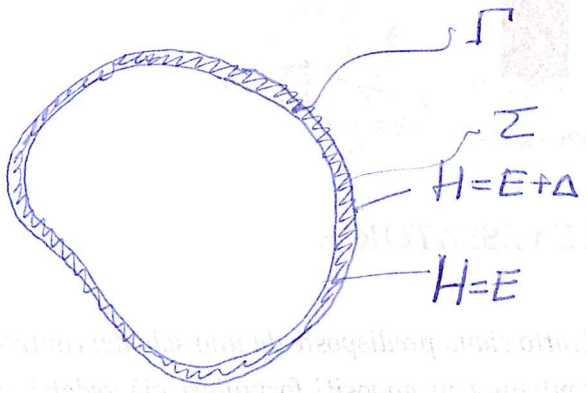
Microcanonical Thermodynamic Potential

It is customary to define the # of microscopic state as result of integration of available phase space on a "volume" in phase space of thickness Δ



the "volume" Γ is $\int_{E<H<E+\Delta} d^{3N}p\, d^{3N}q$

the # of microscopic states is Γ / Volume of a cell

Volume of a "cell" in phase space is Λ^{3N} where Λ has the dimension of an action

$$\Omega_{micro} = \frac{\Gamma}{\Lambda^{3N}} = \Delta \int \frac{d^{3N}p\, d^{3N}q}{\Lambda^{3N}} \delta(H-E)$$

$\Sigma = \int d^{3N}p\, d^{3N}q\, \delta(H-E)$ is the surface of available phase space

$[\Sigma] = \frac{1}{E}$ $[\Delta] = E$ $[\Omega_{micro}] = 1$

$S = k_B \ln \Sigma_{Micro}$

is Extensive and Increasing function of E

Proof of Extensivity

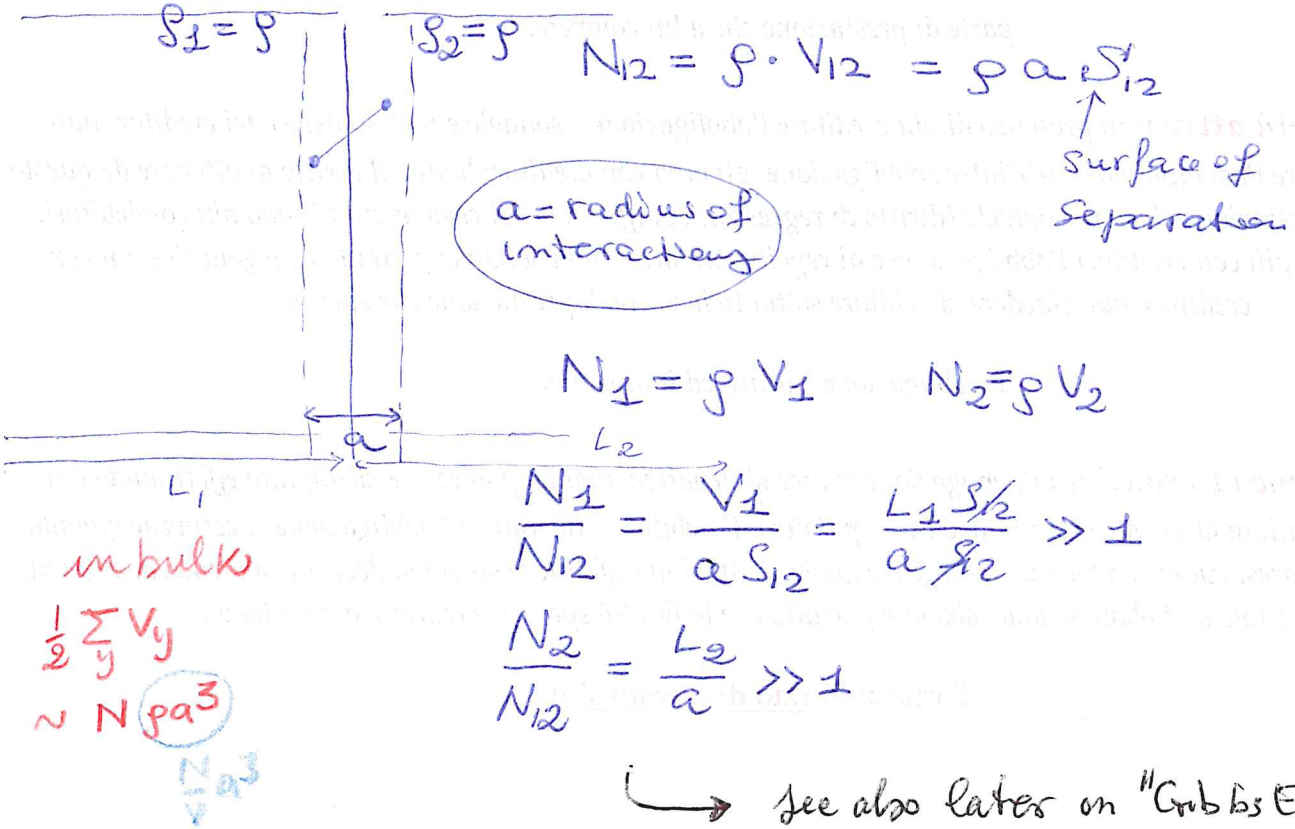
$$H = H_1(p_1 q_1) + H_2(p_2 q_2) + H_{12}(q_1 q_2)$$

