Lecture 12 - More liquids & gasses

Structure Factor

Reminder: example

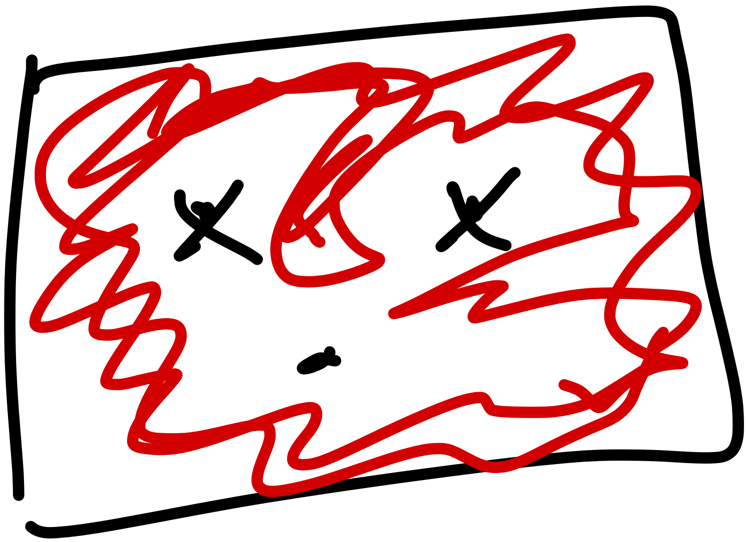
$$P^{(2)}(\vec{q}_1{}', \vec{q}_2{}') = \int d\vec{q}^{\,N-2} \frac{e^{-\beta U(q_1', q_2', \dots q_N)}}{Z}$$

"integrate out other dof...

$$P^{(2)}(q_1', q_2') = \int dq^N \, \delta(q_1 - q_1')\,\delta(q_2 - q_2')\, e^{-\beta U(q)} / Z$$

$$= \langle \delta(q_1 - q_1')\, \delta(q_2 - q_2') \rangle$$

$$\rho^{(n)}(q_1' \ldots q_n') = \left\langle \prod_{i=1}^{n} \delta(q_i - q_i') \right\rangle_{q_1', q_2' \ldots q_n'}$$



product $\longleftrightarrow$ "and"

$$g^{(2)}(q_1', q_2') = \frac{N(N-1)}{\rho^2} \left\langle \delta(q_1 - q_1') \, \delta(q_2 - q_2') \right\rangle$$

$$q_1 = R - \frac{1}{2} r \qquad R = \frac{q_1 + q_2}{2}$$

$$q_2 = R + \frac{1}{2} r \qquad r = q_2 - q_1$$

$$g^{(2)}(r', R') = \frac{(N)(N-1)}{\rho^2} \int dq^{N-2}\, e^{-\beta U(R' - \frac{1}{2} r',\, R' + \frac{1}{2} r',\, q_3 \dots q_N)} \Big/ Z$$

$$= \langle \delta(R - R') \cdot \delta(r - r') \rangle$$

$$g(r') = \frac{1}{V} \int dR\, g^{(2)}(r', R)$$

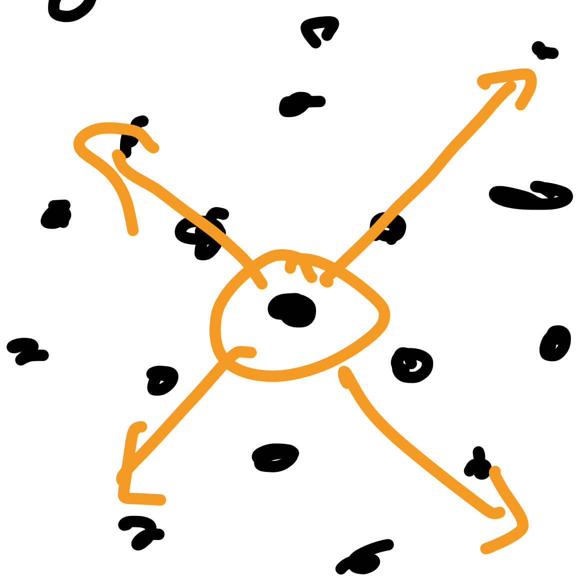
$$= \frac{N(N-1)}{\rho^2} \cdot \frac{1}{V} \langle \delta(r - r') \rangle = \frac{(N-1)}{\rho} \langle \delta(r - r') \rangle$$

