

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

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

where k is Boltzmann's constant. The coefficient p_n is a statistical weighting factor that does not depend on T .

Let us now consider the processes by which a molecule transitions between energy levels. The processes are absorption, induced emission, and spontaneous emission. Let ε_m be an energy level such that $\varepsilon_m > \varepsilon_n$. Let B_n , B_m , and A_m be coefficients of transition rates such that

$$\begin{array}{ccc} \frac{dN_n}{dt} = B_n \rho(\nu) N_n & \frac{dN_m}{dt} = B_m \rho(\nu) N_m & \frac{dN_m}{dt} = A_m N_m \\ \text{absorption} & \text{induced emission} & \text{spontaneous emission} \\ \varepsilon_n \rightarrow \varepsilon_m & \varepsilon_m \rightarrow \varepsilon_n & \varepsilon_m \rightarrow \varepsilon_n \end{array}$$

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

At equilibrium, transition rates between ε_m and ε_n are equal.

$$\begin{array}{ccc} B_n \rho(\nu) N_n = B_m \rho(\nu) N_m + A_m N_m \\ \text{absorption} & \text{induced emission} & \text{spontaneous emission} \\ \varepsilon_n \rightarrow \varepsilon_m & \varepsilon_m \rightarrow \varepsilon_n & \varepsilon_m \rightarrow \varepsilon_n \end{array}$$

Divide through by N to obtain

$$\begin{array}{ccc} B_n \rho(\nu) p_n \exp\left(-\frac{\varepsilon_n}{kT}\right) = B_m \rho(\nu) p_m \exp\left(-\frac{\varepsilon_m}{kT}\right) + A_m p_m \exp\left(-\frac{\varepsilon_m}{kT}\right) \\ \text{absorption} & \text{induced emission} & \text{spontaneous emission} \\ \varepsilon_n \rightarrow \varepsilon_m & \varepsilon_m \rightarrow \varepsilon_n & \varepsilon_m \rightarrow \varepsilon_n \end{array}$$

Note that for increasing T we have

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

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

$$B_n \rho(\nu) p_n = B_m \rho(\nu) p_m + A_m p_m$$

Divide through by $\rho(\nu)$.

$$B_n p_n = B_m p_m + A_m p_m / \rho(\nu)$$

Energy density $\rho(\nu)$ increases with temperature T hence $A_m p_m / \rho(\nu)$ vanishes for $T \rightarrow \infty$ leaving

$$B_n p_n = B_m p_m$$

Einstein reasoned that the above relation is true in general based on the assumption that the factors involved do not depend on T . By substitution in the absorption term we now have

$$\begin{array}{ccc} B_m \rho(\nu) p_m \exp\left(-\frac{\varepsilon_n}{kT}\right) = B_m \rho(\nu) p_m \exp\left(-\frac{\varepsilon_m}{kT}\right) + A_m p_m \exp\left(-\frac{\varepsilon_m}{kT}\right) \\ \text{absorption} & \text{induced emission} & \text{spontaneous emission} \\ \varepsilon_n \rightarrow \varepsilon_m & \varepsilon_m \rightarrow \varepsilon_n & \varepsilon_m \rightarrow \varepsilon_n \end{array}$$

Divide through by $B_m p_m$ and rearrange terms.

$$\underbrace{\rho(\nu) \exp\left(-\frac{\varepsilon_n}{kT}\right)}_{\substack{\text{absorption} \\ \varepsilon_n \rightarrow \varepsilon_m}} - \underbrace{\rho(\nu) \exp\left(-\frac{\varepsilon_m}{kT}\right)}_{\substack{\text{induced emission} \\ \varepsilon_m \rightarrow \varepsilon_n}} = \underbrace{(A_m/B_m) \exp\left(-\frac{\varepsilon_m}{kT}\right)}_{\substack{\text{spontaneous emission} \\ \varepsilon_m \rightarrow \varepsilon_n}}$$

Solve for energy density $\rho(\nu)$.

$$\rho(\nu) = \frac{(A_m/B_m) \exp\left(-\frac{\varepsilon_m}{kT}\right)}{\exp\left(-\frac{\varepsilon_n}{kT}\right) - \exp\left(-\frac{\varepsilon_m}{kT}\right)} = \frac{A_m/B_m}{\exp\left(\frac{\varepsilon_m - \varepsilon_n}{kT}\right) - 1}$$

From Wien's law $\rho(\nu) = \alpha \nu^3 \exp(-h\nu/kT)$ which is accurate for large ν , we have

$$A_m/B_m = \alpha \nu^3$$

and

$$\varepsilon_m - \varepsilon_n = h\nu$$

Planck's law follows directly.

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