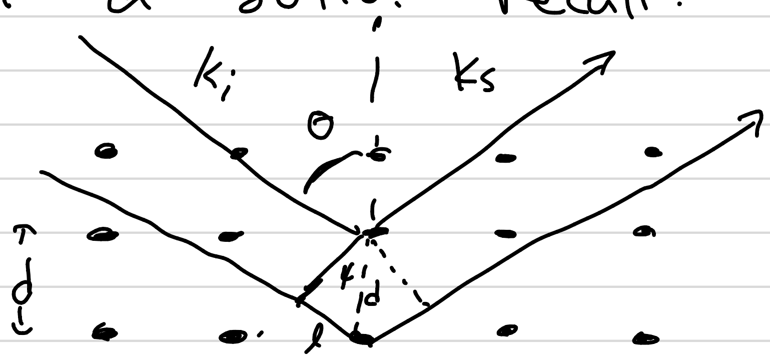
Lecture 8 -

RDFs continued

Last time: characterized liquid / gas structure by $g(r)$, the radial distribution function: $g(r) = \frac{N-1}{4\pi\rho r^2}\langle\delta(r-r')\rangle$

But how do we measure the structure of these systems - do by scattering expt, like for a solid. Recall:



$\ell = d\sin\psi$

path dist $= 2\ell = 2d\sin\psi$

Constructive interpherence when $2d\sin\psi = n\lambda$
(Bragg Scattering)

For a plane wave, $\psi(r) = e^{-ik\cdot r}$, [$k\cdot r$ is phase at a point]

In this scattering experiment, every photon comes in with momentum $|\vec{k}_i| = 2\pi/\lambda$ and leaves with momentum $\vec{k}_s$

Phase at $\vec{r}_1$ is $-\vec{k}_i\cdot\vec{r}_1$ and $\vec{r}_2$ is $-\vec{k}_i\,\vec{r}_2$

Phase diff is $-k_i \cdot (\vec{r}_1 - \vec{r}_2) = \delta\phi_i$

$\delta\phi_i = |k||r_1 - r_2| \cos\theta$ where θ is angle between incoming wave & $\vec{r}_2 - \vec{r}_1$

$= 2\pi/\lambda \, d \cos\theta$

$\delta\phi_s = k_s \cdot (\vec{r}_1 - \vec{r}_2)$

$\delta\phi = \delta\phi_s + \delta\phi_i = (k_s - k_i) \cdot (\vec{r}_1 - \vec{r}_2)$

$= \vec{q} \cdot (r_1 - r_2)$

momentum transfer

for elastic, $\theta_{in} = \theta_{out}$

$\delta\theta = 4\pi/\lambda \, d \cos\theta$

constructive $\delta\theta = 2\pi n$

$\Rightarrow 4\pi/\lambda \, d \cos\theta = 2\pi n \Rightarrow 2d\cos\theta = n\lambda$

Bragg again

Turns out, outgoing wave is sum over all scattering events $\psi(q) = \sum_{j=1}^{N} f_j e^{-i\vec{q}\cdot\vec{R}_j}$

pos of particles

change in wave vec $\vec{k}_s - \vec{k}_i$

f_j is form factor that depends on how atom interacts w/ light

Intensity $= |\psi^* \psi| = \sum_{i=1}^{N} \sum_{j=1}^{N} f_i f_j e^{-iq(R_j - R_i)}$

The "structure factor" is defined by normalizing by $\sum_{i=1}^{N} f_i^2$

$$S(q) = \frac{1}{\sum_{i=1}^{N} f_i^2} \sum_i \sum_j e^{-iq(R_j - R_i)} \cdot f_i f_j$$

if all the same type, $f_i = f$

$$\Rightarrow S(q) = \frac{1}{N f^2} \cdot f^2 \sum_{ij} e^{-iq(R_j - R_i)} = \boxed{\frac{1}{N} \sum_{ij} e^{-iq(R_j - R_i)}}$$

To actually compute, avg over MC motions

$$S(q) = \left\langle \frac{1}{N} \sum_{ij} e^{-iq \cdot \Delta R} \right\rangle \underset{\text{rewrite}}{=} \frac{1}{N} \left\langle \left| \sum_i e^{\overset{\pm \text{ doesn't matter}}{i} q \cdot R_i} \right| \right\rangle$$

