Interaction of X-rays and Neutrons with Matter

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Synopsis

- Advantages/Disadvantages of X-ray and Neutrons
- Scattering Length and Scattering Cross-Section
- Kinematic Theory of Scattering and Definition of Scattering Function S(Q)
- Correlation Functions; Coherent and Incoherent Scattering of Neutrons
- Pair Distribution Function and Scattering from Liquids and Glasses
- Diffraction by Crystals and the Reciprocal Lattice; Bragg and Laue Scattering
  Single Crystal and Powder Diffraction
- Scattering from 1-Dimensional and 2-Dimensional Systems; Adsorbed Monolayers
- Scattering from Disordered Systems; Diffuse Scattering
- Small Angle Scattering
- Reflectivity and Surface Scattering Truncation Rods

Synopsis (Cont.)

- Formal Derivation of Cross-Sections in the Born Approximation
- Inelastic Neutron and X-ray Scattering
- Deep Inelastic (Compton) Scattering
- Quasi-elastic Scattering
- Beam Coherence, Speckle and Dynamical Scattering

Thermal Neutrons

Advantages

1) λ_n ~ Interatomic Spacing

2) Penetrates Bulk Matter (neutral particle)

3) Strong Contrasts Possible (e.g. H/D)

4) E_n ~ Elementary Excitations (phonons, magnons, etc.)

5) Scattered Strongly by Magnetic Moments

Disadvantages

1) Low Brilliance of Neutron Sources-Low Resolution or Intensities; Large Samples; Low Coherence; Surfaces Difficult

2) Some Elements Strongly Absorb (e.g. Cd, Gd, B)

3) Kinematic Restriction on Q for Large E Transfers

4) Restricted to Excitations ≤ 100 meV

Synchrotron X-rays

Advantages

1) λ_n - Interatomic Spacing

2) High Brilliance of X-ray Sources - High Resolution; Small Samples; High Degree of Coherence

3) No Kinematic Restrictions (E,Q uncoupled)

4) No Restriction on Energy Transfer that Can Be Studied

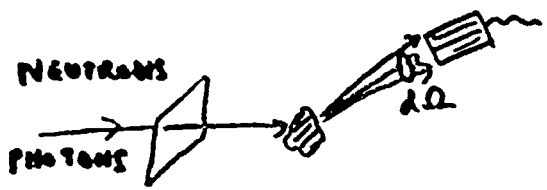
Disadvantages

1) Strong Absorption for Lower Energy Photons

2) Little Contrast for Hydrocarbons or Similar Elements

3) Weak Scattering from Light Elements

4) Radiation Damage to Samples



Cross-Sections

Let Φ = Incident Flux of particles [$\sec^{-1}$ cm^{-2}]

Partial Differential Cross-Section

$$\frac{d^2\sigma}{d\Omega dE'} = \frac{(\text{No. scattered/sec into } d\Omega \text{ with energies between } E' \text{ and } E'+dE)}{\Phi d\Omega dE'}$$

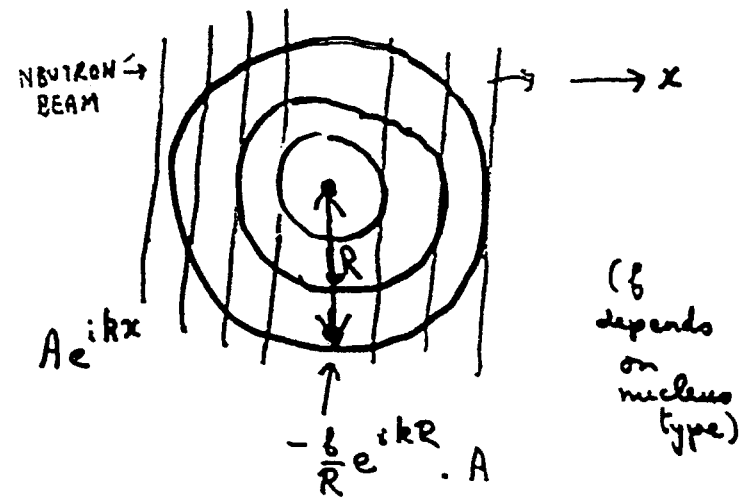
Differential Cross-Section

$$\frac{d\sigma}{d\Omega} = \frac{(\text{No. scattered/sec into } d\Omega)}{\Phi d\Omega} = \int_0^\infty \frac{d^2\sigma}{d\Omega dE'} dE'$$

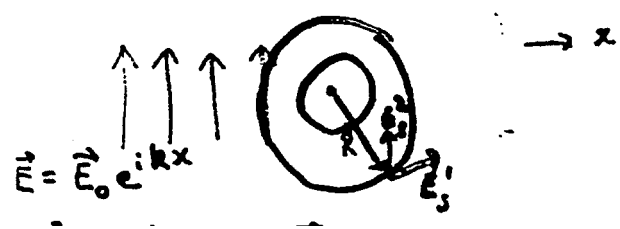
Total Cross-Section

$$\sigma = \frac{(\text{No. scattered/sec})}{\Phi} = \int d\Omega \left(\frac{d\sigma}{d\Omega}\right)$$

Scatttering by a Single Nucleus (assumed fixed)



Scatttering by a Single Free Electron



el. accelern $\rightarrow$ $\vec{a} = \frac{e}{m}\vec{E}_0$

Radiated field $\rightarrow$ $\vec{E}_S^{\,j} = \frac{e}{c^2 R} e^{ikR} \left(\vec{a} \cdot \vec{\varepsilon}_j\right) \vec{E}j$

$$= \left(\frac{e^2}{mc^2}\right) \frac{e^{ikR}}{R} \left(\vec{E}_0 \cdot \vec{\varepsilon}_j\right) \vec{\varepsilon}_j$$

$$b = \left(\frac{e^2}{mc^2}\right) \left(\vec{\varepsilon}_i \cdot \vec{\varepsilon}_j\right)$$

$$\left(\frac{e^2}{mc^2}\right) = r_0 \rightarrow \text{Thomson Scat. length}$$

Neutrons

If v is the velocity of neutrons (before and after scattering),

Number of neutrons passing through dS/sec

$$= vdS\left|\psi_{se}\right|^2 = \frac{vdS}{R^2} b^2 \left|A\right|^2 = vd\Omega b^2 \left|A\right|^2$$

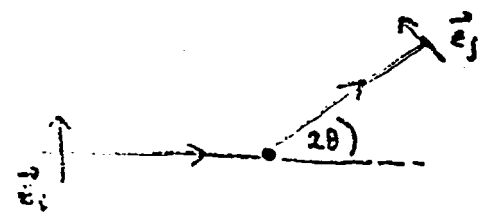
Incident flux $\Phi = v|A|^2$

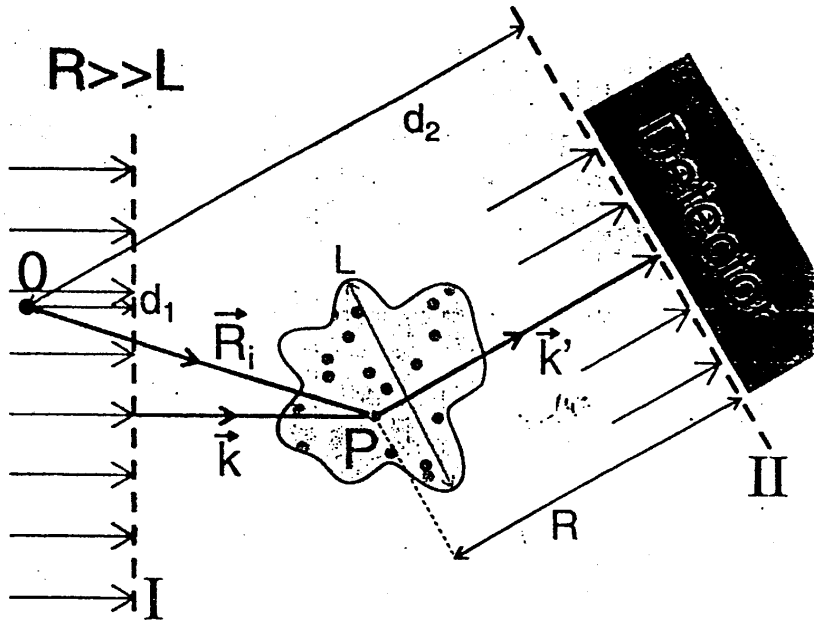
$$\therefore \frac{d\sigma}{d\Omega} = \frac{vb^2 d\Omega \left|A\right|^2}{v\left|A\right|^2 d\Omega} = b^2$$

$$\sigma = 4\pi b^2 = \int \left(\frac{d\sigma}{d\Omega}\right) d\Omega$$

X-rays

$$\frac{d\sigma}{d\Omega} = \underbrace{\left(\frac{e^2}{mc^2}\right)^2}_{r_0^2} \left[\frac{1 + \mathrm{Cos}^2(2\theta)}{2}\right] \leftarrow \text{“Polarization Factor”}$$





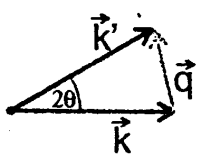
Phase at plane I $= 0$ (per definition)

Phase at P $= e^{i(\vec{k}\cdot\vec{R}_i - kd_1)}$

Phase at plane II $= e^{i(\vec{k}\cdot\vec{R}_i - kd_1)}\, e^{i(k'd_2 - \vec{k}'\cdot\vec{R}_i)}$

$= e^{i(\vec{k}-\vec{k}')\cdot\vec{R}_i}\, e^{i\phi}$ $\quad (\phi = k'd_2 - kd_1)$

$= e^{-i\vec{q}\cdot\vec{R}_i}\, e^{i\phi}$ $\quad (\vec{q} = \vec{k}' - \vec{k})$



Neutrons

Sum of scattered waves on plane II:

$$\psi_{se} = Ae^{i\phi}\sum_i \frac{b_i}{R} e^{-i\vec{q}\cdot\vec{R}_i}$$

$$\frac{d\sigma}{d\Omega} = \frac{vdS|\psi_{se}|^2}{v|A|^2\, d\Omega} = \frac{vdS}{v|A|^2}\frac{|A|^2}{R^2}\frac{1}{d\Omega}\sum_{ij} b_i b_j\, e^{-i\vec{q}\cdot(\vec{R}_i - \vec{R}_j)}$$

$$= \sum_{ij} b_i b_j\, e^{-i\vec{q}\cdot(\vec{R}_i - \vec{R}_j)}$$

X-rays

$$\frac{d\sigma}{d\Omega} = r_0^2 \sum_{ij} e^{-i\vec{q}\cdot(\vec{r}_i - \vec{r}_j)} \times \left(\frac{1+\mathrm{Cos}^2(2\theta)}{2}\right)$$

