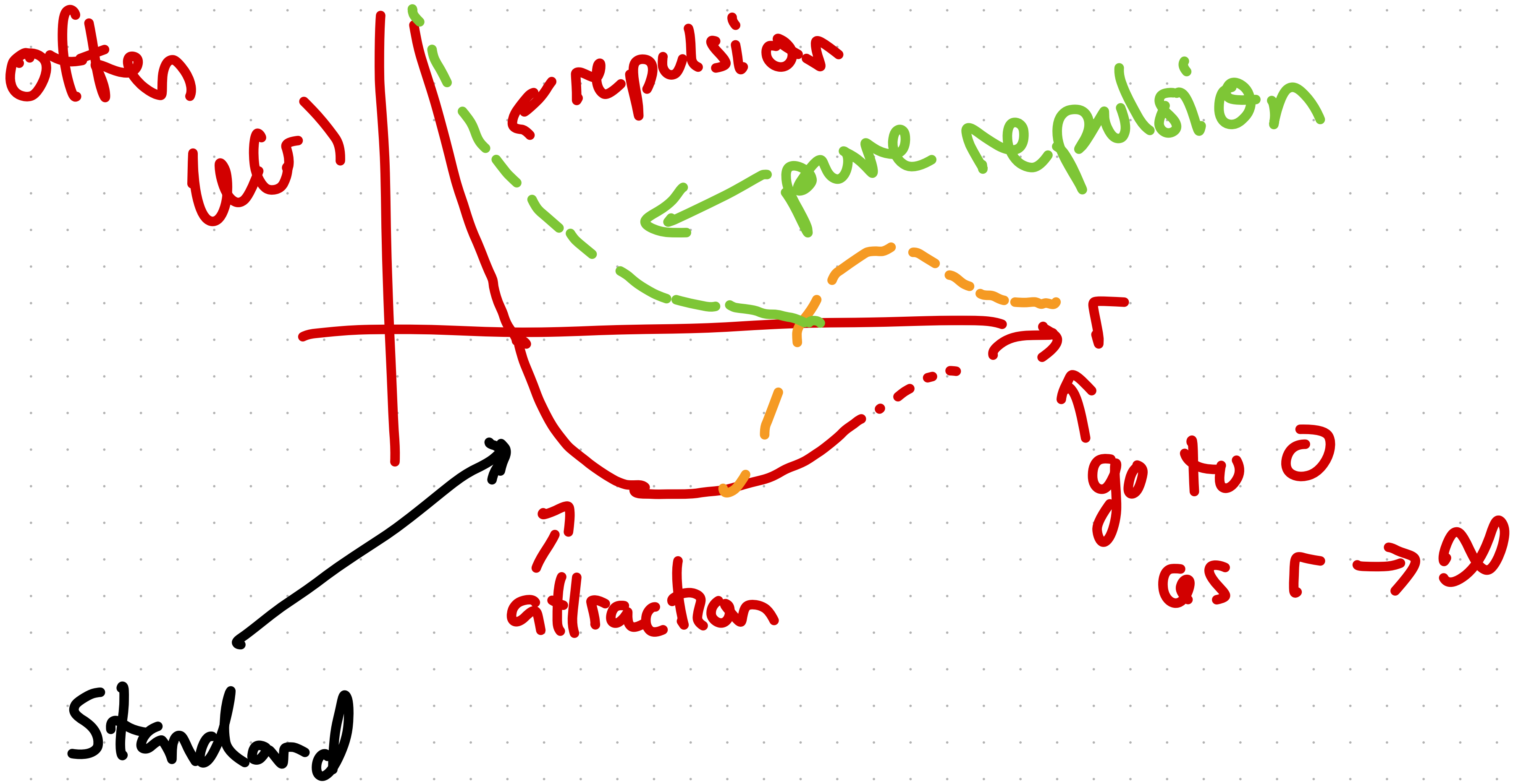
Lecture 7 - "Real" Liquids and Gasses

Interacting systems of molecules

$$\mathcal{H}(\vec{X}) = \underbrace{\sum_{i=1}^{N} \vec{p}_i^{\,2}/2m}_{\text{ideal gas}} + U(\vec{q})$$