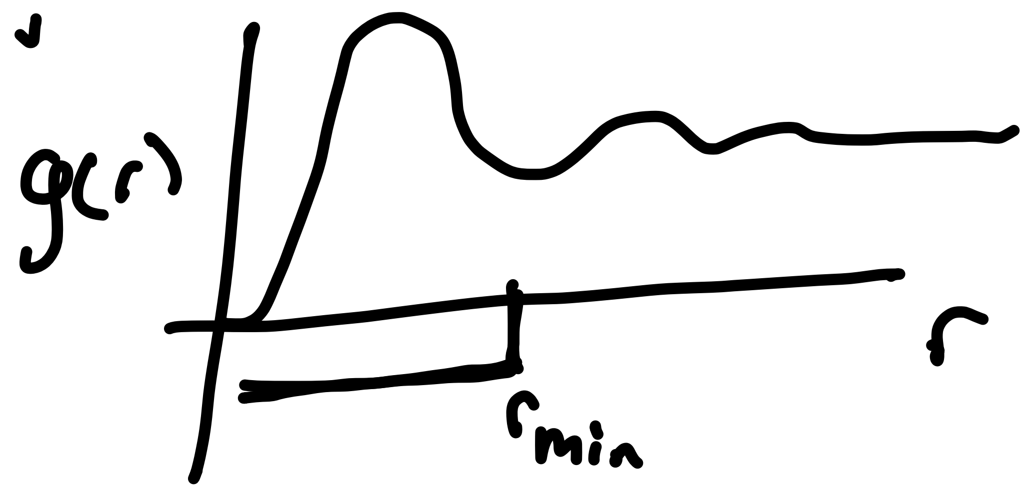
$$g(\vec{r}') = \frac{N-1}{\rho}\langle \delta(\vec{r}' - \vec{r}')\rangle$$

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

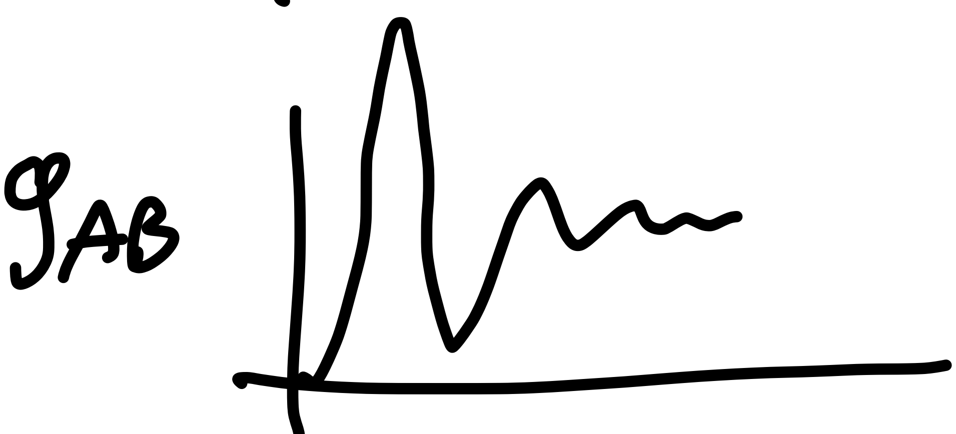
$$\int_0^\infty 4\pi\rho r^2 g(r)\,dr = N-1$$

