

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  $\varepsilon_n$ . 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  $\varepsilon_m$  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  $\nu$ . The  $A$  and  $B$  coefficients are presumed to not depend on temperature  $T$ .

At equilibrium, transition rates between  $\varepsilon_m$  and  $\varepsilon_n$  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 can now eliminate  $B_n p_n$  and obtain

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

Divide through by  $B_m p_m$  and rearrange terms.

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

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  $\nu$ , we have

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

and

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

Planck's law follows directly.

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