Introduction to Neutron and X-Ray Scattering

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and

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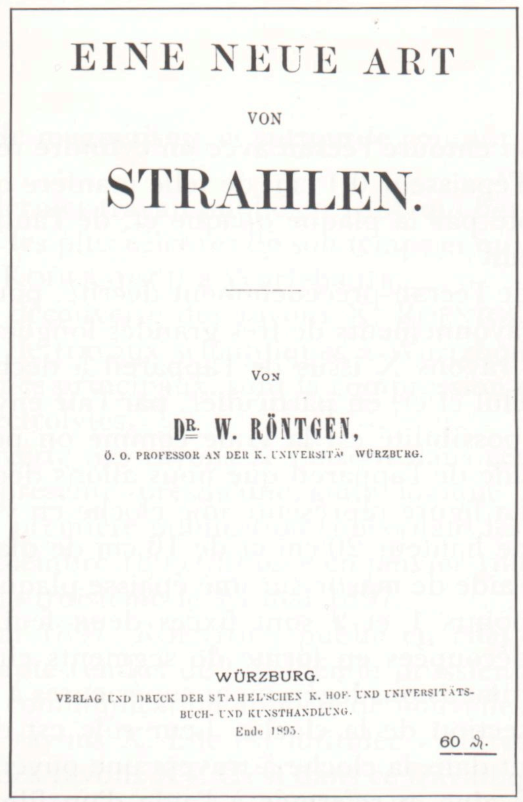
Disclaimer: Thanks to Dr. Roger Pynn (Los Alamos and University of California - Santa Barbara) and Professor Metin Tolan (University of Dortmund) for letting me use some of their slides, of much better quality than my own!

Wilhelm Conrad Röntgen 1845-1923


EINE NEUE ART

VON

STRAHLEN.

Von

Dr. W. RÖNTGEN,

Ö. O. PROFESSOR AN DER K. UNIVERSITÄT WÜRZBURG.

WÜRZBURG.

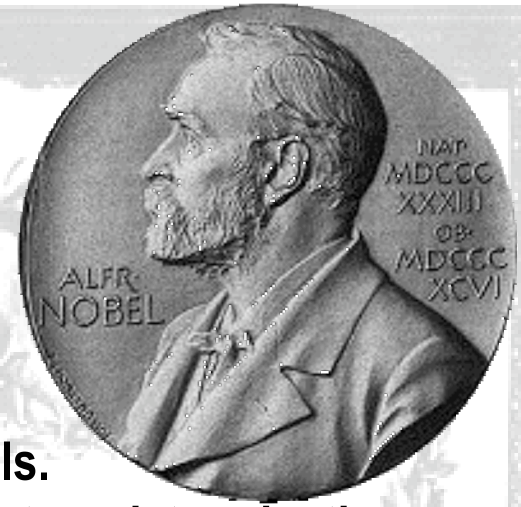
VERLAG UND DRUCK DER STAHEL'SCHEN K. HOF- UND UNIVERSITÄTS-
BUCH- UND KUNSTHANDLUNG.

Ende 1895.

60 ₰.

1895: Discovery of X-Rays

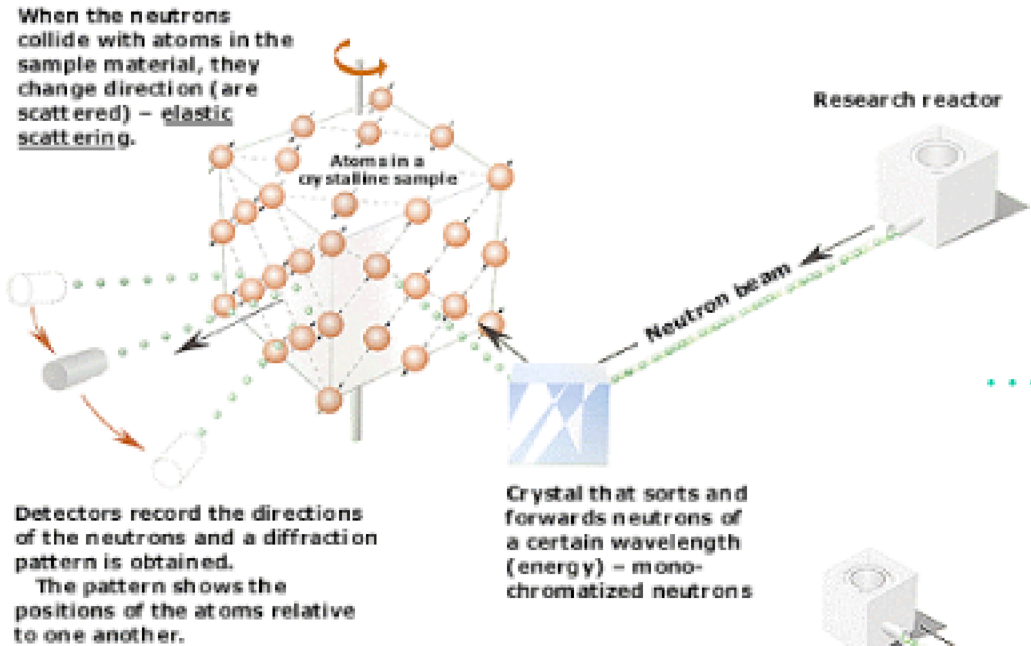
Nobel Prizes for Research with X-Rays

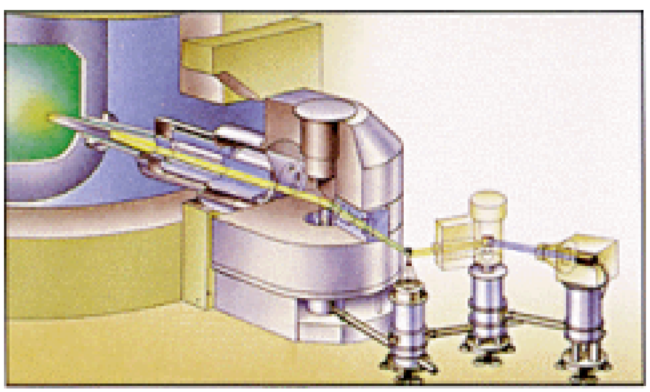


1901 W. C. Röntgen in Physics for the discovery of x-rays.
1914 M. von Laue in Physics for x-ray diffraction from crystals.
1915 W. H. Bragg and W. L. Bragg in Physics for crystal structure determination.
1917 C. G. Barkla in Physics for characteristic radiation of elements.
1924 K. M. G. Siegbahn in Physics for x-ray spectroscopy.
1927 A. H. Compton in Physics for scattering of x-rays by electrons.
1936 P. Debye in Chemistry for diffraction of x-rays and electrons in gases.
1962 M. Perutz and J. Kendrew in Chemistry for the structure of hemoglobin.
1962 J. Watson, M. Wilkins, and F. Crick in Medicine for the structure of DNA.
1979 A. McLeod Cormack and G. Newbold Hounsfield in Medicine for computed axial tomography.
1981 K. M. Siegbahn in Physics for high resolution electron spectroscopy.
1985 H. Hauptman and J. Karle in Chemistry for direct methods to determine x-ray structures.
1988 J. Deisenhofer, R. Huber, and H. Michel in Chemistry for the structures of proteins that are crucial to photosynthesis.

The 1994 Nobel Prize in Physics – Shull & Brockhouse

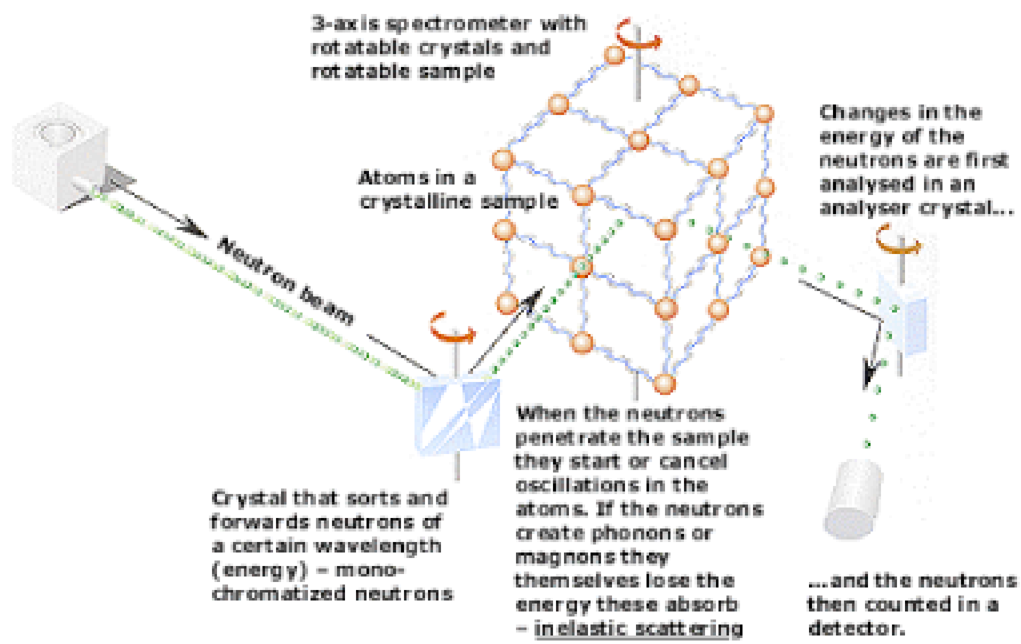
Neutrons show where the atoms are….



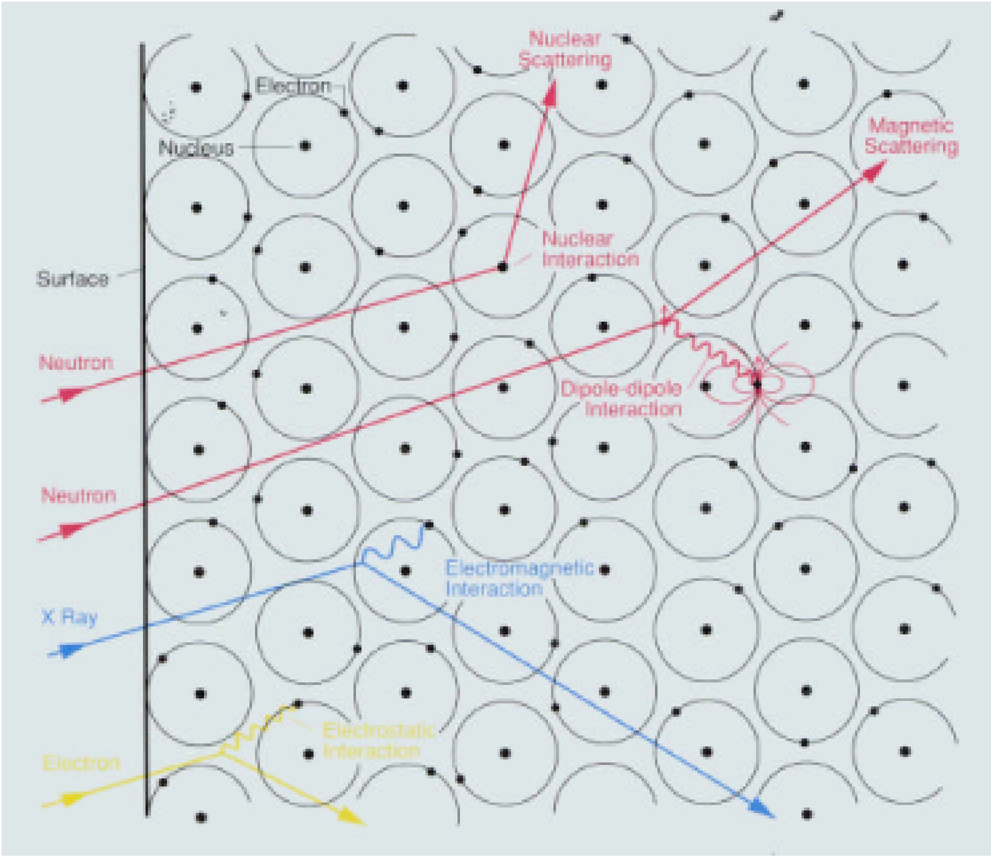


3-axis spectrometer

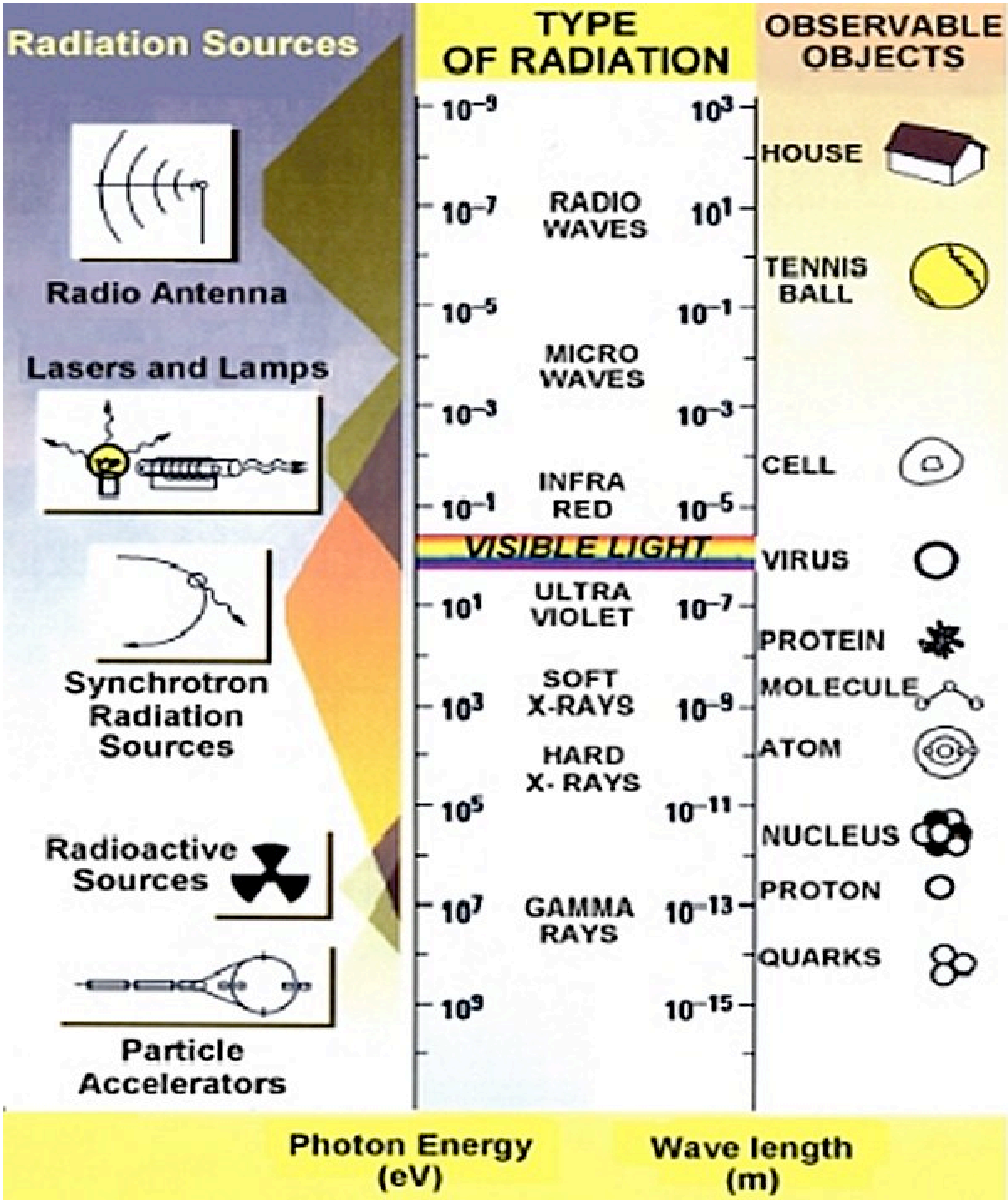
…and what the atoms do.



Interaction Mechanisms



• Neutrons interact with atomic nuclei via very short range (~fm) forces.
• Neutrons also interact with unpaired electrons via a magnetic dipole interaction.



Wavelength
≈
Object Size
≈
Angstroms for Condensed Matter Research

$$\lambda[\text{Å}] = \frac{12.398}{E_{ph}[\text{keV}]}$$

The Neutron has Both Particle-Like and Wave-Like Properties

- Mass: $m_n = 1.675 \times 10^{-27}$ kg
- Charge = 0; Spin = ½
- Magnetic dipole moment: $\mu_n = - 1.913\ \mu_N$
- Nuclear magneton: $\mu_N = eh/4\pi m_p = 5.051 \times 10^{-27}$ J T^{-1}
- Velocity (v), kinetic energy (E), wavevector (k), wavelength (λ), temperature (T).
- $E = m_n v^2/2 = k_B T = (hk/2\pi)^2/2m_n$; $k = 2\ \pi/\lambda = m_n v/(h/2\pi)$

	Energy (meV)	**Temp (K)**	**Wavelength (nm)**
Cold	**0.1 – 10**	**1 – 120**	**0.4 – 3**
Thermal	**5 – 100**	**60 – 1000**	**0.1 – 0.4**
Hot	**100 – 500**	**1000 – 6000**	**0.04 – 0.1**

λ (nm) = 395.6 / v (m/s)

E (meV) = $0.02072\ k^2$ (k in nm^{-1})

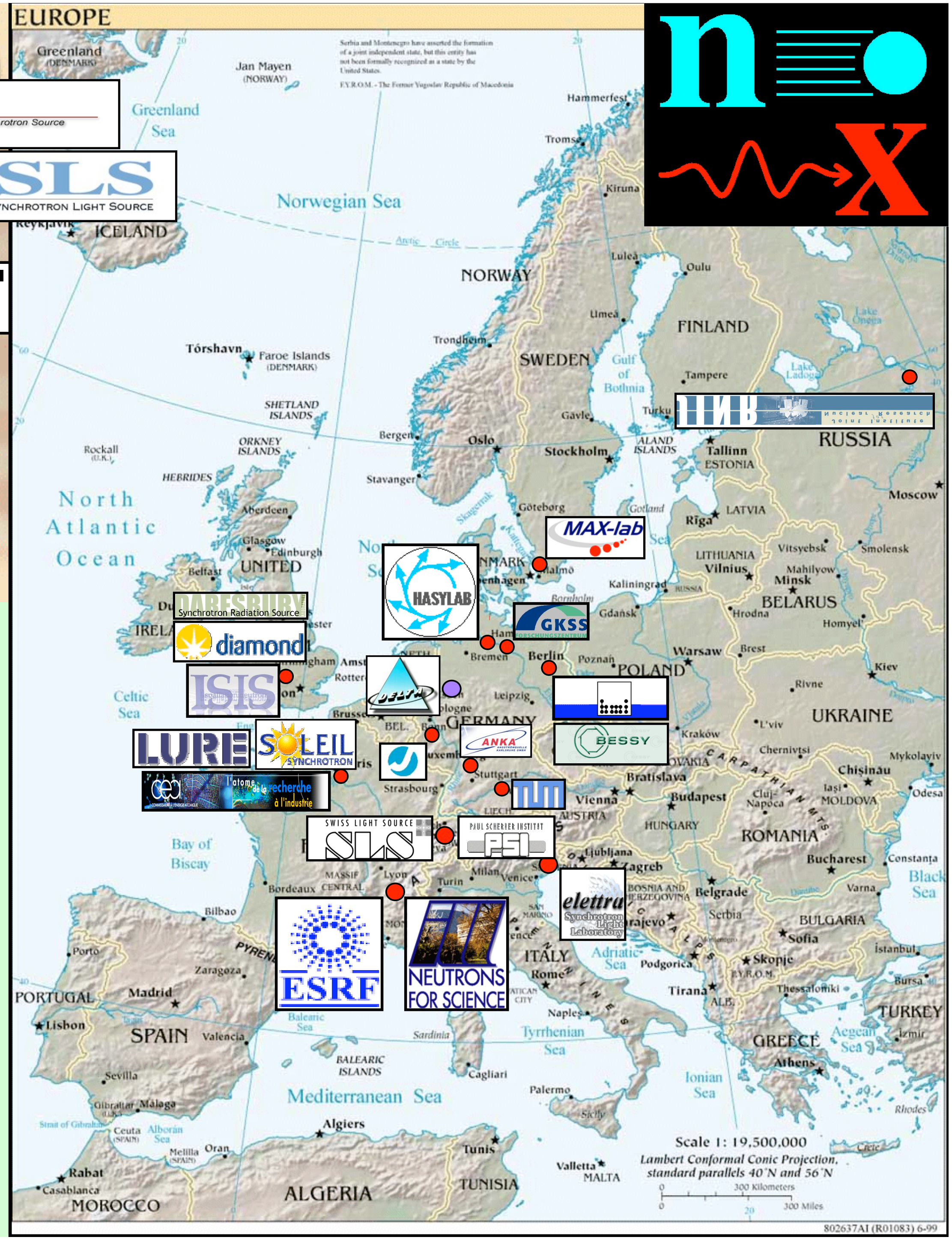
The photon also has wave and particle properties

$E = h\nu = hc/l = hck$

Charge = 0 Magnetic Moment = 0

Spin = 1

E (keV)	λ (Å)
0.8	15.0
8.0	1.5
40.0	0.3
100.0	0.125



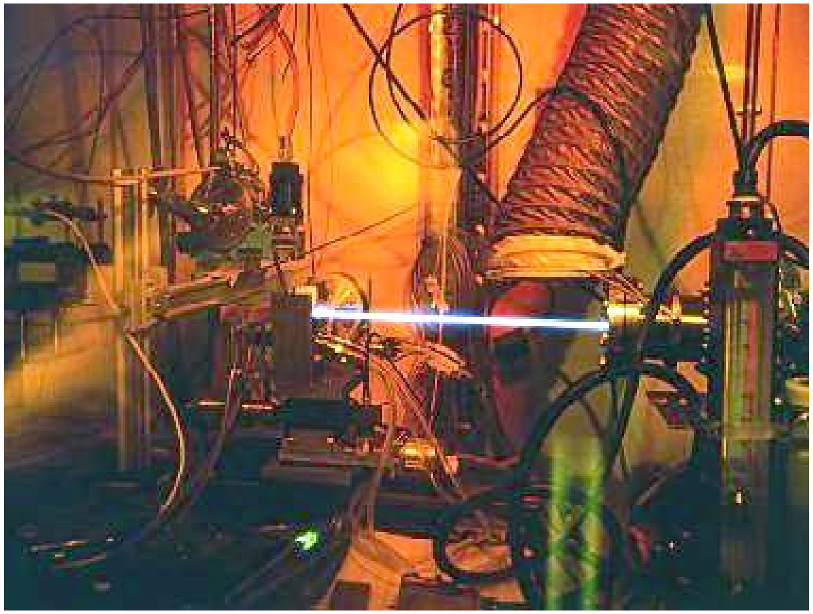
Synchrotron- and Neutron Scattering Places

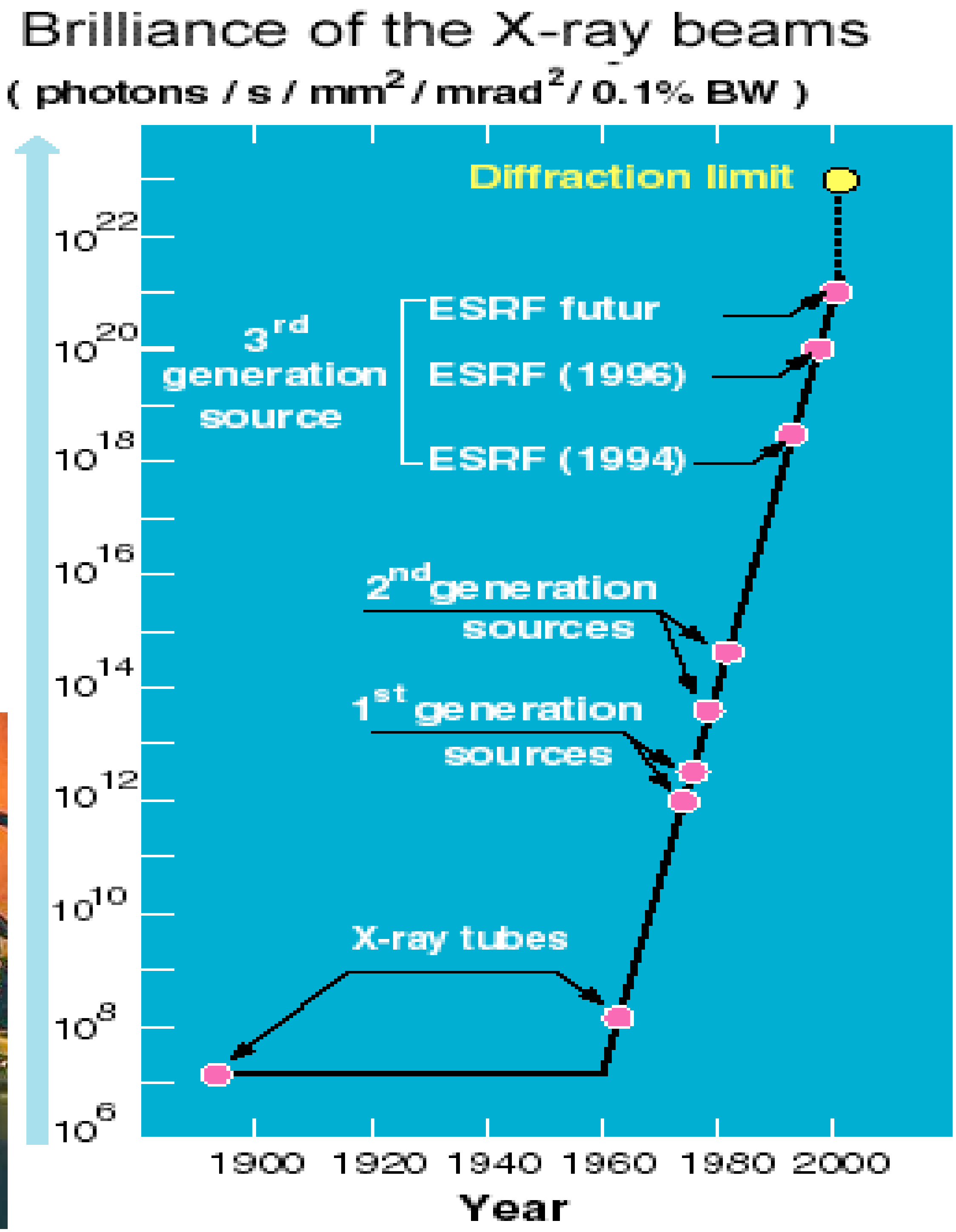
Brightness & Fluxes for Neutron & X-Ray Sources

	Brightness $(s^{-1}m^{-2}ster^{-1})$	dE/E (%)	Divergence $(mrad^2)$	Flux $(s^{-1}m^{-2})$
Neutrons	10^{15}	2	10×10	10^{11}
Rotating Anode	10^{20}	0.02	0.5×10	5×10^{14}
Bending Magnet	10^{27}	0.1	0.1×5	5×10^{20}
Undulator (APS)	10^{33}	10	0.01×0.1	10^{24}

Why Synchrotron-radiation ?

Intensity !!!





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

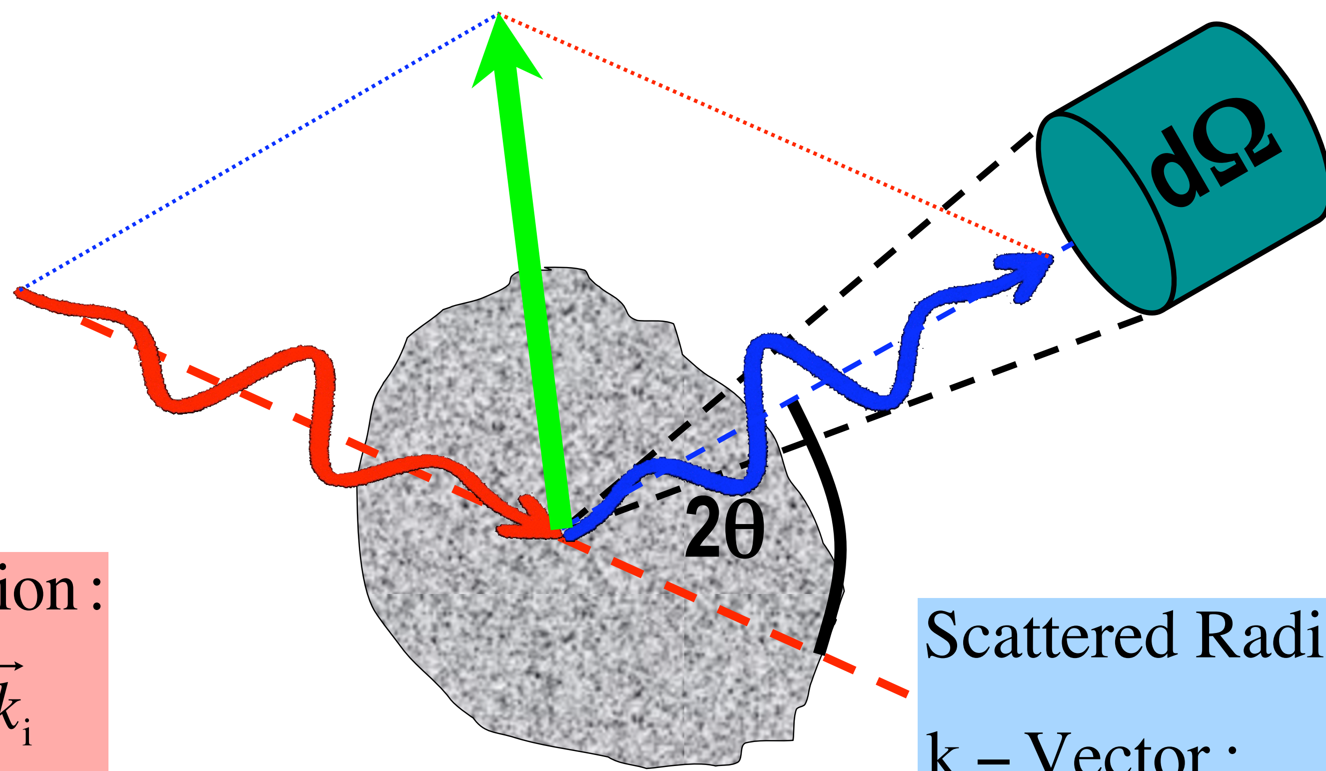
1) Strong Absorption for Lower Energy Photons

2) Little Contrast for Hydrocarbons or Similar Elements

3) Weak Scattering from Light Elements

4) Radiation Damage to Samples

Scattering Geometry



Incident Radiation:

k – Vector: $\vec{k}_{\mathrm{i}}$

$|\vec{k}_{\mathrm{i}}| = 2\pi/\lambda$

Energy: E_{i}

Polarization: $\vec{p}_{\mathrm{i}}$

Scattered Radiation:

k – Vector: $\vec{k}_{\mathrm{f}}$

Energy: E_{f}

Polarization: $\vec{p}_{\mathrm{f}}$

Wavevector Transfer:

$\vec{q} = \vec{k}_{\mathrm{f}} - \vec{k}_{\mathrm{i}}$

Energy Transfer:

$\Delta E = E_{\mathrm{f}} - E_{\mathrm{i}} = \hbar\omega$

Polarization:

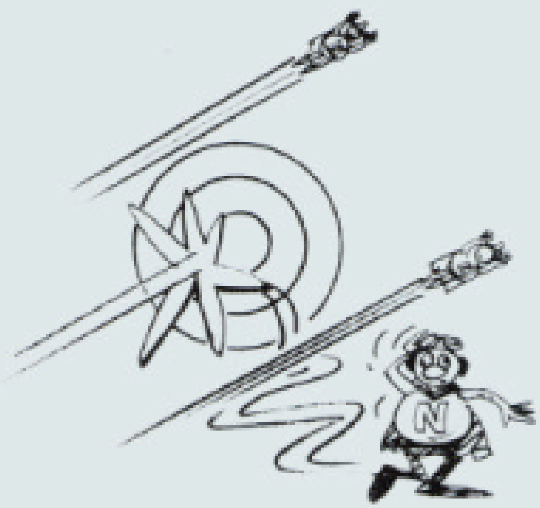
$\vec{p}_{\mathrm{i}} \rightarrow \vec{p}_{\mathrm{f}}$

For X-Rays:

$\Delta E << E_{\mathrm{f}}, E_{\mathrm{i}}$

$\Rightarrow \quad |\vec{q}| = 2k_{\mathrm{i}} \sin(2\theta/2)$

Cross Sections

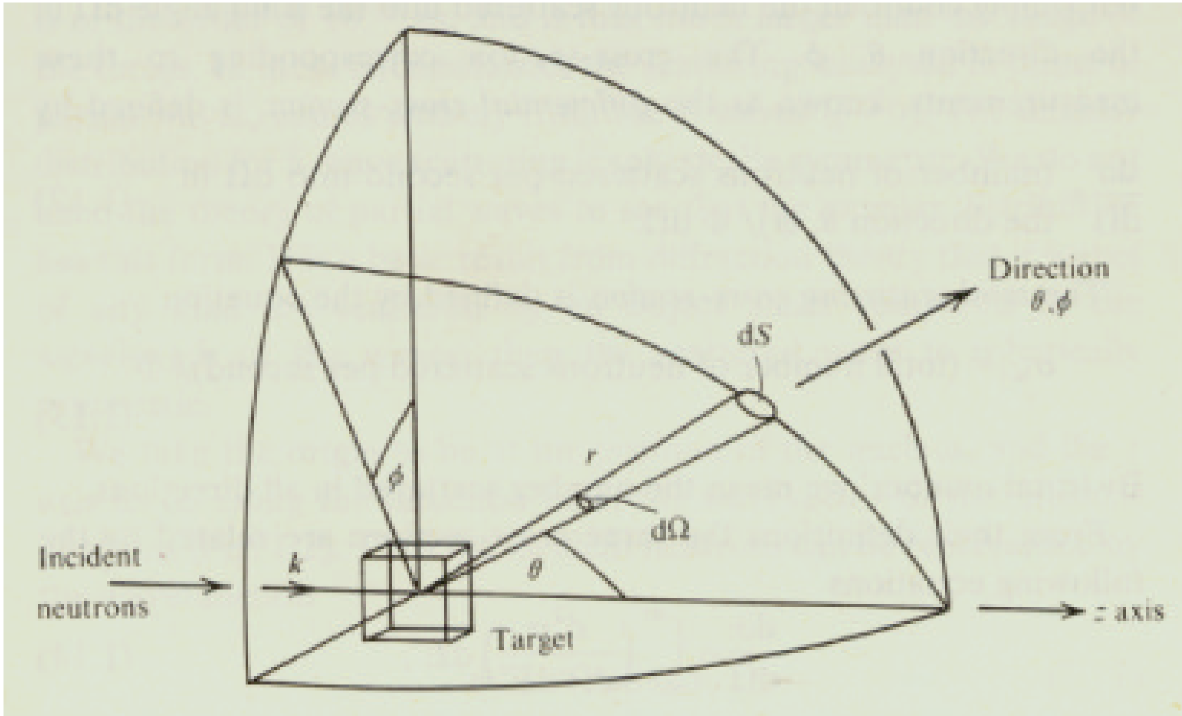


cross section

The effective area presented by a nucleus to an incident neutron. One unit for cross section is the barn, as in "can't hit the side of a barn!"

