Lecture 11 - Interacting gasses & liquids, pt 1

Canonical Ensemble: N, V, T

$$P(\vec{q}, \vec{p}) = e^{-\beta \mathcal{H}(\vec{q}, \vec{p})} \Big/ \int d\vec{q} \int d\vec{p}\, e^{-\beta \mathcal{H}(\vec{q}, \vec{p})}$$

$$\mathcal{H}(\vec{q}, \vec{p}) = \underbrace{\sum_{i=1}^{N} \vec{p}_i^{\,2} / 2m_i}_{\text{ideal gas part}} + \underbrace{U(\vec{q}_1, \vec{q}_2, \dots \vec{q}_N)}_{\text{potential energy}}$$

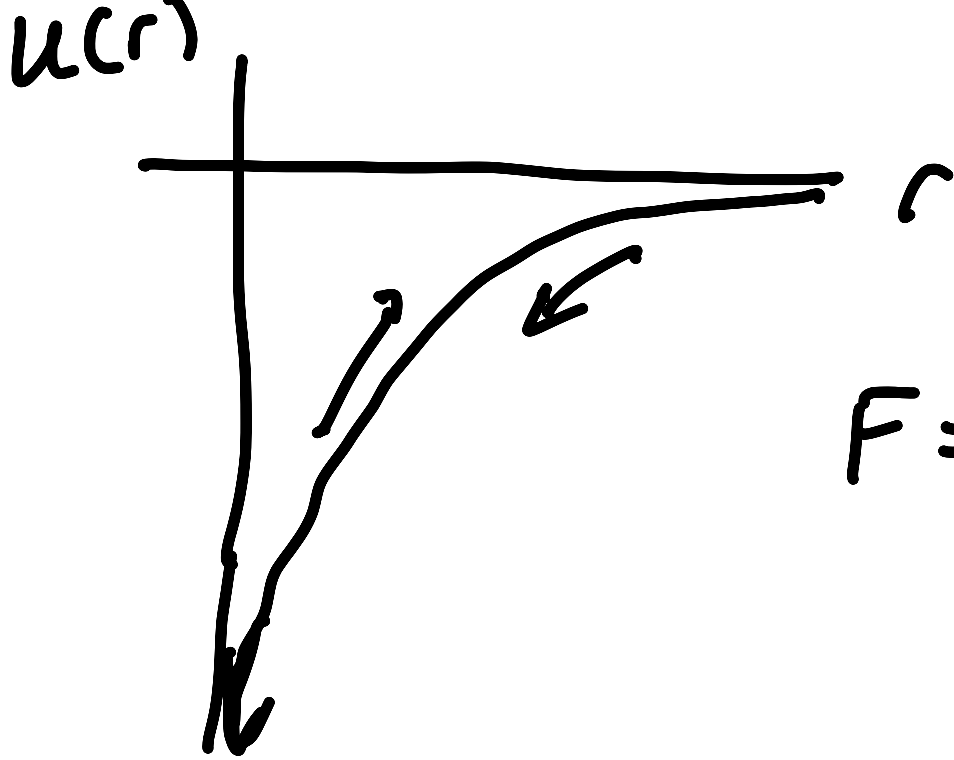
KE - always positive, U can be $\pm$

U can be >0 or <0

Negative energies tend to make molecules stick together

$$U(\vec{q}_1, \vec{q}_2) = -\frac{e^2}{4\pi\epsilon_0 |\vec{q}_1 - \vec{q}_2|}$$

$\oplus$ $\ominus$



$$F = -\frac{\partial u}{\partial r}$$

Remember: A helmholz free energy minimized @ eq.

