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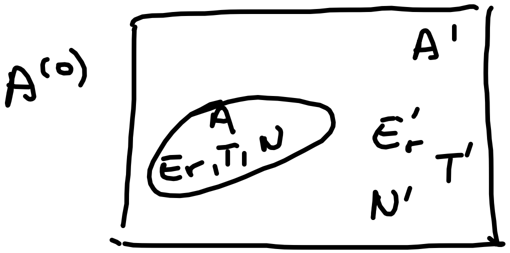
Last time:

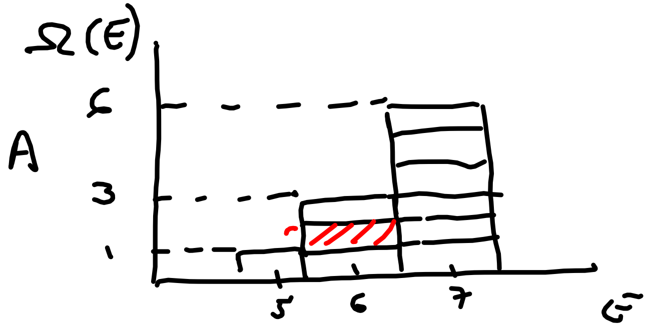


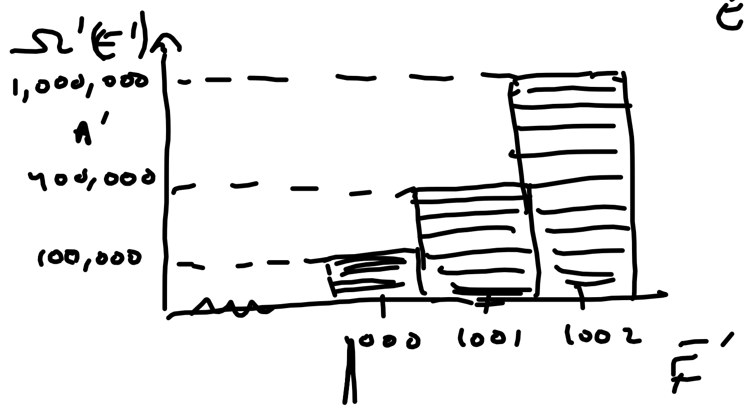
$$A^{(0)} = A + A'$$

$$E^{(0)} = E_r + E_r' \qquad N^{(0)} = N + N'$$

Example:

$E^{(0)} = 1007$





$$P_r \propto \Omega'(E'_r) \equiv \Omega'(E^{(0)} - E_r)$$

We are going to calculate P_r by expanding $\ln \Omega'(E^{(0)} - E_r)$ about $E^{(0)}$ since $E_r \ll E^{(0)}$

$$\ln \Omega'(E'_r) = \underbrace{\ln \Omega'(E^{(0)})}_{\text{constant}} + \underbrace{\frac{\partial \ln \Omega'}{\partial E'}\bigg|_{E'=E^{(0)}}}_{\beta' = \beta \text{ in equilibrium}} \overbrace{E'_r - E^{(0)}}^{-E_r} + \ldots$$

$\beta = \frac{1}{kT}$

$$= C - \beta E_r$$

$\therefore P_r \propto e^{-\beta E_r}$ independent of A'!

since $0 \leq P_r \leq 1$ then

$$P_r = \frac{e^{-\beta E_r}}{\sum_r e^{-\beta E_r}}$$

canonical probability distribution.

↳ sum over ALL the states of system A.

Compare P_r with P_r for the microcanonical ensemble:

$$P_r^{micro} = \begin{cases} \dfrac{1}{\Omega(\bar{E})} & \text{constant normalized to 1 by the number of accessible microstates.} \\ 0 & \text{if } r \text{ is not accessible (not compatible with } \bar{E}) \end{cases}$$

System in canonical ensemble:

$\mathcal{N}$ systems $(1, 2, \ldots \mathcal{N})$ sharing energy $\mathcal{E}$.

$\mathcal{E} = \mathcal{N} U$ $\qquad U = \langle E \rangle$ average value of the energy

E_r $\quad r = 0, 1, 2, \ldots$ are the allowed energies of the system.

n_r = # of systems with energy E_r at a given time t.

