted by the emission formulae (41) or (42) may be inferred from the data of Dousmanis *et al* (1964). They give the electrical current $i_{el} = 5\,\mathrm{mA}$ and applied voltage $V = 1.335\,\mathrm{V}$. At $T = 78\,\mathrm{K}$ the emission peak occurs at $\hbar\omega_p = 1.38\,\mathrm{eV}$ with a half-width of $w = 0.045\,\mathrm{eV}$. The voltage drop due to series resistance is $0.003\,\mathrm{V}$. The chemical potential of the electron–hole pairs in the junction is expected to be $\mu_{eh} \approx 1.332\,\mathrm{eV}$. With the same assumptions of quantum efficiency $\eta \approx 0.01$ and emitting area $A = 10^{-4}\,\mathrm{cm^2}$ which Landsberg and Evans (1963) made in analysing Dousmanis data in terms of effective temperatures, the spectral intensity $I(\hbar\omega_p)$ at the emission peak is estimated to be

$$I(\hbar\omega_p) = \frac{i_e\hbar\omega_p\eta}{eAw} = 15.4\ \mathrm{W\ eV^{-1}\ cm^{-2}}.$$

The chemical potential $\mu_\gamma$ is found from (42)

$$\mu_\gamma = \hbar\omega_p + kT\ln\left(\frac{4\pi^2\hbar^3c^2}{a(\hbar\omega_p)(\hbar\omega_p)^3}I(\hbar\omega_p)\right) = 1.33\ \mathrm{eV}$$

with a typical value for the absorptivity of $a(\hbar\omega_p) \approx 0.5$. With the assumptions about quantum yield and emitting area the chemical potential $\mu_\gamma$ of the emitted photons and the applied voltage $V$ agree very well.

Our analysis of luminescent radiation states that its chemical potential $\mu_\gamma$ is smaller than the photon energy and smaller than or in good junctions at most equal to the applied voltage. In most experiments the applied voltage is larger than the observed photon energies. Their analysis would therefore automatically give the chemical potential of the photons smaller than the applied voltage. In the experiment by Dousmanis *et al* (1964) the photon energy is larger than the electrical energy per electron–hole pair supplied by an external source. Energy conservation requires that heat is removed from the diode with the emitted photon current. This Peltier effect of luminescent radiation is the most interesting aspect of the observations by Dousmanis *et al* (1964).

With the above relations the chemical potential of the emitted photons can be determined experimentally. For a good luminescent diode it is simply given by the voltage across the p–n junction. This makes the chemical potential a much more meaningful quantity than effective radiation temperatures used previously in the thermodynamics of luminescent radiation (Landsberg and Evans 1966, 1968, Landsberg and Tonge 1980).

Our analysis of the radiation from light-emitting diodes shows that for a given material the intensity is only a function of the applied voltage. If there were only radiative recombination processes, then for a given voltage the electrical current would also be fixed. That this is not found experimentally reflects that non-radiative recombination processes are also present and mostly predominant. It is fortunate for our analysis that non-radiative processes occur parallel to radiative processes. Therefore only the elec-

trical current is affected by this additional channel, but the relationship between luminescence intensity and voltage still holds.

## 8. Entropy of radiation

The entropy of isotropic radiation with chemical potential $\mu_\gamma \neq 0$ contained in a reflecting cavity is found from Gibbs's fundamental relation

$$dE(S, V, N_\gamma) = T\,dS - p\,dV + \mu_\gamma\,dN_\gamma. \tag{5}$$

The entropy $S$, the volume $V$ and the particle number $N_\gamma$ are the independent variables. Since the particles of radiation do not react with each other, they are determined by the way they are produced. Except at very high densities the recombination of electron–hole pairs produces single photons and we therefore take them as the particles of radiation. From (5) we have

$$dS(E, V, N_\gamma) = (1/T)(dE + p\,dV - \mu_\gamma\,dN_\gamma). \tag{43}$$

In the following we restrict ourselves to an interval $d\varepsilon$ in the spectrum of photon energies (by using a proper filter when filling the reflecting cavity). All photons then have the energy $\varepsilon$ and

$$dE = \varepsilon\,dN_\gamma. \tag{44}$$

This removes one variable from (43) and we have

$$dS(V, N_\gamma) = (1/T)[(\varepsilon - \mu_\gamma)\,dN_\gamma + p\,dV]. \tag{45}$$