$U \leftarrow$ what is it in general



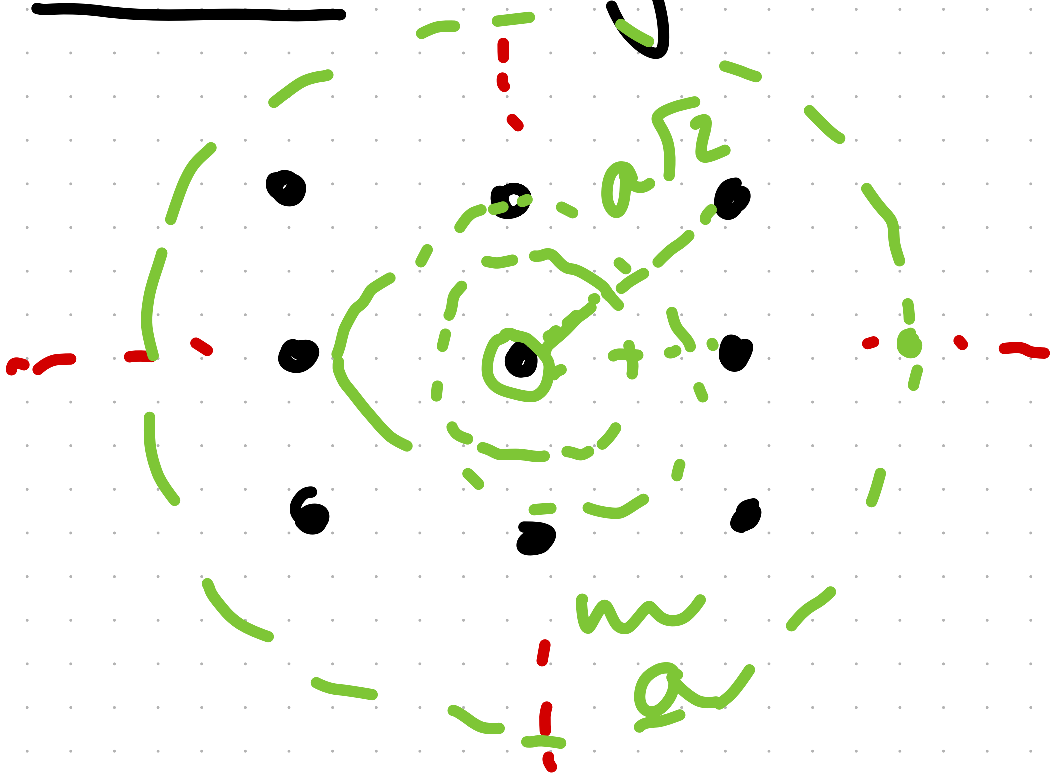
Because there an attraction term condensation (liq, solids) at T↓ P↑

