Light with nonzero chemical potential

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Thermodynamic states and processes involving light are discussed in which the chemical potential of light is nonzero. Light with nonzero chemical potential is produced in photochemical reactions, for example, in a light emitting diode. The chemical potential of black-body radiation becomes negative upon a Joule expansion. The isothermal diffusion of light, which is a common phenomenon, is driven by the gradient in the chemical potential. These and other examples support the idea that light can be interpreted as a gas of photons, with properties similar to a material gas. © *2005 American Association of Physics Teachers.*
[DOI: 10.1119/1.1904623]

I. INTRODUCTION

The thermodynamics of electromagnetic radiation is more than 100 years old. Planck[1] showed that the rules of thermodynamics, established by Clausius, Gibbs, and Thomson, apply to electromagnetic radiation in the same way as to a material gas. In particular, Planck introduced relations between the usual quantities of thermodynamics such as the energy, entropy, volume, temperature, and pressure. In addition, he treated processes with light that are commonly considered when discussing material gases, isothermal and isentropic expansion, as well as free (isoenergetic) expansion into vacuum. However, one of the relevant thermodynamic quantities is not found in Planck's work, the chemical potential μ, introduced by Gibbs in 1873.[2] The reason for Planck's omission is understandable, he discussed only black-body radiation, that is, states of light in which the chemical potential is zero. Planck did discuss the isoenergetic expansion of light, without realizing that the final state could be described by a nonzero chemical potential.[3] We will show that the expansion of light without the presence of a ''carbon particle'' as described by Planck leads to a state in which the temperature of the light is the same before and after the expansion, and the chemical potential is negative.

In typical undergraduate courses on thermodynamics the emphasis is on material gases. In spite of Planck's comprehensive work, light is rarely considered as a gas in much the same way as a material gas. There are several reasons to discuss the thermodynamics of light in addition to that of material ideal gases. Kelly reviewed the thermodynamic processes considered by Planck, derived expressions for quantities such as the heat capacity and compressibility, showed the validity of the third principle of thermodynamics, discussed the Carnot cycle with light as the medium, and stressed that students obtain a one-sided understanding if light is treated only in electrodynamics.[4] Lee pointed out that in addition to a material gas, light is another simple system for demonstrating the formalism of thermodynamics.[5] Leff emphasized that light is both a quantum mechanical and a relativistic system.[6]

In Refs. 1 and 4–8, only states of light are discussed for which the chemical potential of the photons is zero. The similarity of the treatment of a material gas and a photon gas would, however, be more apparent if states are included in which the chemical potential is nonzero,[9–12] and processes are discussed in which the chemical potential is changed. In Sec. II, states of nonzero chemical potential are treated in general terms. In Sec. III we discuss the chemical equilibrium between electromagnetic radiation and the electron-hole gas of a semiconductor diode. The change of the chemical potential in a Joule expansion of light is considered in Sec. IV, and in Sec. V we discuss the isothermal diffusive flow of light.

II. THE CHEMICAL POTENTIAL OF PHOTONS

Several arguments are generally given to show that the chemical potential of light is always zero. All of them are based on the fact, that photons are easily created and annihilated. The essence of the reasoning is that ''...the absence of a conservation law for photons leads to a zero value for the chemical potential.''[7]

However, a thermodynamic treatment of light based on zero chemical potential is correct only for light from incandescent sources. It does not apply to light from sources such as gas discharges, TV screens, light emitting diodes, and lasers. Moreover, nonconservation of particle number by itself is not an argument for a zero chemical potential, because nonconservation of particles is not restricted to photons. For example, consider the reaction

$$2H_2 + O_2 \rightleftharpoons 2H_2O. \tag{1}$$

Although the particle numbers are not conserved, the chemical potentials of the three substances are nonzero. For chemical equilibrium, the chemical potential of water, μ_{H_2O}, is determined by the chemical potential of hydrogen, μ_{H_2}, and oxygen, μ_{O_2}, because

$$2\mu_{H_2} + \mu_{O_2} = 2\mu_{H_2O}. \tag{2}$$

In other words, the chemical potentials of the products adjust to those of the reactants. The same applies to photons. They are created or annihilated in ''reactions'' involving the excitations of matter, such as phonons and electron-hole pairs. The excitations of matter must be involved because although particle number is not conserved, the photon momentum and angular momentum are conserved, which does not allow an unrestricted variation of the photon number. This conservation leads to the well known selection rules for the interac-

tions of photons with the excitations of matter. The photons derive their temperature and chemical potential from these interactions.

