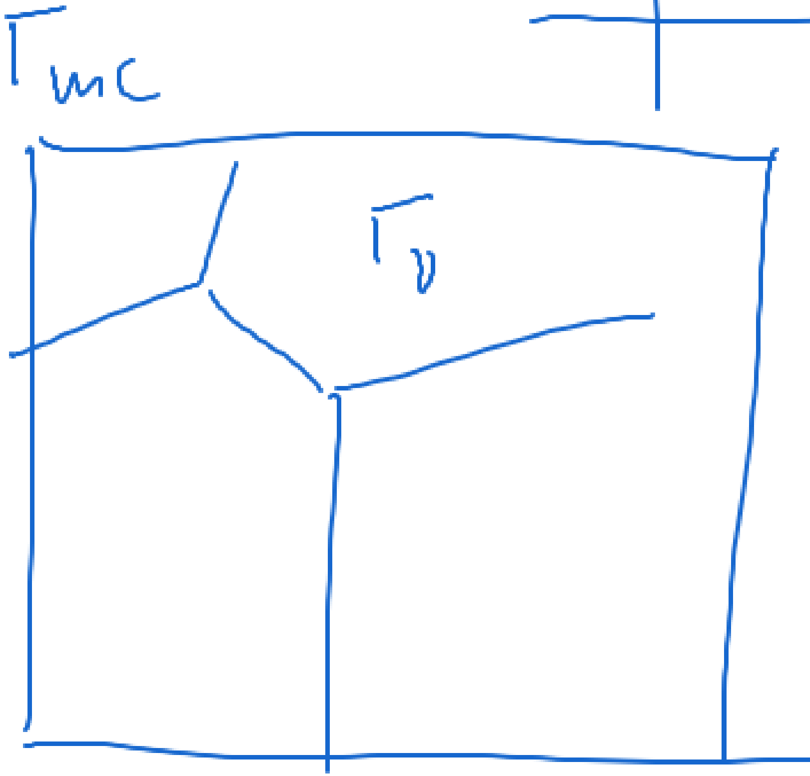
Macro sets



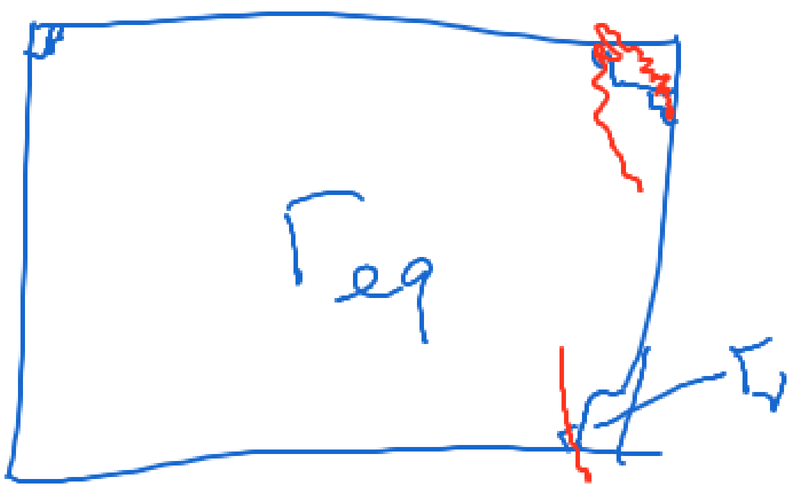
Rule: volumes of Γ_ν are dramatically different

Rule of the dominant macro set

Usually, on each Γ_{mc}, there is 1 macro set that contains most points of Γ_{mc}.

dominant macro set $= \Gamma_{eq}$

nearly 100% of the volume



dom. macro set $\Rightarrow$ macro variables M_j are nearly const. fcts on Γ_{mc}.

i.e. $\exists\, m_j \in \mathbb{R}$ ("thermal eq value of M_j")

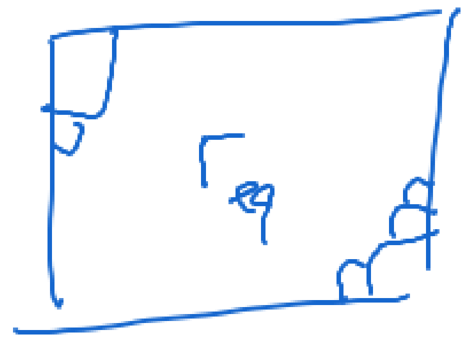
s.t. $$\frac{\mathrm{vol}\{x \in \Gamma_{mc} : M_j(x) = m_j\}}{\mathrm{vol}(\Gamma_{mc})} \approx 1.$$

$$\Rightarrow \langle M_j \rangle_{mc} := \frac{\int_{\Gamma_{mc}} M_j(x)\,dx}{\mathrm{vol}(\Gamma_{mc})} \approx m_j \approx \langle M_j \rangle_E$$

Equiv. of ensembles

$$m_j \approx \langle M_j \rangle_{can(\beta)}$$

for suitable $\beta(E)$.