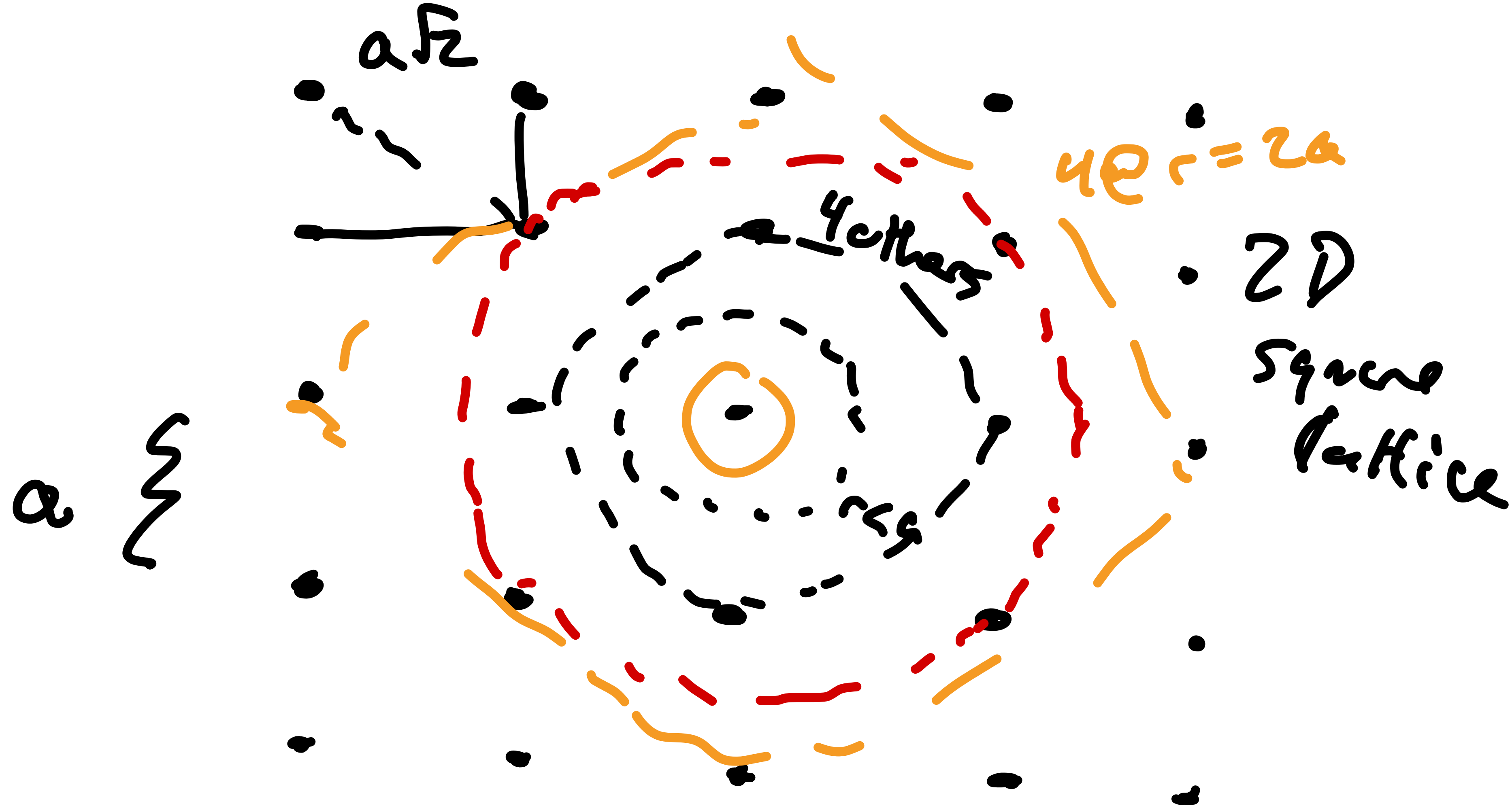
$$A = \mathcal{E} - TS, \quad T > 0$$

Competition btwn lowering $\mathcal{E}$ & S

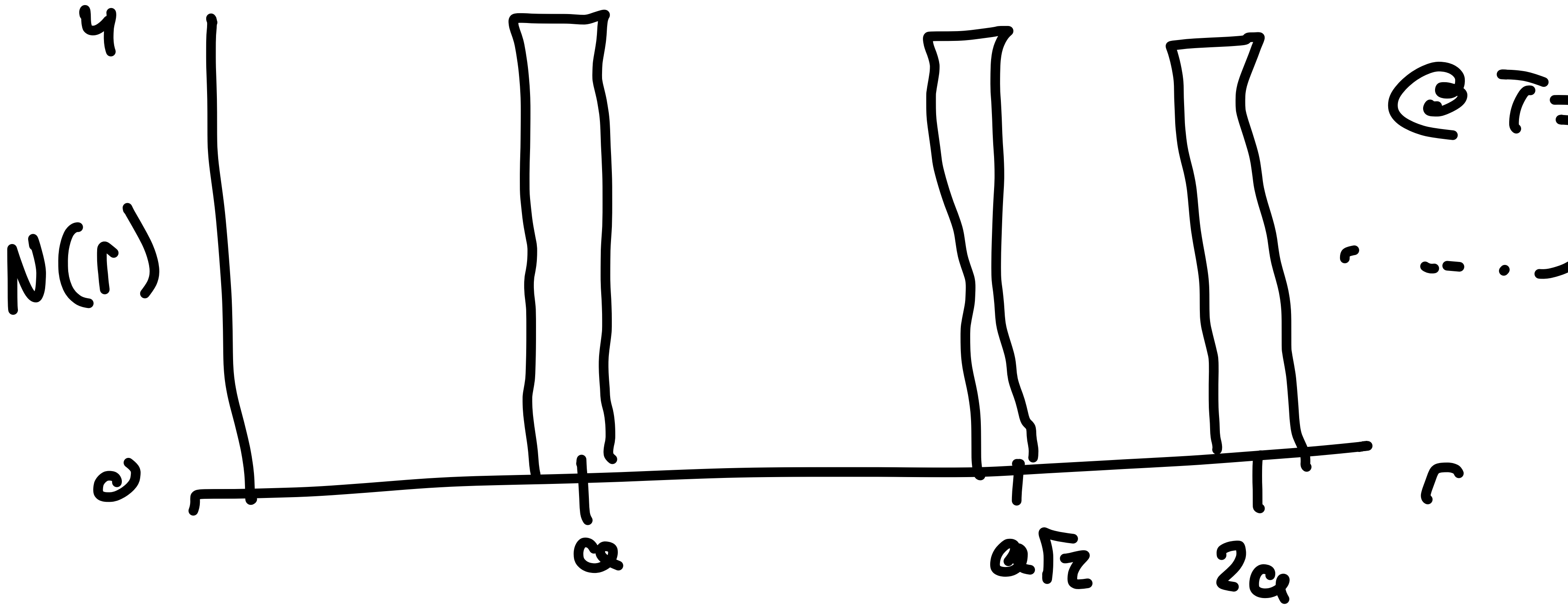
At low T & high P, we expect liquids & solids