States with nonzero chemical potential of the photons, μ_γ, can be realized in two ways. In one way, the light is the result of a photochemical reaction. If the light is in chemical equilibrium with the excitations of matter whose chemical potential is nonzero, for example, the electron-hole pairs in a light emitting diode (LED), then the chemical potential of the light is nonzero as well.

From the chemical reaction of an electron e with a hole h to produce a photon γ,

$$e+h \rightleftharpoons \gamma, \tag{3}$$

it follows that

$$dn_\gamma = -dn_e = -dn_h. \tag{4}$$

For the minimum of the free energy we have

$$\mu_e \, dn_e + \mu_h \, dn_h + \mu_\gamma \, dn_\gamma = 0. \tag{5}$$

By using Eq. (1) we obtain

$$\mu_\gamma = \mu_e + \mu_h. \tag{6}$$

(The sum $\mu_e + \mu_h$ is the difference $\varepsilon_{FC} - \varepsilon_{FV}$ of the quasi-Fermi energies of the electrons in the conduction band and holes in the valence bands, respectively.[10,12])

Another way to realize a nonzero chemical potential is by a thermodynamic process. We start with photons with $\mu_\gamma = 0$ and change the chemical potential in a thermodynamic process. The resulting state with $\mu_\gamma \neq 0$ is preserved as long as the photons do not interact with excitations of matter having zero chemical potential, that is, as long as they are not absorbed.

We recall how the Planck distribution is affected by a nonzero chemical potential:[9,10,12]

$$\frac{d\rho}{d\omega} = \frac{\hbar\omega^3}{\pi^2 c^3} \frac{1}{\left[e^{\beta(\hbar\omega - \mu_\gamma)} - 1 \right]}, \tag{7}$$

where $d\rho/d\omega$ is the energy density per frequency interval and $\beta = 1/kT$. All the other symbols have their usual meaning. Equation (7) is a generalization of Planck's radiation law. The chemical potential μ_γ appears, in addition to the temperature T, as a second parameter in the same way as for other bosons, for example, ^{4}He. Figure 1 shows three spectra of thermal radiation. Curves (a) and (b) correspond to the chemical potential $\mu_\gamma = 0$, but the temperature of (b) is lower than that of (a). Curves (a) and (c) correspond to the same temperature, but to different chemical potentials. The chemical potential of (c) is negative. Note that different values of the chemical potential mainly affect the magnitude of the spectral energy density, but leave the shape of the spectrum essentially unaltered.

If we neglect the term -1 in the denominator of Eq. (7), it simplifies to

$$\frac{d\rho}{d\omega} \approx \frac{\hbar\omega^3}{\pi^2 c^3} e^{-\beta(\hbar\omega - \mu_\gamma)} = a\omega^3 e^{-\beta\hbar\omega} e^{\beta\mu_\gamma}, \tag{8}$$

where $e^{\beta\mu_\gamma}$ appears as a scaling factor. Except for this factor, Eq. (8) is Wien's radiation law.[13] In Eq. (8), the energy density per frequency interval (or the number of photons) increases at each frequency by the same factor when the chemical potential is increased. This approximation trans-
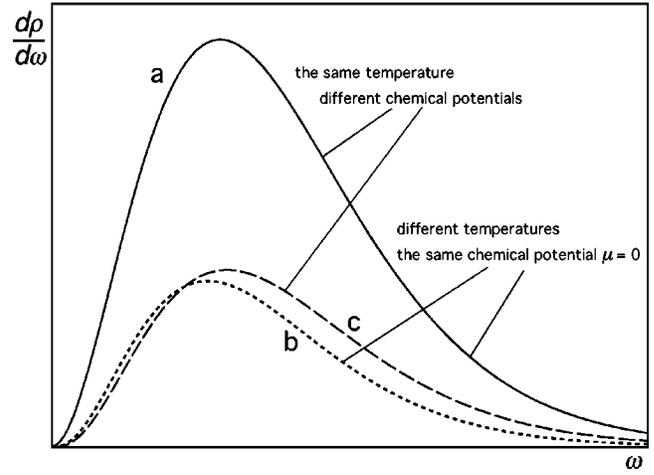

