

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 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_{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 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.

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

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 ν)

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

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 ν .