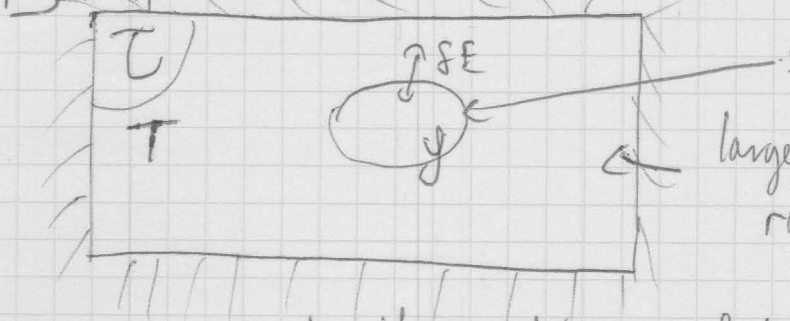
Chap 5 : Canonical ensemble

Intro : So far, we started with the isolated system => E fixed microcanonical
=> then we release some constraints between 2 isolated systems
The goal was to look at the final state reached when we release a constraint. However in realistic systems, the energy is not fixed
What is fixed then?

I. The canonical ensemble

1) Proof



=> Under these conditions, what is the distribut° of the microstates ?

$$E_{tot} = E_T + E_S = E_T + E \quad \text{fixed.}$$

Let us fix E. # microstates $= \Omega_S(E) \cdot \Omega_T(E_{tot} - E)$

$$\Omega_{T\otimes S}(E_{tot}) = \sum_E \Omega_S(E)\,\Omega_T(E_{tot}-E)$$

Here we neglect weak interactions at the border between S and T
(this is justified for macroscopic systems)

The proba distribut° of a state $\ell \in S$ is given by the total nb of states in $T \otimes S$ when S being in state ℓ

For fixed E_ℓ $\quad P_\ell = \dfrac{\Omega_T(E_{tot}-E_\ell)}{\sum_{E_\ell} \Omega_T(E_{tot}-E_\ell)\,\Omega_T(E_\ell)} \propto e^{\frac{1}{k_B} S_T^*(E_{tot}-E_\ell)}$ ← entropy

However $S_T^*(E_{tot}-E_\ell) \simeq S_T^*(E_{tot}) - E_\ell \left.\dfrac{\partial S_T^*}{\partial E}\right|_{E_{tot}} + O(E_\ell^2)$

$$S_\tau^*(E_{tot} - E_\ell) = S_\tau^*(E_{tot}) - \frac{E_\ell}{T_\tau^*} + O(E_\ell^2)$$

Here $\boxed{T = T_\tau^*}$ microcanonical temp of larger system.

$$\boxed{p_\ell^c = \frac{1}{Z} e^{-\beta E_\ell}} \quad \text{with} \quad \boxed{\beta = \frac{1}{k_B T}}$$

normalization: $\boxed{Z = \sum_\ell e^{-\beta E_\ell}}$ canonical partition function

The thermostat is only encoded through β

2) Another proof

let us use the maximized entropy principle

$$S = -k_B \sum_\ell p_\ell \ln p_\ell \quad \text{with} \quad \sum_\ell p_\ell = 1$$

$\{\ell\}$ labels the microstates of $\mathcal{S}$ in contact with a thermostat τ

we allow exchange of energy of $\mathcal{S}$ with τ such that only $\langle E \rangle$ is fixed.

$$\sum_\ell E_\ell p_\ell = \langle E \rangle = E$$

Consider $\mathcal{A}(\{p_\ell\}) = -k_B \sum_\ell p_\ell \ln p_\ell + \alpha k_B \left(\sum_\ell p_\ell - 1 \right) + \beta k_B \left(\sum_\ell p_\ell E_\ell - E \right)$

$$\frac{\partial \mathcal{A}}{\partial p_\ell} = 0 \Rightarrow -k_B \ln p_\ell - k_B - \alpha k_B - \beta k_B E_\ell = 0$$

$$\Rightarrow p_\ell = \frac{e^{-\beta E_\ell}}{1+\alpha} \qquad \alpha, \beta \in \mathbb{R}$$

$$\sum_\ell p_\ell = 1 \Rightarrow e^{1+\alpha} = \sum_k e^{-\beta E_k} \Rightarrow p_\ell = \frac{e^{-\beta E_\ell}}{\sum_\ell e^{-\beta E_\ell}} = \frac{e^{-\beta E_\ell}}{Z}$$