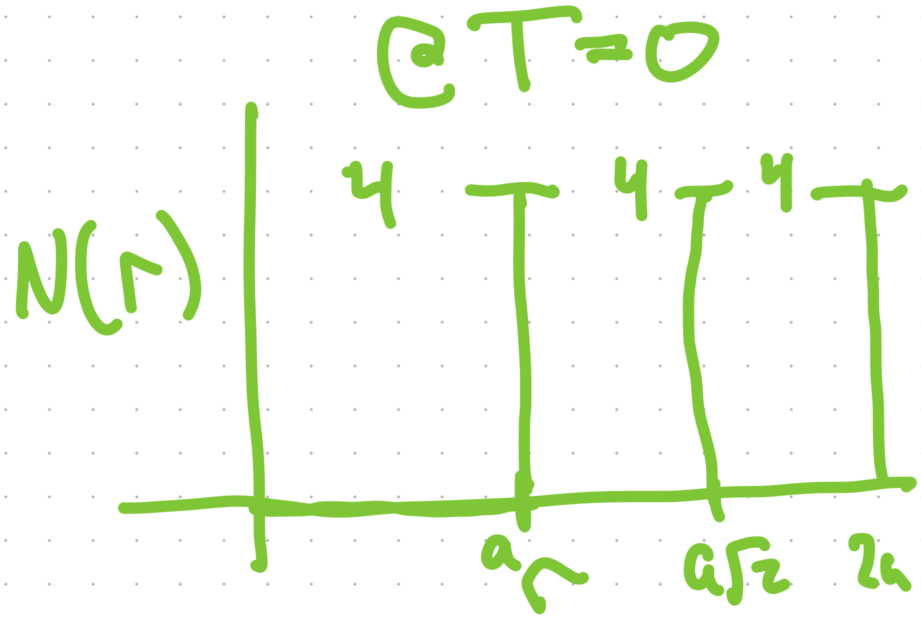
"structure" of liquids and gasses

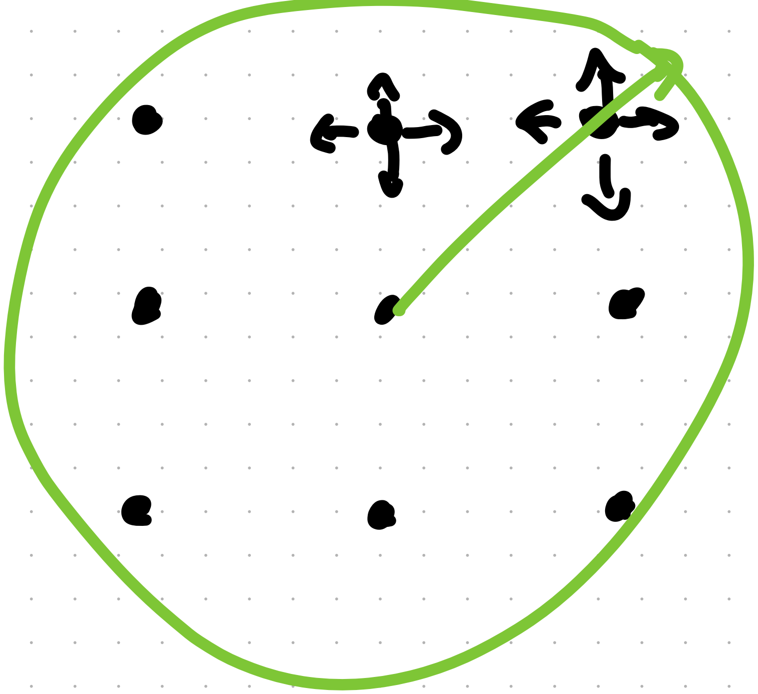
turn on interactions

→ average arrangement of molecules

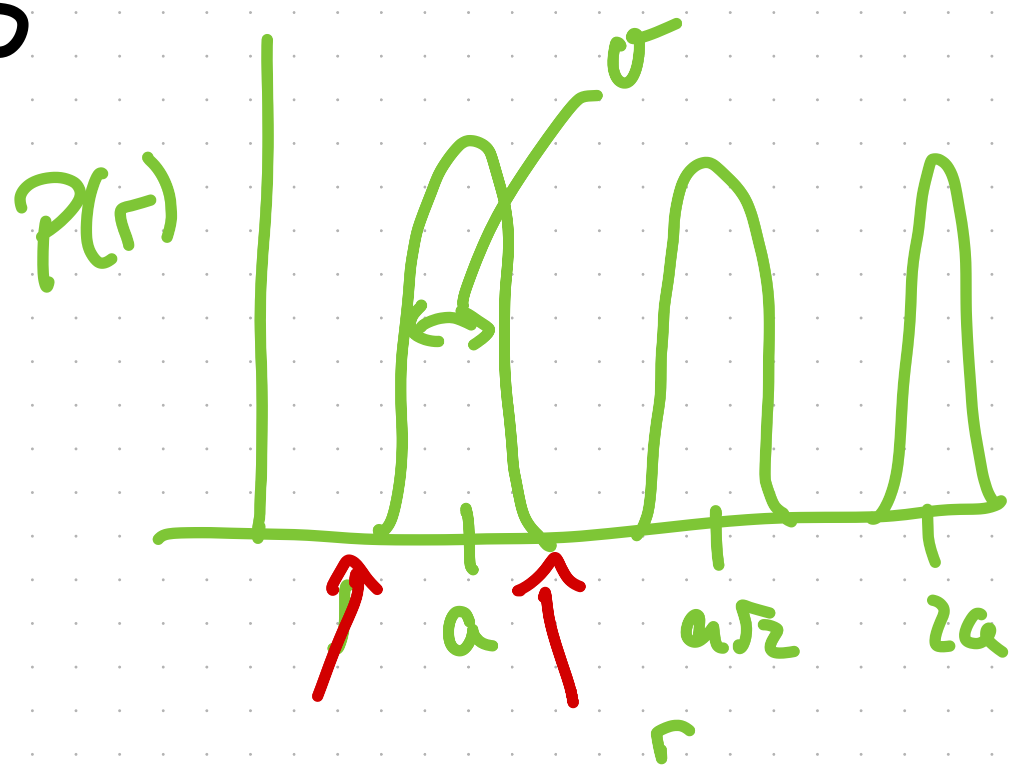
Solid Eg 2d square crystal