Rem arbitrariness becomes better as $N \to \infty$

Analogy Γ_{eq}

strings $\in \{0,1\}^N$

$\boxed{01}\,\boxed{10}\,\boxed{00}\,\boxed{10}\,11\,0\,1110\,0$

0 1 0 1 0 1 0 1 0 1 0 1 0 1 0 1 0 1

"look random"

0 0 0 0 0 0 0 0 0 1 1 1 1 1 1 1 1 1

1) $\mathbb{P}$(look random) < 1

2) def complicated, arbitrary, becomes better as $N \to \infty$

Entropy

introduced by Rudolf Clausius in 1865

thermod. fct $\quad S(E,V,N)$

$\{\text{th. eq. states}\} \longleftrightarrow [0,\infty)^3$

Def Boltzmann's fundamental entropy formula

$$S(x) = S(\nu) = k \log \operatorname{vol} \Gamma_\nu . \quad \text{for } x \in \Gamma_\nu$$

$\mathrm{vol} = \mathrm{vol}$ in ${}^N\Gamma_1$ or $\frac{\mathrm{vol}_0}{N!}$ $\quad \Gamma_1^N = \Gamma_0$

ordered

<u>Rem</u> $\quad [\mathrm{vol}\, \Gamma_v] = \left([\text{length}] \cdot [\text{momentum}]\right)^{3N}$

1) In QM, $\mathrm{vol}\,\Gamma_v \longrightarrow \dim \mathcal{H}_v$

2) In CM, choose a unit of length · momentum, e.g., $h = 2\pi\hbar$

3) In thermod., S is def'd up to add. of a const.

$$\Gamma_V^{\Delta E} = \text{"}\,\Gamma_V \times [E, E+\Delta E)\,\text{"}$$

Γ_V'

$$k \log \underbrace{\mathrm{Vol}\, \Gamma_V^{\Delta E}}_{\lambda_E(\Gamma_V)\,\Delta E}$$

$$= k \log \lambda_E(\Gamma_V) + \cancel{k \log \Delta E}$$

$$\mu_E(B) = \frac{\lambda_E(B)}{\lambda_E(\Gamma_E)}.$$

$k \log \lambda_E(\Gamma_E)$ not const.

micro

macro

~~macro-can~~

micro-can.

can.

grand-can.

dom macro set, fund. entropy formula

$\Longrightarrow$ $S(eq)$ is max. among $S(\nu)$

in Γ_{mc}

$$\frac{\mathrm{vol}(\Gamma_{eq})}{\mathrm{vol}(\Gamma_{mc})} \approx 1, \quad \text{so } k \log \mathrm{vol}\,\Gamma_{eq} \approx k \log \mathrm{vol}(\Gamma_{mc})$$

$$S(eq) \approx k \log \mathrm{vol}(\Gamma_{mc})$$

Def $\Omega(E) = \lambda_E(\Gamma_E) = \frac{1}{N!} \lambda^0_E(\Gamma^0_E)$

$$= \frac{1}{N!} \frac{d}{dE} \mathrm{vol}_0 \left(\Gamma^0_{\le E}\right)$$

Ex ideal gas $\Gamma^{\circ}_{\leq E} = \Lambda^N \times B^{3N}_{\sqrt{2mE}}$

energy dependence:

$$\mathrm{vol}_0 \left(\Gamma^{\circ}_{\leq E} \right) \propto E^{3N/2}$$

$$\Rightarrow \quad \Omega(E) = C(V,N) \; E^{3N/2 - 1}$$

$$S(eq) = S(E,V,N) = S(E) = k \log \Omega(E)$$

$$\Gamma_{mc} = \text{“} \Gamma_E \times [E, E+\Delta E] \text{”}$$

$$\mathrm{vol}\left(\Gamma_{mc}\right) = \Omega(E)\, \Delta E$$

$$S(eq) = k \log \mathrm{vol}\, \Gamma_{mc}$$

$$= \underline{k \log \Omega(E)} + \cancel{k \log \Delta E}$$

$$\Rightarrow S(E) = k \frac{3}{2}(N-2) \log E + \cancel{\underset{(V,N)}{\mathrm{const}}}.$$

$$\underline{\frac{\partial S}{\partial E}} = \frac{3k(N-2)}{2E} = \frac{3k\cancel{N}}{2\bar{e}\cancel{N}} - \frac{3k2}{2\bar{e}N}$$

$$= \underline{\frac{1}{T}} + \cancel{O(N^{-1})}$$

$$\bar{e} = \frac{3}{2}kT$$

$$dS = \frac{dQ}{T} \qquad (\text{Clausius } 1865)$$

<u>Extensive</u> (additive)

$$S_{A \cup B}(V_A, V_B) = k \log \operatorname{vol}\big(\underbrace{\Gamma_{V_A} \times \Gamma_{V_B}}_{= \Gamma_{V_A, V_B}}\big) = S_A(V_A) + S_B(V_B)$$

under which conditions?

i) $A \cap B = \emptyset$, ii) need that permutations don't mix A, B.

$\Leftarrow$ 1) different types of particles

2) disjoint regions in space

iii) interaction energy negligible

2nd law (qualitative)

Rule of small macro sets

$$\Gamma_{<\nu} = \bigcup_{\nu' : S(\nu') < S(\nu)} \Gamma_{\nu'}$$

$$\mathrm{vol}\left(\Gamma_{<\nu}\right) \ll \mathrm{vol}\left(\Gamma_{\nu}\right)$$

"The number of small macro sets does not compensate their smallness."

B.'s expl. 2nd law: $S(T^t_x)$ increases

$t_1, \; t_2 = t_1 - t$

at t_1, Γ_ν, $A_t = T^t \Gamma_\nu$, $\mathrm{vol}(A_t) = \mathrm{vol}(\Gamma_\nu)$

$$\frac{\mathrm{vol}(A_t \cap \Gamma_{<\nu})}{\mathrm{vol}(\Gamma_\nu)} \leq \frac{\mathrm{vol}(\Gamma_{<\nu})}{\mathrm{vol}(\Gamma_\nu)} \ll 1.$$

$\Longrightarrow S(x(t_2)) \geq S(x(t_1))$ for most $x(t_1) \in \Gamma_\nu$.