However β? $\quad S = -k_B \sum_\ell p_\ell \ln p_\ell$

$$= -k_B \sum_\ell p_\ell \left(-\beta E_\ell - \ln Z \right) = \beta k_B \underbrace{\langle E \rangle}_{E} + k_B \ln Z$$

$$\frac{\partial S}{\partial \langle E \rangle} = \frac{1}{T} = \beta k_B \Rightarrow \underline{\beta = \frac{1}{k_B T}} \quad \|$$

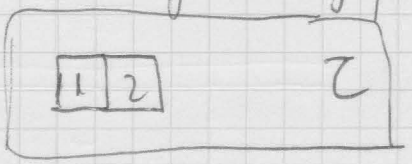
Here T is not really the microcanonical temperature but more some average T which is the thermostat temp. if in contact with τ

3) Helmotz free energy and extensivity

$$Z = e^{-\beta F^c} \Leftrightarrow F_c = -k_B T \ln Z(T,V,N)$$

F will be interpreted as the generating function of thermodynamic properties

F is extensive



If we neglect interactions between 1 and 2 $\{\ell_{1,2}\} \simeq \{\ell\}_1 \otimes \{\ell\}_2$

Then $E_{1,2} = E_1 + E_2$

$$Z = \sum_{\ell_1,\ell_2} e^{-\beta(E_{\ell_1}+E_{\ell_2})} = \left(\sum_{\ell_1} e^{-\beta E_{\ell_1}}\right)\left(\sum_{\ell_2} e^{-\beta E_{\ell_2}}\right) = Z_1 Z_2$$

$$\Rightarrow F = -k_B T \ln Z = F_1 + F_2$$

We can generalize it if $\mathcal{S} \simeq \mathcal{S}_1 \otimes \mathcal{S}_2 \otimes \dots \otimes \mathcal{S}_N$

Then $E_{\ell_1,\ell_2,\dots,\ell_N} \simeq \sum_{i=1}^{N} E_{\ell_i}$

same reasoning $Z = \prod_{i=1}^{N} z_i \Rightarrow F = -k_B T \sum_{i=1}^{N} \ln z_i$

$$\Rightarrow \boxed{F = \sum_{i=1}^{N} F_i}$$

If the subsystems are distinguishable and identical $Z = z^N \Rightarrow F = -N k_B T \ln z = N f$

extensivity: $F(T, \lambda V, \lambda N) = \lambda F(T,V,N)$

which implies $F(T,V,N) = N f\left(T, \frac{V}{N}\right)$ ($\frac{V}{N}$ ← intensive)

F depends on only 2 variables! (T ← intensive)

4) Average energy and higher cumulants

$$\bar{E}^c = \sum_\ell p_\ell^c E_\ell = \frac{1}{Z}\sum_\ell E_\ell e^{-\beta E_\ell} = \frac{-1}{Z}\frac{d}{d\beta}\sum_\ell e^{-\beta E_\ell}$$

$$\Rightarrow \boxed{\bar{E}^c = -\frac{1}{Z}\frac{dZ}{d\beta} = -\frac{d\ln Z}{d\beta}}$$

$$\langle E^2\rangle_c^* = \overline{E^2}^c = \frac{1}{Z}\sum_\ell E_\ell^2 e^{-\beta E_\ell} = \frac{1}{Z}\frac{d^2}{d\beta^2}\left(\sum_\ell e^{-\beta E_\ell}\right)$$

$$= \frac{1}{Z}\frac{d^2 Z}{d\beta^2}$$

$$(\sigma_E)^2 = \langle E^2\rangle_c^* - \langle E\rangle_c^2 = \frac{1}{Z}\frac{d^2Z}{d\beta^2} - \frac{1}{Z^2}\left(\frac{dZ}{d\beta}\right)^2$$

$\sigma_E^2 = \mathrm{var}(E)$

$$= \left(-\frac{d}{d\beta}\right)^2 \ln Z = -\frac{d\bar{E}^c}{d\beta}$$

$$\mathrm{var}(E) = \sigma_E^2 = \boxed{-\frac{d\bar{E}^c}{d\beta}} = \left(-\frac{d}{d\beta}\right)^2 \ln Z$$

