

where $N_0(T)$ is given by (62.1). Expanding the integrand and using the fact that μ is small near the point $T = T_0$, and therefore the important part of the integral arises from the region where ε is small, we find that the integral is equal to

$$T\mu \int_0^\infty \frac{d\varepsilon}{\sqrt{\varepsilon(\varepsilon + |\mu|)}} = -\pi T \sqrt{|\mu|}. \quad (1)$$

Substituting this value and then expressing μ in terms of $N - N_0$, we have

$$-\mu = \frac{2\pi^2 \hbar^6}{g^2 m^3} \left(\frac{N_0 - N}{TV} \right)^2.$$

To the same accuracy we can write

$$\frac{\partial E}{\partial \mu} = -\frac{3}{2} \frac{\partial \Omega}{\partial \mu} = \frac{3}{2} N \cong \frac{3}{2} N_0,$$

whence

$$E = E_0 + \frac{3}{2} N_0 \mu = E_0 - \frac{3\pi^2 \hbar^6}{g^2 m^3} N_0 \left(\frac{N_0 - N}{TV} \right)^2,$$

where $E_0 = E_0(T)$ denotes the energy for $\mu = 0$, i.e. the function (62.5). The second derivative of the second term with respect to temperature will clearly give the required discontinuity. The result of the calculation is

$$\Delta \left(\frac{\partial C_v}{\partial T} \right)_V = -\frac{6\pi^2 \hbar^6}{g^2 m^3 V^2} \left[N_0 \left(\frac{1}{T} \frac{\partial N_0}{\partial T} \right)^2 \right]_{T=T_0} = -3.66 N/T_0. \quad (2)$$

The value of the derivative $(\partial C_v / \partial T)_V$ for $T = T_0 - 0$ is, from (62.5), $+2.89 N/T_0$, and for $T = T_0 + 0$ it is therefore $-0.77 N/T_0$.

§ 63. Black-body radiation

The most important application of Bose statistics relates to electromagnetic radiation which is in thermal equilibrium—called *black-body radiation*. Such radiation may be regarded as a gas consisting of photons. The linearity of the equations of electrodynamics expresses the fact that photons do not interact with one another (the principle of superposition for the electromagnetic field), so that the photon gas is an ideal gas. Because the angular momentum of the photons is integral, this gas obeys Bose statistics.

If the radiation is not in a vacuum but in a material medium, the condition for an ideal photon gas requires also that the interaction between radiation and matter should be small. This condition is satisfied in gases throughout the radiation spectrum except for frequencies in the neighbourhood of absorption lines of the material, but at high densities of matter it may be violated except at very high temperatures.

It should be remembered that at least a small amount of matter must be present if thermal equilibrium is to be reached in the radiation, since the interaction between the photons themselves may be regarded as completely absent.[†] The mechanism by which equilibrium can be established consists in the absorption and emission of photons by matter. This results in an important specific property of the photon gas: the number of photons N in it is variable, and not a given constant as in an ordinary gas. Thus N itself must be determined from the conditions of thermal equilibrium. From the condition that the free energy of the gas should be a minimum (for given T and V), we obtain as one of the necessary conditions $\partial F/\partial N = 0$. Since $(\partial F/\partial N)_{T,V} = \mu$, this gives

$$\mu = 0, \quad (63.1)$$

i.e. the chemical potential of the photon gas is zero.

The distribution of photons among the various quantum states with definite values of the momentum $\hbar\mathbf{k}$ and energies $\varepsilon = \hbar\omega = \hbar ck$ (and definite polarisations) is therefore given by formula (54.2) with $\mu = 0$:

$$\bar{n}_{\mathbf{k}} = 1/(e^{\hbar\omega/T} - 1). \quad (63.2)$$

This is called *Planck's distribution*.

Assuming that the volume is sufficiently large, we can make the usual change (see *Fields*, § 52) from the discrete to the continuous distribution of eigenfrequencies of the radiation. The number of modes of oscillation for which the components of the wave vector $\mathbf{k}$ lie in the intervals $d^3k = dk_x dk_y dk_z$ is $V d^3k/(2\pi)^3$, and the number of modes for which the absolute magnitude of the wave vector lies in the range dk is correspondingly $V \cdot 4\pi k^2 dk/(2\pi)^3$. Using the frequency $\omega = ck$ and multiplying by 2 (for the two independent directions of polarisation of the oscillations), we obtain the number of quantum states of photons with frequencies between ω and $\omega + d\omega$:

$$V\omega^2 d\omega/\pi^2 c^3. \quad (63.3)$$

Multiplying the distribution (63.2) by this quantity, we find the number of photons in this frequency interval:

$$dN_\omega = \frac{V}{\pi^2 c^3} \frac{\omega^2 d\omega}{e^{\hbar\omega/T} - 1}, \quad (63.4)$$

and a further multiplication by $\hbar\omega$ gives the radiation energy in this segment of the spectrum:

$$dE_\omega = \frac{V\hbar}{\pi^2 c^3} \frac{\omega^3 d\omega}{e^{\hbar\omega/T} - 1}. \quad (63.5)$$

[†] Apart from the entirely negligible interaction (the scattering of light by light) which is due to the possible production of virtual electron-positron pairs.

