6.1 Boltzmann Factor

Let us look at how a small system interacting with reservoir behaves when it can only exchange energy with the reservoir.

The system has energies $E_1, E_2, E_3, \ldots$ (maybe an ∞ number of states)

An energy level is called degenerate when an energy level corresponds to more than one independent state.
For example, non relatistic hydrogen atom the energies are $E_n = -13.6\,eV/n^2$ and the number of states at energy E_n is n^2 $\Rightarrow$ there are 9 states with energy $E_3 = -1.5\,eV$

I will follow the formulation of the book where the focus is on the states of the system and not on the energy levels of the system. When systems are degenerate you need to remember to count all of the states.

What is the probability the system is in the state s_a?

$$\mathcal{P}(s_a) = \underbrace{C}_{\text{some constant}} \cdot \overbrace{1}^{\text{multiplicity of system}} \cdot \underbrace{\Omega_{Res}}_{\text{multiplicity of reservoir}}(E - E(s_a)) \qquad U = E_{Rese} + E_{sys}$$

$E(s_a)$ = energy of state a

$$\Rightarrow \frac{\mathcal{P}(s_a)}{\mathcal{P}(s_b)} = \frac{\Omega_{Res}(U - E(s_a))}{\Omega_{Res}(U - E(s_b))} = \frac{e^{S_R(U-E(s_a))/k_B}}{e^{S_R(U-E(s_b))/k_B}} = e^{[S_R(U-E(s_a)) - S_R(U-E(s_b))]/k_B}$$

This doesn't help much until you realize U is an extensive quantity which is proportional to N so $|U| >> E(s_a), E(s_b)$

$$\Rightarrow S_R(U - E(s_a)) \cong S_R(U) - E(s_a)\left(\frac{\partial S_R}{\partial U}\right)_{N,V} = S_R(U) - \frac{E(s_a)}{T}$$

$$\Rightarrow \mathcal{P}(s_a)/\mathcal{P}(s_b) = e^{-E(s_a)/k_BT} / e^{-E(s_b)/k_BT}$$

$\Rightarrow$ the canonical distribution (Boltzmann distribution)

$$\mathcal{P}(s_a) = \frac{1}{Z} e^{-E(s_a)/k_BT}$$

Z is called the partition function.

The partition function is from $\sum_s P(s) = 1$

$$\Rightarrow Z = \sum_s e^{-E(s)/k_BT}$$

Very important: suppose all of the energies levels of the system are shifted by energy E_0. Does Z change? Does $P(s)$ change?

$$Z = \sum_s e^{-[E(s)+E_0]/k_BT} = \sum_s e^{-E(s)/k_BT} e^{-E_0/k_BT} = e^{-E_0/k_BT} \sum_s e^{-E(s)/k_BT}$$
$$= e^{-E_0/k_BT} Z_{old}$$

$$P(s) = \frac{e^{-[E(s)+E_0]/k_BT}}{Z} = \frac{e^{-E(s)/k_BT} e^{-E_0/k_BT}}{Z_{old} e^{-E_0/k_BT}} = P_{old}(s)$$

Prob 6.5 $\frac{.05eV}{k_B 300k} = 1.93$

pg 225 a) $Z = e^{+1.93} + e^0 + e^{-1.93} = 8.03$

b) $-.05eV$ $P = e^{1.93}/8.03 = 0.86$, 0 $P = 0.12$, $0.05eV$ $P = 0.02$

c) Z will be $e^{1.93}$ x bigger all probabilities will be same

Prob 6.10 $f = 4.8 \times 10^{13}$ Hz for harmonic oscillator.

pg 228 Energies are $\frac{1}{2}hf$, $\frac{3}{2}hf$, $\frac{5}{2}hf$ and are not degenerate.

shift to $0, hf, 2hf, \ldots$

a) at 300 k $hf/k_BT = \frac{4.8\times10^{13}\text{Hz}\ 6.626\times10^{-34}\text{Js}}{1.381\times10^{-23}\text{J/k}\ 300k} = 7.68$

$Z = e^0 + e^{-7.68} + e^{-2\times7.68} \cong 1.00046$

$P(0) = 1/1.00046 = 0.99954$ $\quad P(1) = 0.00046$ $\quad P(2) = 2\times10^{-7}$

b) at 700 K $hf/k_BT = 3.29$

$Z = e^0 + e^{-3.29} + e^{-2\times3.29} + e^{-3\times3.29} = 1.039$

$P(0) = 1/1.039 = 0.963$, $P(1) = 0.036$, $P(2) = 0.001$

At low T, how does Z and P behave? Use levels

Define $E_1 = 0$ and Ω_1 = multiplicity of level 1 ; $E_2 > E_1$; Ω_2 = multiplicity of level 2

$$Z = \Omega_1 e^0 + \Omega_2 e^{-E_2/k_BT} + \ldots = \Omega_1 + \Omega_2 e^{-E_2/k_BT} + \Omega_3 e^{-E_3/k_BT} + \ldots$$

But $1 \gg e^{-E_2/k_BT} \gg e^{-E_3/k_BT} \gg \ldots$

$\Rightarrow Z \simeq \Omega_1 + \Omega_2 e^{-E_2/k_BT}$

$P(1) = \Omega_1/Z \cong \left(1 + \frac{\Omega_2}{\Omega_1} e^{-E_2/k_BT}\right)^{-1} = 1 - \frac{\Omega_2}{\Omega_1} e^{-E_2/k_BT}$

$P(2) = \Omega_2 e^{-E_2/k_BT} \cong (\Omega_2/\Omega_1) e^{-E_2/k_BT}$

Remember E_2 is energy of level 2 above level 1