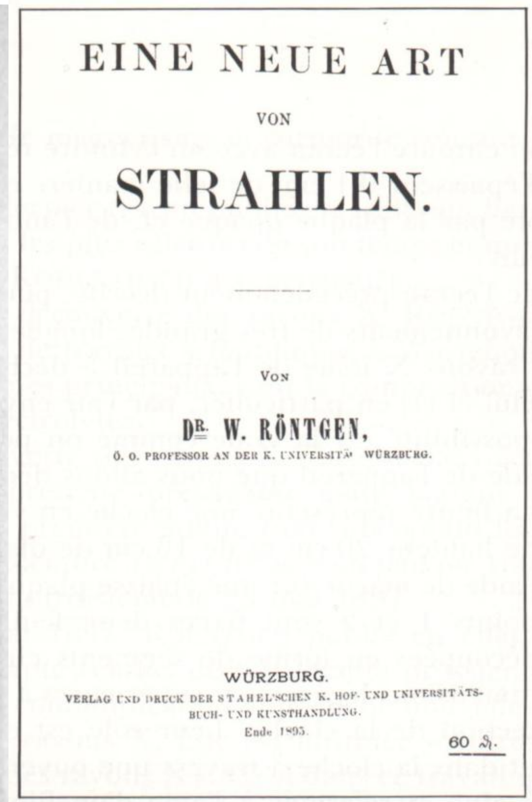
Introduction to Neutron and X-Ray Scattering

Sunil K. Sinha

UCSD/LANL

Acknowledgements: Prof. R.Pynn(Indiana U.)
Prof. M.Tolan (U. Dortmund)

Wilhelm Conrad Röntgen 1845-1923


EINE NEUE ART

VON

STRAHLEN.

Von

Dr. W. RÖNTGEN,

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

WÜRZBURG.

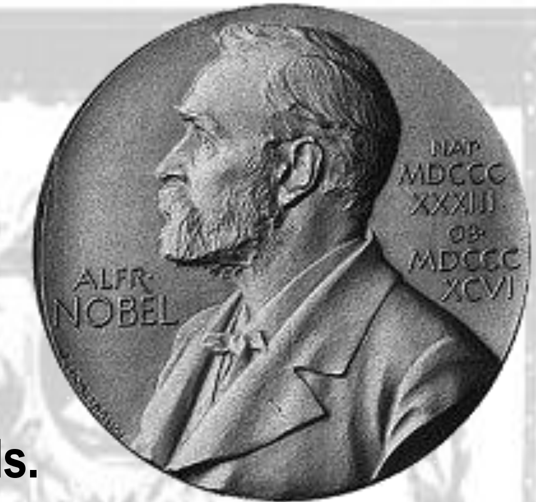
VERLAG UND DRUCK DER STAHEL'SCHEN K. HOF- UND UNIVERSITÄTS-BUCH- UND KUNSTHANDLUNG.

Ende 1895.

60 Pf.

1895: Discovery of X-Rays

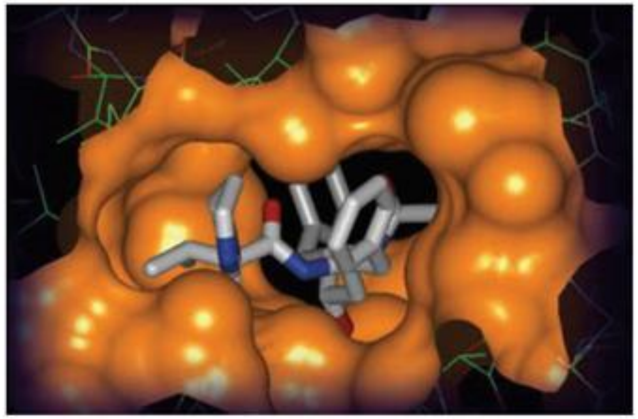
Nobel Prizes for Research with X-Rays



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.
2006 R. Kornberg in Chemistry for studies of the molecular basis of eukaryotic

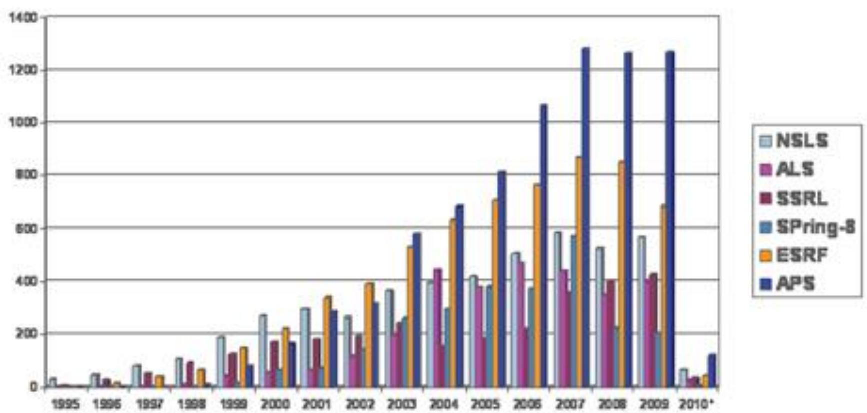
Synchrotron research on proteins has led to major advances in drugs to battle infection, HIV, cancer

Renal cancer drug pazopanib™ developed in part based on APS research (GlaxoSmithKline)



Close-up view of the drug binding site within HIV protease (Kaletra®, Abbott).

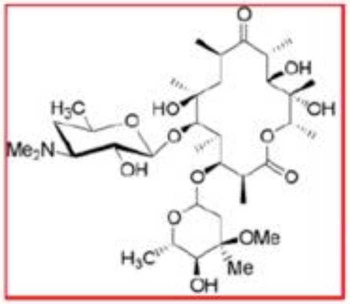
Ramakrishnan, Steitz and Yonath
2009 Chemistry Nobel Laureates



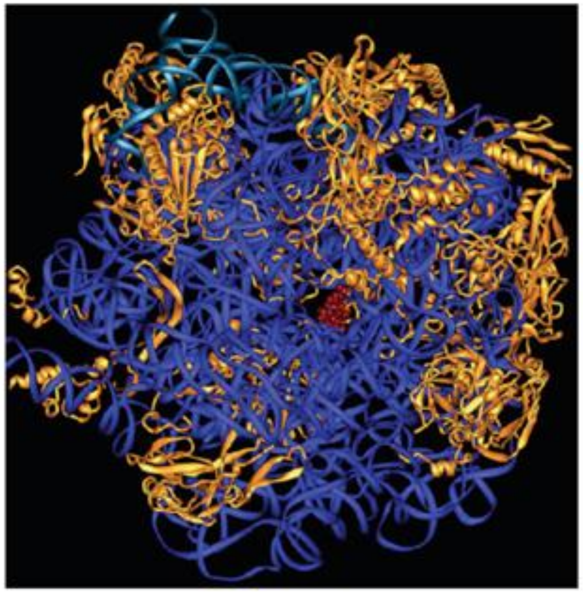
APS protein structure output is almost twice that of any other light source

