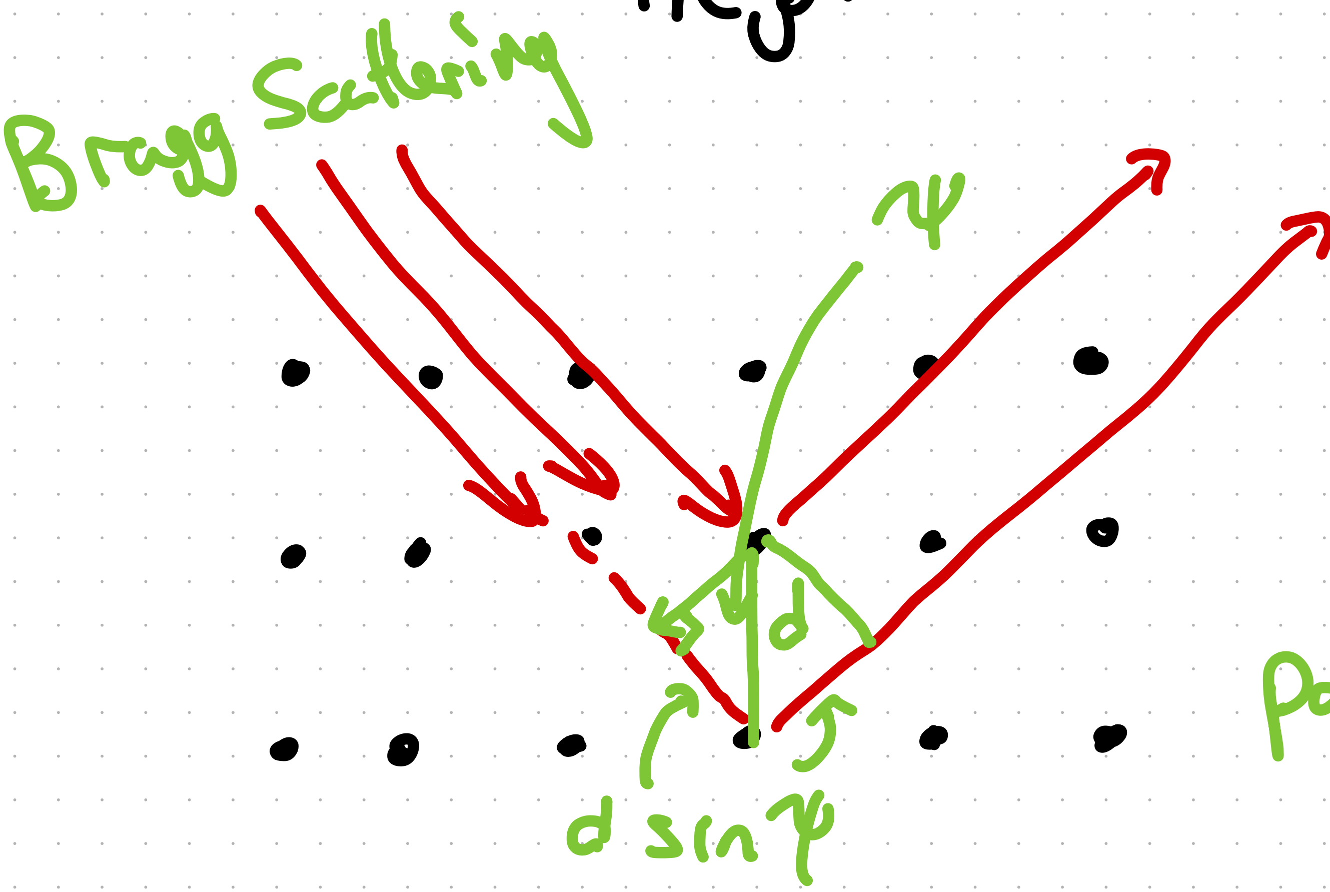
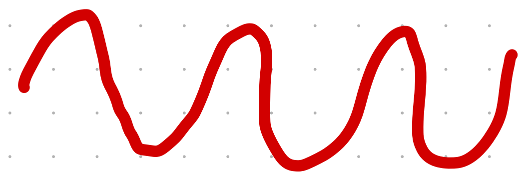
Lecture 9 - RDF connected to scattering + avg energy

