

In his 1917 paper, “On the Quantum Theory of Radiation,” Einstein uses the following argument to derive Planck’s law.

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 E_n . By the Maxwell-Boltzmann distribution we have

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

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 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 $N_{m \rightarrow n}/\Delta t$ 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 with dimensions such that

$$\frac{N_{n \rightarrow m}}{\Delta t} = \underset{\text{absorption}}{B_{nm}N_n\rho(\nu, T)}, \quad \frac{N_{m \rightarrow n}}{\Delta t} = \underset{\text{induced emission}}{B_{mn}N_m\rho(\nu, T)} + \underset{\text{spontaneous emission}}{A_{mn}N_m}$$

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.

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

Hence

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

Divide through by N .

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

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

$$\underset{\text{absorption}}{B_{nm}p_n\rho(\nu, T)\exp\left(-\frac{E_n}{kT}\right)} = \underset{\text{induced emission}}{B_{mn}p_m\rho(\nu, T)\exp\left(-\frac{E_m}{kT}\right)} + \underset{\text{spontaneous emission}}{A_{mn}p_m\exp\left(-\frac{E_m}{kT}\right)} \quad (2)$$

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

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

Note that for increasing T we have

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

It follows that for $T \rightarrow \infty$ 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 $T \rightarrow \infty$ 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 . By substitution in the absorption term we can now eliminate $B_{nm}p_n$ and obtain

$$\underbrace{B_{mn}p_m\rho(\nu, T) \exp\left(\frac{E_m - E_n}{kT}\right)}_{\text{absorption}} = \underbrace{B_{mn}p_m\rho(\nu, T)}_{\text{induced emission}} + \underbrace{A_{mn}p_m}_{\text{spontaneous emission}}$$

Divide both sides by $B_{mn}p_m$.

$$\underbrace{\rho(\nu, T) \exp\left(\frac{E_m - E_n}{kT}\right)}_{\text{absorption}} = \underbrace{\rho(\nu, T)}_{\text{induced emission}} + \underbrace{\frac{A_{mn}}{B_{mn}}}_{\text{spontaneous emission}}$$

Rearrange terms.

$$\underbrace{\rho(\nu, T) \exp\left(\frac{E_m - E_n}{kT}\right)}_{\text{absorption}} - \underbrace{\rho(\nu, T)}_{\text{induced emission}} = \underbrace{\frac{A_{mn}}{B_{mn}}}_{\text{spontaneous emission}}$$

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

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

and

$$E_m - E_n = h\nu$$

Then by substitution we obtain Planck's law.

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

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 $2p \leftrightarrow 1s$ we have

$$A_{21} = \frac{e^{10} m_e}{26244 \pi^5 \epsilon_0^5 \hbar^6 c^3} = 6.27 \times 10^8 \text{ second}^{-1}$$

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 $2p \leftrightarrow 1s$ we have

$$\begin{aligned} g_1 &= 2 & (\ell = 0, m_s = 1/2) \\ g_2 &= 6 & (\ell = 1, m_s = 1/2) \end{aligned}$$

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