Fig. 1. The influence of the temperature and the chemical potential on the spectrum of light. The continuous and the dotted line correspond to zero chemical potential. The continuous and the broken line correspond to the same temperature.

forms the Bose distribution into the Boltzmann distribution. All the equations derived in the following are correct within this approximation. (Einstein used Wien's law as an approximation when he proved the existence of the photons,[14] although Planck's law was already known to him.)

For photons with nonzero chemical potential, Eq. (8) is valid for states with $\hbar\omega - \mu_\gamma > kT$. A spectrum containing all photon energies can therefore have only a negative chemical potential. A positive chemical potential must be restricted to a photon energy range $\hbar\omega > \mu_\gamma + kT$. In textbooks, the chemical potential of a system of bosons is shown to be negative, because the zero of the chemical potential scale is assumed to coincide with the origin of the kinetic energy. If the origin of the chemical potential scale is taken to be the origin of the total energy, as in our case for photons, then the chemical potential can have positive values as well, but must be smaller than the total energy. This restriction holds for LEDs. Their emission spectrum contains only photons with energies larger than the band gap of the LED.

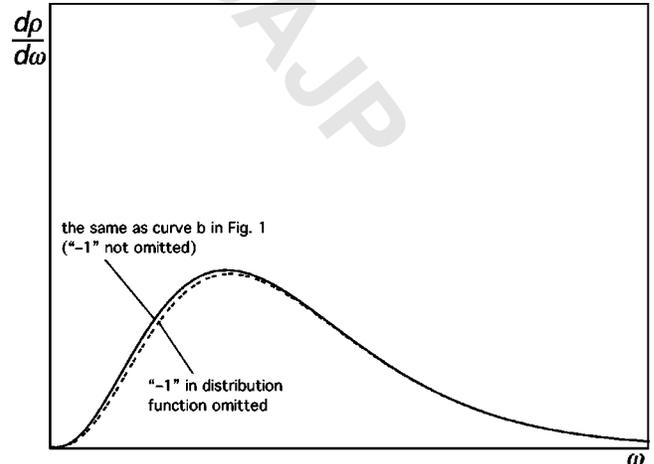Figure 2 illustrates the error that is caused by neglecting

Fig. 2. The neglect of -1 in the distribution function causes only minor changes in the spectrum.

the term -1 in the denominator of Eq. (7). From Eq. (8), the energy density is obtained by integrating over the frequency,

$$\rho(\mu_\gamma) = a e^{\beta\mu_\gamma} \int \omega^3 e^{-\beta\hbar\omega} \, d\omega. \tag{9}$$

If we express the energy density $\rho(\mu_\gamma)$ in terms of the energy density ρ_0 of a photon gas with $\mu_\gamma = 0$, we obtain

$$\rho(\mu_\gamma) = \rho_0 e^{\beta\mu_\gamma}. \tag{10}$$

Because the pressure is proportional to the energy density, a similar relation holds for the pressure,

$$p(\mu_\gamma) = p_0 e^{\beta\mu_\gamma}. \tag{11}$$

We solve for the chemical potential in Eq. (11) and find

$$\mu_\gamma(p) = kT \ln\left(\frac{p}{p_0}\right), \tag{12}$$

where p_0 is the pressure of a photon gas with $\mu_\gamma = 0$. The counterpart of Eq. (12) for a material ideal gas is[15]

$$\mu(p) - \mu(p_0) = kT \ln\left(\frac{p}{p_0}\right). \tag{13}$$

In contrast to Eq. (12), Eq. (13) does not allow us to calculate the absolute value of $\mu(p)$ for a given pressure p, but only the deviation from the chemical potential $\mu(p_0)$ for the reference pressure p_0. Equation (13) is valid for light as well, if the state with $\mu_\gamma = 0$ is taken as the reference. (In general, such a choice cannot be made for a material gas.)