For processes with $V = V_0 = \text{const}$ as imposed by the cavity it is

$$dS(V_0, N_\gamma) = \frac{\varepsilon - \mu_\gamma}{T}\,dN_\gamma. \tag{46}$$

From our radiation formula (16)

$$\frac{\varepsilon - \mu}{T} = k \ln\left(\frac{\kappa^3 \varepsilon^2 V_0}{\pi^2 \hbar^3 c^3 N_\gamma} + 1\right) \tag{47}$$

and equation (46) can be integrated and yields

$$S(V_0, N_\gamma) = kN_\gamma\left\{\frac{\varepsilon - \mu_\gamma}{kT} - \left[\exp\left(\frac{\varepsilon - \mu_\gamma}{kT}\right) - 1\right]\ln\left[1 - \exp\left(-\frac{\varepsilon - \mu_\gamma}{kT}\right)\right]\right\}. \tag{48}$$

The entropy $S$ does not depend on the volume explicitly, and we finally have for the entropy per photon in a cavity $\sigma = S/N$

$$\sigma = \frac{\varepsilon - \mu_\gamma}{T} - k\left[\exp\left(\frac{\varepsilon - \mu_\gamma}{kT}\right) - 1\right]\ln\left[1 - \exp\left(-\frac{\varepsilon - \mu_\gamma}{kT}\right)\right]. \tag{49}$$

This entropy per photon is for $\varepsilon - \mu_\gamma \gg kT$,

$$\sigma \approx \frac{\varepsilon - \mu_\gamma}{T} + k \approx \frac{\varepsilon - \mu_\gamma}{T}$$

which is the relation for an ideal gas.

In the other limit $\varepsilon - \mu_\gamma \ll kT$,

$$\sigma \approx \frac{\varepsilon - \mu_\gamma}{T}\left[1 - \ln\left(\frac{\varepsilon - \mu_\gamma}{kT}\right)\right]$$

the photons do not form an ideal gas and the entropy per photon tends to zero. That this has some connection to laser radiation will be discussed later. Here we note that for thermal radiation with $\mu_\gamma = 0$ Planck's expression (4) is obtained from (49).

The entropy is an important quantity for the determination of the 'thermodynamic' temperature as used by Landsberg and Tonge (1980) and references therein. By not considering $\mu_\gamma \, dN_\gamma$ as a separate form of energy of a photon gas in Gibbs's equation (5) the 'thermodynamic' temperature is defined as $1/T = (\partial S/\partial E)_V$. This definition treats luminescent radiation as if it were black-body radiation. Having shown that the chemical potential $\mu_\gamma$ is a non-vanishing variable of photons in luminescent radiation, the temperature must be defined as $1/T = (\partial S/\partial E)_{V,N}$, which keeps the otherwise undetermined variable $N$ constant.

It must be emphasised that the above expression for the entropy (49) is valid for radiation contained in a cavity. It may not be valid for a current of radiation as is seen from the following arguments. For $\mu_\gamma = 0$ the integration of the entropy per photon $\sigma$ over all photons in the cavity leads to the well known relation (Planck 1906)

$$TS = \tfrac{4}{3}E. \tag{50}$$

Entropy currents are commonly written in analogy to energy currents, which are $j_E(\hbar\omega) = \hbar\omega j_\gamma(\hbar\omega)$, as $j_S(\hbar\omega) = \sigma j_\gamma(\hbar\omega)$ (Landsberg and Evans 1966, 1968, Press 1976, Henry 1980, deVos and Pauwels 1981). An integration over all photon energies then yields for the total black-body thermal entropy current a relation in analogy to (50)