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





Section 4.6.2 (Tuck)

path diff $2d\sin\psi = n\lambda$

Plane wave $\psi(\vec{r}) = e^{\pm i \vec{k}\cdot\vec{r}} \cdot A$

$\vec{k}$ "wave vector", momentum

$\vec{k}\cdot\vec{r}$ phase of the wave at position $\vec{r}$

$$e^{ix} = \cos \underline{x} + i \sin x$$

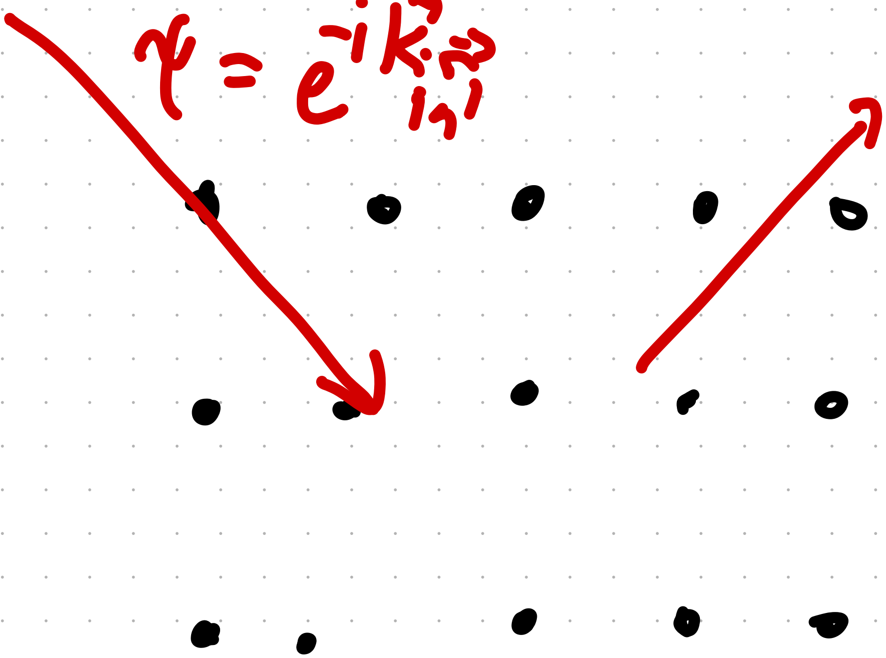
Intensity: $|\psi^* \psi| = A e^{2 + ikr} e^{-ikr}$

$= A^2(\cos^2 x + \sin^2 x) = A^2$

Book shows still get bragg scattering writing it this way

Elastic scattering

$$\Theta_{in} = \Theta_{out}$$



$$\psi = e^{-i\vec{k}_{in}\cdot\vec{r}_1}$$

$$e^{+i\vec{k}_{out}\cdot\vec{r}_2}$$

$$\delta\theta = \underbrace{(\vec{k}_s - \vec{k}_i)}_{\vec{q}} \cdot (\vec{r}_1 - \vec{r}_2)$$

"momentum trans."

Outgoing wave can be written as a sum over all scattering events

$$\psi_{out} = \sum_{j=1}^{N} f_j e^{-i\vec{q}\cdot\vec{R}_j}$$

position

$\vec{k}_s - \vec{k}_i$

form factor

how nuc interacts with light

$$\psi = \sum_j f_j e^{-i\vec{q}\cdot\vec{R}_j}$$

$$I = |\psi^* \psi| = \sum_i \sum_j f_i f_j e^{-i\vec{q}(\vec{R}_j - \vec{R}_i)}$$