Designing antibiotics –

difference between bacterial and eukaryotic ribosomes is one amine group in the 2.5MD ribosome



Erythromycin – a macrolide antibiotic that blocks protein synthesis by binding to bacterial ribosomes but not to eukaryotic ribosomes

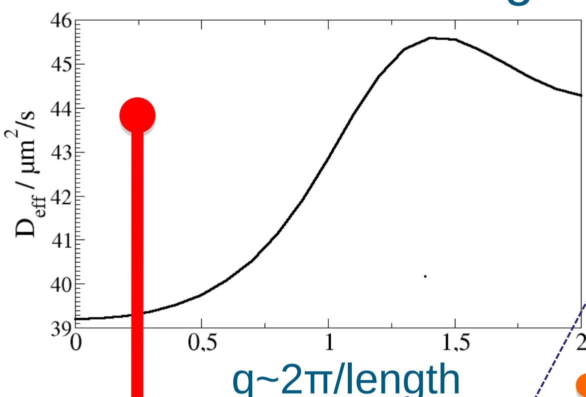


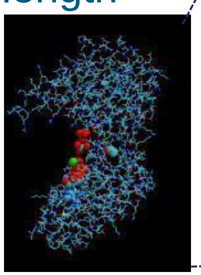
www.molgen.mpg.de

Functional domain dynamics in proteins

NSE

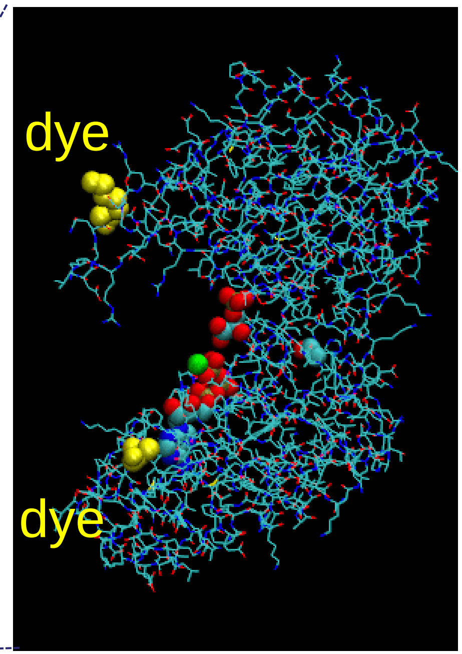
0.5-50 nm length scale
ps - µs time scale
orientational average





FRET

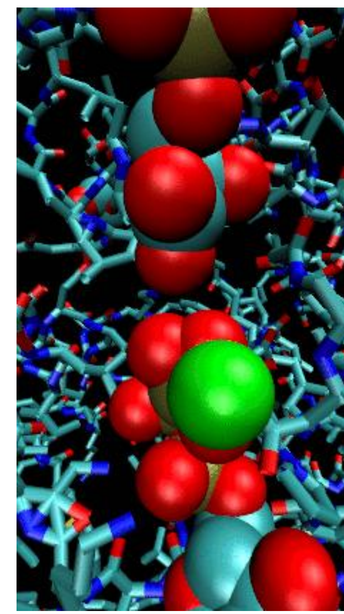
fixed defined position
> µs timescale



phosphoglycerate kinase

NMR

ps - ms timescale
small proteins



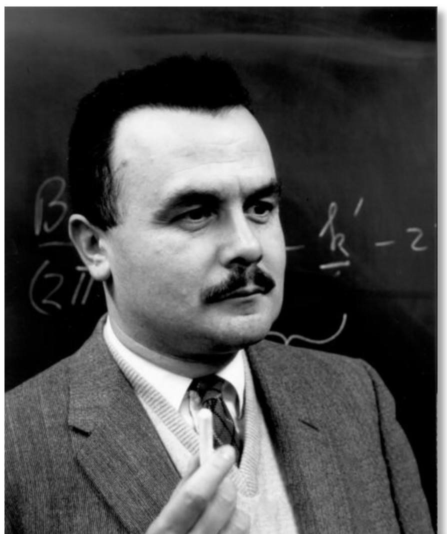
Neutron Advantages

- Penetrating, but does no damage to sample
- H/D contrast matching can be used to study macromolecules in solution, polymers, etc.
- Strongly interacts with magnetic moments
- Energies match those of phonons, magnons,rotons, etc.

Nobel Prize in Physics, 1994

Awarded for "pioneering contributions to the development of neutron scattering techniques for studies of condensed matter"

