Last time: state i, energy ε_i, occupation n_i, $\Omega = N! / \prod_i n_i!$

Max Entropy $\rightarrow$ $n_i = e^A e^{-\beta \varepsilon_i}$

Constraints: $N = \sum_i n_i = e^A \sum_i e^{-\beta \varepsilon_i}$

$$\Rightarrow \quad e^A = N / \sum_i e^{-\beta \varepsilon_i} = \frac{N}{Z} \quad \text{where} \quad \boxed{Z = \sum_i e^{-\beta \varepsilon_i}}$$

Therefore: $n_i = \frac{N}{Z} e^{-\beta \varepsilon_i}$ or $P_i = \frac{n_i}{N} = e^{-\beta \varepsilon_i}$.

Z is known as the Partition Function. (normalisation of probabilities from $0 \rightarrow 1$).

$$\mathcal{U} = \sum_i n_i \varepsilon_i = N/_Z \sum_i \underline{\varepsilon_i e^{-\beta \varepsilon_i}}$$

Let's take the derivative of Z with respect to $-\beta$.

$$-\frac{dZ}{d\beta} = -\frac{d}{d\beta} \sum_i e^{-\beta \varepsilon_i} = \sum_i \underline{\varepsilon_i e^{-\beta \varepsilon_i}}$$

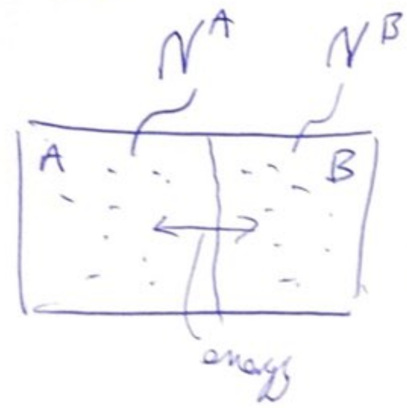
If we combine these we get $\mathcal{U} = -\frac{N}{Z} \frac{dZ}{d\beta} = -N \frac{d}{d\beta} \ln Z$

β is the Lagrange multiplier constraining energy and Z constrains particle number (via α, A).

Thermodynamic definitions T (temperature) and F (free energy)

i.e. $\frac{1}{T} = \left.\frac{\partial S}{\partial U}\right|_V$ and $F = U - TS$

Consider two systems, A and B, which can exchange energy but not particles and is otherwise isolated.



Total particle number $N = N^A + N^B$.

Let's have energy levels ε_i^A, ε_i^B and distributions $\{n_i^A\}$, $\{n_i^B\}$.

Entropy: $S = S^A + S^B$

$$\Rightarrow \quad S^A/k_B = N^A \ln N^A - \sum_i n_i^A \ln n_i^A$$

$$S^B/k_B = N^B \ln N^B - \sum_i n_i^B \ln n_i^B$$

Thermal equilibrium occurs at maximum entropy, so let's maximise subject to constraints of constant N^A (Lagrange multiplier α)

" N^B (" " α')

" U (" " β).

Maximize with constraints :

$$-\alpha\underbrace{\sum_i n_i^A}_{N^A} - \alpha'\underbrace{\sum_i n_i^B}_{N^B} - \beta\underbrace{\left[\sum_i n_i^A \varepsilon_i^A + \sum_i n_i^B \varepsilon_i^B\right]}_{U}$$

$$+ \underbrace{\left[N^A \ln N^A - \sum_i n_i^A \ln n_i^A\right]}_{S^A} + \underbrace{\left[N^B \ln N^B - \sum_i n_i^B \ln n_i^B\right]}_{S^B}$$

– We take derivatives with respect to n_i^A (i.e. $\partial/\partial n_i^A \to 0$)

and do the same for n_i^B (i.e. $\partial/\partial n_i^B \to 0$).

All of the sum disappear, just the i^{th} terms surviving

as before giving.

$$\frac{n_i^A}{N^A} = \frac{e^{-\beta \varepsilon_i^A}}{Z^A} \quad \text{with} \quad Z^A = \sum_i e^{-\beta \varepsilon_i^A}$$

and $$\frac{n_i^B}{N^B} = \frac{e^{-\beta \varepsilon_i^B}}{Z^B} \quad \text{with} \quad Z^B = \sum_i e^{-\beta \varepsilon_i^B}$$

with $$U = \frac{N^A}{Z^A} \sum_i \varepsilon_i^A e^{-\beta \varepsilon_i^A} + \frac{N^B}{Z^B} \sum_i \varepsilon_i^B e^{-\beta \varepsilon_i^B}$$

This system is in thermal equilibrium & is at some temperature.

Note that systems A and B have the same β.

$\Rightarrow$ β and T are related.

Essentially $\boxed{\beta = 1/k_B T}$ (we'll show this later).

Consider a system A with 1 particle in it and a system B with $N-1$ particles where N is very large. B is so much larger than A that it acts as a constant temperature heat ~~ba~~ bath.

(AB) is in the (N, U, V) macrostate (microcanonical ensemble).

Probability of a particle being in state i with energy ε_i is

$$P_i = \frac{e^{-\beta \varepsilon_i}}{Z}$$

Probability of the particle in A being in state i is

$$P_i^A = \frac{\Omega(\varepsilon_i)}{\sum_i \Omega(\varepsilon_i)},$$

where $\Omega(\varepsilon_i)$ is the number of microstates of (AB) where A has energy ε_i.

If the particle in A has energy ε_i, then B has energy $U - \varepsilon_i$

The number of microstates of A is $\Omega^A = 1$, so $\Omega(\varepsilon_i)$ is the number of microstates which has energy $U - \varepsilon_i$ distributed with the $N-1$ particles in B.

So $S^B = k_B \ln \Omega(\varepsilon_i)$, $U^B = U - \varepsilon_i$

and we know $\frac{1}{T} = \left.\frac{\partial S}{\partial U}\right|_V$

$$\Rightarrow \frac{1}{T} = \left.\frac{\partial S^B}{\partial U^B}\right|_V = -k_B \frac{d}{d\varepsilon_i} \ln \Omega(\varepsilon_i)$$

$$\Rightarrow \text{(integrate wrt } \varepsilon_i\text{)} : \ln \Omega(\varepsilon_i) = -\varepsilon_i/k_B T + \text{const.}$$

$$\Rightarrow \Omega(\varepsilon_i) = C\, e^{-\varepsilon_i/k_B T}$$

Compare this expression to previous $\boxed{\beta \Leftrightarrow 1/k_B T}$