What is the "structure" of liquids, gasses (& solids)

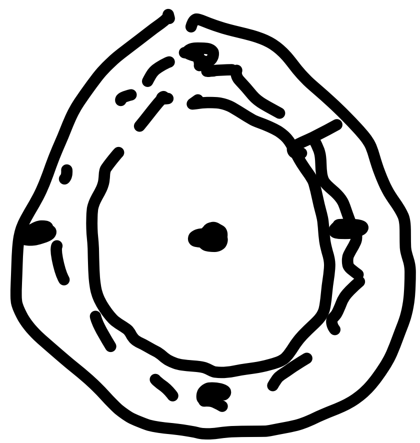
Think about a crystal



What is environment of "tagged molecule"



@ $T = 0$



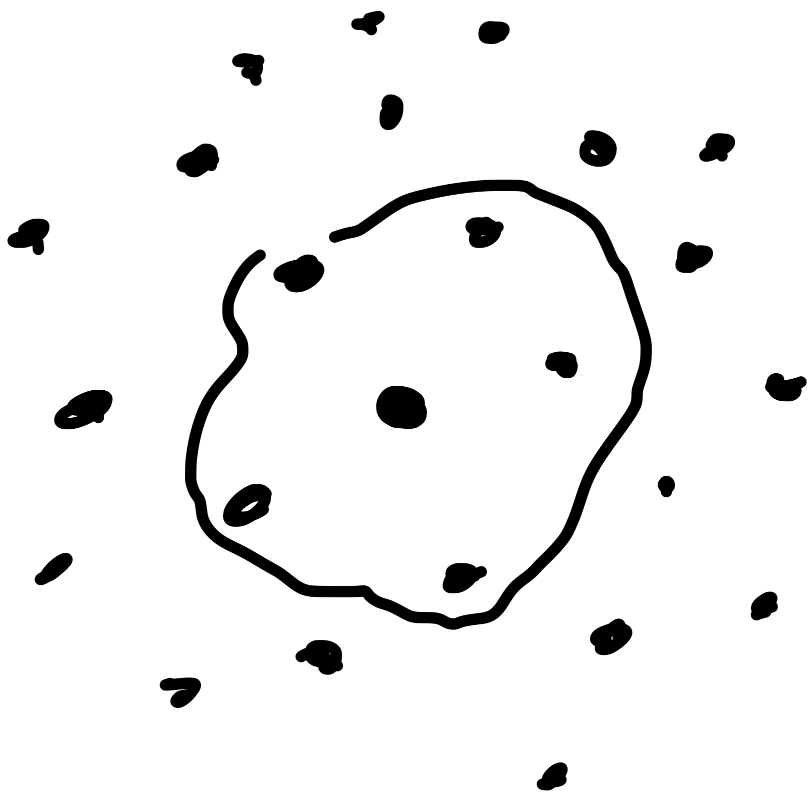
$a - \Delta < r < a + \Delta$

$$\int_{a-2\sigma}^{a+2\sigma} dr\, P(r) \approx 4$$

Liquid long range attraction

