How Einstein derived Planck's law

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

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

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 $N_{m\to n}/\Delta t$ 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 such that

$$\frac{N_{n\to m}}{\Delta t} = \underset{\text{absorption}}{\rho B_{nm} N_n}, \qquad \frac{N_{m\to n}}{\Delta t} = \underset{\substack{\text{induced}\\ \text{emission}}}{\rho B_{mn} N_m} + \underset{\substack{\text{spontaneous}\\ \text{emission}}}{A_{mn} N_m}$$

Absorption and induced emission are proportional to radiant energy density ρ. The A and B coefficients do not depend on T.

At equilibrium, the transition rates are equal.

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

Hence

$$\underset{\text{absorption}}{\rho B_{nm} N_n} = \underset{\substack{\text{induced}\\ \text{emission}}}{\rho B_{mn} N_m} + \underset{\substack{\text{spontaneous}\\ \text{emission}}}{A_{mn} N_m}$$

Divide through by N.

$$\underset{\text{absorption}}{\rho B_{nm} \frac{N_n}{N}} = \underset{\substack{\text{induced}\\ \text{emission}}}{\rho B_{mn} \frac{N_m}{N}} + \underset{\substack{\text{spontaneous}\\ \text{emission}}}{A_{mn} \frac{N_m}{N}}$$

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

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

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

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

Note that for increasing T we have

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

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

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

Divide through by ρ.

$$B_{nm}p_n=B_{mn}p_m+\frac{A_{mn}p_m}{\rho}$$

Energy density ρ increases with temperature T hence $A_{mn}p_m/\rho$ vanishes for $T\to\infty$ leaving

$$B_{nm}p_n=B_{mn}p_m \tag{3}$$

We find equation (3) to be independent of T since the factors involved do not depend on T. Hence we can substitute $B_{mn}p_m$ into the absorption term and write

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

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

$$\rho\exp\left(\frac{E_m-E_n}{kT}\right)=\rho+\frac{A_{mn}}{B_{mn}}$$

Rearrange terms.

$$\rho\exp\left(\frac{E_m-E_n}{kT}\right)-\rho=\frac{A_{mn}}{B_{mn}}$$

Factor out ρ.

$$\rho\left(\exp\left(\frac{E_m-E_n}{kT}\right)-1\right)=\frac{A_{mn}}{B_{mn}}$$

Solve for ρ.

$$\rho=\frac{A_{mn}}{B_{mn}}\frac{1}{\exp\left(\frac{E_m-E_n}{kT}\right)-1}$$

We now consider the case of large exponentials such that

$$\exp\left(\frac{E_m-E_n}{kT}\right)\approx\exp\left(\frac{E_m-E_n}{kT}\right)-1$$

Hence for large exponentials

$$\rho\approx\frac{A_{mn}}{B_{mn}}\exp\left(-\frac{E_m-E_n}{kT}\right)$$

By equivalence with Wien's law (which is accurate for large ν) we have

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

Hence

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

and

$$E_m - E_n = h\nu$$

Then by substitution we obtain Planck's law.

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

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 hydrogen transition $2p \rightarrow 1s$ we have

$$A_{21} = \frac{16e^8}{6561\varepsilon_0^4 h^4 c^3 a_0} = 6.26 \times 10^8 \,\text{second}^{-1}$$

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 $2p \rightarrow 1s$ we have

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

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