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

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

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

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

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

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

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

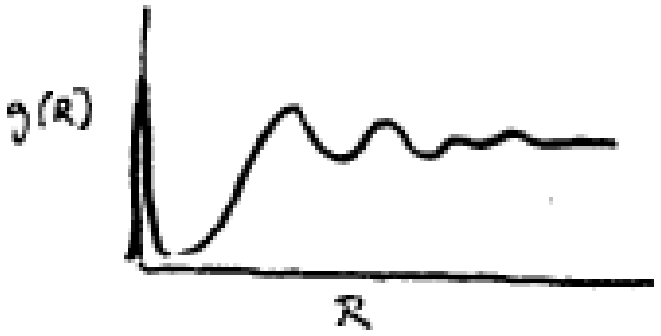
$g(\vec{R})$ = Pair-distribution function

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

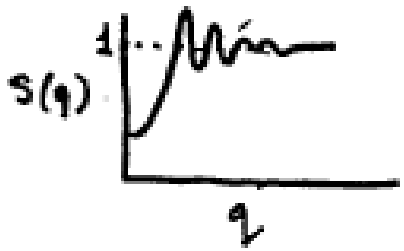
$\Rightarrow$ Probability that given a particle at $\vec{r}$, there is distance $\vec{R}$ from it (per unit volume)

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

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



Liquids and Glasses



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

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

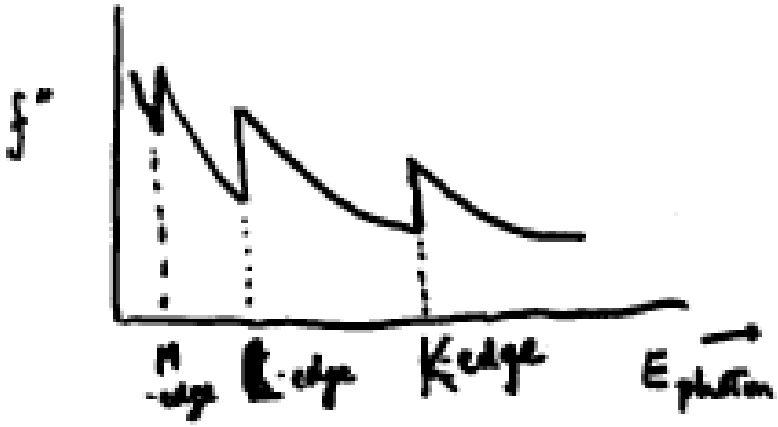
$$= 4\pi \int_0^\infty dq\, q^2 \frac{\mathrm{Sin}(qR)}{(qR)} [S(q) - 1]$$

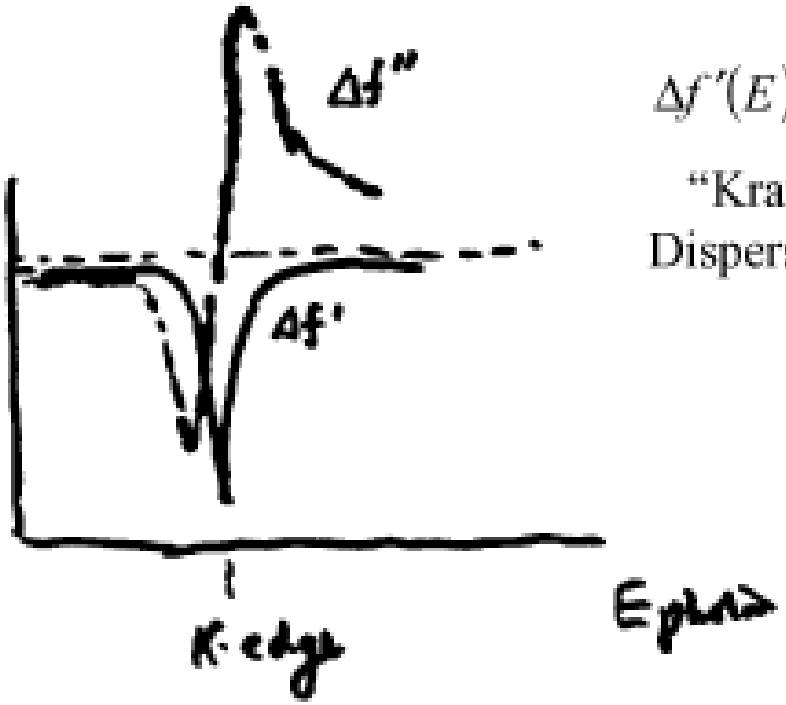
X-rays

$$f = f_0 + \Delta f' + i\Delta f''$$

"Scattering factor" $= Zf(q)$

"anomalous" big at edges





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

"Kramers-Kronig Dispersion Relations

$$S(q) = \left\langle |\rho_N(\bar{q})|^2 \right\rangle \qquad \left[\times |f(q)|^2 \right] \text{for x-rays} \quad *Z^2$$

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

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

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

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

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

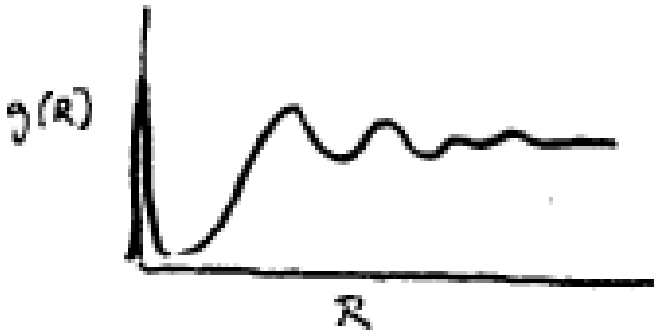
$g(\bar{R})$ = Pair-distribution function

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

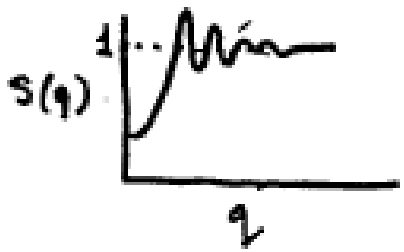
$\Rightarrow$ Probability that given a particle at $\bar{r}$, there is distance $\bar{R}$ from it (per unit volume)

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

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



Liquids and Glasses



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

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

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

S(Q) and g(r) for Simple Liquids

- Note that S(Q) and g(r)/ρ both tend to unity at large values of their arguments
- The peaks in g(r) represent atoms in "coordination shells"
- g(r) is expected to be zero for r < particle diameter – ripples are truncation errors from Fourier transform of S(Q)

Fig. 5.1 The structure factor $S(\kappa)$ for ^{36}Ar at 85 K. The curve through the experimental points is obtained from a molecular dynamics calculation of Verlet based on a Lennard-Jones potential. (After Yarnell *et al.*, 1973.)

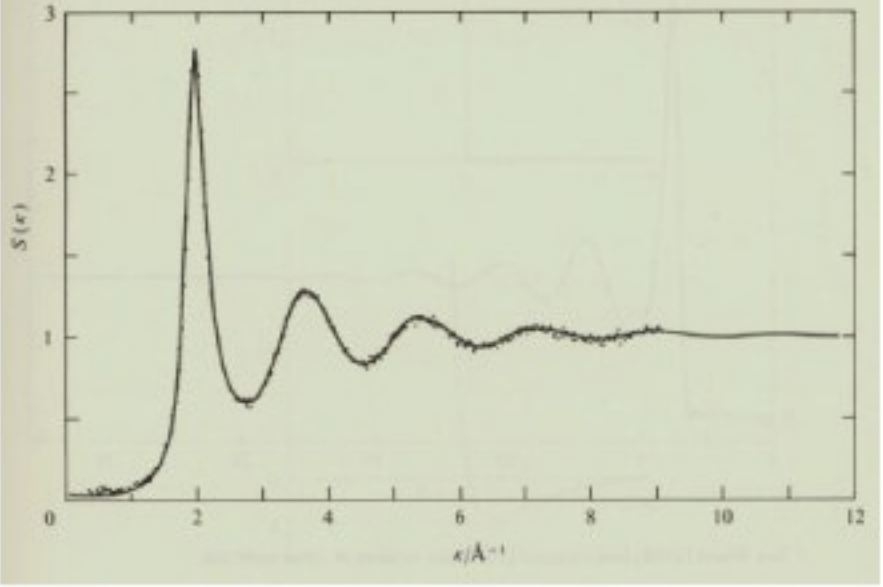
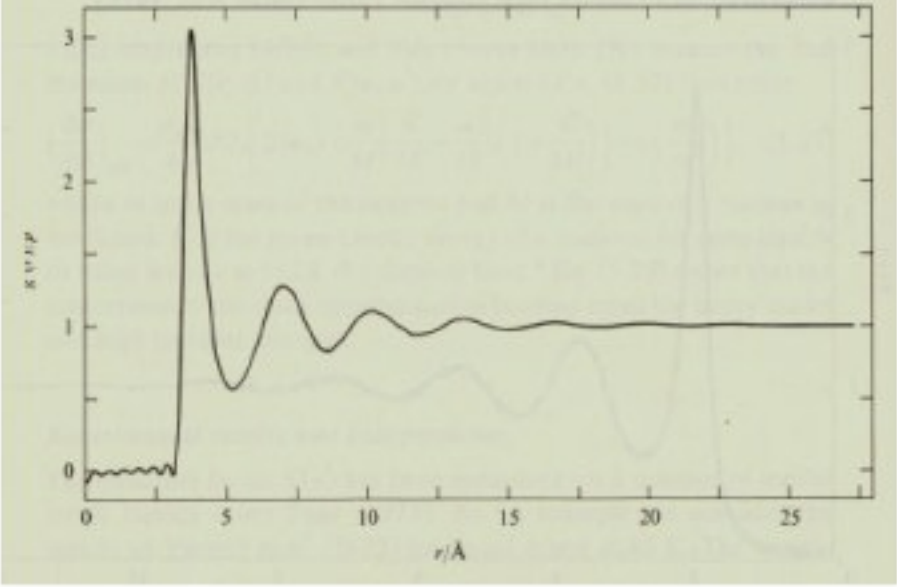


Fig. 5.2 The pair-distribution function $g(r)$ obtained from the experimental results in Fig. 5.1. The mean number density is $\rho = 2.13 \times 10^{28}$ atoms m^{-3}. (After Yarnell *et al.*, 1973.)