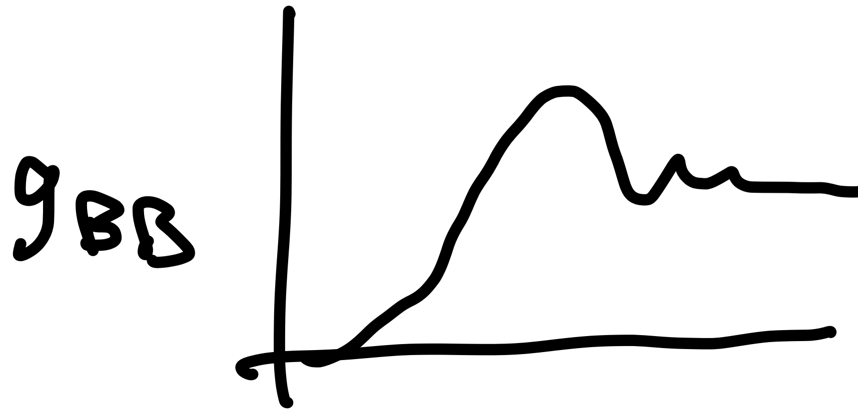
$$\approx N$$

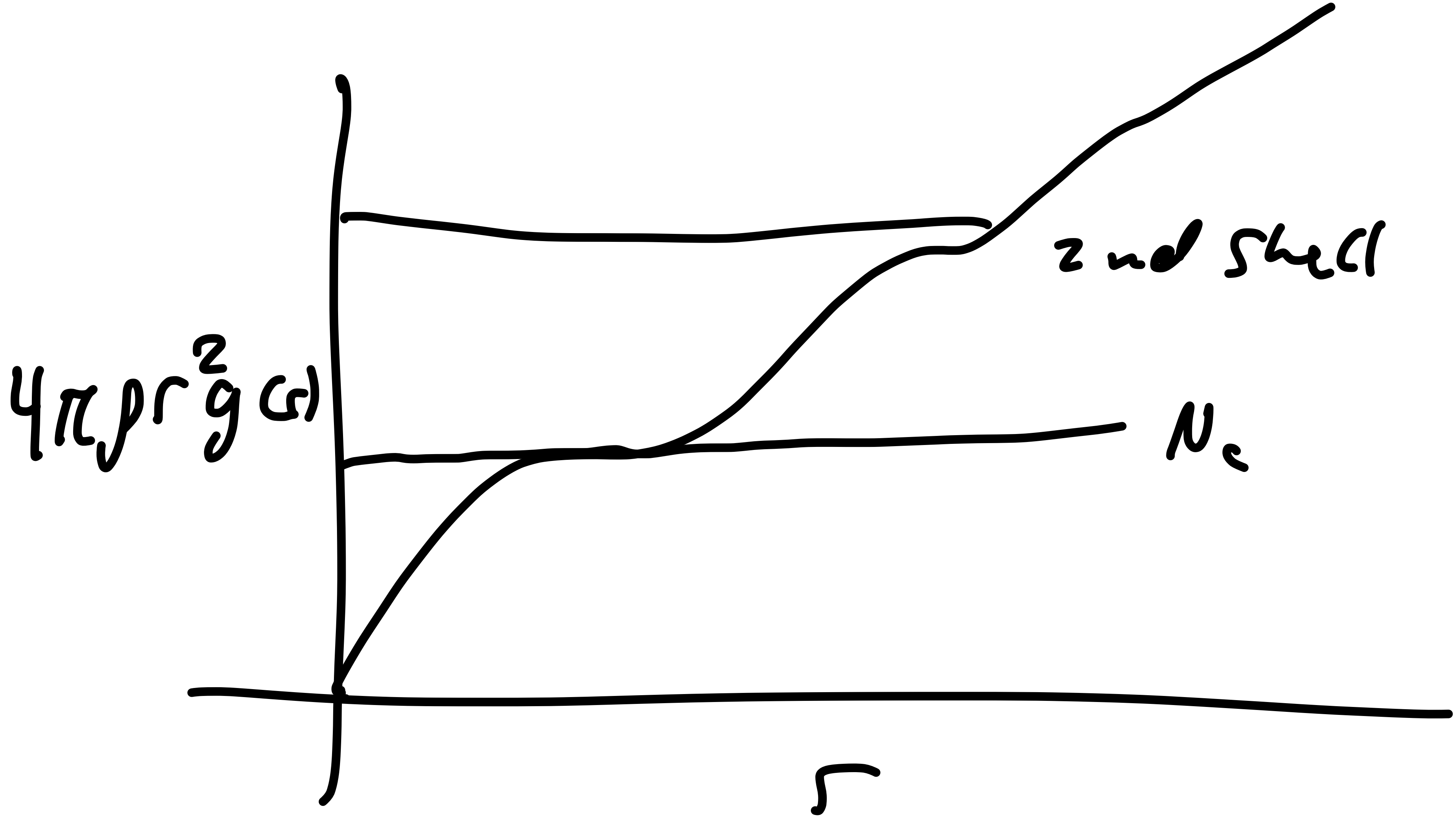




$$N_c = \int_0^{r_{min}} 4\pi \rho r^2 g(r)\, dr$$



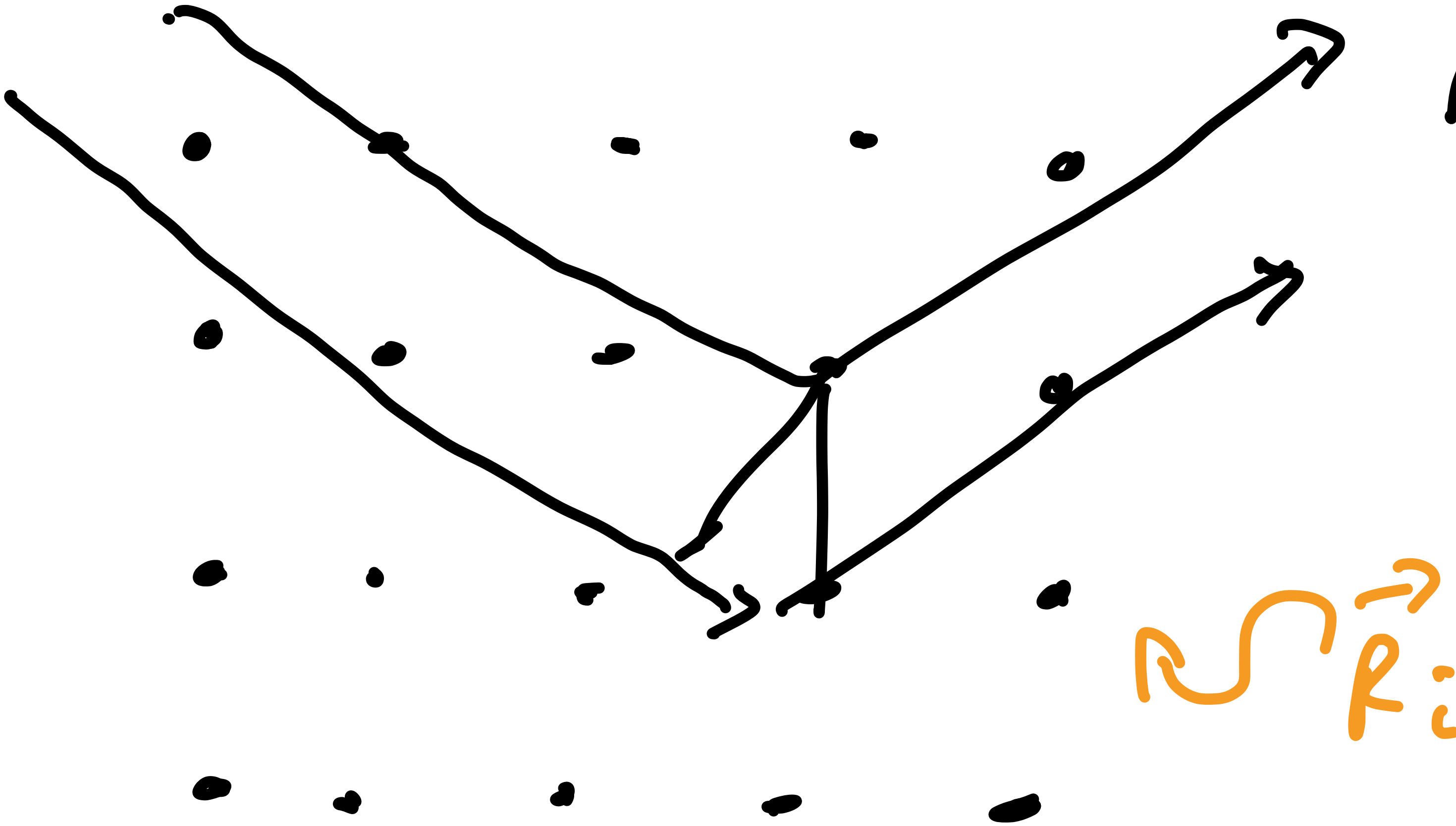




$4\pi\rho r^2 g(r)$
2nd shell
N_c
r

Getting g(r) from experiment

[Sec 4.6.2]



Plane wave: $\psi(r) = e^{-ik\cdot r}$

$= \cos(-kr) + i\sin(-kr)$