$\vec{r}_i \rightarrow$ electron coordinates

For neutrons, b_i depends on nucleus (isotope, spin relative to neutron ($\uparrow\uparrow$ or $\downarrow\uparrow$)), etc. Even for one type of atom,

$b_i = \langle b \rangle + \delta b_i \leftarrow$ random variable

$$b_i b_j = \langle b \rangle^2 + \langle b \rangle \left[\underbrace{\delta b_i + \delta b_j}_{\text{zero}} \right] + \underbrace{\delta b_i \, \delta b_j}_{\text{zero unless } i = j}$$

$$\left\langle \delta b_i^2 \right\rangle = \left\langle b^2 \right\rangle - \langle b \rangle^2$$

$$\therefore \frac{d\sigma}{d\Omega} = \underbrace{\langle b \rangle^2}_{\sigma_{coh}/4\pi} \sum_{ij} e^{-i\vec{q}\cdot\left(\vec{R}_i - \vec{R}_j\right)} + \underbrace{\left[\left\langle b^2 \right\rangle - \langle b \rangle^2 \right]}_{\sigma_{inc}/4\pi} N$$

"coherent" "incoherent"

In most cases, we must do a thermodynamic or ensemble average

$$\frac{d\sigma}{d\Omega} = \langle b \rangle^2 S(q) \qquad S(q) = \left\langle \sum_{ij} e^{-i\vec{q}\cdot\left(\vec{R}_i - \vec{R}_j\right)} \right\rangle$$

$\{R_i\}$ = nuclear posns

X-rays

$$\frac{d\sigma}{d\Omega} = Z^2 r_0^2 \left(\frac{1 + Cos^2(2\theta)}{2} \right) S(q) \qquad S(q) = \frac{1}{Z^2} \left\langle \sum_{ij} e^{-i\vec{q}\cdot\left(\vec{r}_i - \vec{r}_j\right)} \right\rangle$$

$\{r_i\}$ = electron posns

H has large <u>incoherent</u> σ (10.2×10^{-24} cm^2)

but small <u>coherent</u> σ (1.8×10^{-24} cm^2).

D has larger <u>coherent</u> σ (5.6×10^{-24} cm^2)

and small <u>incoherent</u> σ (2.0×10^{-24} cm^2).

C,O have completely coherent σ's.

V almost completely incoherent

($\sigma_{coh} = 0.02 \times 10^{-24}$ cm^2 $\quad \sigma_{inc} = 5.0 \times 10^{-24}$ cm^2)

NOTE: $\sum_i e^{-i\vec{q}\cdot\vec{R}_i} = \rho_N(\vec{q})$ F.T. of nuclear density function

<u>PROOF</u>: $\rho_N(\vec{q}) = \int d\vec{r}\, e^{-i\vec{q}\cdot\vec{r}} = \int d\vec{r}\, e^{-i\vec{q}\cdot\vec{r}} \rho_N(\vec{r})$

$$= \int d\vec{r}\, e^{-i\vec{q}\cdot\vec{r}} \sum_i \delta\left(\vec{r}_i - \vec{R}_i\right) = \sum_i e^{-i\vec{q}\cdot\vec{R}_i}$$

Similarly for electrons.

$$\boxed{S(q)_{neut} = \left\langle \rho_N(\vec{q}) \rho_N^*(\vec{q}) \right\rangle \;\Big\|\; S(q)_{x-ray} = \frac{1}{Z^2} \left\langle \rho_{el}(\vec{q}) \rho_{el}^*(\vec{q}) \right\rangle}$$

If electrons are bound to atoms centered on $\vec{R}_i$

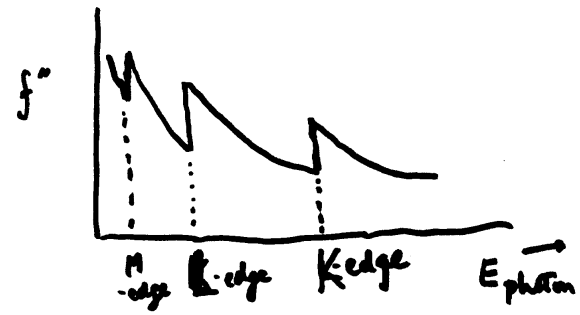
$$\rho_{el}(\vec{r}) = \sum_i f_{el}(\vec{r} - \vec{R}_i)$$

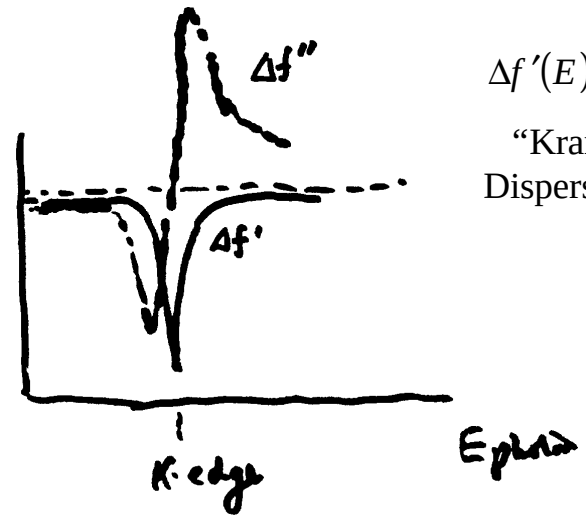
$$\rho_{el}(\vec{q}) = \int d\vec{r}\, e^{-i\vec{q}\cdot\vec{r}} \sum_i f(\vec{r} - \vec{R}_i)$$

$$= \sum_i \left[\int d\vec{r}\, e^{-i\vec{q}\cdot(\vec{r}-\vec{R}_i)} f(\vec{r} - \vec{R}_i) \right] e^{-i\vec{q}\cdot\vec{R}_i}$$

$$= Zf(\vec{q}) \sum_i e^{-i\vec{q}\cdot\vec{R}_i} = Zf(\vec{q})\,\rho_N(\vec{q})$$

atomic form factor





$$\Delta f'(E) = 2\pi \int \frac{\Delta f''(E')}{E - E'} dE'$$

"Kramers-Kronig Dispersion Relations

<u>X-rays</u>

$$f = f_0 + \underbrace{\Delta f' + i\Delta f''}$$

"Scattering factor" = $Zf(q)$

"anomalous" big at edges

$$S(q) = \left\langle \left| \rho_N(\vec{q}) \right|^2 \right\rangle \qquad \left[\times \left| f(q) \right|^2 \right] \text{for x–rays}$$

$$\rho_N(\vec{q}) = \int d\vec{r}\, e^{-i\vec{q}\cdot\vec{r}} \rho_N(\vec{r})$$

$$\Rightarrow S(q) = \iint d\vec{r}\, d\vec{r}\,' e^{-i\vec{q}\cdot(\vec{r}-\vec{r}\,')} \langle \rho_N(r) \rho_N(r') \rangle$$

If $\langle \rho_N(\vec{r}) \rho_N(r') \rangle$ = Fn. of $(r - r')$ only,

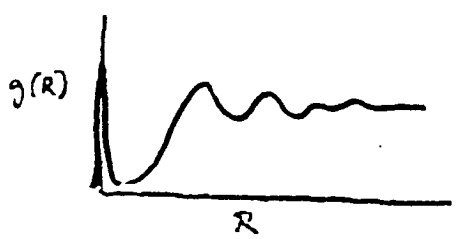
$$S(q) = V \int d\vec{r}\,' e^{-i\vec{q}\cdot\vec{R}} \langle \rho_N(\vec{r}) \rho_N(\vec{r} - \vec{R}) \rangle$$

$$= \int d\vec{R}\, e^{-i\vec{q}\cdot\vec{R}} g(\vec{R})$$

$g(\vec{R})$ = Pair-distribution function

$$= V \langle \rho_N(\vec{r}) \rho_N(\vec{r} - \vec{R}) \rangle$$

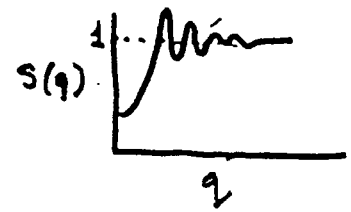
$\Rightarrow$ Probability that given a particle at $\vec{r}$, there is one at a distance $\vec{R}$ from it (per unit volume)



$$g(\vec{R}) = \delta(\vec{R}) + g_d(\vec{R}) \qquad S(q) - 1 = \int d\vec{R}\, e^{-i\vec{q}\cdot R} g_d(\vec{R})$$

$$g_d(\vec{R})_{R\to\infty} \to V \langle \rho \rangle^2$$

Liquids and Glasses



$g(\vec{R})$ and hence $S(q)$ are isotropic.

$g_d(R)$ = Reverse F.T. of $[S(q) - 1]$

$$= 4\pi \int_0^\infty dq\, q^2 \frac{\sin(qR)}{(qR)} [S(q) - 1]$$

For compounds, alloys,

Neutrons

$$I(q) \equiv \frac{d\sigma}{d\Omega} = \sum_{K,K'} b_K b_{K'} S_{KK'}(q)$$

$K, K' \to$ different atomic types

X-rays

$$I(q) = \sum_{K,K'} (r_0)^2 Z_{K'}, Z_{K'}, f_K(q) f^*_{K'}(q) S_{KK'}(q)$$

$$\times \left[1 + \frac{\mathrm{Cos}^2(2\theta)}{2} \right]$$

(K,K' = Different atomic types)

$$S_{KK'}(q) = \left\langle \sum_{i(K)j(K')} e^{-i\vec{q}\cdot\left[\vec{R}_i(K) - \vec{R}_j(K')\right]} \right\rangle$$

$\Rightarrow$ partial structure factor

These can be unscrambled by simultaneous measurements of $\frac{d\sigma}{d\Omega}$ for neutrons, different isotopes + x-rays.

Reciprocal Lattice

Lattice Vectors $\vec{R}_\ell = m_1\vec{a}_1 + m_2\vec{a}_2 + m_3\vec{a}_3$

$\vec{a}_1, \vec{a}_2, \vec{a}_3 \rightarrow$ primitive translation vectors of unit cell.