$$\Sigma_{Micro} = \Delta \int d1\, d2\, \delta(E - H_1 - H_2 - H_{12})$$

E is extensive

① & ② are thermodynamically large

H_{12} will involve on average a # of particles proportional to the surface of separation btw ① & ② for Short Range forces



$N_{12} = \rho \cdot V_{12} = \rho\, a\, S_{12}$ ← surface of separation

a = radius of interaction

$N_1 = \rho V_1 \qquad N_2 = \rho V_2$

$$\frac{N_1}{N_{12}} = \frac{V_1}{a S_{12}} = \frac{L_1 S_{12}}{a S_{12}} \gg 1$$

$$\frac{N_2}{N_{12}} = \frac{L_2}{a} \gg 1$$

in bulk

$\frac{1}{2}\sum_j V_j \sim N \rho a^3$

$\frac{N}{V} a^3$

↳ see also later on "Gibbs Ensembles"

interaction energy $\langle H_{12} \rangle$ scales with N_{12}

while $\langle H_1 \rangle \sim N_1$ $\quad \langle H_2 \rangle \sim N_2$

To evaluate the equilibrium # of microscopic states we safely neglect the H_{12} contribution

This is however not correct if we want to calculate equilibration times

$$\mathcal{Z}_{micro} = \Delta \int d1\, d2\, \delta(E - H_1 - H_2 - H_{12}) =$$

$$= \Delta \int d1 \int d2 \int_0^E dE_1\, \delta(E - E_1 - H_2)\, \delta(E_1 - H_1)$$

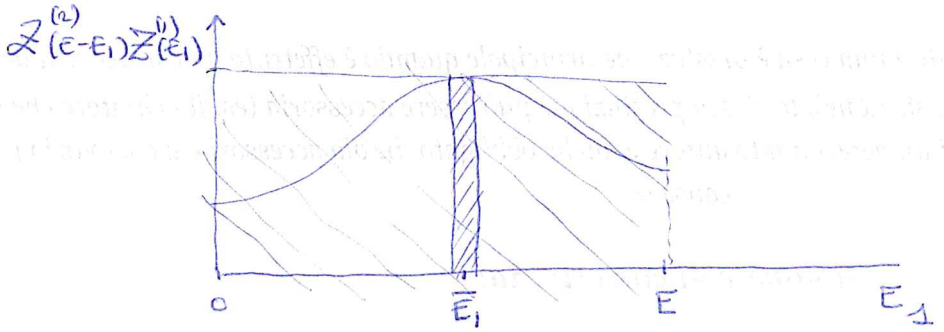
$$= \frac{1}{\Delta} \int_0^E dE_1\, \mathcal{Z}^{(1)}_{micro}(E_1)\, \mathcal{Z}^{(2)}_{micro}(E - E_1)$$

both $\mathcal{Z}^{(1)}$ & $\mathcal{Z}^{(2)}$ are positive we assume that within E $\exists$ $\bar{E}_1$ such that

$$\mathcal{Z}^{(2)}_{micro}(E - \bar{E}_1)\, \mathcal{Z}^{(1)}_{micro}(\bar{E}_1) \geq \mathcal{Z}^{(2)}_{micro}(E - E_1)\, \mathcal{Z}^{(1)}_{micro}(E_1) \quad \forall E_1$$

then

$$\mathcal{Z}_{micro}(E - \bar{E}_1)\, \mathcal{Z}_{micro}(\bar{E}_1) \leq \mathcal{Z}_{micro}(E) \leq \frac{E}{\Delta}\, \mathcal{Z}^{(2)}_{micro}(E - \bar{E}_1)\, \mathcal{Z}^{(1)}_{micro}(\bar{E}_1)$$