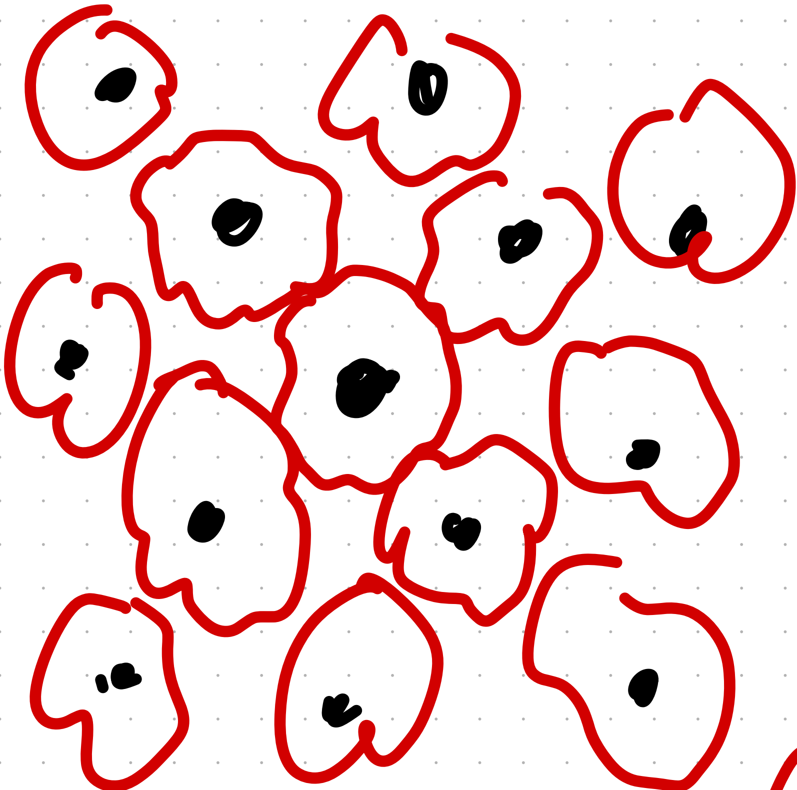


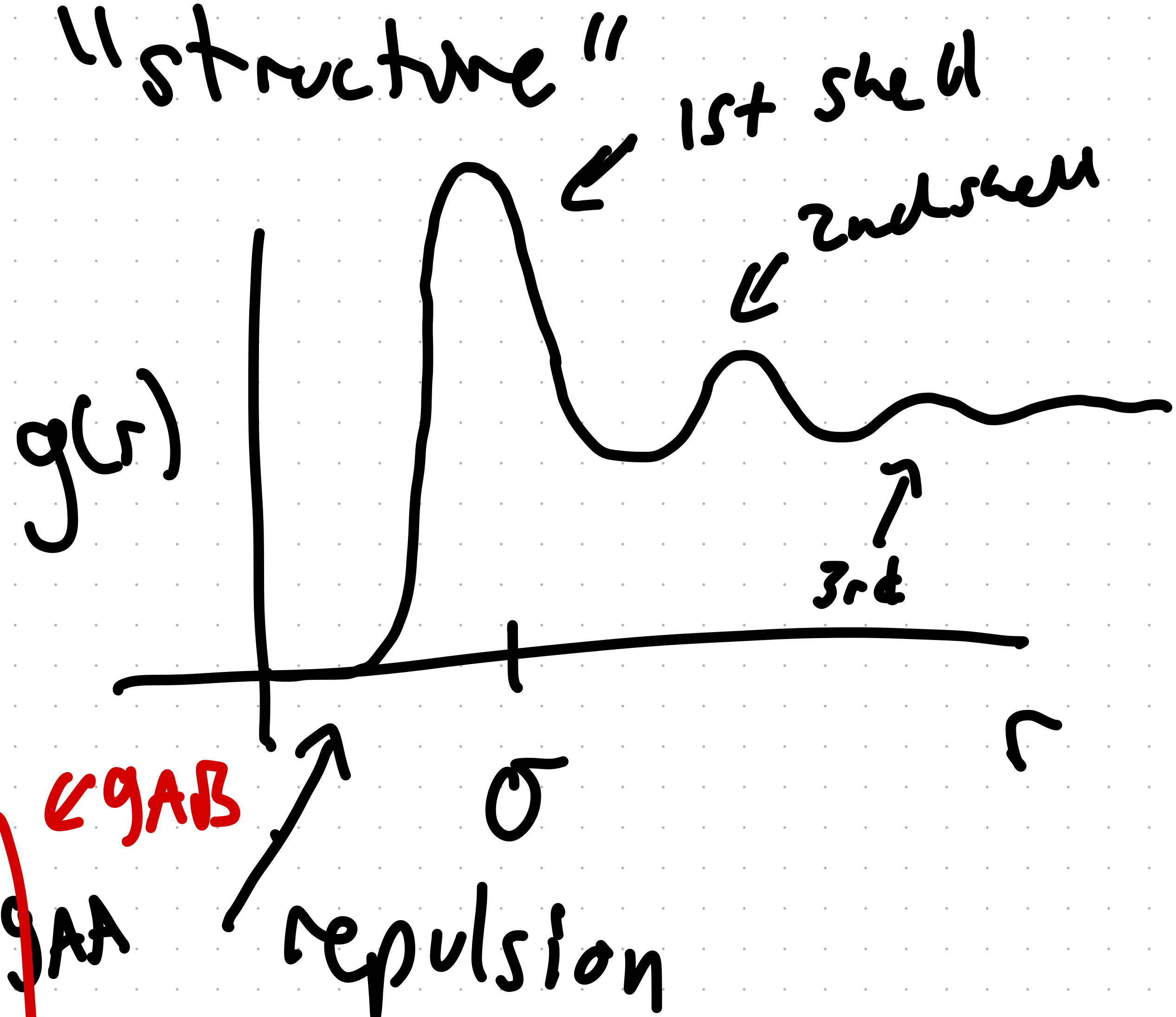
$T > 0$



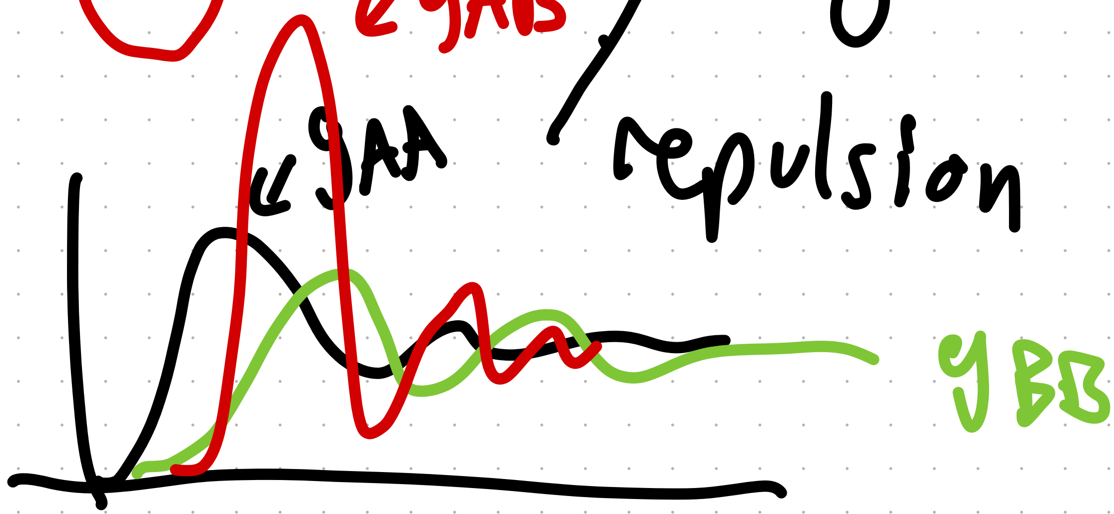
$$N(r) = \int_{a-3\sigma}^{a+3\sigma} dr\, P(r) \approx 4$$

In a liquid, what is equivalent form of "structure"