Neutrons

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

X-rays

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

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

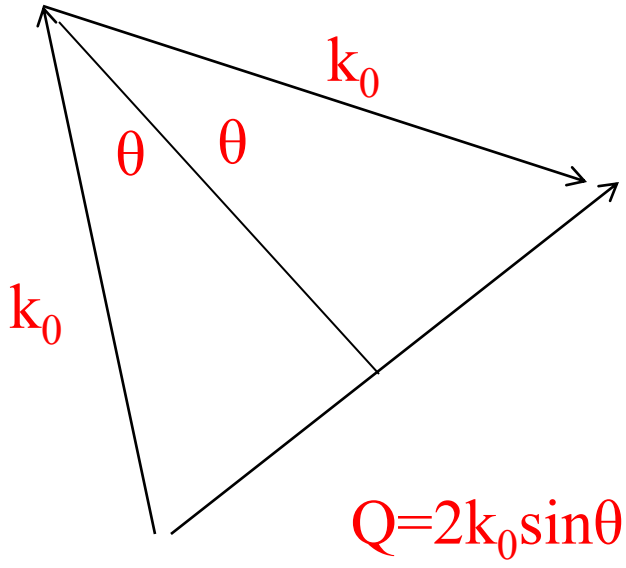
More than one type of atom

(K,K' = Different atomic types)

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

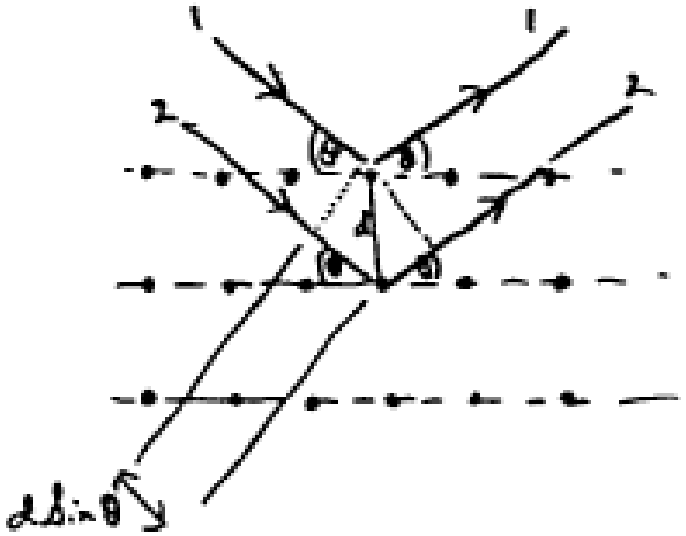
$\Rightarrow$ partial structure factor

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


k_0
θ
θ
k_0
$Q=2k_0\sin\theta$

In general, in a scattering experiment

$$|\vec{q}| = 2k \sin\theta = \frac{4\pi}{\lambda}\sin\theta$$

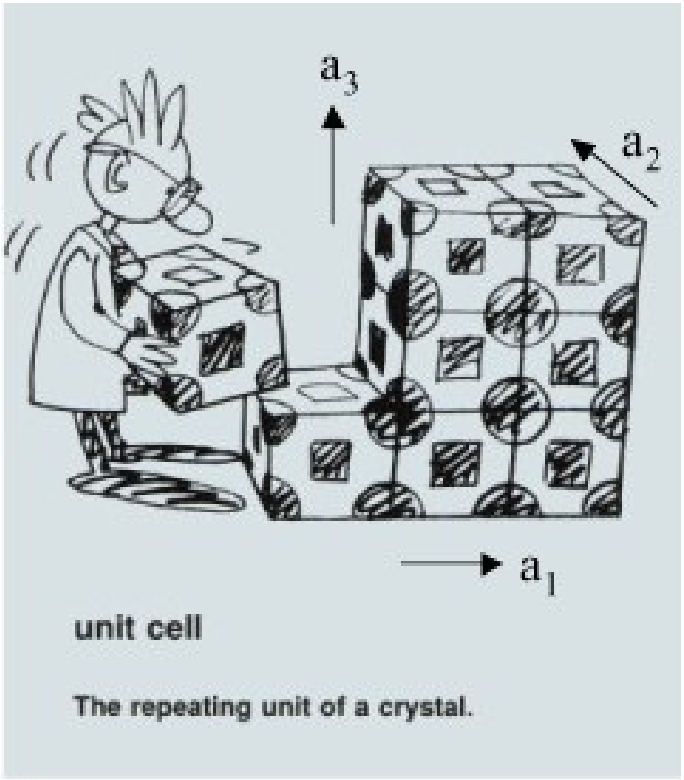


A simple way to see Bragg's Law:

Path length difference between rays reflected from successive planes (1 and 2) = $2d \sin\theta$

$\therefore$ Constructive interference when

$$n\lambda = 2d \sin\theta$$



Define 3 other vectors:

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

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

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

$v_0 = \bar{a}_1 \cdot (\bar{a}_2 \times \bar{a}_3)$ = unit cell vol.

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

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

$$\bar{G} = n_1\bar{b}_1 + n_2\bar{b}_2 + n_3\bar{b}_3$$

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

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

Reciprocal Lattice

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

$\bar{a}_1, \bar{a}_2, \bar{a}_3 \rightarrow$ primitive translation vectors of unit ce

S.K. Sinha

OR

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

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:

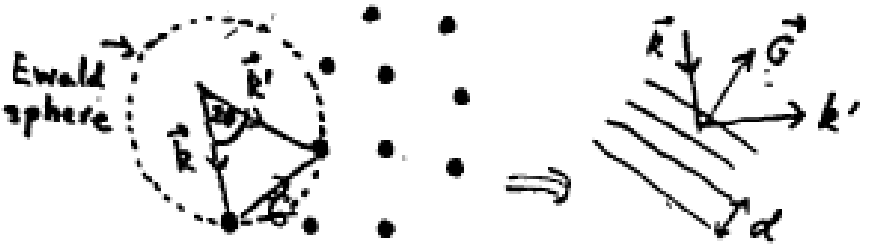
$$e^{-i\vec{G}\cdot\vec{R}_\ell} = e^{in\cdot 2\pi} = 1]$$

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

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

Similarly,

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

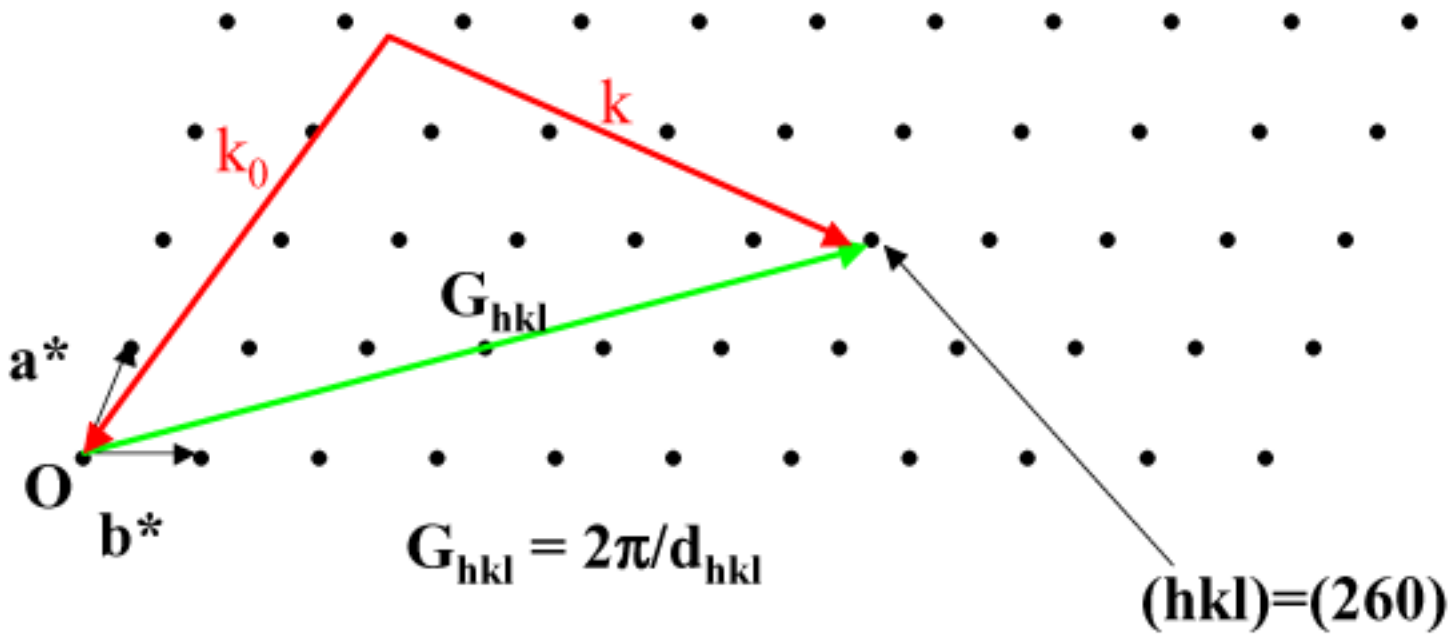


Bragg Reflections: $\vec{k}' - \vec{k} = \vec{G}$

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

$$n\lambda = 2d\,\mathrm{Sin}\theta$$ Bragg's Law

Reciprocal Space – An Array of Points (hkl) that is Precisely Related to the Crystal Lattice



$a^* = 2\pi(b \times c)/V_0$, etc.

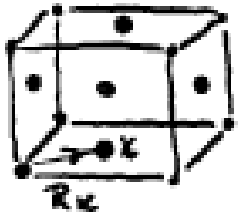
A single crystal has to be aligned precisely to record Bragg scattering

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

Generalization

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

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



$$= \left| \sum_K b_K e^{-i\bar{q}\cdot\bar{R}_K} e^{-2W_K} \right|^2 \sum_{\ell\ell'} e^{-i\bar{q}\cdot(R_\ell - R_{\ell'})}$$

F (structure factor)

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

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

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

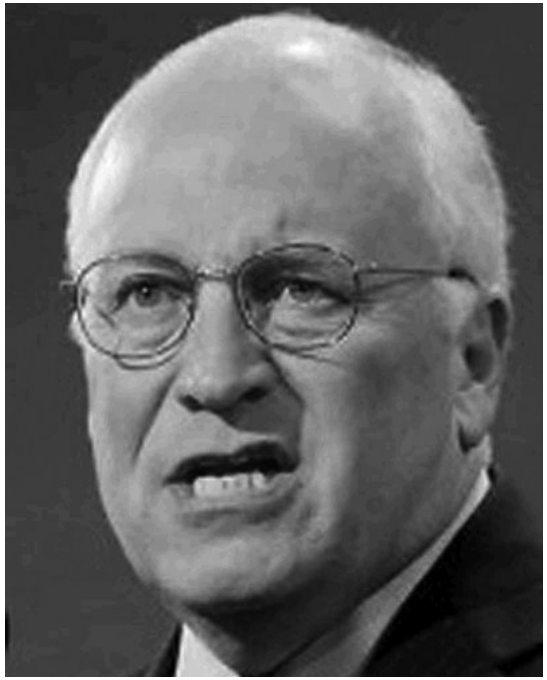
BUT what is measured is $|F_G|^2$ **NOT** F_G!