$$Tj_S = \tfrac{4}{3}j_E. \tag{51}$$

If this relation were valid, it would have the consequence that heat radiation could only be converted into electricity with an efficiency smaller than the Carnot efficiency (Press 1976). This is remarkable since the conversion of heat into electricity then depends on the way in which the heat is transported from the source to the receiver, since the Carnot efficiency is obtained for heat conduction. Henry (1980) argues that this is due to irreversibilities in emission and absorption processes. If that were true, a body could not be heated by radiation up to the temperature of the radiation source, which is possible, however, if both are in a cavity, as was shown by Kirchhoff (1860).

Moreover, if the relation (50) were valid for radiation currents, a violation of the second principle of thermodynamics can be devised in a process where the heat engine receives heat via conduction and gives off heat via radiation. With an energy current $j_{E_1}$ this heat engine would take up an entropy current $j_S = j_{E_1}/T$. In an isentropic process the engine emits this same entropy current $j_S$ via radiation which is therefore accompanied by an energy current $j_{E_2} = \tfrac{4}{3}Tj_S$. Although the engine operates between identical temperatures $T$ it would nevertheless produce work at a rate $j_{E_1} - j_{E_2} = \tfrac{1}{3}Tj_S$ i.e. with an efficiency of 25%. This is a violation of the second principle, and we can conclude that a proper expression for entropy currents associated with radiation does not yet exist. The discrepancy between entropy in a cavity and entropy currents is most pronounced for small photon energies and vanishes for photons with $\varepsilon - \mu_\gamma \gg kT$.

## 9. Laser radiation

A laser amplifies radiation and a necessary condition is that the rate of stimulated emission is larger than the rate of absorption. From (18) we see that this implies a negative absorption coefficient, $\alpha(\hbar\omega) < 0$. Under which condition this occurs is most easily seen for a two-level system with energies per electron $\varepsilon_v$ and $\varepsilon_c$, which differ by $\hbar\omega$. The absorption coefficient in (25) is for the two-level system

$$\alpha(\hbar\omega, \mu_{eh}) = (\kappa/c)MN(\varepsilon_v)N(\varepsilon_c)\{f(\varepsilon_v) - f(\varepsilon_c)\} \tag{52}$$

There are always as many electrons with energy $\varepsilon_c$ as there are holes with energy $(-\varepsilon_v)$. For this intrinsic system using (6) we obtain

$$\alpha(\hbar\omega, \mu_{eh}) = (\kappa/c)MN(\varepsilon_v)N(\varepsilon_c)\frac{\sinh[(\hbar\omega - \mu_{eh})/2kT]}{1 + \cosh[(\hbar\omega - \mu_{eh})/2\,kT]} \tag{53}$$

where $\mu_{eh}$ is the chemical potential of the electron–hole pairs. The absorption coefficient $\alpha(\hbar\omega, \mu_{eh})$ of the two-level system is shown in figure 6. It is negative if $\mu_{eh} > \hbar\omega$. In this state which is usually called inversion, the two-level system amplifies radiation, incident or spontaneously emitted. In a reflecting cavity the energy density of radiation would increase beyond all limits. Therefore, there cannot be equilibrium between the photons and the electron–hole pairs, if their chemical potential is $\mu_{eh} > \hbar\omega$. Equilibrium can exist only for $\alpha(\hbar\omega, \mu_{eh}) > 0$ with $\mu_{eh} = \mu_\gamma < \hbar\omega$. $\mu_\gamma = \hbar\omega$ represents the limiting case, in which the entropy per photon is zero, and the density of photons is infinite.

As long as $\mu_{eh} < \hbar\omega$ the intensity of the emitted radiation depends only on the state in which the emitter is, i.e. on the temperature and chemical potential of its electron–hole system, provided the emitter is thicker than $1/\alpha$. If, however, $\mu_{eh} > \hbar\omega$ the intensity of the emitted radiation not only depends on the state of the emitter, but also on the photon density inside the emitter, which triggers stimulated emission processes.