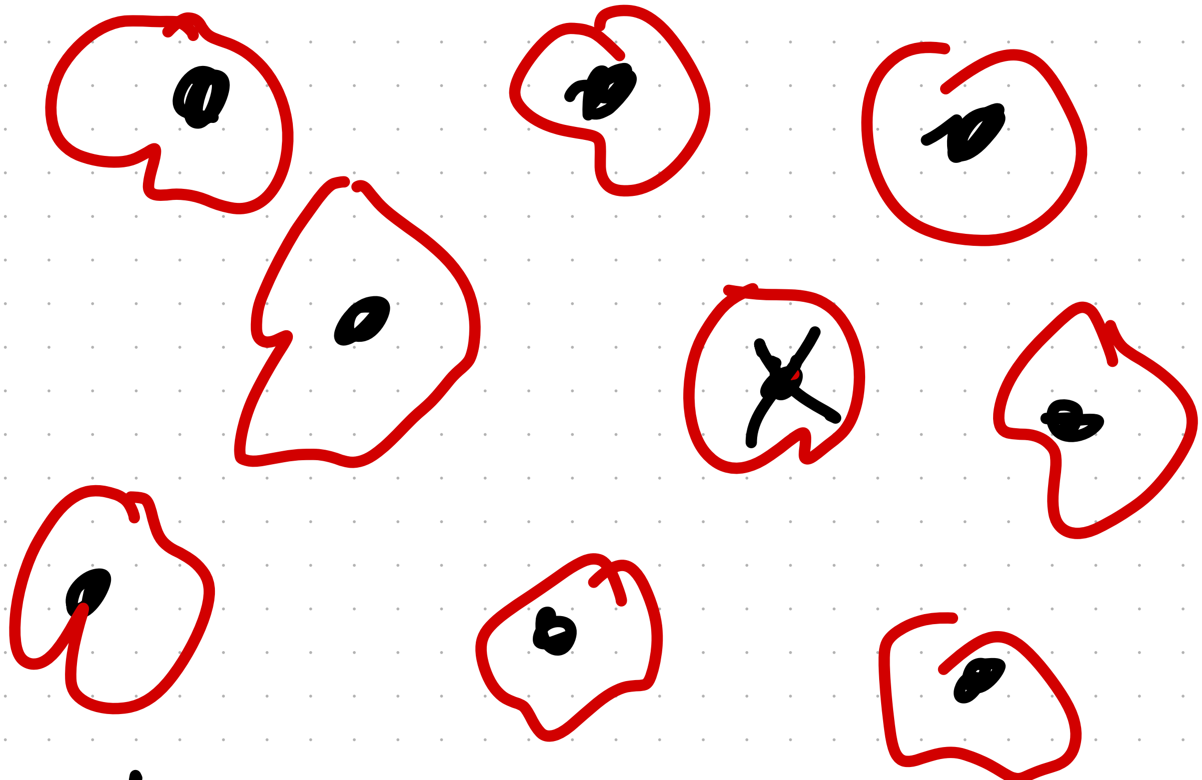


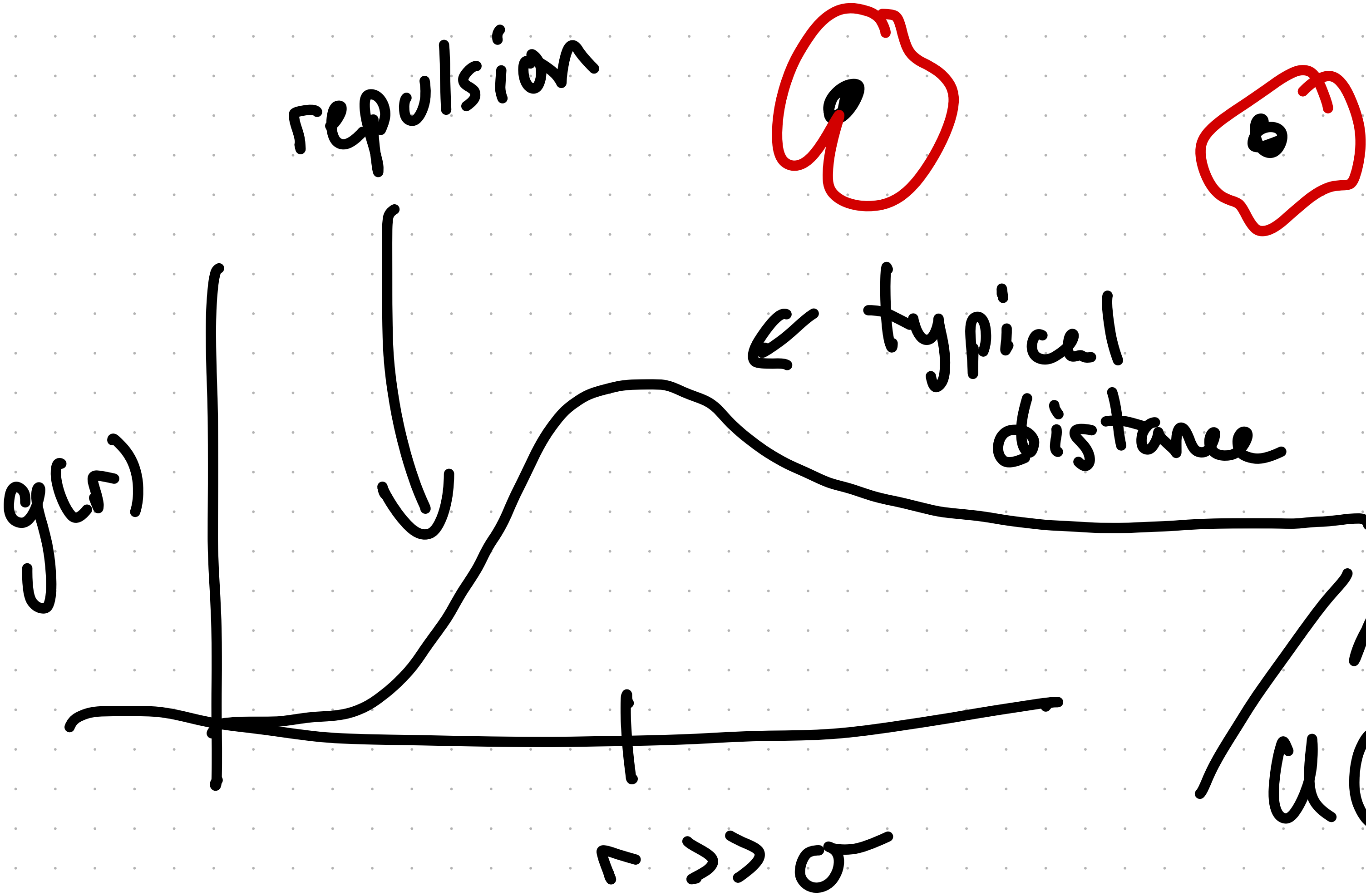


2 types



In a gas

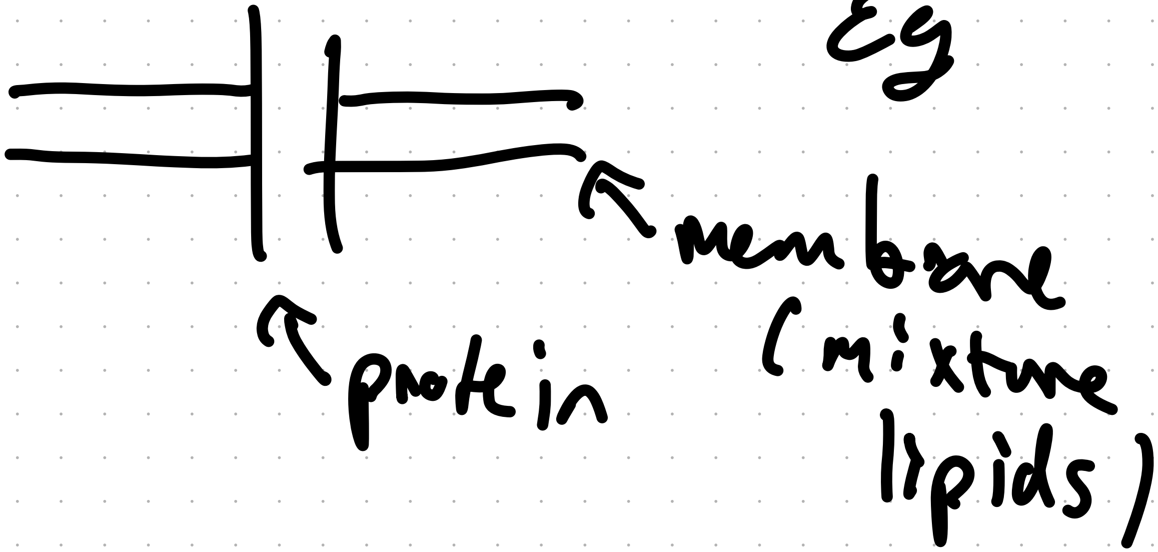


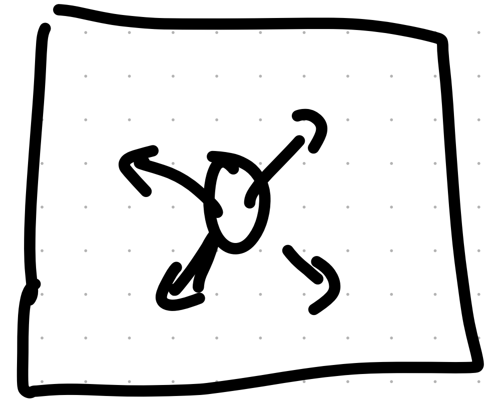


no θ dependenc

$U(r)$ radially symmetric

Eg





$$Q(N,V,T) = \frac{1}{N!\,h^{3N}} \int dp^{3N} \int dq^{3N}\, e^{-\beta \mathcal{H}(\vec{p},\vec{q})}$$

$$\beta = \frac{1}{k_B T}$$

$$\mathcal{H} = KE + PE \leftarrow u(\vec{q})$$

$$\int d\vec{X}\, e^{-\beta(KE + PE)}$$

$$= \left(\int d\vec{p}\, e^{-\beta(KE)}\right)\left(\int dq\, e^{-\beta u}\right)$$

