General characteristics of Entropy in Microcanonical Ensemble

1) $S = k_B \ln \Gamma_{micro}$ — # of microscopic state to a macroscopic state

is extensive (for that we need correct Boltzmann counting)

2) S is an increasing function of E

since Γ is an increasing function of E

$\Rightarrow$ we may define a Temperature

$$\frac{1}{T} = \frac{\partial S}{\partial E}$$

3) satisfies the 2nd principle in particular spontaneous transformation such as adiabatic expansion leads to an increase of the entropy

1) S is extensive provided the CCB in the perfect gas limit

$$Z_{micro} = \Delta \int \frac{dp^{3N} dq^{3N}}{\Lambda^{3N}} \delta(E-H)$$

$$\int_{E \leq H \leq E+\Delta} dp^{3N} dq^{3N} = \Delta \int dp^{3N} dq^{3N} \delta(E-H)$$

$$H = \sum_1^N \frac{p_i^2}{2m}$$ indep on q

$$Z_{micro} = \Delta V^N \underbrace{\int \frac{d^{3N}p}{\Lambda^{3N}} \delta\left(E - \sum_i \frac{p_i^2}{2m}\right)}_{\text{Scales as } \left(\frac{E}{N}\right)^{3N/2}}$$

(extensive)^N

$\ln Z_{micro} \sim N \ln V$
more than extensive!

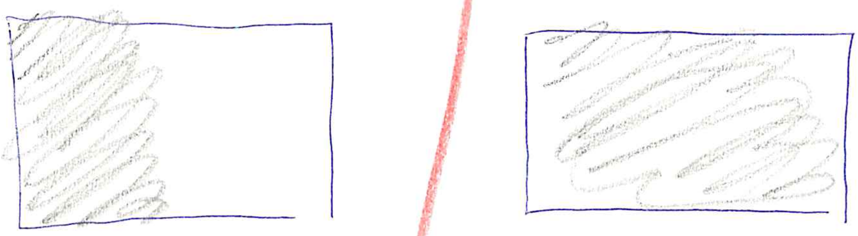
while dividing by $N!$ we get

$$\frac{V^N}{N!} \simeq \left(\frac{V}{N}\right)^N \frac{1}{e^{-N}\sqrt{2\pi N}}$$ can be associated to this

if $\quad S \simeq k_B \ln \dfrac{\Omega(E)}{N!\,\Lambda^{3N}}$

then

$$\Omega(E) = \int d^{3N}p\, d^{3N}q \; \underbrace{\Theta(E-H)}_{E=\mathrm{const}}$$



V_1 $\qquad\qquad$ V_2

domain of integration for q varies

SHORT RANGE INTERACTIONS

the average potential energy is extensive for short range interactions

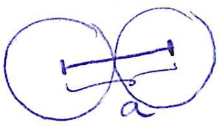
$$V = \frac{1}{2} \sum_{i \neq j} v(\vec{r}_i - \vec{r}_j)$$

there are $N\frac{(N-1)}{2}$ terms but

$\langle V \rangle$ do not scale as N^2 !!

because

$$v(|r_i - r_j|) \cong 0 \quad \text{if} \quad |\vec{r}_i - \vec{r}_j| > a$$



a radius of interaction (diameter of an hard sphere!!)

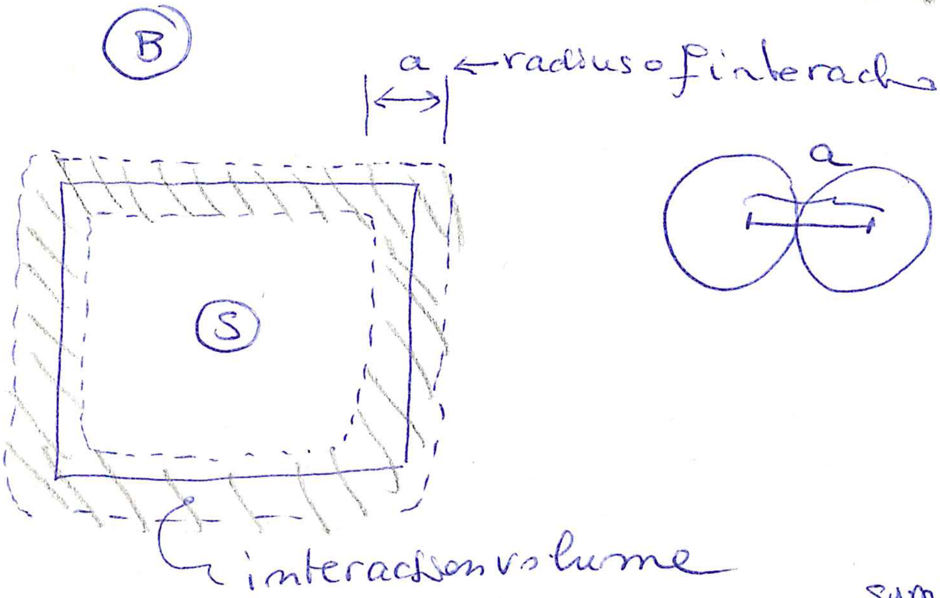
$$\langle V \rangle = \frac{1}{2} \sum_{i=1}^{N} \underbrace{\sum_j \langle v(|r_i - r_j|) \rangle}_{\text{is} \neq 0 \text{ only if } |r_i - r_j| < a}$$

$$\langle V \rangle \sim N \rho a^3 \langle v \rangle$$

ρ # density (number density)

scales with N and not N^2

SURFACE INTERACTIONS



$$\langle H_{SB} \rangle \sim N_S^{(a)} \cdot \underbrace{\rho_B a^3}_{\text{\# of Bath particle in the interaction zone (given a system particle at distance a)}} \simeq \overbrace{\rho_S \rho_B}^{\text{symm}} a^4 S$$

scales with the surface not with the volume

$N_S^{(a)}$: # of system particle in the interaction volume

$\rho_S S \cdot a$