III. THE PHOTON GAS IN CHEMICAL EQUILIBRIUM WITH AN ELECTRON–HOLE GAS

When a chemical reaction is in chemical equilibrium, the sum of the chemical potentials of the substances on the left-hand side of the reaction equation is equal to the sum of the right-hand side potentials. In an LED an electron e and a hole h recombine to produce a photon γ, or they are generated when a photon is absorbed as in Eq. (3). If the absorptivity of the light emitting layer is close to one, emission and reabsorption processes are frequent, and thus the reaction is in chemical equilibrium and Eq. (6) holds. For an LED with no series resistance, the sum of the chemical potentials, $\mu_e + \mu_h$, and the difference of the quasi-Fermi energies $\varepsilon_{FC} - \varepsilon_{FV}$, is related to the voltage V between the terminals of the LED by

$$\varepsilon_{FC} - \varepsilon_{FV} = \mu_e + \mu_h = \mu_\gamma = eV. \tag{14}$$

It might be argued that applying a voltage and having a current is not consistent with the concept of equilibrium. In fact, equilibrium relations are valid as long as the equilibrium exchange rates are much larger than the disturbing rates. An equilibrium description as in Eq. (3) is based on well-defined Fermi distributions for the electrons in the conduction band and for the holes in the valence band, a very good approximation in LEDs.

The light emitted by an LED is known as luminescent radiation. Figure 3(a) shows the idealized absorptivity, $a(\hbar\omega)$, of a thick semiconductor, which, according to Kirchhoff, is equal to its emissivity. Photons with $\hbar\omega < \varepsilon_G$, the band gap of the LED, cannot be absorbed by generating electron–hole pairs resulting in $a(\hbar\omega < \varepsilon_G) = 0$, whereas all photons with $\hbar\omega > \varepsilon_G$ are absorbed resulting in $a(\hbar\omega$
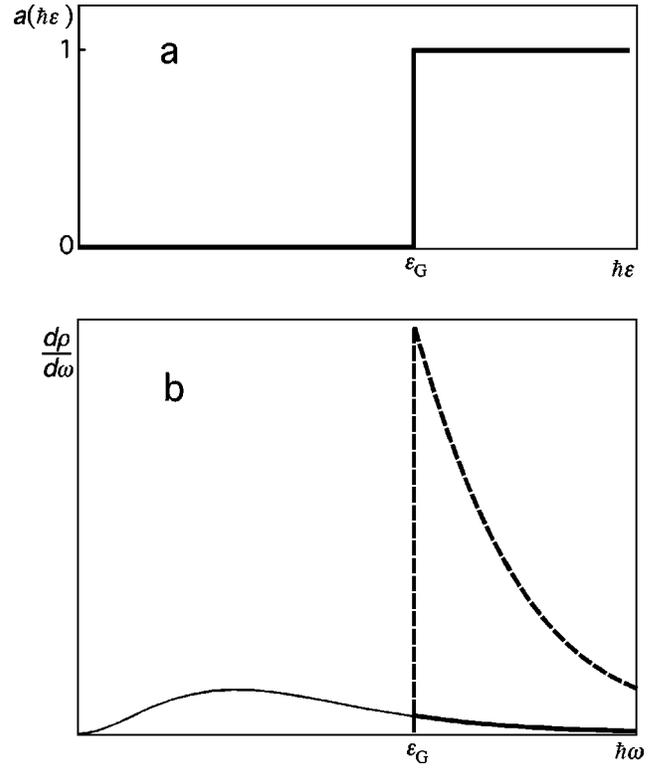

Fig. 3. (a) Idealized absorptivity $a(\hbar\omega)$ of a thick semiconductor. (b) The thin line is the black-body spectrum for $T = 300$ K and $\mu_\gamma = 0$. The thick line represents the part of the black-body spectrum that is emitted by an LED in equilibrium with its 300 K surroundings. The broken line shows schematically the emission spectrum of the LED when a voltage is applied. (For clarity, the gap energy ε_G in the figure is assumed to be much smaller than it really is.)