→ "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 pairs of atoms

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

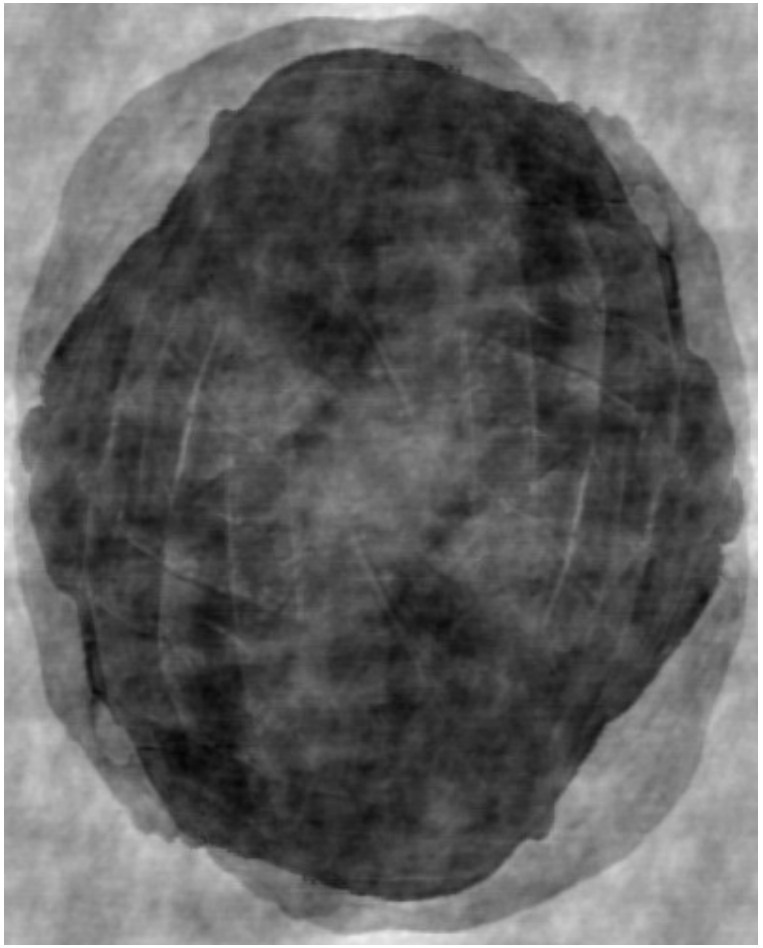


The “Phase Problem”

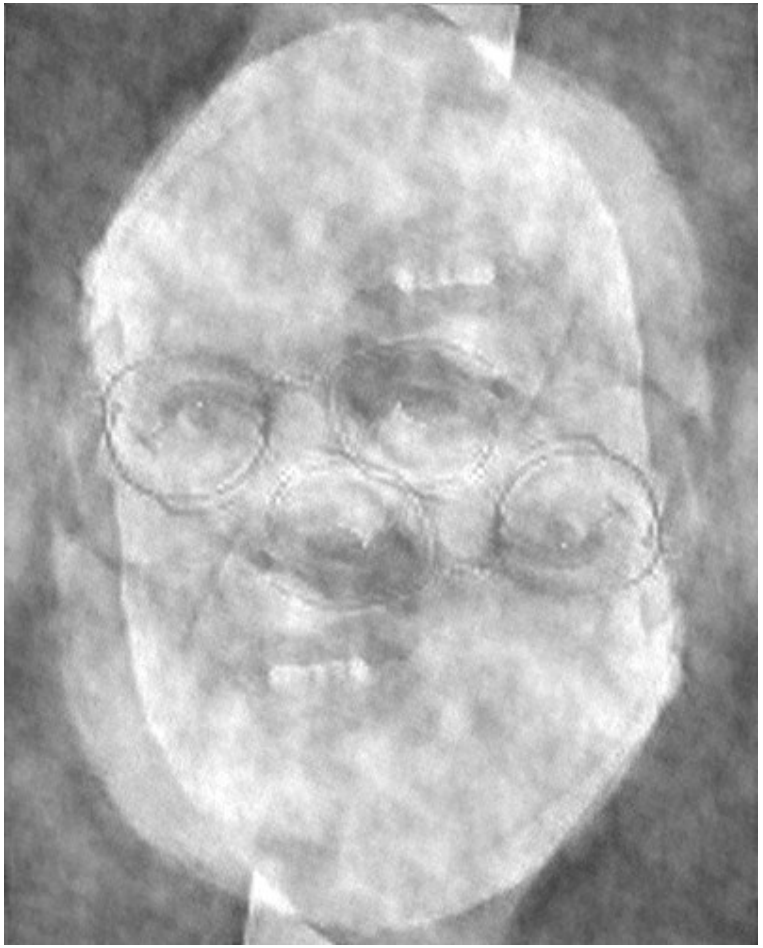
Object
A

Object
B

Fourier Reconstruction with phases of object A and phases of Object B

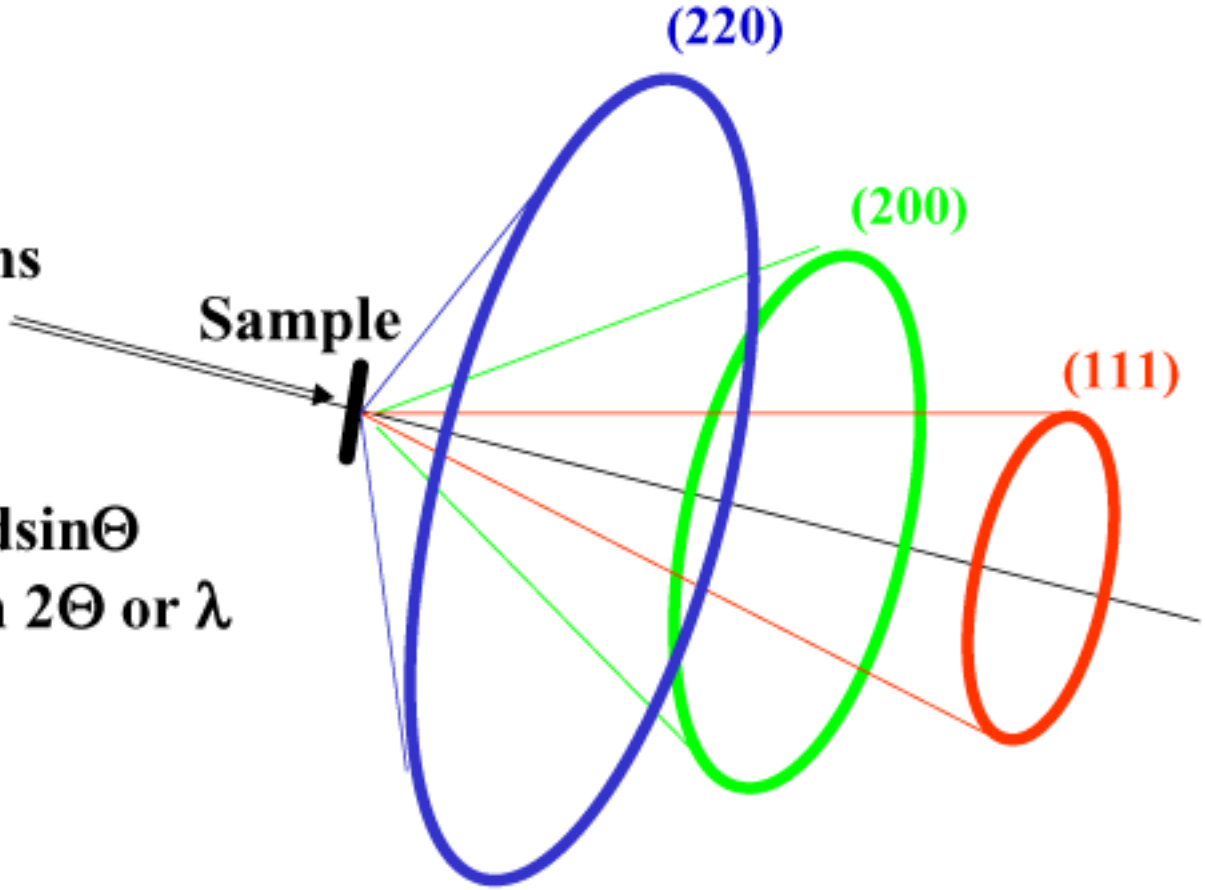


Fourier Reconstruction with phases of object B and phases of Object A



Powder Diffraction gives Scattering on Debye-Scherrer Cones

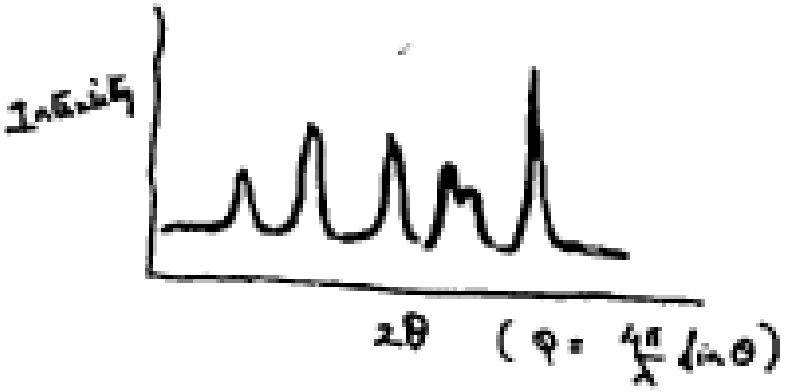
Incident beam
x-rays or neutrons



Bragg's Law $\lambda = 2d\sin\Theta$

Powder pattern – scan 2Θ or λ

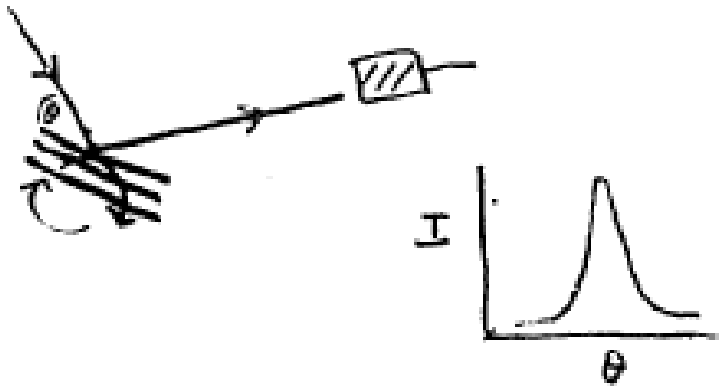
For a given $\vec{k}$, $\vec{k}'$ will lie on a cone (Debye-Scherrer cone) traced out by a $\vec{G}$ on the Ewald sphere as it is oriented randomly about the origin of reciprocal space.



