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

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

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 $N_{m\to n}/\Delta t$ 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

$$\underbrace{\frac{N_{n\to m}}{\Delta t} = B_{nm}N_n\rho(\nu, T)}_{\text{absorption}}, \qquad \frac{N_{m\to n}}{\Delta t} = \underbrace{B_{mn}N_m\rho(\nu, T)}_{\substack{\text{induced} \\ \text{emission}}} + \underbrace{A_{mn}N_m}_{\substack{\text{spontaneous} \\ \text{emission}}}$$

Absorption and induced emission are proportional to $\rho(\nu, T)$ which is the radiant energy density of the gas as a function of radiant frequency ν and temperature T. The A and B coefficients do not depend on T.

At equilibrium, the transition rates are equal.

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

Hence

$$\underbrace{B_{nm}N_n\rho(\nu, T)}_{\text{absorption}} = \underbrace{B_{mn}N_m\rho(\nu, T)}_{\substack{\text{induced} \\ \text{emission}}} + \underbrace{A_{mn}N_m}_{\substack{\text{spontaneous} \\ \text{emission}}}$$

Divide through by N.

$$\underbrace{B_{nm}\frac{N_n}{N}\rho(\nu, T)}_{\text{absorption}} = \underbrace{B_{mn}\frac{N_m}{N}\rho(\nu, T)}_{\substack{\text{induced} \\ \text{emission}}} + \underbrace{A_{mn}\frac{N_m}{N}}_{\substack{\text{spontaneous} \\ \text{emission}}}$$

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

$$B_{nm}p_n\rho(\nu, T)\exp\left(-\frac{E_n}{kT}\right)$$

absorption

$$= B_{mn}p_m\rho(\nu, T)\exp\left(-\frac{E_m}{kT}\right) + A_{mn}p_m\exp\left(-\frac{E_m}{kT}\right) \quad (2)$$

induced
emission

spontaneous
emission

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

$$B_{nm}p_n\rho(\nu, T)\exp\left(\frac{E_m - E_n}{kT}\right) = B_{mn}p_m\rho(\nu, T) + A_{mn}p_m$$

absorption

induced
emission

spontaneous
emission

Note that for increasing T we have

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

It follows that for $T \to \infty$ 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 $T \to \infty$ 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

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

absorption

induced
emission

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 an approximation of $\rho(\nu, T)$ for the case of a large exponential term.

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

Then by equivalence with Wien's law (which is accurate for large ν)

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

we have

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

and

$$E_m - E_n = h\nu$$

Then by substitution we obtain Planck's law.

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

$$= \frac{2h\nu^3}{c^2} \frac{1}{\exp\left(\frac{h\nu}{kT}\right) - 1}$$

3

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 the hydrogen transition $2p \to 1s$ 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 $2p \to 1s$ we have

$$g_1 = 2 \qquad (\ell = 0,\ m_s = 1/2)$$
$$g_2 = 6 \qquad (\ell = 1,\ m_s = 1/2)$$

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