$$\psi_{out}(\vec{q}) = \sum_{j=1}^{N} f_j e^{-i\vec{q}\cdot R_j}$$

$$\psi_{out}(\vec{q}) = \sum_{j=1}^{N} f_j e^{-i q \cdot R_j}$$

depends on interaction of mc w/ wave

position of each one

$\vec{q} = \vec{k}_{out} - \vec{k}_{in}$

$\vec{k}$ = momentum of wave

$= 2\pi/\lambda \ \hat{k}$

Intensity:

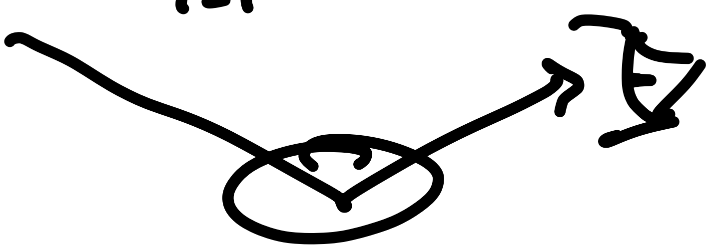
$$|\psi^* \psi| = \sum_{i=1}^{N} \sum_{j=1}^{N} f_i f_j e^{-i \vec{q} \cdot (\vec{R}_j - \vec{R}_i)}$$