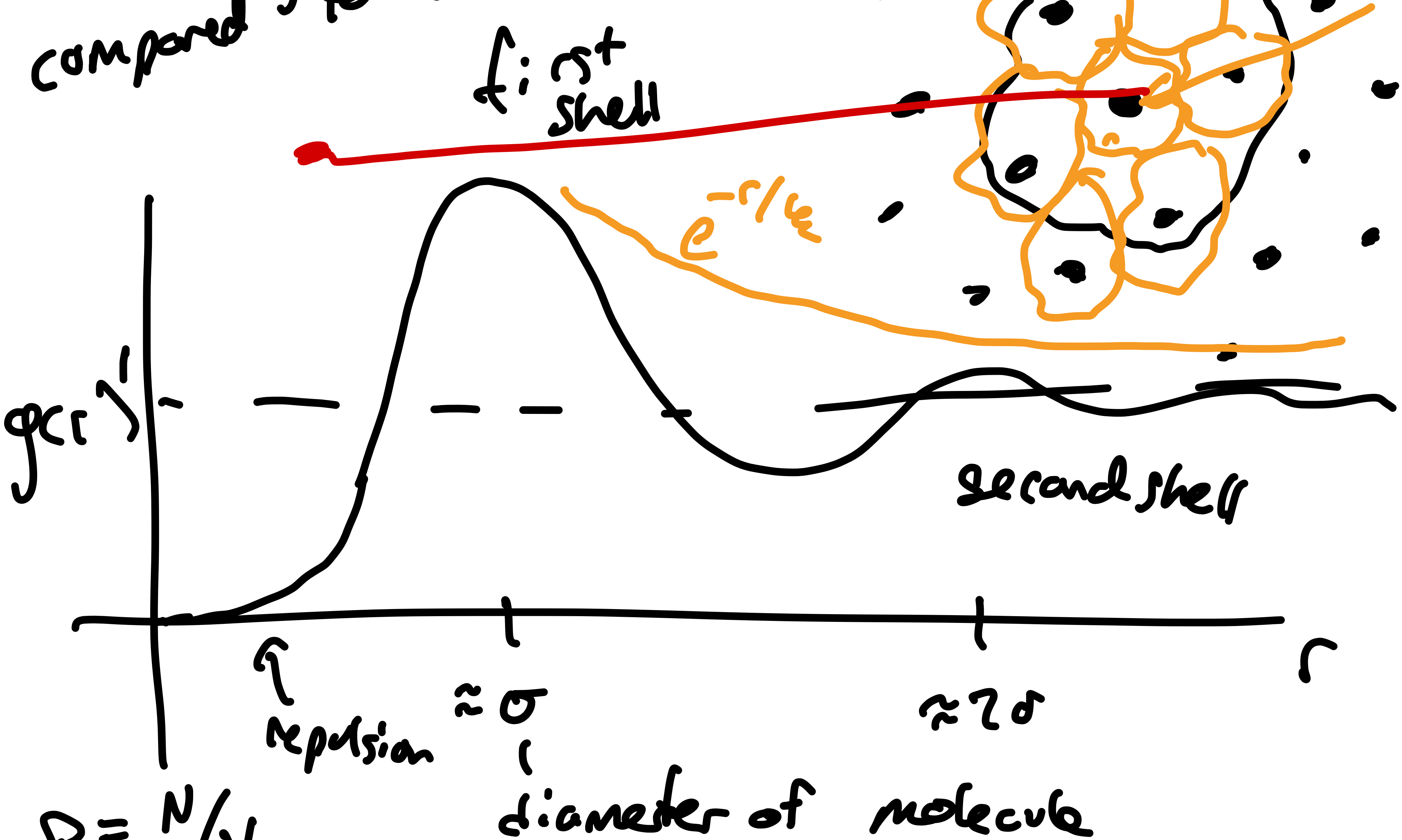
Short range repulsion

$u(\,)$ — between molecules



No long range order

Relative prob of finding a mc @ dist r compared to uniform density



$\rho = N/V$

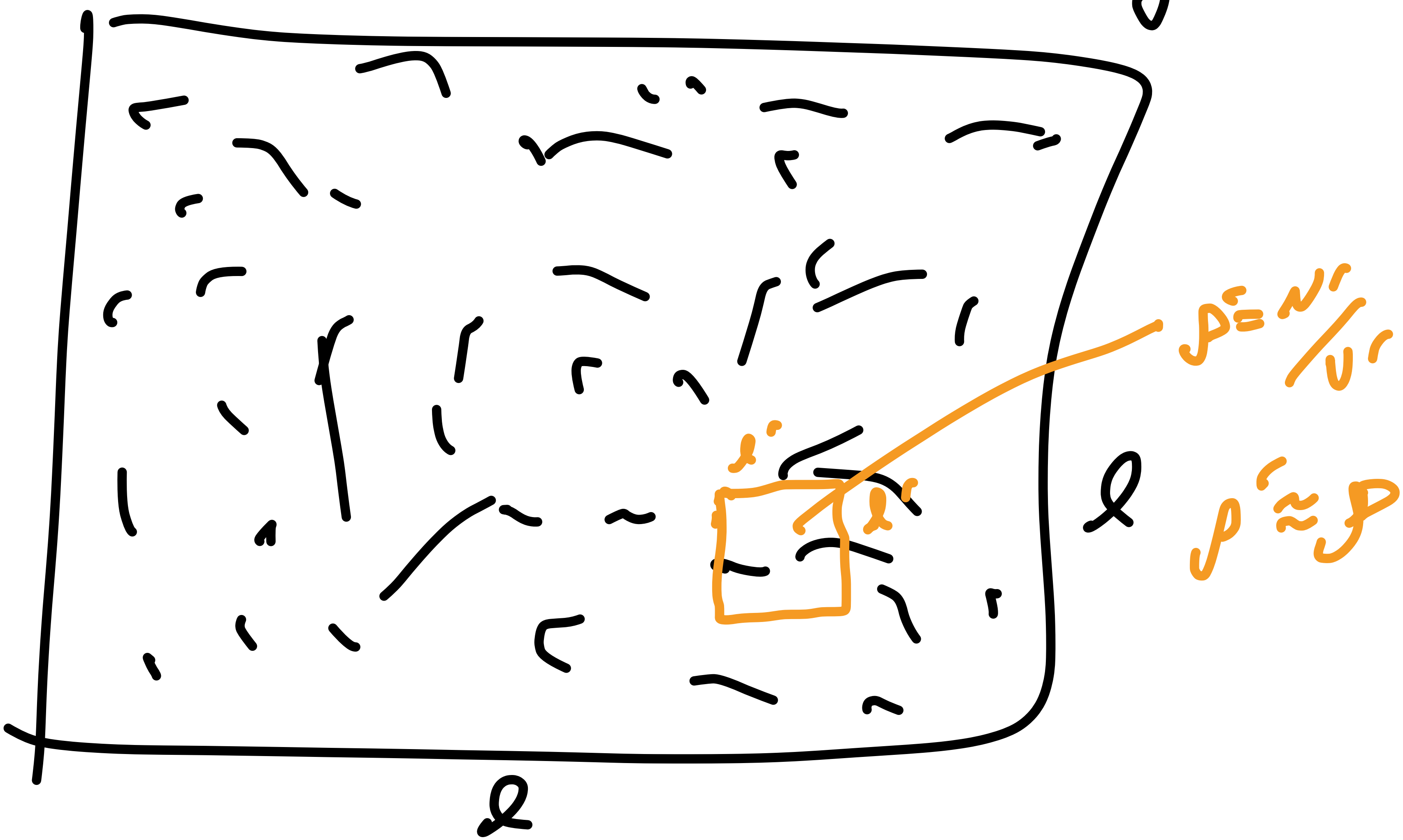
For a liquid: $\qquad N, V, T$

Isotropic $\leftarrow \rho \approx N/V$