Define 3 other vectors:

$$\vec{b}_1 = 2\pi(\vec{a}_2 \times \vec{a}_3)/v_0$$

$$\vec{b}_2 = 2\pi(\vec{a}_3 \times \vec{a}_1)/v_0 \qquad v_0 = \vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)$$

= unit cell vol.

$$\vec{b}_3 = 2\pi(\vec{a}_1 \times \vec{a}_2)/v_0$$

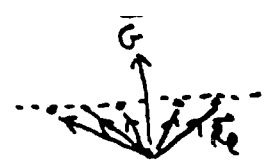
These have the property that $\vec{a}_i \cdot \vec{b}_j = 2\pi\delta_{ij}$

So if we choose any vector $\vec{G}$ on the lattice defined by $\vec{b}_1, \vec{b}_2, \vec{b}_3$:

$$\vec{G} = n_1\vec{b}_1 + m_2\vec{b}_2 + m_3\vec{b}_3$$

then for any $\vec{G}, \vec{R}_\ell$,

$\vec{G} \cdot \vec{R}_\ell = 2\pi \times \text{integer} \rightarrow$ Implies $\vec{G}$ is normal to sets of planes of atoms spaced $2\pi/G$ apart.



OR

$$e^{i\vec{G}\cdot\vec{R}_\ell} = 1$$

Crystals (Bravais or Monotonic)

$$\left(\frac{d\sigma}{d\Omega}\right)_{neutrons} = \langle b\rangle^2 \left\langle \sum_{\ell\ell'} e^{-i\vec{q}\cdot(\vec{R}_\ell - \vec{R}_{\ell'})} \right\rangle$$

where $\vec{R}_\ell$ denotes a lattice site

$$= N\langle b\rangle^2 \left\langle \sum_{\ell} e^{-i\vec{q}\cdot\vec{R}_\ell} \right\rangle$$

Now

$$\boxed{\sum_{\ell} e^{-i\vec{q}\cdot\vec{R}_\ell} = \frac{(2\pi)^3}{v_0}\sum_{\vec{G}} \delta(\vec{q}-\vec{G})}$$

v_0 = Vol. of unit cell; $\vec{G}$ = Reciprocal Lattice Vector

[Property of reciprocal lattices and direct lattices:

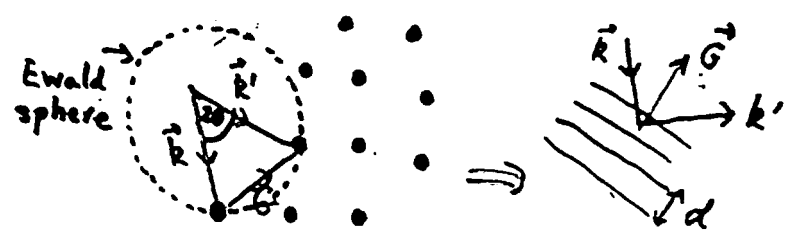
$$e^{-i\vec{G}\cdot\vec{R}_\ell} = e^{in\cdot 2\pi} = 1]$$

$$\boxed{\left(\frac{d\sigma}{d\Omega}\right)_{neutrons} = \langle b\rangle^2 N \cdot \frac{(2\pi)^3}{v_0}\sum_{\vec{G}} \delta(\vec{q}-\vec{G}) e^{-2W}}$$

(Introduce e^{-2W} = "Form factor" for thermal smearing of atoms = $e^{-\langle(\vec{q}\cdot\vec{u})^2\rangle}$ $\Rightarrow$ Debye-Waller factor)

Similarly,

$$\boxed{\left(\frac{d\sigma}{d\Omega}\right)_{x-rays} = Z^2 r_0^2 \left(\frac{1+\mathrm{Cos}^2(2\theta)}{2}\right) f^2(\vec{q}) e^{-2W} \quad N\cdot\frac{(2\pi)^3}{v_0}\sum_{\vec{G}} \delta(\vec{q}-\vec{G})}$$



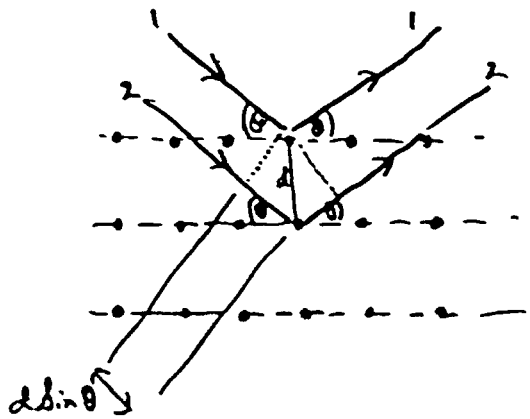
Bragg Reflections: $\vec{k}' - \vec{k} = \vec{G}$

$$2k\,\mathrm{Sin}\,\theta = G = \frac{2\pi}{d}$$

$$\rightarrow \boxed{\lambda = 2d\,\mathrm{Sin}\theta} \quad \text{Bragg's Law}$$

In general, in a scattering experiment

$$\boxed{|\vec{q}| = 2k\,\mathrm{Sin}\,\theta = \frac{4\pi}{\lambda}\mathrm{Sin}\,\theta}$$



A simple way to see Bragg's Law:

Path length difference between rays reflected from successive planes (1 and 2) = $2d\,\mathrm{Sin}\,\theta$

$\therefore$ Constructive interference when

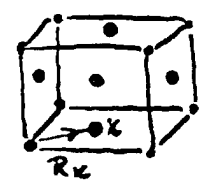
$$\boxed{n\lambda = 2d\,\mathrm{Sin}\,\theta}$$

Crystals with Complex Unit Cells (more than one type of atom/cell)

<u>Generalization</u>

$$\left(\frac{d\sigma}{d\Omega}\right) = \left\langle \sum_{\substack{\ell\ell' \\ KK'}} b_K\, b_{K'}\, e^{-i\vec{q}\cdot\left(\vec{R}_\ell + \vec{R}_K - \vec{R}_{\ell'} - \vec{R}_{K'}\right)} \right\rangle$$

where b_K is coherent scattering length $\langle b \rangle$ for K-type atom in unit cell at position $\vec{R}_K$.



$$= \left| \sum_K \underbrace{f_K\, e^{-i\vec{q}\cdot\vec{R}_K}}_{\text{F (structure factor)}} e^{-2W_K} \right|^2 \sum_{\ell\ell'} e^{-i\vec{q}\cdot\left(R_\ell - R_{\ell'}\right)}$$

$$\left(\frac{d\sigma}{d\Omega}\right)_{neutron} = \frac{N\cdot(2\pi)^3}{v_0}\sum_G |F_G|^2\,\delta(\vec{q}-\vec{G})$$

$$\left(\frac{d\sigma}{d\Omega}\right)_{x-ray} = \frac{N\cdot(2\pi)^3}{v_0}\sum_G |F_G|^2\,\delta(\vec{q}-\vec{G})\left(\frac{1+\mathrm{Cos}^2(2\theta)}{2}\right)$$

where

$$\boxed{F_G = \sum_K Z_K\, f_K(\vec{G})\, r_0\, e^{-2W_K}\, e^{-i\vec{G}\cdot\vec{R}_K}}$$ – x-ray structure factor

Measurement of Structure Factors → Structure

<u>BUT</u> what is measured is $|F_G|^2$ **<u>NOT</u>** F_G!

→ "Phase Problem" → Special Methods

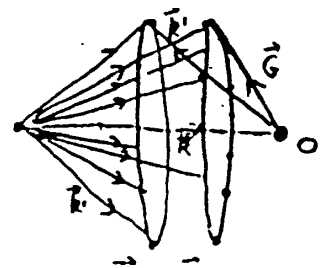
Note that $|F_G|^2$ can be written $\sum_{KK'} \mu_K \mu_{K'}\, e^{-i\vec{G}\cdot(\vec{R}_K-\vec{R}_{K'})}$

so that its F.T. yields information about <u>pairs</u> of atoms

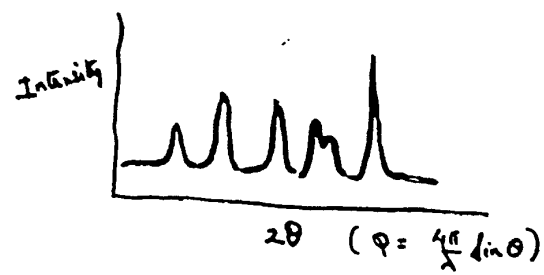
separated by $\vec{R}_K - \vec{R}_{K'} \Rightarrow$ Patterson Function.

<u>Methods of Measuring Bragg Peaks:</u>

A. <u>Powder Diffraction</u>



For a given $\vec{k}$, $\vec{k}'$ will lie on a cone (Debye-Scherrer cone) traced out by a $\vec{G}$ on the Ewald sphere as it is oriented randomly about the origin of reciprocal space.



2θ = scattering angle

Peaks whenever $\mathrm{Sin}\,\theta = \dfrac{\lambda}{2d_{hk\ell}}$ for all sets of planes indexable by (h,k,ℓ) with spacing $d_{hk\ell}$ (provided $|F_{hk\ell}|^2 \neq 0$)

(Integrated) Intensity of peak associated with (h,k,ℓ) can be shown to be given by:

$$I_{hk\ell} = \phi \frac{d}{2\pi R \operatorname{Sin}(2\theta)} \frac{V}{v_0^2} \frac{\lambda^3}{4 \operatorname{Sin}\theta} |F_{hk\ell}|^2 \sigma_{hk\ell}$$

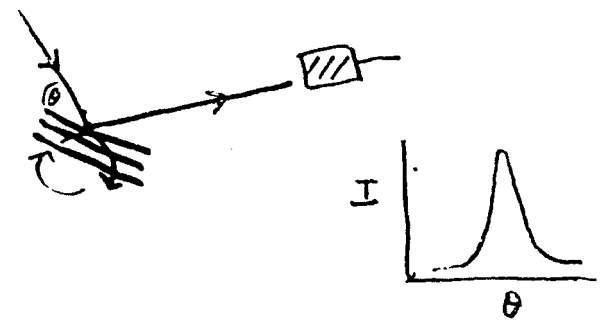
ϕ = Incident Flux on sample
d = Detector height
R = Detector Distance
$\sigma_{hk\ell}$ = Number of relections with same $d_{hk\ell}$
(degeneracy factor)

Sometimes, (2θ) is held fixed and we vary λ. Whenever $\lambda = 2d_{hk\ell} \operatorname{Sin}\theta$, we get peaks.

(Energy Dispersive X-Ray Powder Diffraction;
Neutron Time-of-Flight P.D.)