If we consider the slab in figure 2 to contain the two-level system in a state with $\mu_{eh} > \hbar\omega$, with no photons incident from the left, the photon current emitted to the right is from (27) and (24) for $R = 0$

$$j_\gamma(\hbar\omega, \mu_{eh}) = [\exp(-\alpha(\hbar\omega)d) - 1]\frac{(\hbar\omega)^2}{4\pi^2\hbar^3c^2}\left[1 - \exp\left(-\frac{\mu_{eh} - \hbar\omega}{kT}\right)\right]^{-1}. \tag{54}$$
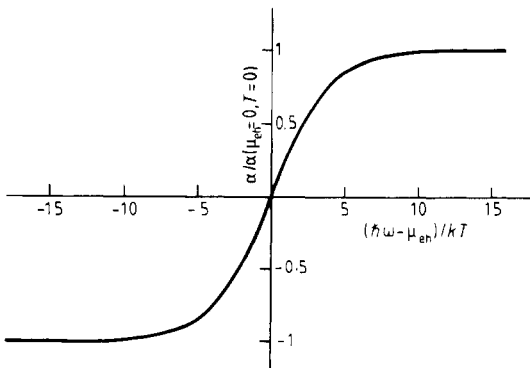


**Figure 6.** Absorption coefficient $\alpha$ of a two-level system with energies $\varepsilon_c - \varepsilon_v = \hbar\omega$ as a function of the chemical potential $\mu_{eh}$ of electron–hole pairs.

The photon current increases exponentially with the thickness $d$ of the slab because the absorption coefficient is $\alpha(\hbar\omega, \mu_{eh}) < 0$. The above expression for the emitted photon current describes what is called superfluorescence.

The previous discussion was limited to a two-level system, because for this system there is a simple analytical expression for the influence of the chemical potential of electron–hole pairs on the absorption coefficient. The results are, however, valid in general. To show this, we eliminate the matrix elements from the emission and absorption rates in (8), (9), (10) by the absorption coefficient (25). The rate of spontaneous emission per photon energy interval in a semiconductor with a chemical potential $\mu_{eh}$ of its electron–hole system is then given by (26).

For a two-level system with $\alpha(\hbar\omega, \mu_{eh})$ given by (53) and shown in figure 6 this spontaneous emission rate $r_{sp}$ is shown as a function of $\mu_{eh}$ in figure 7.

The rate of stimulated emission per photon energy interval depends also on the density of photons characterised by their chemical potential $\mu_\gamma$ and is

$$r_{st} = r_{sp}(\hbar\omega)\left[\exp\left(\frac{\hbar\omega - \mu_\gamma}{kT}\right) - 1\right]^{-1}. \tag{55}$$

The absorption rate finally is

$$r_a = r_{sp}(\hbar\omega)\exp\left(\frac{\hbar\omega - \mu_{eh}}{kT}\right)\left[\exp\left(\frac{\hbar\omega - \mu_\gamma}{kT}\right) - 1\right]^{-1}. \tag{56}$$

We again see that in equilibrium of the electron–hole pair/photon reaction, where

$$r_{sp} + r_{st} - r_a = r_{sp}(\hbar\omega, \mu_{eh})\left\{1 - \left[\exp\left(\frac{\hbar\omega - \mu_{eh}}{kT}\right) - 1\right]\left[\exp\left(\frac{\hbar\omega - \mu_\gamma}{kT}\right) - 1\right]^{-1}\right\}$$

$$= 0 \tag{57}$$

the chemical potentials of photons and electron–hole pairs are equal ($\mu_\gamma = \mu_{eh}$).