Structure factor

$$I \Big/ \sum_{i=1}^{N} f_i^2 \Rightarrow S(q) = \frac{1}{\sum_{i=1}^{N} f_i^2} \sum_{i,j} \overset{f_i f_j}{\downarrow} e^{-i\vec{q}(\vec{R}_j - \vec{R}_i)}$$

if all atoms are identical

for identical

$$\boxed{S(q) = \frac{1}{N} \sum_{i,j} e^{-i\vec{q}\,(\vec{R}_j - \vec{R}_i)}}$$

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

± doesn't matter

$$= \frac{1}{N} \left\langle \left| \sum_{i} e^{i\vec{q}\cdot\vec{R}_i} \right|^2 \right\rangle$$

$$\rho(\vec{r}) = \sum_{i=1}^{N} \delta(\vec{r} - \vec{R}_i)$$

$$FT[f(x)] = \int_{-\infty}^{\infty} e^{-i\vec{q}\vec{x}} f(x)$$

$$\rho_q = FT(\rho(\vec{r})) = \sum_{i=1}^{N} e^{-i\vec{q}\cdot\vec{R}_i}$$

$$A = \sum_i x_i \qquad A^2 = \left(\sum_i x_i\right)\left(\sum_i x_i\right)$$

$$= \sum_i \sum_j x_i x_j$$

$$\left|\sum e^{ikx_i}\right|^2$$

c.c.

$$= \sum_i \sum_j e^{ikx_i} \, e^{-ikx_j}$$

$$S(q) = \frac{1}{N}\left\langle \sum_i \sum_j e^{-i\vec{q}(R_j - R_i)} \right\rangle$$

2 kinds of terms

$i = j$, $R_j - R_i = 0$, $e^{(\,)} = 1$

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

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

$$S(q) = 1 + (N-1)\left\langle e^{-iq(R_2 - R_1)} \right\rangle_{N,V,T}$$

$$\simeq 1 + (N-1)\cdot\frac{1}{Z}\int d\vec{R}_N \, e^{-i\vec{q}(\vec{R}_2-\vec{R}_1)} \, e^{-\beta U(\vec{R})}$$

$$= 1 + (N-1)\int d\vec{R}_1 \, d\vec{R}_2 \, e^{-i\vec{q}(\vec{R}_2-\vec{R}_1)} \times \underbrace{\left[\int d\vec{R}_3 \ldots d\vec{R}_N \, \frac{e^{-\beta U(\vec{R})}}{Z}\right]}_{\rho^2 g^{(2)}(\vec{R}_1,\vec{R}_2)\cdot\frac{1}{N(N-1)}}$$

$$S(\vec{q}) = 1 + \frac{1}{N} \int dR_1 \int dR_2 \, \rho^2 g^{(2)}(R_1, R_2) e^{-ik(\vec{R}_2 - \vec{R}_1)}$$

$$\vec{r} = \vec{R}_2 - \vec{R}_1 \quad \rightsquigarrow \int d\vec{r} \int d\vec{R}_{com}$$

If system is isotropic

care about mag.