Structures often obtained by <u>Rietveld Analysis</u>
(least squares fitting)

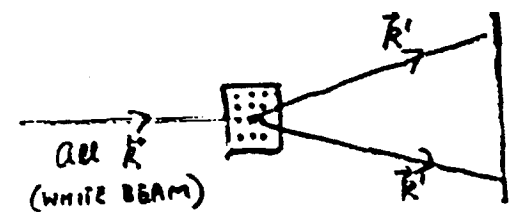
B. <u>Single Crystal Bragg Methods</u>



Integrated Intensity under Bragg Peak

$$I_{hk\ell} = \phi \frac{V}{v_0^2} \frac{\lambda^3}{\operatorname{Sin}(2\theta)} |F_{hk\ell}|^2$$

C. <u>Laue Method</u>



$$I_{hk\ell} - \phi(\lambda)\frac{V}{v_0^2}\frac{\lambda^4}{2\,\mathrm{Sin}^2\,\theta}\left|F_{hk\ell}\right|^2$$

$\phi(\lambda)d\lambda =$ Incident flux between λ, λ+dλ

2-D Crystals (Adsorbed Monolayers, Films)

If $\vec{R}_\ell$ are all restricted to say the (x,y) plane, z-component of $\vec{q}$ will not affect

$$S(\vec{q}) = \sum_{\ell\ell'} e^{i\vec{q}\cdot\left(\vec{R}_\ell - \vec{R}_{\ell'}\right)}$$

which is thus <u>independent</u> of q_z.

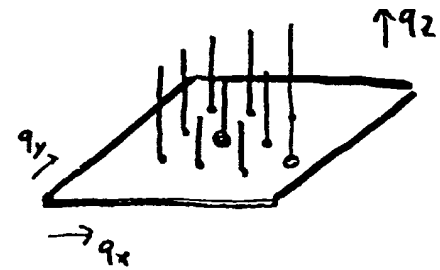
$$S(q) \propto \sum_{G_{||}} \delta\left(\vec{q}_{||} - \vec{G}_{||}\right)$$

where

$\vec{G}_{||}$ is 2-D reciprocal lattice vector in plane

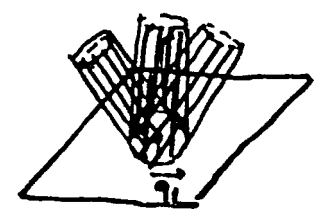
$\vec{q}_{||}$ is (x,y) plane component of $\vec{q}$

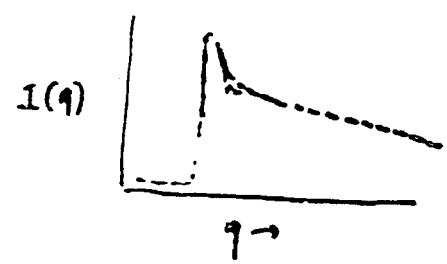
$\Rightarrow$ diffraction is on <u>rods</u> in reciprocal space through the $\vec{G}_{||}$ and parallel to z-axis



Only q_z-dependence of I along rod is due to $f(\vec{q})e^{-2W}$ (functions of q_z but slowly varying)

<u>Powders of 2-D Crystals</u>

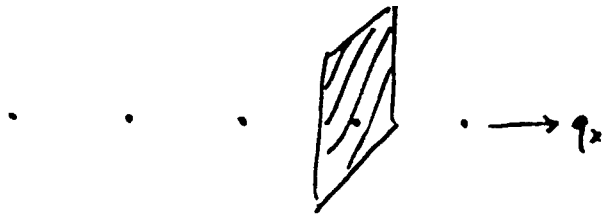




asymmetric (saw-tooth) powder peak shape

(Warren)

1-D Crystals



$S(\vec{q})$ independent of q_z and q_y. Planes of scattering in reciprocal space.

Charge Density Waves/Phonons (x-rays only!)*

These give rise to sinusoidal modulations of the atoms in the crystals about their equilibrium positions.

$$\vec{R}_\ell \to \vec{R}_\ell + \vec{u}_\ell$$

Consider a simple Bravais (monatomic) lattice which has such a modulation:

$$S(\vec{q}) = \left\langle \sum_{\ell\ell'} e^{i\vec{q}\cdot\left(\vec{R}_\ell - \vec{R}_{\ell'} + \vec{u}_\ell - \vec{u}_{\ell'}\right)} \right\rangle$$

$$= \sum_{\ell\ell'} e^{i\vec{q}\cdot\left(\vec{R}_\ell - \vec{R}_{\ell'}\right)} \left\langle e^{i\vec{q}\cdot\left(\vec{u}_\ell - \vec{u}_{\ell'}\right)} \right\rangle$$

ℓ is either fixed ℓ (static CDW) or

Theorem for Gaussian Variables *u*:

$$\left\langle e^{u} \right\rangle = e^{\frac{1}{2}\left\langle u^2 \right\rangle}$$

$$\therefore \left\langle e^{i\vec{q}\cdot\left(\vec{u}_\ell - \vec{u}_{\ell'}\right)} \right\rangle = \underbrace{e^{-\frac{1}{2}\left\langle \left(\vec{q}\cdot\vec{u}_\ell\right)^2 \right\rangle}}_{e^{-W}} e^{-\frac{1}{2}\left\langle \left(\vec{q}\cdot\vec{u}_{\ell'}\right)^2 \right\rangle} e^{\left\langle \left(\vec{q}\cdot\vec{u}_\ell\right)\left(\vec{q}\cdot\vec{u}_{\ell'}\right) \right\rangle}$$

---

* For neutrons, phonons can exchange significant amounts of energy with neutrons, so “instantaneous” correlation functions are not measured directly, unless neutron energy is integrated over.

$$\therefore \left\langle e^{i\vec{q}\cdot(\vec{u}_\ell - \vec{u}_{\ell'})} \right\rangle = e^{-2W} e^{\langle (\vec{q}\cdot\vec{u}_\ell)(\vec{q}\cdot\vec{u}_{\ell'}) \rangle}$$

$$= e^{-2W}\left[1 + \sum_{\alpha\beta} q_\alpha q_\beta \left\langle u_{\ell,\alpha} u_{\ell'\beta} \right\rangle + \ldots\right]$$

$$\boxed{u_{\ell,\alpha} = \varepsilon_\alpha e^{i\vec{q}_0\cdot\vec{R}_\ell} + \varepsilon_\alpha^* e^{-i\vec{q}_0\cdot\vec{R}_\ell}}$$

$$= e^{-2W}\Big[1 + (\vec{q}\cdot\vec{\varepsilon}_0)^2 e^{i\vec{q}_0\cdot(\vec{R}_\ell + \vec{R}_{\ell'})}$$

$$+ \left(\vec{q}\cdot\vec{\varepsilon}_0^*\right)^2 e^{-i\vec{q}_0\cdot(\vec{R}_\ell + \vec{R}_{\ell'})}$$

$$+ (q\cdot\vec{\varepsilon}_0)\left(\vec{q}\cdot\vec{G}_0^*\right) e^{i\vec{q}_0\cdot(\vec{R}_\ell + \vec{R}_{\ell'})}$$

$$+ \left(\vec{q}\cdot\vec{G}_0^*\right)\left(q\cdot\vec{G}_0\right) e^{-i\vec{q}_0\cdot(\vec{R}_\ell + \vec{R}_{\ell'})} + \ldots\Big]$$

So,

$$S(\vec{q}) = e^{-2W}\Big[\sum_{\ell\ell'} e^{i\vec{q}\cdot(\vec{R}_\ell - \vec{R}_{\ell'})} + (\vec{q}\cdot\vec{\varepsilon}_0)^2$$

$$\sum_{\ell\ell'} e^{i(\vec{q}+\vec{q}_0)\cdot\vec{R}_\ell} e^{-i(\vec{q}-\vec{q}_0)\cdot\vec{R}_{\ell'}} + \ldots$$

$$+ |\vec{q}\cdot\vec{\varepsilon}_0|^2 \sum_{\ell\ell'} e^{i(\vec{q}+\vec{q}_0)\cdot(\vec{R}_\ell - \vec{R}_{\ell'})}$$

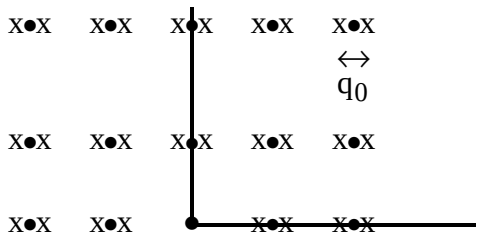
$$+ |\vec{q}\cdot\vec{\varepsilon}_0|^2 \sum_{\ell\ell'} e^{-i(\vec{q}+\vec{q}_0)\cdot(\vec{R}_\ell - \vec{R}_{\ell'})} + \ldots\Big]$$

Bragg Peak satellites

$$S(\vec{q}) = e^{-2W}\frac{(2\pi)^3}{v_0}\Big[\sum_{\vec{G}}\{\delta(\vec{q} - \vec{G}) + |\vec{q}\cdot\vec{\varepsilon}_0|^2 \delta(\vec{q} + \vec{q}_0 - \vec{G})$$

$$+ |\vec{q}\cdot\vec{\varepsilon}_0|^2 \delta(\vec{q} - \vec{q}_0 - \vec{G})\Big]$$

$\Rightarrow$ satellites at $\vec{q} = \vec{G} \pm \vec{q}_0$ and Bragg Peak at $\vec{q} = \vec{G}$



Intensity of peak at $\vec{q} = \vec{G} + \vec{q}_0$ is

$$\boxed{e^{-2W} \frac{(2\pi)^3}{v_0} \left|\vec{q} \cdot \vec{\varepsilon}_0\right|^2}$$

If modulation is due to phonons,

$$\varepsilon_0^2 = \frac{1}{2M} \frac{1}{\omega_{q_0}} \left(2\bar{n}_{q_0} + 1\right) \qquad \bar{n}_{q_0} = \frac{1}{e^{\beta\omega_{q_0} - 1}}$$

$$= \frac{1}{M\omega_{q_0}} \left[\frac{e^{\beta\omega_{q_0}}}{e^{\beta\omega_{q_0} - 1}} \right] \qquad \beta = \frac{1}{kT}$$

For $\beta\omega_{q_0} << 1$, $\varepsilon_0^2 \simeq \dfrac{kT}{M\omega_{q_0}^2} \simeq \dfrac{kT}{Mc^2} \dfrac{1}{q_0^2}$

Alloys, Crystals with Defects (vacancies, impurities, etc.)

$$\frac{d\sigma}{d\Omega} = \left\langle \sum_{\ell\ell'} b_\ell b_{\ell'} e^{-i\vec{q}\cdot\left(\vec{R}_\ell - \vec{R}_{\ell'}\right)} \right\rangle$$

[For neutrons, b_ℓ = (Sc. length of nucleus at site ℓ) $\times e^{-W_\ell}$.
For x-rays, $b_\ell = Zf(q)e^{-W_\ell} r_0$ for atom at site ℓ.]