Separate into self, $i=j$, $R_i - R_j = 0$ & distinct

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

$N \cdot N-1$ terms $e^{i\vec{q} \cdot \vec{R}_j - \vec{R}_i}$

$\langle e^{iq \cdot R_j - R_i} \rangle = \langle e^{i\vec{q} \cdot \vec{R}_2 - \vec{R}_1} \rangle$ avg value doesn't depend on particle pair

$$\Rightarrow S(q) = 1 + (N-1) \langle e^{-i\vec{q}(\vec{R}_2 - \vec{R}_1)} \rangle$$

$$= 1 + (N-1) \cdot \int \frac{dR_1 \, dR_2 \ldots dR_N \, e^{-i\vec{q}(\vec{R}_2 - \vec{R}_1)} e^{-\beta u(\vec{x})}}{Z}$$

$$= 1 + (N-1) \cdot \int dR_1 \int dR_2 \, e^{-iq(R_2 - R_1)} \underbrace{\int dR^{N-2} \, e^{-\beta u(x)} / Z}_{\frac{\rho^2 g^2(R_1 R_2)}{N \cdot N-1}}$$

switched to k

$$S(k) = 1 + \frac{1}{N} \cdot \int dr_1 \int dr_2\, \rho^2 g^{(2)}(r_1, r_2)\, e^{-ik(\vec{r}_2 - \vec{r}_1)}$$

$$= 1 + \frac{1}{N} \int d\vec{R}\, d\vec{r}\, \rho^2 g(\vec{r}, \vec{R})\, e^{i\vec{k}\cdot\vec{r}} \qquad \vec{r} = \vec{r}_2 - \vec{r}_1$$

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

$$= 1 + \frac{1}{\rho} \int d\vec{r}\, \rho^2 g(\vec{r})\, e^{-i\vec{k}\vec{r}}$$

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

Reminder: $\tilde{f}(k) = FT[f(x)] = \int_{-\infty}^{\infty} dx\, e^{-ikx} f(x)$

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

$u = -\cos\theta$

$du = +\sin\theta\, d\theta$

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

$$\int e^{ax} = \frac{1}{a} e^{ax}$$

$$= 1 + 2\pi\rho \int_0^{\infty} dr\, r^2 g(r) \cdot \frac{1}{ikr} \cdot \left[e^{+ikru} \right]_{u=-1}^{1} \qquad \left| \quad \frac{e^{+iax} - e^{-iax}}{2i} = +\sin(ax) \right.$$

$$= 1 + 4\pi\rho \int_0^{\infty} dr \cdot r^2 g(r) \frac{\sin(kr)}{kr}$$

← can predict S(k) from liquid struct

Thermodynamic Quantities from $g(r)$

Very interesting result: $g(R) = e^{-\beta w(R)}$

Reversible work theorem, $w(r)$ is work to move two particles from infinite separation to separation r – reversibly, const N, V, T

work $= \Delta A$ in process

work done by the force $= \int_{+\infty}^{R} F(r)\,dr$, $w(r)$ work you have to do $= \int_{R}^{\infty} F(r)\,dr$

But what is F?, $-\nabla U(r)$ averaged over positions of other particles, if reversibly slow

$$\left\langle -\frac{\partial U(r_{12})}{\partial r_{12}} \right\rangle = \int dr_3\,dr_4 \ldots dr_N \; -\frac{dU}{dr_{12}}\, e^{-\beta U(r)} \Big/ \int dr_3\,dr_4 \ldots dr_N\, e^{-\beta U(r)}$$

$$= \int dr^{N-2} \cdot \frac{1}{\beta} \frac{d}{dr_{12}} e^{-\beta U(r)} \Big/ \int dr^{N-2} e^{-\beta U(r)}$$

r_1, r_2 fixed

$r_{12} = r_2 - r_1$

$$= k_B T \frac{d}{dr_{12}} \log \left[\int dr^{N-2} e^{-\beta U(r)} \right]$$

$$\left[g^{(2)}(r_1, r_2) = Z \rho^2 \cdot \frac{1}{N(N-1)} \int dr^{N-2} e^{-\beta U(r)} \right]$$

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

$$\Rightarrow w(R) = \int_R^\infty k_B T \left[\frac{d}{dr} \log g(r)\right] dr$$

$$= k_B T \log g(r) \Big|_R^\infty = 0 - \underline{k_B T \log g(R)}$$

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

$w(R)$ is called the "potential of mean force" $\rightarrow \langle -\frac{\partial u}{\partial r} \rangle = -\frac{d}{dr} w(r)$

and it is what we often want to calculte in free energy methods & what we fit for course grained forces

Example