Bertram N. Brockhouse



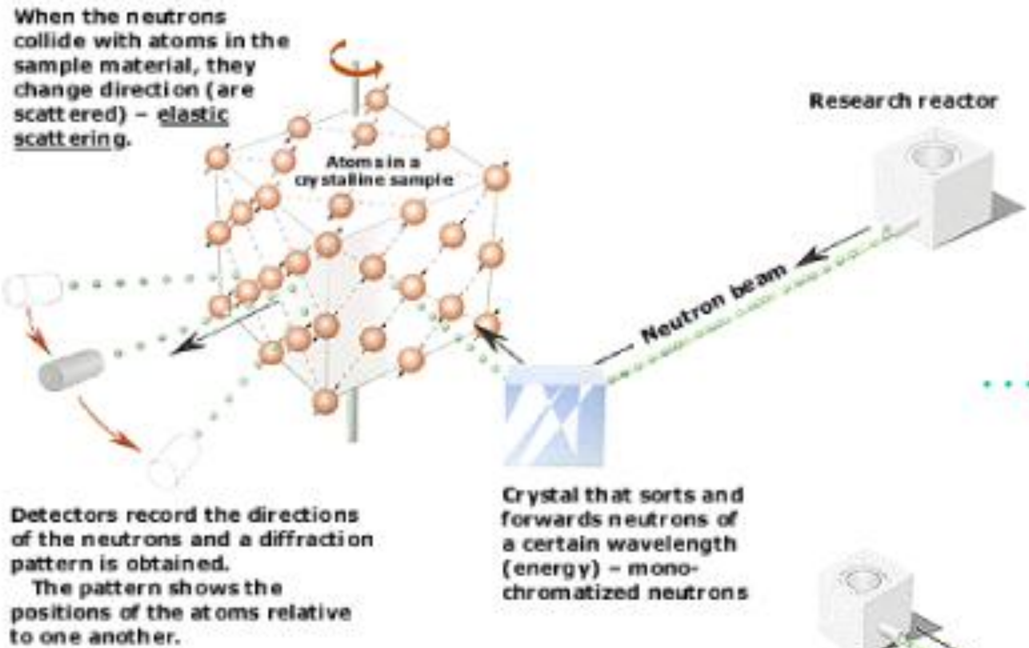
Development of neutron spectroscopy

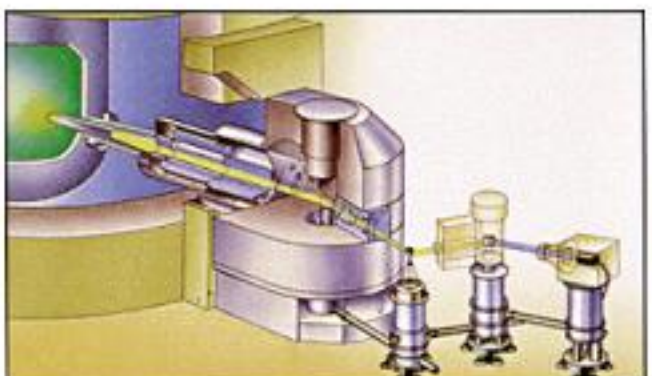
Clifford G. Shull

Development of the neutron diffraction technique

The 1994 Nobel Prize in Physics – Shull & Brockhouse

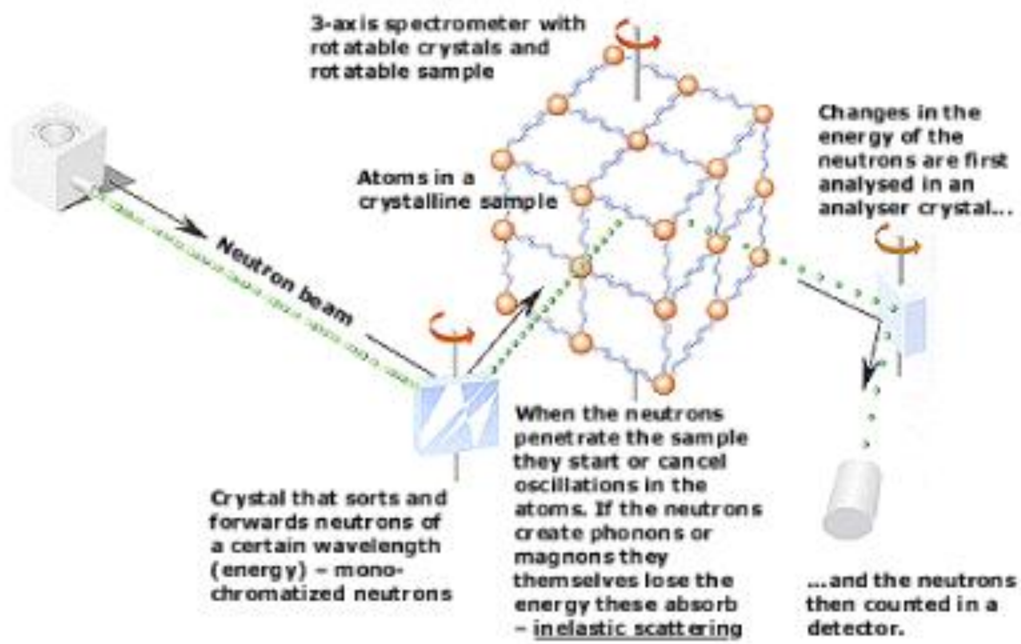
Neutrons show where the atoms are….



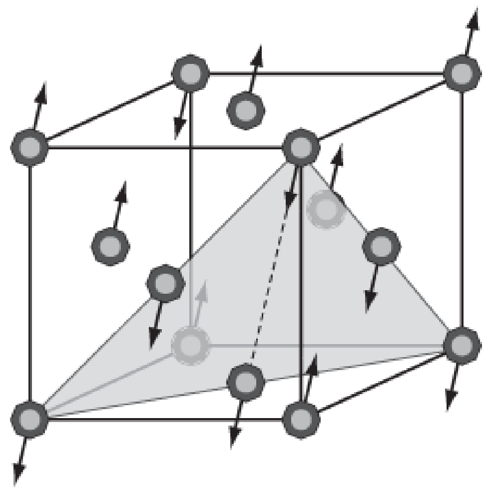


3-axis spectrometer

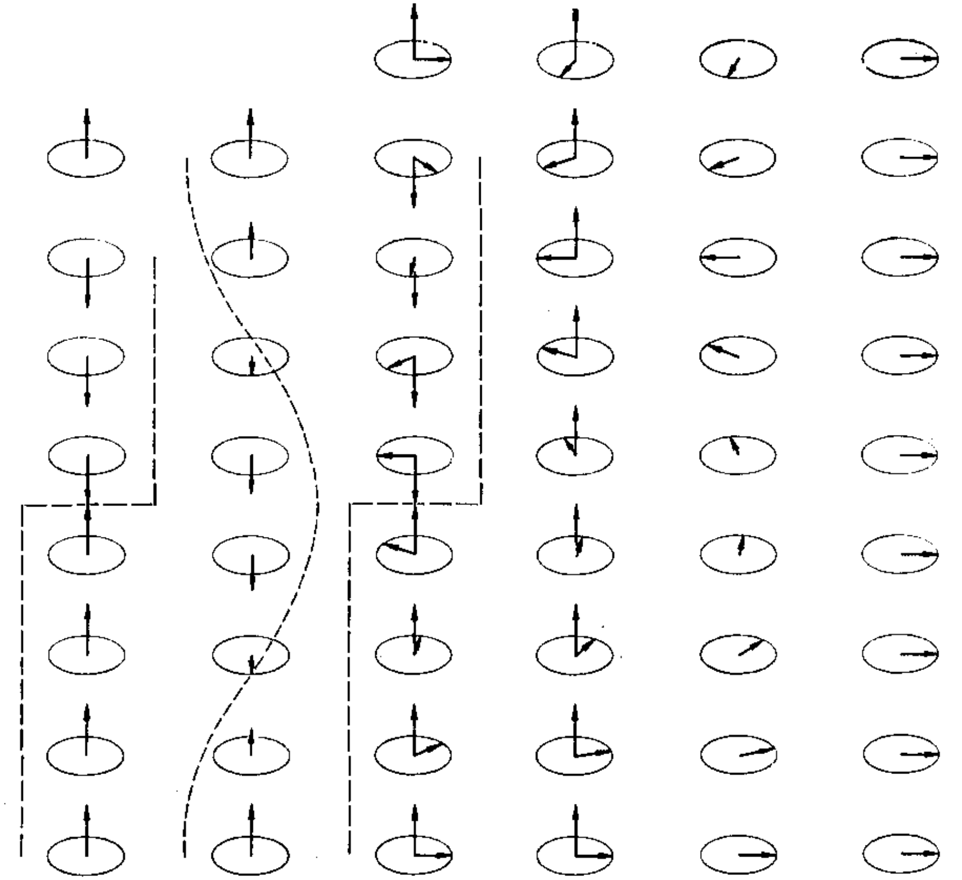
…and what the atoms do.