For 2 types of atoms 1,2 with b_1, b_2

$$\frac{d\sigma}{d\Omega} = \left\langle \sum_{\ell\ell'} \left[b_1 \rho_\ell + b_2(1-\rho_\ell)\right]\left[b_1 \rho_{\ell'} + b_2(1-\rho_{\ell'})\right] \times \left[e^{-i\vec{q}\cdot\left(\vec{R}_\ell - \vec{R}_{\ell'}\right)}\right] \right\rangle$$

where

ρ_ℓ = probability of occupn. by atom 1 on site ℓ.

$\rho_\ell = c + \delta\rho_\ell$

$c = \langle \rho_\ell \rangle$ = Concn. of type 1.

$$\boxed{\frac{d\sigma}{d\Omega} = \left(\bar{b}\right)^2 S_0(\vec{q}) + \sum_{\ell\ell'} (f_1 - f_2)^2 \left\langle \delta\rho_\ell \delta\rho_{\ell'} e^{-i\vec{q}\cdot\left(\vec{R}_\ell - \vec{R}_{\ell'}\right)} \right\rangle}$$

where

$\bar{b} = b_1 c + b_2 (1-c)$ = <u>average</u> b

$$S_0(\vec{q}) = \frac{(2\pi)^3}{v_0} \sum_{\vec{G}} \delta\left(\vec{q} - \vec{G}\right) \quad \text{[Bragg Peaks]}$$

2nd term $\rightarrow$ Diffuse Scattering

If $\delta\rho_\ell, \delta\rho_{\ell'}$ uncorrelated, $\langle \delta\rho_\ell \delta\rho_{\ell'} \ldots \rangle \sim \delta_{\ell\ell'}$

2nd term = $(f_1 - f_2)^2 \left\langle \delta\rho_\ell^2 \right\rangle = \boxed{(f_1 - f_2)^2 c(1-c)}$

Small Angle Scattering $\begin{pmatrix} \textbf{SANS} \\ \textbf{SAXS} \end{pmatrix}$

<u>Length scale</u> probed in a scattering experiment at wave-vector transfer $\vec{q}$ is ~ $\boxed{\left(\frac{2\pi}{q}\right)}$ (e.g., Bragg scattering $d_{hk\ell} \sim \frac{2\pi}{G_{hk\ell}}$)

Thus <u>small</u> $\vec{q}$ scattering probes large length scales, <u>not atomic or molecular</u> structure.

At small q, one can consider "smeared out" nuclear or electron density varying relatively slowly in space.

$$\boxed{I(\vec{q}) \propto \iint d\vec{r} d\vec{r}' e^{-i\vec{q}\cdot\left(\vec{r} - \vec{r}'\right)} \langle \rho_s(\vec{r}) \rho_s(\vec{r}') \rangle}$$

where

$\rho_s(\vec{r})$ = scattering length (average) density for neutrons

= electron density for electrons.

Since uniform $\rho_s(\vec{r})$ would give only forward scattering, we use the deviations (contrast) from the <u>average</u> density

$$\boxed{I(q) \propto \iint d\vec{r}\, d\vec{r}\,' e^{-i\vec{q}\cdot(\vec{r}-\vec{r}\,')} \langle \delta\rho_s(\vec{r}) \delta\rho_s(\vec{r}\,') \rangle}$$

<u>Single Particles (Dilute Limit)</u>

Let ρ_0 be average $s\ell d$ (e.g., embedding media or solvent)

ρ_1 be average $s\ell d$ of particle (assume uniform)

$$\boxed{I(\vec{q}) \propto (\rho_1 - \rho_0)^2 \left| \int_V d\vec{r} e^{-i\vec{q}\cdot\vec{r}} \right|^2 = (\rho_1 - \rho_0)^2 |f(\vec{q})|}$$

where V is over volume of particle, $f(\vec{q})$ is determined by <u>shape</u> of particle, e.g., for sphere of radius R,

$$\boxed{f(q) = (V_0) \frac{\mathrm{Sin}(qR) - qR\,\mathrm{Cos}(qR)}{(qR)^3}}$$

V_0 = Particle Volume

origin of $\vec{r}$ is taken as centroid of particle.

Expanding exponential,

$$\int_V d\vec{r} e^{-i\vec{q}\cdot\vec{r}} = V_0 - i\vec{q}\cdot\cancel{\int_V \vec{r} d\vec{r}} - \frac{1}{2}\int_V d\vec{r} (\vec{q}\cdot\vec{r})^2 + \ldots$$

$$\simeq V_0 \left[1 - \frac{1}{2} \frac{\int_V d\vec{r} (\vec{q}\cdot\vec{r})^2}{\int_V d\vec{r}} + \ldots \right]$$

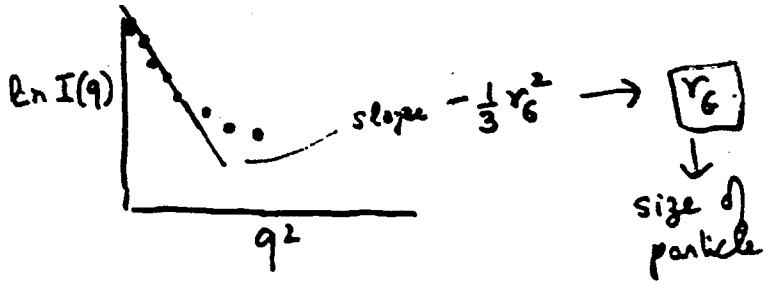
$$= V_0 \left[1 - \frac{q^2}{6} \underbrace{\frac{\int_V d\vec{r}\, r^2}{\int_V d\vec{r}}}_{r_G^2} + \ldots \right]$$

r_G = radius of gyration

so $I(\vec{q}) \propto (\rho_1 - \rho_0)^2 V_0^2 = \left[1 - \frac{1}{3} q^2 r_G^2 + \ldots \right]$ approx.

$$\boxed{I(\vec{q}) \simeq A(\rho_1 - \rho_0)^2 V_0^2 e^{-\frac{1}{3} q^2 r_G^2}}$$

Guinier Approxn.



Small-Angle Scattering Is Used to Study:

- $\left\{\begin{matrix}\text{Sizes}\\ \text{Shapes}\end{matrix}\right\}$ of particles in dilute solution (Polymers, Micelles, Colloids, Proteins, Precipitates, …)
- Correlation between particles in concentrated solutions (Aggregates, Fractals, Colloidal Crystals and Liquids)
- 2-component or multicomponent systems (Binery fluid mixtures, Porous Media, Spinodal Decomposition)

For colliodal, micellar liquids:

$$S(\vec{q}) = \sum_{\ell\ell'} f_\ell(\vec{q}) f_{\ell'}^*(\vec{q}) e^{i\vec{q}\cdot(\vec{R}_\ell - \vec{R}_{\ell'})}$$

Form Factor $= |f_\ell(\vec{q})|^2 S_0(\vec{q})$ Structure Factor

$$S_0(\vec{q}) = \sum_{\ell\ell'} e^{i\vec{q}\cdot(\vec{R}_\ell - \vec{R}_{\ell'})}$$ = S.F. of centers of particles

→ Liquid- or glass-like

Fractals

These are systems which are scale-invarient (usually in a statistically averaged sense) i.e., $R \to \kappa R$, the object resembles itself ("self-similarity")

Property: If $n(R)$ is number of particles inside a sphere of radius R

$$\boxed{n(R) \sim R^D}$$

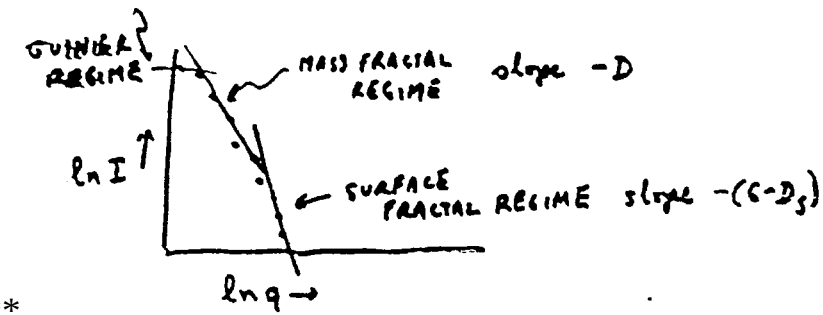
D = Fractal (Hausdorff) Dimension

It follows that

$4\pi R^2 d\,R g(R) = C R^{D-1} dR$ C = constant

$$\therefore g(R) = \frac{C}{4\pi} R^{D-3} = \frac{C}{4\pi}\frac{1}{R^{3-D}}$$

$$\boxed{\therefore S_0(\vec{q}) = \int d\vec{R} e^{-i\vec{q}\cdot\vec{R}} g(R) = \text{Const} \times \frac{1}{q^D}}$$



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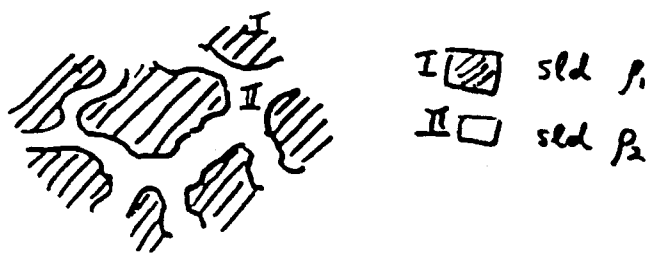
Examples: Aggregates of micelles, colloids, granular materials, rocks*

* Surface fractals $S(q) \sim \dfrac{1}{q^{S-D_S}}$

Porous Media



ϕ_1 = Vol. fraction of I

ϕ_2 = Vol. fraction of II = $1 - \phi_1$

V = Sample Volume

$$I(q) \propto V\phi_1\phi_2(\rho_1 - \rho_2)^2 \iint d\vec{r}\,d\vec{r}\,' e^{-i\vec{q}\cdot(\vec{r}-\vec{r}\,')}\gamma_0(\vec{r}-\vec{r}\,')$$

$\gamma_0(\vec{r})$ = Debye correlation fn.