For a laser two conditions must be met:

(i) It must amplify radiation, i.e.

$$r_{st}/r_a = \exp\left(\frac{\mu_{eh} - \hbar\omega}{kT}\right) > 1 \tag{58}$$
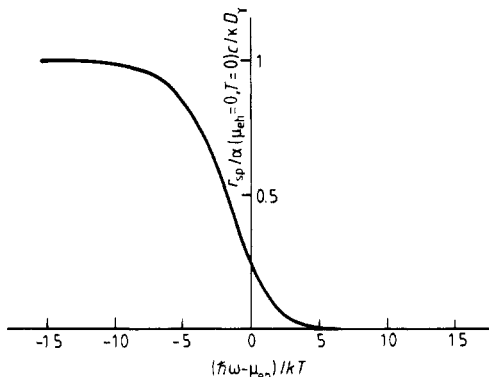


**Figure 7.** Spontaneous emission rate $r_{sp}$ of a two-level system with an absorption coefficient $\alpha$ as shown in figure 6. $r_{sp}$ rises with increasing chemical potential $\mu_{eh}$ of electron–hole pairs and saturates at four times the rate at the lasing threshold ($\mu_{eh} = \hbar\omega$), where $\alpha$ changes its sign.

which requires $\mu_{eh} > \hbar\omega$. By comparing (58) with (18) we recognise that this condition implies in any system

$$\alpha(\hbar\omega, \mu_{eh}) < 0 \qquad \text{simultaneous with } \mu_{eh} > \hbar\omega.$$

The above condition ensures superfluorescence. For a laser, which is to emit coherent radiation, the rate of stimulated emission at $\hbar\omega$ must exceed the rate of spontaneous emission. This gives the second condition

$$(ii) \qquad r_{st}/r_{sp} = \left[ \exp\left(\frac{\hbar\omega - \mu_\gamma}{kT}\right) - 1 \right]^{-1} > 1 \tag{59}$$

which requires $\mu_\gamma > \hbar\omega - kT \ln 2$.

The large photon density necessary to fulfil this condition is achieved by inserting the laser material into a resonator, an almost perfect reflecting cavity for photons belonging to the mode, which is consistent with the standing wave between the mirrors. The mirrors accomplish a feedback by reflecting the emitted photons back into the laser material and thus achieve a selective amplification in the mode for which the quality of the resonator is highest. Due to this selective feedback photons in different modes are not in equilibrium with each other and have different chemical potentials. In the mode which is amplified selectively, the emitted radiation is well approximated by a plane wave, which is known to carry no entropy. In this mode, $\mu_\gamma$ is very close to $\hbar\omega$. Although it appears that the expression for the entropy per photon in a cavity (58) is not valid for photon currents, its tendency towards zero for $\mu_\gamma \rightarrow \hbar\omega$ is as expected for the emission of laser radiation.

## 10. Conclusion

By introducing the chemical potential $\mu_\gamma$ of photons the thermodynamic treatment developed by Planck (1906) for thermal radiation is extended to radiation of any kind. As a result equation (16) gives the photon density per photon energy interval in equilibrium with a luminescing material and equation (27) gives the photon current density per photon energy interval emitted by a luminescing material. For the derivation of the thermodynamic relations a semiconductor was used as a model substance. A gap in the distribution of states in energy is recognised as a necessity for non-thermal radiation to occur. The results for the semiconductor model with its gap between conduction and valence bands may therefore easily be transferred to other systems with energy gaps as for example atoms and molecules in gas discharges and deep levels in metals involved in x-ray emission. The concept of a chemical potential $\mu_\gamma$ as the only thermodynamic quantity of relevance besides the real temperature makes use of internal thermal and chemical equilibria within subsystems like the electrons and the holes of a semiconductor. In systems where more than one electron subsystem and more than one hole subsystem are involved in emission processes more than one chemical potential might be necessary for the description of the emission spectrum, if there is insufficient entropy and particle exchange between the electron subsystems or the hole subsystems.

The theory presented is most powerful in describing the interaction of radiation with semiconductors. In this paper we have applied the formalism to the conversion of electrical energy, as the free energy of electron–hole pairs, into light emitted by luminescent diodes. The reverse process, the conversion of light into free energy of

electron–hole pairs and subsequently into electricity by solar cells has already been discussed (Ruppel and Würfel 1980).

## Acknowledgment

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