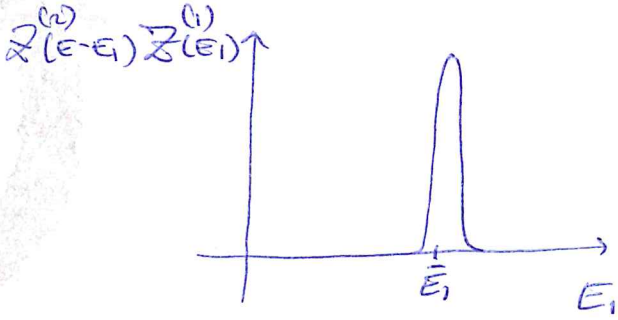
$$S^{(2)}(E-\bar{E}_1) + S^{(1)}(\bar{E}_1) \leq S^{(1+2)}(E) \leq S^{(2)}(E-\bar{E}_1) + S^{(1)}(\bar{E}_1) + k_B \ln \frac{E}{\Delta}$$

Thermodynamically irrelevant

$$\sim \ln N$$

therefore

$$S^{(1+2)}(E) = S^{(1)}(\bar{E}_1) + S^{(2)}(\bar{E}_2)$$



with $\bar{E}_2 = E - \bar{E}_1$

definition of $\bar{E}_1$ imply

$$\frac{\partial}{\partial E_1} Z^{(2)}(E-E_1)\, Z^{(1)}(E_1)\Big|_{E_1=\bar{E}_1} = 0$$

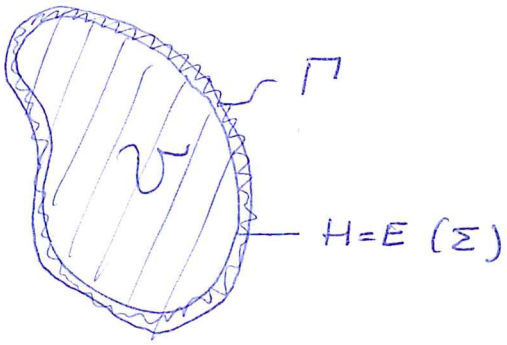
$$\frac{\partial}{\partial E_1} e^{S^{(2)}(E-E_1)/k_B}\, e^{S^{(1)}(E_1)/k_B} = 0$$

$$\frac{\partial}{\partial E_1} S^{(2)}(E-E_1) + S^{(1)}(E_1) = 0$$

$$\frac{\partial S^{(1)}(E_1)}{\partial E_1}\Big|_{\bar{E}_1} = \frac{\partial S^{(2)}(E_2)}{\partial E_2}\Big|_{E_2=E-\bar{E}_1} \Rightarrow \frac{1}{T_1} = \frac{1}{T_2}$$

Thermal Equilibrium

Proof of increasing $S(E)$



change $V \to \Omega$ to avoid confusion with physical volume

in the thermodynamic limit

$$S = \begin{cases} k_B \ln \Gamma / h^{3N} \\ k_B \ln V / h^{3N} \end{cases}$$ are equivalent

if $E = n\Delta$

$$V = \underbrace{\Gamma(E) + \Gamma(E-\Delta) + \cdots \Gamma(\Delta)}_{n \text{ terms}}$$ ← positive

but Γ is increasing function of E and positive $\Rightarrow V$ is increasing function of E

$$\Gamma(E) \leq V(E) \leq \frac{E}{\Delta}\Gamma(E)$$

$$S_\Gamma = k_B \ln \Gamma \leq S_V = k_B \ln V \leq S_\Gamma + k_B \ln \frac{E}{\Delta}$$