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

$k \cdot r = kr\cos\theta$

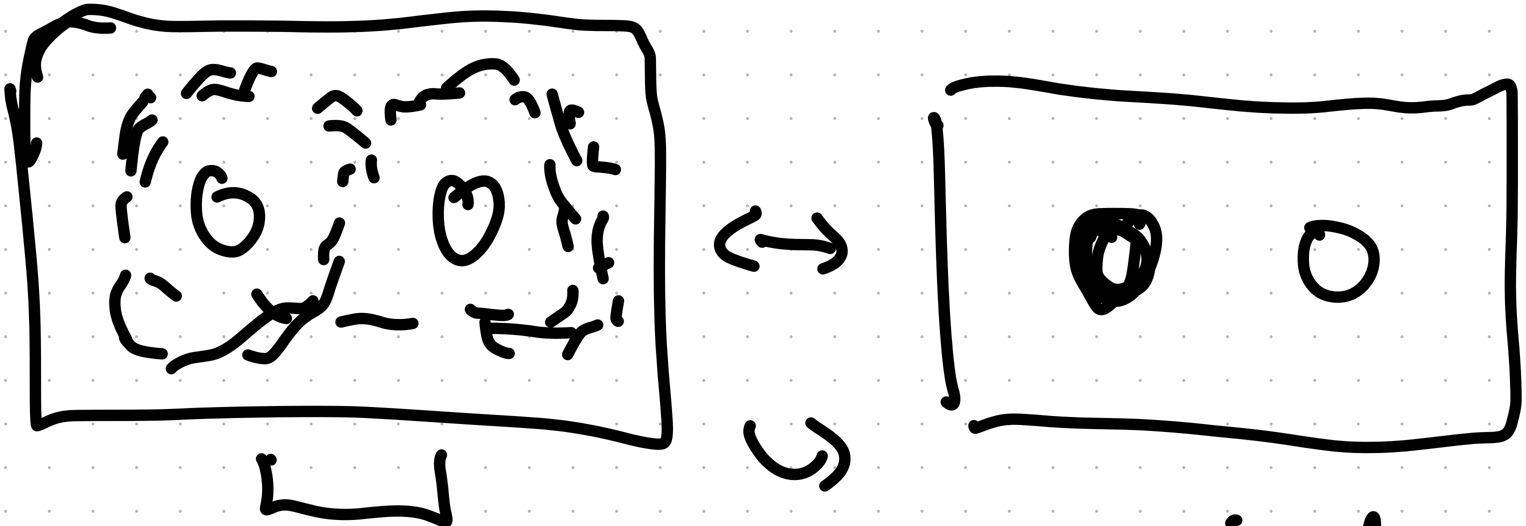
$$= 1 + 4\pi\rho \int_0^\infty dr \, r^2 g(r) \frac{\sin(kr)}{kr}$$

Thermodynamic quantities from g(r)

Reversible work theorem

$g(r') = e^{-\beta w(r')}$ / $w(r') = -k_BT \log g(r')$

$w(r)$ is work to bring 2 particles from $r = \infty$ to $r = r'$ reversibly in N, V, T



coarse grained

$$W = \pm\int \vec{F} \cdot d\vec{r}$$

work done
by the force

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

$-1 \times$ for we do.

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

$$W(R) = \int_R^\infty F(r)\,dr$$

$$F(r_{12}) = \left\langle -\frac{\partial U}{\partial r_{12}} \right\rangle_{r_1, r_2} \quad \text{b/c reversible}$$

$$\left\langle -\frac{\partial U}{\partial r_{12}} \right\rangle = \frac{1}{Z'} \int dr_3\, dr_4 \cdots dr_N \, -\frac{dU}{dr_{12}} e^{-\beta U(r)} .$$

avg over $r_3 - r_N$

$$= \frac{1}{Z'} \int dr^{N-2} \frac{1}{\beta} \left(\frac{d}{dr_{12}} \right) \left(e^{-\beta U(r)} \right)$$

$$Z' = \int dr^{N-2} e^{-\beta U(r)}$$

$$\left\langle -\frac{du}{dr_{12}} \right\rangle_{r_1, r_2} = \frac{\int dr^{N-2} \frac{1}{\beta} \frac{d}{dr_{12}} e^{-\beta u(r)}}{\int dr^{N-2} e^{-\beta u(r)}}$$

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

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

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

$$F = \left\langle -\frac{\partial u}{\partial r_{12}} \right\rangle_{\vec{r}_1, \vec{r}_2} = -k_B T \frac{d}{dr_{12}} \log(g(r_{12}))$$

$$r_{12} = |\vec{r}_1 - \vec{r}_2|$$

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

$$\left[\int_a^b dx \left[\frac{d}{dx} f\right] = f(b) - f(a) \right.$$

$$= \left[\log[g(\infty)] - \log[g(R)] \right] k_B T$$

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

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

$$\left\langle \underbrace{-\frac{du}{dr}}_{\text{mean force}} \right\rangle = -\underbrace{\frac{d}{dr}}\, \underbrace{w(r)}$$

"potential of mean force"

(PMF)

$$\left\langle -\frac{\partial \mathcal{H}}{\partial r} \right\rangle$$

$$= \left\langle -\frac{d}{dr}\left[KE \right] + \frac{d}{dr}\left[U(r) \right] \right\rangle$$

only depends on p

$$= \left\langle -\frac{d}{dr} U(r) \right\rangle$$