$$|\psi^*\psi| = \sum_{i=1}^{N}\sum_{j=1}^{N} f_i f_j \, e^{-i\vec{q}\cdot(\vec{R}_j-\vec{R}_i)}$$

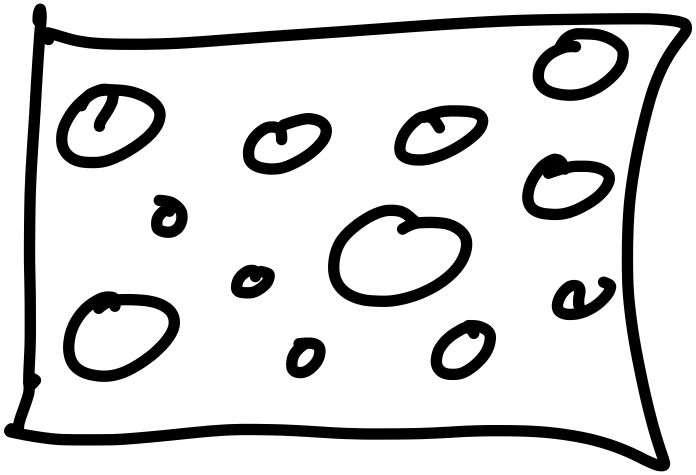
$$S(\vec{q}) = \frac{|\psi^*\psi|}{\sum_{i=1}^{N} f_i^2} \overset{\sim f^2}{=} \left\langle \frac{1}{N}\sum_{i=1}^{N}\sum_{j=1}^{N} e^{-i\vec{q}\cdot(\vec{R}_j-\vec{R}_i)} \right\rangle$$