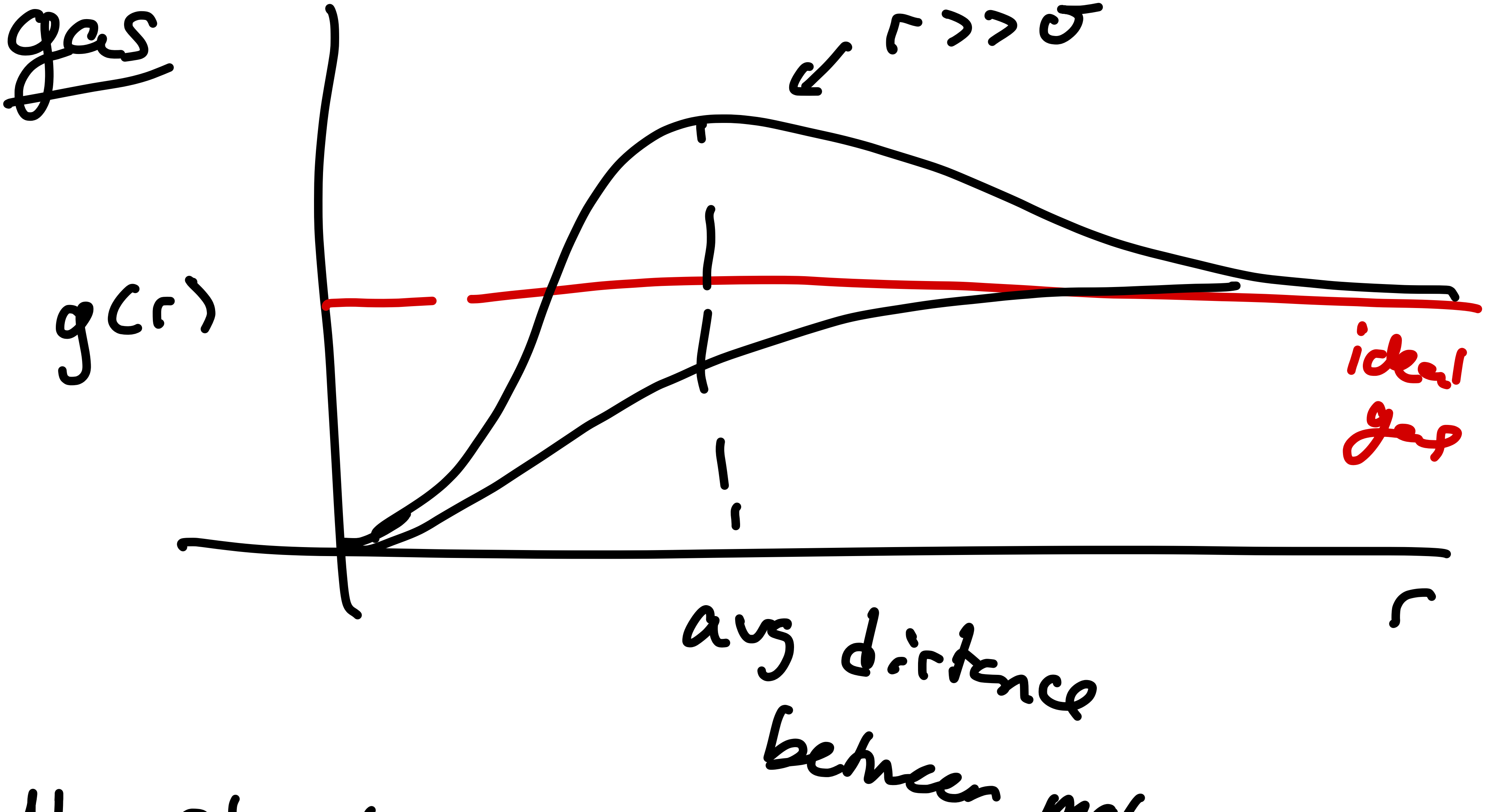
Translationally invariant

$\rho = N/V$

$V = \ell^d$



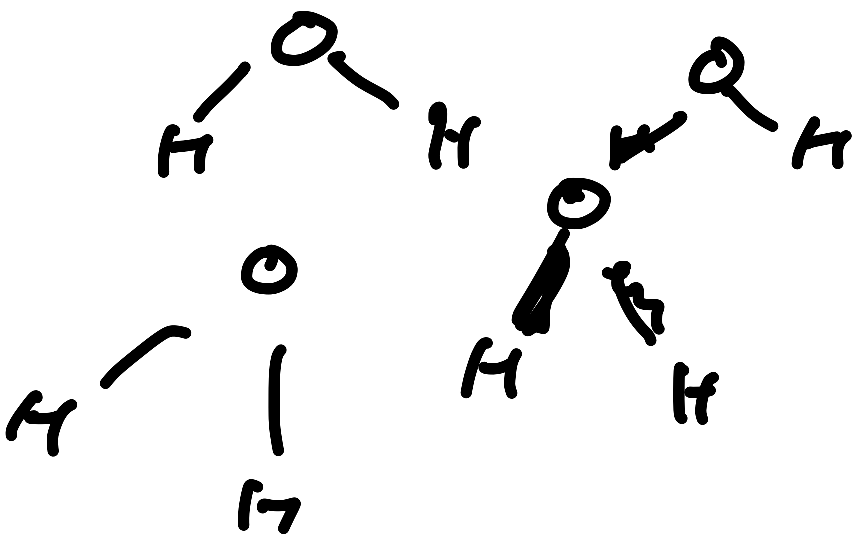
gas



No structure related to molecule properties

$g(r)$ relative prob @ dist r

averaged over angles



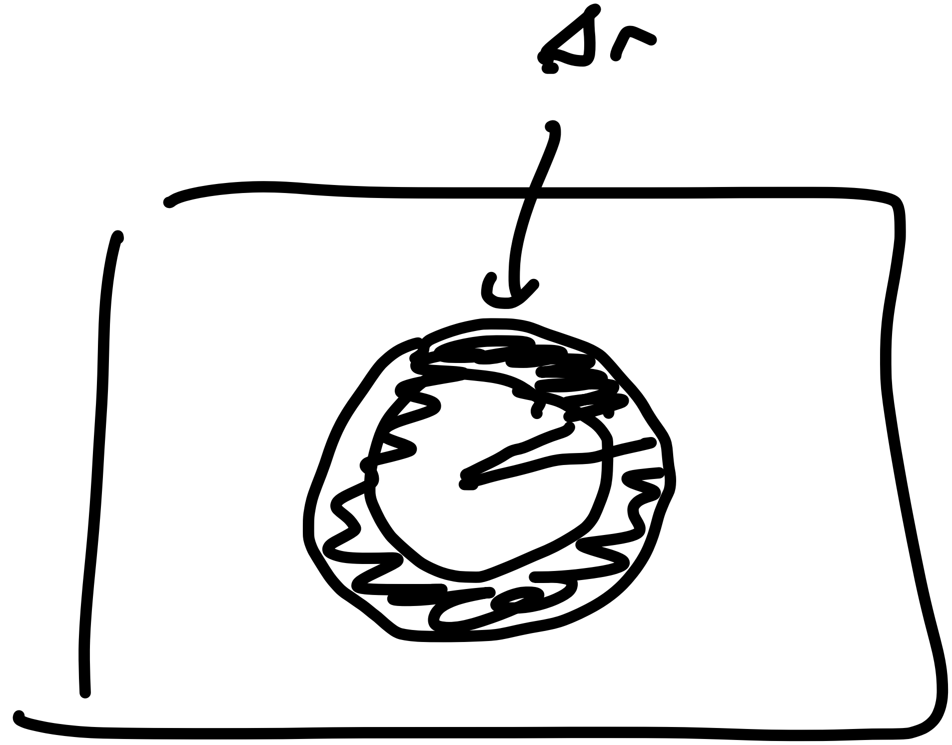
ideal gas, same ρ

inside sphere