First Study of an Antiferromagnetic Structure



Antiferromagnetic Structure of MnO
(Shull and Wollan Phys. Rev. 83, 333 (1951)



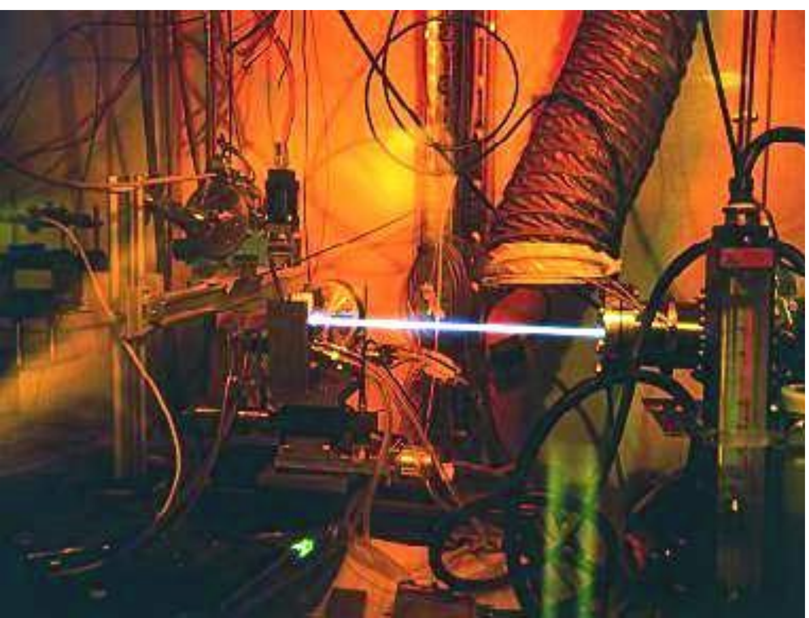
Magnetic Structure of the Rare Earth Metals
(W.C. Koehler (1965))

Science with X-Rays

- Diffraction and crystal structures
- Structure Factors of liquids and glasses
- Structures of Thin Films
- ARPES
- EXAFS, XANES
- Studies of Magnetism with resonant XMS
- Inelastic X-ray scattering: phonons, electronic excitations
- X-ray Photon Correlation Spectroscopy
- Microscopy
- Imaging/Tomography

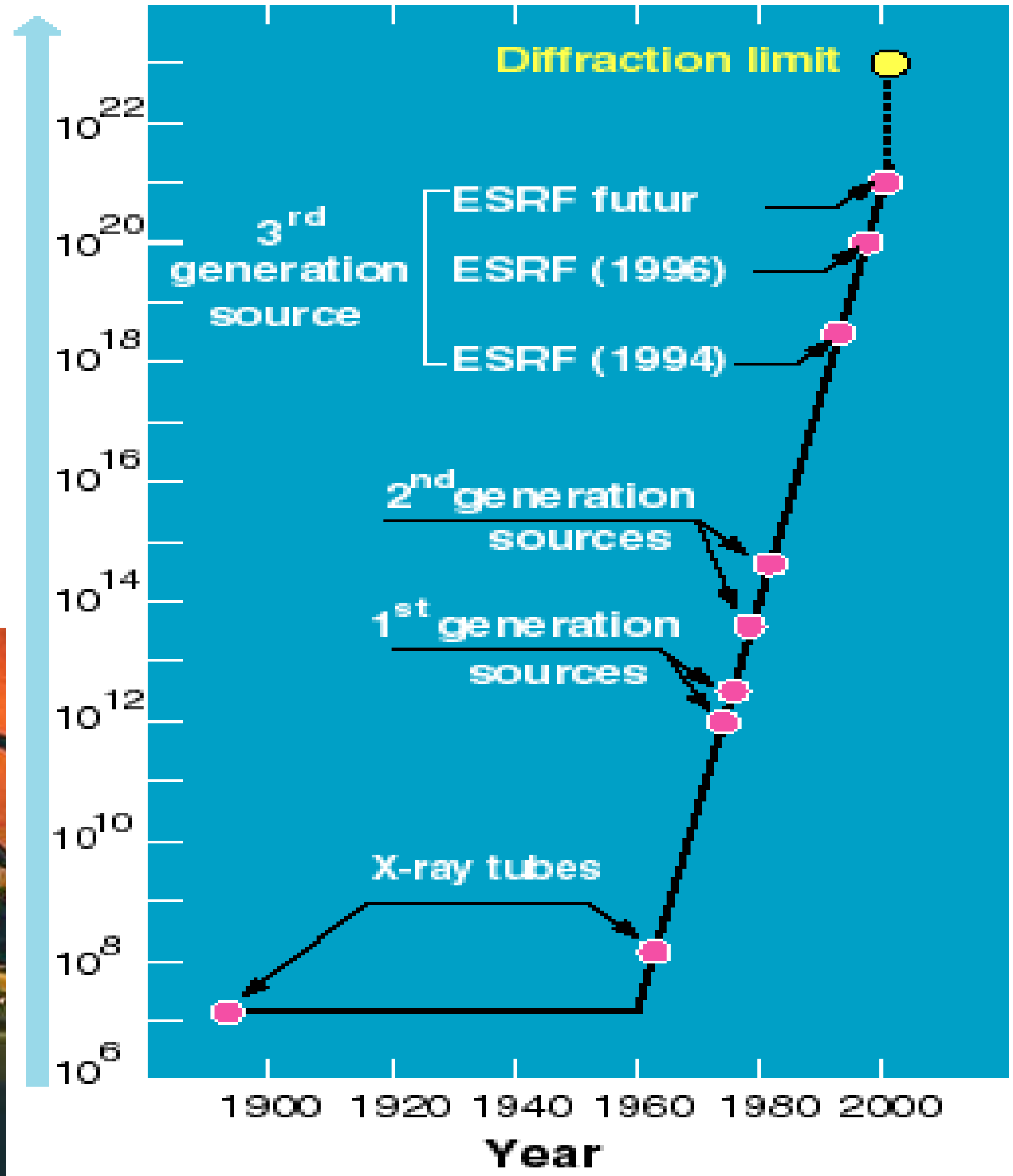
Why Synchrotron-radiation ?

Intensity !!!