σ measured in barns:
1 barn = 10^{-24} cm^2

Attenuation = $\exp(-N\sigma t)$
N = # of atoms/unit volume
t = thickness



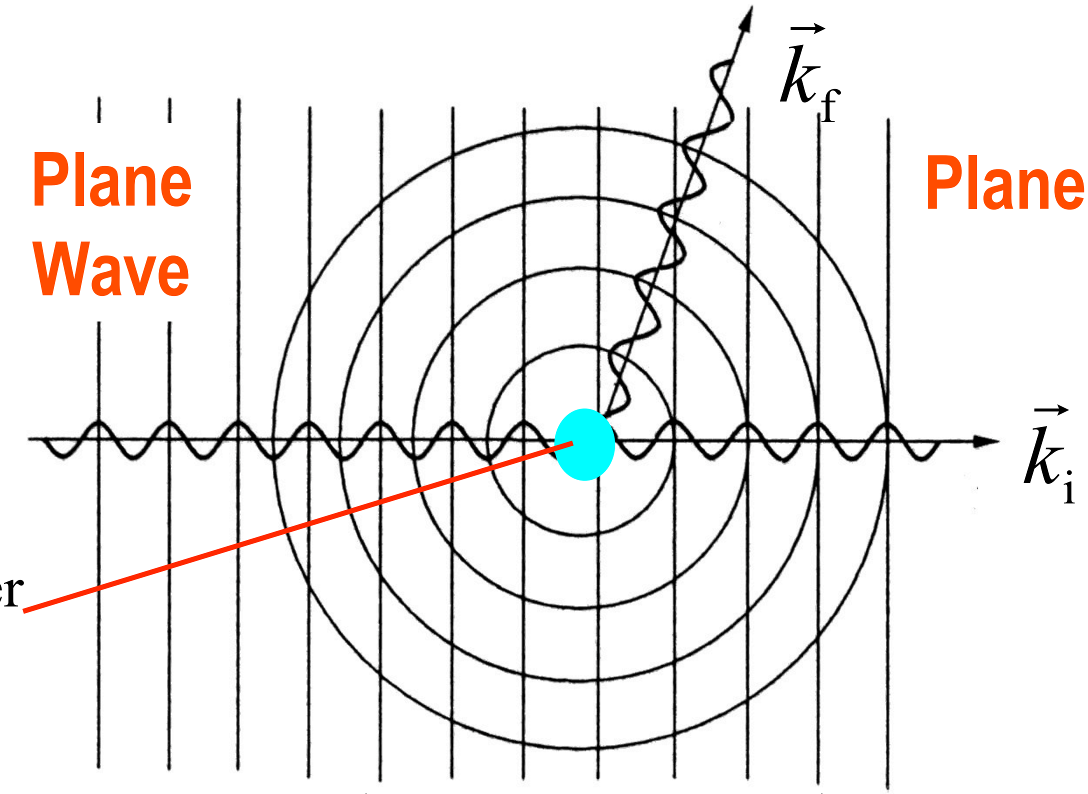
$$\Phi = \text{number of incident neutrons per cm}^2 \text{ per second}$$

$$\sigma = \text{total number of neutrons scattered per second} / \Phi$$

$$\frac{d\sigma}{d\Omega} = \frac{\text{number of neutrons scattered per second into d}\Omega}{\Phi \,\text{d}\Omega}$$

$$\frac{d^2\sigma}{d\Omega dE} = \frac{\text{number of neutrons scattered per second into d}\Omega \text{ \& dE}}{\Phi \,\text{d}\Omega \,\text{dE}}$$

Intrinsic Cross Section



Plane & Spherical Wave

Scattering Center at $\vec{r} = 0$

$$e^{i\vec{k}_i\cdot\vec{r}} \rightarrow e^{i\vec{k}_i\cdot\vec{r}} + f(\Omega)\frac{e^{i\vec{k}_f\cdot\vec{r}}}{r}$$

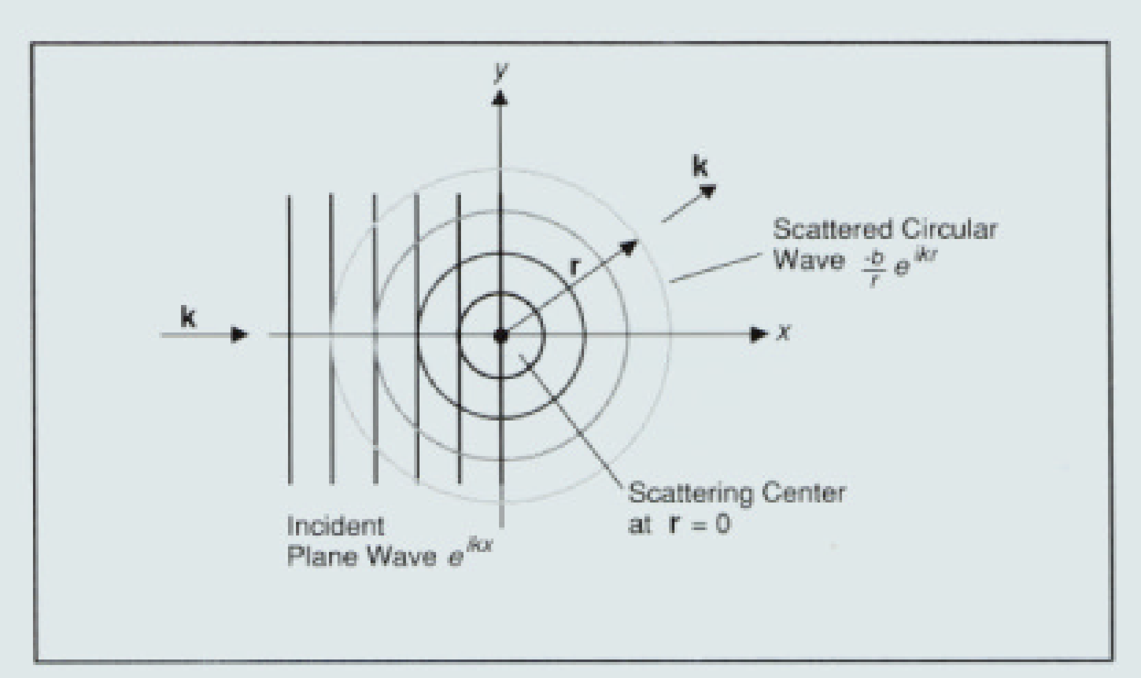
Total Cross Section :

$$\sigma = \iint \left(\frac{d\sigma}{d\Omega}\right)_0 d\Omega$$

$$\sigma = \int_0^{2\pi}\int_0^{\pi} \left|f(\vartheta,\phi)\right|^2 \sin\vartheta \, d\vartheta \, d\phi$$

$$\left(\frac{d\sigma}{d\Omega}\right)_0 = \left|f(\Omega)\right|^2$$

Scattering by a Single (fixed) Nucleus



- range of nuclear force (~ 1fm) is << neutron wavelength so scattering is "point-like"
- energy of neutron is too small to change energy of nucleus & neutron cannot transfer KE to a fixed nucleus => scattering is elastic
- we consider only scattering far from nuclear resonances where neutron absorption is negligible

If v is the velocity of the neutron (same before and after scattering), the number of neutrons passing through an area dS per second after scattering is :

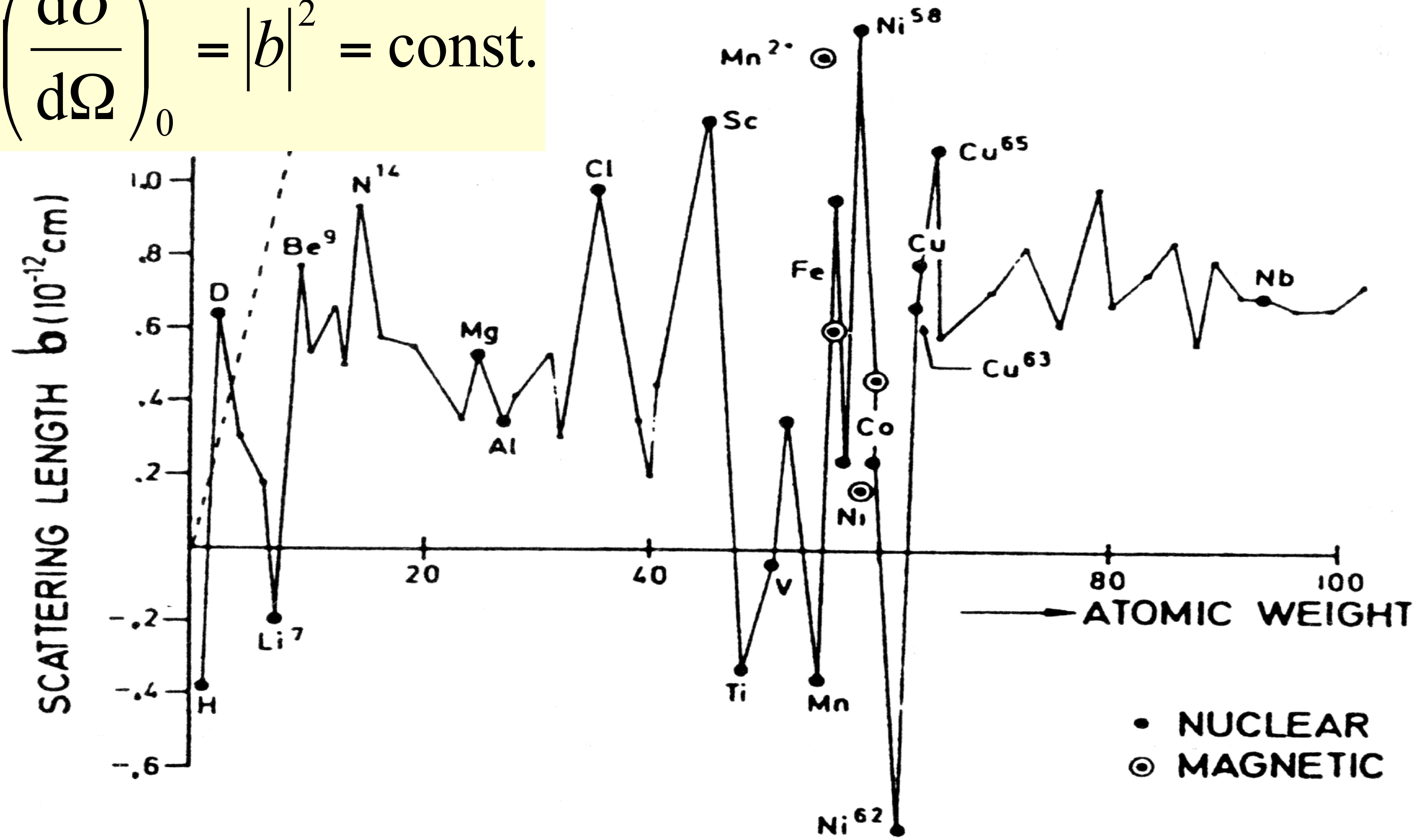
$$v\, dS\, |\psi_{scat}|^2 = v\, dS\, b^2/r^2 = v\, b^2\, d\Omega$$

Since the number of incident neutrons passing through unit area is : $\Phi = v|\psi_{incident}|^2 = v$

$$\frac{d\sigma}{d\Omega} = \frac{v\, b^2\, d\Omega}{\Phi d\Omega} = b^2 \qquad \text{so } \sigma_{total} = 4\pi b^2$$

Intrinsic Cross Section: Neutrons

$$\left(\frac{d\sigma}{d\Omega}\right)_0 = |b|^2 = \text{const.}$$



Intrinsic Cross Section: X-Rays

$$\vec{E}_{\text{in}} = \vec{E}_0\, e^{\mathrm{i}(\vec{k}\cdot\vec{r}-\omega t)}$$

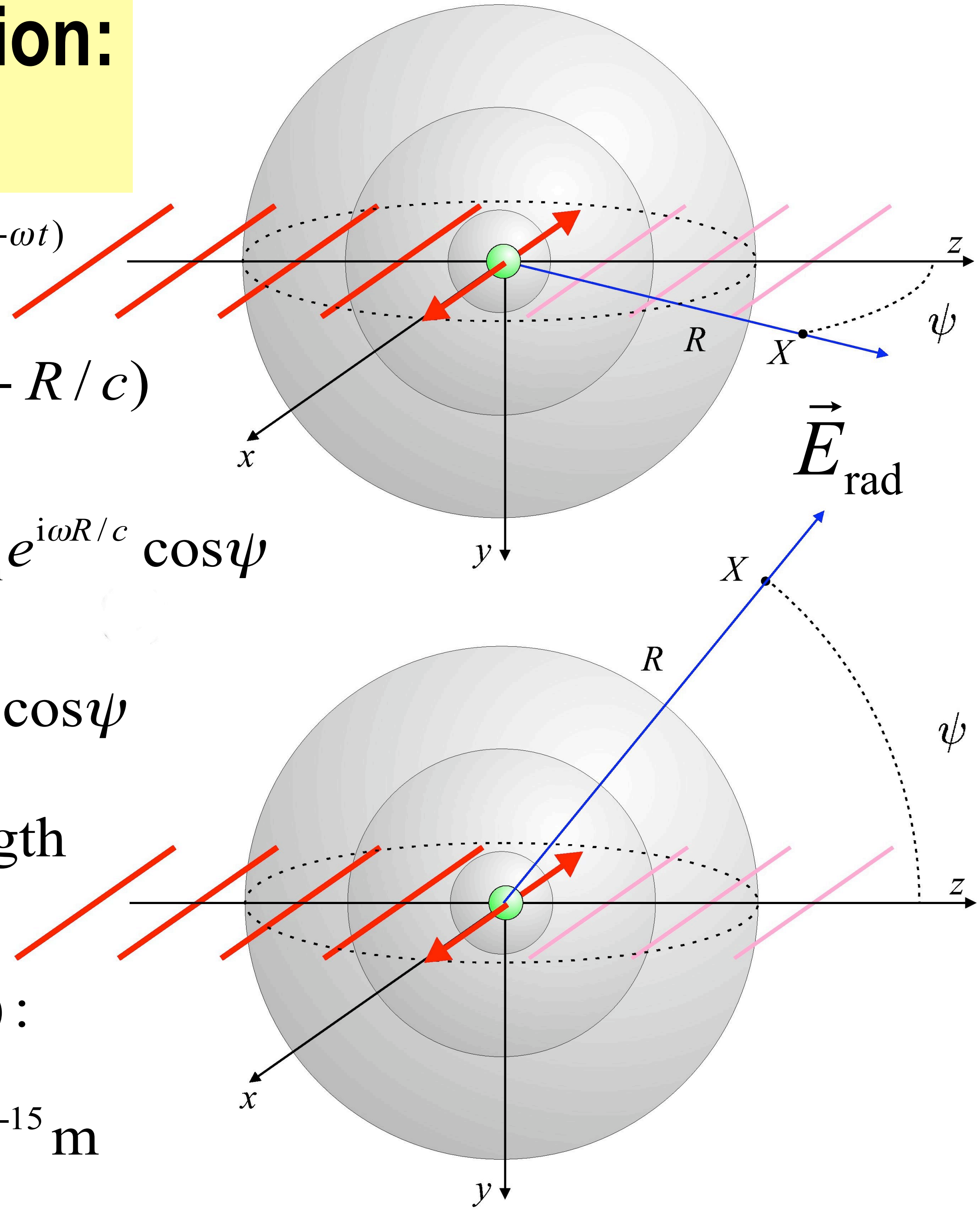
$$E_{\text{rad}}(R,t) = \frac{e}{4\pi\varepsilon_0 c^2 R}\,\ddot{x}(t-R/c)$$

$$\ddot{x}(t-R/c) = -\frac{e}{m}\alpha(\omega)E_{\text{in}}e^{\mathrm{i}\omega R/c}\cos\psi$$

$$\frac{E_{\text{rad}}(R,t)}{E_{\text{in}}} = -r_0\alpha(\omega)\frac{e^{\mathrm{i}kR}}{R}\cos\psi$$

Thomson Scattering Length of the Electron (classical electron radius):

$$r_0 = \frac{e^2}{4\pi\varepsilon_0 mc^2} = 2.82\times10^{-15}\,\mathrm{m}$$

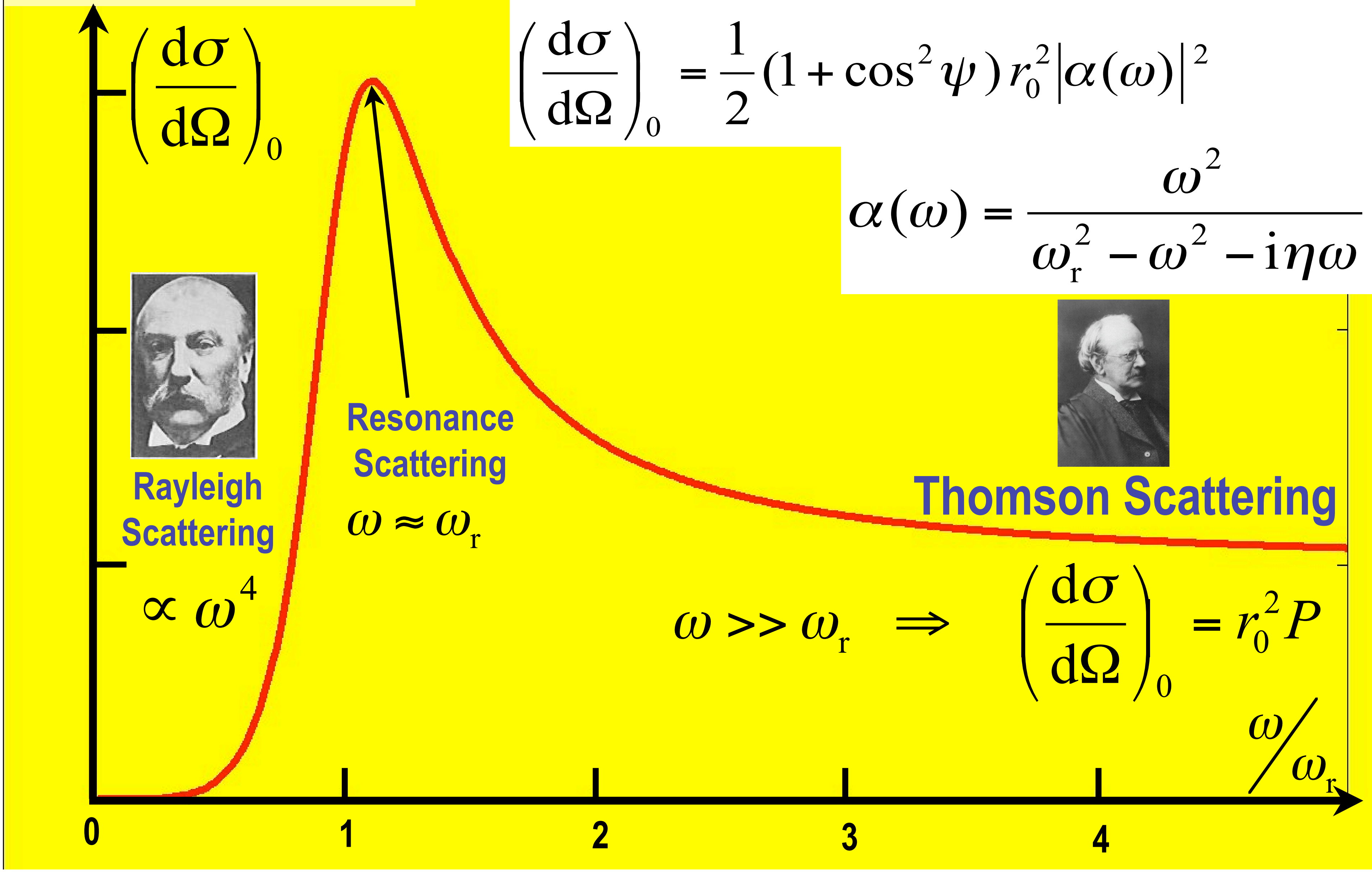


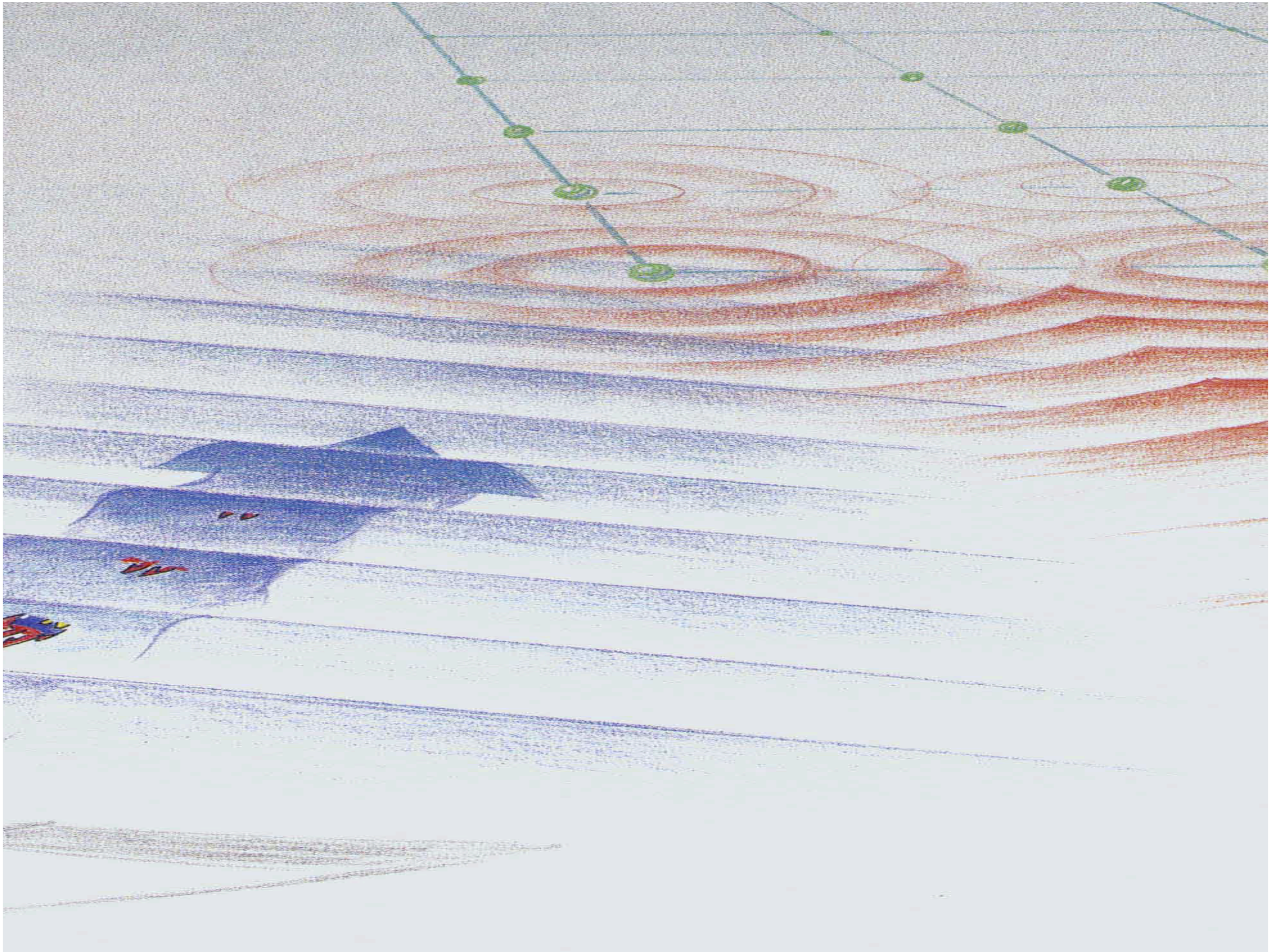
Intrinsic Cross Section: X-Rays

$$\left|\frac{E_{\mathrm{rad}}(R,t)}{E_{\mathrm{in}}}\right|^2 = \frac{r_0^2}{R^2}\left|\alpha(\omega)\right|^2 P(\psi) = \frac{\left|f(\Omega)\right|^2}{R^2}$$

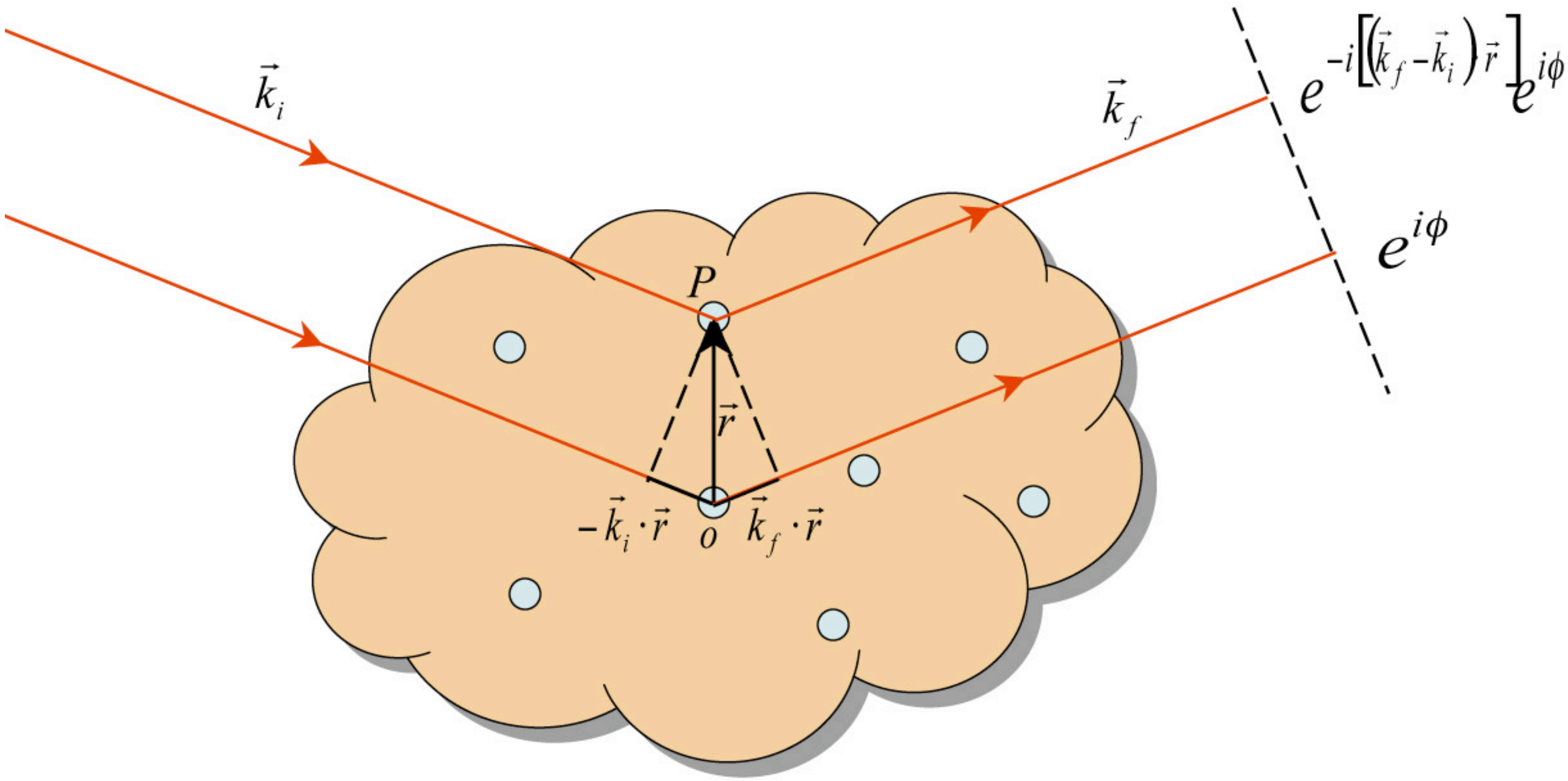
$$\left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\right)_0 = \frac{1}{2}\left(1+\cos^2\psi\right) r_0^2 \left|\alpha(\omega)\right|^2$$

$$\alpha(\omega) = \frac{\omega^2}{\omega_{\mathrm{r}}^2 - \omega^2 - \mathrm{i}\eta\omega}$$





Adding up phases at the detector of the wavelets scattered from all the scattering centers in the sample:



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 <u>neutrons</u>, 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

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

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

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

"coherent" "incoherent"

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

Coherent Part

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

X-rays

$$\frac{d\sigma}{d\Omega} = r_0^2 \left[\frac{1 + \cos^2(2\theta)}{2}\right] S(\mathbf{q})$$

$$S(\mathbf{q}) = \left\langle \Sigma_{ij} \exp[-i\mathbf{q}.(\mathbf{r}_i - \mathbf{r}_j)] \right\rangle$$

$\{\mathbf{r}_i\}$ == electron positions.

