# Entropy Revisited:

- Previously we considered each microstate of the full system to be equally likely. Thus

$$P_m = C$$

probability to be in microstate $m$ is constant

Then $\sum_m P_m = 1$ or $C \sum_m 1 = 1$

this litterally counts the states

or

$$C\,\Omega(E) = 1 \quad \text{and} \quad \boxed{P_m = \frac{1}{\Omega(E)}}$$

Thus

$$S = k \ln \Omega = -k \ln P_m$$

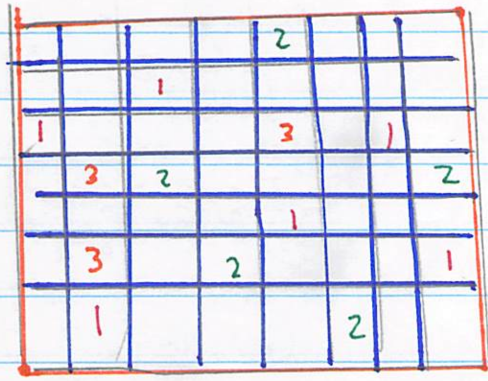
- Now we have a subsystem with probabilies $P_m \propto e^{-\mathcal{E}_m/kT}$. We would to find the mean entropy for the subsystems, with this probdlity distribution

The generalzation is (as we show below)

$$\boxed{S = -\langle k \ln P_m \rangle = -k \sum_m P_m \ln P_m}$$

Let's work it out!

Consider a large number of subsystems




$N$ subsystems: (blue boxes)

$N_1$ in state 1:

$N_2$ in state 2, etc

for example, probability to be in state 1 $\longrightarrow P_1 = \dfrac{N_1}{N} \propto e^{-\varepsilon_1/kT}$

- $S_{TOT} = k \ln(\#\text{ configurations with } N_1, N_2, \ldots \text{ fixed})$

$$= k \ln \frac{N!}{N_1!\, N_2! \ldots N_m!}$$

$$\simeq k\left( N \ln N - N - \sum_m (N_m \ln N_m - N_m) \right)$$

- So using $\sum_m N_m = N$ we have

$$S_{TOT} = k \sum_m N_m \ln N - N_m \ln N_m$$

Using $\ln N - \ln N_m = -\ln N_m/N = -\ln P_m$ we have

$$S_{TOT} = -k \sum_m N_m \ln P_m$$

- Finally the mean entropy for one subsystem is

$$S = \frac{S_{TOT}}{N} = -k \sum_m \frac{N_m}{N} \ln P_m = -k \sum_m P_m \ln P_m$$

So we have an important result:

$$\boxed{S = -k \sum_m P_m \log P_m}$$

this expression for $S$ is valid for any probality distribution, $P_m$

Notes

1. If $P_m = \frac{1}{\Omega}$ is the microcanonical (or equally likely distribution)

Then

$$S = -k \sum_m \frac{1}{\Omega} \log \frac{1}{\Omega} = -k \log \Omega \underbrace{\sum_m \frac{1}{\Omega}}$$

Sum over states divided by # of states

$$S = -k \log \Omega$$ ← This is what we had before:

2. If $P_m = \frac{1}{Z} e^{-\beta E_m}$, this is the canonical ensemble

Then

$$S = -k \sum_m \frac{1}{Z} e^{-\beta E_m} \log \left( \frac{1}{Z} e^{-\beta E_m} \right)$$

$$= -k \frac{1}{Z} \sum_m (-\beta E_m) e^{-\beta E_m} + k \log Z \overbrace{\frac{1}{Z} \sum_m e^{-\beta E_m}}^{1}$$

$$\boxed{S = k\beta \bar{E} + k \log Z}$$

So

$$\boxed{S = \frac{\bar{E}}{T} + k \log Z}$$

this is how the entropy can be computed from the partition function $Z$

$$\bar{E} = \frac{-1}{Z}\frac{\partial Z}{\partial \beta}$$

- Finally lets calculate the entroply of the Einstein Model with $E = 400\hbar\omega$, $N = 400$

$$\boxed{S_{\text{one site}} = \frac{\bar{E}}{T} + k\ln Z}$$

this is general.

$$\frac{S_{\text{one site}}}{k} = \frac{\bar{E}}{kT} + \ln Z$$

- Putting in $\bar{E} = \hbar\omega/(e^{\hbar\omega/kT} - 1)$ $\quad Z = \dfrac{1}{1 - e^{-\hbar\omega/kT}}$

we have

$$\boxed{\frac{S_{\text{one}}}{k} = \frac{\beta\hbar\omega_0}{e^{\beta\hbar\omega_0} - 1} - \ln\left(1 - e^{-\hbar\omega_0\beta}\right)}$$

entropy of SHO at temperature $T$

Using $\hbar\omega_0/\ln 2 = k_B T$ and multiplying by $N = 400$

we have, $\beta\hbar\omega_0 = \ln 2$

$$\frac{S}{k} = N\frac{S_{\text{one site}}}{k} = N\,2\ln 2 \simeq 554.$$

this is in agreement with the direct counting result we quoted earlier.