Brilliance of the X-ray beams

(photons / s / mm^2 / $mrad^2$ / 0.1% BW)



Compare the evolution of high intensity optical and x-ray sources

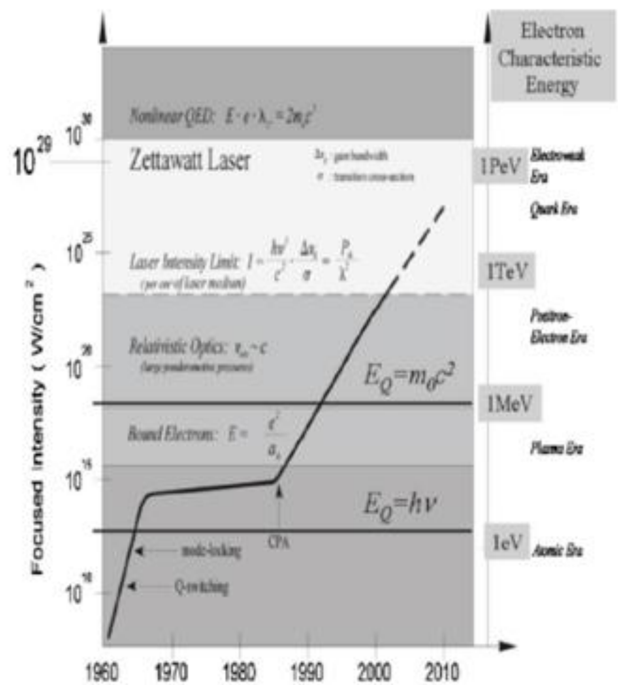
Hign-intensity at optical wavelengths
- high harmonic generation
- tabletop coherent x-ray radiation
- attosecond pulses

High-intensity at x-ray wavelengths

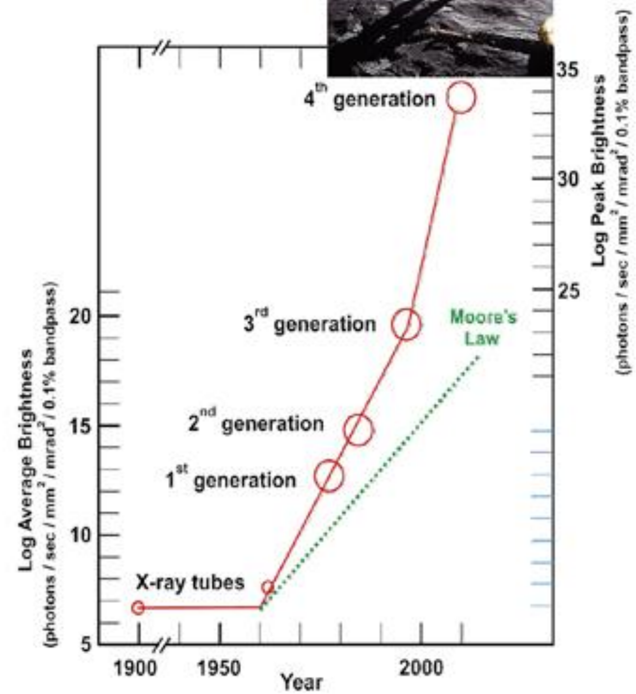
?

?

?



G. Mourou RMP 2006



D. Moncton, George Brown

Example 1: X-Ray Diffraction & structural biology

- D.C. Phillips presents the 3-D structure of lysozyme to the Royal Society in **1965**
- Linear polypeptide chain
- Folded model of the same amino acid sequence
- July 2009: 58,588 structures in Protein Data Bank

A single protein structure used to be the project of a scientific lifetime

Synchrotron Radiation - 8301 structures solved in 2009

Advantages of Neutrons and X-Rays

- Penetrating/ Non Destructive N (X)
- Right wavelength/energy N,X
- Magnetic probe N,X
- Contrast matching N
- Weakly interacting-Born approxn. N,X
- *Global* Statistical information N,X
- Buried Interfaces—depth dependence N,X

Neutron and X-ray Scattering:

"small" science at big facilities!

Historic accomplishments (Neutrons)

- Antiferromagnetic Structures
- Rare earth spirals and other spin structures
- Spin wave dispersion
- Our whole understanding of the details of exchange interactions in solids
- Magnetism and Superconductivity
- Phonon dispersion curves in crystals; quantum crystals and anharmonicity
- Crystal fields
- Excitations in normal liquids
- Rotons in superfluid helium
- Condensate fraction in helium

Recent Applications

- Quantum Phase Transitions and Critical points
- Magnetic order and magnetic fluctuations in the high-Tc cuprates
- Gaps and low-lying excitations (including phonons) in High-Tc
- Magnetic Order and spin fluctuations in highly-correlated systems
- Manganites
- Magnetic nanodot/antidot arrays
- Exchange bias

Applications in Soft Matter and Materials

- Scaling Theory of polymers
- Reptation in Polymers
- Alpha and beta relaxation in glasses
- Structures of surfactants and membranes
- Structure of Ribozome
- Excitations and Phase transitions in confined Systems (phase separation in Vycor glass; Ripplons in superfluid He films, etc.)
- Momentum Distributions
- Materials—precipitates, steels, cement, etc.

Recent Applications (contd.)

- Proton motion in carbon nanotubes
- Protein dynamics
- Glass transition in polymer films
- Protonation states in biological macromolecules from nuclear density maps
- Studies of protein diffusive motion in hydrated enzymes
- Boson peaks in glasses
- Phase diagrams of surfactants
- Lipid membranes

Applications of Surface/Interface Scattering

- study the morphology of surface and interface roughness
- wetting films
- film growth exponents
- capillary waves on liquid surfaces (polymers, microemulsions, liquid metals, etc.)
- islands on block copolymer films
- pitting corrosion
- magnetic roughness
- study the morphology of magnetic domains in magnetic films.
- Nanodot arrays
- Tribology, Adhesion, Electrodeposition

