Lecture 12 - More liquids & gasses

Reminder - want prob or relative prob of n- molecules in some location

Defined $$P^{(2)}(q_1, q_2) = \int d\vec{q}^{\,N-2} \frac{e^{-\beta U(\vec{q}_1 \ldots, \vec{q}_N)}}{Z}$$

("integrate out")

Convenient way to write & physical meaning

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

$$\Rightarrow P^{(n)}(q \ldots q_n) = \left\langle \prod_i \delta(\vec{q}_i - \vec{q}_i') \right\rangle_{q_i' \ldots}$$

Thermal average counting things in that exact position [remember micro partition function]

Product $\rightleftarrows$ "and", all true at once

Therefore $$g^{(2)}(\vec{q}_1', \vec{q}_2') = \frac{N(N-1)}{\rho^2} \langle \delta(q_1 - q_1') \, \delta(q_2 - q_2') \rangle$$

Rewriting with coords

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

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

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

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

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

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

$\sim$

Need this formal def^n later

For just dist:

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

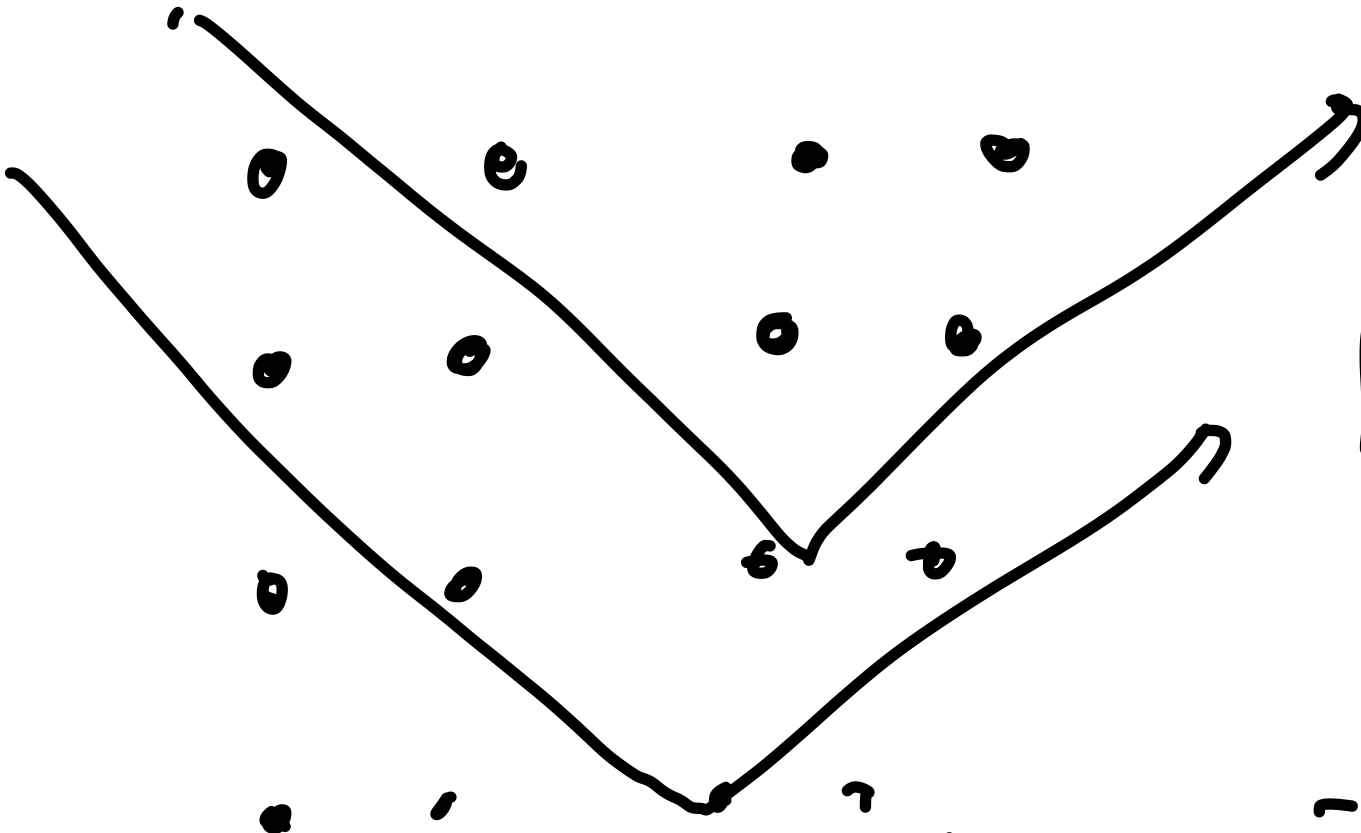
particles up to dist a =

$$4\pi\rho \int_0^a r^2 g(r)\, dr \quad \sim \text{ if } a = r_{min}$$

$$= N_c$$

as $a \to \infty \rightarrow N-1$, total non "tagged" particles

How do we measure $g(r)$ in xpt



[see 4.6.2]

