CHAPTER 12

RADIATION

§12.01 *General considerations*

There are several alternative ways of approach to the thermodynamics of radiation. We shall choose the one according to which the radiation is regarded as a collection of photons. Each photon is characterized by a frequency, a direction of propagation, and a plane of polarization. In empty space all photons have equal speeds c. Each photon has an energy U_i related to its frequency ν_i by Planck's relation

$$U_i = h\nu_i \qquad 12.01.1$$

and a momentum of magnitude $h\nu_i/c$. It is convenient to group together all the species of photons having equal frequencies, and so equal energies, but different directions of propagation and planes of polarization. We denote by g_i the number of distinguishable kinds of photons having frequencies ν_i and energies U_i. More precisely $g_i \mathrm{d}\nu_i$ denotes the number of distinguishable kinds of photons having frequencies between ν_i and $\nu_i + \mathrm{d}\nu_i$ and energies between U_i and $U_i + \mathrm{d}U_i$. By purely geometrical considerations it can be shown* that in an enclosure of volume V

$$g_i \mathrm{d}\nu_i = 2 \times 4\pi V c^{-3} \nu_i^2 \mathrm{d}\nu_i \qquad 12.01.2$$

the factor 2 being due to the two independent planes of polarization.

§12.02 *Energy and entropy in terms of g_i's*

We denote by N_i the number of photons having energy U_i and frequency ν_i interrelated by (12.01.1). Then the total energy U is given by

$$U = \sum_i N_i U_i. \qquad 12.02.1$$

* Brillouin, Die Quantenstatistik, Springer 1931 ch. 2; Fowler and Guggenheim, Statistical Thermodynamics, Cambridge University Press 1939 §§ 401–403.

From the fact that photons obey Bose–Einstein statistics it can be shown* that the entropy S of the system is given by

$$S/k=\sum_i \ln\{(g_i+N_i)!/g_i!\,N_i!\}. \qquad 12.02.2$$

Differentiating (1) and (2) at constant g_i, that is to say constant V, we have

$$\mathrm{d}U=\sum_i U_i \mathrm{d}N_i \qquad 12.02.3$$

$$\mathrm{d}S/k=\sum_i \ln\{(g_i+N_i)/N_i\}\mathrm{d}N_i. \qquad 12.02.4$$

The condition for equilibrium is according to (1.35.1) that S should be a maximum for given U, V. Hence for the most general possible variation, the expressions (3) and (4) must vanish simultaneously. It follows that

$$U_i/\ln\{(g_i+N_i)/N_i\}=U_k/\ln\{(g_k+N_k)/N_k\} \quad (\text{all } i, k) \qquad 12.02.5$$

and consequently using (3) and (4)

$$U_i/\ln\{(g_i+N_i)/N_i\}=\sum_i U_i \mathrm{d}N_i/\sum_i \ln\{(g_i+N_i)/N_i\}\mathrm{d}N_i$$

$$=k\mathrm{d}U/\mathrm{d}S=kT \qquad 12.02.6$$

since at constant volume

$$\mathrm{d}U=T\mathrm{d}S \qquad (V \text{ const.}). \qquad 12.02.7$$

From (6) we have

$$N_i/(g_i+N_i)=\exp(-U_i/kT) \qquad 12.02.8$$

and so

$$N_i=g_i/\{\exp(U_i/kT)-1\}. \qquad 12.02.9$$

Substituting (9) into (1), we obtain

$$U=\sum_i g_i U_i/\{\exp(U_i/kT)-1\}. \qquad 12.02.10$$

For the entropy we obtain from (2), using Stirling's approximation for the factorials, and by use of (8)

$$S=\sum_i N_i \ln\{(g_i+N_i)/N_i\}+\sum_i g_i \ln\{(g_i+N_i)/g_i\}$$

$$=\sum_i N_i U_i/kT-\sum_i g_i \ln\{1-\exp(-U_i/kT)\}. \qquad 12.02.11$$

For the Helmholtz function $Æ$ we deduce from (1) and (11)

$$Æ=kT\sum_i g_i \ln\{1-\exp(-U_i/kT)\}. \qquad 12.02.12$$

* Brillouin, Die Quantenstatistik, Springer 1931 ch. 6.