$\ln Z$ ← generating function of the cumulants

In usual thermodynamics, $C_V^{th} = \left(\frac{\partial E}{\partial T}\right)_{N,V}$

We have shown that the thermo def and μ-canonical def make sense.

$$C_V^c = \frac{\partial \bar{E}^c}{\partial T} = -k_B\beta^2\frac{\partial \bar{E}^c}{\partial \beta} = \frac{1}{k_B T^2}\sigma_E^2$$

$$\boxed{C_V = \frac{1}{k_B T^2}\sigma_E^2}$$

C_V: thermo; σ_E^2: fluctuat°

We have established a relation between the specific heat and the fluctuat° of energy of the system. (particular type of a more general relat° which relates the fluctuations of the system to the way it dissipate (exchange energy with the outside)

5) Application to the paramagnetic crystal

μ-canonical

$\uparrow \pm +$ $\quad \downarrow -$ $\quad \vec{B}$

$\varepsilon_B > 0$

$N = N_+ + N_-$

$E = (-N_+ + N_-)\varepsilon_B$

$\Rightarrow N_\pm = \frac{1}{2}\left(N \mp \frac{E}{\varepsilon_B}\right)$

$\Omega = \frac{N!}{N_+! N_-!} \Rightarrow S^* = k_B \ln \Omega$

$\frac{1}{T^*} = \frac{\partial S^*(E)}{\partial E} = \frac{k_B}{2\varepsilon_B} \ln \frac{N\varepsilon_B - E}{N\varepsilon_B + E}$

Invert this relat°

$2\beta^* \varepsilon_B = \ln \frac{N\varepsilon_B - E}{N\varepsilon_B + E}$

$\Leftrightarrow E = -N\varepsilon_B \tanh \beta^* \varepsilon_B$

canonical

$E = \pm \varepsilon_B$

$\zeta = e^{-\beta\varepsilon_B} + e^{\beta\varepsilon_B}$

$\left(\Rightarrow Z = (\zeta)^N = (2\cosh \beta\varepsilon_B)^N\right.$

$F = -N k_B T \ln(2\cosh \beta\varepsilon_B)$

$\bar{E}^c = -\frac{d \ln Z}{d\beta} = -N\varepsilon_B \tanh(\beta\varepsilon_B)$

Notice that the calculat° are trivial

Let us compare the two results: They agree if:

E	$=$	$\bar{E}^c$
T^*	$=$	T

Basically we go from μ-canonical to canonical by replacing E by $\bar{E}^c$ and T^* by T.

6) Entropy of a canonical ensemble

$$S = -k_B \sum_\ell P_\ell^c \ln P_\ell^c = -k_B \sum_\ell P_\ell^c (-\ln Z - \beta E_\ell)$$

$$= k_B \ln Z + \frac{1}{T}\bar{E}^c = \frac{\bar{E}^c - F}{T}$$

$$\boxed{S = \frac{\bar{E}^c - F}{T}}$$

$F = -k_B T \ln Z \Rightarrow \frac{dF}{dT} = -k_B \ln Z + \frac{1}{Z}\frac{dZ}{dT}(-k_B T)$

and $\frac{d\ln Z}{dT} = \frac{d\ln Z}{d\beta}\frac{d\beta}{dT} = -\frac{1}{k_B T^2}\frac{d\ln Z}{d\beta} = \frac{\bar{E}^c}{k_B T^2}$

Therefore $\frac{dF}{dT} = -k_B \ln Z - k_B T \frac{\bar{E}^c}{k_B T^2} = -k_B \ln Z - \frac{\bar{E}^c}{T} = -S$

Thus $\boxed{S = -\frac{dF}{dT}}$ Also Ex $C_v = T\frac{\partial S^c}{\partial T} = -T\frac{\partial^2 F}{\partial T^2}$

We have found $S = \frac{\bar{E}^c - F}{T} \Leftrightarrow F^c = \bar{E}^c - TS$

This is fully analogous to thermo where $F = U - TS$

RQ: In thermodynamics $\Delta S \geq \int \frac{\delta Q}{T}$

if T fixed $\Delta S \geq \frac{Q}{T} \Leftrightarrow Q \leq T\Delta S$

$T\Delta S$ defines some upper limit to the heat received.