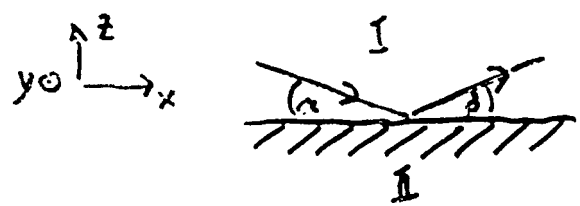
For small R (large q), $\gamma_0(R) \sim 1 - R/\bar{\ell}$

so asymptotically for large q,

$$I(q) \sim \frac{2\pi A_S}{q4} \qquad (A_S = \text{Internal Surface Area})$$

Porod's law for smooth (D_S = 2) surfaces

Reflectivity



$n = 1$

$n = 1 - \delta - i\beta$

For x-rays, neutrons

$$n = 1 - \frac{\rho}{2\pi}\lambda^2 \bar{b}$$

$\bar{b}$ = Av. nucl. scattering length for neutrons

ρ = No. of nuclei/volume for neutrons

$\bar{b} = r_0$ or $\left(e^2 / mc^2\right)$ for x-rays

ρ = No. of Electrons/Volume

Proof (for x-rays)

$$\varepsilon(\omega) = 1 - \frac{\omega_P^2}{\omega^2} \qquad \omega_P = \text{Plasma Frequency}$$

At x-ray frequencies

$$w_P^2 = \frac{4\pi e^2}{m}\rho \qquad \omega = \frac{2\pi c}{\lambda}$$

$$E(\omega) = 1 - \frac{\omega_P^2}{\omega^2} = 1 - \frac{4\pi e^2}{m\omega^2}\rho\frac{\lambda^2}{4\pi^2 e^2} = 1 - \left(\frac{e^2}{mc^2}\right)\left(\frac{\rho\lambda^2}{\pi}\right)$$

$$= 1 - \frac{\rho\lambda^2}{\pi} r_0$$

$$n = \sqrt{E} \simeq 1 - \underbrace{\frac{r_0}{2\pi}\rho\lambda^2}_{\sim 10^{-6}} - \underbrace{i\beta}_{\sim 10^{-8}} \longleftarrow \text{For absorption}$$

<u>Neutrons</u> obey Schrödinger Eqn.

$$-\frac{\hbar^2}{2m}\nabla^2\phi(\vec{r}) + (V - E)\phi(r) = 0$$

$$\text{or } \nabla^2\phi(r) + \frac{2m}{\hbar^2}(E - V)\phi(\vec{r}) = 0$$

$$V = \frac{2\pi\hbar^2}{m}\rho\bar{b} \qquad E = \frac{\hbar^2}{2m}k_0^2$$

$$\therefore \frac{2m}{\hbar^2}(E - V) = k_0^2 - 4\pi\rho b = k_0^2\left(1 - \frac{4\pi\rho\bar{b}}{k_0^2}\right) = k_0^2\underbrace{\left(1 - \frac{\rho\lambda^2\bar{f}}{\pi}\right)}_{n^2}$$

$$= n^2(\vec{r})k_0^2$$

Also wave-eqn. for x-rays ("s" poln.)

$$\phi(\vec{r}) = E_y(\vec{r})$$

$$\boxed{\therefore \nabla^2\phi(\vec{r}) + n^2(\vec{r})k_0^2\phi(\vec{r}) = 0}$$

For single smooth surface $\left[n(\vec{r}) = 1 \text{ in region I} \right.$
$\left. = n \text{ in region II}\right]$

matching boundary conditions

$$\left(\phi \text{ continuous}, \frac{\partial\phi}{\partial z} \text{ continuous at boundary}\right)$$

gives for incident wave $e^{i\vec{k}_i\cdot\vec{r}}$, a reflected wave $re^{i\vec{k}_r\cdot\vec{r}}$, and transmitted wave $te^{i\vec{k}_t\cdot\vec{r}}$

$$(k_i)_y = (k_r)_y = (k_t)_y = 0$$

we have

$$\left.\begin{aligned} (k_i)_x &= (k_r)_x = (k_t)_x \\ (k_r)_z &= -(k_i)_z \end{aligned}\right] \leftarrow \text{specular reflectivity } (\alpha = \beta)$$

$$(k_t)_z = \sqrt{(k_i)_z^2 - k_i^2\left(1 - n^2\right)}$$

$$\boxed{r = \frac{(k_i)_z - (k_t)_z}{(k_i)_z + (k_t)_z} \qquad t = \frac{2(k_i)_z}{(k_i)_z + (k_t)_z}}$$

$R = |r|^2 = R_F$ "Fresnel Theory (smooth flat surface)

If $(k_i)_z^2 < k_i^2\left(1 - n^2\right)$, $(k_t)_z$ is <u>purely imaginary</u>
(evenescent wave in medium II)

$$k_i^2 \operatorname{Sin}^2\alpha < k_i^2\left(1 - n^2\right)$$

or $\operatorname{Sin}^2\alpha < \left(1 - n^2\right) = \dfrac{\rho\lambda^2\bar{b}}{\pi} = \operatorname{Sin}^2\alpha_c$

or $\alpha < \alpha_c \qquad \alpha_c \simeq \lambda\left(\dfrac{\rho\bar{b}}{\pi}\right)^{1/2}$ (critical angle for total external reflection)

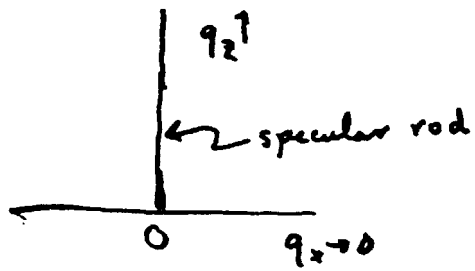
then

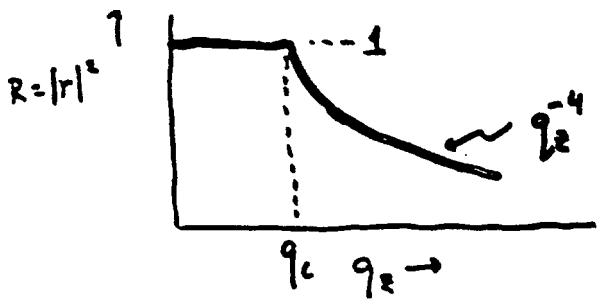
$|r|^2 = 1 \rightarrow$ total external reflection

For reflectivity process,

$$\vec{q} = \vec{k}_r - \vec{k}_i = \left(0, 0, 2(k_i)_z\right)$$

i.e., along q_z only





$$q_c = 2k_i \operatorname{Sin}\alpha_c = \frac{4\pi}{\lambda}\operatorname{Sin}\alpha_c = 4\left(\pi\rho\bar{b}\right)^{1/2}$$

independent of λ

Approximate effect of roughness $\left(\overline{\delta z^2} = \sigma^2\right)$

$$R = R_F e^{-q_z^2\sigma^2} \qquad (q_z >> q_c)$$

Born Approximation for Specular Reflectivity

Suppose nuclear or electron density is fn. of z only.

$$\frac{d\sigma}{d\Omega} = \bar{b}^2\left|\int d\vec{r}\rho(z)e^{-i\vec{q}\cdot\vec{r}}\right|^2$$

$$= \bar{b}^2\left|\iiint dxdydz\rho(z)e^{-i\left(q_x x + q_y y + q_z z\right)}\right|$$

$$= \left(\bar{b}\right)_A^2 4\pi^2\delta(q_x)\delta(q_y)\left|\int_{-\infty}^{\infty} dz\rho(z)e^{-iq_z z}\right|^2$$

A = area of surface

$$R = \frac{\int \frac{d\sigma}{d\Omega} d\Omega\, \Phi}{\Phi\, A_0}$$

A_0 = Cross-section of incident beam

$d\Omega$ = Solid Angle subtened by detector

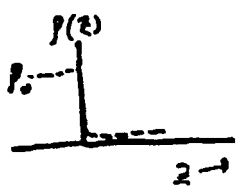
$$d\Omega = \frac{1}{k_i^2 \operatorname{Sin}\alpha} dq_x dq_y \qquad A_0 = A \operatorname{Sin}\alpha$$

$$\text{or } R = \frac{16\pi^2 \bar{b}^2 \rho_0}{q_z^4} \left| \frac{1}{\rho_0} \int_{-\infty}^{\infty} dz \frac{d\rho(z)}{dz} e^{-iq_z z} \right|^2$$

$$\boxed{R \simeq R_F(q_z) \left| \frac{1}{\rho_0} \int_{-\infty}^{\infty} dz \frac{d\rho(z)}{dz} e^{-iq_z z} \right|^2}$$

<u>Simple cases:</u>

$$\rho(z) = \rho_0 \;\; z > 0$$
$$= 0 \;\; z \geq 0$$

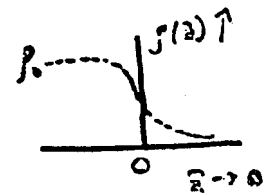


smooth surface

$$\frac{d\rho(z)}{dz} = -\rho_0 \delta(z) \rightarrow \boxed{R = R_F(q_z)}$$

$$\rho(z) = Erf(z/r)$$

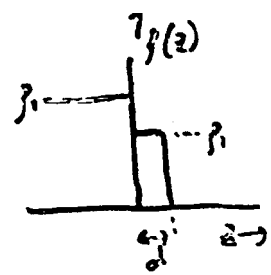
$$\frac{d\rho(z)}{dz} = -\frac{\rho_0}{\sqrt{2\pi\sigma}} e^{-z^2/2\sigma^2}$$



rough surfaces

$$\boxed{R = R_F(q_z) e^{-q_z^2 \sigma^2}}$$

$$\rho(z) = \rho_0 \;\; z < 0$$
$$= \rho_1 \;\; 0 < z < d$$
$$= 0 \;\; z > d$$



smooth thin film

$$\frac{d\rho}{d_z} = -(\rho_0 - \rho_1)\delta(z) - \rho_1 \delta(z - d)$$

$$R = R_F\left(1 - \frac{4\rho_1(\rho_0-\rho_1)}{\rho_0^2}\mathrm{Sin}^2\frac{(q_z d)}{2}\right)$$

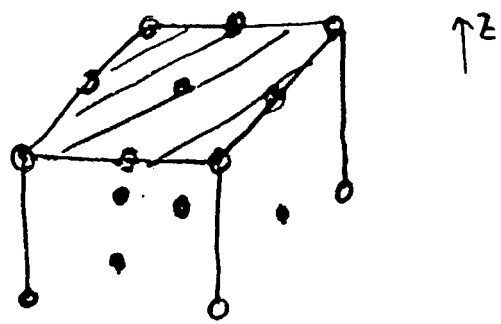
$$S(q) = \left\langle \sum_{\ell\ell'} e^{-i\vec{q}\cdot(\vec{R}_\ell - \vec{R}_{\ell'})} \right\rangle \qquad \delta(q_x - G_x) \qquad \delta(q_y - G_y)$$

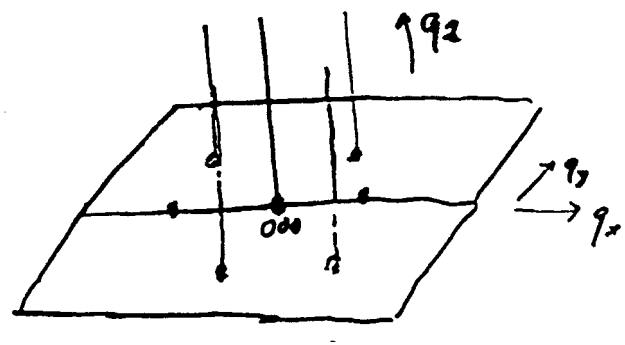
$$= \sum\sum_{n_x, n_{x'} + -\infty}^{\infty} \sum\sum_{n_y, n_{y'} = -\infty}^{\infty} e^{-iq_x(n_x - n'_x)a} e^{-iq_y(n_y - n'_y)a}$$

$$\times \sum_{n_z,}^{0} \sum_{n'_z z = -\infty}^{0} e^{-iq_z(n_z - n'_z)a}$$

$$(q_z - G_z)^{-2}$$

Crystal Truncation rods





Formal Theory of Scattering

Neutrons

ψ_k incident neutron wave fn.

