

Consider a gas at temperature  $T$ . Let  $N$  be the number of gas molecules and let  $N_n$  be the number of molecules with energy  $E_n$ . By the Maxwell-Boltzmann distribution we have

$$\frac{N_n}{N} = p_n \exp\left(-\frac{E_n}{kT}\right) \quad (1)$$

Coefficient  $p_n$  is a statistical weighting factor that does not depend on  $T$ .

Let us now consider the processes by which an atom or molecule transitions between energy levels. The processes are absorption, induced emission, and spontaneous emission. Let  $E_m$  and  $E_n$  be energy levels such that  $E_m > E_n$ . Let  $N_{m \rightarrow n}/\Delta t$  be the number of atoms or molecules that transition from energy level  $E_m$  to  $E_n$  in time  $\Delta t$ . Finally, let  $B_{nm}$ ,  $B_{mn}$ , and  $A_{mn}$  be coefficients such that

$$\frac{N_{n \rightarrow m}}{\Delta t} = \underbrace{\rho B_{nm} N_n}_{\text{absorption}}, \quad \frac{N_{m \rightarrow n}}{\Delta t} = \underbrace{\rho B_{mn} N_m}_{\text{induced emission}} + \underbrace{A_{mn} N_m}_{\text{spontaneous emission}}$$

Absorption and induced emission are proportional to radiant energy density  $\rho$ . The  $A$  and  $B$  coefficients do not depend on  $T$ .

At equilibrium, the transition rates are equal.

$$\frac{N_{n \rightarrow m}}{\Delta t} = \frac{N_{m \rightarrow n}}{\Delta t}$$

Hence

$$\underbrace{\rho B_{nm} N_n}_{\text{absorption}} = \underbrace{\rho B_{mn} N_m}_{\text{induced emission}} + \underbrace{A_{mn} N_m}_{\text{spontaneous emission}}$$

Divide through by  $N$ .

$$\underbrace{\rho B_{nm} \frac{N_n}{N}}_{\text{absorption}} = \underbrace{\rho B_{mn} \frac{N_m}{N}}_{\text{induced emission}} + \underbrace{A_{mn} \frac{N_m}{N}}_{\text{spontaneous emission}}$$

Then by the Maxwell-Boltzmann distribution (1) we have

$$\underbrace{\rho B_{nm} p_n \exp\left(-\frac{E_n}{kT}\right)}_{\text{absorption}} = \underbrace{\rho B_{mn} p_m \exp\left(-\frac{E_m}{kT}\right)}_{\text{induced emission}} + \underbrace{A_{mn} p_m \exp\left(-\frac{E_m}{kT}\right)}_{\text{spontaneous emission}} \quad (2)$$

Multiply both sides by  $\exp(E_m/kT)$ .

$$\underbrace{\rho B_{nm} p_n}_{\text{absorption}} \exp\left(\frac{E_m - E_n}{kT}\right) = \underbrace{\rho B_{mn} p_m}_{\text{induced emission}} + \underbrace{A_{mn} p_m}_{\text{spontaneous emission}}$$

Note that for increasing  $T$  we have

$$\lim_{T \rightarrow \infty} \exp\left(\frac{E_m - E_n}{kT}\right) = 1$$

It follows that for  $T \rightarrow \infty$  the equilibrium formula is

$$\rho B_{nm} p_n = \rho B_{mn} p_m + A_{mn} p_m$$

Divide through by  $\rho$ .

$$B_{nm} p_n = B_{mn} p_m + \frac{A_{mn} p_m}{\rho}$$

Energy density  $\rho$  increases with temperature  $T$  hence  $A_{mn} p_m / \rho$  vanishes for  $T \rightarrow \infty$  leaving

$$B_{nm} p_n = B_{mn} p_m \quad (3)$$

Einstein reasoned that equation (3) is true in general based on the assumption that the factors involved do not depend on  $T$ . Hence we can substitute  $B_{mn} p_m$  into the absorption term and write

$$\underbrace{\rho B_{mn} p_m}_{\text{absorption}} \exp\left(\frac{E_m - E_n}{kT}\right) = \underbrace{\rho B_{mn} p_m}_{\text{induced emission}} + \underbrace{A_{mn} p_m}_{\text{spontaneous emission}}$$

Divide both sides by  $B_{mn} p_m$ .

$$\rho \exp\left(\frac{E_m - E_n}{kT}\right) = \rho + \frac{A_{mn}}{B_{mn}}$$

Rearrange terms.

$$\rho \exp\left(\frac{E_m - E_n}{kT}\right) - \rho = \frac{A_{mn}}{B_{mn}}$$

Factor out  $\rho$ .

$$\rho \left( \exp\left(\frac{E_m - E_n}{kT}\right) - 1 \right) = \frac{A_{mn}}{B_{mn}}$$

Solve for  $\rho$ .

$$\rho = \frac{A_{mn}}{B_{mn}} \frac{1}{\exp\left(\frac{E_m - E_n}{kT}\right) - 1}$$

We now consider the case of large exponentials such that

$$\exp\left(\frac{E_m - E_n}{kT}\right) \approx \exp\left(\frac{E_m - E_n}{kT}\right) - 1$$

Hence for large exponentials

$$\rho \approx \frac{A_{mn}}{B_{mn}} \exp\left(-\frac{E_m - E_n}{kT}\right)$$

By equivalence with Wien's law (which is accurate for large  $\nu$ ) we have

$$\rho = \frac{2h\nu^3}{c^2} \exp\left(-\frac{h\nu}{kT}\right)$$

Hence

$$\frac{A_{mn}}{B_{mn}} = \frac{2h\nu^3}{c^2} \quad (4)$$

and

$$E_m - E_n = h\nu$$

Then by substitution we obtain Planck's law.

$$\begin{aligned} \rho &= \frac{A_{mn}}{B_{mn}} \frac{1}{\exp\left(\frac{E_m - E_n}{kT}\right) - 1} \\ &= \frac{2h\nu^3}{c^2} \frac{1}{\exp\left(\frac{h\nu}{kT}\right) - 1} \end{aligned}$$

Let us now consider the values of the  $A$  and  $B$  coefficients. The coefficient for spontaneous emission can be computed from quantum mechanics. For example, for hydrogen transition  $2p \rightarrow 1s$  we have

$$A_{21} = \frac{16e^8}{6561\varepsilon_0^4 h^4 c^3 a_0} = 6.26 \times 10^8 \text{ second}^{-1}$$

The coefficient for induced emission can be obtained from equation (4).

$$B_{mn} = \frac{c^2}{2h\nu^3} A_{mn}$$

The coefficient for absorption can be computed from equation (3).

$$B_{nm} = \frac{p_m}{p_n} B_{mn}$$

The ratio  $p_m/p_n$  is equal to  $g_m/g_n$  where  $g$  is the multiplicity for quantum numbers  $\ell$  and  $m_s$ .

$$g = (2\ell + 1)(2m_s + 1)$$

Hence for hydrogen  $2p \rightarrow 1s$  we have

$$\begin{aligned} g_1 &= 2 & (\ell = 0, m_s = 1/2) \\ g_2 &= 6 & (\ell = 1, m_s = 1/2) \end{aligned}$$

(Recall that  $\ell = 0$  for orbital  $s$  and  $\ell = 1$  for orbital  $p$ .)