§12.03 *Thermodynamic functions*

In the previous section we obtained formulae for the energy, the entropy, and the Helmholtz function in terms of the U_i's and g_i's without making any use of (12.01.1) or (12.01.2). If we now substitute the values of U_i and g_i, given by these formulae, into the relations of the previous section we obtain

$$\mathcal{F} = 8\pi V c^{-3} kT \int_0^\infty \ln\{1 - \exp(-h\nu/kT)\}\nu^2\,\mathrm{d}\nu \qquad 12.03.1$$

$$U = 8\pi V c^{-3} \int_0^\infty h\nu^3\{\exp(h\nu/kT) - 1\}^{-1}\,\mathrm{d}\nu. \qquad 12.03.2$$

We can write (2) in the form

$$U = \int_0^\infty U_\nu\,\mathrm{d}\nu \qquad 12.03.3$$

$$U_\nu = 8\pi V c^{-3} h\nu^3\{\exp(h\nu/kT) - 1\}^{-1} \qquad 12.03.4$$

which is *Planck's formula* from which quantum theory originated.

§12.04 *Evaluation of integrals*

We can rewrite (12.03.1) as

$$\mathcal{F} = -8\pi V k^4 T^4 h^{-3} c^{-3} I \qquad 12.04.1$$

where I is the integral defined by

$$I \equiv -\int_0^\infty \xi^2 \ln\{1 - \exp(-\xi)\}\mathrm{d}\xi. \qquad 12.04.2$$

Using the power series for the logarithm and then integrating term by term, we obtain

$$I = \int_0^\infty \sum_{n=1}^\infty n^{-1}\xi^2 \exp(-n\xi)\mathrm{d}\xi = \sum_{n=1}^\infty n^{-4} \int_0^\infty \eta^2 \exp(-\eta)\mathrm{d}\eta$$

$$= 2\sum_{n=1}^\infty n^{-4} = \pi^4/45. \qquad 12.04.3$$

Substituting (3) into (1) we obtain finally

$$\mathcal{F} = -(8\pi^5 k^4/45c^3h^3)T^4 V. \qquad 12.04.4$$

§12.05 *Stefan–Boltzmann law*

We could obtain formulae analogous to (12.04.4) for U and S by evaluation of the relevant integrals, but it is more convenient to obtain these formulae by differentiation of (12.04.4).

We first abbreviate (12.04.4) to

$$\mathcal{F} = -\tfrac{1}{3}aT^4V \qquad 12.05.1$$

where a is a universal constant defined by

$$a = 8\pi^5k^4/15c^3h^3 = 7.5646\times10^{-16}\ \mathrm{J\ m^{-3}\ K^{-4}}. \qquad 12.05.2$$

From (1) we deduce immediately

$$S = \tfrac{4}{3}aT^3V \qquad 12.05.3$$

$$U = aT^4V \qquad 12.05.4$$

$$P = \tfrac{1}{3}aT^4 = \tfrac{1}{3}U/V \qquad 12.05.5$$

$$G = U - TS + PV = 0. \qquad 12.05.6$$

Formula (5) can be derived from classical electromagnetic theory. Formula (4) was discovered by Stefan and derived theoretically by Boltzmann. It is called the *Stefan–Boltzmann law.*

From (4) we see that aT^4 is the equilibrium value of the radiation per unit volume in an enclosure. If a small hole is made in such an enclosure then it can be shown by geometrical considerations that the radiation emitted through the hole per unit area and per unit time is σT^4, where σ is given by

$$\sigma = \tfrac{1}{4}ac = 5.670\times10^{-8}\ \mathrm{J\ m^{-2}\ s^{-1}\ K^{-4}} \qquad 12.05.7$$

in which c denotes the speed of light. This constant σ is called the *Stefan–Boltzmann constant.*

§12.06 *Adiabatic changes*

Suppose that radiation is confined by perfectly reflecting walls and that the volume of the container is altered by moving a piston. If the radiation remains in thermal equilibrium its temperature will change. For such a reversible adiabatic change, we have

$$S = \text{const.} \qquad 12.06.1$$

From (12.05.3) and (1) it follows that

$$VT^3 = \text{const.} \qquad \text{(adiabatic).} \qquad 12.06.2$$

From (12.05.4) and (12.05.5) we have

$$P/T^4 = \text{const.} \qquad 12.06.3$$

so that

$$PV/T = \text{const.} \qquad \text{(adiabatic)} \qquad 12.06.4$$

and

$$PV^{\frac{4}{3}} = \text{const.} \qquad \text{(adiabatic).} \qquad 12.06.5$$

From (2), (3), (4), (5) it appears that the relations for a reversible adiabatic change in radiation are formally similar to those for a perfect gas such that the ratio C_P/C_V has the constant value $\frac{4}{3}$. This apparent resemblance is however accidental, for the ratio C_P/C_V of radiation is not $\frac{4}{3}$. In fact for radiation

$$C_V = (\partial U/\partial T)_V = T(\partial S/\partial T)_V = 4aT^3V \qquad 12.06.6$$

while

$$C_P = T(\partial S/\partial T)_P \rightarrow \infty \qquad 12.06.7$$

since no increase in S, however great, can increase T without increasing P.