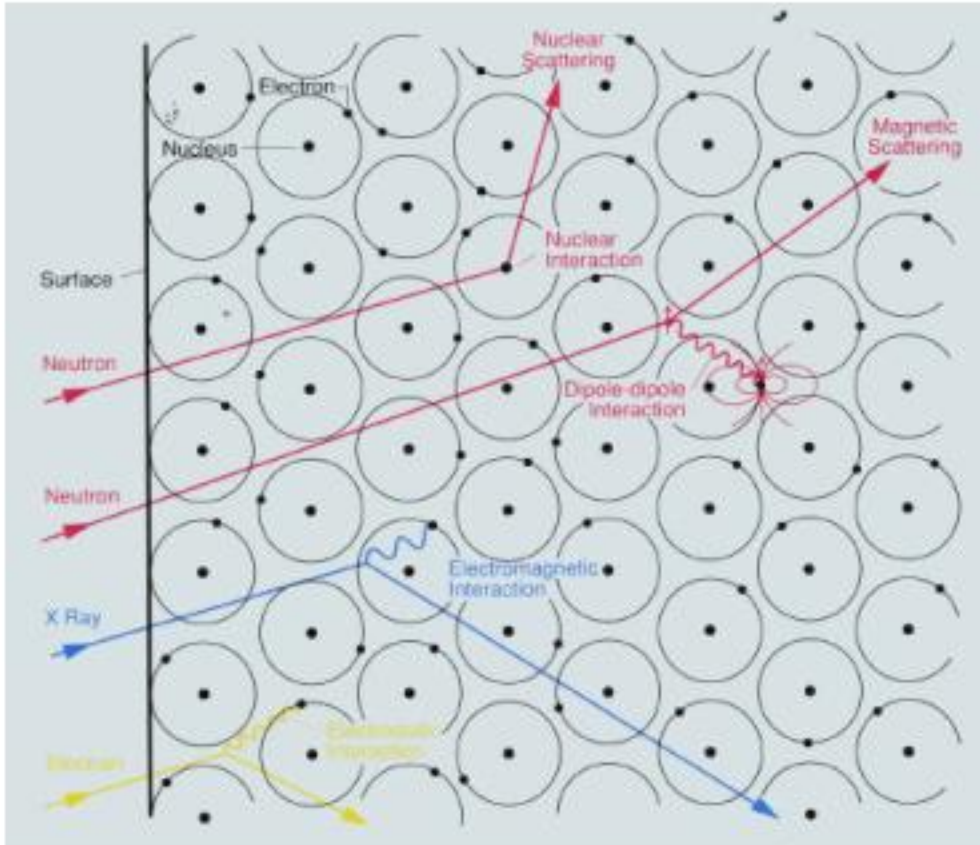
X-rays and neutrons are complementary to SPM's

- Yield GLOBAL statistical properties about assemblies of particles
- Can be used to study BURIED interfaces or particles
- Impervious to sample environmental conditions, magnetic fields, etc.
- Can also be used to study single nanoparticles (synchrotron nanoprobe)

S.R. and neutron based research can help us to understand:

- How the constituent molecules self-assemble to form nanoparticles.
- How these self-organize into assemblies
- How structure and dynamics lead to function
- How emergent or collective properties arise

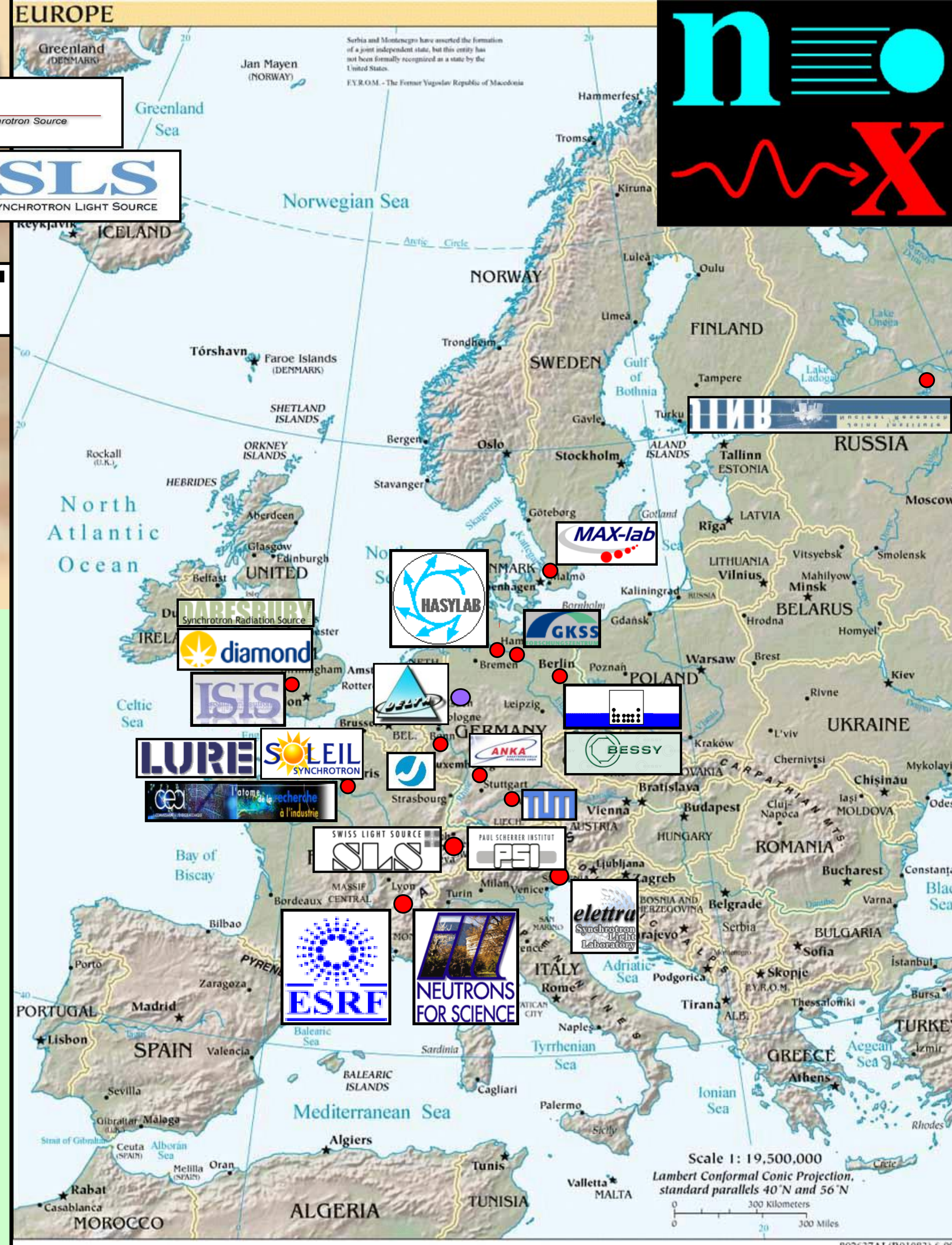
Interaction Mechanisms



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

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}



Synchrotron- and Neutron Scattering Places

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

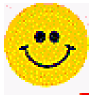
$E = h\nu = hc/\lambda = hck$

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

Thermal Neutrons

Advantages 

1) λ_n ~ Interatomic Spacing

2) Penetrates Bulk Matter (neutral particle)

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

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

5) Scattered Strongly by Magnetic Moments

Disadvantages 

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

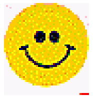
2) Some Elements Strongly Absorb (e.g. Cd, Gd, B)