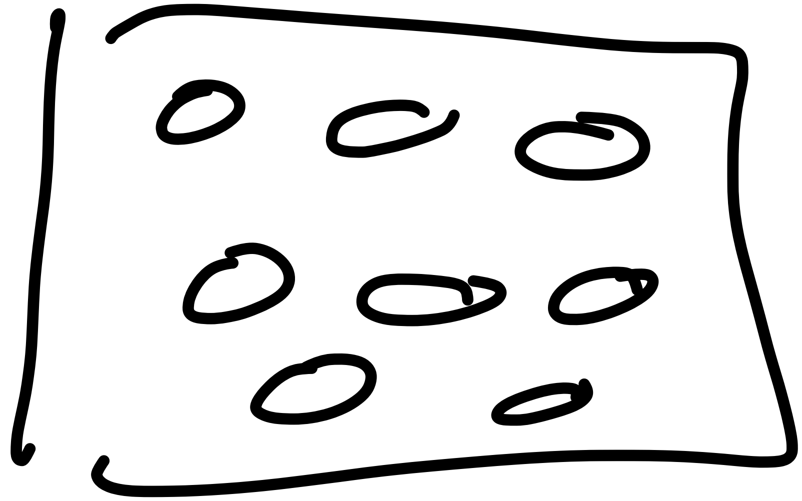
if all f_i same

$$\sum_{i=1}^{N} f_i^2 = N f^2$$



S_{AB}





Liq Ar

$$S(q) = \left\langle \frac{1}{N} \sum_{i,j} e^{-i\vec{q}\cdot(\vec{R}_j - \vec{R}_i)} \right\rangle$$

Self part , rest $\quad i=j$

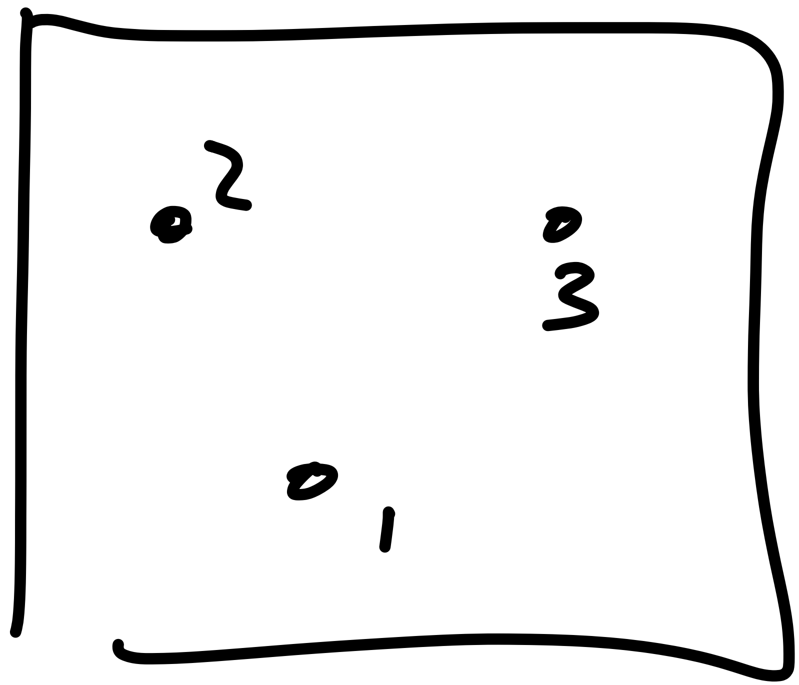
$$= 1 + \left\langle \frac{1}{N} \sum_{i \neq j} e^{-i\vec{q}\cdot(\vec{R}_j - \vec{R}_i)} \right\rangle$$