Now, $\Sigma_i \exp[-i\mathbf{q}.\mathbf{R_i}] = \rho_N(\mathbf{q})$ Fourier Transform of nuclear density
[sometimes also referred to as $F(\mathbf{q})$]

Proof:

$$\rho_N(\mathbf{r}) = \Sigma_i \,\delta(\mathbf{r} - \mathbf{R_i})$$

$$\rho_N(\mathbf{q}) = \int \rho_N(\mathbf{r}) \exp[-i\mathbf{q}.\mathbf{r}]\, d\mathbf{r} = \int \Sigma_i \,\delta(\mathbf{r} - \mathbf{R_i}) \exp[-i\mathbf{q}.\mathbf{r}]\, d\mathbf{r}$$

$$= \Sigma_i \exp[-i\mathbf{q}.\mathbf{R_i}]$$

Similarly,

$\Sigma_i \exp[-i\mathbf{q}.\mathbf{r_i}] = \rho_{el}(\mathbf{q})$ Fourier Transform of electron density

So, for neutrons, $S(\mathbf{q}) = \langle \rho_N(\mathbf{q})\, \rho_N^*(\mathbf{q}) \rangle$

And, for x-rays, $S(\mathbf{q}) = \langle \rho_{el}(\mathbf{q})\, \rho_{el}^*(\mathbf{q}) \rangle$

Values of σ_{coh} and σ_{inc}

Nuclide	σ_{coh}	σ_{inc}	Nuclide	σ_{coh}	σ_{inc}
^{1}H	1.8	80.2	V	0.02	5.0
^{2}H	5.6	2.0	Fe	11.5	0.4
C	5.6	0.0	Co	1.0	5.2
O	4.2	0.0	Cu	7.5	0.5
Al	1.5	0.0	^{36}Ar	24.9	0.0

- Difference between H and D used in experiments with soft matter (contrast variation)
- Al used for windows
- V used for sample containers in diffraction experiments and as calibration for energy resolution
- Fe and Co have nuclear cross sections similar to the values of their magnetic cross sections
- Find scattering cross sections at the NIST web site at:

  http://webster.ncnr.nist.gov/resources/n-lengths/

If electrons are bound to atoms centered on nuclei at $\mathbf{R_i}$

$$\rho_{el}(\mathbf{r}) = \Sigma_i f_{el}(\mathbf{r} - \mathbf{R_i})$$

$$\rho_{el}(\mathbf{q}) = \int d\mathbf{r} \exp[-i\mathbf{q}.\mathbf{r}] \Sigma_i f_{el}(\mathbf{r} - \mathbf{R_i})$$

$$= \Sigma_i \{ \int d\mathbf{r} \exp[-i\mathbf{q}.(\mathbf{r} - \mathbf{R_i})] f_{el}(\mathbf{r} - \mathbf{R_i}) \} \exp[-i\mathbf{q}.\mathbf{R_i}]$$

$$= f(\mathbf{q}) \Sigma_i \exp[-i\mathbf{q}.\mathbf{R_i}]$$

$$= f(\mathbf{q}) \rho_N(\mathbf{q})$$

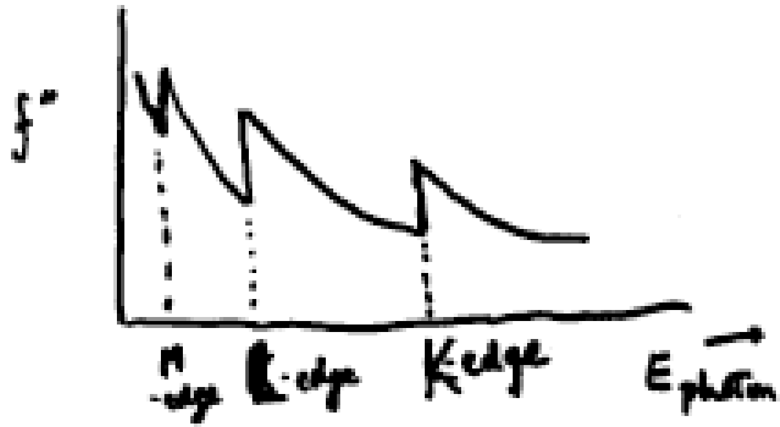
$f(\mathbf{q})$ is called the **Atomic Form Factor**

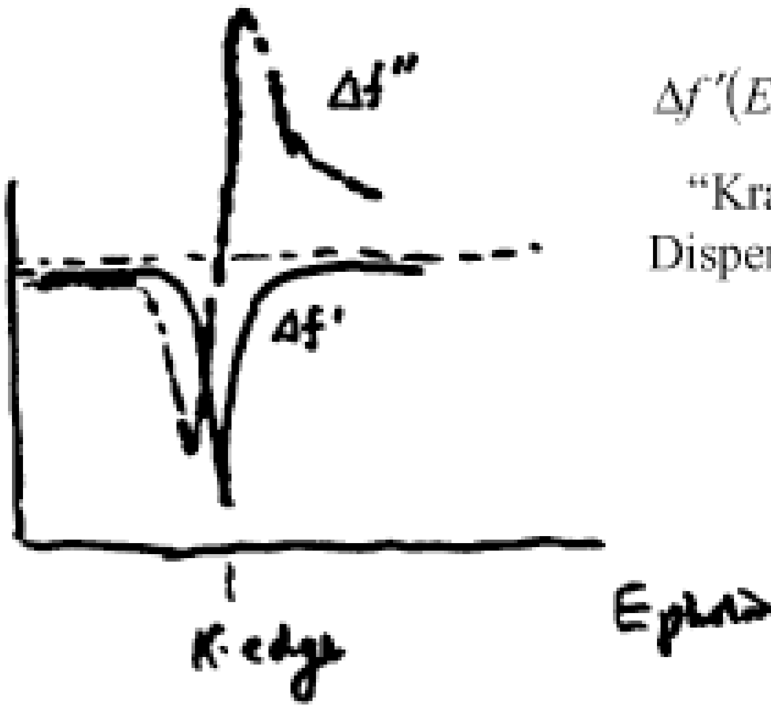
X-rays

$$f = f_0 + \underbrace{\Delta f' + i\Delta f''}_{\text{"anomalous" big at edges}}$$

"Scattering factor" $= Zf(q)$

"anomalous" big at edges

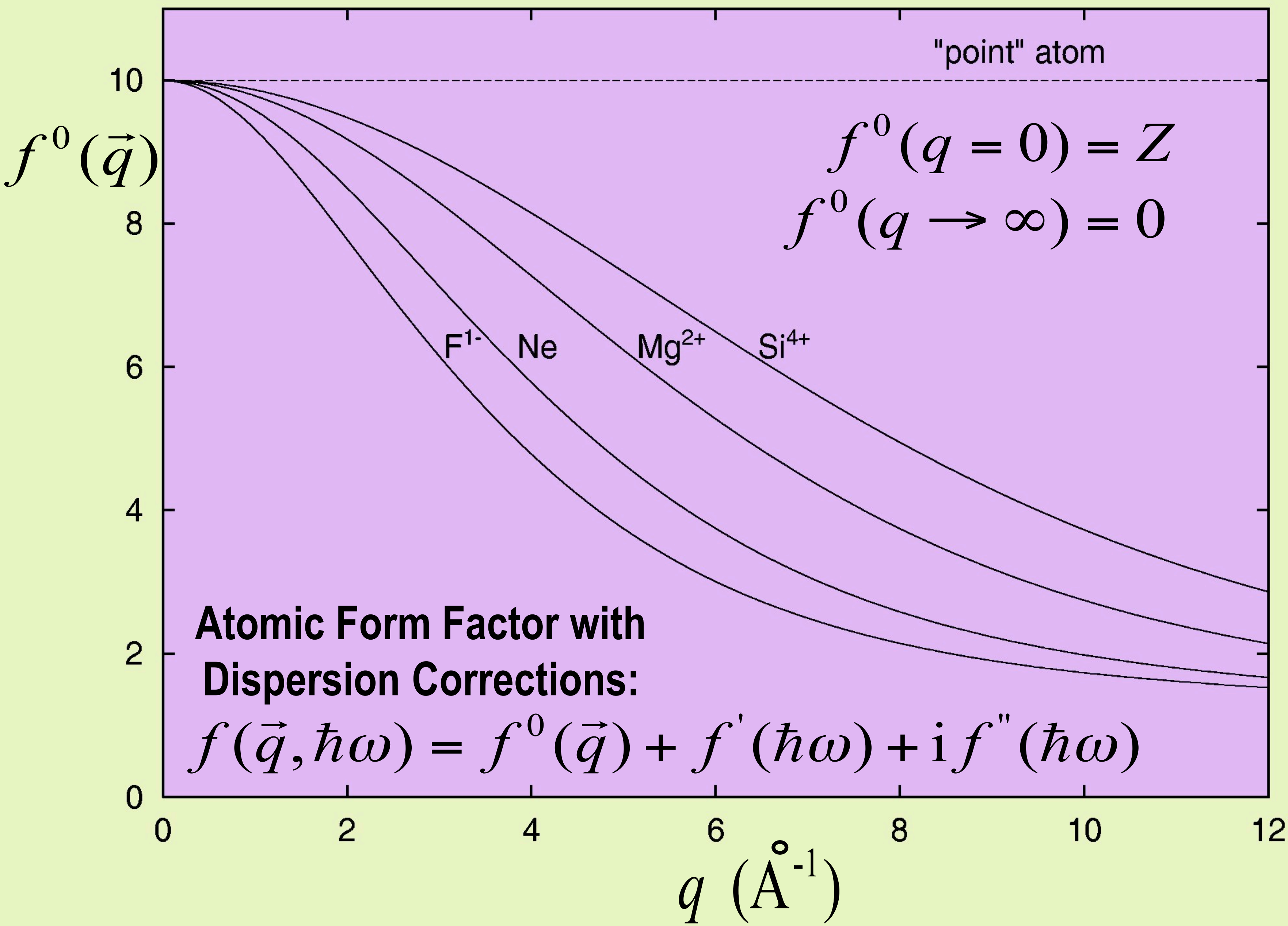




$$\Delta f'(E) = 2\pi \int \frac{\Delta f''(E')}{E - E'}\, dE'$$

"Kramers-Kronig Dispersion Relations

Atomic Form Factor: $f^{0}(\vec{q}) = \int \rho(\vec{r})\, e^{i\vec{q}\cdot\vec{r}}\, \mathrm{d}V$



$$f^{0}(\vec{q})$$

$$q\ (\text{Å}^{-1})$$

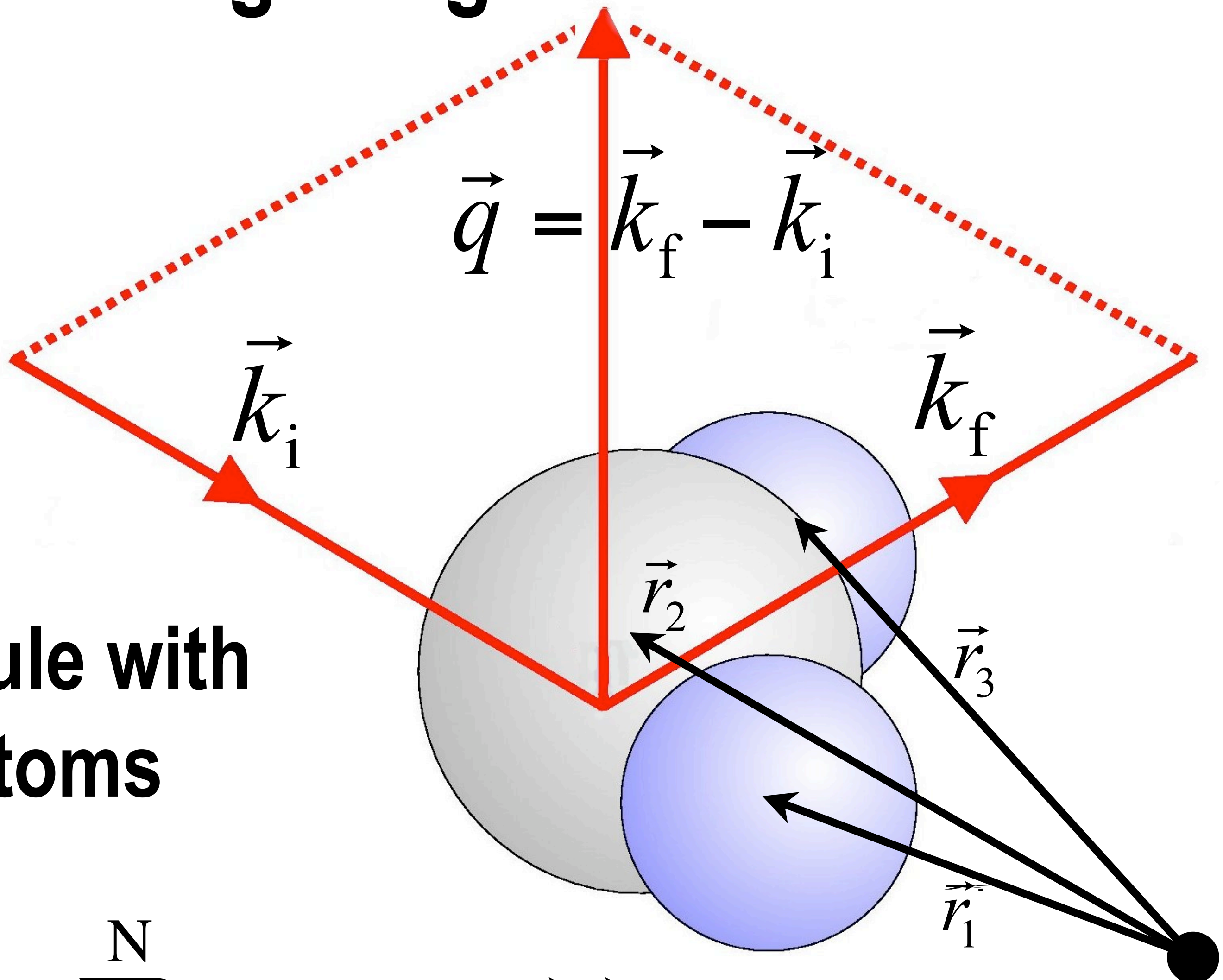
$$f^{0}(q = 0) = Z$$

$$f^{0}(q \rightarrow \infty) = 0$$

Atomic Form Factor with Dispersion Corrections:

$$f(\vec{q}, \hbar\omega) = f^{0}(\vec{q}) + f^{'}(\hbar\omega) + \mathrm{i}\, f^{''}(\hbar\omega)$$

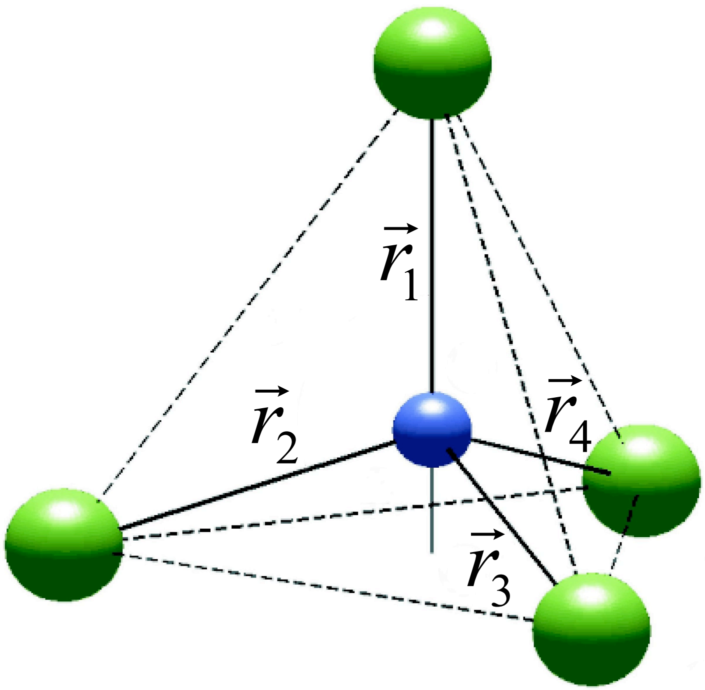
Scattering Length of a Molecule

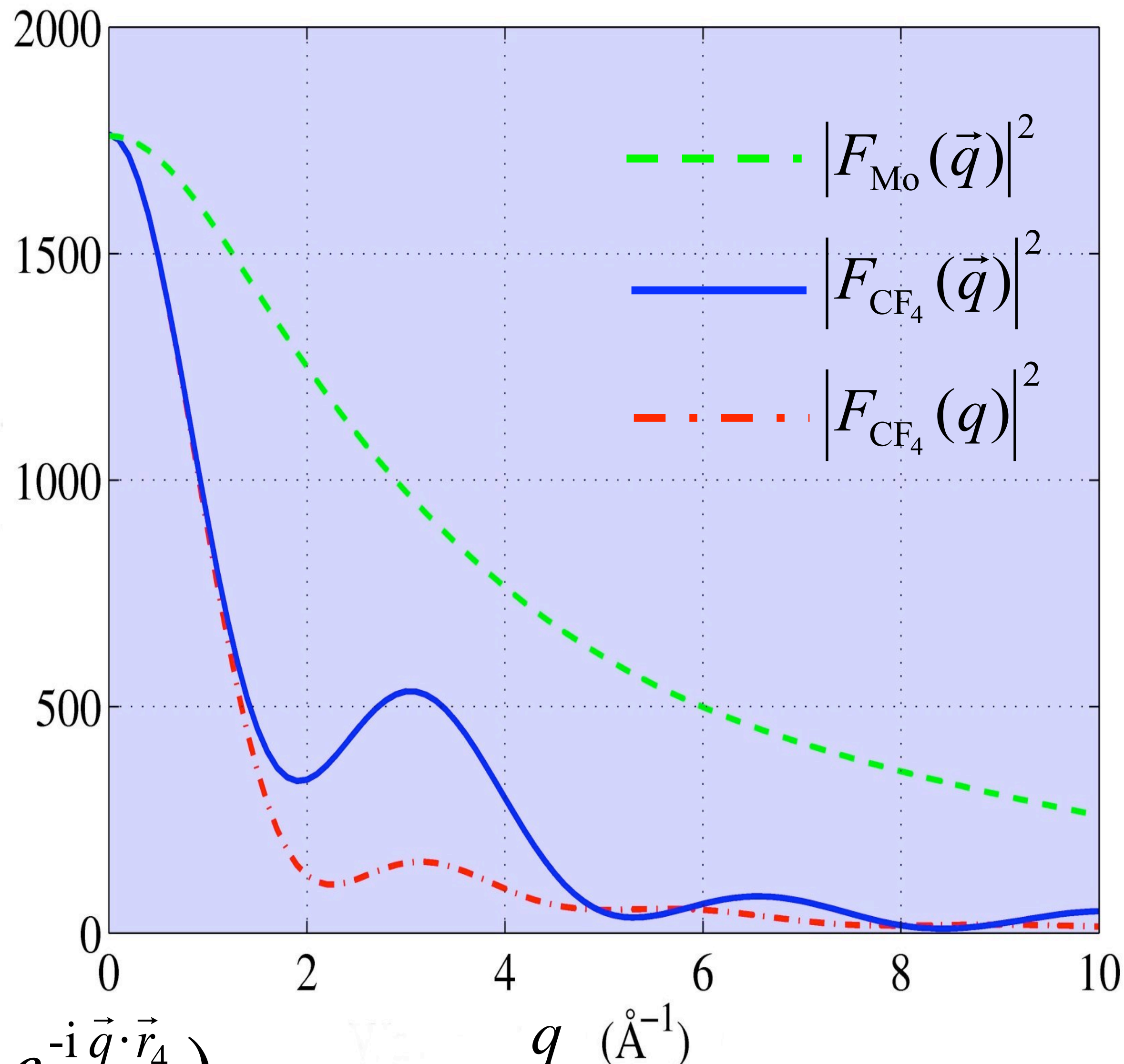


Molecule with N Atoms

$$F_{\text{mol.}}(\vec{q}) = \sum_{j=1}^{N} f_j(\vec{q})\, e^{-i\,\vec{q}\cdot\vec{r}_j}$$

Example: CF_4 - Molecule

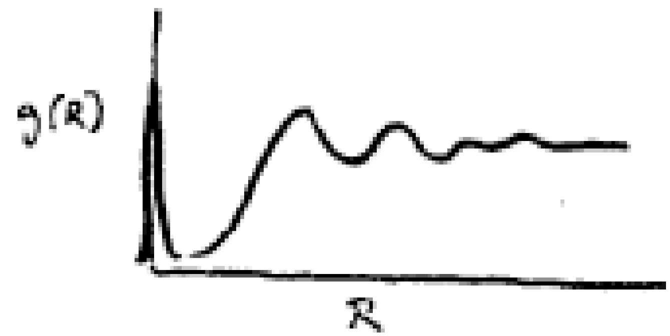




$$F_{\mathrm{CF_4}}(\vec{q}) = f_{\mathrm{C}}(\vec{q}) + \\ + f_{\mathrm{F}}(\vec{q})(e^{-i\,\vec{q}\cdot\vec{r}_1} + \\ + e^{-i\,\vec{q}\cdot\vec{r}_2} + e^{-i\,\vec{q}\cdot\vec{r}_3} + e^{-i\,\vec{q}\cdot\vec{r}_4})$$

Liquids and Glasses

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



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

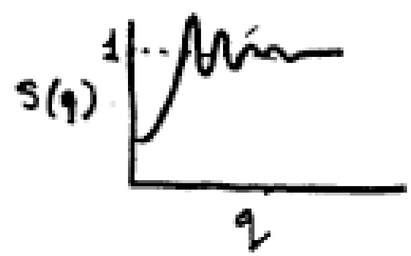
$$\Rightarrow S(q) = \iint d\vec{r}\, d\vec{r}\,'\, e^{-i\vec{q}\cdot(\vec{r}-\vec{r}\,')} \langle \rho_N(r)\rho_N(r')\rangle$$

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

Liquids and Glasses

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

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



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

$g(\vec{R})$ = 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)

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

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

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

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

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)

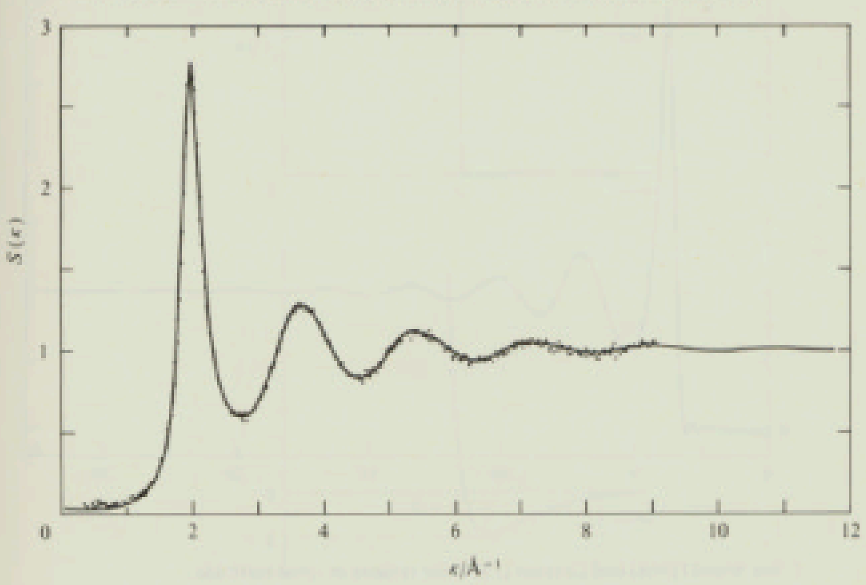


Fig. 5.1 The structure factor $S(\kappa)$ for ^{36}Ar at 85 K. The curve through the experimental points is obtained from a molecular dynamics calculation of Verlet based on a Lennard-Jones potential. (After Yarnell *et al.*, 1973.)

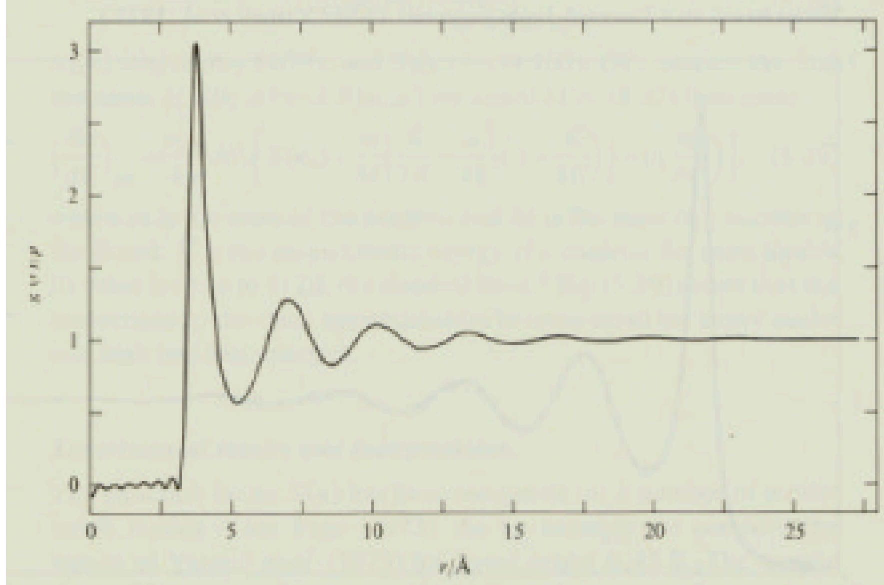


Fig. 5.2 The pair-distribution function $g(r)$ obtained from the experimental results in Fig. 5.1. The mean number density is $\rho = 2.13 \times 10^{28}$ atoms m^{-3}. (After Yarnell *et al.*, 1973.)

Neutrons

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

More than one kind of atom

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)

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

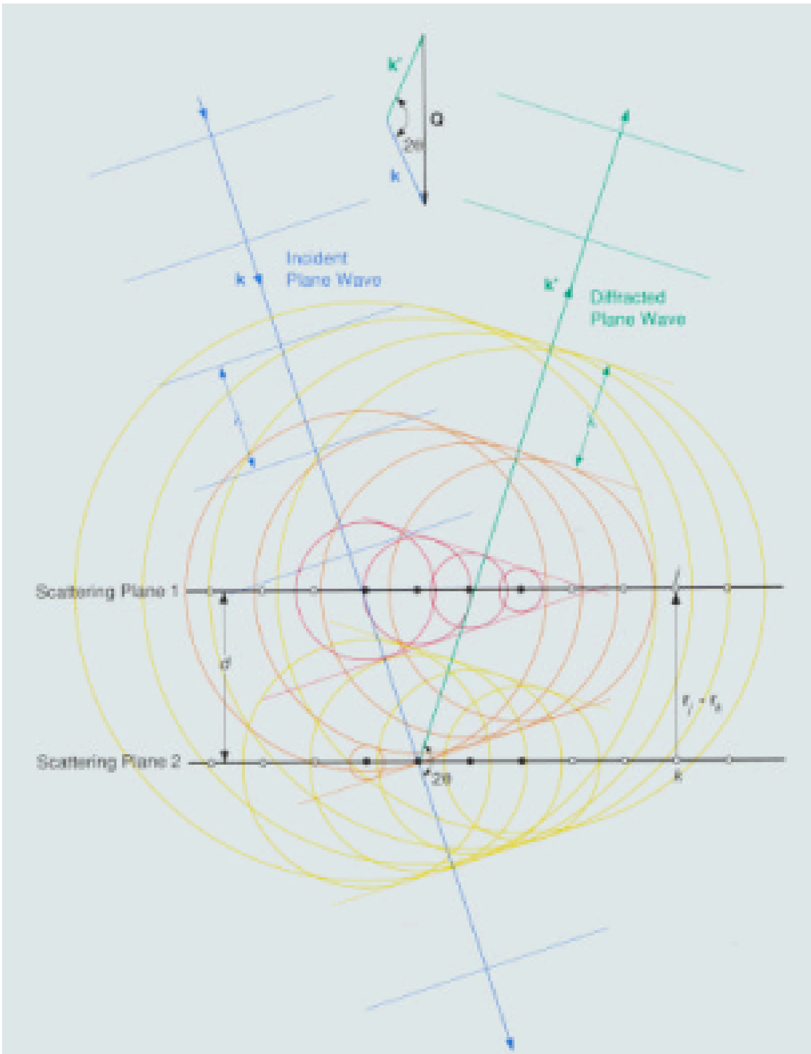
$\Rightarrow$ partial structure factor

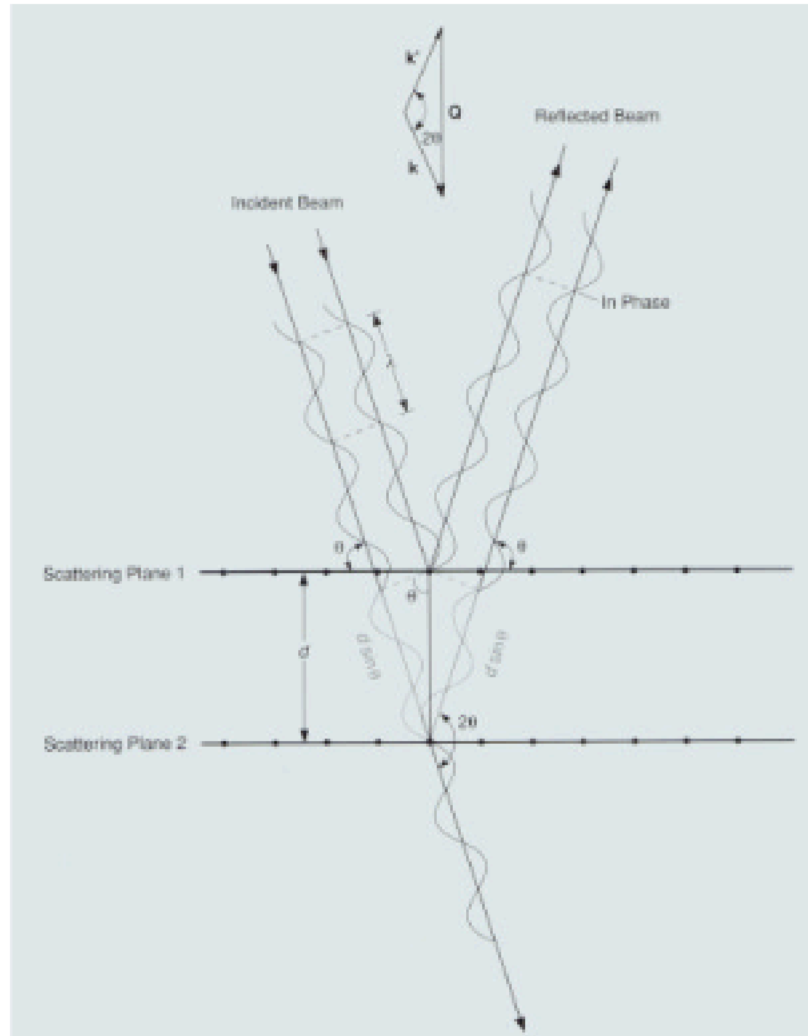
These can be unscrambled by simultaneous measurements of $\frac{d\sigma}{d\Omega}$ for neutrons, different isotopes + x-rays.

CRYSTALS

For Periodic Arrays of Nuclei, Coherent Scattering Is Reinforced Only in Specific Directions Corresponding to the Bragg Condition:

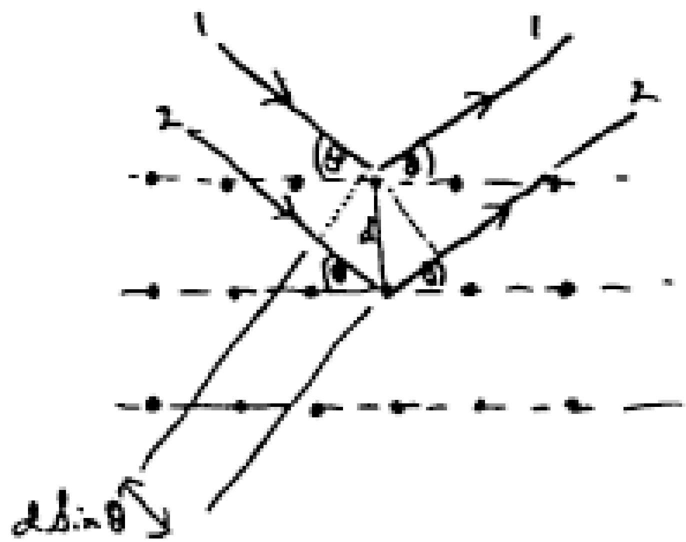
$$\lambda = 2\, d_{hkl} \sin(\theta) \text{ or } 2\, k \sin(\theta) = G_{hkl}$$





In general, in a scattering experiment

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



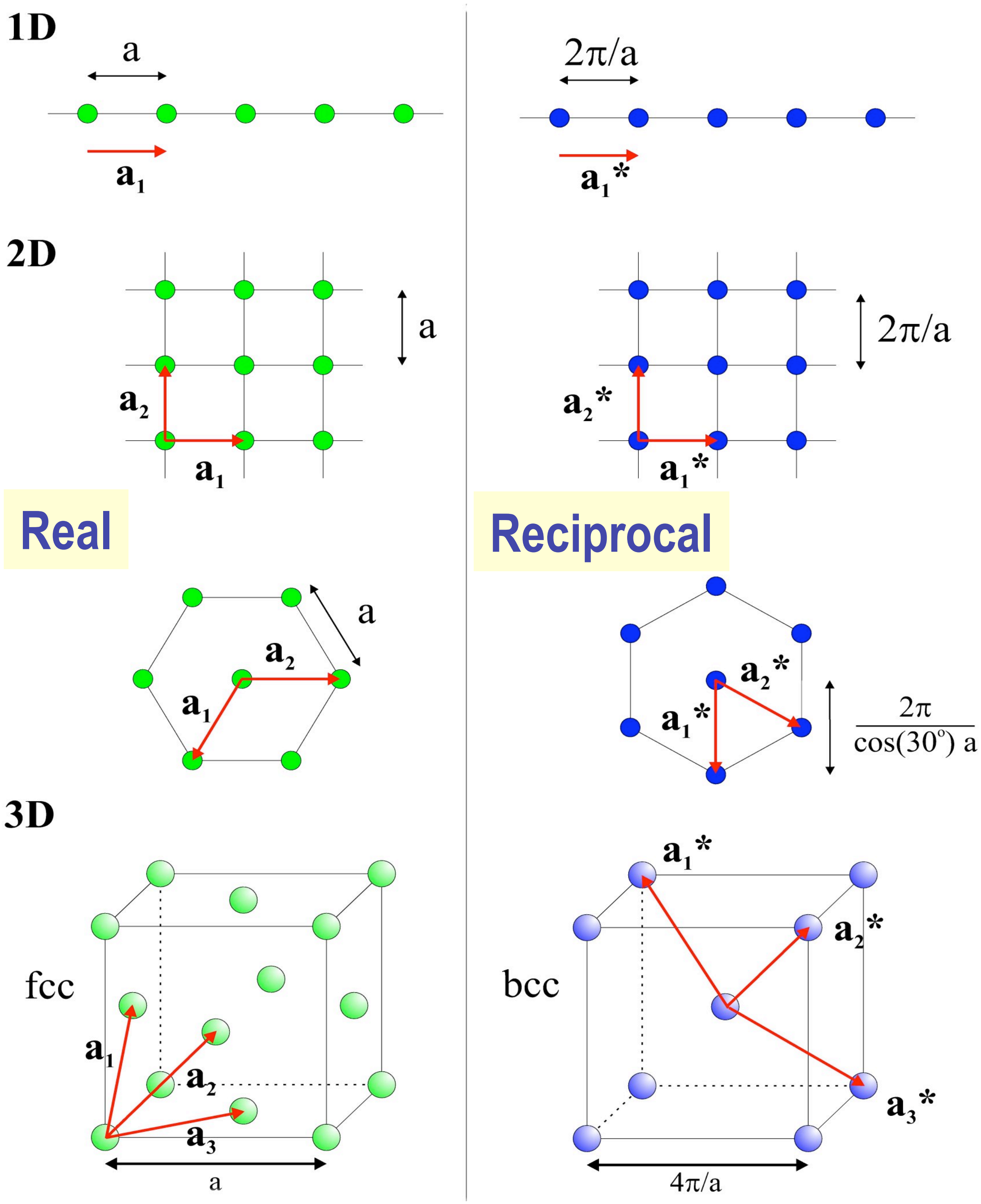
A simple way to see Bragg's Law:

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

$\therefore$ Constructive interference when

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

Reciprocal Lattice:



$$V_c = \vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)$$

$$\vec{a}_1^* = \frac{2\pi}{V_c} \vec{a}_2 \times \vec{a}_3$$

$$\vec{a}_2^* = \frac{2\pi}{V_c} \vec{a}_3 \times \vec{a}_1$$

$$\vec{a}_3^* = \frac{2\pi}{V_c} \vec{a}_1 \times \vec{a}_2$$

Define 3 other vectors:

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

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

$$v_0 = \vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)$$
= 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 $\vec{G}, \vec{R}_\ell$,

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

$|\mathbf{G}| = n\, 2\pi/d$ ←←←←

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 = $e^{-\left\langle (\bar{q}\cdot\bar{u})^2 \right\rangle}$ $\Rightarrow$ Debye-Waller factor)

Similarly,

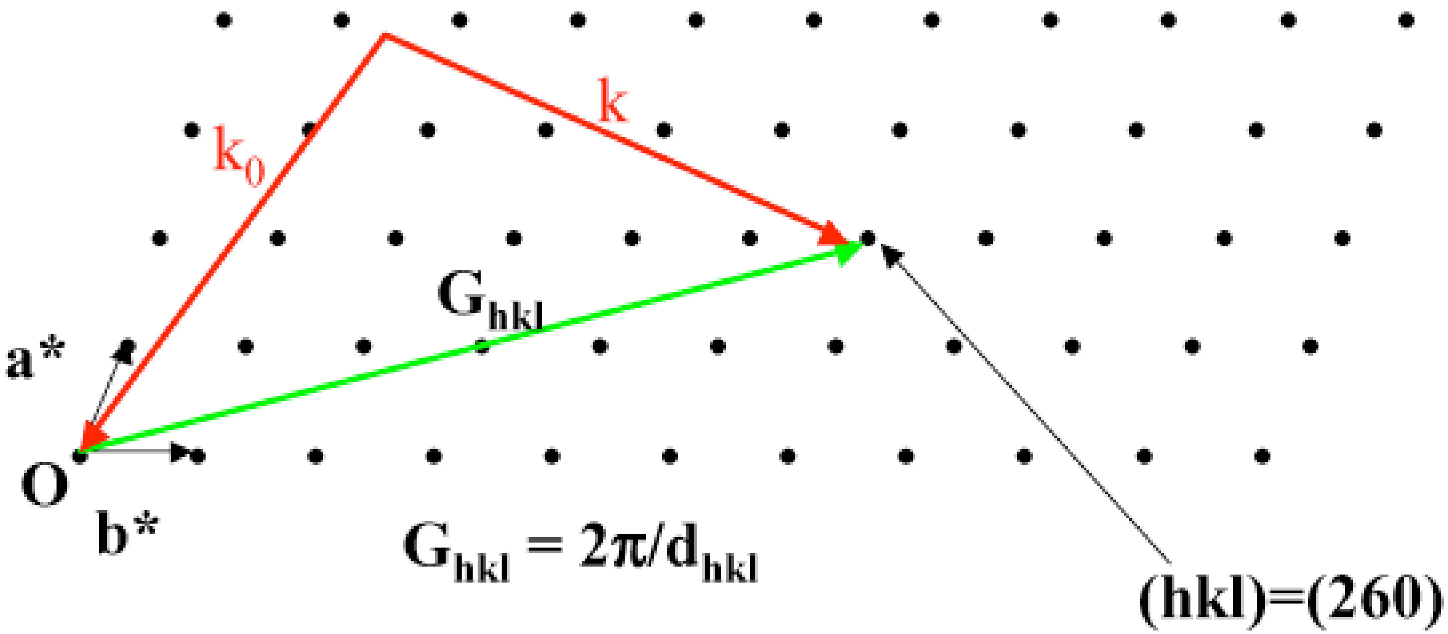
$$\boxed{\begin{aligned}\left(\frac{d\sigma}{d\Omega}\right)_{x-rays} = Z^2 r_0^2 \left(\frac{1+\mathrm{Cos}^2(2\theta)}{2}\right) f^2(\bar{q})e^{-2W} \\ N\cdot\frac{(2\pi)^3}{v_0}\sum_{\bar{G}}\delta(\bar{q}-\bar{G})\end{aligned}}$$

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

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

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

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

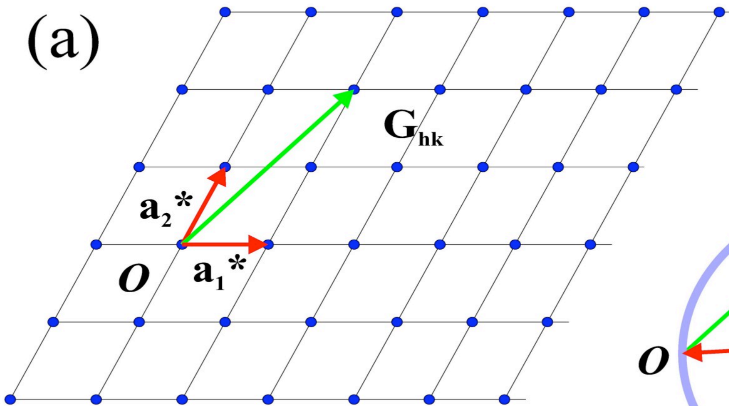


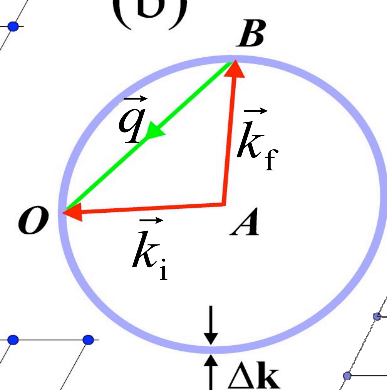
$$G_{hkl} = 2\pi/d_{hkl}$$

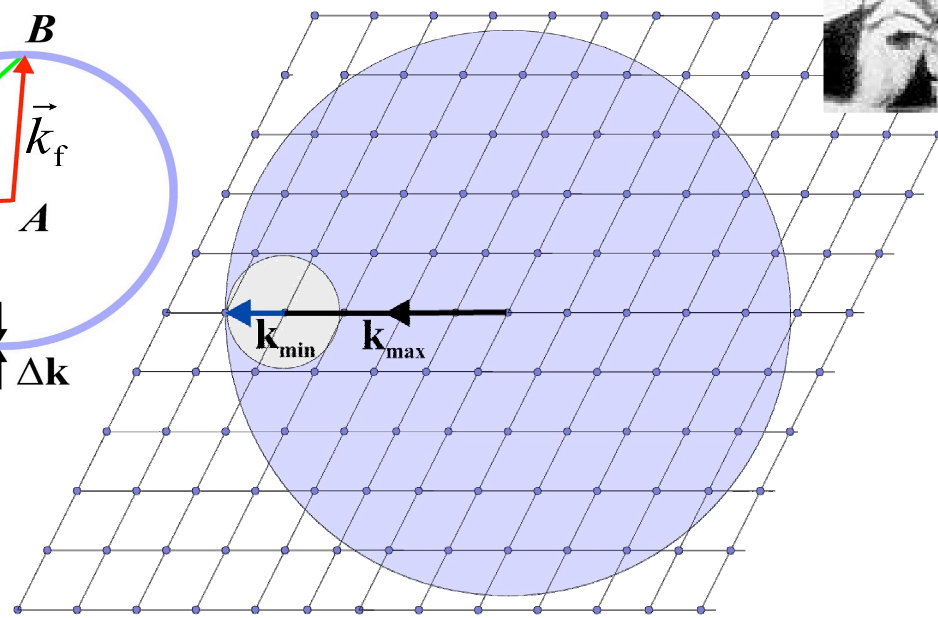
$$a^* = 2\pi(b \times c)/V_0, \text{ etc.}$$

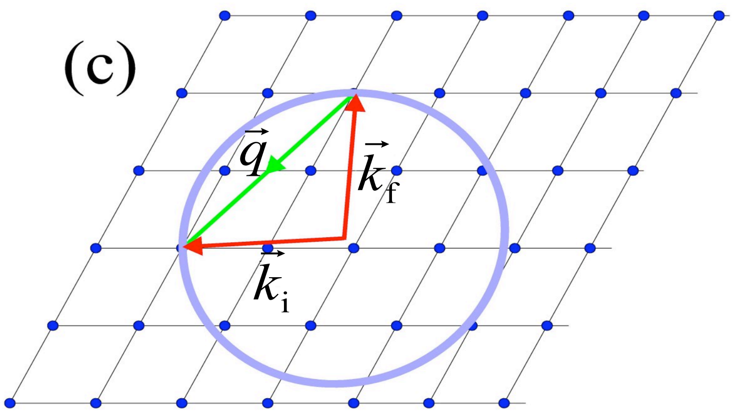
A single crystal has to be aligned precisely to record Bragg scattering

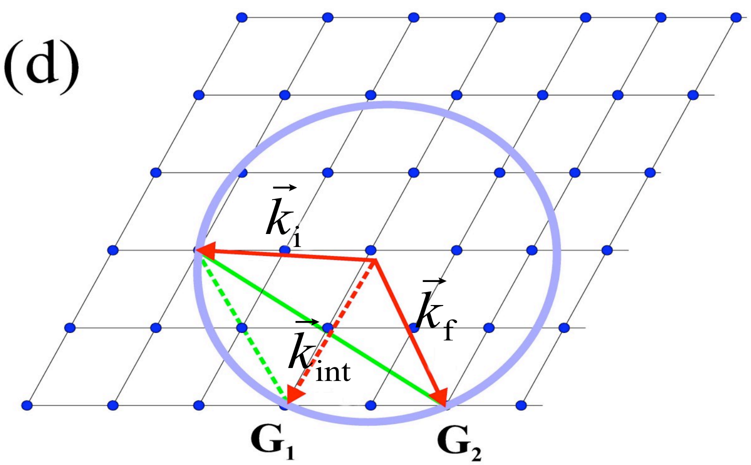
Ewald-Construction

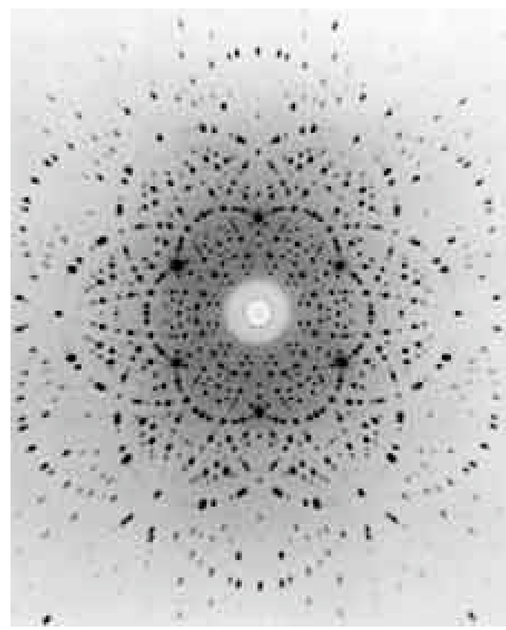












Laue Pattern of Beryllium-Aluminum-Silicate ("Beryl")

Elastic Scattering from a Crystal

Differential Scattering Cross Section

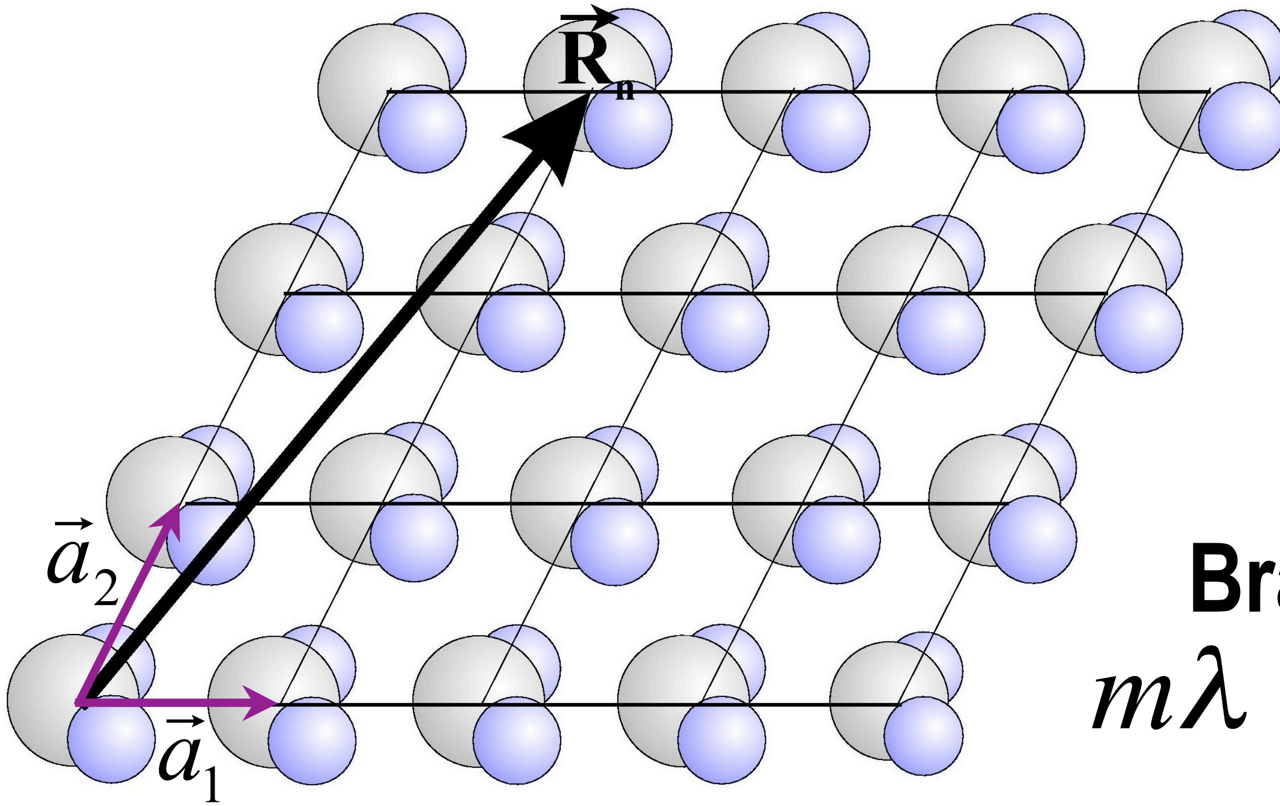
$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = \left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\right)_0 S(\vec{q})$$

Intrinsic Cross Section
Coupling Beam ⇔ Sample

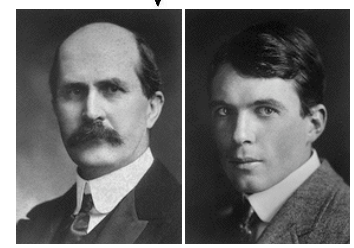
Properties of the Sample without Beam

$$S(\vec{q}) = \left|F_{\mathrm{crystal}}(\vec{q})\right|^2$$

Scattering from a Crystal



d



Bragg's Law:

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

$$F_{\text{crystal}}(\vec{q}) = \left(\sum_{j=1}^{N} f_j(\vec{q})\, e^{i\,\vec{q}\cdot\vec{r}_j}\right)\cdot\left(\sum_{n=1}^{M} e^{i\,\vec{q}\cdot\vec{R}_n}\right)$$

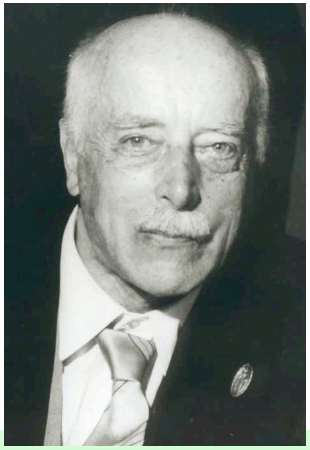
Unit Cell Structure Factor $F_{uc}(\vec{q})$

Lattice Sum

$$F_{\text{crystal}}(\vec{q}) = \left(\sum_{j=1}^{N} f_j(\vec{q})\, e^{-i\,\vec{q}\cdot\vec{r}_j}\right)\cdot\left(\sum_{n=1}^{M} e^{-i\,\vec{q}\cdot\vec{R}_n}\right)$$

Unit Cell Structure Factor — Lattice Sum

$$\sum_{n=1}^{M} e^{-i\,\vec{q}\cdot\vec{R}_n} \approx \begin{cases} M \gg 1 & \text{for } \vec{q}\cdot\vec{R}_n = 2\pi\times\text{integer} \\ 0 & \text{otherwise} \end{cases}$$



Reciprocal Lattice:

$$\vec{R}_n = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$$

$$\vec{a}_i\cdot\vec{a}_j^{\,*} = 2\pi\delta_{ij} \qquad i,j = 1,2,3$$

$$\vec{G}_{hkl} = h\vec{a}_1^{\,*} + k\vec{a}_2^{\,*} + l\vec{a}_3^{\,*}$$

$$\vec{G}_{hkl}\cdot\vec{R}_n = 2\pi(hn_1 + kn_2 + ln_3)$$

Laue Condition

$$\vec{q} = \vec{G}_{hkl}$$

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

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

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 $\rightarrow$ Structure

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

$\rightarrow$ "Phase Problem" $\rightarrow$ 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.

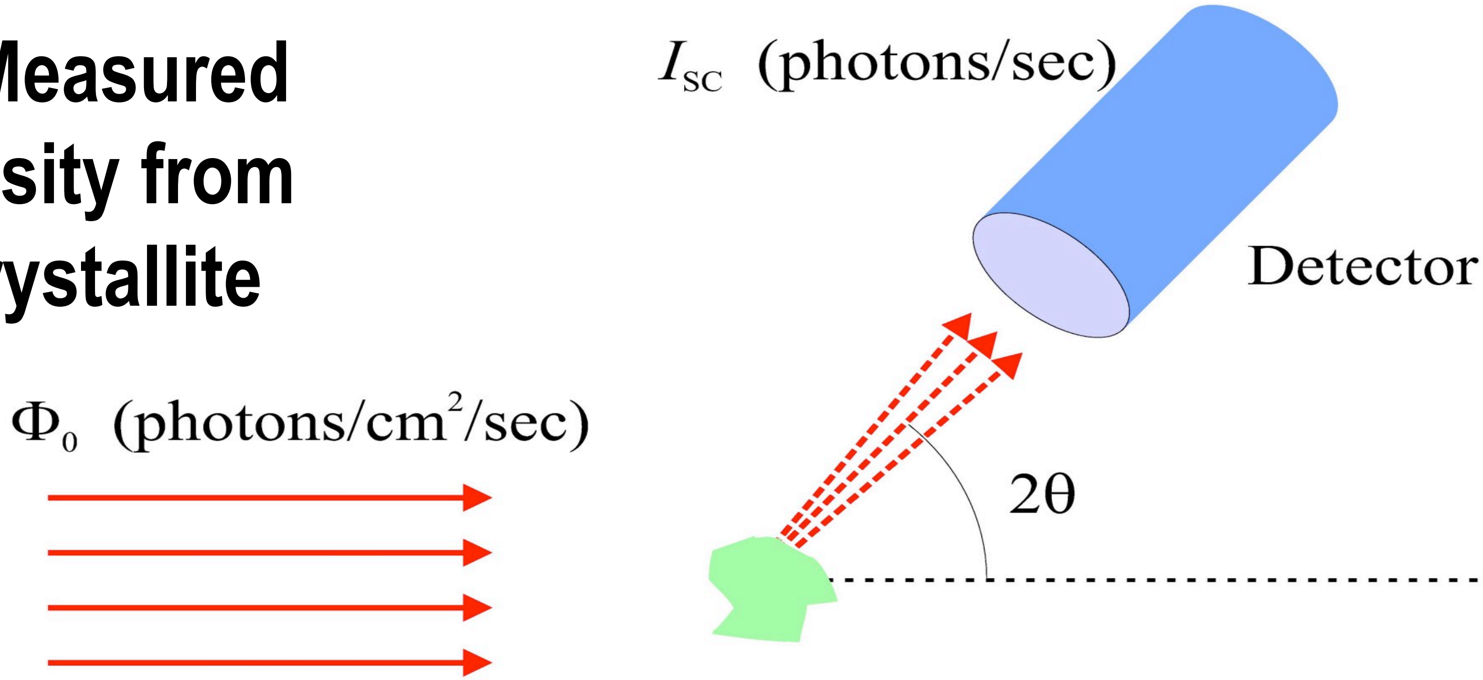
We would be better off if diffraction measured phase of scattering rather than amplitude! Unfortunately, nature did not oblige us.

Figure 1.2

A graphic illustration of the phase problem: (a) and (b) are the original images. (c) is the (Fourier) reconstruction which has the Fourier phases of (a) and Fourier amplitudes of (b); (d) is the reconstruction with the phases of (b) and the amplitudes of (a).

Picture by courtesy of D. Sivia

The Measured Intensity from a Crystallite



$$\left(\frac{d\sigma}{d\Omega}\right) = \frac{\text{Number of Photons Scattered per Second into } d\Omega}{(\text{Incident Flux})\,(d\Omega)}$$

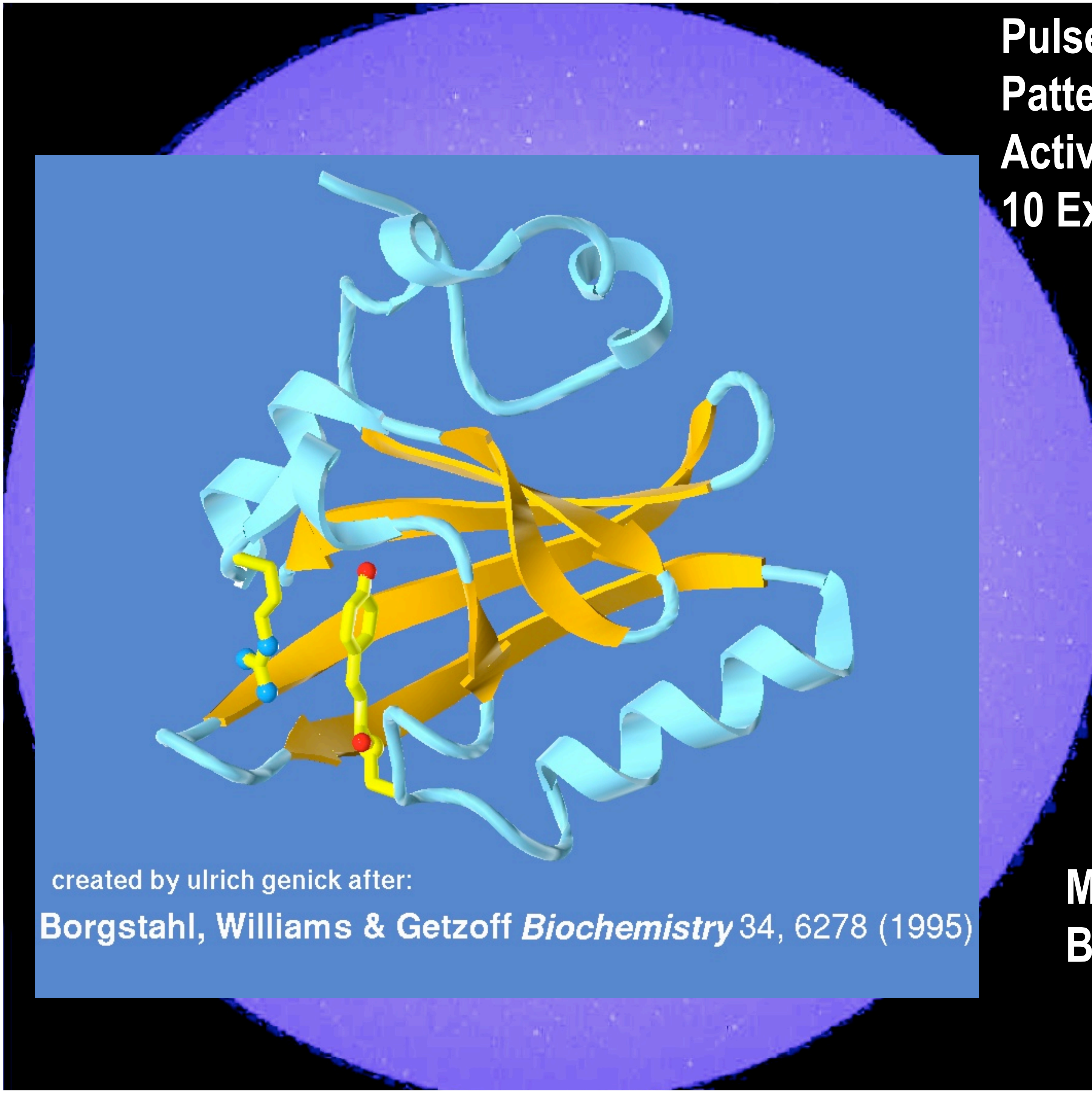
$$\left(\frac{d\sigma}{d\Omega}\right) = r_0^2 P \left|F_{hkl}(\vec{q})\right|^2 M V_c^* \,\delta(\vec{q} - \vec{G}_{hkl})$$

Thomson Scattering of an Electron

Structure Factor of the Unit Cell

Number of Unit Cells

Reciprocal Space Unit Cell Volume



created by ulrich genick after:
Borgstahl, Williams & Getzoff *Biochemistry* 34, 6278 (1995)

Pulsed Laue Diffraction Pattern from the Photo-Active Yellow Protein: 10 Exposures of 100 ps

↓

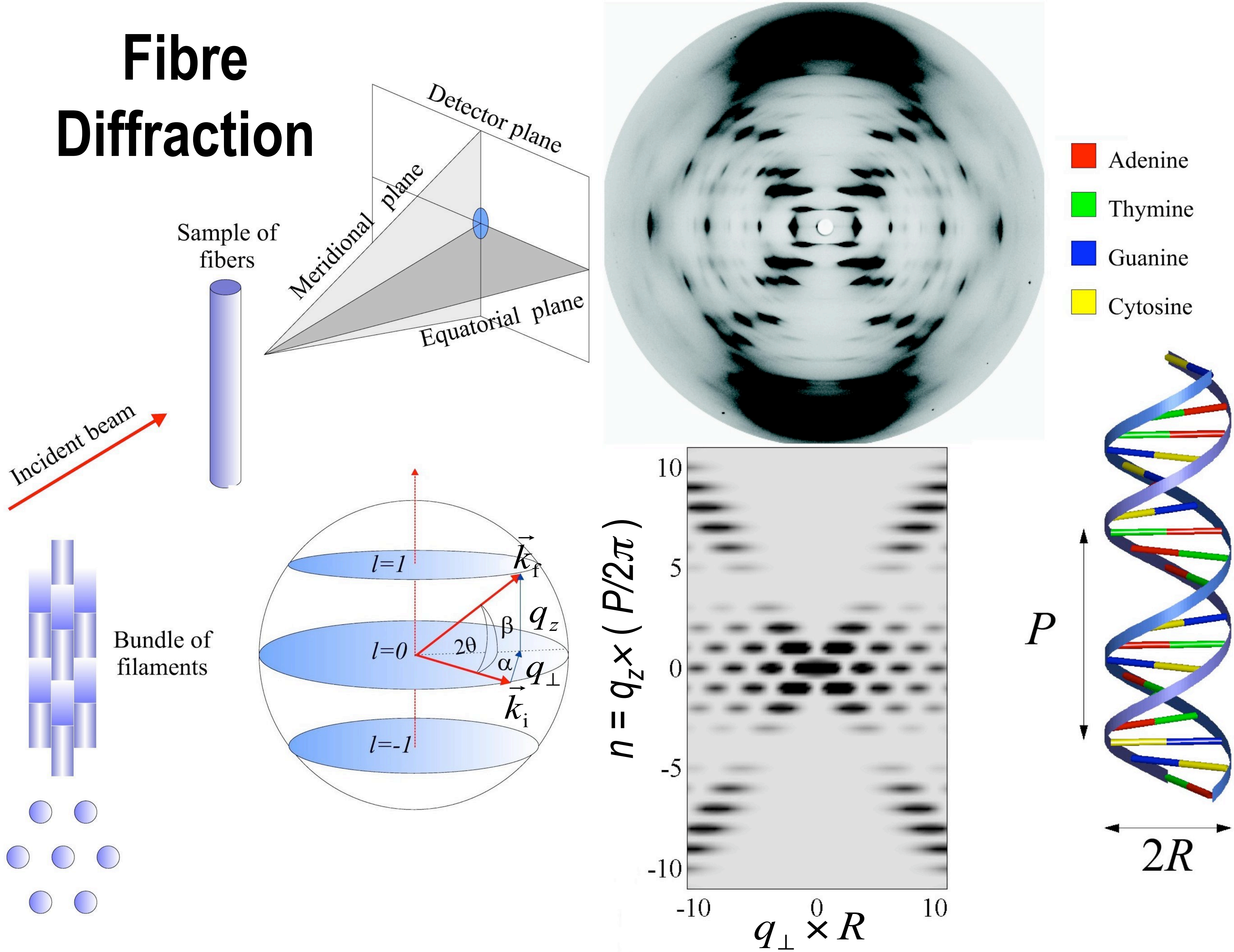
3700 Reflections with $|F_{hkl}(q)|^2$

↓

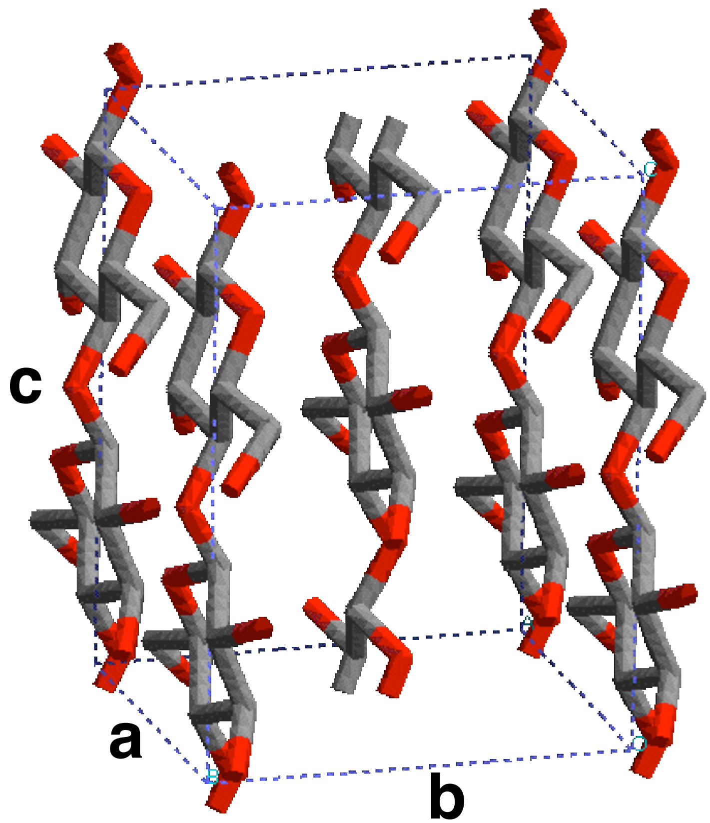
STRUCTURE

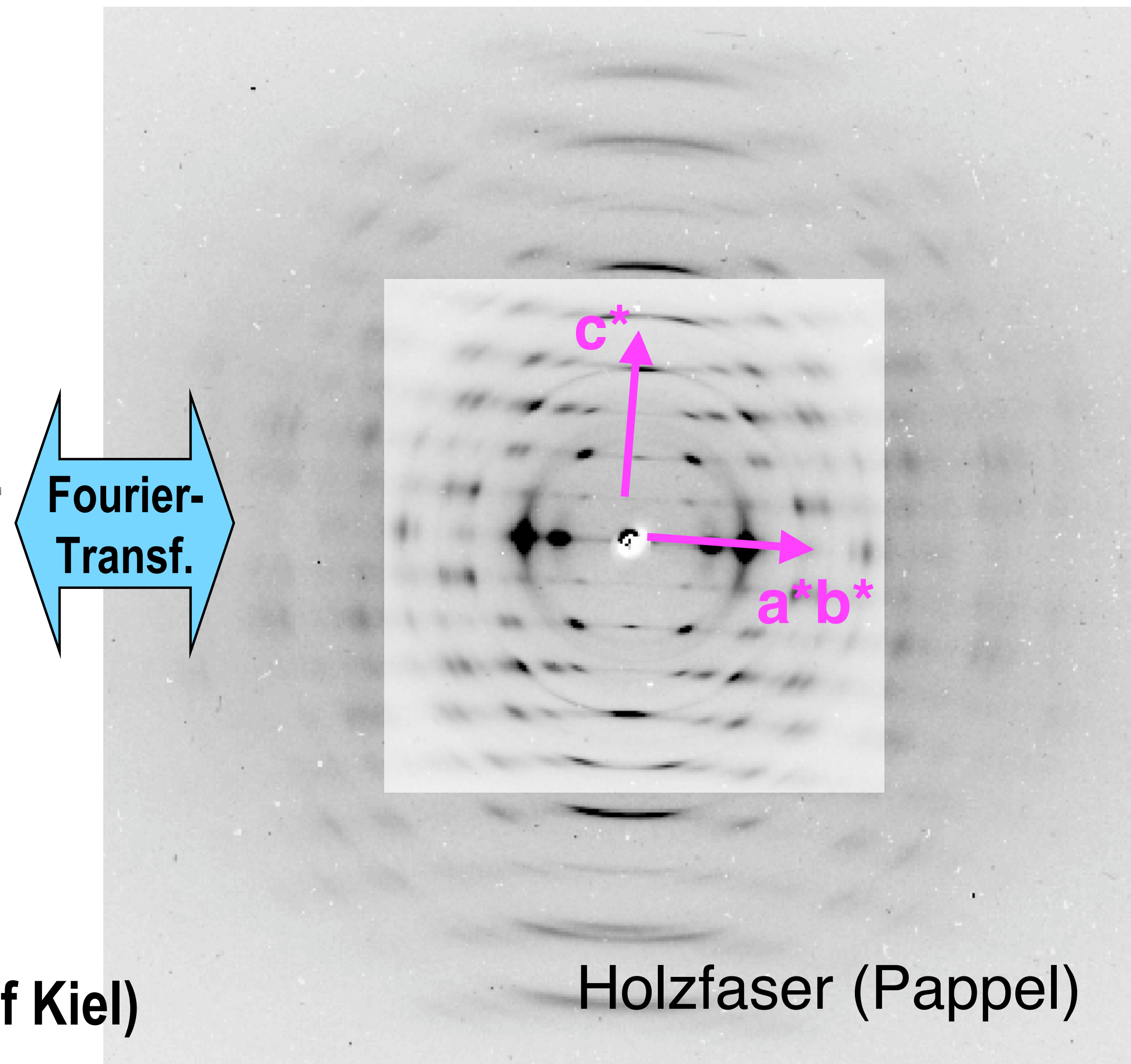
M. Wulff (ESRF)
B. Perman (Univ. of Chicago)