This formula for the spectral energy distribution of black-body radiation is called *Planck's formula*.[†] In terms of the wavelength $\lambda = 2\pi c/\omega$, it becomes

$$dE_\lambda = \frac{16\pi^2 c \hbar V}{\lambda^5} \frac{d\lambda}{e^{2\pi \hbar c / T \lambda} - 1}. \quad (63.6)$$

At low frequencies ($\hbar\omega \ll T$), formula (63.5) gives

$$dE_\omega = V(T/\pi^2 c^3) \omega^2 d\omega. \quad (63.7)$$

This is the *Rayleigh-Jeans formula*. It should be noticed that formula (63.7) does not contain the quantum constant $\hbar$, and can be derived by multiplying by T the number of modes (63.3); in this sense it corresponds to classical statistics, in which an energy T must correspond to each “vibrational degree of freedom”—the law of equipartition (§ 44).

In the opposite limiting case of high frequencies ($\hbar\omega \gg T$), formula (63.5) becomes

$$dE_\omega = V(\hbar/\pi^2 c^3) \omega^3 e^{-\hbar\omega/T} d\omega. \quad (63.8)$$

This is *Wien's formula*.

Figure 7 shows a graph of the function $x^3/(e^x - 1)$, corresponding to the distribution (63.5).

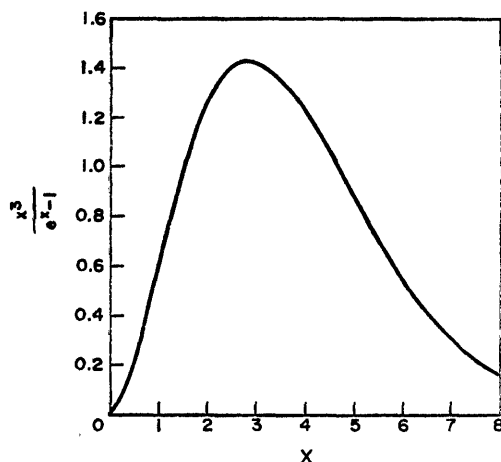


FIG. 7

The density of the spectral frequency distribution of the energy of black-body radiation, $dE_\omega/d\omega$, has a maximum at a frequency ω_m given by

$$\hbar\omega_m/T = 2.822. \quad (63.9)$$

[†] The discovery of this law by M. Planck (1900) was the foundation of the quantum theory.

Thus, when the temperature rises, the position of the maximum of the distribution is displaced towards higher frequencies in proportion to T (the *displacement law*).[†]

Let us calculate the thermodynamic quantities for black-body radiation. For $\mu = 0$, the free energy is the same as Ω (since $F = \Phi - PV = N\mu + \Omega$). According to formula (54.4), in which we put $\mu = 0$ and change in the usual way (by means of (63.3)) from summation to integration, we obtain

$$F = T \frac{V}{\pi^2 c^3} \int_0^\infty \omega^2 \log(1 - e^{-\hbar\omega/T}) d\omega. \quad (63.10)$$

With the new variable of integration $x = \hbar\omega/T$, integration by parts gives

$$F = -V \frac{T^4}{3\pi^2 \hbar^3 c^3} \int_0^\infty \frac{x^3 dx}{e^x - 1}.$$

The integral is equal to $\pi^4/15$ (see the second footnote to § 58). Thus

$$\begin{aligned} F &= -V \cdot \pi^2 T^4 / 45 (\hbar c)^3 \\ &= -4\sigma V T^4 / 3c. \end{aligned} \quad (63.11)$$

If T is measured in degrees, the coefficient σ (called the *Stefan-Boltzmann constant*) is

$$\begin{aligned} \sigma &= \pi^2 k^4 / 60 \hbar^3 c^2 \\ &= 5.67 \times 10^{-5} \text{ g/sec}^3 \text{ deg}^4. \end{aligned} \quad (63.12)$$

The entropy is

$$S = -\partial F / \partial T = 16\sigma V T^3 / 3c, \quad (63.13)$$

and is proportional to the cube of the temperature. The total radiation energy $E = F + TS$ is

$$E = 4\sigma V T^4 / c = -3F. \quad (63.14)$$

This expression could, of course, be derived also by direct integration of the distribution (63.5). Thus the total energy of black-body radiation is proportional to the fourth power of the temperature. This is *Boltzmann's law*.

For the specific heat of the radiation C_v we have

$$C_v = (\partial E / \partial T)_V = 16\sigma T^3 V / c. \quad (63.15)$$

[†] The wavelength distribution density $dE_\lambda/d\lambda$ also has a maximum, but at a different value of the corresponding ratio: $2\pi\hbar c/T\lambda_m = 4.965$. Thus the maximum λ_m of the wavelength distribution is displaced in inverse proportion to the temperature.