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 $|F_{hk\ell}|^2 \neq 0$)

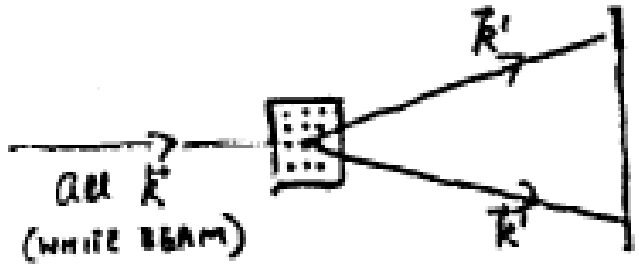
B. Single Crystal Bragg Methods



Integrated Intensity under Bragg Peak

$$I_{hk\ell} = \phi \frac{V}{\nu_0^2} \frac{\lambda^3}{\mathrm{Sin}(2\theta)} |F_{hk\ell}|^2$$

C. Laue Method

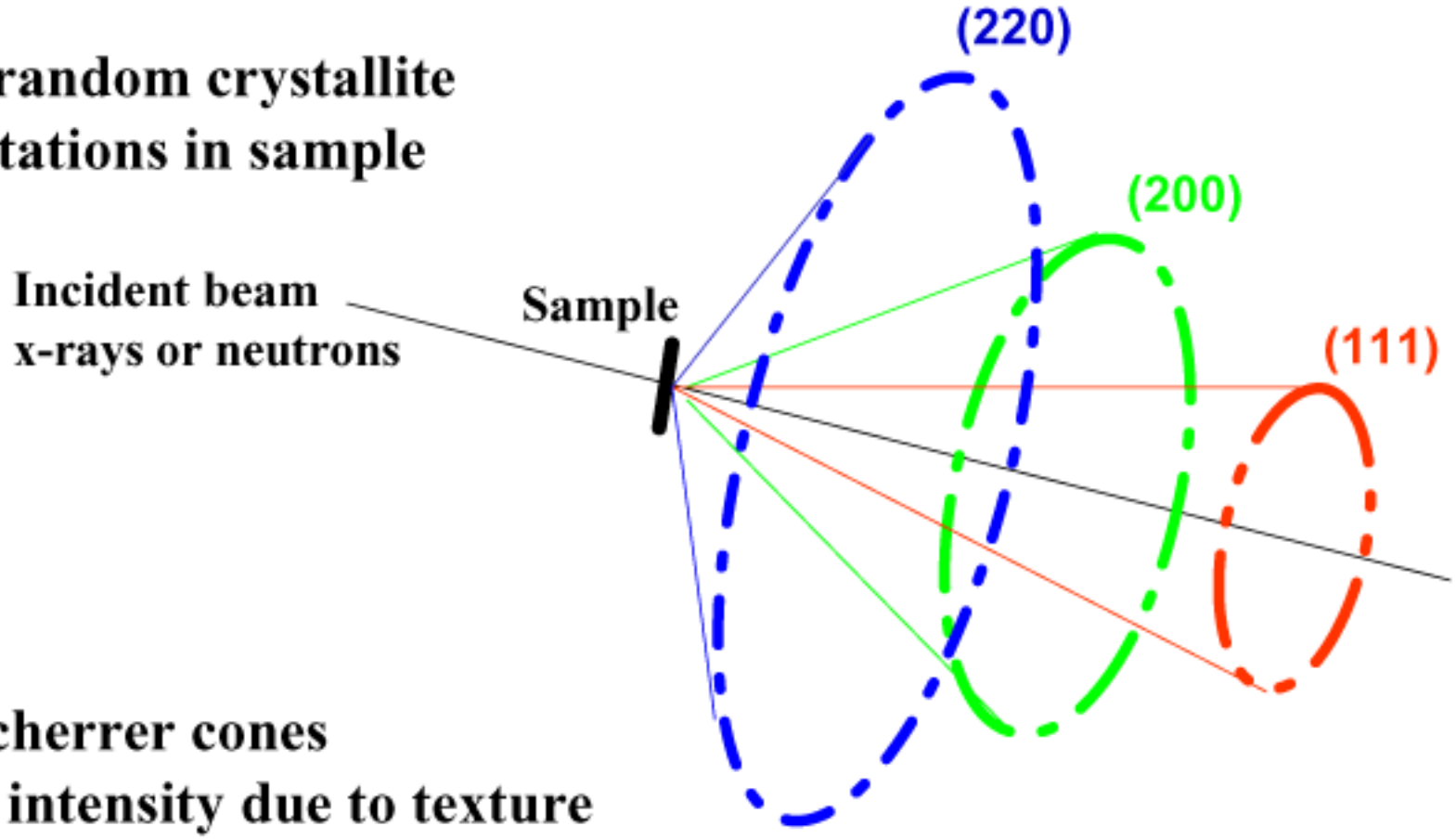


$$I_{hk\ell} - \phi(\lambda) \frac{V}{\nu_0^2} \frac{\lambda^4}{2\mathrm{Sin}^2\theta} |F_{hk\ell}|^2$$

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

Texture Measurement by Diffraction

Non-random crystallite orientations in sample



Debye-Scherrer cones

- **uneven intensity due to texture**
- **different pattern of unevenness for different hkl's**
- **intensity pattern changes as sample is turned**

2-D Crystals (Adsorbed Monolayers, Films)

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

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

which is thus independent of q_z.

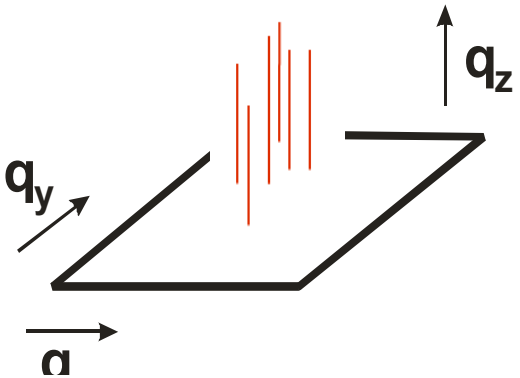
$$S(q) \propto \sum_{G_\parallel} \delta(\bar{q}_\parallel - \bar{G}_\parallel)$$

where

$\bar{G}_\parallel$ is 2-D reciprocal lattice vector in plane

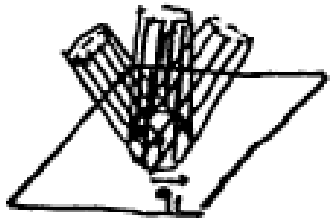
$\bar{q}_\parallel$ is (x,y) plane component of $\bar{q}$

$\Rightarrow$ diffraction is on rods in reciprocal space through the $\bar{G}_\parallel$ and parallel to z-axis



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

Powders of 2-D Crystals



asymmetric (saw-tooth) powder peak shape

(Warren)

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

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

[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

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

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.

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

where

$$\bar{b} = b_1 c + b_2 (1-c) = \underline{\text{average}}\ b$$

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

2^{nd} term $\rightarrow$ Diffuse Scattering

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

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

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

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

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

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

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

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 average density

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

Single Particles (Dilute Limit)

Let ρ_0 be average *sld* (e.g., embedding media or solvent)

ρ_1 be average *sld* of particle (assume uniform)

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

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

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

V_0 = Particle Volume

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

Expanding exponential,

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

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

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

$\rightarrow r_G^2$ $\quad r_G$ = 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.

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

$\downarrow$

Guinier Approxn.

Scattering for Spherical Particles

The particle form factor $\left|F(\vec{Q})\right|^2 = \left|\int_V d\vec{r} e^{i\vec{Q}\cdot\vec{r}}\right|^2$ is determined by the particle shape.

For a sphere of radius R, F(Q) only depends on the magnitude of Q:

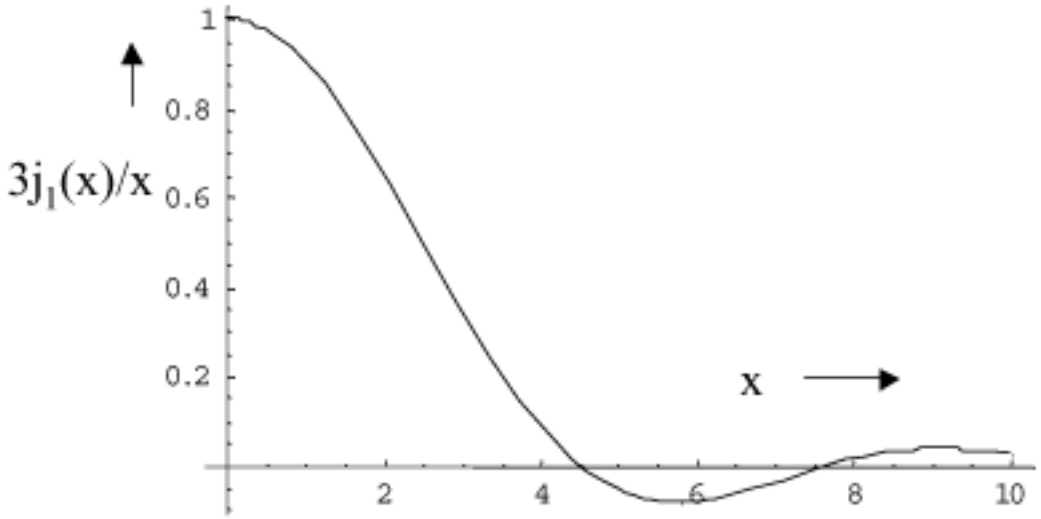
$$F_{sphere}(Q) = 3V_0\left[\frac{\sin QR - QR\cos QR}{(QR)^3}\right] \equiv \frac{3V_0}{QR} j_1(QR) \rightarrow V_0 \text{ at } Q = 0$$

Thus, as $Q \rightarrow 0$, the total scattering from an assembly of uncorrelated spherical particles [i.e. when $G(\vec{r}) \rightarrow \delta(\vec{r})$] is proportional to the square of the particle volume times the number of particles.

For elliptical particles replace R by:

$R \rightarrow (a^2 \sin^2\vartheta + b^2 \cos^2\vartheta)^{1/2}$

where ϑ is the angle between the major axis (a) and $\vec{Q}$



Determining Particle Size From Dilute Suspensions

- Particle size is usually deduced from dilute suspensions in which inter-particle correlations are absent
- In practice, instrumental resolution (finite beam coherence) will smear out minima in the form factor
- This effect can be accounted for if the spheres are mono-disperse
- For poly-disperse particles, maximum entropy techniques have been used successfully to obtain the distribution of particles sizes

