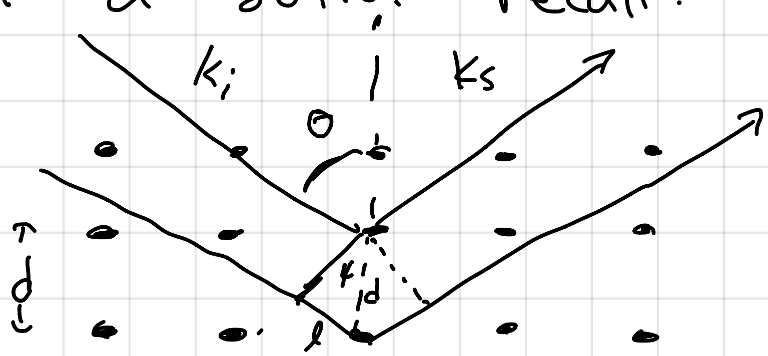
Lecture 8 — Scattering & Energy from RDF

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:



$l = d\sin\psi$

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

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 $\delta\theta = 2\pi n$

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

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

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

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

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

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

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

$\vec{r} = \vec{r}_2 - \vec{r}_1$

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

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

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

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

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

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

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

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

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

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

$$\frac{e^{+iax} - e^{-iax}}{2i} = +\sin(ax)$$

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

← 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 $= \int_{R}^{\infty} F(r)\,dr$ ($w(r)$)

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

$r_{12} = r_2 - r_1$

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

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

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

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

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

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

$W(R)$ 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 calculate in free energy methods & what we fit for course grained forces

---

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

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

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

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

So to get potential energy, only need configurational partition function

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

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

but by relabeling can just write

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

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

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

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

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

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

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

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 $\cdot N/2$