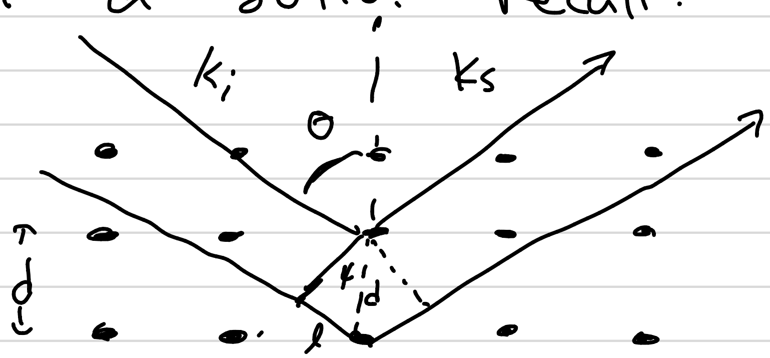
Lecture 8 -

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

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

Bragg again

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

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

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, $f_i = f$

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

To actually compute, avg over MC motions

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

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

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

$r_{12} = r_2 - r_1$

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

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

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

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

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

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

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

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

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Lets look at how the RDF is connected to the avg energy

first $E = -\frac{\partial \log Q}{\partial \beta}$, $Q = Z / N! \lambda^{3N}$, $\lambda = \sqrt{\frac{2\pi m}{\beta h^2}}$

$$E = -\frac{\partial}{\partial \beta}\left[\log Z - \frac{3}{2} N \log \beta + \text{const}\right]$$

$$= \underbrace{\frac{3}{2} N k_B T}_{\langle \text{kinetic } E \rangle} - \underbrace{\frac{\partial \log Z}{\partial \beta}}_{\langle U \rangle}$$

So to get potential energy, only need configurational partition function

Now let's consider potentials $U_{pair}(\vec{r}) = \sum_i \sum_{j>i} u(r_{ij})$
(pairwise)

then $$\langle U_{pair} \rangle = \frac{1}{Z} \sum_i \sum_{j>i} \underbrace{\int dr^N\, u(r_i - r_j)\, e^{-\beta U_{pair}(r)}}$$

but by relabeling can just write

$$\int dr^N\, u(r_1 - r_2)\, e^{-\beta U(r)}$$

$$= \frac{N \cdot (N-1)}{2} \cdot \frac{1}{Z} \int dr^N\, u(r_{12})\, e^{-\beta U_{pair}(r)}$$

$$= \frac{1}{2} \int dr_1 dr_2\, u(r_{12})\, \frac{N \cdot N-1}{Z} \int dr^{N-2}\, e^{-\beta U_{pair}(r)}$$

$$= \rho^2/2 \int d\vec{r}_1 d\vec{r}_2\, u(\vec{r}_{12})\, g^{(2)}(\vec{r}_1, \vec{r}_2)$$

like before $$= \frac{\rho^2 V}{2} \int d\vec{r}\, u(\vec{r})\, g(\vec{r})$$

or L, if short range $u \to 0$ before L

$$\underset{\text{if isotropic}}{=} \frac{N^2}{2V} \cdot 4\pi \int dr\, r^2 u(r) g(r) = \boxed{2\pi N \rho \int_0^\infty dr\, r^2 u(r) g(r)}$$

note - kind of what you expect,

N particles dist away is $4\pi\rho \int dr\, g(r)\, r^2$

so this is energy at that dist $\times$ # pairs at that dist $\cdot N/2$

What about pressure?

$$P = kT \frac{\partial}{\partial V} \ln Q(N,V,T) = kT \frac{\partial}{\partial V} \log Z(N,V,T)$$

$$Z(N,V,T) = \int_V dr^N e^{-\beta U(r)}$$ | so where is volume dependence

Imagine changing volume as moving everything closer ~~together~~ or farther apart

Say $\vec{s}_i = \frac{1}{V^{1/3}} \vec{r}_i$

$$\Rightarrow Z(N,V,T) = V^N \int ds_N \, e^{-\beta U(V^{1/3}\vec{s}_1, V^{1/3}\vec{s}_2 \ldots, V^{1/3}\vec{s}_N)}$$

$$\frac{dZ}{dV} = N V^{N-1} \int ds_N \ldots \quad + \quad V^N \int ds_N \cdot -\beta \frac{dU}{dV}(V^{1/3}\ldots) e^{-\beta U(\,)}$$

$$= \frac{N}{V} \cdot Z$$

chain rule $$\frac{dU}{dV} = \sum_{i=1}^{N} \frac{\partial U}{\partial (V^{1/3} s_i)} \frac{\partial V^{1/3} s_i}{\partial V} = \sum_{i=1}^{N} \left(\tfrac{1}{3} V^{-2/3} s_i\right) \frac{\partial U}{\partial r_i}$$