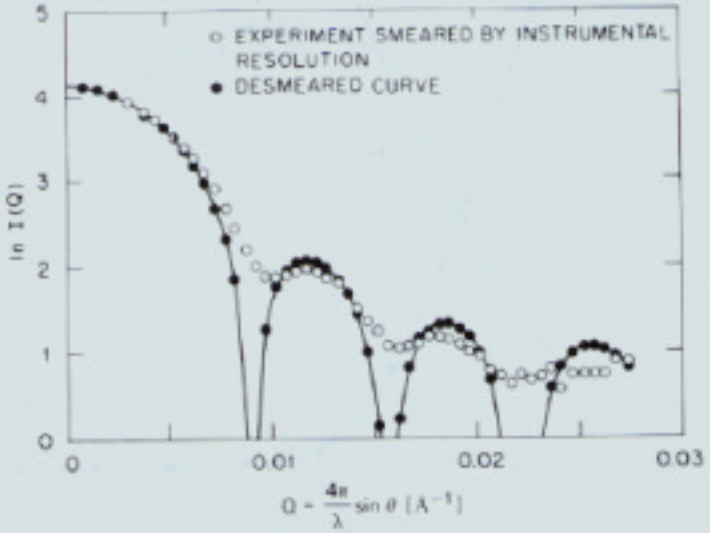
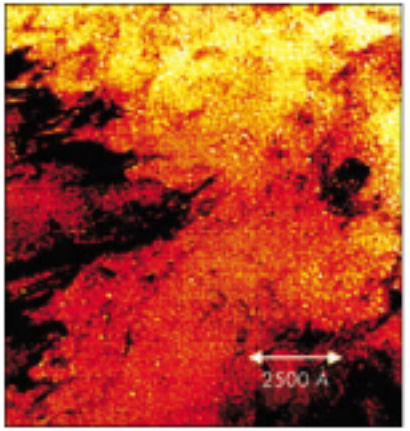
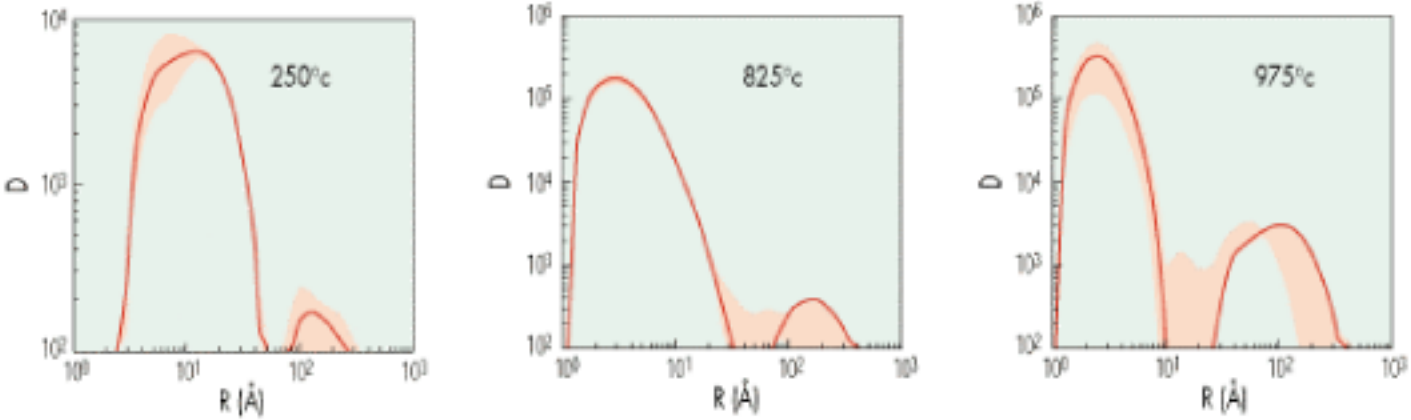


Fig. 4. Plot of ln $I(Q)$ *vs* Q for 3·98 vol.% monodisperse PMMA-H spheres (core *C*1) in D_2O/H_2O mixtures.

Size Distributions Have Been Measured for Helium Bubbles in Steel

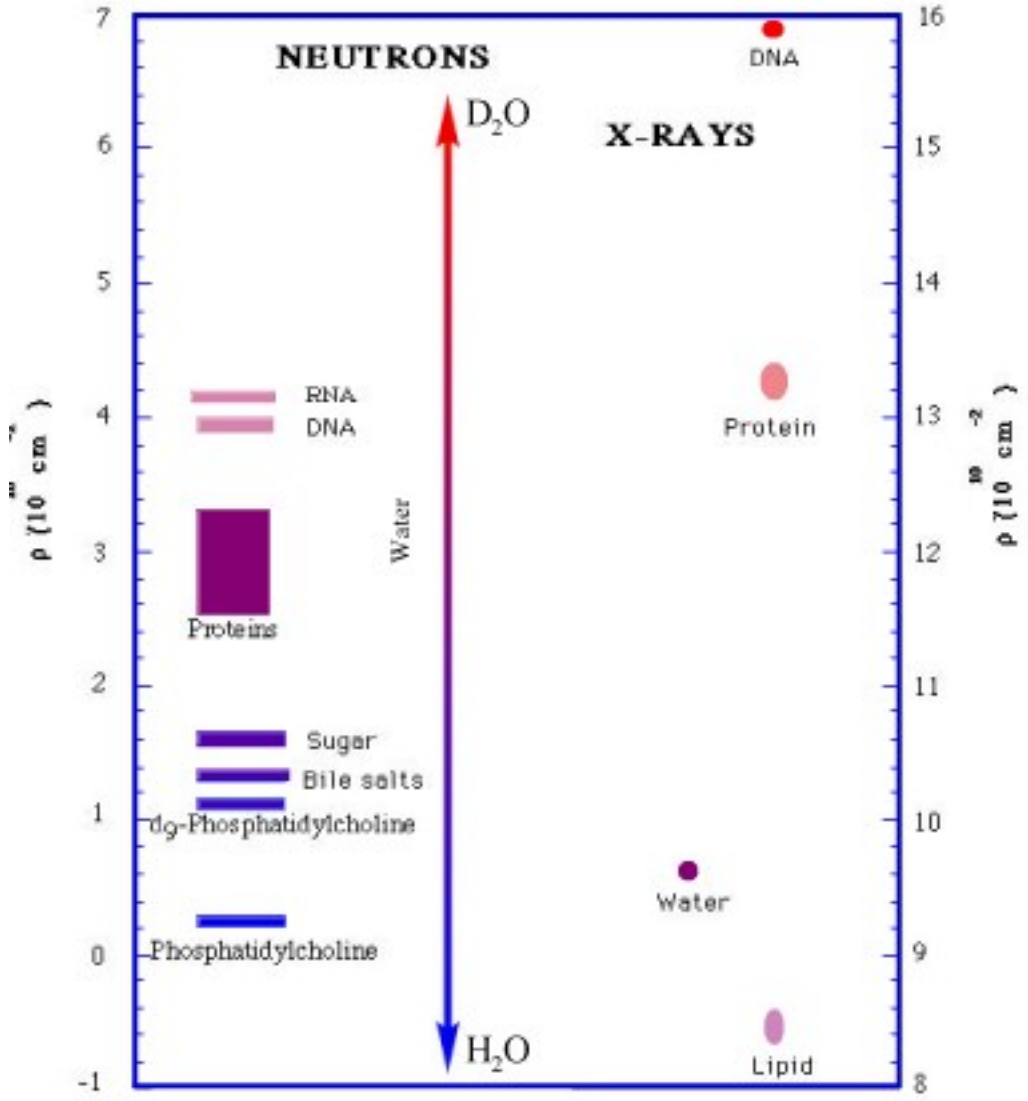
- The growth of He bubbles under neutron irradiation is a key factor limiting the lifetime of steel for fusion reactor walls
  - Simulate by bombarding steel with alpha particles
- TEM is difficult to use because bubble are small
- SANS shows that larger bubbles grow as the steel is annealed, as a result of coalescence of small bubbles and incorporation of individual He atoms



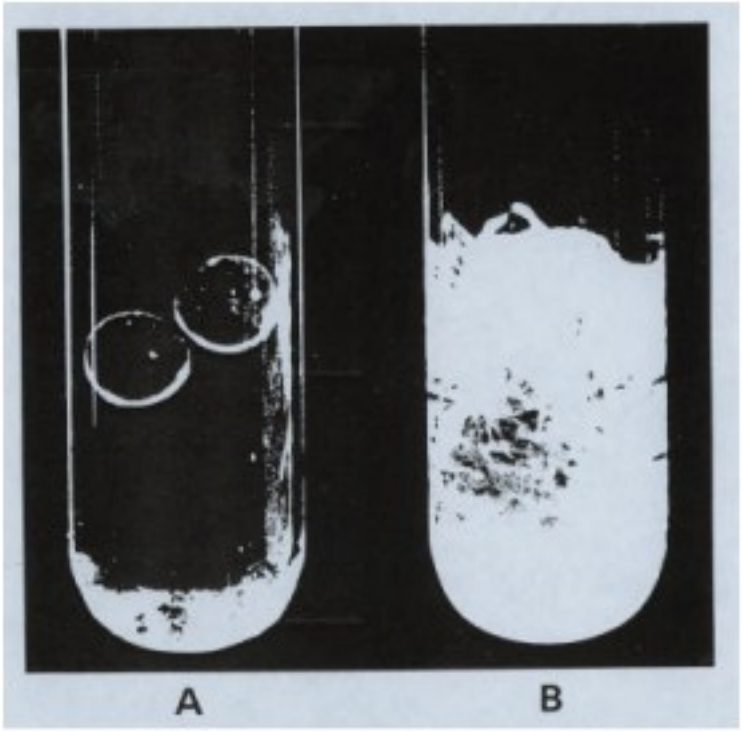


SANS gives bubble volume (arbitrary units on the plots) as a function of bubble size at different temperatures. Red shading is 80% confidence interval.

Contrast & Contrast Matching



* Chart courtesy of Rex Hjelm

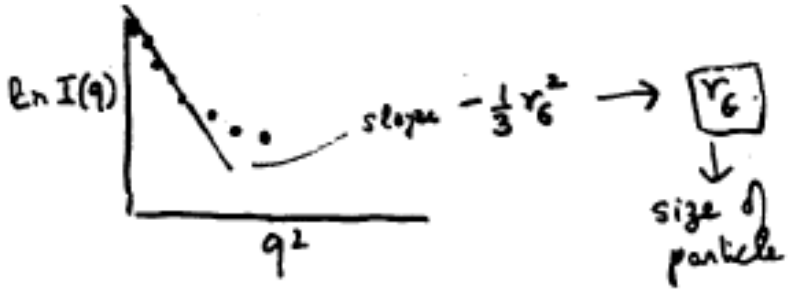


Both tubes contain borosilicate beads + pyrex fibers + solvent. (A) solvent refractive index matched to pyrex;. (B) solvent index different from both beads and fibers – scattering from fibers dominates

Isotopic Contrast for Neutrons

Hydrogen Isotope	Scattering Length b (fm)
^{1}H	-3.7409 (11)
^{2}D	6.674 (6)
^{3}T	4.792 (27)

Nickel Isotope	Scattering Lengths b (fm)
^{58}Ni	15.0 (5)
^{60}Ni	2.8 (1)
^{61}Ni	7.60 (6)
^{62}Ni	-8.7 (2)
^{64}Ni	-0.38 (7)



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:

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

Form Factor / Structure Factor

$$= \left|f_\ell(\bar{q})\right|^2 S_0(\bar{q})$$

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

$\rightarrow$ Liquid- or glass-like

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

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

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

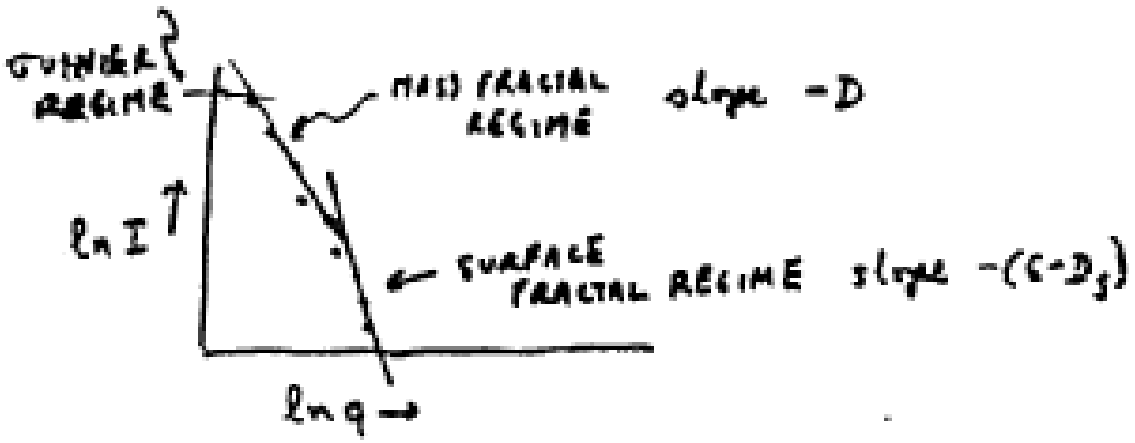
D = Fractal (Hausdorff) Dimension

It follows that

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

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

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

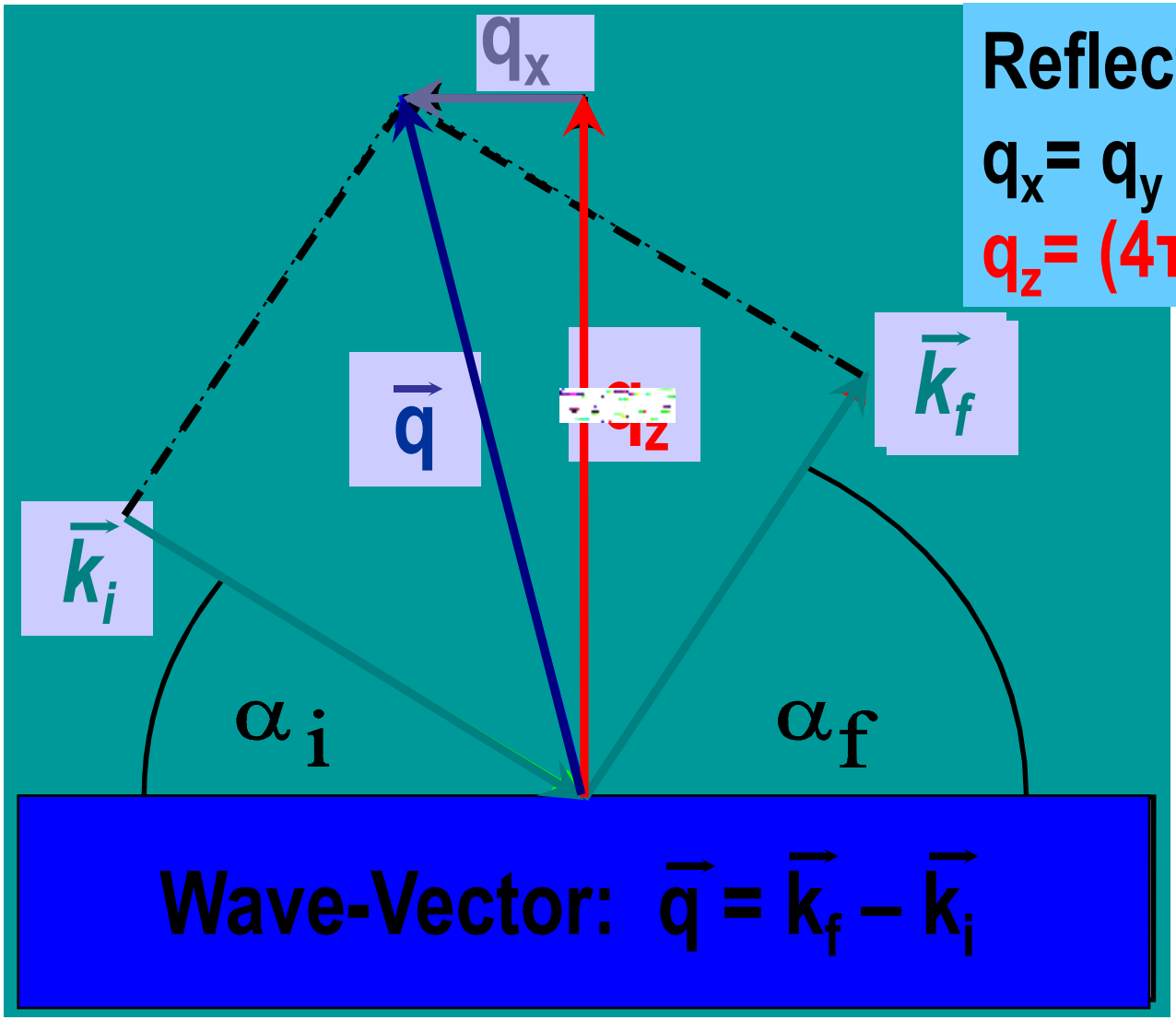


:**

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

Surface fractals $S(q) \sim \frac{1}{q^{6-D_S}}$

Scattering Geometry & Notation



Reflectivity:

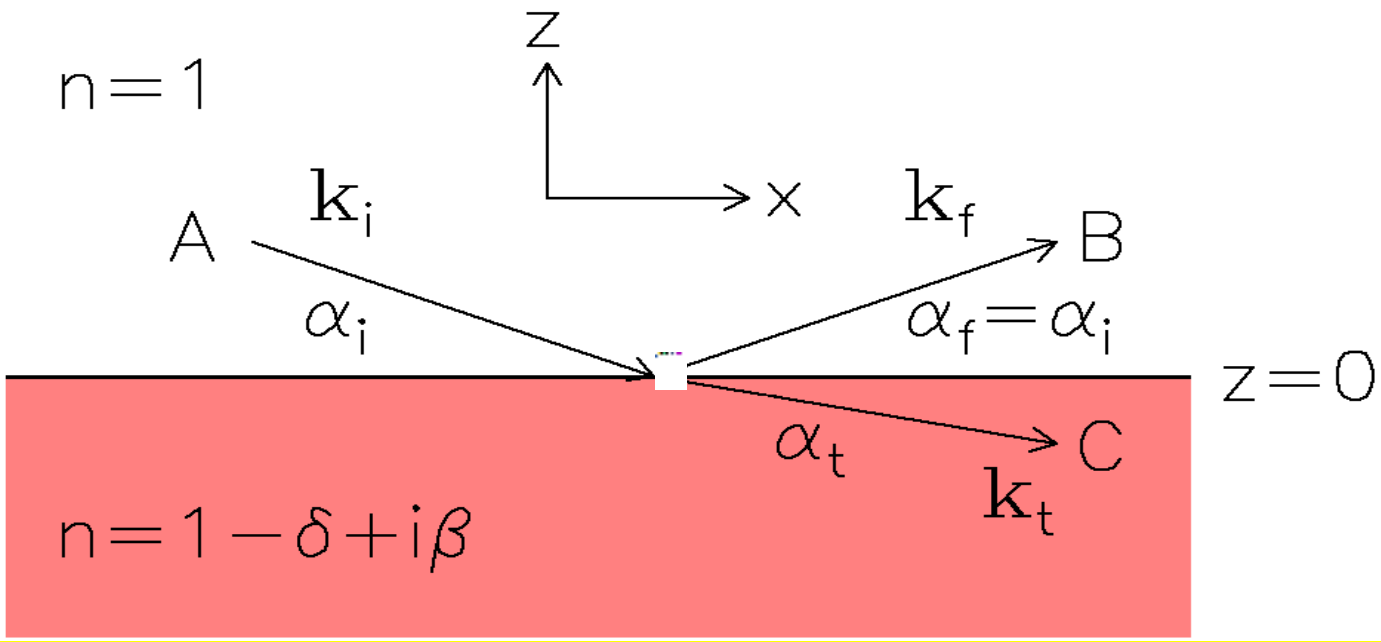
$q_x = q_y = 0$

$q_z = (4\pi\lambda/\sin\theta)$

Reflection of Visible Light

Perfect & Imperfect „Mirrors“

Basic Equation: X-Rays



Helmholtz-Equation & Boundary Conditions

$$\nabla^2 E(r) + k^2 n^2(r) E(r) = 0$$

Refractive Index: X-Rays & Neutrons

$$n_{\mathrm{x}}^2(\vec{r}) = 1 + N\,\frac{e^2}{m\,\varepsilon_0}\,\frac{f(\vec{r},E)}{\omega_0^2-\omega^2-2\mathrm{i}\,\eta_0\,\omega}$$ + magnetic part

$$n_{\mathrm{n}}^2(\vec{r}) = 1 - \frac{2\,m\,\lambda^2}{h^2}\,V(\vec{r})$$ + magnetic part

$$n(\vec{r}) = 1 - \delta(\vec{r}) + \mathrm{i}\,\beta(\vec{r})$$

Minus!!

Dispersion

Absorption

Derivation of n for neutrons:

Consider Schrodinger Eqn.

$-(\hbar^2/2m)\nabla^2\psi + (V - E)\,\psi = 0 \quad E = (\hbar^2/2m)k_0^2$

can be written:

$$\nabla^2\psi + [1 - (2m/[\hbar^2 k_0^2])V]\, k_0^2\psi = 0$$

$V = (2\pi\hbar^2/m)b\,N; \qquad k_0 = 2\pi/\lambda$

so:

$n^2 = (1 - (2m/[\hbar^2 k_0^2])V) = 1 - (\lambda^2 b/\pi)\,N$

2nd term $<<1$, so $n = 1 - (\lambda^2 b/2\pi)\,N$

Refractive Index: X-Rays

$$n(z) = 1 - \frac{\lambda^2}{2\pi} r_e \varrho(z) + \mathrm{i}\,\frac{\lambda}{4\pi}\mu(z)$$

$$\varrho(z) = \langle \varrho(x,y,z) \rangle_{x,y}$$

	$r_e\varrho\,(10^{10}\mathrm{cm}^{-2})$	$\delta(10^{-6})$	$\mu\,(\mathrm{cm}^{-1})$	$\alpha_c(^\circ)$
Vacuum	0	0	0	0
PS $(C_8H_8)_n$	9.5	3.5	4	0.153
PMMA $(C_5H_8O_2)_n$	10.6	4.0	7	0.162
PVC $(C_2H_3Cl)_n$	12.1	4.6	86	0.174
PBrS $(C_8H_7Br)_n$	13.2	5.0	97	0.181
Quartz (SiO_2)	18.0–19.7	6.8–7.4	85	0.21–0.22
Silicon (Si)	20.0	7.6	141	0.223
Nickel (Ni)	72.6	27.4	407	0.424
Gold (Au)	131.5	49.6	4170	0.570

E = 8 keV λ = 1.54 Å

Electron Density *Profile* !