χ_λ initial sample wave fn.

$\psi_{k\phi}$ scattered neutron wave fn.

$\chi_{\lambda'}$ final sample wave fn.

$$\boxed{\left(\frac{d\sigma}{d\Omega}\right)_{\lambda\to\lambda'} = \frac{1}{\Phi}\frac{1}{d\Omega}\sum_{k'}^{d\Omega} W_{\vec{k}\lambda\to\vec{k}'\lambda'}} \qquad (1)$$

$W_{k\lambda\to k'\lambda'}$ = Number of transitions $k\lambda \to k'\lambda'$ per second

Use Fermi's Golden Rule:

$$\boxed{\sum_{k'}^{d\Omega} W_{\vec{k}\lambda\to\vec{k}'\lambda'} = \frac{2\pi}{\hbar} v_{k'} \left|\left\langle \vec{k}'\lambda' \middle| V \middle| \vec{k}\lambda \right\rangle\right|^2} \qquad (2)$$

$v_{k'}$ = Number of neutron momentum states in $d\Omega$ per unit energy range at $\vec{k}'$.

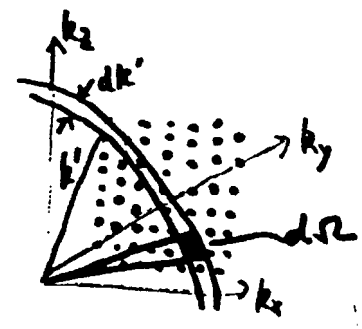
V = Interaction potential of neutron with the sample.

$$H = H_{neutrons}\left(\frac{P_N^2}{2m_N}\right) + H_{sample} + V$$

Quantize states in box of side L with periodic boundary conditions:

$$\vec{k} = \frac{2\pi}{L}\left(n_x, n_y, n_z\right)$$

Density of k-pts / unit vol. of k-space = $\dfrac{L^3}{(2\pi)^3}$



$$E' = \frac{\hbar^2}{2m}k'^2$$

$$dE' = \frac{\hbar^2}{m}k'dk$$

Now $v_{k'}dE'$ = Number of k-pts inside $d\Omega$ with energy between E', and $E' + dE'$

$$= (k')^2 dk' d\Omega \frac{L^3}{(2\pi)^3}$$

$$\therefore v_{k'} = \frac{L^3}{(2\pi)^3}\frac{m}{\hbar^2}k'd\Omega$$

Incident neutron wave fn. $\psi_k = L^{-3/2} e^{i\vec{k}\cdot\vec{r}}$

Incident flux $\Phi = v|\psi_k|^2 = \frac{\hbar}{m} k \frac{1}{L^3}$

Thus, by Eqs. (1), (2),

$$\boxed{\left(\frac{d\sigma}{d\Omega}\right)_{\lambda\to\lambda'} = \frac{k'}{k}\left(\frac{m}{2\pi\hbar^2}\right)^2 L^6 \left|\langle \vec{k}'\lambda'|V|\vec{k}\lambda\rangle\right|^2} \qquad (3)$$

Use energy conservation law,

$$\boxed{\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{\lambda\to\lambda'} = \frac{k'}{k}\left(\frac{m}{2\pi\hbar^2}\right)^2 \left|\langle k'\lambda'|V|k\lambda\rangle\right|^2 L^6 \, \delta(E_\lambda - E_{\lambda'} + E - E')} \qquad (4)$$

Formally represent interaction between neutron and nucleus by a delta-fn. (Fermi pseudopotential)

$$V(r_n - R_i) = a\,\delta(\vec{r}_n - \vec{R}_i)$$

Consider elastic scattering again from a single fixed nucleus:

Elastic $\begin{matrix} k' = k \\ \lambda' = \lambda \end{matrix} \langle k'\lambda'|V|k\lambda\rangle = a$

(3) gives $\frac{d\sigma}{d\Omega} = \left(\frac{m}{2\pi\hbar^2}\right)^2 a^2$

Comparing this with the result $\frac{d\sigma}{d\Omega} = b^2$

$$\boxed{a = \left(\frac{2\pi\hbar^2}{m}\right) b}$$

Thus $V(r) = \left(\frac{2\pi\hbar^2}{m}\right) b\,\delta(\vec{r})$ is the <u>effective</u> interaction between a neutron at $\vec{r}$ and a fixed nucleus at the origin.

Scattering by an assembly of nuclei:

$$V(\dot{r}) = \left(\frac{2\pi\hbar^2}{m}\right)\sum_{j=1}^{N} b_j\,\delta\left(\vec{r} - \vec{R}_j\right) \text{ for neutron at } \vec{r}\,.$$

$$\boxed{\begin{aligned}\left\langle k'\lambda'\middle|V\middle|\vec{k}\lambda\right\rangle &= \frac{1}{L^3}\int d\vec{r}\,e^{-i\left(\vec{k}'-\vec{k}\right)\cdot\vec{r}}\int\ldots\iint dR_1\ldots dR_N \\ &\qquad \chi^*_{\lambda'}\chi_\lambda\sum_{j=1}^{N} b_j\,\delta\left(\vec{r}-\vec{R}_j\right)\times\left(\frac{2\pi\hbar^2}{m}\right) \\ &= \frac{1}{L^3}\left(\frac{2\pi\hbar^2}{m}\right)\sum_{j=1}^{N} b_j\left\langle\lambda'\middle|e^{-i\vec{q}\cdot\vec{R}_j}\middle|\lambda\right\rangle\end{aligned}}$$

Thus from Eq. (4)

$$\boxed{\begin{aligned}\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{\lambda\to\lambda'} &= \frac{k'}{k}\sum_{i,j=1}^{N} b_i b_j\left[\left\langle\lambda\middle|e^{-i\vec{q}\cdot\vec{R}_i}\middle|\lambda'\right\rangle\right. \\ &\qquad \left.\left\langle\lambda'\middle|e^{i\vec{q}\cdot\vec{R}_j}\middle|\lambda\right\rangle\right] \\ &\qquad \delta\left(E_\lambda - E_{\lambda'} + \hbar\omega\right)\end{aligned}} \qquad (5)$$

where

$\hbar w = E - E'$ = Neutron energy loss

Summing over all possible final states λ' of the sample and <u>averaging</u> over all initial states λ, we obtain

$$\left(\frac{d^2\sigma}{d\Omega dE'}\right) = \frac{k'}{k}\sum_{ij} b_i b_j \sum_{\lambda\lambda'} P_\lambda\left\langle\lambda\middle|e^{-i\vec{q}\cdot\vec{R}_i}\middle|\lambda'\right\rangle\left\langle\lambda'\middle|e^{i\vec{q}\cdot\vec{R}_j}\middle|\lambda\right\rangle$$

$$\delta\left(E_\lambda - E_{\lambda'} + \hbar\omega\right)$$

$$P_\lambda = Z^{-1}e^{-E_\lambda/kT} \qquad Z = \sum_\lambda e^{-E_\lambda/kT}$$

b_i depends on nucleus (isotope, spin relative to neutron $\uparrow\uparrow$ or $\downarrow\downarrow$), etc. Even for a monatomic system

$$b_i = \langle b\rangle + \delta b_i \leftarrow \text{random sample}$$

$$b_i b_j = \langle b\rangle^2 + \langle b\rangle\left[\underbrace{\delta b_i + \delta b_j}_{\text{zero}}\right] + \underbrace{\delta b_i\,\delta b_j}_{\text{zero unless } i = j}$$

$$\left\langle\delta b_i^2\right\rangle = \left\langle b^2\right\rangle - \langle b\rangle^2$$

$$\text{So } \left(\frac{d^2\sigma}{d\Omega dE'}\right) = \left(\frac{d^2\sigma}{d\Omega dE'}\right)_{\text{coh}} + \left(\frac{d^2\sigma}{d\Omega dE'}\right)_{\text{inc}}$$

$$\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{\text{coh}} = \underbrace{\frac{k'}{k}\langle b\rangle^2}_{\sigma_{\text{coh}}/4\pi} \sum_{\lambda\lambda'} P_\lambda \left\langle \lambda \left| \sum_i e^{-i\vec{q}\cdot\vec{R}_i} \right| \lambda' \right\rangle \left\langle \lambda' \left| \sum_j e^{i\vec{q}\cdot\vec{R}_j} \right| \lambda \right\rangle \delta\left(E_\lambda - E_{\lambda'} + \hbar\omega\right)$$

$$\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{\text{inc}} = \underbrace{\frac{k'}{k}\left[\left\langle b^2\right\rangle - \langle b\rangle^2\right]}_{\sigma_{\text{inc}}/4\pi} \sum_{\lambda\lambda'} P_\lambda \sum_i \left\langle \lambda \left| e^{-i\vec{q}\cdot\vec{R}_i} \right| \lambda' \right\rangle \times \left\langle \lambda' \left| e^{i\vec{q}\cdot\vec{R}_i} \right| \lambda \right\rangle \times \delta\left(E_\lambda - E_{\lambda'} + \hbar\omega\right)$$

Write it as

$$\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{\text{coh}} = \frac{k'}{k}\frac{\sigma_{\text{coh}}}{4\pi} N S_{\text{coh}}(\vec{q},\omega)$$

$$\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{\text{inc}} = \frac{k'}{k}\frac{\sigma_{\text{inc}}}{4\pi} N S_{\text{inc}}(\vec{q},\omega)$$

$$\boxed{\begin{aligned} S_{\text{coh}}(\vec{q},\omega) &= \frac{1}{N}\sum_{\lambda\lambda'} P_\lambda \left\langle \lambda \left| \sum_i e^{-i\vec{q}\cdot\vec{R}_i} \right| \lambda' \right\rangle \left\langle \lambda' \left| \sum_j e^{i\vec{q}\cdot\vec{R}_j} \right| \lambda \right\rangle \delta\left(E_\lambda - E_{\lambda'} + \hbar\omega\right) \\ S_{\text{inc}}(\vec{q},\omega) &= \frac{1}{N}\sum_{\lambda\lambda'} P_\lambda \sum_i \left\langle \lambda \left| e^{-i\vec{q}\cdot\vec{R}_i} \right| \lambda' \right\rangle \left\langle \lambda' \left| e^{i\vec{q}\cdot\vec{R}_i} \right| \lambda \right\rangle \delta\left(E_\lambda - E_{\lambda'} + \hbar\omega\right) \end{aligned}} \quad (6)$$

Heisenberg Time-Dependent Operators

If A is any operator, and H is the system Hamiltonian

$$A(t) = e^{iHt/\hbar} A e^{-iHt/\hbar}$$

is the corresponding time-dependent Heisenberg operator.