$$= \sum_{i=1}^{N} \frac{1}{3V} \cdot r_i \frac{\partial U}{\partial r_i} = -\frac{1}{3V} \sum_{i=1}^{N} r_i \cdot F_i$$

$$\frac{dZ}{dV} = \frac{N}{V} Z + \int dr^N \cdot \frac{\beta}{3V} \sum_{i=1}^{N} r_i \cdot F_i \, e^{-\beta U(r)}$$

virial

$$P = k_B T \frac{\partial \log Z}{\partial V} = k_B T \cdot \frac{1}{Z} \frac{dZ}{dV} = \frac{N k_B T}{V} + \frac{1}{3V} \left\langle \sum_{i=1}^{N} r_i \cdot F_i \right\rangle$$

$$\left\langle \sum p_i^2/2m \right\rangle = \tfrac{3}{2} N k_B T \Rightarrow$$

$$P = \frac{1}{3V} \left\langle \sum_{i=1}^{N} \frac{p_i^2}{m} + r_i \cdot F_i \right\rangle$$ ~ pressure estimator in MD

Lastly, consider $U_{pair} = \frac{1}{2}\sum_i \sum_j u(r_{ij})$

$$F_i = \sum_{j=1}^{N} -\frac{\partial u(r_{ij})}{\partial r_i} = \sum_{j=1}^{N} f_{ij}$$, note $f_{ij} = -f_{ji}$

$$\frac{1}{3V}\left\langle \sum_{i=1}^{N} r_i F_i \right\rangle = \frac{1}{3V}\cdot\frac{1}{Z}\int dr^N \sum_{i=1}^{N}\sum_{j=1}^{N} r_i f_{ij} \quad e^{-\beta U_{pair}}$$

$$= \frac{1}{3V}\cdot\frac{1}{Z}\int dr^N \sum_{i>j} r_{ij} f_{ij}\, e^{-\beta U_{pair}}$$

each integral identical by swapping particles

$$= \frac{N(N-1)}{2}\cdot\frac{1}{3V}\cdot\frac{1}{Z}\int dr_1 dr_2\, r_{12} f_{12} \int dr^{N-2} e^{-\beta u(r)}$$

$$= -\frac{\rho^2}{2}\cdot\frac{1}{3V}\cdot\int dr_1 dr_2\, r_{12}\frac{du}{dr_{12}}\, g(r_1, r_2)$$

$$= -\frac{\rho^2}{6V}\int dr\, dR\; r\frac{du}{dr}\, g(r, R)$$

$$= -\rho^2/6 \int d\vec{r}\;\vec{r}\,\frac{du}{dr}\, g(r)$$

isotropic
$$= -\rho^2/6 \cdot 4\pi \int dr\, r^3 \frac{du}{dr} g(r)$$

$$P/kT = \rho - \frac{2\pi\rho^2}{3k_BT}\int_0^\infty dr\, r^3\left(\frac{du}{dr}\right) g(r) \qquad \star$$

$g(r)$ depends on ρ & T

Imagine $g(r)$ can be written as

$$g(r,\rho) = \sum_{j=0}^{\infty} \rho^j g_j(r)$$ g_j somehow related to $d^jg/d\rho^j$

Then $P/k_BT = \rho + \sum_{j=0}^{\infty} B_{j+2}\,\rho^{j+2}$

$$B_{j+2}(T) = -\frac{2\pi}{3k_BT}\int_0^\infty r^3\, u'(r)\, g_j(r_1,T)$$

at small ρ, $\beta P \approx \rho + \rho^2 B_2$

$$B_2 \approx -\frac{2\pi}{3k_BT}\int_0^\infty dr\, r^3\, u'(r)\, g(r)$$

one can show for low ρ, $g(r) \approx e^{-\beta u(r)}$

HW? prob 4.5

$u(r) = -k_BT \log g(r)$

$$B_2 \approx +\frac{2\pi}{3}\int_0^\infty dr\ \underbrace{r^3}_{u} \cdot \underbrace{\frac{d[g(r)-1]}{dr}}_{dv}$$

$$\left\{\begin{array}{l} \dfrac{dg(r)}{dr} = -\beta\dfrac{du(r)}{dr}\,g(r) \\[2ex] \dfrac{d[g(r)-1]}{dr} = \dfrac{dg(r)}{dr} \end{array}\right.$$

$$= \frac{2\pi}{3}\left[r^3[g(r)-1]\Big|_0^\infty - \int_0^\infty 3r^2(g(r)-1)\,dr\right]$$

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

Low ρ, $g(r) = e^{-\beta u(r)}$