Incoming plane wave $\psi(r) = e^{-ik \cdot r}$

Turns out, can write outgoing wave as sum over all scattering events:

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

R_j ← position of particle

q ← change in wave vec $k_{out} - k_{in}$

Intensity:

$$|\Psi^*\Psi| = \sum_i \sum_j f_i f_j e^{-iq(R_j - R_i)}$$

$$S(q) = \frac{|\Psi^*\Psi|}{\sum_{i=1}^{N} f_i^2} \text{, if all same} = \frac{1}{N}\sum_{i,j} e^{-iq(R_j - R_i)}$$

Actually, an average over molecular motion

$$S(q) = \left\langle \frac{1}{N} \sum_{ij} e^{-iq(R_j - R_i)} \right\rangle$$

$$= \frac{1}{N} \left\langle \left| \sum e^{iq \cdot R_i} \right|^2 \right\rangle$$

shows purely real

self, $i=j$ & $i \neq j$

$N \cdot (N-1)$ terms

$$S(q) = 1 + \left\langle \frac{1}{N} \sum_{i \neq j} e^{-iq(R_j - R_i)} \right\rangle$$

$$S(q) = 1 + (N-1)\langle e^{-iq(R_2-R_1)}\rangle$$

could be same for any 2

$$= 1 + (N-1)\int dR_1 dR_2 \left[e^{-iq(R_2-R_1)}\right] \underbrace{\int dR^{N-2} e^{-\beta U(R^N)}}_{\frac{\rho^2 g_2(R_1,R_2)}{N(N-1)}}$$

$$S(q) = 1 + \frac{1}{N}\int dR_1 \int dR_2\, \rho^2 g_2(R_1, R_2)\, e^{-iq\underbrace{(R_2-R_1)}_{=r}}$$

$$\Rightarrow \; = 1 + \frac{1}{N}\int dr \int dR\, \rho^2 g_2(r, R)\, e^{-iqr}$$

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

$$[Vg(r) = \int dR\, g(r, R)]$$

Reminder $f(\vec{q}) = FT(f(x)) = \int_{-\infty}^{\infty} dx\, e^{-iqx} f(x)$

so $S(q) \leftrightarrow g(r)$ by FT

$$= 1 + \rho \int_0^{\pi} d\theta \int_0^{2\pi} d\phi \int_0^{\infty} dr\, r^2 \sin\theta\, g(r) e^{-iqr\cos\theta}$$

$u = -\cos\theta \quad du = \sin\theta\, d\theta$

$$= 1 + 2\pi\rho \int_{-1}^{1} du \int_0^{\infty} dr\, r^2 g(r)\, e^{iqru}$$

$$= 1 + 2\pi\rho \int_0^{\infty} dr\, r^2 g(r) \frac{}{iqr} \left[e^{iqru} \right]_{-1}^{1}$$

$$\left[e^{iax} - e^{-iax} \right/ 2i = \sin(ax)$$

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

Thermo from $g(r)$

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

Rev work thm! $w(r)$ is work

to have to move from inf separation

brought to sep R reversibly @ const N, V, T

work is ΔA for process

Work done by a force! $\int_{\infty}^{R} F(r)\,dr$

work to do $= \int_{R}^{\infty} F(r)\,dr$

But what is F? = $-\nabla u$ averaged over all other particle cfgs

$$F(r_{12}) = \left\langle -\frac{\partial u(r_1 \ldots r_N)}{\partial r_{12}} \right\rangle_{3-N} \qquad r_1, r_2 \text{ fixed}$$

$$= \int dr^{N-2} \left[-\frac{\partial u}{\partial r_{12}} e^{-\beta u(r)} \right] \Big/ \int dr^{N-2} e^{-\beta u(r)}$$

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

$$= k_B T \frac{d}{dr_{12}} \ln g^{(2)}(r_1, r_2) = k_B T \frac{d}{dr} \ln g(r)$$

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

$$= k_B T \left[\ln g(r) \right]_{r=R}^{\infty}$$

$$= -k_B T \ln g(R) \qquad \Rightarrow F(R) = -\frac{d}{dR} w(R)$$

$$\Rightarrow \quad g(R) = e^{-\beta w(R)} \qquad \checkmark$$

$w(r)$ is "potential mean force", b/c

$-\frac{d}{dr} w(r) = \left\langle -\frac{\partial u}{\partial r} \right\rangle$: ~~key~~ for FE calcs & CG sims