$A(0) = A$.

Write $\delta(E_\lambda - E_{\lambda'} + \hbar\omega) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dt\, e^{-i\omega t} e^{i(E_{\lambda'} - E_\lambda)t/\hbar}$

Then

$$\sum_{\lambda'} \langle\lambda|A|\lambda'\rangle \langle\lambda'|B|\lambda\rangle\, \delta(E_\lambda - E_{\lambda'} + \hbar\omega)$$

$$= \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dt\, e^{-i\omega t} \sum_{\lambda'} \langle\lambda|A|\lambda'\rangle \langle\lambda'|B|\lambda\rangle e^{i(E_{\lambda'} - E_\lambda)t/\hbar}$$

$$\left[e^{-iHt/\hbar}|\lambda\rangle = e^{-iE_\lambda t/\hbar}|\lambda\rangle \right]$$

$$= \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dt\, e^{-i\omega t} \sum_{\lambda'} \langle\lambda|A|\lambda'\rangle \langle\lambda'|B|\lambda\rangle$$

$$= \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dt\, e^{-i\omega t} \langle\lambda|A(0)B(t)|\lambda\rangle$$

$$\sum_{\lambda} P_\lambda \langle\lambda|A(0)B(t)|\lambda\rangle \equiv \langle A(0)B(t)\rangle$$ ← T.D. Correlation function

Thus, by (6),

$$S_{\text{coh}}(\vec{q},\omega)=\frac{1}{N}\frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}dt\,e^{-i\omega t}\sum_{\lambda}P_{\lambda}\left\langle\lambda\left|\sum_{i}e^{-i\vec{q}\cdot\vec{R}_i(0)}\right.\right.$$

$$\left.\left.\times\sum_{j}e^{i\vec{q}\cdot\vec{R}_j(t)}\right|\lambda\right\rangle$$

$$=\frac{1}{N}\frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}dt\,e^{-i\omega t}\left\langle\sum_{ij}e^{-i\vec{q}\cdot\vec{R}_i(0)}e^{i\vec{q}\cdot\vec{R}_j(t)}\right\rangle$$

$$S_{\text{inc}}(\vec{q},\omega)=\frac{1}{N}\frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}dt\,e^{-i\omega t}\sum_{i}P_{\lambda}\left\langle\lambda\left|e^{-i\vec{q}\cdot\vec{R}_i(0)}e^{i\vec{q}\cdot\vec{R}_i(t)}\right|\lambda\right\rangle$$

$$=\frac{1}{N}\frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}dt\,e^{-i\omega t}\left\langle\sum_{i}e^{-i\vec{q}\cdot\vec{R}_i(0)}e^{i\vec{q}\cdot\vec{R}_i(t)}\right\rangle$$

Let $\rho_N(\vec{r})$ be density fn. of nuclei,

$$\rho_N(\vec{r})=\sum_{i}\delta(\vec{r}-\vec{R}_i)$$

It's Fourier Transform

$$\rho_N(\vec{q})=\int d\vec{r}\,e^{-i\vec{q}\cdot\vec{r}}=\sum_{i}e^{-i\vec{q}\cdot\vec{R}_i}$$

Thus,

$$S_{\text{coh}}(\vec{q}\cdot\omega)=\frac{1}{N}\frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}dt\,e^{-i\omega t}\left\langle\rho_N(\vec{q},0)\rho_N^{+}(\vec{q},t)\right\rangle \qquad (7)$$

$$\left\langle\rho_N(\vec{q},0)\rho_N^{+}(\vec{q},t)\right\rangle=\int d\vec{r}\,e^{-i\vec{q}\cdot\vec{r}}G(\vec{r},t)$$

$$G(\vec{r},t)=\sum_{ij}\int d\vec{r}\,'\left\langle\delta(\vec{r}-\vec{r}\,'-\vec{R}_i(0))\delta(\vec{r}\,'+\vec{R}_j(t))\right\rangle$$

$$\Downarrow$$

Van-Hove space-time correlation function of system

$$\boxed{S_{\text{coh}}(\vec{q},\omega)=\frac{1}{N}\frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}dt\,e^{-i\omega t}\int d\vec{r}\,e^{-i\vec{q}\cdot\vec{r}}G(\vec{r},t)} \qquad (8)$$

NOTE: $R_i(0)$, $R_j(t)$ are not <u>commuting</u> operators in general, so care must be exercised!

X-rays

$$H = \frac{1}{2m}\sum_i \left(\vec{P}_i + \frac{e}{c}\vec{A}(\vec{r})\delta(\vec{r}-\vec{r}_i)\right)\cdot\left(\vec{P}_i + \frac{e}{c}\vec{A}(r)\delta(\vec{r}-\vec{r}_i)\right)$$

$$+ \sum_i V(r_i) + V_{\text{int}}^{e-e}$$

(P_i = electron momentum,
$\vec{A}$ = vector potential

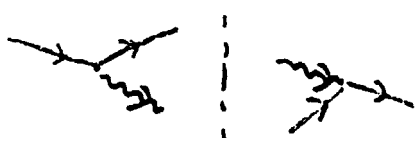
$$= \frac{1}{2m}\sum_i \left(P_i^2 + V(r_i)\right) + V_{\text{int}}^{e-e} \leftarrow H_{e\ell}$$

$$+ \frac{e}{2mc}\sum_i \left\{\vec{P}_i\cdot\vec{A}(\vec{r})\delta(\vec{r}-\vec{r}_i) + \vec{A}(\vec{r})\delta(r-r_i)\cdot\vec{P}_i\right\}$$

$$H_{\text{int}}^{(1)}$$

$$+ \frac{e^2}{2mc^2}\sum_i \delta(\vec{r}-\vec{r}_i)\vec{A}(\vec{r})\cdot\vec{A}(\vec{r}) \leftarrow H_{\text{int}}^{(2)} \qquad (9)$$

$$\vec{A}(\vec{r}) = \sum_{\vec{k},\alpha}\left(\frac{\hbar}{\omega_k}\right)^{1/2} c\left\{\vec{\varepsilon}_\alpha a_{\vec{k},\alpha}^{+} e^{i\vec{k}\cdot\vec{r}} + \vec{\varepsilon}_\alpha^{*} a_{\vec{k},\alpha} e^{-i\vec{k}\cdot\vec{r}}\right\} \qquad (10)$$

$H_{\text{int}}^{(1)} \rightarrow$ 

In 1st order → 1-photon absorption, emission

In 2nd order → scattering

$H_{\text{int}}^{(2)} \rightarrow$

In 1st order → scattering

Using $H_{\text{int}}^{(2)}$,

$$\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{\substack{\vec{k}\alpha\to\vec{k}'\beta \\ \lambda\to\lambda'}} = \left(\frac{e^2}{mc^2}\right)^2 \left|\vec{\varepsilon}_\alpha\cdot\vec{\varepsilon}_\beta^{*}\right|^2 \left\langle\lambda\left|\sum_i e^{-i\vec{q}\cdot\vec{r}_i}\right|\lambda'\right\rangle \qquad (11)$$

$$\left\langle\lambda'\left|\sum_j e^{i\vec{q}\cdot\vec{r}_j}\right|\lambda\right\rangle$$

"Thomson" Scattering

$$\delta(E_\lambda - E_{\lambda'} + \hbar\omega)$$

$$\left(\frac{d^2\sigma}{d\Omega dE'}\right) = \left(\frac{e^2}{mc^2}\right)^2 S_{e\ell}(\vec{q},\omega)\left|\vec{\varepsilon}_\alpha\cdot\vec{\varepsilon}_\beta^{*}\right|^2$$

$$S_{e\ell}(\vec{q},\omega) = \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} dt\, e^{-i\omega t}\left\langle \rho_{e\ell}(\vec{q},0)\rho_{e\ell}^{+}(\vec{q},t)\right\rangle \qquad (12)$$

Elastic Scattering: $\omega = 0 \rightarrow$ "Infinite time average."

Often what we measure is $\int \frac{d^2\sigma}{d\Omega dE'} dE' = \frac{d\sigma}{d\Omega}$

$$\left(\frac{d\sigma}{d\Omega}\right)_{\text{coh}} = \frac{\hbar}{2\pi\hbar}\int d\omega e^{-i\omega t}\int_{-\infty}^{\infty} dt \left\langle \rho(\vec{q},0)\rho^{+}(\vec{q},t)\right\rangle$$

$$\begin{cases} \times \frac{k'}{k}\langle b\rangle^2 \rightarrow \text{neutrons} \\ \times\left(\frac{e^2}{mc^2}\right)^2 \left|\vec{\varepsilon}_\alpha \cdot \vec{\varepsilon}_\beta^{\,*}\right|^2 \rightarrow \text{x–rays} \end{cases} \qquad (13)$$

$$\int d\omega e^{-i\omega t} = 2\pi\delta(t)$$

$$\left(\frac{d\sigma}{d\Omega}\right)_{wh} = S(\vec{q})\begin{cases} \times\langle b\rangle^2 \rightarrow \text{neutrons} \\ \times\left(\frac{e^2}{mc^2}\right)\left|\vec{\varepsilon}_\alpha \cdot \vec{\varepsilon}_\beta^{\,*}\right|^2 \rightarrow \text{x–rays} \end{cases} \qquad (14)$$

$$S(q) = \left\langle \rho(q,0)\rho^{+}(q,0)\right\rangle \equiv \left\langle \rho(q)\rho^{+}(q)\right\rangle$$

(Equal-Time Correlation Function)