

In his 1917 paper, “On the Quantum Theory of Radiation,” Einstein uses the following argument to derive Planck’s law. The argument requires induced emission, a process which was a theoretical discovery by Einstein. Prior to Einstein, no one was aware that induced emission existed.

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  $B_{nm}$ ,  $B_{mn}$ , and  $A_{mn}$  be coefficients of transition rates such that

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

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.

$$\begin{array}{ccc} B_{nm}\rho(\nu)N_n = B_{mn}\rho(\nu)N_m + & A_{mn}N_m \\ \text{absorption} & \text{induced emission} & \text{spontaneous emission} \\ \varepsilon_n \rightarrow \varepsilon_m & \varepsilon_m \rightarrow \varepsilon_n & \varepsilon_m \rightarrow \varepsilon_n \end{array}$$

Divide through by  $N$  to obtain

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

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

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

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

$$B_{nm}p_n = B_{mn}p_m + A_{mn}p_m/\rho(\nu)$$

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

$$B_{nm}p_n = B_{mn}p_m \tag{1}$$

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  $B_{nm}p_n$  and obtain

$$\underbrace{B_{mn}\rho(\nu)p_m \exp\left(-\frac{\varepsilon_n}{kT}\right)}_{\substack{\text{absorption} \\ \varepsilon_n \rightarrow \varepsilon_m}} = \underbrace{B_{mn}\rho(\nu)p_m \exp\left(-\frac{\varepsilon_m}{kT}\right)}_{\substack{\text{induced emission} \\ \varepsilon_m \rightarrow \varepsilon_n}} + \underbrace{A_{mn}p_m \exp\left(-\frac{\varepsilon_m}{kT}\right)}_{\substack{\text{spontaneous emission} \\ \varepsilon_m \rightarrow \varepsilon_n}}$$

Divide through by  $B_{mn}p_m$  and rearrange terms.

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

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

$$\begin{aligned} \rho(\nu) &= \frac{A_{mn}}{B_{mn}} \frac{\exp\left(-\frac{\varepsilon_m}{kT}\right)}{\exp\left(-\frac{\varepsilon_n}{kT}\right) - \exp\left(-\frac{\varepsilon_m}{kT}\right)} \\ &= \frac{A_{mn}}{B_{mn}} \frac{1}{\exp\left(\frac{\varepsilon_m - \varepsilon_n}{kT}\right) - 1} \end{aligned}$$

We now consider the limit of  $\rho(\nu)$  for large  $\varepsilon_m - \varepsilon_n$ .

$$\lim \rho(\nu) = \frac{A_{mn}}{B_{mn}} \exp\left(-\frac{\varepsilon_m - \varepsilon_n}{kT}\right)$$

Then by equivalence with Wien's law (which is accurate for large  $\nu$ )

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

we have

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

and

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

Substitution yields Planck's law.

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

Coefficient  $A_{mn}$  can be computed from first principles of quantum mechanics. Then  $B_{mn}$  can be obtained using equation (2).

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

Then  $B_{nm}$  can be computed from equation (1).

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

The ratio  $p_m/p_n$  is equal to the multiplicity ratio and hence is determined by the atomic species. Note that  $B_{mn}$  and  $B_{nm}$  depend on frequency  $\nu$ .