$> \varepsilon_G) = 1$. The thin line in Fig. 3(b) is the black-body spectrum with $T = 300$ K and $\mu_\gamma = 0$, and the thick solid line is the part of the black-body spectrum that the LED absorbs and emits in equilibrium with the 300 K surroundings when no voltage is applied to the LED. The emission spectrum with an applied voltage, that is, for $\mu_\gamma > 0$, has the same shape as for $\mu_\gamma = 0$, but it is much more intense as shown by the broken line in Fig. 3(b). If a potential difference of 1 V is applied, the intensity is increased by a factor of $\exp(1 \text{ eV}/kT) = 5 \times 10^{16}$.

From Eq. (7) it can be seen that, although there is no lower bound, the chemical potential cannot be higher than the smallest photon energy of the corresponding spectrum. Otherwise, a negative energy density would result. Therefore, radiation with a positive chemical potential cannot contain all photon energies. It can exist only above the energy threshold. Atoms, molecules, and semiconductors, which are able to emit luminescent radiation, are characterized by such a threshold.

IV. JOULE EXPANSION

In Refs. 1, 4, and 5 isothermal and isentropic processes are discussed with light. Kelly[4] and Planck[1] considered isoenergetic expansion into the vacuum, known as Joule expansion. To ensure that the light is black-body radiation with $\mu_\gamma = 0$ before and after the expansion, Planck employed his famous black dust particle. The particle is assumed to be so small that its entropy can be neglected with respect to that of the
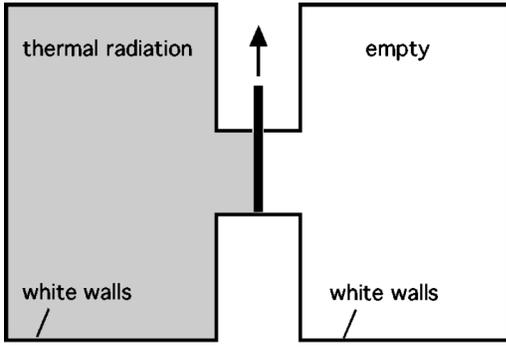
Fig. 4. Joule experiment with black-body radiation. The white walls of the container guarantee the isotropy of the radiation at any time.

radiation. The black particle serves two purposes in the expansion process: It ensures that the spectral distribution of the light remains a black-body spectrum, and it ensures that the light remains isotropic.

Because we want the chemical potential to be nonzero, we realize the expansion without Planck's dust particle, which would fix the chemical potential at its black-body value of zero. To make sure that the light is isotropic after the expansion, we assume the walls of the container to be perfectly white. As mentioned in Sec. I, Planck[3] discussed such a process, without realizing that the final state could be described by a nonzero chemical potential.

In the following, values in the initial state have the index 0, and the final state has index 1. For comparison, we first consider a material gas. After the expansion, the temperature has the same value as before, while the pressure and chemical potential have decreased. From the equation of state we obtain

$$p_1 = \frac{V_0}{V_1} p_0, \tag{15}$$

and Eq. (13) becomes

$$\mu(p_1) - \mu(p_0) = kT \ln\left(\frac{p_1}{p_0}\right). \tag{16}$$

Thus, when the volume increases by a factor of 2, the pressure is reduced to half of its initial value and the chemical potential decreases by $kT \ln 2$.

We now realize the expansion with electromagnetic radiation, as shown in Fig. 4. Initially, the left compartment has been filled with black-body radiation with $\mu_\gamma = 0$. Because this radiation is isotropic, its state remains unaltered by scattering of the photons with the white walls of the compartment. The right compartment is empty, that is, it contains no radiation. When the partition between the two compartments is removed, the light is diluted by a factor of V_0/V_1. Therefore, its spectral energy density for all photon energies is reduced by the same factor for all photon energies, and the distribution of the photons is still isotropic. The pressure is reduced in the same way as it would be for a material gas

$$p_1 = \frac{V_0}{V_1} p_0. \tag{17}$$

Likewise, according to Eq. (12), the change of the chemical potential is the same as for a material gas,

$$\mu_\gamma(p_1) = kT \ln\left(\frac{p_1}{p_0}\right). \tag{18}$$

It is seen that for light, as well as for a material gas, the chemical potential is reduced by free expansion. Because we started with black-body radiation with $\mu_\gamma = 0$, the chemical potential becomes negative upon expansion.