3) Kinematic Restriction on Q for Large E Transfers

4) Restricted to Excitations ≤ 100 meV

Synchrotron X-rays

Advantages



1) λ_n - Interatomic Spacing

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

3) No Kinematic Restrictions (E,Q uncoupled)

4) No Restriction on Energy Transfer that Can Be Studied

Disadvantages

1) Strong Absorption for Lower Energy Photons

2) Little Contrast for Hydrocarbons or Similar Elements

3) Weak Scattering from Light Elements

4) Radiation Damage to Samples

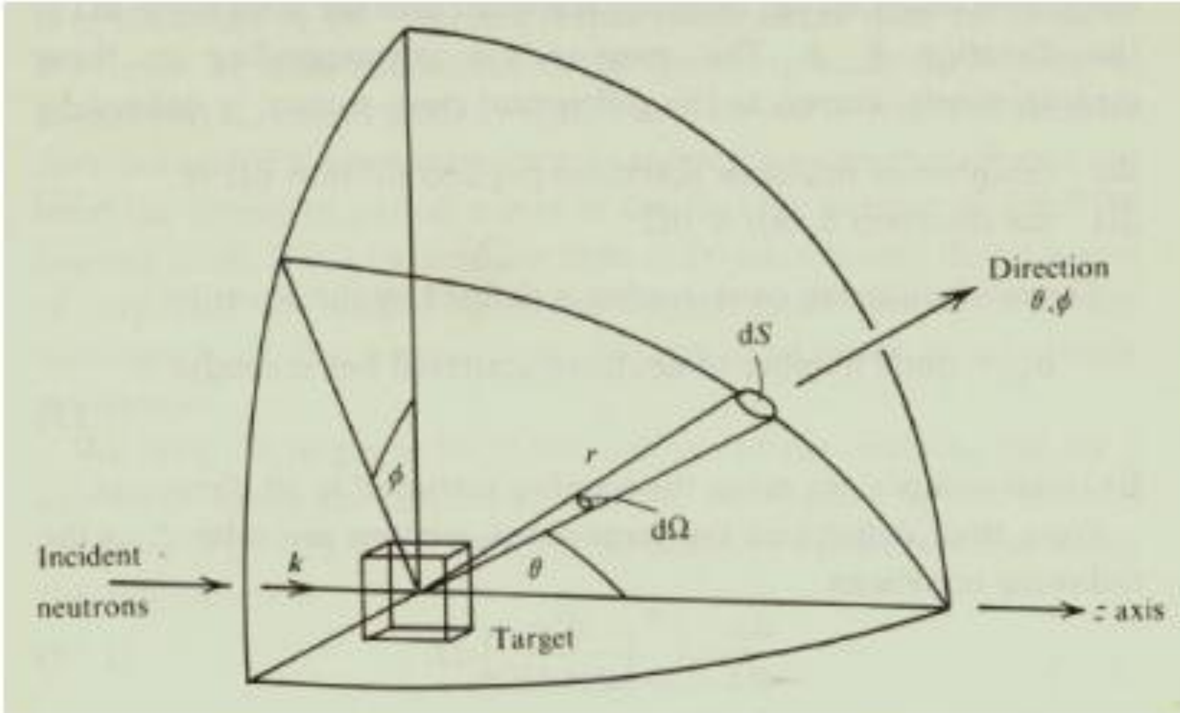
Cross Sections

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



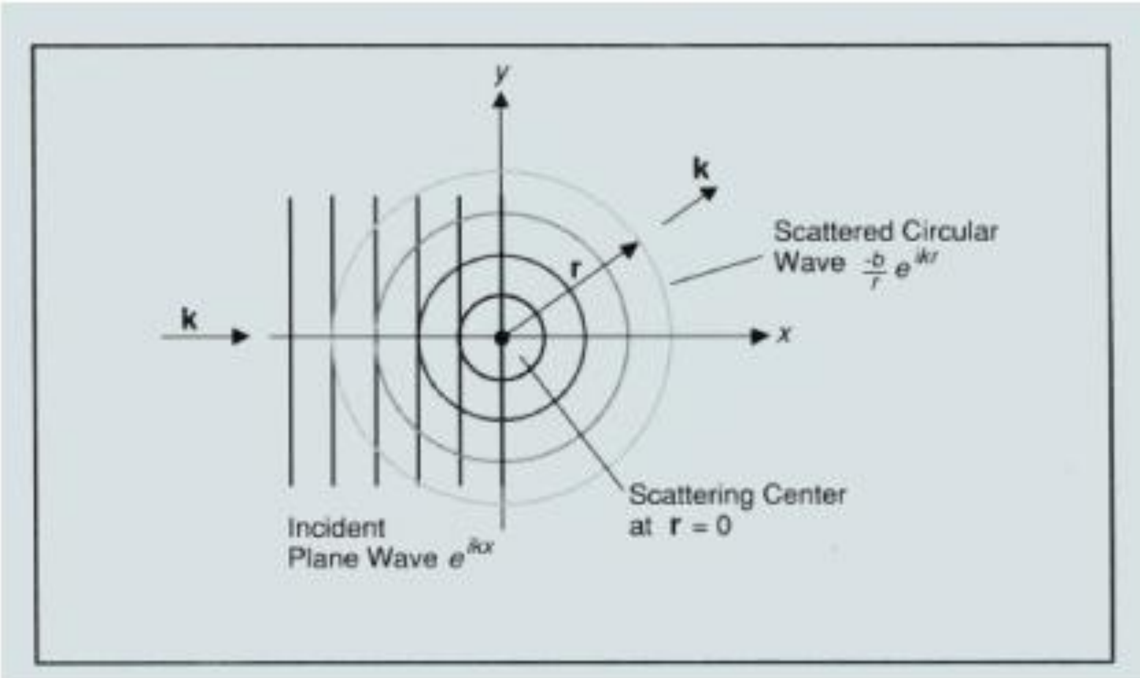
$$\Phi = \text{number of incident neutrons per cm}^2 \text{ per second}$$