$\langle N \rangle = \frac{4}{3}\pi r^3 \rho$

bigger sphere

$\langle N_2 \rangle = \frac{4}{3}\pi (r+\Delta r)^3 \rho$



in shell of size Δr

$$\frac{4}{3}\pi (r+\Delta r)^3 \rho - \frac{4}{3}\pi r^3 \rho$$

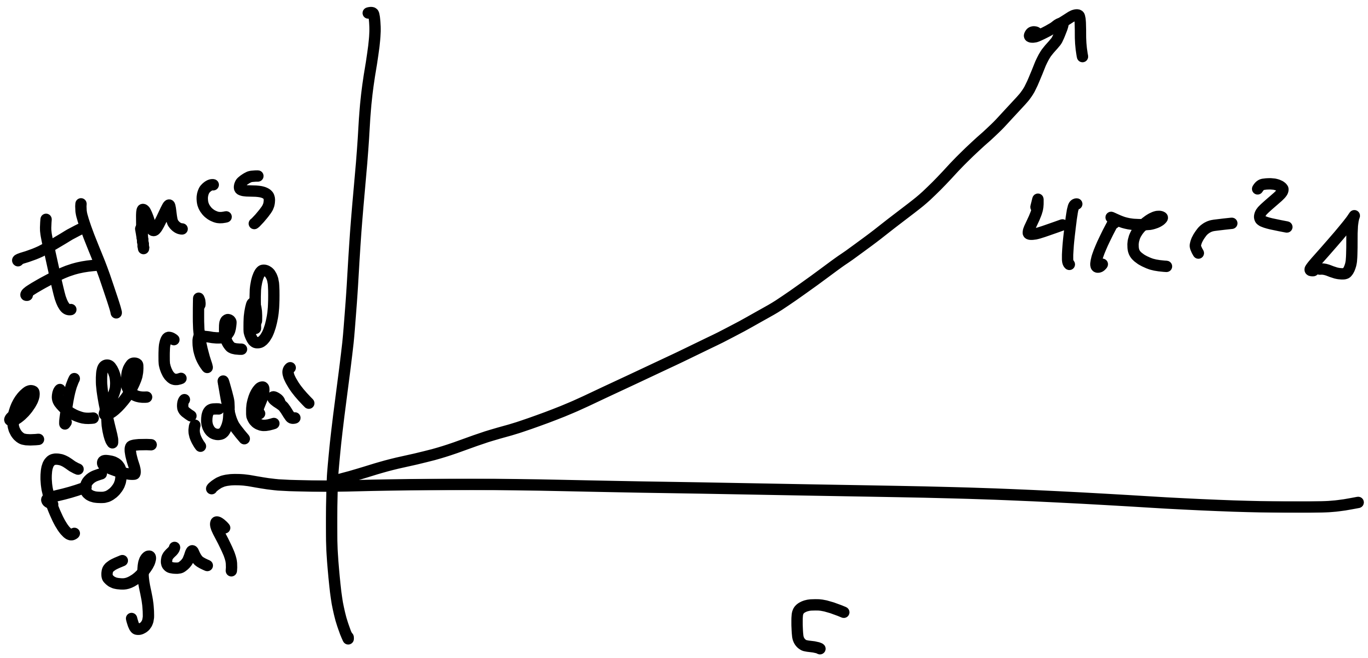
$$\frac{4}{3}\pi \left[r^3 + 3\Delta r r^2 + 3r(\Delta r)^2 + \Delta r^3 \right] \rho$$