$\Delta F = \Delta E - T\Delta S = \Delta U - T\Delta S = W + Q - T\Delta S \leq W$

$W_{available} = -W \leq -\Delta F$ upper limit of the work which is available

The relations between F^c and S^c is called a Legendre transform

S^c is the derivative of F with respect to T

(T, S) are conjugate variable $\Rightarrow$ Mathematical tool in SVP

In thermodynamics, we go from thermodynamical potential to another one by a Legendre transform.

$dE = TdS - pdV + \mu dN$

$F = E - TS \Rightarrow dF = dE - TdS - SdT$

$\Leftrightarrow dF = -SdT - pdV + \mu dN$

$\hookrightarrow S = -\left(\frac{\partial F}{\partial T}\right)_{V,N}$

7) Relations with Thermodynamics (1st and 2nd principle)

$$d\bar{E}^c = d\left(\sum_\ell p_\ell E_\ell\right) = \sum_\ell dp_\ell E_\ell + \sum_\ell dE_\ell p_\ell$$

Let us consider a reversible transformation

Since $U \overset{h}{\leftrightarrow} \bar{E}^c \Rightarrow dU = \delta Q + \delta W$

could we identify $d\bar{E}^c = \underbrace{\sum_\ell E_\ell dp_\ell}_{\delta Q} + \underbrace{\sum_\ell p_\ell dE_\ell}_{\delta W}$?

Not obvious a priori

$$S = -k_B \sum_\ell p_\ell \ln p_\ell \Rightarrow dS = -k_B \sum_\ell (\ln p_\ell + 1)\, dp_\ell$$

$$= k_B \sum_\ell (-1 + \ln Z_\ell + \beta E_\ell)\, dp_\ell$$

$$\overset{\sum dp_\ell = 0}{\Rightarrow} dS = k_B \beta \sum_\ell E_\ell dp_\ell = \frac{1}{T} \sum_\ell E_\ell dp_\ell$$

$$\Rightarrow \delta Q^{rev} = \sum_\ell E_\ell dp_\ell$$

Therefore $\delta W^{rev} = \sum p_\ell dE_\ell$

This provides a microscopic interpretation of the 1st principle

⚠ We use a transformation which is reversible

Ex: Let us come back to our paramagnetic crystal.

$$F = -k_B T N \ln\left(2\cosh(\beta\varepsilon_B)\right) \Rightarrow S = -\frac{\partial F}{\partial T} = N k_B \left[\ln(2\cosh(\beta\varepsilon_B)) - \beta\varepsilon_B \tanh(\beta\varepsilon_B)\right]$$

Ex: Compare it to μ-canonical

$$H = -\varepsilon_B \sum_{i=1}^{N} s_i \text{ with } s_i = \pm 1 \Rightarrow M = \mu_B \sum s_i \Rightarrow \bar{M}^c = \mu_B N \tanh(\beta\varepsilon_B)$$

$\varepsilon_B = \frac{1}{2}\mu_B B$

$$\bar{m}^c = \frac{\bar{M}^c}{N} = \mu_B \tanh(\beta\varepsilon_B) \; ; \; \chi(\beta) = \frac{\partial \bar{m}^c}{\partial B} = \beta\mu_B^2 \left(1 - \tanh^2(\beta\varepsilon_B)\right)$$

$$\chi(0) = \beta\mu_B^2 = \frac{\mu_B^2}{k_B T} \xrightarrow{T \to 0} \infty \neq \lim_{T\to 0} \chi(B) \sim \frac{\mu_B^2}{k_B T} e^{-\frac{2\mu_B B}{k_B T}} \to 0$$

8) About the third principle.

The 3rd principle is actually an abuse of language for the Nernst thm

$$S(T) \underset{T \to 0}{\longrightarrow} 0$$

However $\begin{cases} S^*(T) \longrightarrow \\ S^c(T) \xrightarrow[T \to 0]{} \end{cases} k_B \ln \Omega_0$ where Ω_0 is the ground state degeneracy

by def

However, one may reasonably expect that the degeneracy of the ground state to be non extensive. such that

$$\lim_{T \to 0} \frac{1}{N} S(T) \longrightarrow 0 \quad \text{Nernst thm}$$

However, we know systems where the degeneracy of the ground state can be extremely large such that $\lim_{T \to 0} \frac{S(T)}{N} = \text{finite}$.

Ex: Glasses, spin liquids, ...