$$= 1 + \left\langle \frac{1}{N} \sum_{i \neq j} e^{-i\vec{q}\cdot(\vec{R}_j - \vec{R}_i)} \right\rangle$$

$$\langle A \rangle = \int_{-\infty}^{\infty} \frac{dR_1\, dR_2 \ldots dR_N\, e^{-\beta U(\vec{R})} \cdot A}{Z}$$

$$= 1 + \frac{N(N-1)}{N} \left\langle e^{-i\vec{q}\cdot(\vec{R}_2 - \vec{R}_1)} \right\rangle$$

$$= 1 + (N-1) \int d\vec{R}_1 \int d\vec{R}_2\, e^{-i\vec{q}(\vec{R}_2 - \vec{R}_1)} \underbrace{\int \frac{dR^{N-2}\, e^{-\beta U(\vec{R})}}{Z}}_{\frac{\rho^2}{N(N-1)} g^{(2)}(R_1, R_2)}$$



$$\langle r_{ij} \rangle$$

$$\left\langle \frac{r_{12}+r_{23}+r_{13}}{3} \right\rangle$$

$$\int_{-\infty}^{\infty} dq_1 \int_{-\infty}^{\infty} dq_2 \int_{-\infty}^{\infty} dq_3 \, \frac{r_{12}+r_{23}+r_{13}}{3} e^{-\beta U(q_1 q_2 q_3)} = \frac{3}{3}\langle r_{12} \rangle$$

$r_{12} = |q_2 - q_1|$ $\quad r_{23} = |q_3 - q_2|$ $\quad r_{13} = |q_3 - q_1|$

$$S(q) = 1 + \frac{1}{N}\int d\vec{R}_1 \int d\vec{R}_2\, \rho^2 g_2(R_1, R_2)\, e^{-iq(R_2 - R_1)}$$

$$= 1 + \frac{1}{N}\int d\vec{R} \int d\vec{r}\, \rho^2 g_2(R, r)\, e^{-i\vec{q}\cdot\vec{r}}$$

$$\vec{r} = \vec{R}_2 - \vec{R}_1 \leftarrow \quad R = \frac{\vec{R}_1 + \vec{R}_2}{2}$$

$$V g(\vec{r}) = \int d\vec{R}\, g(\vec{r}, \vec{R})$$

$$= 1 + \rho \int d\vec{r}\, g(r)\, e^{-i\vec{q}\cdot\vec{r}}$$

$$\frac{S(q) - 1}{\rho} = \int d\vec{r}\, g(r)\, e^{-i\vec{q}\cdot\vec{r}}$$

$$g(r) = IFT\left[\frac{S(q) - 1}{\rho}\right]$$

$\to \to \quad 1 + 4\pi\rho \int_0^\infty dr\, r^2 g(r) \frac{\sin(qr)}{qr}$

Reversible work theorem

$$g(R) = e^{-\beta w(R)}$$

$$w(R) = -k_B T \ln g(R)$$

Work to bring 2 mcs together from "infinite" separation to distance R @ const N, V, T $\quad [\Delta A]$

Work done by a force

$$\int_{\infty}^{R} F(r) \cdot dr$$, work we have to do is $$\int_{R}^{\infty} F(r) \cdot dr$$

