

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 Δt . Finally, let B_{nm} , B_{mn} , and A_{mn} be coefficients such that

$$\frac{N_{n \rightarrow m}}{\Delta t} = \underset{\text{absorption}}{B_{nm} N_n \rho_\nu(T)}, \quad \frac{N_{m \rightarrow n}}{\Delta t} = \underset{\text{induced emission}}{B_{mn} N_m \rho_\nu(T)} + \underset{\text{spontaneous emission}}{A_{mn} N_m}$$

Absorption and induced emission are proportional to $\rho_\nu(T)$ which is the radiant energy density of the gas for frequency ν and temperature T . 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

$$\underset{\text{absorption}}{B_{nm} N_n \rho_\nu(T)} = \underset{\text{induced emission}}{B_{mn} N_m \rho_\nu(T)} + \underset{\text{spontaneous emission}}{A_{mn} N_m}$$

Divide through by N .

$$\underset{\text{absorption}}{B_{nm} \frac{N_n}{N} \rho_\nu(T)} = \underset{\text{induced emission}}{B_{mn} \frac{N_m}{N} \rho_\nu(T)} + \underset{\text{spontaneous emission}}{A_{mn} \frac{N_m}{N}}$$

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

$$\begin{aligned}
& \underbrace{B_{nm}p_n\rho_\nu(T) \exp\left(-\frac{E_n}{kT}\right)}_{\text{absorption}} \\
&= \underbrace{B_{mn}p_m\rho_\nu(T) \exp\left(-\frac{E_m}{kT}\right)}_{\text{induced emission}} + \underbrace{A_{mn}p_m \exp\left(-\frac{E_m}{kT}\right)}_{\text{spontaneous emission}} \quad (2)
\end{aligned}$$

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

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

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

$$B_{nm}p_n\rho_\nu(T) = B_{mn}p_m\rho_\nu(T) + A_{mn}p_m$$

Divide through by $\rho_\nu(T)$.

$$B_{nm}p_n = B_{mn}p_m + \frac{A_{mn}p_m}{\rho_\nu(T)}$$

Energy density $\rho_\nu(T)$ increases with temperature T hence $A_{mn}p_m/\rho_\nu(T)$ 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 $B_{mn}p_m$ for $B_{nm}p_n$ in the absorption term and write

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

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

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

Rearrange terms.

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

Factor out $\rho_\nu(T)$.

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

Solve for $\rho_\nu(T)$.

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

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

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

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

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

Hence

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

and

$$E_m - E_n = h\nu$$

Then by substitution we obtain Planck's law.

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

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 ℓ 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 .)