Fibre Diffraction



Fibre Diffraction: Cellulose

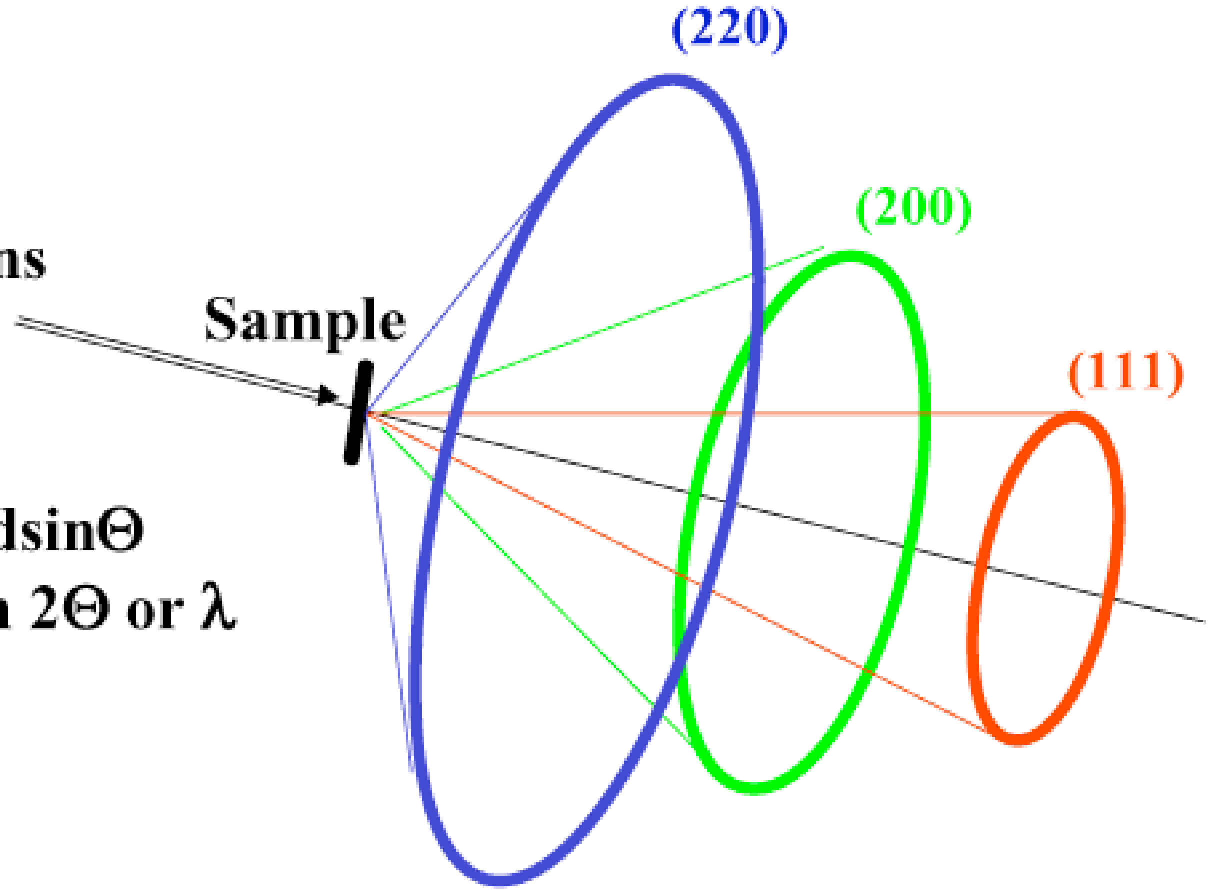




M. Müller et al. (University of Kiel)

Powder Diffraction gives Scattering on Debye-Scherrer Cones

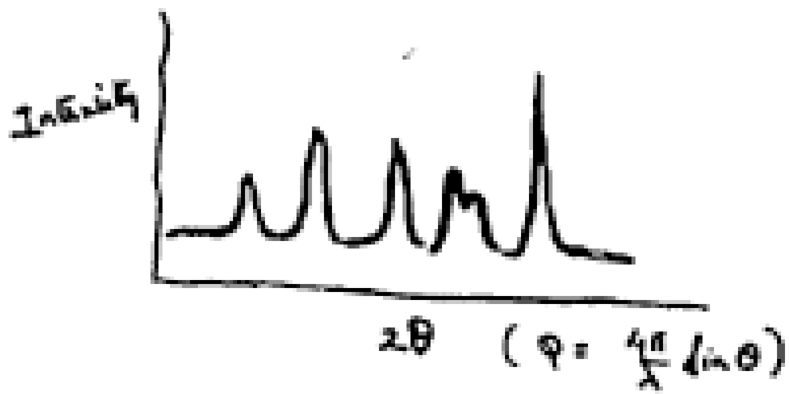
Incident beam
x-rays or neutrons



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.

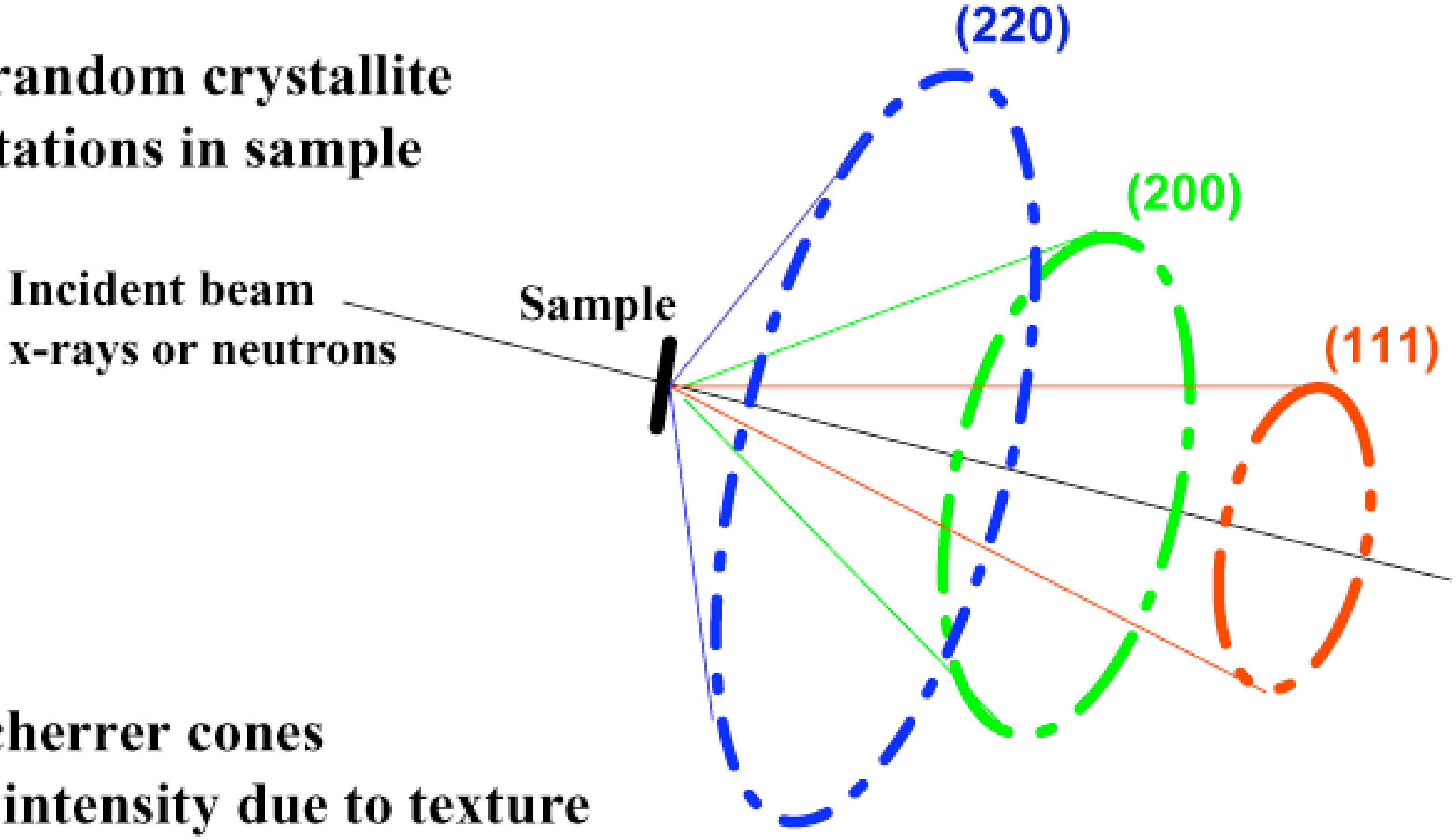


$2\theta =$ scattering angle

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

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 <u>independent</u> of q_z.

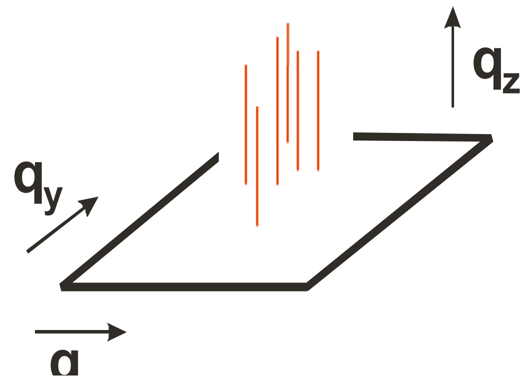
$$S(q) \propto \sum_{G_{||}} \delta\left(\bar{q}_{||} - \bar{G}_{||}\right)$$

where

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

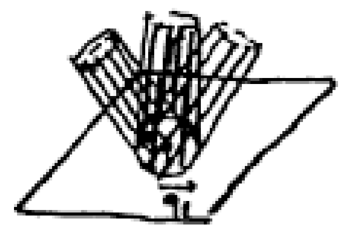
$\bar{q}_{||}$ is (x,y) plane component of $\bar{q}$

$\Rightarrow$ diffraction is on <u>rods</u> in reciprocal space through the $\bar{G}_{||}$ 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)

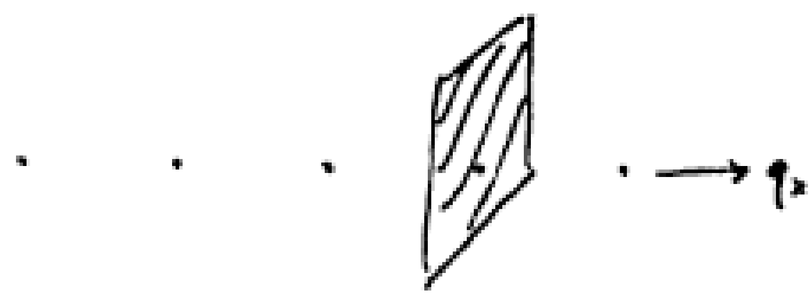
<u>Powders of 2-D Crystals</u>



asymmetric (saw-tooth) powder peak shape

(Warren)

1-D Crystals



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

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

$$\frac{d\sigma}{d\Omega} = \left\langle \sum_{\ell\ell'} [b_1\rho_\ell + b_2(1-\rho_\ell)][b_1\rho_{\ell'} + b_2(1-\rho_{\ell'})] \right.$$

$$\left. \times \left[e^{-i\vec{q}\cdot\left(\vec{R}_\ell - \vec{R}_{\ell'}\right)} \right] \right\rangle$$

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

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

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

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

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

2^{nd} 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 (SANS,SAXS)

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

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

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

Single Particles (Dilute Limit)

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)

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

where V is over volume of particle, $f(\bar{q})$ 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 $\bar{r}$ is taken as centroid of particle.

Expanding exponential,

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

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

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

r_G^2 $\quad$ r_G = radius of gyration

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

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

Guinier Approxn.

Scattering for Spherical Particles

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

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

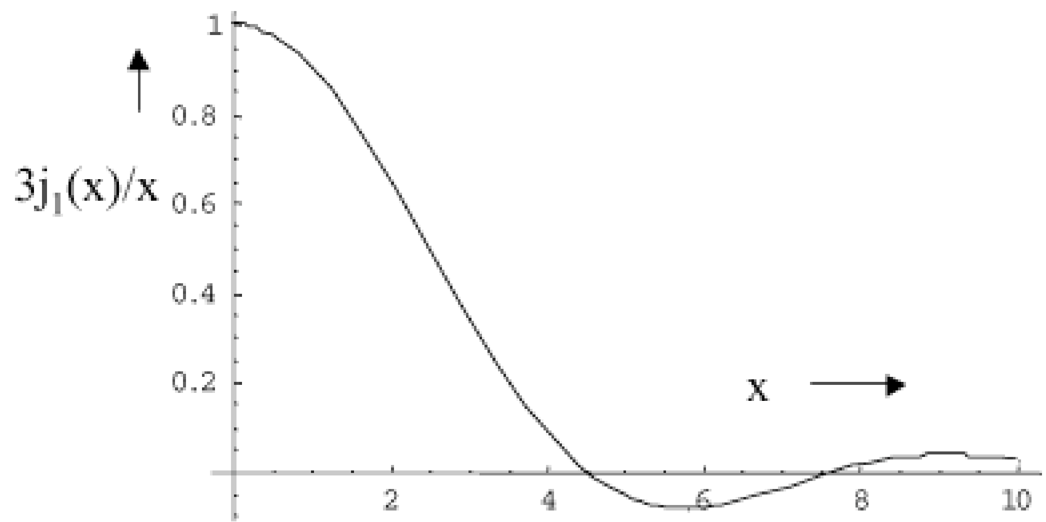
$$\boxed{F_{sphere}(Q) = 3V_0\left[\frac{\sin QR - QR\cos QR}{(QR)^3}\right] \equiv \frac{3V_0}{QR} j_1(QR) \rightarrow V_0 \text{ at } Q = 0}$$

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

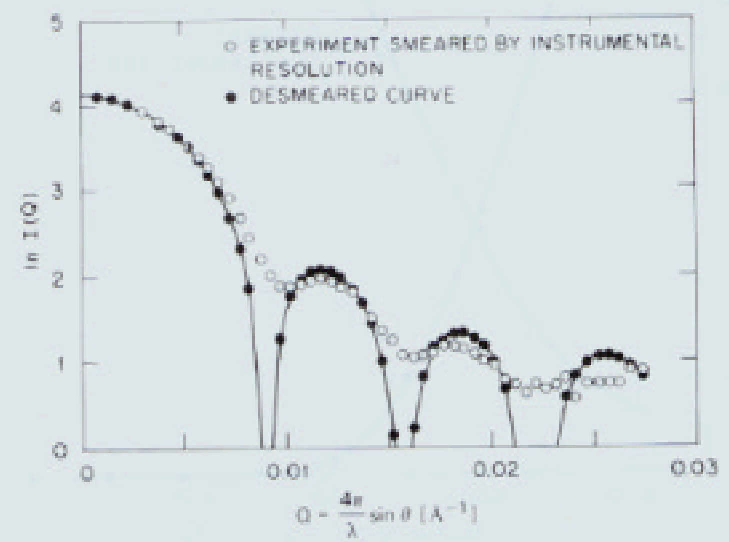
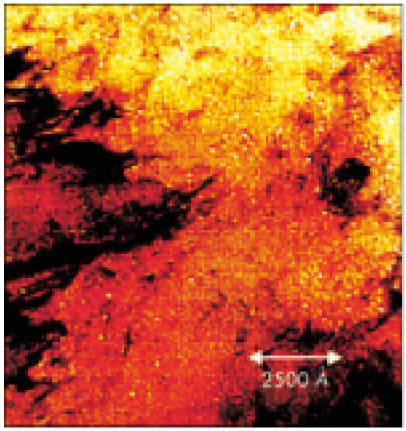
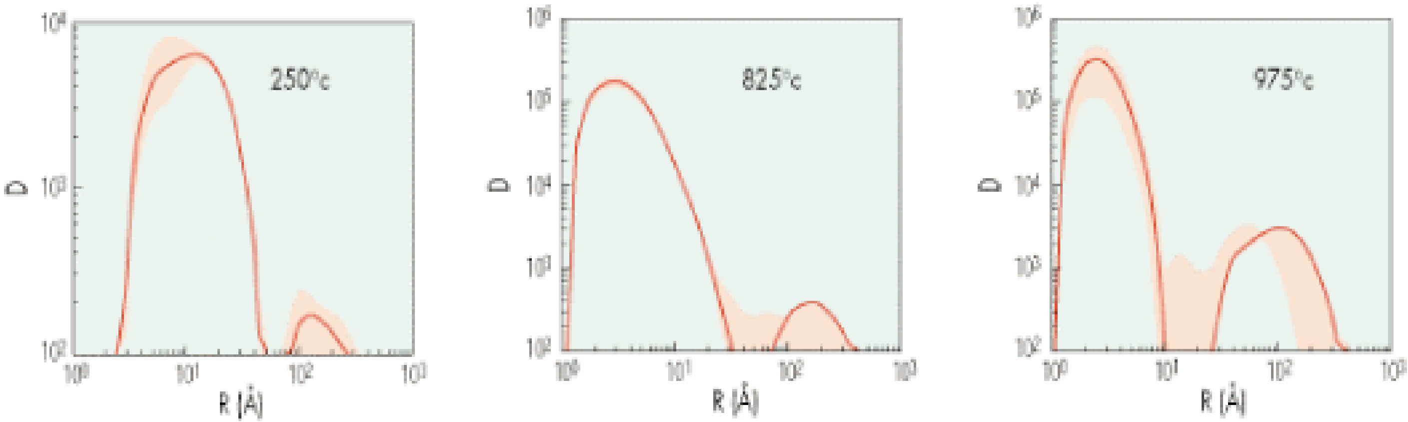


Fig. 4. Plot of ln $I(Q)$ *vs* Q for 3·98 vol.% monodisperse PMMA-H spheres (core $C1$) in D_2O/H_2O mixtures.

Size Distributions Have Been Measured for Helium Bubbles in Steel

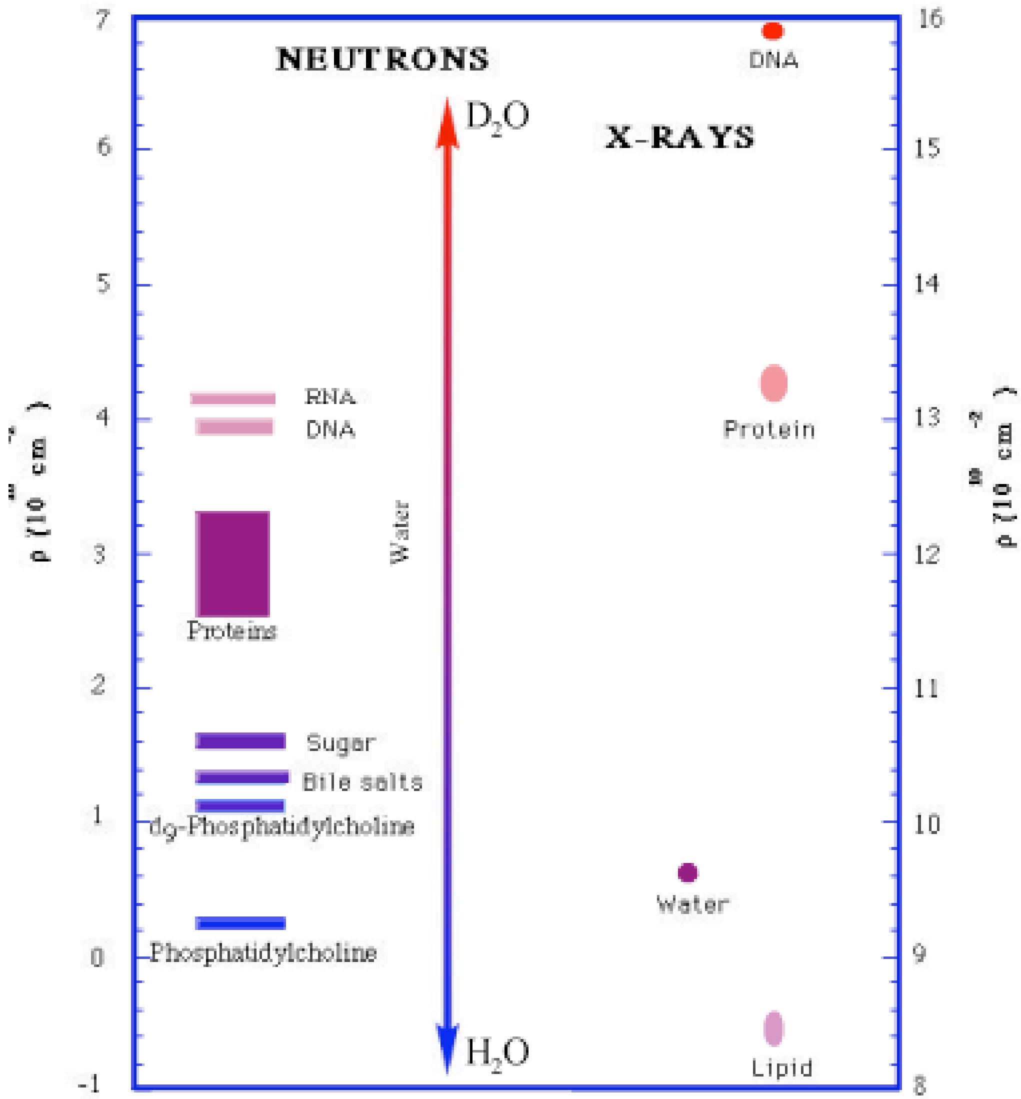
- The growth of He bubbles under neutron irradiation is a key factor limiting the lifetime of steel for fusion reactor walls
  - Simulate by bombarding steel with alpha particles
- TEM is difficult to use because bubble are small
- SANS shows that larger bubbles grow as the steel is annealed, as a result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



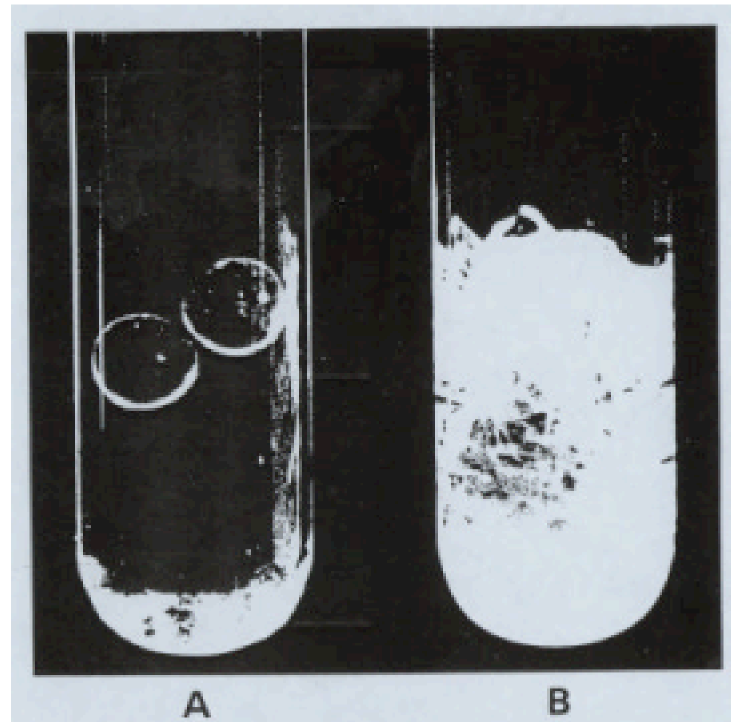


SANS gives bubble volume (arbitrary units on the plots) as a function of bubble size at different temperatures. Red shading is 80% confidence interval.

Contrast & Contrast Matching



* Chart courtesy of Rex Hjelm

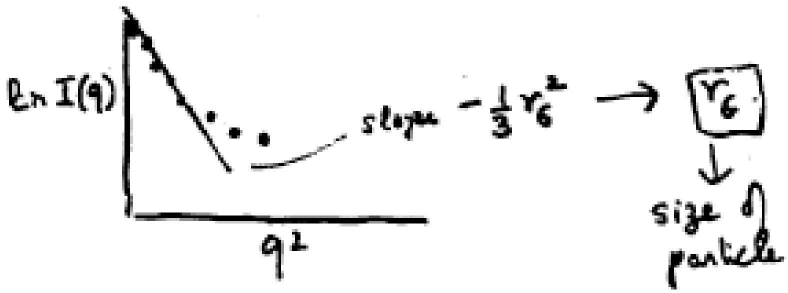


Both tubes contain borosilicate beads + pyrex fibers + solvent. (A) solvent refractive index matched to pyrex;. (B) solvent index different from both beads and fibers – scattering from fibers dominates

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:

- $\begin{Bmatrix}\text{Sizes}\\ \text{Shapes}\end{Bmatrix}$ 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 → Structure Factor ←