$\{n_r\}$ satisfies:

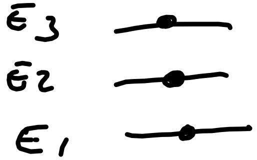
$$① \begin{cases} \sum_r n_r = \mathcal{N} \\ \sum_r n_r E_r = \mathcal{E} = \mathcal{N} U \quad \therefore \quad U = \dfrac{\mathcal{E}}{\mathcal{N}} \end{cases}$$

Any $\{n_r\}$ satisfying ① is a valid configuration.

However, each $\{n_r\}$ will have a weight related with the number of ways in which we can exchange the members of the ensemble from the occupied energy levels. (the ensemble members are equivalent).

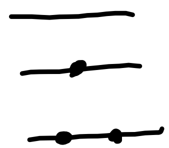
Example:

$\mathcal{N} = 3$



$W = \mathcal{N}! = 6$

degeneracy



$$W = \frac{\mathcal{N}!}{n_1!\, n_2!\, n_3!} = \frac{3!}{2!\, 1!\, 0!} = 3$$

So in general

$$W_{\{n_r\}} = \frac{N!}{n_0!\, n_1!\, n_2! \cdots}$$

$N!$ → total # of possible permutations

$n_0!\, n_1!\, n_2! \cdots$ → corrects in case that there are more than 0 or 1 particle in state r.

Notice that all the distributions $\{n_r\}$ that satisfy 1 are equally likely which means that the configuration $\{n_r\}$ with the largest $W_{\{n_r\}}$ will be the most likely in which we are going to find our ensemble at any time t.

One way of obtaining the most probable configuration of $\{n_r\}$ is by finding $\{n_r^*\}$ which is the configuration that maximizes $W_{\{n_r\}}$.

Also:

sum over $\{n_r\}$ satisfying ①.

$$\langle n_r \rangle = \frac{\sum'_{\{n_r\}} n_r W\{n_r\}}{\sum'_{\{n_r\}} W\{n_r\}}$$

We will find $\{n_r^*\}$ and $\langle n_r \rangle$ and we will see that when $N \to \infty$ $\{n_r^*\} \equiv \langle n_r \rangle$

1) Method of most probable values:

We want to find $\{n_r\} = \{n_r^*\}$ that maximizes

$W_{\{n_r\}}$

$$\ln W = \ln\left[\frac{N!}{\prod_r n_r!}\right] = \ln N! - \sum_r \ln n_r!$$

Now consider that $N \to \infty$ so we can use

that $\ln n! \simeq n \ln n - n$ (Stirling's approximation)

$$\ln W \simeq N \ln N - N - \left(\sum_r n_r \ln n_r - n_r\right) =$$

$$= N \ln N - \cancel{N} - \sum_r n_r \ln n_r + \underbrace{\sum_r n_r}_{\cancel{N}} =$$

$$= N \ln N - \sum_r n_r \ln n_r$$

We will calculate the variation of $\ln W$ produced by a $\delta\{n_r\}$ of the ensemble distribution

$$\delta(\ln W) = -\sum_r \left(\delta n_r \ln n_r + n_r \frac{1}{n_r}\delta n_r\right) =$$

$$= -\sum_r (\ln n_r + 1)\,\delta n_r$$

At a maximum we know that $\delta(\ln W) = 0$

δn_r satisfy the constrain equations 1:

$$\sum_r n_r = N \Rightarrow \sum_r \delta n_r = 0$$

$$\sum_r n_r \epsilon_r = \mathcal{E} \Rightarrow \sum_r \epsilon_r \delta n_r = 0$$

Using Lagrange multipliers we can make the δn_r independent:

$$\delta(\ln W) = 0 = \sum_r \left[-(\ln n_r + 1) - \alpha - \beta\epsilon_r\right] \delta n_r$$

now they are independent!