Single Interface: Vacuum/Matter

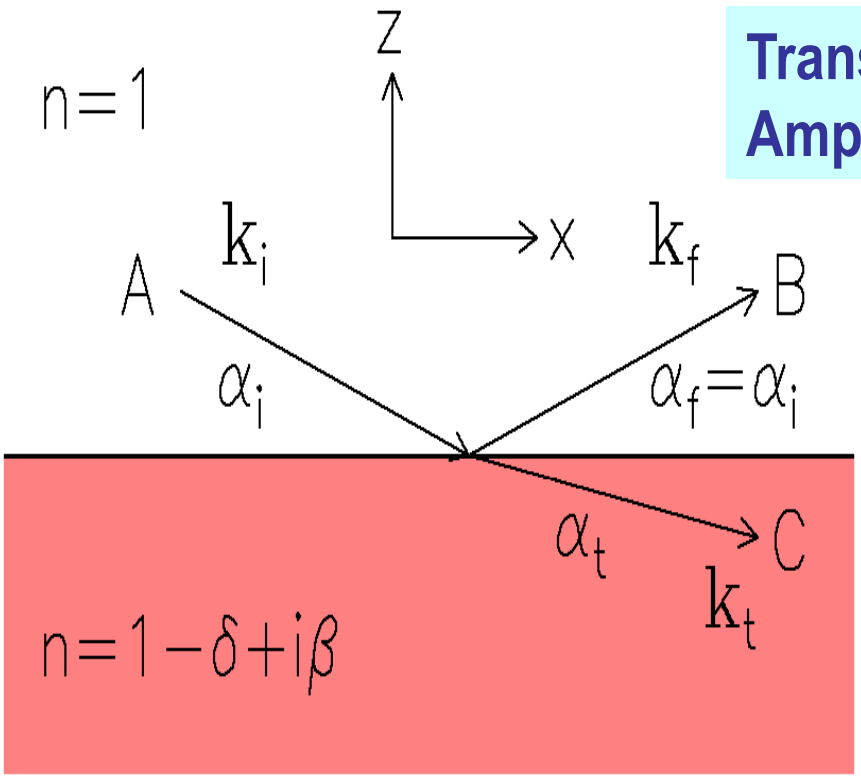
Fresnel-Formulae

Reflected Amplitude

$$r = \frac{B}{A} = \frac{k_{\mathrm{i},z} - k_{\mathrm{t},z}}{k_{\mathrm{i},z} + k_{\mathrm{t},z}}$$

Transmitted Amplitude

$$t = \frac{C}{A} = \frac{2\,k_{\mathrm{i},z}}{k_{\mathrm{i},z} + k_{\mathrm{t},z}}$$