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

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

→ Liquid- or glass-like

$\boxed{\text{Fractals}}$ 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

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

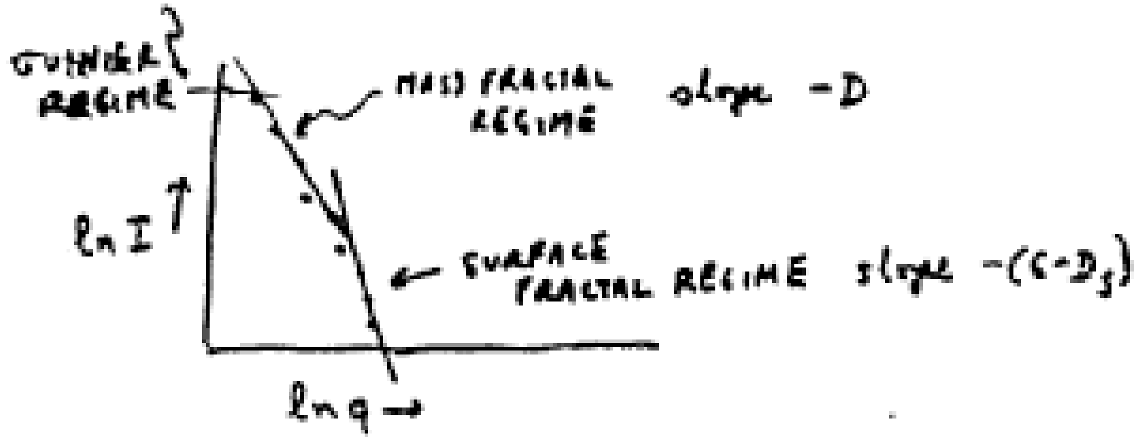
D = Fractal (Hausdorff) Dimension

It follows that

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

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

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



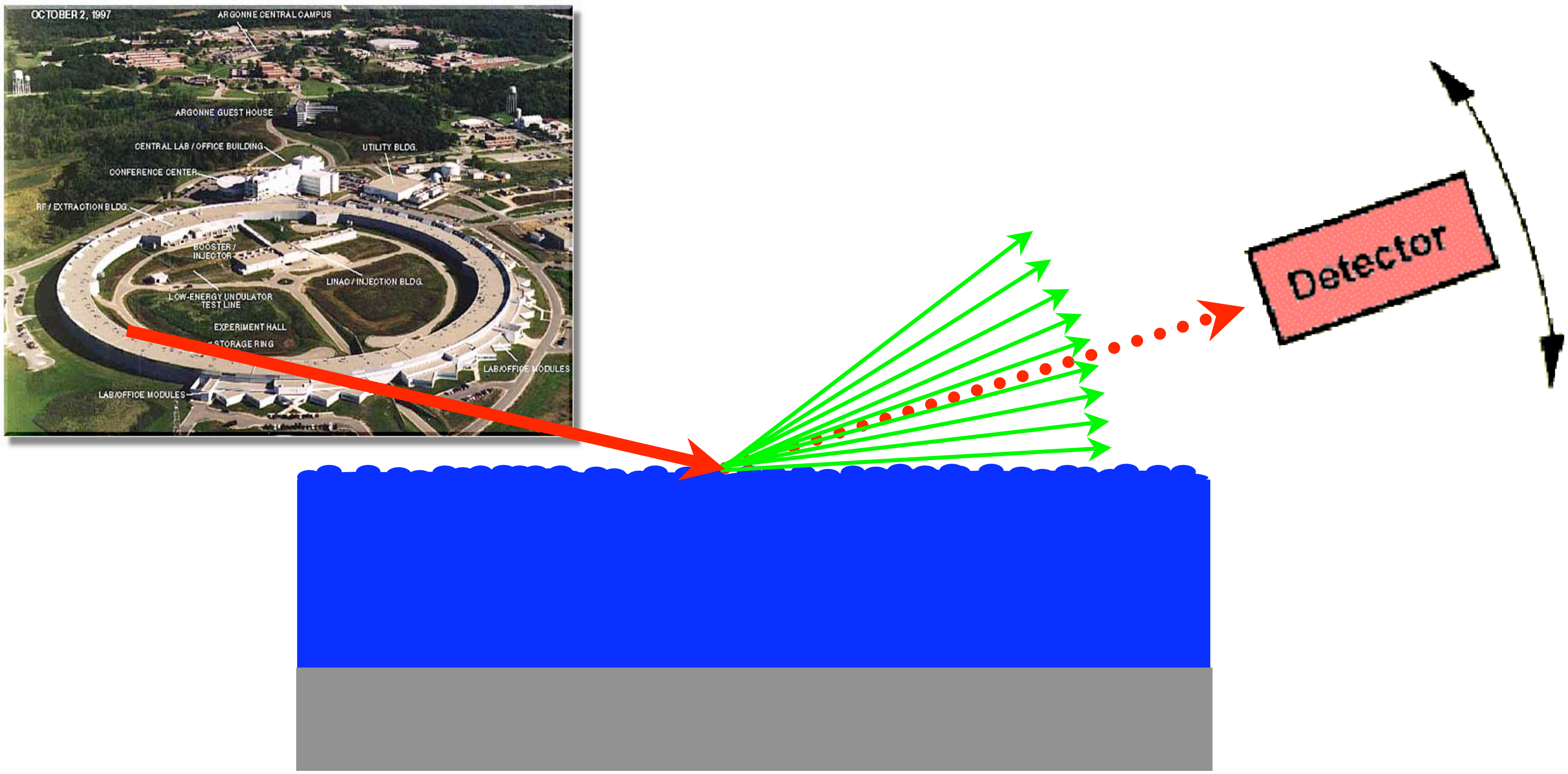
**

<u>Examples</u>: Aggregates of micelles, colloids, granular materials, rocks*

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

SURFACES and THIN FILMS

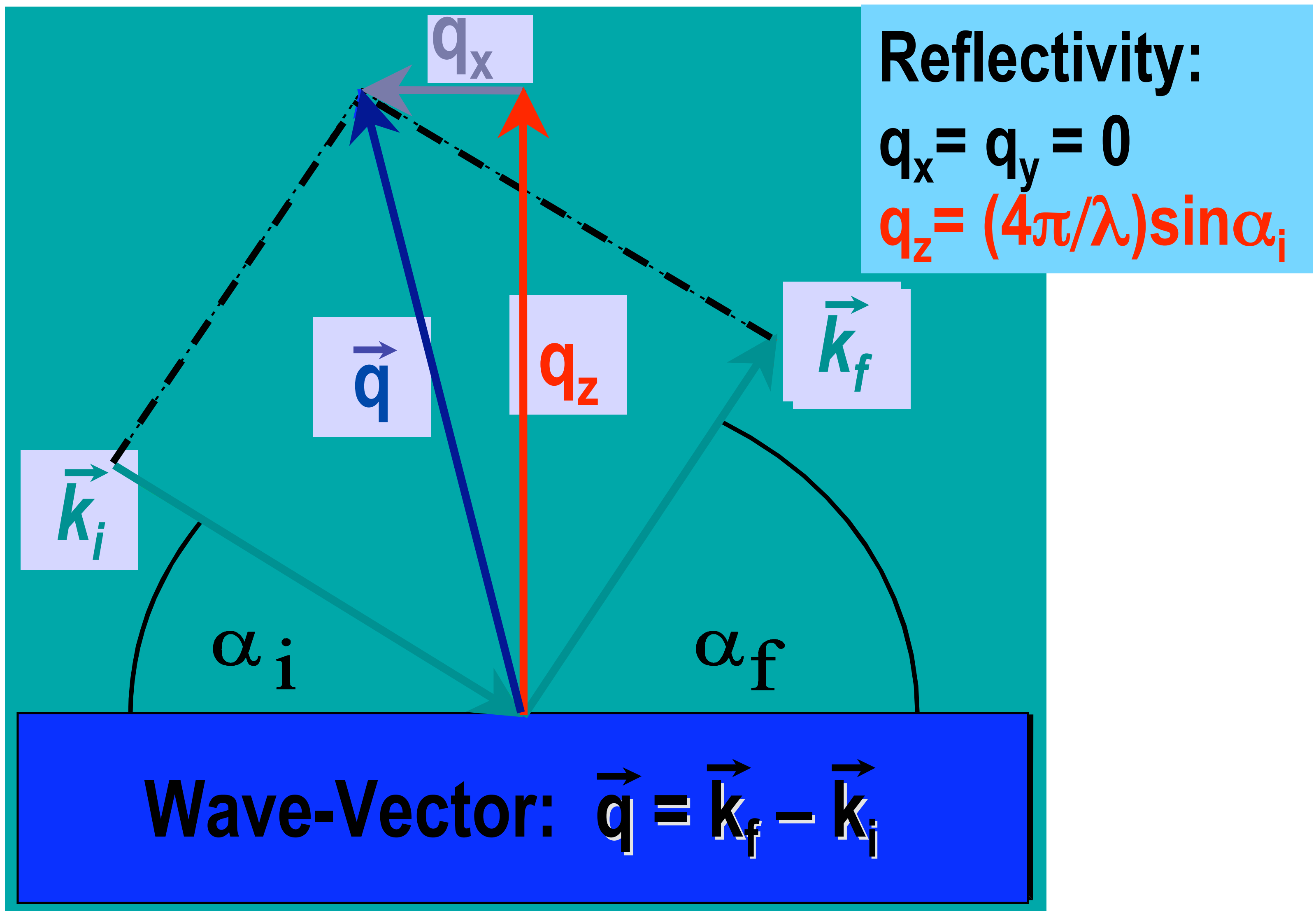
X-Ray Scattering Scheme



Scattering ~ Power Spectral Density

$$I(q_x,q_y) \sim S(q_x,q_y) = FT\,(\,C(X,Y)\,)$$

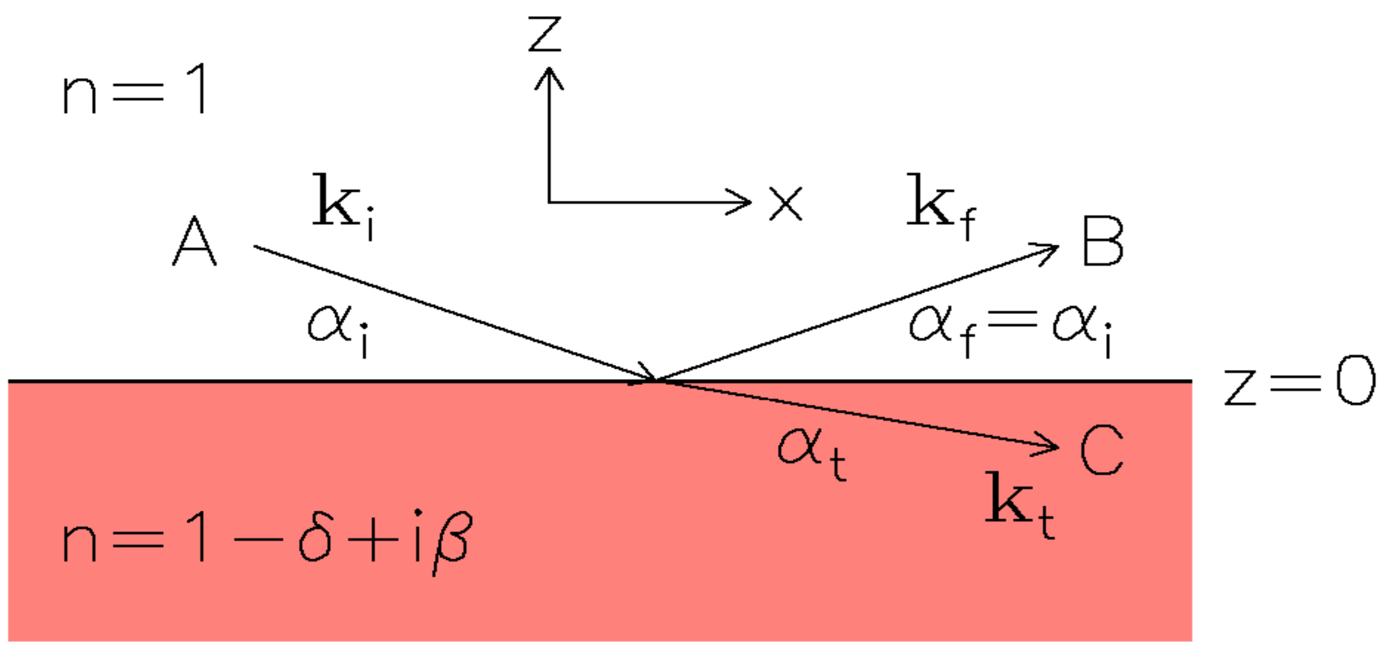
Scattering Geometry & Notation



Reflection of Visible Light

Perfect & Imperfect „Mirrors“

Basic Equation: X-Rays



Helmholtz-Equation & Boundary Conditions

$$\Delta E(\vec{r}) + k^2\, n_{\mathrm{X}}^2(\vec{r})\, E(\vec{r}) = 0$$

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

Refractive Index: X-Rays

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

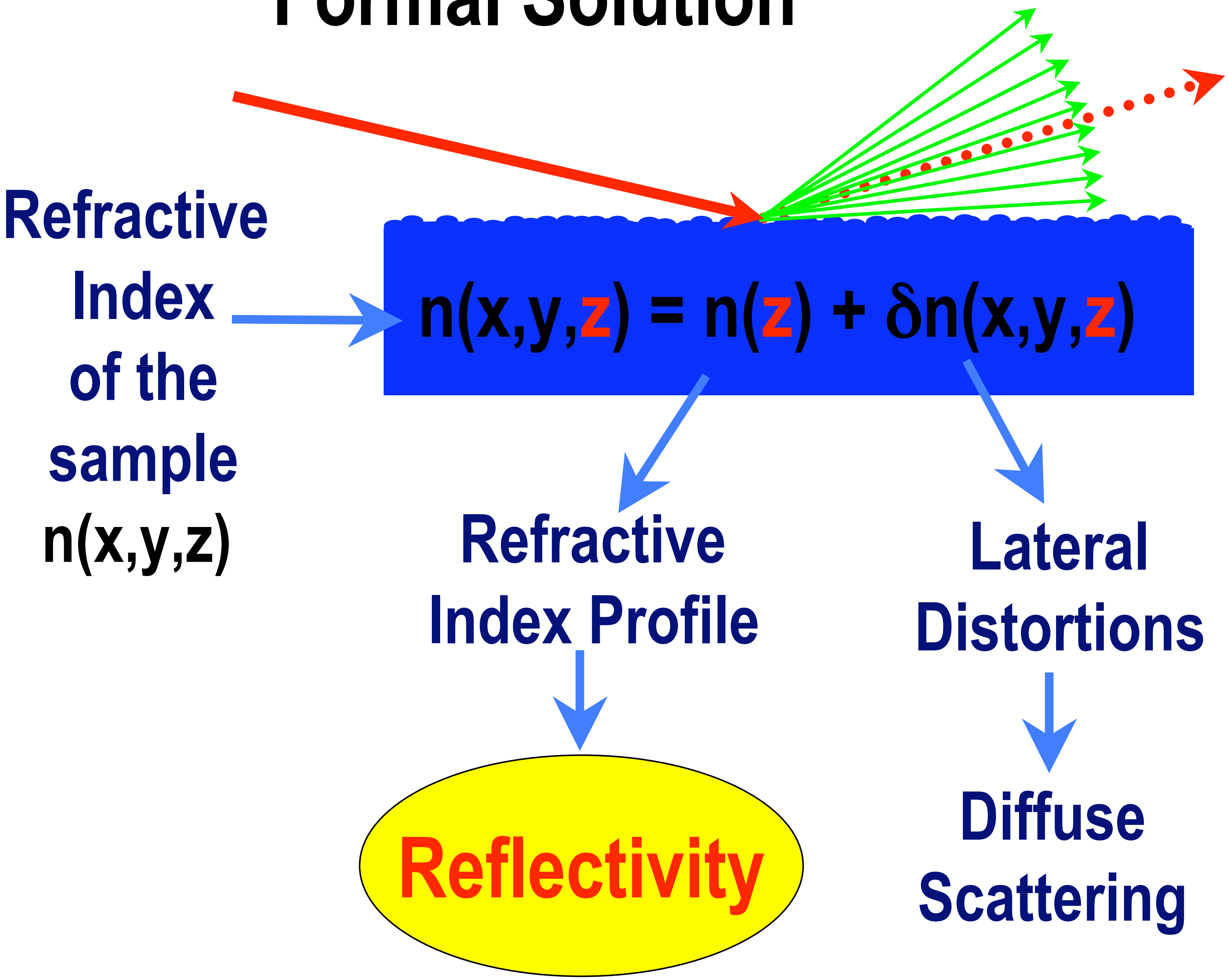
$$\varrho(z) = \langle \varrho(x,y,z) \rangle_{x,y}$$

	$r_e\varrho\,(10^{10}\mathbf{cm}^{-2})$	$\delta(10^{-6})$	$\mu\,(\mathbf{cm}^{-1})$	$\alpha_c(^\circ)$
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* !

Formal Solution

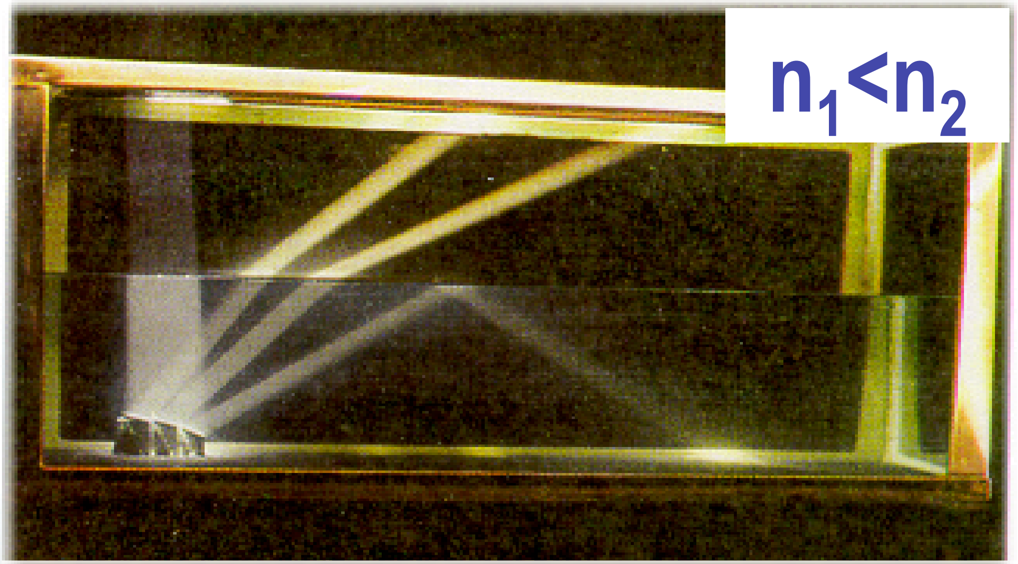


X-Ray Reflectivity: Principle

Visible Light Reflectivity:
$n_2 > 1$

n_1

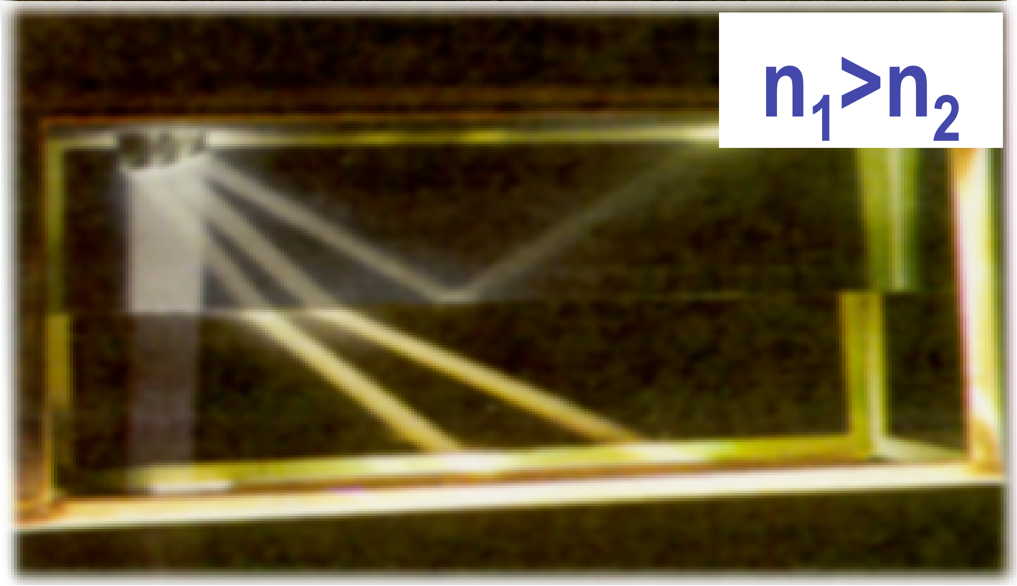
n_2



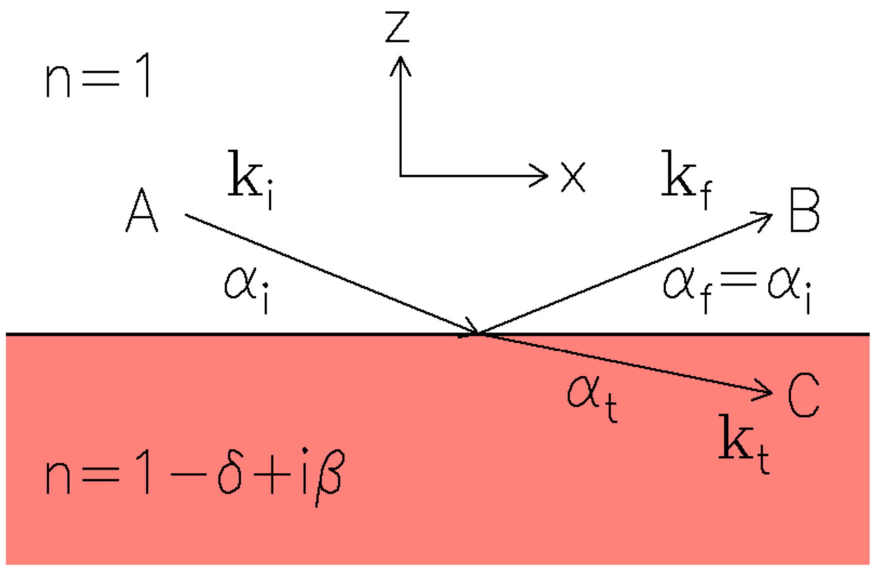
X-Ray Reflectivity:
$n_2 < 1$

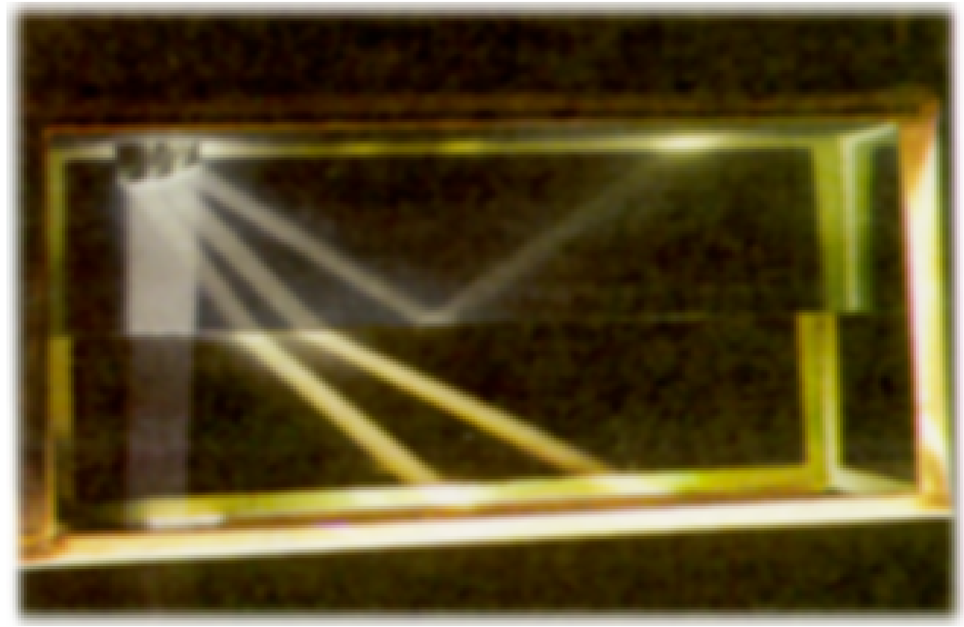
n_1

n_2



Total External Reflection





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

$\alpha_t=0$

Critical Angle:
$$\alpha_c \approx \sqrt{2\delta} \sim 0.3°$$

GRAZING ANGLES !!!

Single Interface: Vacuum/Matter

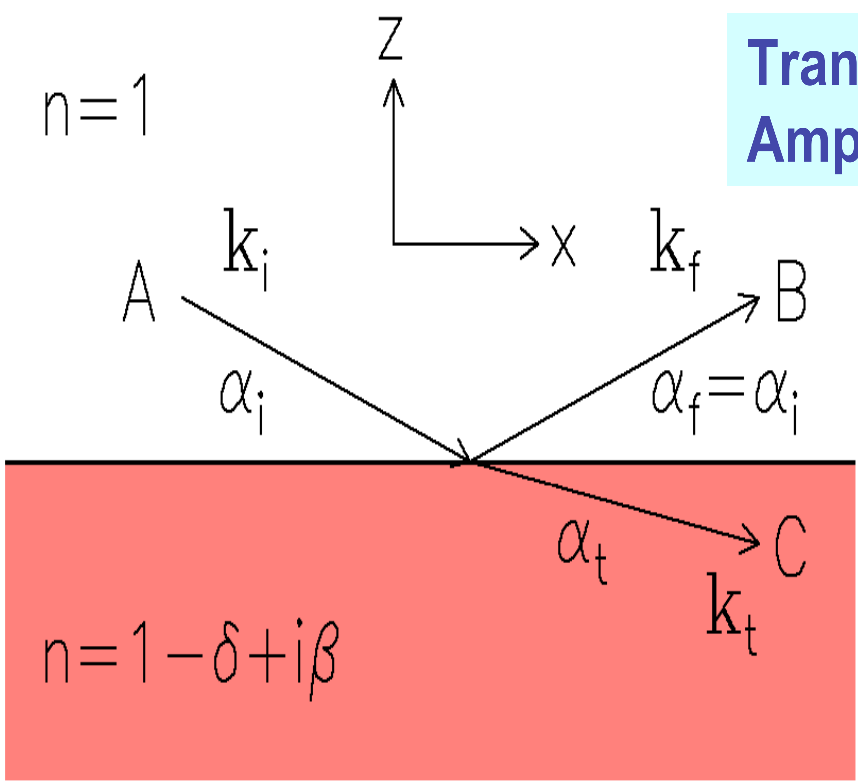
Fresnel-Formulae

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

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

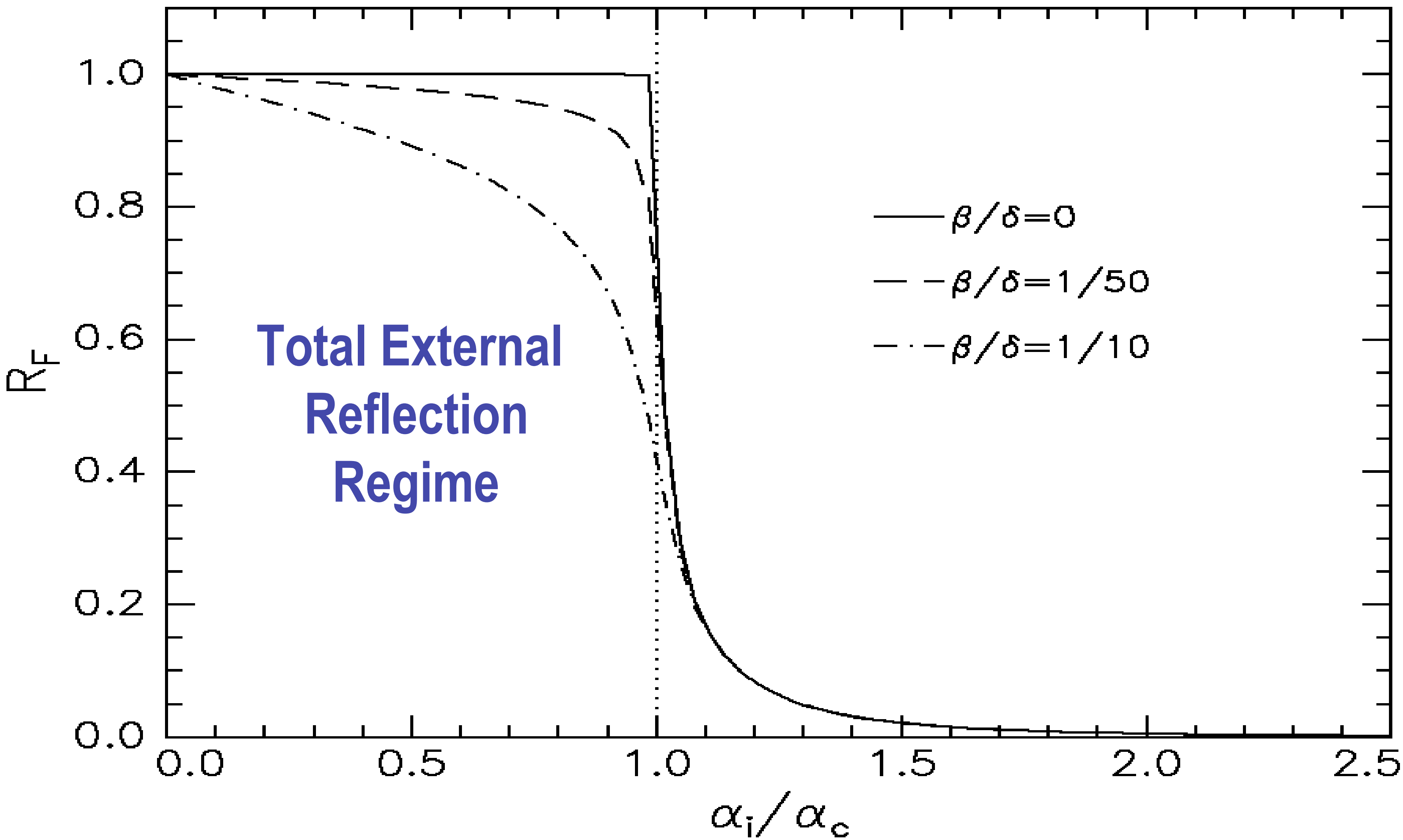


Wave-Vectors

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

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

Fresnel Reflectivity: $R_F(\alpha_i)$



The „Master Formula“

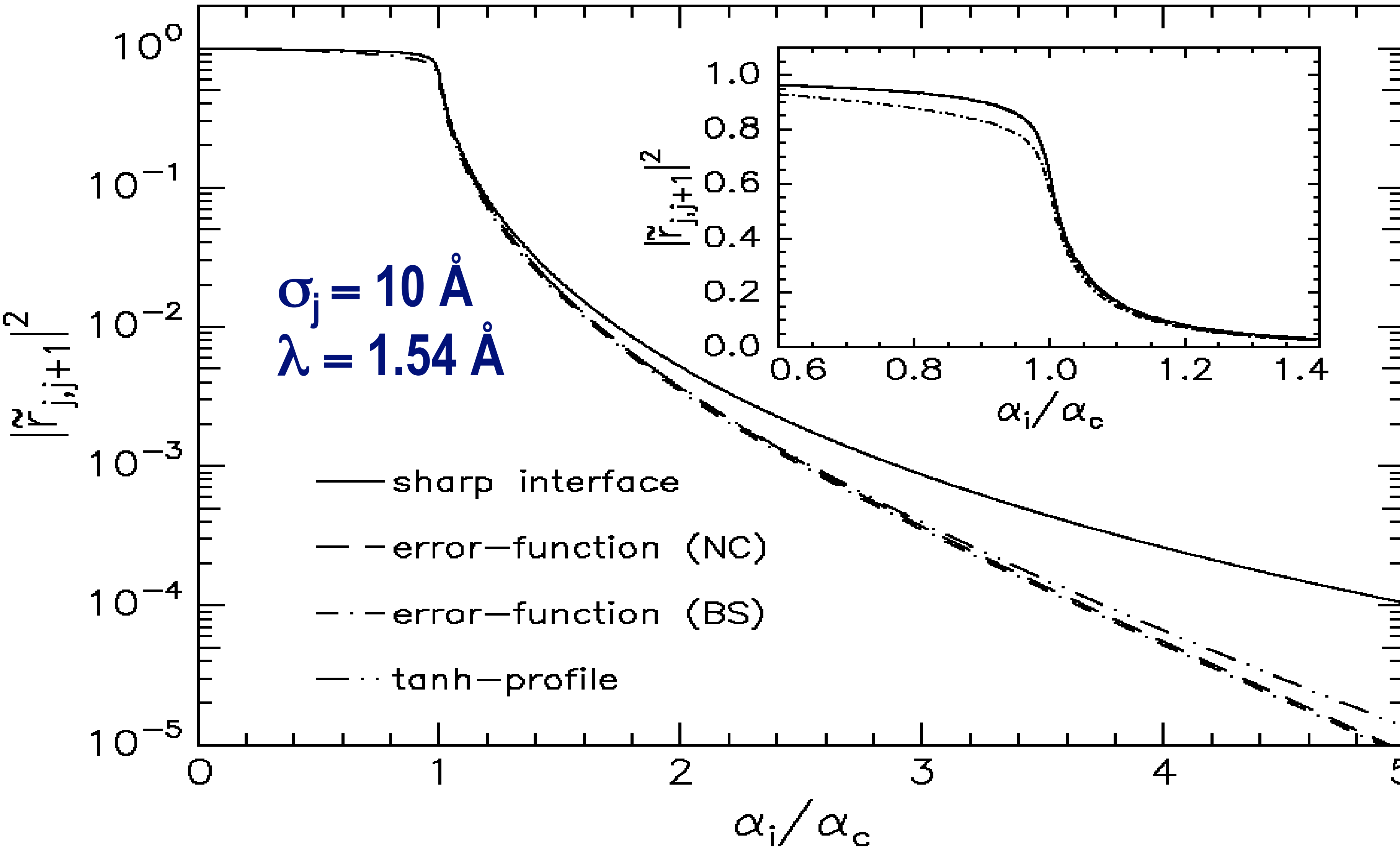
Reformulation for Interfaces

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

Fresnel-Reflectivity of the Substrate

Electron Density Profile

Roughness Damps Reflectivity

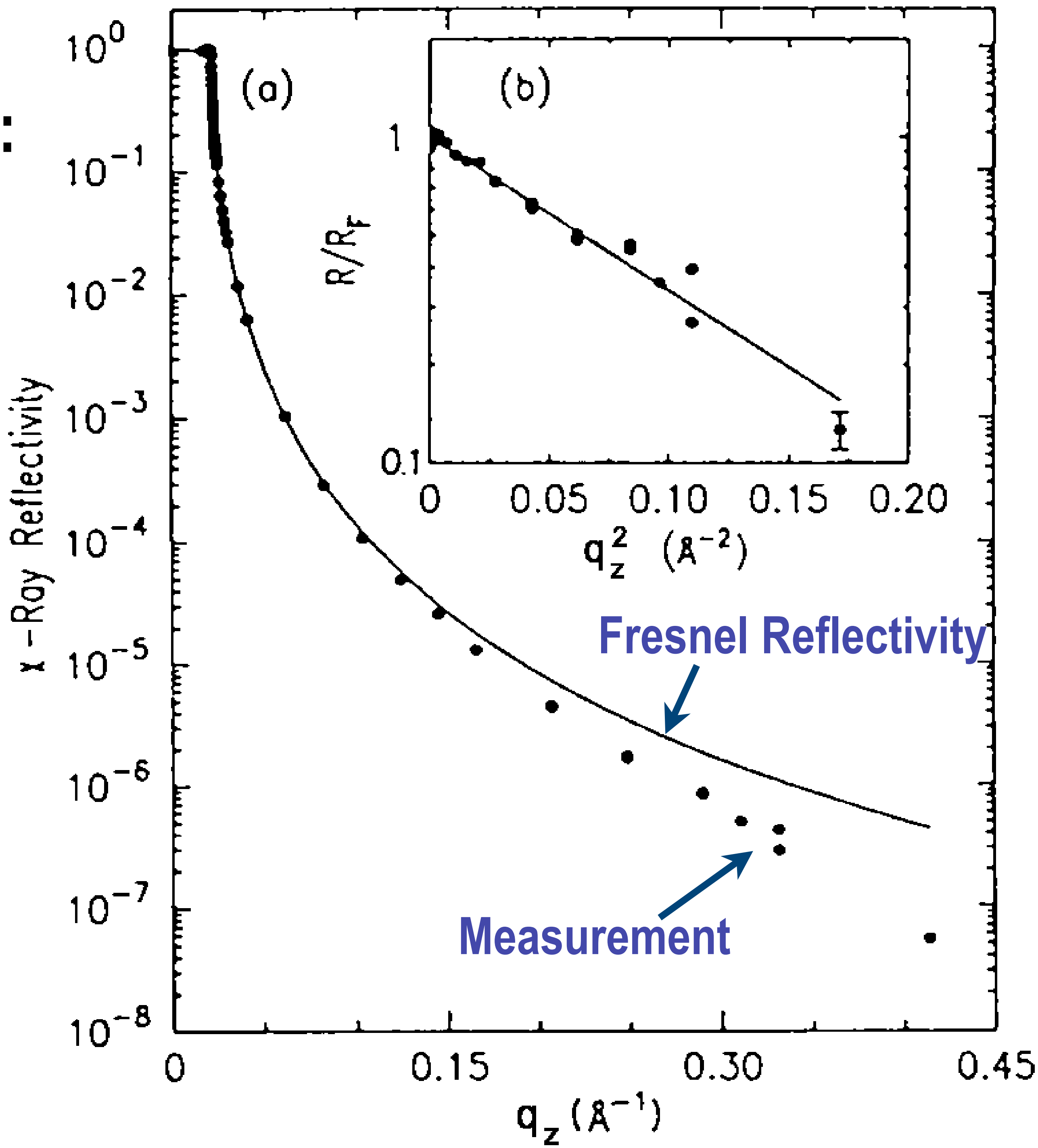


X-Ray Reflectivity: Water Surface

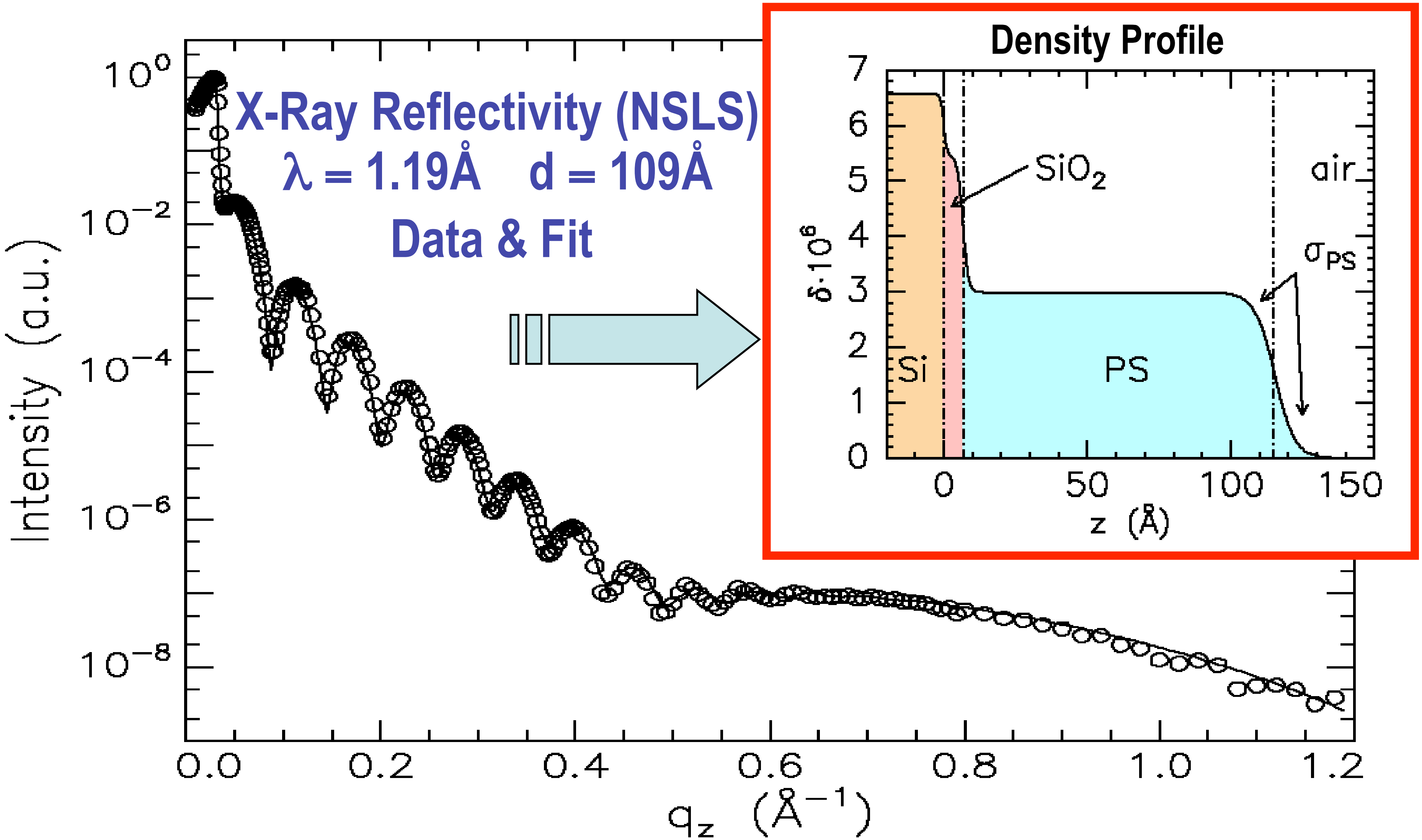
Difference Experiment-Theory:

Roughness !!