For light, the isoenergetic expansion can be followed by another irreversible process: We just have to add Planck's black dust particle. The chemical potential of the light will now go to zero, while the temperature decreases and the photon number increases. At the end, the photon gas is in the same state as if the light had been in Planck's version of the experiment with the black particle present all the time.

The temperature change is found by taking into account that the energy of the photon gas does not change during the expansion. Because the energy density of black-body radiation is proportional to T^4, we obtain,

$$V_0 T_0^4 = V_1 T_1^4, \tag{19}$$

from which the final temperature is obtained,

$$T_1 = T_0 \left(\frac{V_0}{V_1}\right)^{1/4}. \tag{20}$$

V. DIFFUSIVE FLOW OF LIGHT

In Sec. IV we considered the expansion of a well-defined amount of black-body radiation. However, the expansion process also can be considered as a continuous flow. We consider here the isothermal flow of light, which can be realized when light propagates through a medium that is scattering but not absorbing. An example is diffuse light, incident onto a cloud from above. When penetrating into the cloud, the photons are multiple scattered. Some of them return to the upper surface and escape. Others reach the lower surface. As a result, the photon density decreases from the upper to the lower surface of the cloud. With increasing depth, the spectral intensity decreases by the same factor at all photon energies. As a result, the temperature of the light remains constant, but its pressure and chemical potential decrease.

Again, we see that light behaves like a material gas, molecules flow, at constant temperature, from a location of high pressure to one of low pressure or, correspondingly, from high to small chemical potential. A further realization of the isothermal flow of light has been discussed in Ref. 16 in which light diffuses through a pipe, whose walls are perfectly white on the inside.

These examples can be viewed in the same way as the flow of a material gas through a resistive pipe: A gradient of the chemical potential is considered to be the cause or the ''driving force'' of a diffusive flow.[7,17] As long as no other driving forces are present, a substance diffuses from high to low values of the chemical potential.[18]

Finally, we mention another flow process that can be realized with light: A diffusive flow that is driven by a temperature gradient, while the gradient of the chemical potential is zero. This flow corresponds to the expansion discussed in the preceding paragraph, when a black dust particle is present. In this case the light remains black-body radiation, but it propagates from higher to lower temperature. Such a flow is realized in the interior of stars and is the dominant energy transport mechanism when no convection takes place. In the sun,

the heat flow is convective only in the outer 10% of the radius. In the remaining inner 90%, a diffusive flow of light with zero chemical potential is driven by a temperature gradient.

VI. SUMMARY

States of light and processes involving light have been discussed in which the chemical potential of the photons is nonzero. Light can be produced directly with nonzero chemical potential by making use of chemical equilibrium with excitations of matter. If the chemical potential of the excitations is nonzero, then the chemical potential of the emitted light is nonzero as well. In these cases, the light has a temperature not far from room temperature, and its chemical potential is greater than zero. Another way to obtain a nonzero chemical potential is to consider the expansion of blackbody radiation, that is, light with $\mu_\gamma = 0$, in which the number of the photons in any spectral interval is kept constant while the concentration decreases. The chemical potential of the resulting light is less than zero. An example of such a process is scattering without absorption (elastic scattering). The introduction of the chemical potential as a nontrivial thermodynamic variable of light enables us to characterize not only black-body radiation, but also other common types of radiation, such as diffuse white light or luminescent light.

For the approximations we have made, the pressure dependence of the chemical potential in a Joule expansion is the same as for the isoenergetic expansion of a material gas. An isothermal diffusive flow of light is driven by a gradient of the chemical potential in the same way as the flow of a material gas. This close correspondence can help students to understand the similarity between a photon and a material gas.

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[17] G. Job, *Neudarstellung der Wärmelehre* (Akademische Verlagsgesellschaft, Frankfurt, 1972), p. 117.

[18] The gradient of the concentration often is considered to be the cause or "driving force" of diffusive flow. This interpretation is possible only if the chemical potential depends monotonically on the concentration. It does not work if the transport crosses a phase interface. There the chemical potential is indispensable.