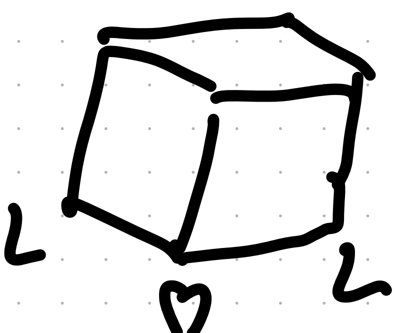
$$\to \frac{1}{h^{3N}} \int d\vec{p}^{\,3N}\, e^{-\beta \sum p_i^2/2m} \sim \left(\frac{2\pi m k_B T}{h^2}\right)^{3N/2}$$

$$\Lambda = \sqrt{\frac{h^2}{2\pi m k_B T}}$$

$$Q(N,V,T) = \frac{1}{N!} \cdot \frac{1}{\lambda^{3N}} \int_V d\vec{q}\, e^{-\beta U(\vec{q})}$$

$$\int_0^L dq_1 \int_0^L dq_2 \cdots \int_0^L dq_{3N}\, e^{-\beta U(q_1, q_2, \ldots, q_{3N})}$$

$$U(\vec{q}) = \begin{cases} U(\vec{q}) & \text{if } \vec{q} \text{ in box} \\ \infty & \text{if any } q_i < 0 \text{ or } q_i > L \end{cases}$$



also say

$$\int_{-\infty}^{\infty} dq_1 \int_{-\infty}^{\infty} dq_2 \cdots \int_{-\infty}^{\infty} dq_{3N}\, e^{-\beta U(\vec{q})}$$

$$Q = \frac{1}{N!}\frac{1}{\lambda^{3N}} \int_V \underbrace{dq^{3N}\, e^{-\beta U(q)}}$$

$$Z(N,V,T) = (\;\;) = Q \cdot N! \cdot \lambda^{3N}$$

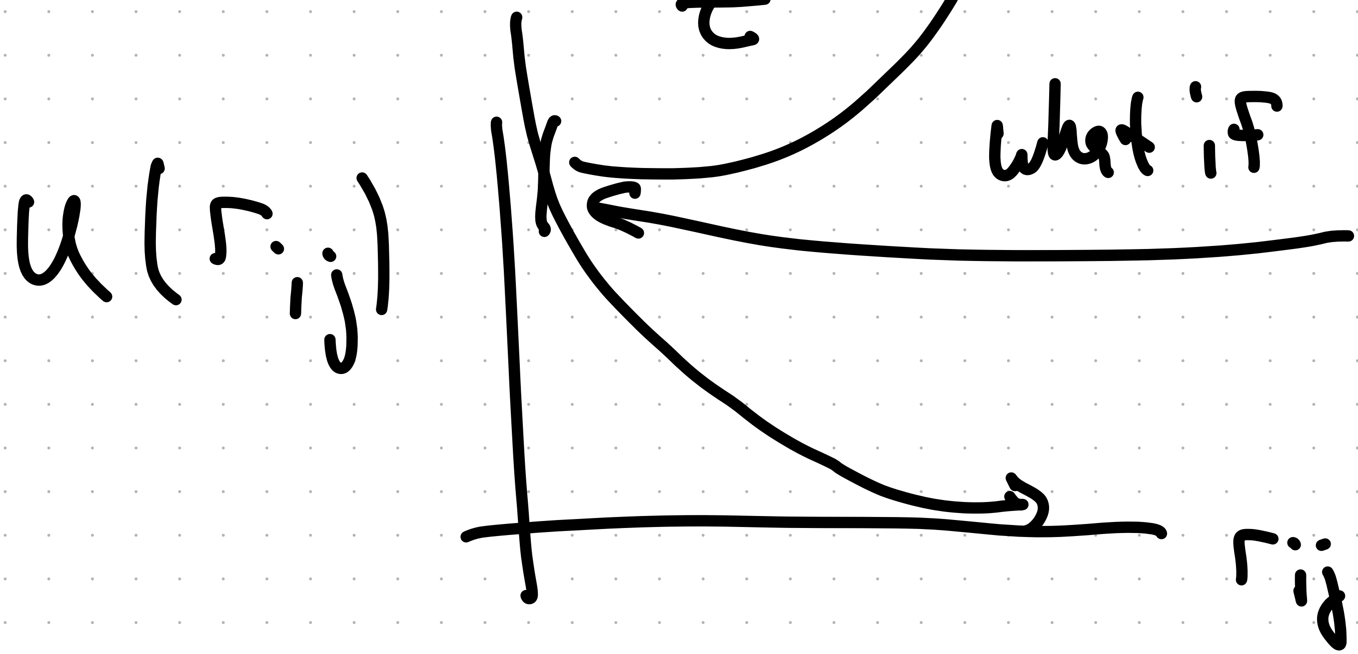
configurational partition funct.

What is the prob. of finding every particle within $d\vec{q}$ of

$$\vec{q} = (\vec{q}_1, \vec{q}_2, \ldots, \vec{q}_N)$$

$$P(\vec{q})\,d\vec{q} = \frac{1}{Z} e^{-\beta U(\vec{q})} \quad d\vec{q}_1 d\vec{q}_2 \ldots d\vec{q}_N$$