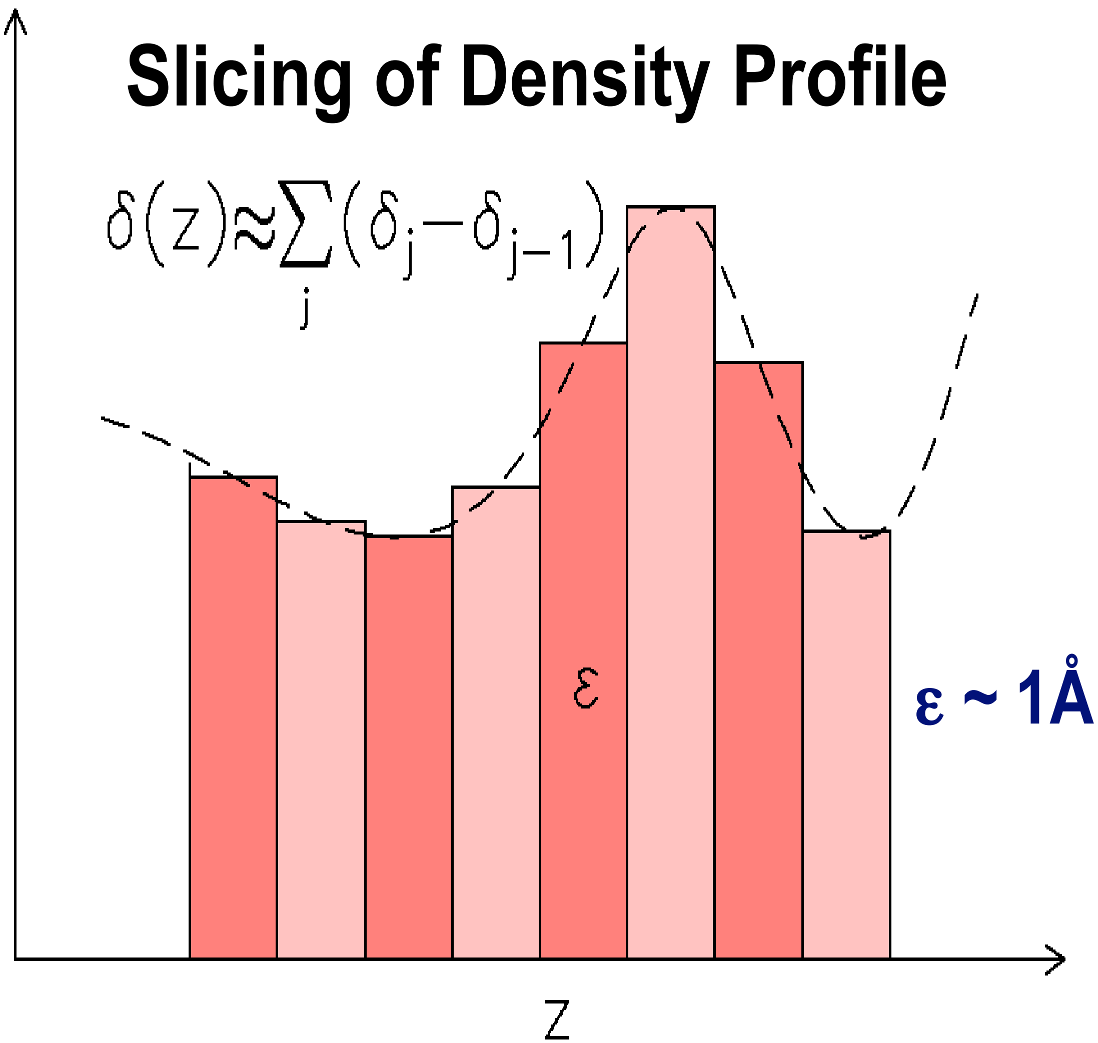
Braslau et al.
PRL *54*, 114 (1985)



Example: PS Film on Si/SiO_2



Calculation of Reflectivity

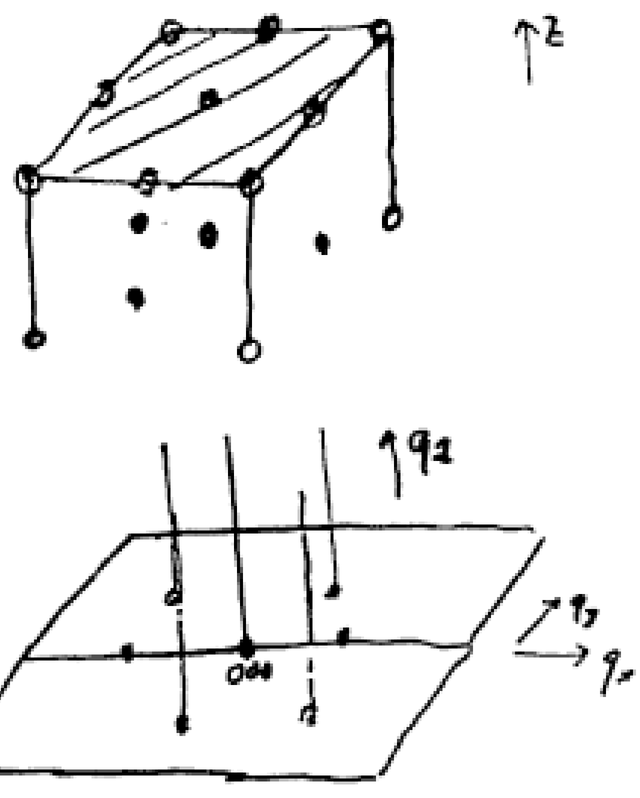


Slicing
&
Parratt-Iteration

Reflectivity from Arbitrary Profiles !

- **Drawback:** Numerical Effort !

Crystal Truncation rods

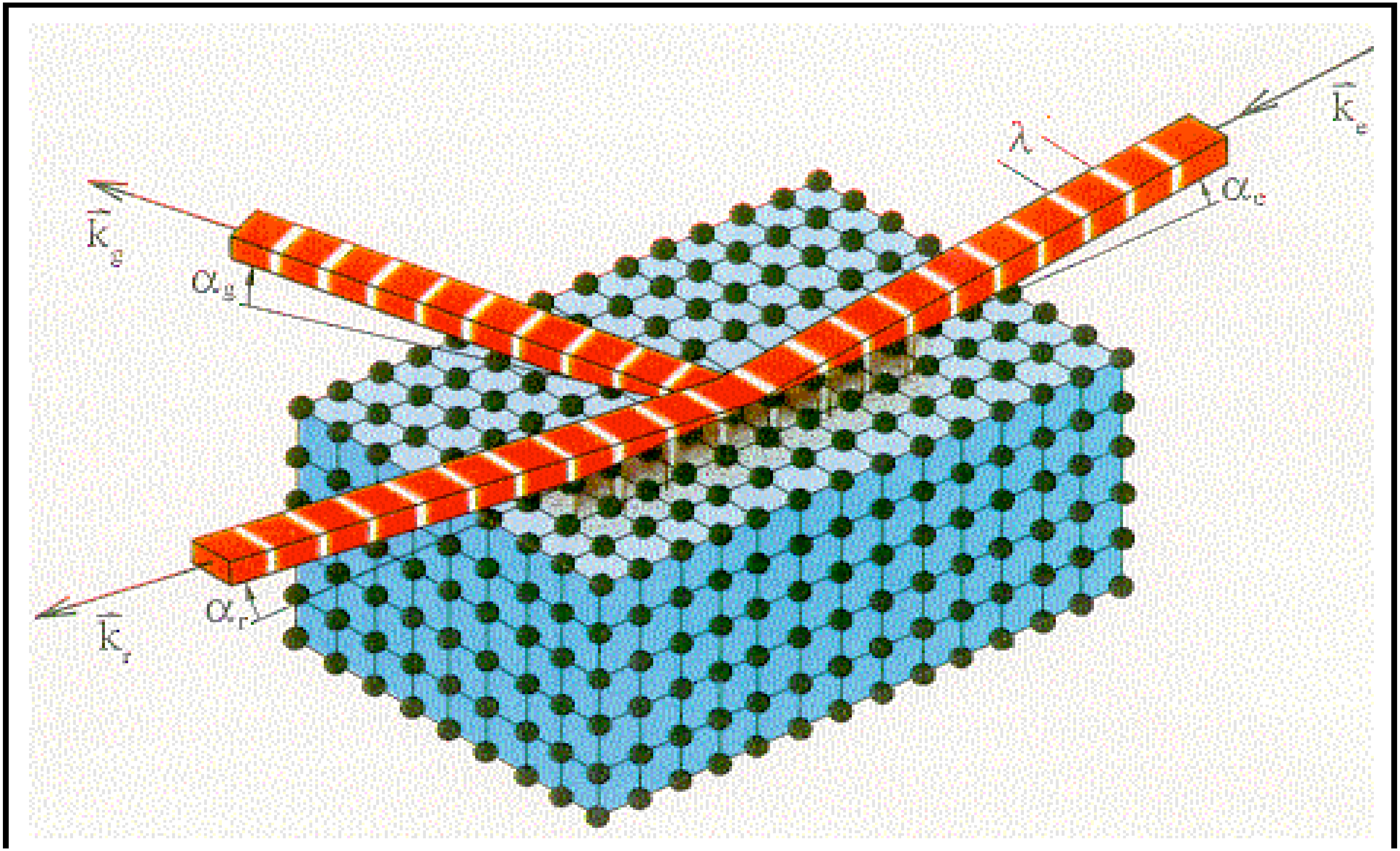


$$S(q) = \left\langle \sum_{\ell \ell'} e^{-i\vec{q}\cdot\left(\vec{R}_\ell - \vec{R}_{\ell'}\right)} \right\rangle$$

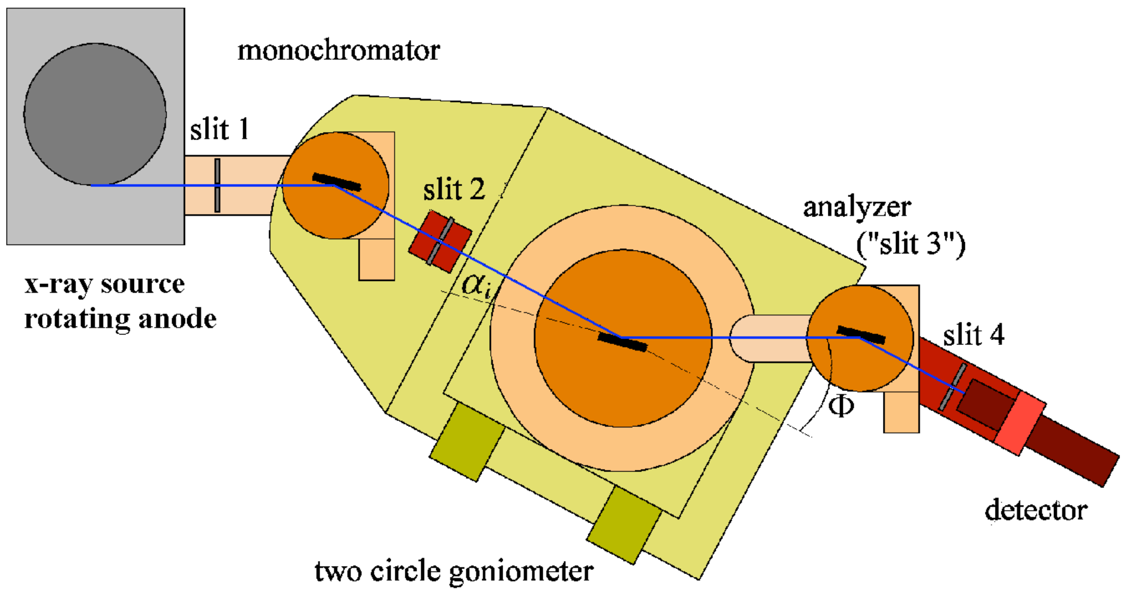
$$= \sum \sum_{n_x, n_{x'} +-\infty}^{\infty} \sum \sum_{n_y, n_{y'} = -\infty}^{\infty} \overbrace{e^{-iq_x (n_x - n'_x) a}}^{\delta(q_x - G_x)} \, \overbrace{e^{-iq_y (n_y - n'_y) a}}^{\delta(q_y - G_y)}$$

$$\times \sum_{n_z,}^{0} \sum_{n'_z z = -\infty}^{0} \underbrace{e^{-iq_z (n_z - n'_z) a}}_{(q_z - G_z)^{-2}}$$

Grazing-Incidence-Diffraction

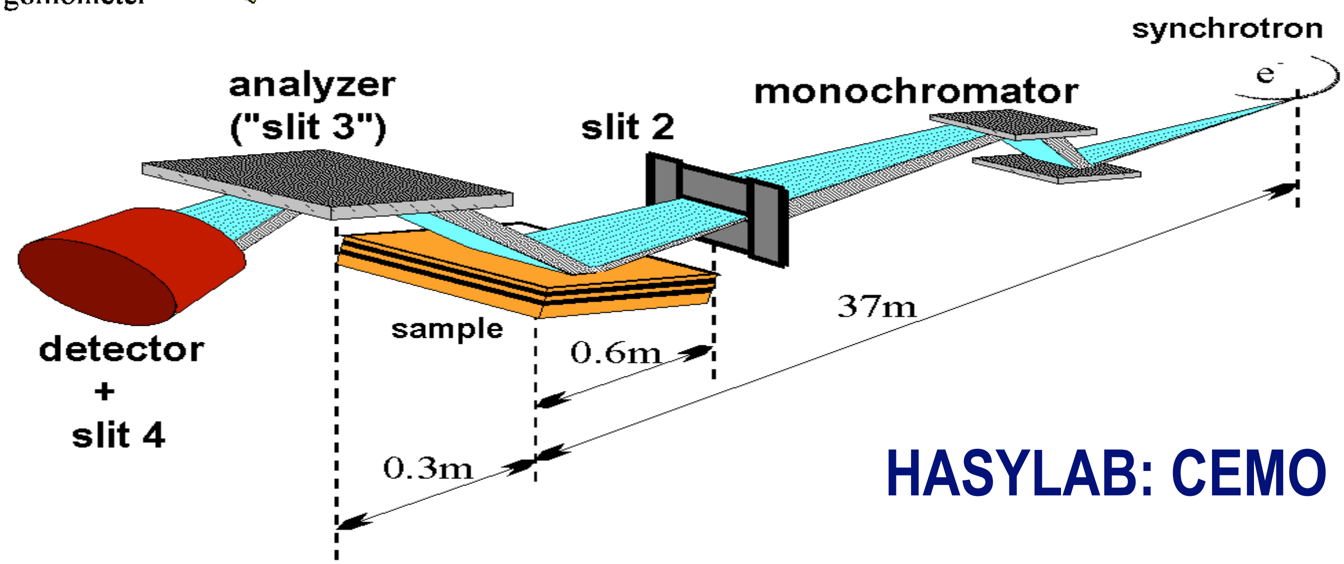


X-Ray Reflectometers



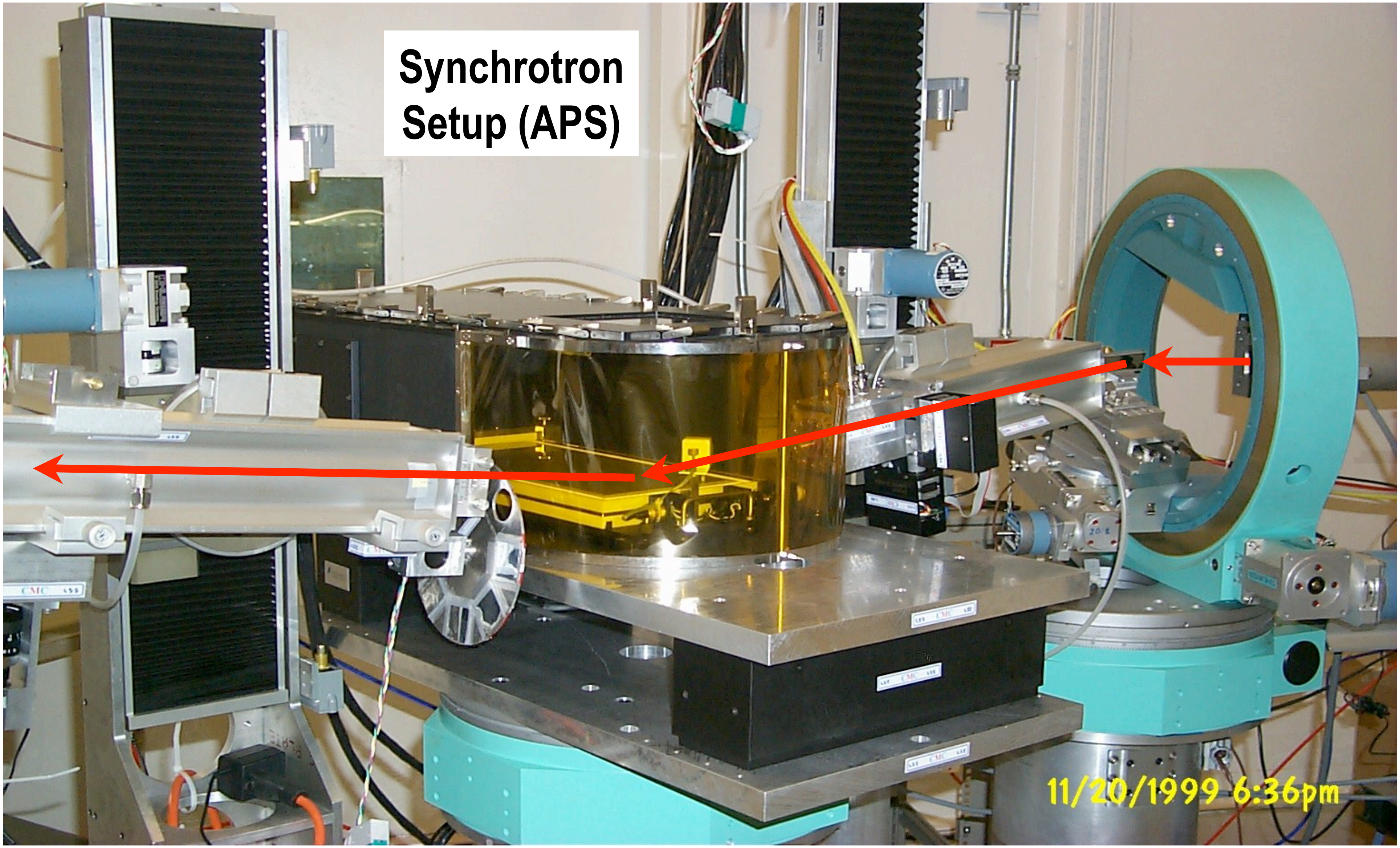
Laboratory Setup

Synchrotron Setup



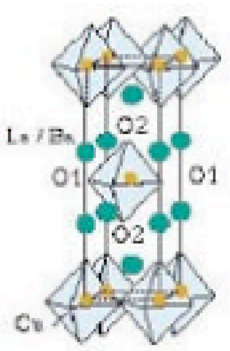
HASYLAB: CEMO

Reflectivity from Liquids I

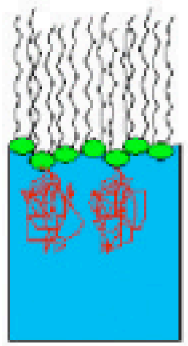


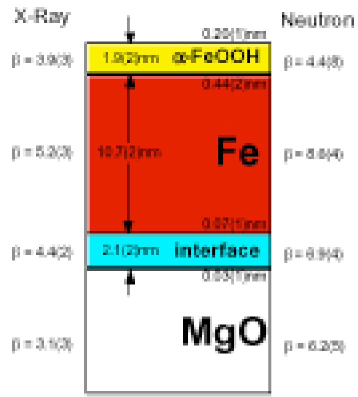
INELASTIC SCATTERING

We Have Seen How Neutron Scattering Can Determine a Variety of Structures

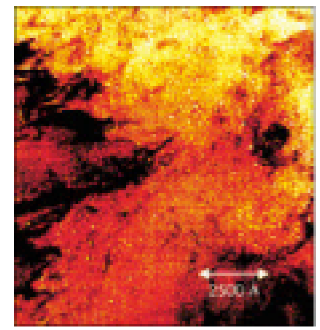


crystals

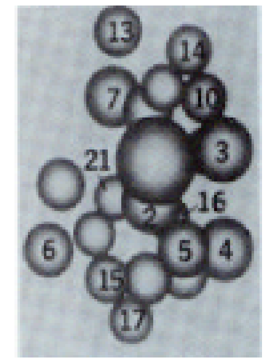




surfaces & interfaces

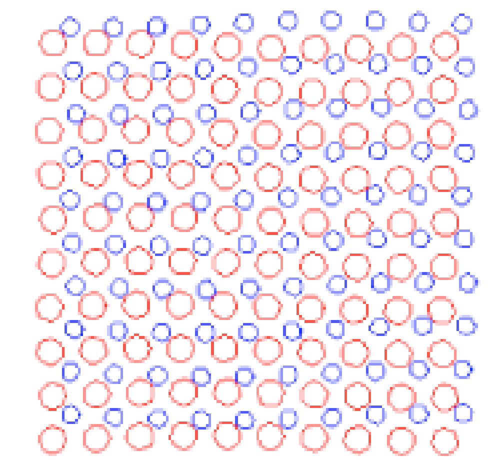


disordered/fractals



biomachines

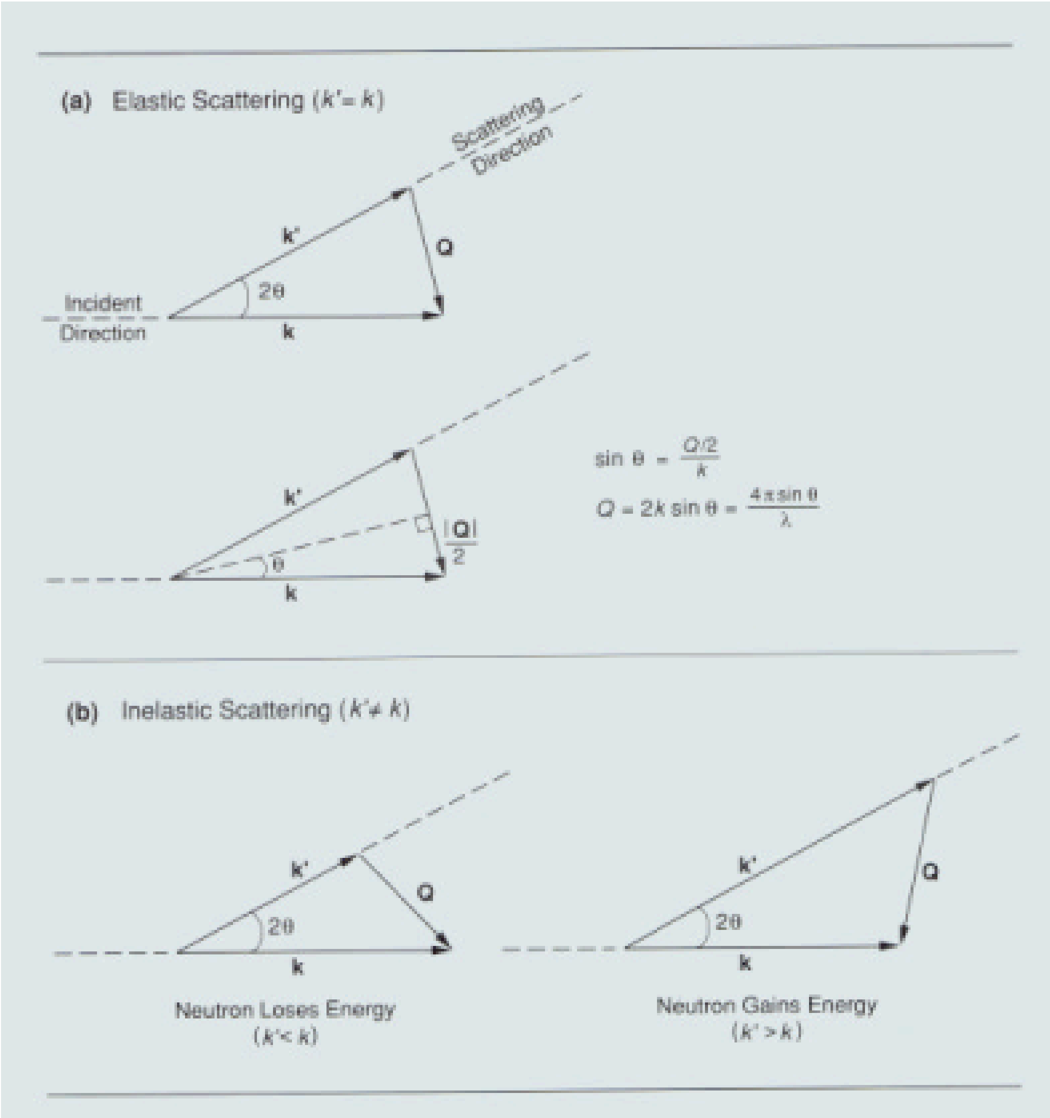
but what happens when the atoms are moving?



Can we determine the directions and time-dependence of atomic motions?
Can well tell whether motions are periodic?
Etc.

These are the types of questions answered by inelastic neutron scattering

The Neutron Changes Both Energy & Momentum When Inelastically Scattered by Moving Nuclei



inelastic scattering

Scattering in which exchange of energy and momentum between the incident neutron and the sample causes both the direction and the magnitude of the neutron's wave vector to change.

The Elastic & Inelastic Scattering Cross Sections Have an Intuitive Similarity

- The intensity of elastic, coherent neutron scattering is proportional to the spatial Fourier Transform of the Pair Correlation Function, G(r) I.e. the probability of finding a particle at position r if there is simultaneously a particle at r=0

- The intensity of inelastic coherent neutron scattering is proportional to the space *and time* Fourier Transforms of the *time-dependent* pair correlation function function, G(r,t) = probability of finding a particle at position r *at time t* when there is a particle at r=0 and *t=0*.

- For inelastic *incoherent* scattering, the intensity is proportional to the space and time Fourier Transforms of the *self-correlation* function, $G_s(r,t)$ I.e. the probability of finding a particle at position r at time t when *the same* particle was at r=0 at t=0

The Inelastic Scattering Cross Section

Recall that $\left(\dfrac{d^2\sigma}{d\Omega.dE}\right)_{coh} = b_{coh}^2 \dfrac{k'}{k} NS(\vec{Q},\omega)$ and $\left(\dfrac{d^2\sigma}{d\Omega.dE}\right)_{inc} = b_{inc}^2 \dfrac{k'}{k} NS_i(\vec{Q},\omega)$

where $S(\vec{Q},\omega) = \dfrac{1}{2\pi\hbar}\iint G(\vec{r},t)e^{i(\vec{Q}.\vec{r}-\omega t)}d\vec{r}dt$ and $S_i(\vec{Q},\omega) = \dfrac{1}{2\pi\hbar}\iint G_s(\vec{r},t)e^{i(\vec{Q}.\vec{r}-\omega t)}d\vec{r}dt$

and the correlation functions that are intuitively similar to those for the elastic scattering case:

$G(\vec{r},t) = \dfrac{1}{N}\int\left\langle \rho_N(\vec{r},0)\rho_N(\vec{r}+\vec{R},t)\right\rangle d\vec{r}$ and $G_s(\vec{r},t) = \dfrac{1}{N}\sum_j \int\left\langle \delta(\vec{r}-\vec{R}_j(0))\delta(\vec{r}+\vec{R}-\vec{R}_j(t))\right\rangle d\vec{r}$

The evaluation of the correlation functions (in which the ρ's and δ - functions have to be treated as non - commuting quantum mechanical operators) is mathematically tedious. Details can be found, for example, in the books by Squires or Marshal and Lovesey.

Examples of $S(Q,\omega)$ and $S_s(Q,\omega)$

- Expressions for $S(Q,\omega)$ and $S_s(Q,\omega)$ can be worked out for a number of cases e.g:
  - Excitation or absorption of one quantum of lattice vibrational energy (phonon)
  - Various models for atomic motions in liquids and glasses
  - Various models of atomic & molecular translational & rotational diffusion
  - Rotational tunneling of molecules
  - Single particle motions at high momentum transfers
  - Transitions between crystal field levels
  - Magnons and other magnetic excitations such as spinons
- Inelastic neutron scattering reveals details of the shapes of interaction potentials in materials

A Phonon is a Quantized Lattice Vibration

- Consider linear chain of particles of mass M coupled by springs. Force on n'th particle is

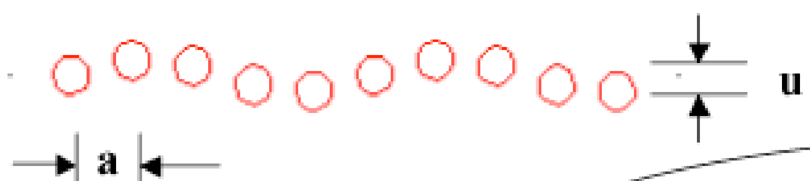
$$F_n = \alpha_0 u_n + \alpha_1(u_{n-1} + u_{n+1}) + \alpha_2(u_{n-2} + u_{n+2}) + \ldots$$

First neighbor force constant

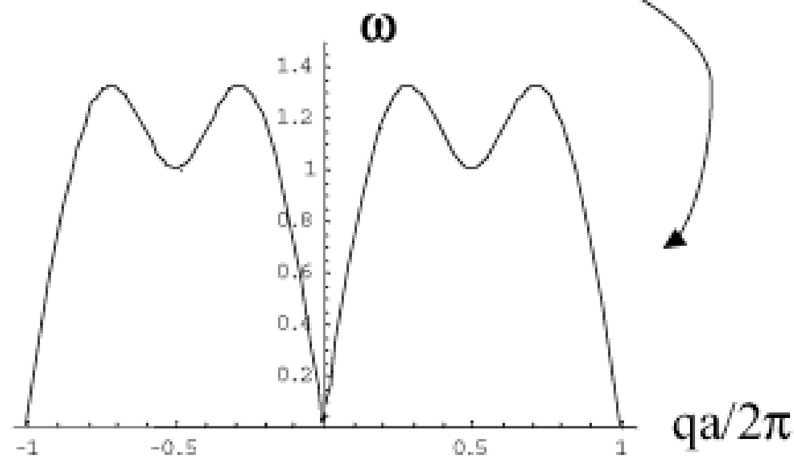
displacements

- Equation of motion is $F_n = M\ddot{u}_n$
- Solution is: $u_n(t) = A_q e^{i(qna-\omega t)}$ with $\omega_q^2 = \frac{4}{M}\sum_\nu \alpha_\nu \sin^2(\frac{1}{2}\nu qa)$

$$q = 0, \pm\frac{2\pi}{L}, \pm\frac{4\pi}{L}, \ldots\ldots \pm\frac{N}{2}\frac{2\pi}{L}$$



Phonon Dispersion Relation:
Measurable by inelastic neutron scattering



Inelastic Magnetic Scattering of Neutrons

- In the simplest case, atomic spins in a ferromagnet precess about the direction of mean magnetization

$$H = \sum_{l,l'} J(\vec{l} - \vec{l}\,')\vec{S}_l . \vec{S}_{l'} = H_0 + \sum_q \hbar\omega_q b_q^+ b_q$$

exchange coupling

ground state energy

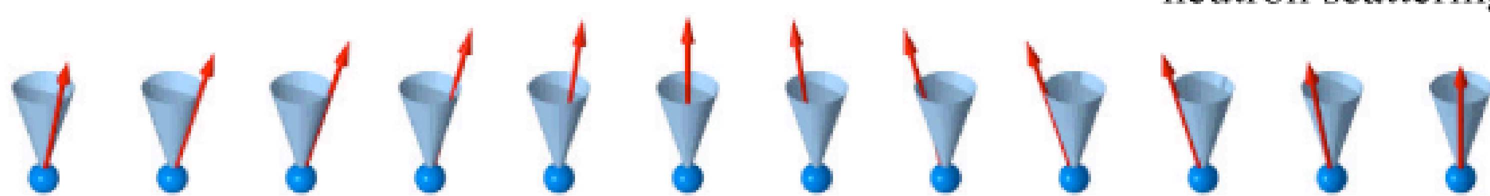
spin waves (magnons)

with

$$\hbar\omega_q = 2S(J_0 - J_q) \qquad \text{where} \quad J_q = \sum_l J(\vec{l}\,)e^{i\vec{q}.\vec{l}}$$

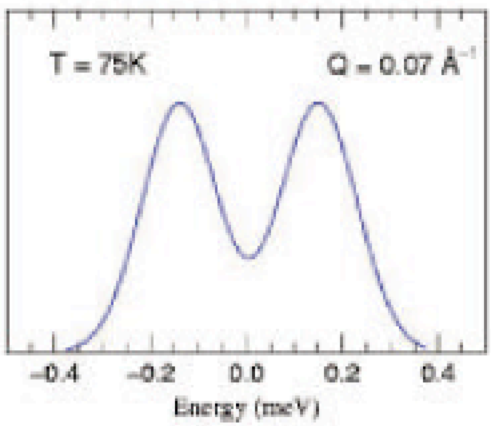
$\hbar\omega_q = Dq^2$ is the dispersion relation for a ferromagnet