Then for each r we have that for $\{n_r^*\}$

$$\ln n_r^* + 1 = -\alpha - \beta\epsilon_r$$

$$\ln n_r^* = -(\alpha+1) - \beta\epsilon_r \Rightarrow n_r^* = e^{-(\alpha+1)} e^{-\beta\epsilon_r}$$

Then

$$n_r^* = c\, e^{-\beta \epsilon_r}$$

Let's find c and β:

$$N = \sum_r n_r = \sum_r n_r^* = c \sum_r e^{-\beta \epsilon_r}$$

$$\therefore\ c = \frac{N}{\sum_r e^{-\beta \epsilon_r}}$$

Then:

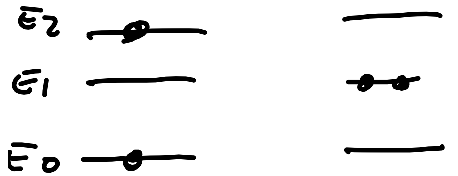
$$\frac{n_r^*}{N} = \frac{e^{-\beta \epsilon_r}}{\sum_r e^{-\beta \epsilon_r}}$$

Same as P_r obtained before.

Example:

$\epsilon_0 = 0 \quad \epsilon_1 = \varepsilon \quad \epsilon_2 = 2\varepsilon$

$N = 2 \quad E = 2\varepsilon$



$W = 2 \qquad W = 1$

this is $n_0 = 1, n_1 = 0, n_2 = 1 \to \{n_r^*\}$

$n_0 = 0, n_1 = 2, n_2 = 0$ have a smaller weight.

Also

$$\to \frac{n_r^*}{\mathcal{N}} = \frac{e^{-\beta \epsilon_r}}{\sum_r e^{-\beta \epsilon_r}}$$

$$\mathcal{N} U = \mathcal{E} = \sum_r \epsilon_r n_r = \sum_r \epsilon_r n_r^* =$$

$$= \sum_r \epsilon_r \frac{\mathcal{N} e^{-\beta \epsilon_r}}{\sum_r e^{-\beta \epsilon_r}} = \mathcal{N} \frac{\sum_r \epsilon_r e^{-\beta \epsilon_r}}{\sum_r e^{-\beta \epsilon_r}}$$

$$\therefore U = \frac{\mathcal{E}}{\mathcal{N}} = \frac{\sum_r \epsilon_r e^{-\beta \epsilon_r}}{\sum_r e^{-\beta \epsilon_r}}$$

Now if you know U (the average energy of the system you can obtain β).

We will see later that $\beta \equiv \frac{1}{kT}$ (using thermodynamics).

Method of Mean Values

we will evaluate $\langle n_r \rangle = \dfrac{\sum'_{\{n_r\}} n_r W\{n_r\}}{\sum'_{\{n_r\}} W\{n_r\}}$

Define :

$$\tilde{W}\{n_r\} = \frac{N!\, w_0^{n_0} w_1^{n_1} w_2^{n_2} \cdots}{n_0!\, n_1!\, n_2! \cdots}$$

Notice that

$$\tilde{W}\{n_r\}\Big|_{\substack{w_i = 1 \\ \forall i}} = W\{n_r\}$$

Notice that $\omega_r = 1$ at the end but we will able to calculate derivatives of $\tilde{W}$:

Define: $$\Gamma(N, U) = \sum_{\{n_r\}}' \tilde{W}\{n_r\}$$

We can see that

$$\langle n_r \rangle = \omega_r \frac{\partial}{\partial \omega_r} (\ln \Gamma) \Big|_{\forall \omega_r = 1}$$

$$\overset{D/}{=} \omega_r \frac{\partial}{\partial \omega_r} \ln \sum_{\{n_r\}}' \frac{N!\, \omega_0^{n_0}\, \omega_1^{n_1} \cdots}{n_0!\, n_1! \cdots} \Big|_{\forall \omega_r = 1} =$$

$$= \omega_r \frac{\sum_{\{n_r\}}' n_r\, \omega_r^{n-1}\, \tilde{W}'\{n_r\}}{\sum_{\{n_r\}} \tilde{W}\{n_r\}} \Big|_{\forall \omega_r = 1} =$$

$$= \frac{\sum' n_r W\{n_r\}}{\sum'_{\{n_r\}} W\{n_r\}}$$