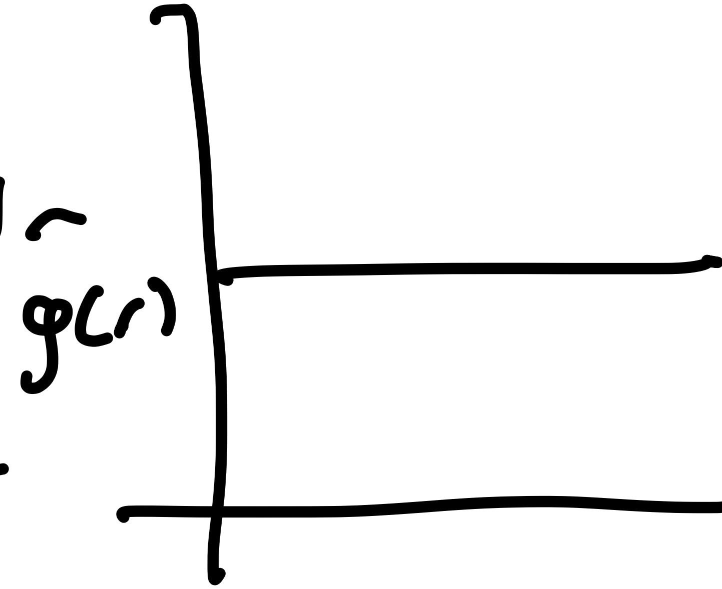
$$- \frac{4}{3}\pi r^3 \rho$$

$$= \left[4r^2 \Delta r + 4r(\Delta r)^2 + \frac{4}{3}(\Delta r)^3 \right] \rho\pi$$

$$= 4\pi r^2 \Delta r \rho + O(\Delta r^2)$$

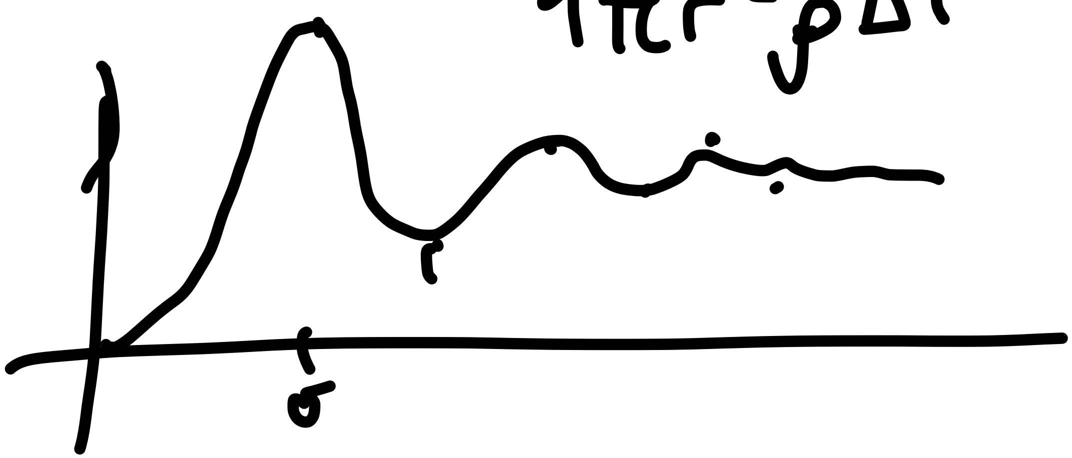
S.A. sphere





$$g(r) = \frac{h(r)}{4\pi r^2 \rho \Delta r}$$

$\leftarrow$ hist $r - \Delta r < r < r + \Delta r$



Connect to partition function:

$$Z_{(conf)} = \int d\vec{q}^{\,N} e^{-\beta U(\vec{q}_1, \vec{q}_2 \ldots \vec{q}_N)}$$