What is the "force"

$$F(r) = \left\langle -\frac{\partial U(r_1, \ldots, r_N)}{\partial r_{12}} \right\rangle_{\substack{r_1, r_2 \text{ fixed} \\ r_3 \ldots r_N \text{ averaged over}}}$$

$$= \frac{\int dr^{N-2} \left[-\frac{dU}{dr_{12}} e^{-\beta U(r_1, \ldots, r_N)} \right]}{\int dr^{N-2} e^{-\beta U(r)}}$$

$$= k_B T \frac{d}{dr_{12}} \ln \Big[\underbrace{\int dr^{N-2} e^{-\beta U(r)}}_{\propto\, g^{(2)}(r_1, r_2) \,\propto\, g(r_{12})} \Big]$$

$$= k_B T \frac{d}{dr} \ln [g(r)]$$

$$w(R) = \int_R^\infty k_B T \frac{d}{dr} \ln(g(r))\, dr$$

$$= k_B T \ln(g(r)) \Big|_R^\infty$$

$$= k_B T \ln(1) - k_B T \ln(g(R))$$

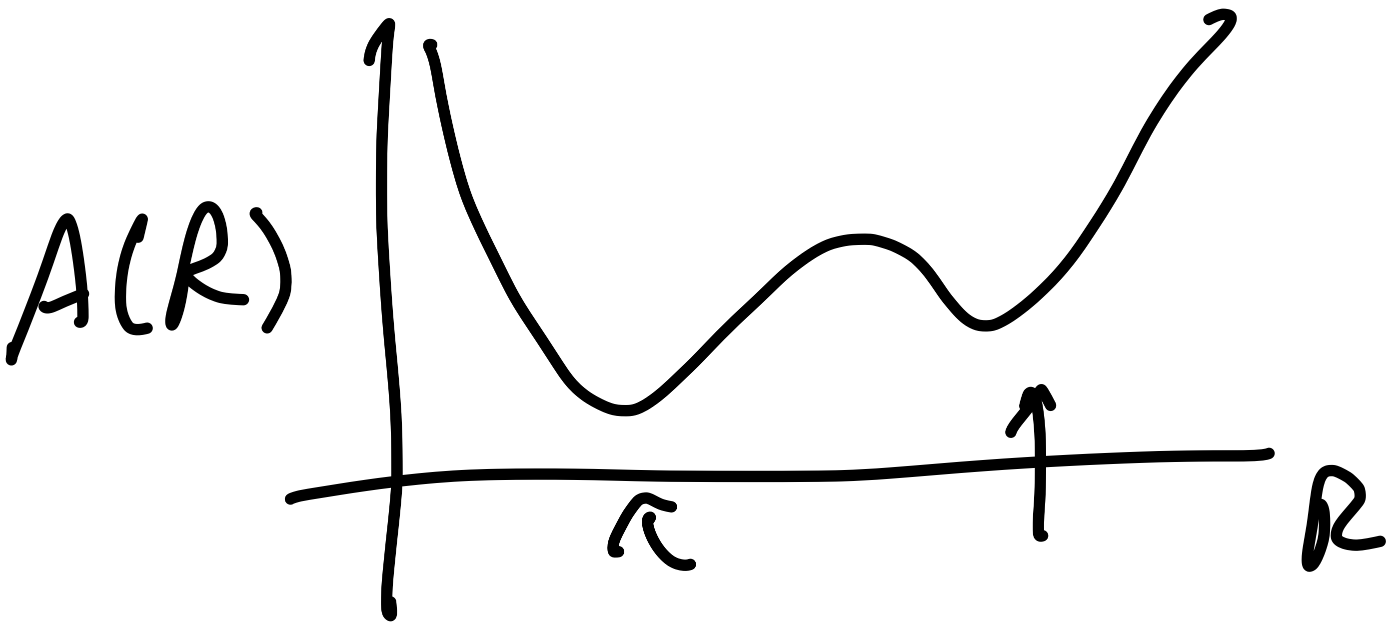
$$= -k_B T \ln(g(R))$$

$w(R)$ call "potential of mean force"

$$F(R) = -\frac{d}{dR} w(R)$$

PMF:

Free energy calculations



Coarse graining

U(R)