what if $\vec{q}_1 \approx \vec{q}_2$

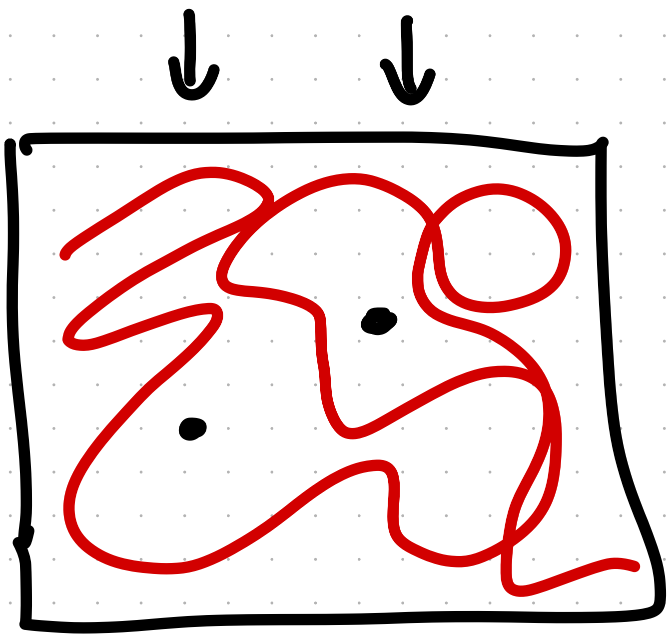


Prob of $\quad$ mc 1 @ q_1

mc 2 @ q_2

etc

averaged over all other particle positions



$$P^{(n)}(q_1, q_2, \ldots, q_n) = \int d\vec{q}_{n+1}\, d\vec{q}_{n+2} \cdots d\vec{q}_N \left(e^{-\beta U(\vec{q})} / Z \right)$$

$n < N$

if we don't care about particle identity

$$\rho^{(n)}(\vec{q}_1, \ldots \vec{q}_n) = \frac{N!}{(N-n)!} \cdot P^{(n)}(\vec{q}_1, \ldots, \vec{q}_n)$$

rho

nice way of writing:

$$\frac{1}{Z}\int d\vec{q}_{n+1}\, d\vec{q}_{n+2} \cdots d\vec{q}_N\, e^{-\beta U(\vec{q})}$$

$$= \frac{1}{Z}\int d\vec{q}_N\, e^{-\beta U(\vec{q})}\, \underbrace{\delta(q_1-q_1')\cdot\delta(q_2-q_2')\ \text{etc}}_{\prod_{i=1}^{n}\delta(\vec{q}_i-\vec{q}_i')}$$

$$= \left\langle \prod_{i=1}^{n} \delta(\vec{q}_i-\vec{q}_i') \right\rangle_{q_1', q_2' \cdots q_n'}$$

1 last quantity:

$$g^{(n)}(\vec{q}_1, \ldots, \vec{q}_n) = \frac{\rho^{(n)}(\vec{q}_1, \ldots, \vec{q}_n)}{\rho^n}$$

$$\rho = N/V$$

interested in $g^{(1)}$, $g^{(2)}$

(eg $g^{(1)} = \rho^{(1)}/\rho$)

$$P^{(1)}(\vec{q}_1) = \int d\vec{q}_2\, d\vec{q}_3 \cdots d\vec{q}_N\, e^{-\beta U(\vec{q})} \Big/ Z$$

number

$$\int d\vec{q}_1\, P^{(1)}(\vec{q}_1) = Z/Z = 1$$

$$\int d\vec{q}_1\, \rho^{(1)}(\vec{q}_1) = \int d\vec{q}_1 \left[N P^{(1)}(\vec{q}_1) \right]$$

$$= N \cdot \int d\vec{q}_1\, P^{(1)}(\vec{q}_1) = N$$

"Isotropic" approximatric

$$P^{(1)}(\vec{q}) = P^{(1)} = 1/V \Rightarrow \rho^{(1)} = N P^{(1)} = N/V$$

$$g^{(2)}(\vec{q}_1, \vec{q}_2) = \frac{N(N-1)}{\rho^2} \langle \delta(\vec{q}-\vec{q}_1)\delta(\vec{q}-\vec{q}_2) \rangle_{\vec{q}_1, \vec{q}_2}$$

in isotropic system

$\vec{q}_1 - \vec{q}_2$ matters

$$\vec{R} = (\vec{q}_1 + \vec{q}_2) \cdot \frac{1}{2}$$

$$\vec{r} = (\vec{q}_1 - \vec{q}_2)$$

$$g(\vec{r}) = \frac{N-1}{\rho} \langle \delta(\vec{r} - \vec{r}') \rangle$$

if angle doesn't matter

integrating out , θ , ϕ , $\vec{R}$

after all integrals

$$g(r) = \frac{N-1}{4\pi\rho r^2} \langle \delta(r - r') \rangle$$

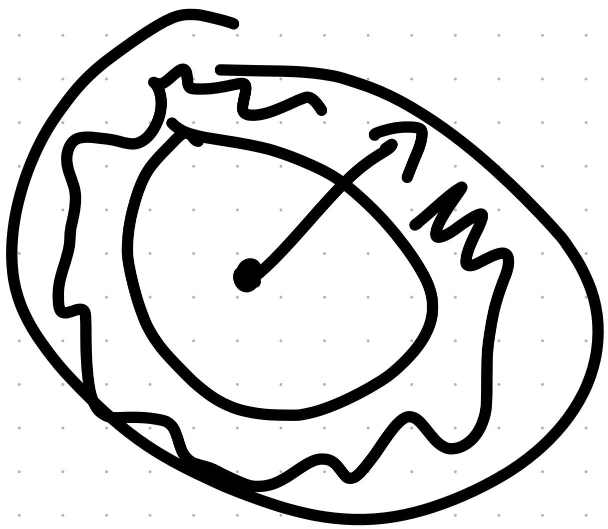
in practice

histogram of how often

2 distances are between

r and $r + \Delta r$

compare to



$4\pi r^2 \Delta r$ = volume of shell

$\# = \rho \cdot 4\pi r^2 \Delta r$

$$\frac{\text{count}}{\text{expected }\#}$$