Fluctuating spin is perpendicular to mean spin direction => spin-flip neutron scattering

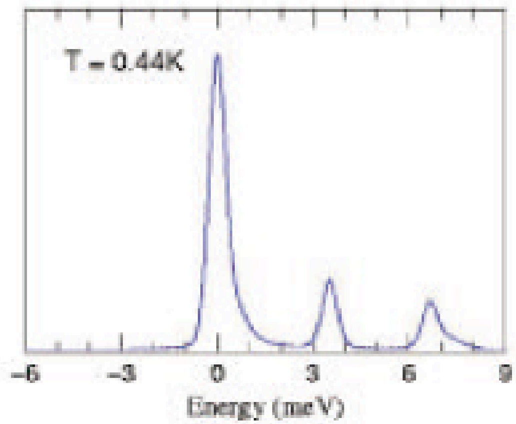


Spin wave animation courtesy of A. Zheludev (ORNL)

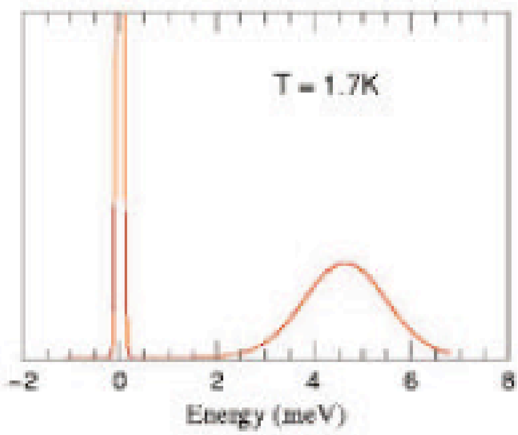
Measured Inelastic Neutron Scattering Signals in Crystalline Solids Show Both Collective & Local Fluctuations*



Spin waves – collective excitations



Crystal Field splittings ($HoPd_2Sn$) – local excitations

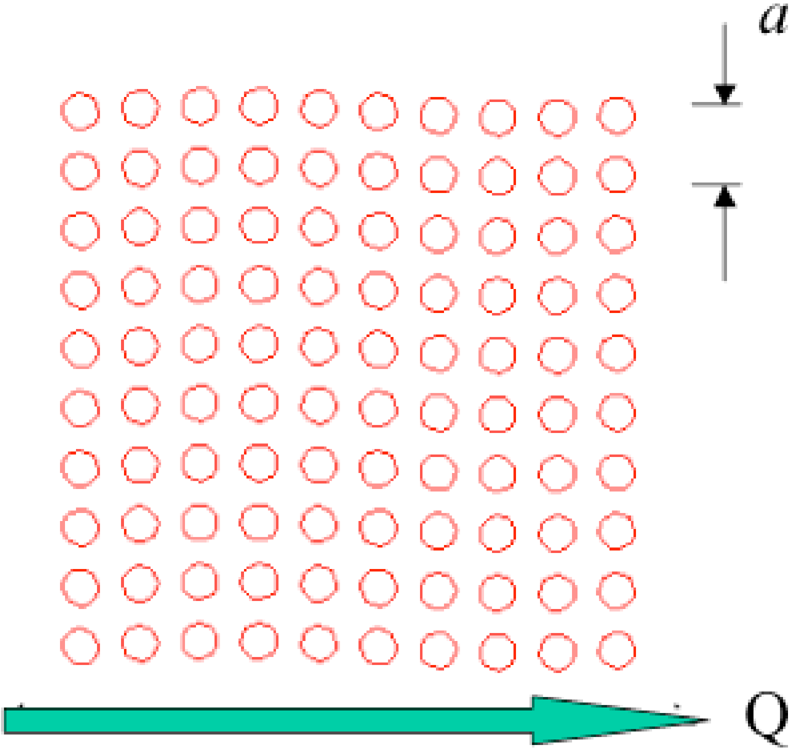


Local spin resonances (e.g. $ZnCr_2O_4$)

* Courtesy of Dan Neumann, NIST

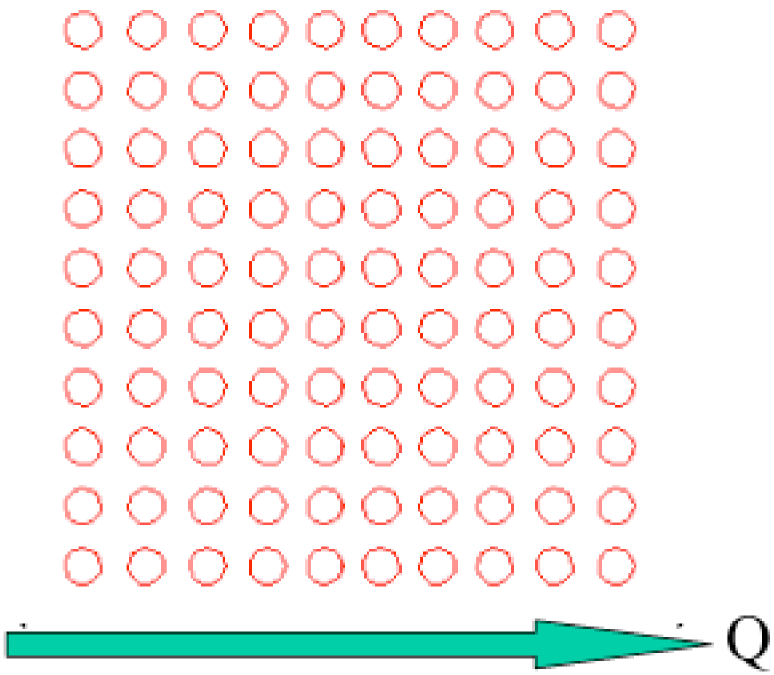
Atomic Motions for Longitudinal & Transverse Phonons

$$\vec{Q} = \frac{2\pi}{a}(0.1,0,0)$$



Transverse phonon

$$\vec{e}_T = (0,0.1,0)a$$



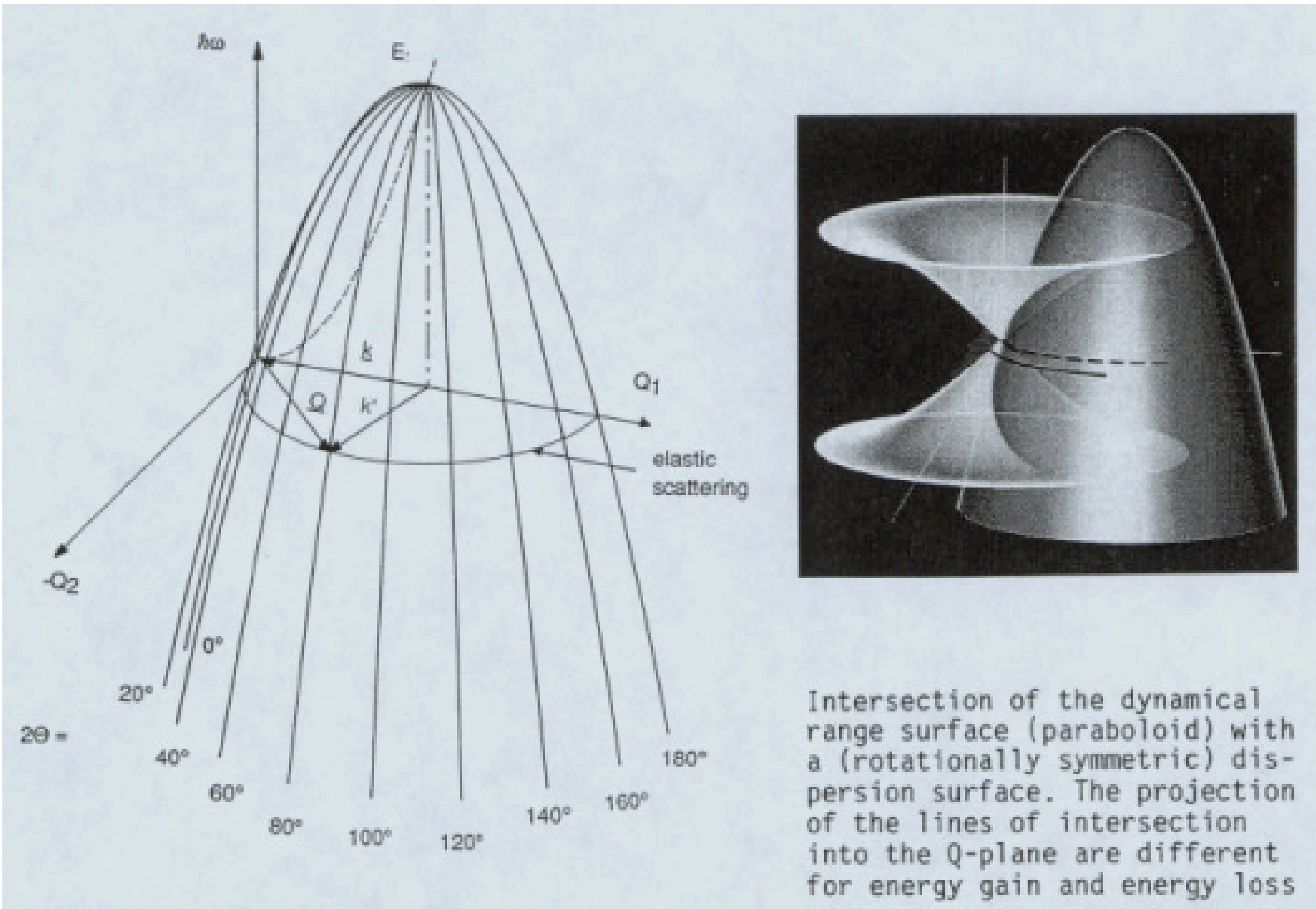
Longitudinal phonon

$$\vec{e}_L = (0.1,0,0)a$$

$$\vec{R}_l = \vec{R}_{l0} + \vec{e}_s e^{i(\vec{Q}.\vec{R}_l - \omega t)}$$

The Accessible Energy and Wavevector Transfers Are Limited by Conservation Laws

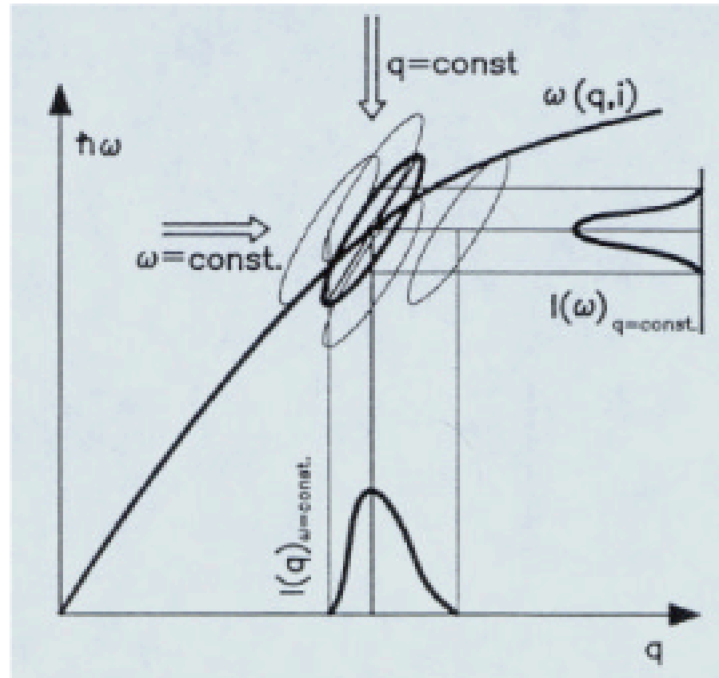
- Neutron cannot lose more than its initial kinetic energy & momentum must be conserved

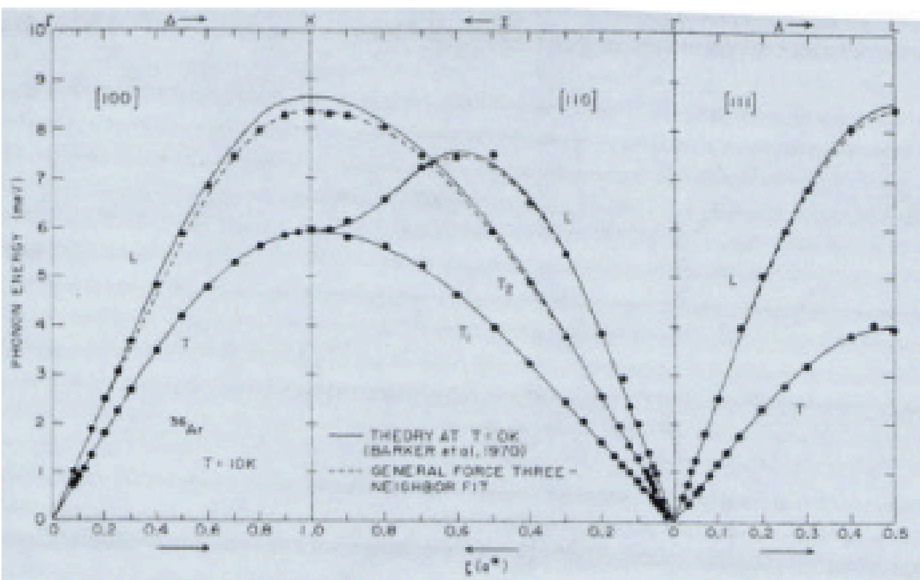


Intersection of the dynamical range surface (paraboloid) with a (rotationally symmetric) dispersion surface. The projection of the lines of intersection into the Q-plane are different for energy gain and energy loss

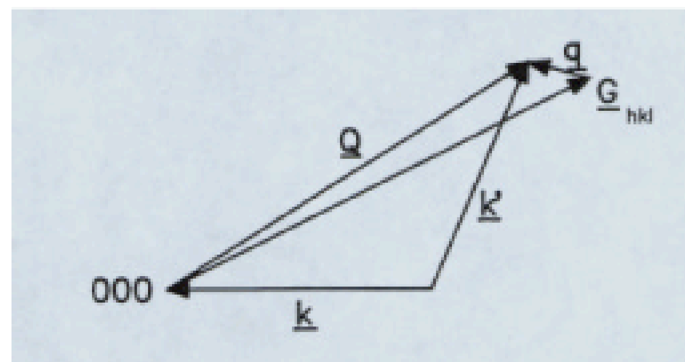
Triple Axis Spectrometers Have Mapped Phonons Dispersion Relations in Many Materials

- Point by point measurement in (Q,E) space
- Usually keep either k_I or k_F fixed
- Choose Brillouin zone (I.e. G) to maximize scattering cross section for phonons
- Scan usually either at constant-Q (Brockhouse invention) or constant-E

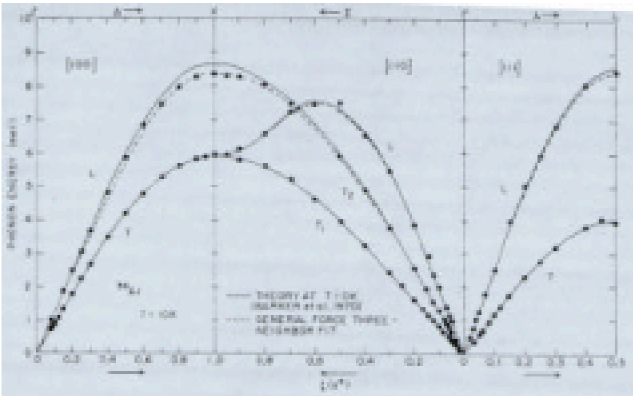




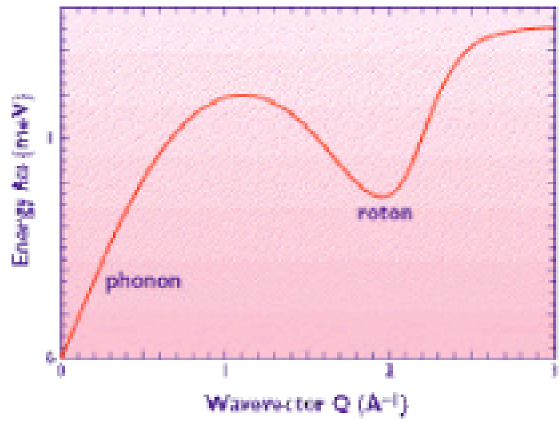
Phonon dispersion of ^{36}Ar



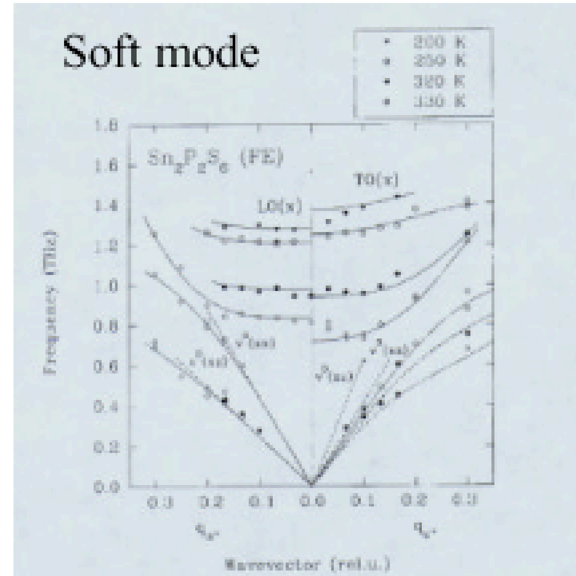
Examples of Phonon Measurements



Phonons in ^{36}Ar – validation of LJ potential



Roton dispersion in ^{4}He



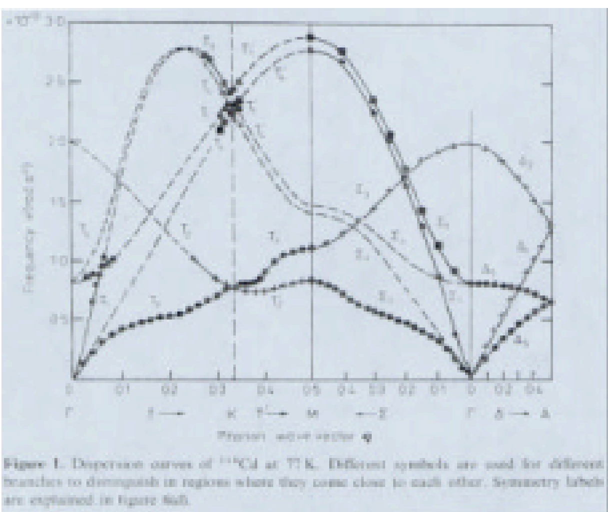
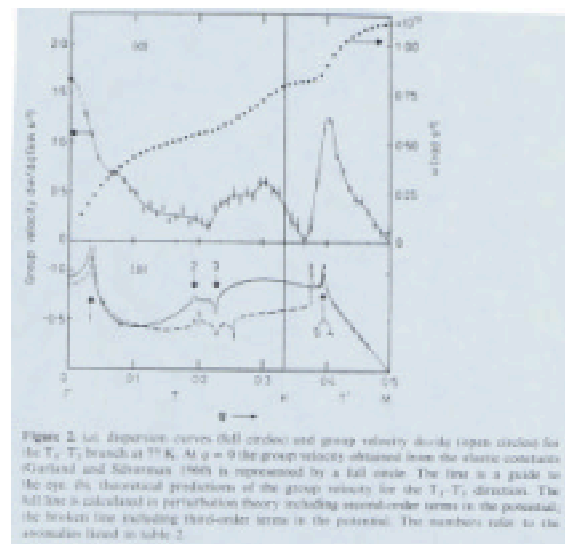


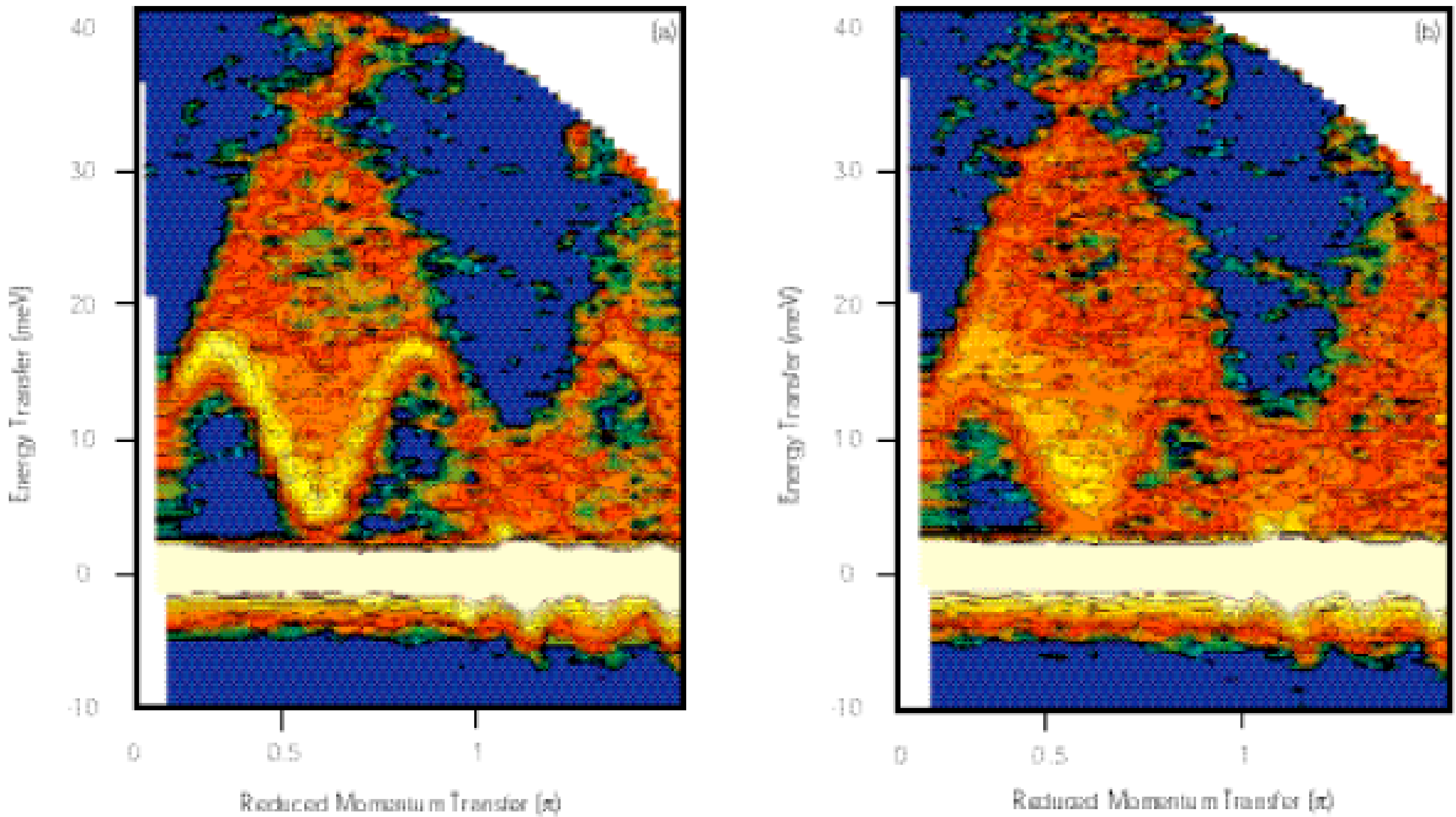
Figure 1. Dispersion curves of ^{110}Cd at 77 K. Different symbols are used for different branches to distinguish in regions where they come close to each other. Symmetry labels are explained in figure 6(d).

Phonons in ^{110}Cd

Kohn anomalies in ^{110}Cd

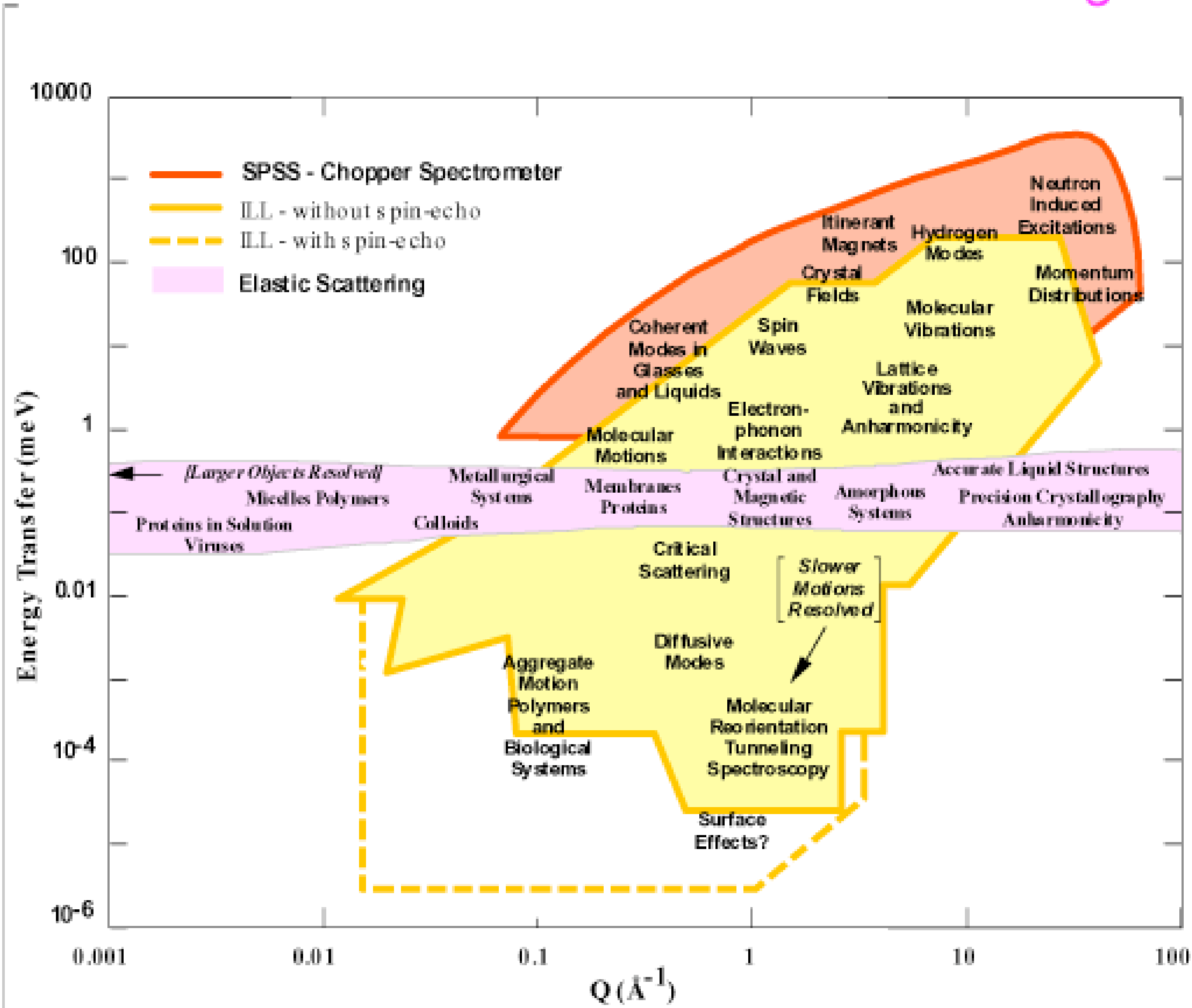


Time-of-flight Methods Can Give Complete Dispersion Curves at a Single Instrument Setting in Favorable Circumstances



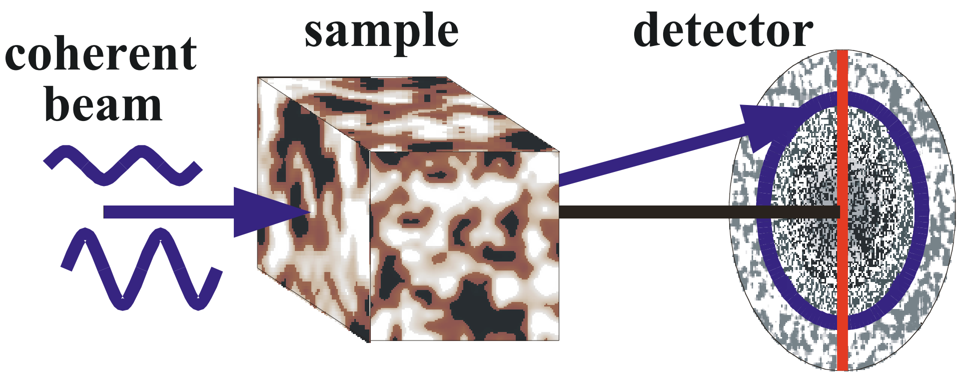
$CuGeO_3$ is a 1-d magnet. With the unique axis parallel to the incident neutron beam, the complete magnon dispersion can be obtained

Much of the Scientific Impact of Neutron Scattering Has Involved the Measurement of Inelastic Scattering

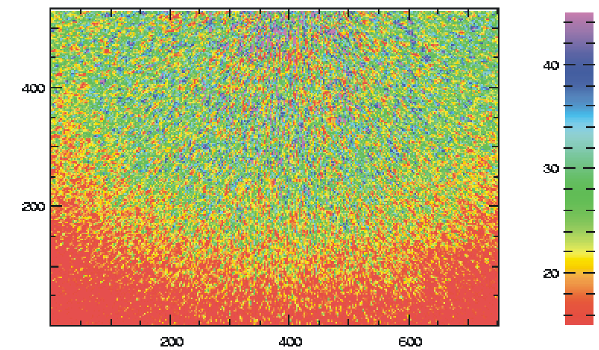


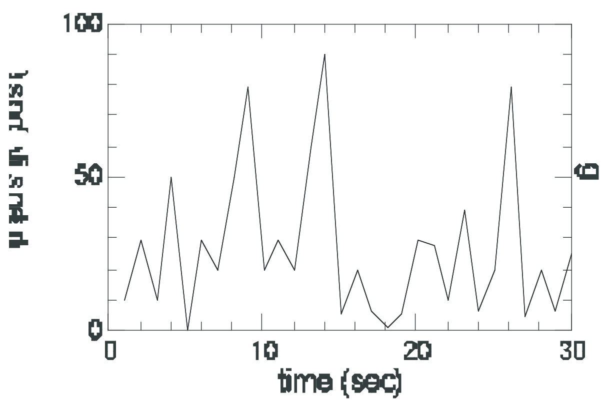
Energy & Wavevector Transfers accessible to Neutron Scattering

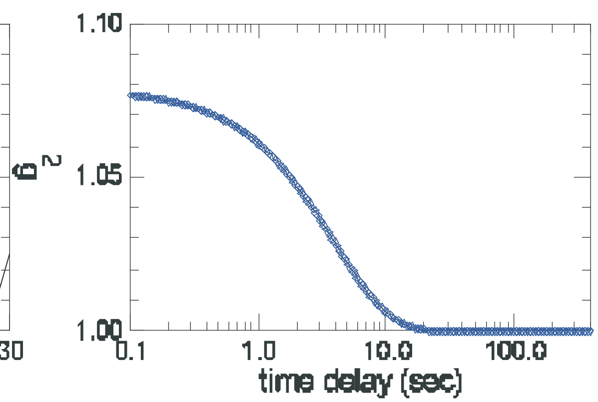
Photon Correlation Spectroscopy



X-ray speckle pattern from a static silica aeroge







$$g_2(q,t) = \frac{\langle I(q,t')I(q,t'+t)\rangle}{\langle I(q,t')\rangle^2}$$

$$g_2(t) = 1 + \beta \exp(-2\Gamma t)$$
$$= 1 + \beta \exp(-2t/\tau)$$

β:speckle contrast

Formal Theory of Scattering

Neutrons

ψ_k incident neutron wave fn.

χ_λ initial sample wave fn.

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

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

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

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

Use Fermi's Golden Rule:

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

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

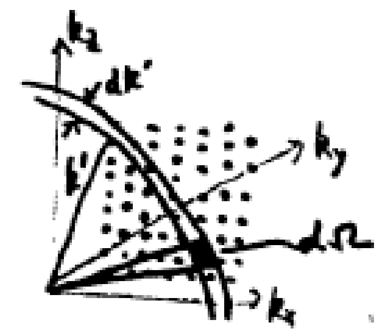
V = Interaction potential of neutron with the sample.

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

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

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

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

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

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

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

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

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

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

Use energy conservation law,

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

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

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

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

Scattering by an assembly of nuclei:

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

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

Thus from Eq. (4)

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

where

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

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

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

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

b_i depends on nucleus (isotope, spin relative to neutron ↑↑ or ↓↓), etc. Even for a monatomic system

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

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

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

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

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

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

Write it as

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

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

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

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

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

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

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

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

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

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

Thus, by (6),

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

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

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

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

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

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

It's Fourier Transform

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

Thus,

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

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

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

$\Downarrow$

Van-Hove space-time correlation function of system

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

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

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

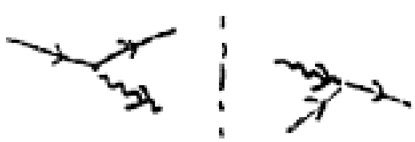
$$+ \frac{e}{2mc}\sum_i \left\{\vec{P}_i\cdot\vec{A}(\vec{r})\delta(\vec{r}-\vec{r}_i) + \vec{A}(\vec{r})\delta(r-r_i)\cdot\vec{P}_i\right\}$$

$$H_{\text{int}}^{(1)} \swarrow \tag{9}$$

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

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

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



In 1st order $\rightarrow$ 1-photon absorption, emission

In 2nd order $\rightarrow$ scattering

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

In 1st order $\rightarrow$ scattering

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

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

"Thomson" Scattering

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

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

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

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

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

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

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

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

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

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

(Equal-Time Correlation Function)