$$P(\vec{q}_1, \vec{q}_2 \ldots, \vec{q}_N)\, d\vec{q}^{\,N}$$

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

$$P^{(n)}(\vec{q}_1, \vec{q}_2 \ldots \vec{q}_n) = \int d\vec{q}_{n+1} d\vec{q}_{n+2} \ldots d\vec{q}_N\, e^{-\beta U(q \ldots)} / Z$$

$$P^{(1)}(\vec{q}_1) = \int d\vec{q}^{\,N-1}\, e^{-\beta U(q)} / Z$$

$$\int d\vec{q}_i = \int_0^L dx_i \int_0^L dy_i \int_0^L dz_i = V$$

$$\int d\vec{q}_1\, P^{(1)}(q_1) = 1$$

isotropic, $P^{(1)}$ const

$$P^{(1)}(q_1) = 1/V$$

$$d\vec{q}^{\,N-n} = d\vec{q}_{n+1}\, d\vec{q}_{n+2} \cdots d\vec{q}_N$$

$$\rho^{(n)}(\vec{q}_1 \ldots \vec{q}_n) = \underbrace{\frac{N!}{(N-n)!}}_{\text{\# ways to label them}} P^{(n)}(\vec{q}_1 \ldots \vec{q}_n)$$

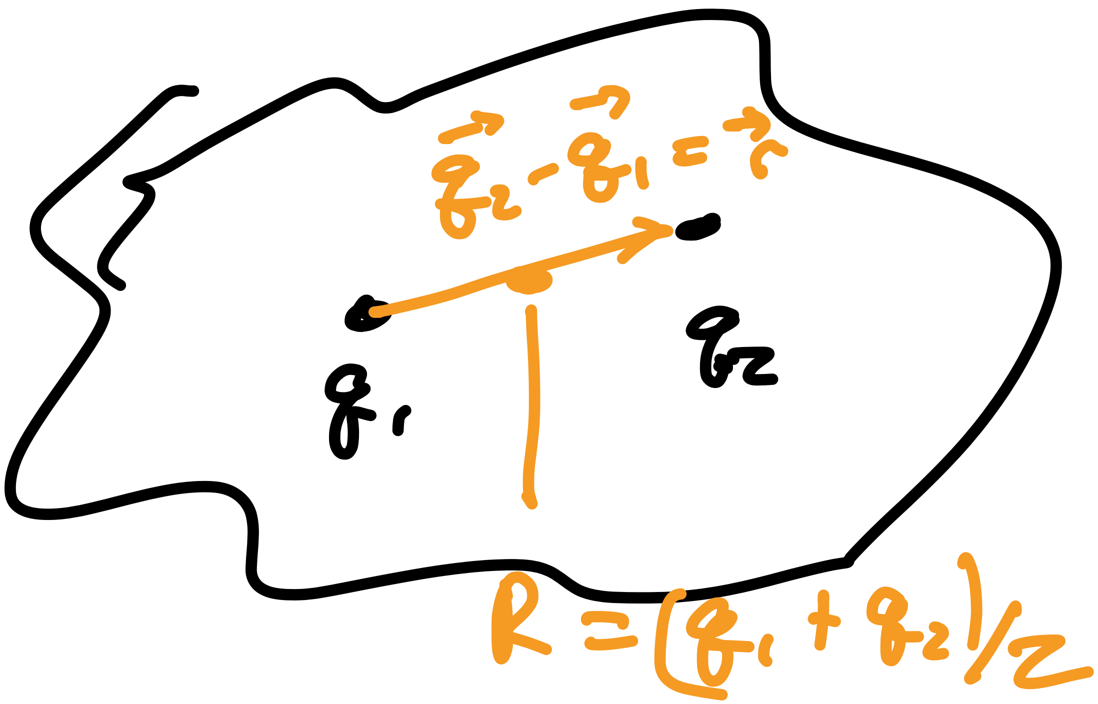
$$\rho^{(1)} = \frac{N!}{(N-1)!} P^{(1)} = N P^{(1)} = N/V$$

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

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

$$= \frac{N(N-1)}{\rho^2} \int d\vec{q}^{\,N-2} e^{-\beta U(q_1, \dots, q_N)} / Z$$

looks like depends on 2 position



$$q_1 = \vec{R} - \frac{1}{2}\vec{r}$$

$$q_2 = \vec{R} + \frac{1}{2}\vec{r}$$

$$g(\vec{r},\vec{R}) = g(q_1, q_2)$$

b/c isotropic, can't depend on $\vec{R}$

$$g(\vec{r}) = \frac{1}{V}\int d\vec{R}\; g^{(2)}(\vec{r},\vec{R})$$

$$\vec{r} = \vec{x}^2 + \vec{y}^2 + z^2$$

$$dx\,dy\,dz = r^2 \sin\theta\, dr\, d\theta\, d\phi$$

integrate $\theta, \phi \rightarrow 4\pi$

$$\int d\theta \int d\phi\; g(\vec{r})\, d\vec{r} = 4\pi r^2 dr\; g(r)$$

$$g(r)\,dr = \underbrace{\frac{(N-1)}{4\pi\rho r^2} \langle \delta(\vec{r}-\vec{r}')\rangle}_{h(r)}$$

histogram

finish next time)

$$\frac{N(N-1)\rho^{(2)}}{(N/V)^2}$$