Thermodynamically irrelevant

but now V is an increasing function of the physical volume

$$V = \int_{H \leq E} d_p^{3N} d_q^{3N} \to \text{perfect gas} \to V = \int_{H \leq E} d_p^{3N} V^N$$

$$\Gamma = \int d^{3N}p\, d^{3N}q \underbrace{\Theta(E - H(pq))}_{\Theta \geq 0}$$

$$\int_A dx\, f(x) \geq \int_B dx\, f(x)$$

if $\mu(A) \geq \mu(B)$ and $f(x) \geq 0$

Spontaneous transformations at fixed E, N imply increasing V therefore S is the thermodynamic Entropy

for short range interaction (e.g. pair) we can prove that

$$\int d^{3N}q\, f(V) \simeq f(0) V^N + \alpha V (a^3)^{N-1}$$

(V: potential; V: volume; N: number; a: radius of interaction; V: volume)

therefore

$$\Gamma = \int d^{3N}p \underbrace{\int d^{3N}q\, \Theta(E - T - V)}_{\int d^{3N}q\, f(V) \sim V^N}$$

$$\int d^{3N}q \left(f(V) - f(0) + f(0)\right) = V^N + \underbrace{\int d^{3N}q \left(f(V) - 1\right)}_{f(0)}$$

$$V = \frac{1}{2}\sum_{ij} v(|q_i - q_j|)$$

$$\int d^3Q \int \prod_i^{N-1} d^3q_i' \left(f(V) - 1\right)$$

$\downarrow$

V

$\uparrow$ different from

Short range interaction & scaling of $\bar{V}$

$$\bar{V} = \frac{1}{2}\sum_{i\neq j} v(|\vec{r}_i - \vec{r}_j|) = \sum_i \sum_{j>i} V(|r_i - r_j|)$$

$\bar{V}$: function which depends on $(N-1)$ 3d positions

3 particles

$$V(|r_1 - r_2|) + V(|r_2 - r_3|) = \bar{V}$$

2 relative coordinate variables

$$\int \prod_1^N d^3 r_i \left\{ [f(\bar{V}) - f(0)] + f(0) \right\}$$

$$= f(0) V^N + \underbrace{\int \prod_1^N d^3 r_i \, [f(\bar{V}) - f(0)]}_{\sim V a^{(N-1)3}}$$

3 particles

$u_2 = r_2 - r_1$

$$\int \prod_1^3 d^3 r_i \left[f\left(V(r_1 - r_2) + V(r_2 - r_3) \right) - f(0) \right] =$$

$$= \underbrace{\int d^3 r_1}_{V} \int d^3 u_2 \int d^3 u_3 \left[f\left(V(|u_2|) + V(|u_3|) \right) - f(0) \right]$$

$V(|u_2|) \neq 0$ only if $|u_2| < a^3$

$V(|u_3|) \neq 0$ only if $|u_3| < a^3$

$$= V \underbrace{\int_{|u_2| \leq a^3} a^3 u_2 \int_{|u_3| \leq a^3} d^3 u_3 \left[f(\bar{V}) - f(0) \right]}_{\sim (a^3)^2}$$

$$\int d^{3N} r \, f(\bar{V}) \sim f(0) V^N + V a^{3(N-1)} \, g$$

$f(0)$: q.p.; g: number

Configurational entropy in microcanonical ensemble

If $H = T(p) + V(q)$ — N particles!

then we can separate for classical particles

$S = S_{kin} + S_{conf}$ ← configurational ⇐ q variables

↑ the perfect gas ⇐ p variables

$$Z = \int \frac{d^{3N}p\, d^{3N}q}{h^{3N} N!}\, \delta(E - T - V) = \int_0^E dE_c \int \frac{d^{3N}p\, d^{3N}q}{h^{3N} N!}\, \delta(E_c - T)\, \delta(E - E_c - V)$$

$$= \int_0^E dE_c \left[\int \frac{d^{3N}q}{V^N}\, \delta(E - E_c - V(q))\right] \left[V^N \int \frac{d^{3N}p}{N!\, h^{3N}}\, \delta(E_c - T(p))\right]$$

conf g — perfect gas

$$= \int_0^E dE_c\, Z_{cfg}(E - E_c)\, Z_{pg}(E_c)$$

If $\bar{E}_c$ is such that $\max_{E_c} Z_{cfg}(E - E_c)\, Z_{gp}(E_c) = Z_{cfg}(E - \bar{E}_c)\, Z_{gp}(\bar{E}_c)$

then up to non extensive corrections

$$S = S_{gp} + S_{cfg}$$

$$S_{gp} = k_B \ln Z_{gp}(\bar{E}_c) \qquad S_{cfg} = k_B \ln Z_{cfg}(E - \bar{E}_c)$$

($E - \bar{E}_c$: potential energy)