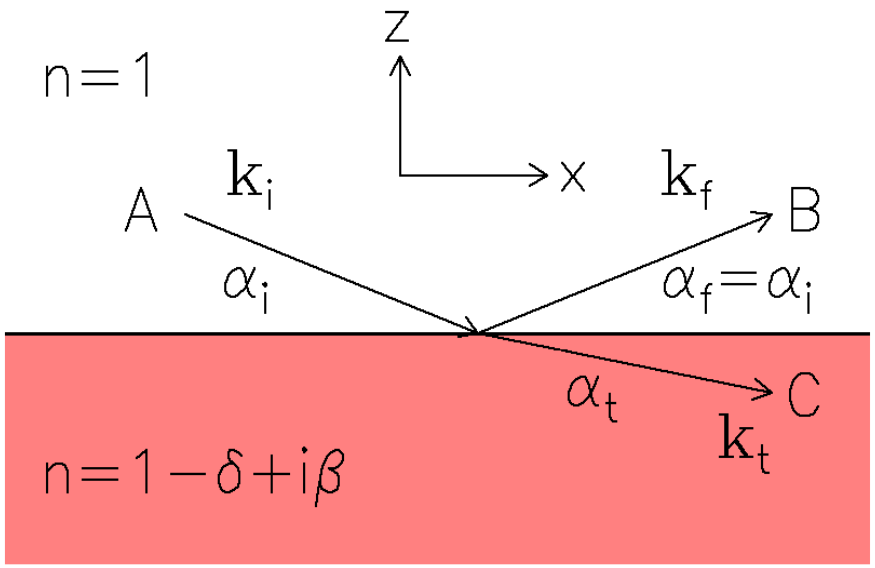


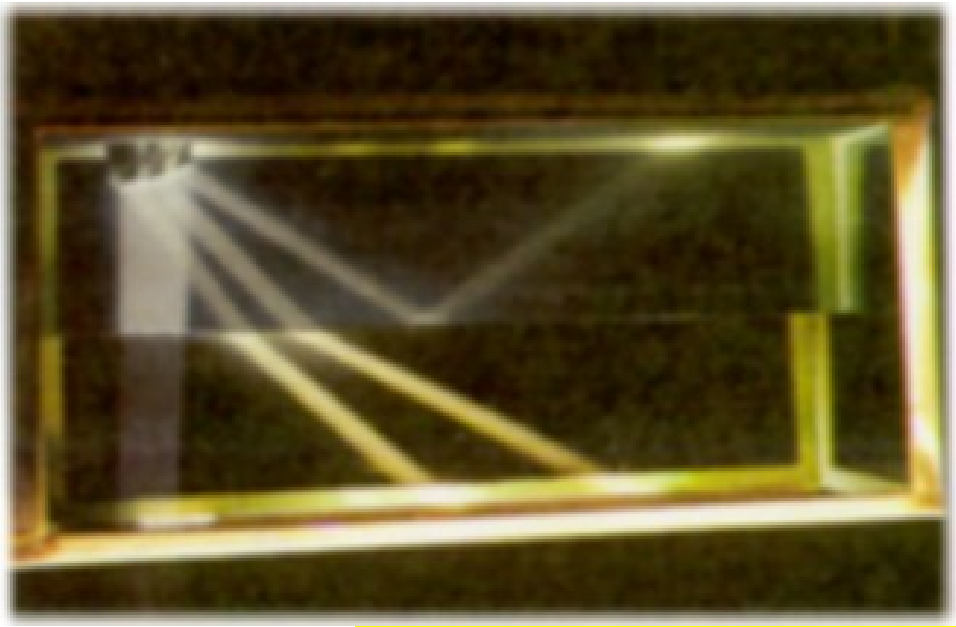
Wave-Vectors

$$k_{\mathrm{i},z} = k \sin\alpha_{\mathrm{i}}$$

$$k_{\mathrm{t},z} = k\left(n^2 - \cos^2\alpha_{\mathrm{i}}\right)^{1/2}$$

Total External Reflection

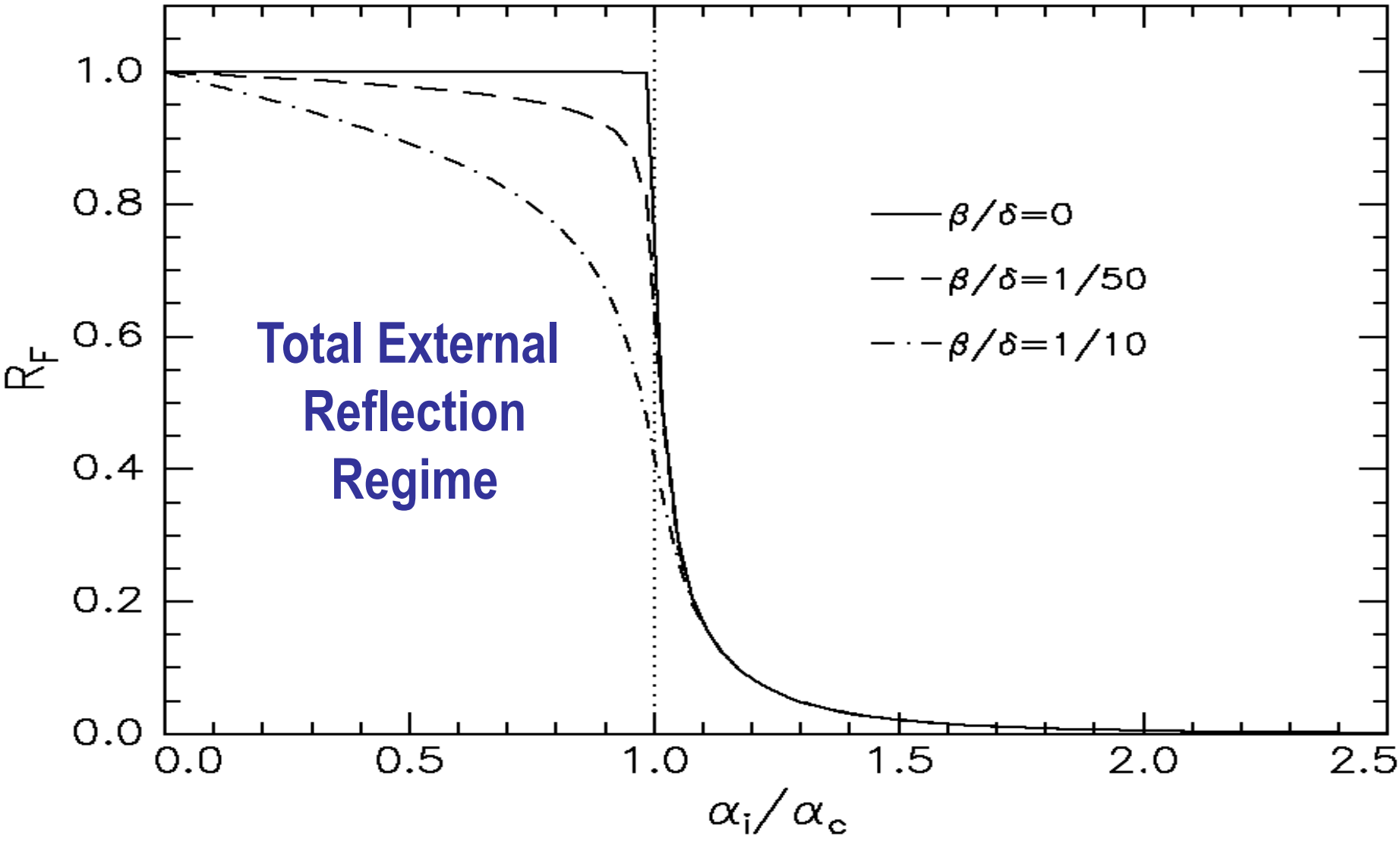




$\cos \alpha_i = (1 - \delta) \cos \alpha_t$

Critical Angle:
$\alpha_c = (2\delta)^{1/2} \sim 0.3°$

Fresnel Reflectivity: $R_F(\alpha_i)$



The „Master Formula“

Reformulation for Interfaces

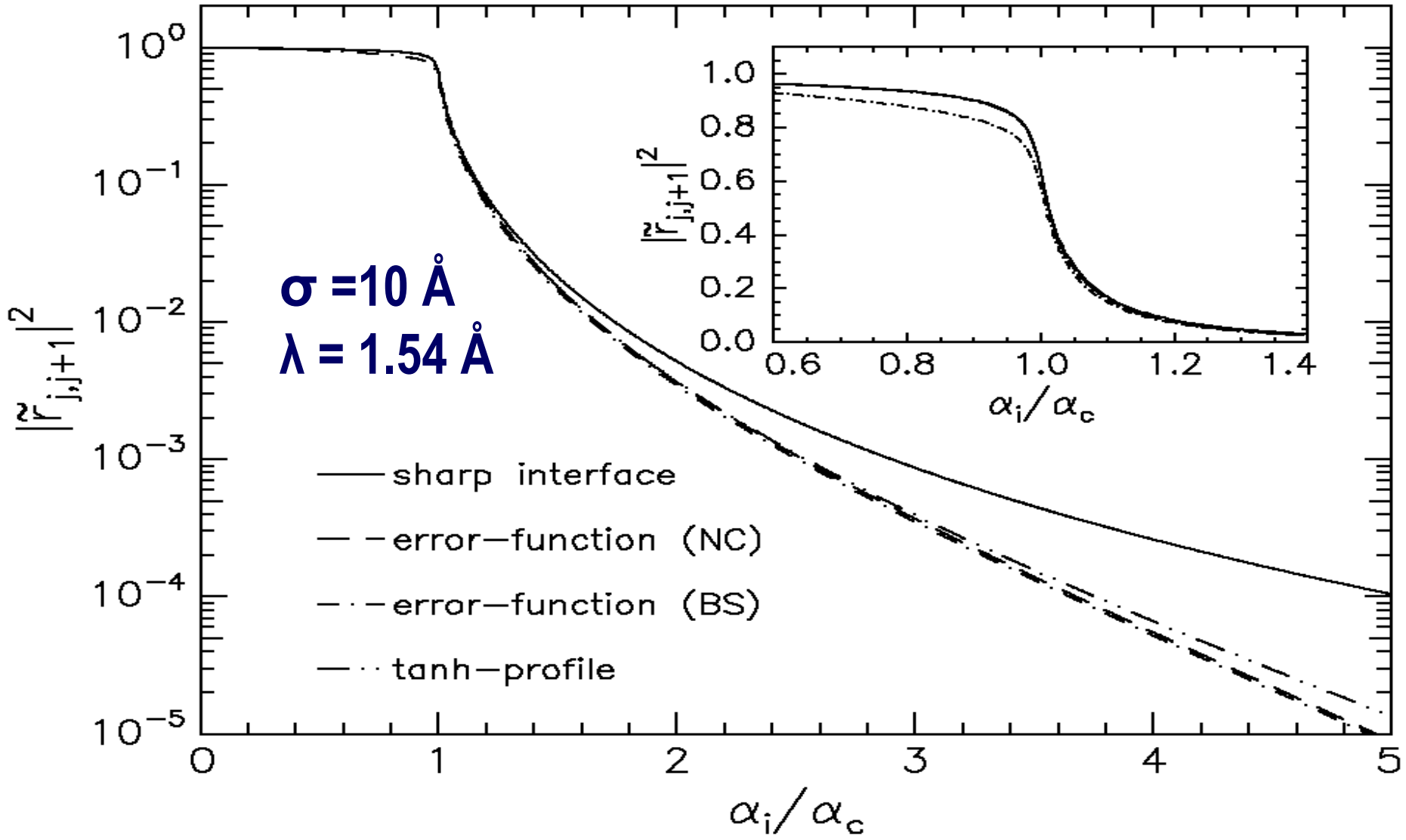
$$R(q_z) = R_{\mathrm{F}}(q_z) \left| \frac{1}{\varrho_\infty} \square \frac{\mathrm{d}\varrho(z)}{\mathrm{d}z} \exp(\mathrm{i}\, q_z z)\, \mathrm{d}z \right|^2$$

Fresnel-Reflectivity of the Substrate

Electron Density Profile

$R(q_z) = R_F \exp(-q_z^2 \sigma^2)$

Roughness Damps Reflectivity

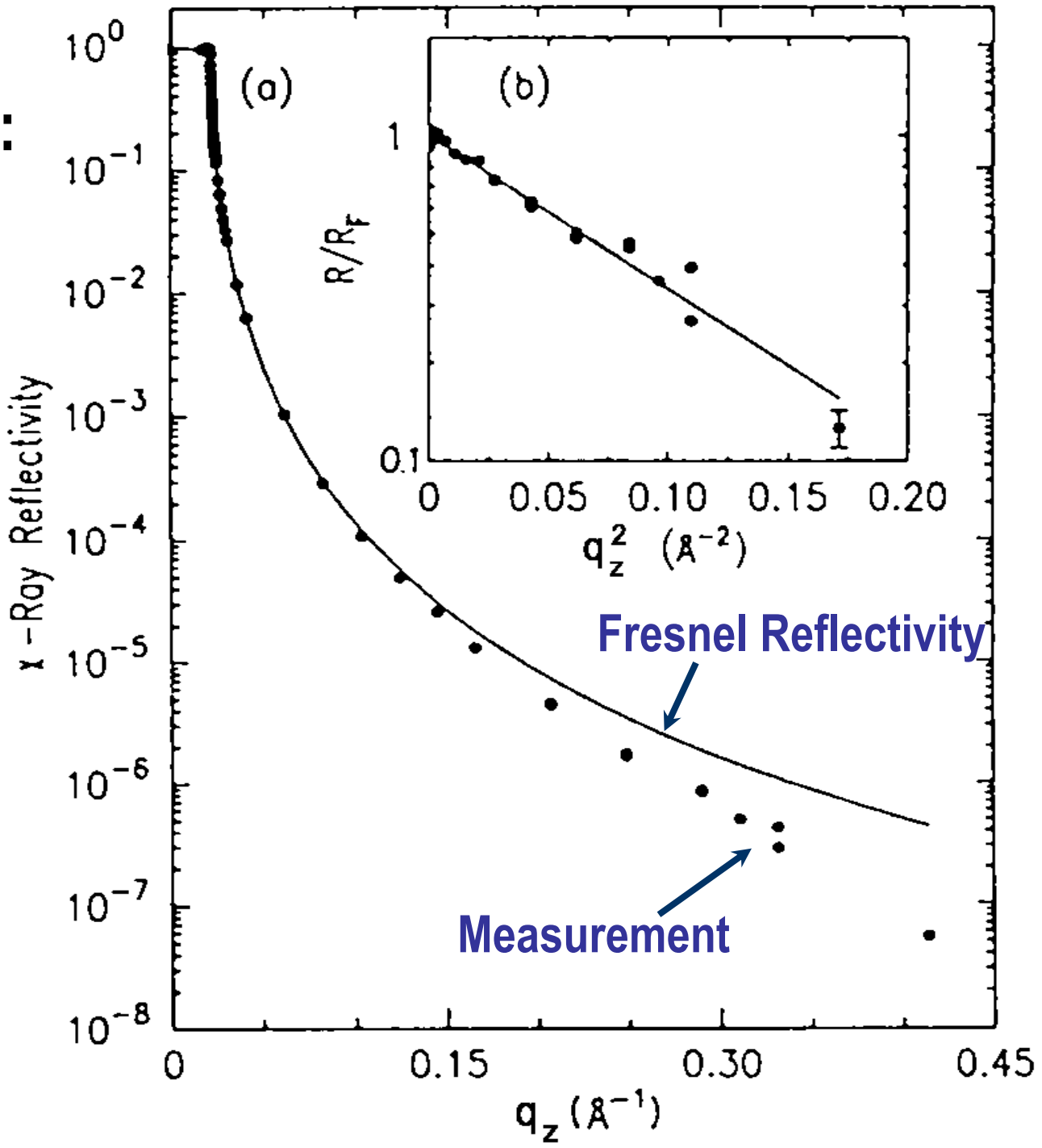


X-Ray Reflectivity: Water Surface

Difference Experiment-Theory:

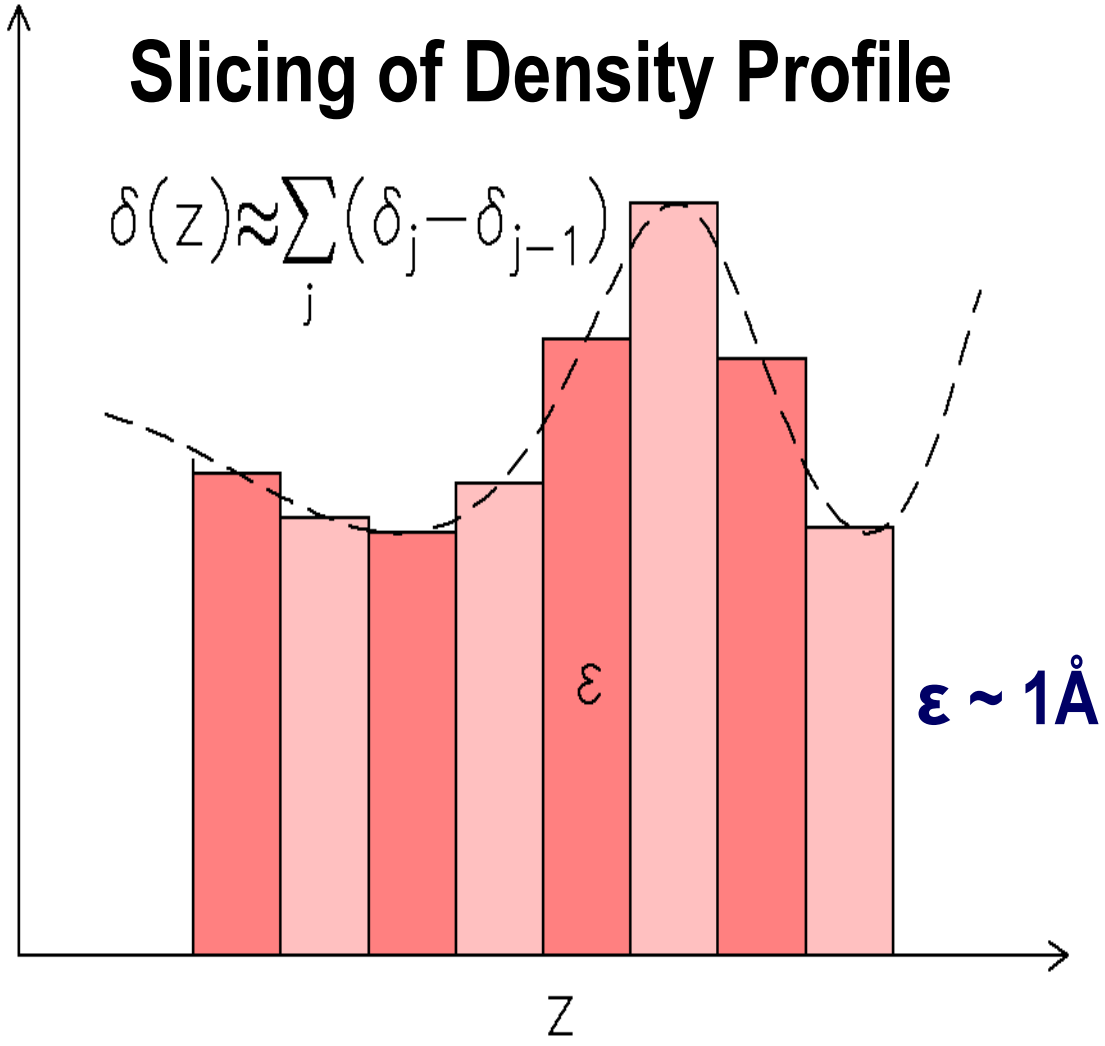
Roughness !!

Braslau et al.
PRL *54*, 114 (1985)



Calculation of Reflectivity

Slicing of Density Profile



Slicing
&
Parratt-Iteration

Reflectivity from Arbitrary Profiles !

- **Drawback: Numerical Effort !**

Example: PS Film on Si/SiO_2