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

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

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

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

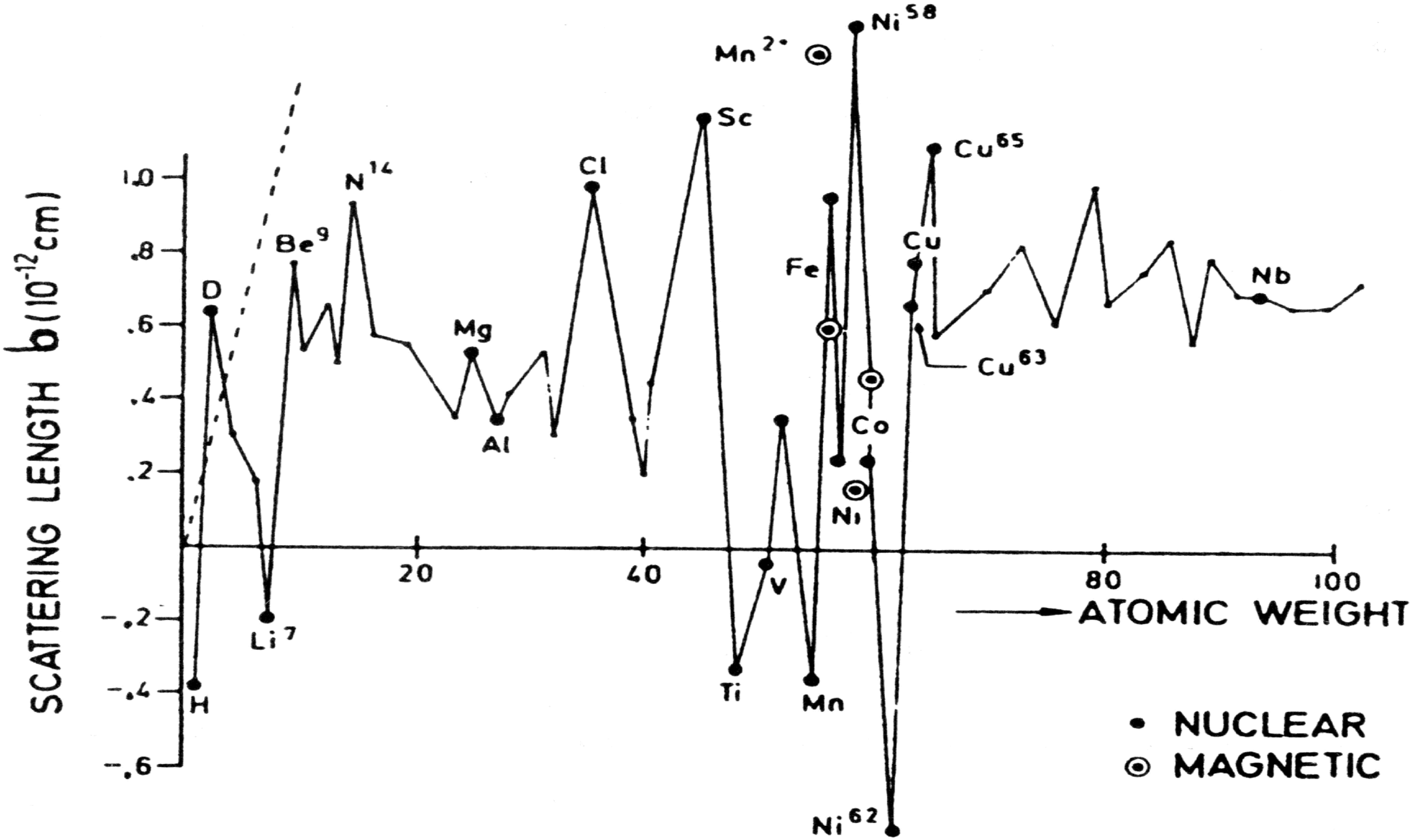
If v is the velocity of the neutron (same before and after scattering), the number of neutrons passing through an area dS per second after scattering is :

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

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

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

Intrinsic Cross Section: Neutrons



Scatttering by a Single Free Electron

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

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

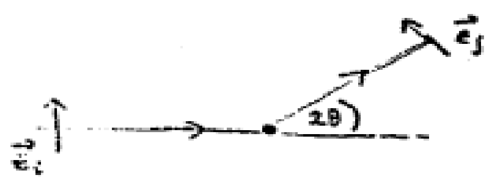
$$= \left(\frac{e^2}{mc^2}\right)\frac{e^{ikR}}{R}\left(\bar{E}_0\cdot\bar{\varepsilon}_j\right)\bar{\varepsilon}_j$$

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

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

$\uparrow$

r_0^2



Intrinsic Cross Section: X-Rays

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

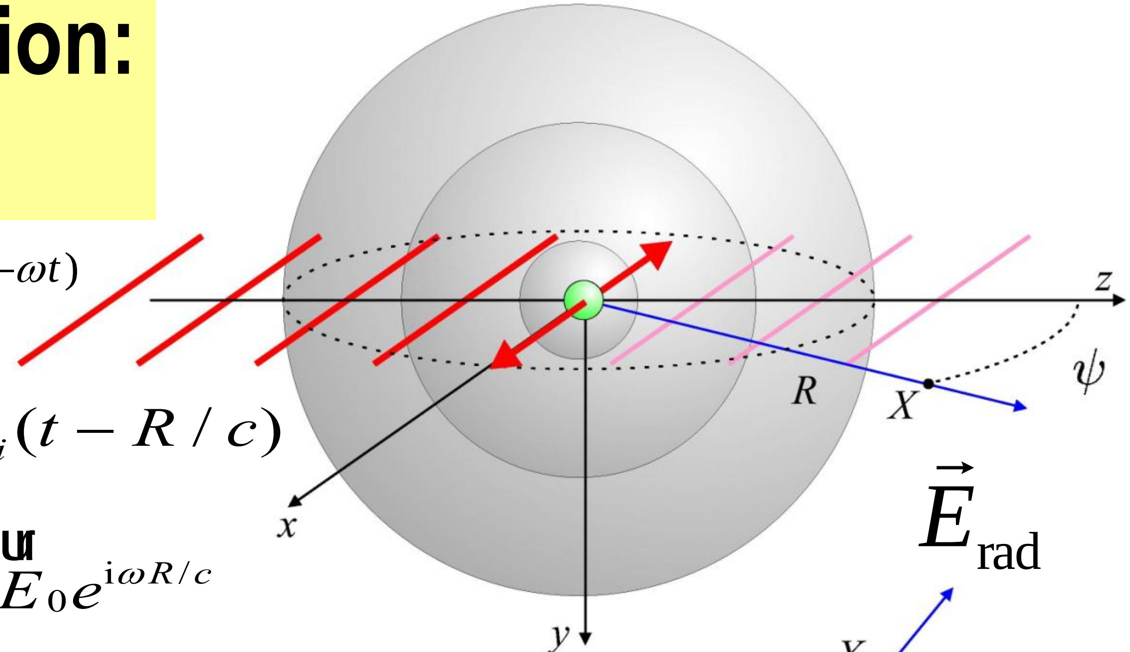
$$E_{i,\text{rad}}(R,t) = \frac{e}{4\pi\varepsilon_0 c^2 R}\, a_i(t - R/c)$$

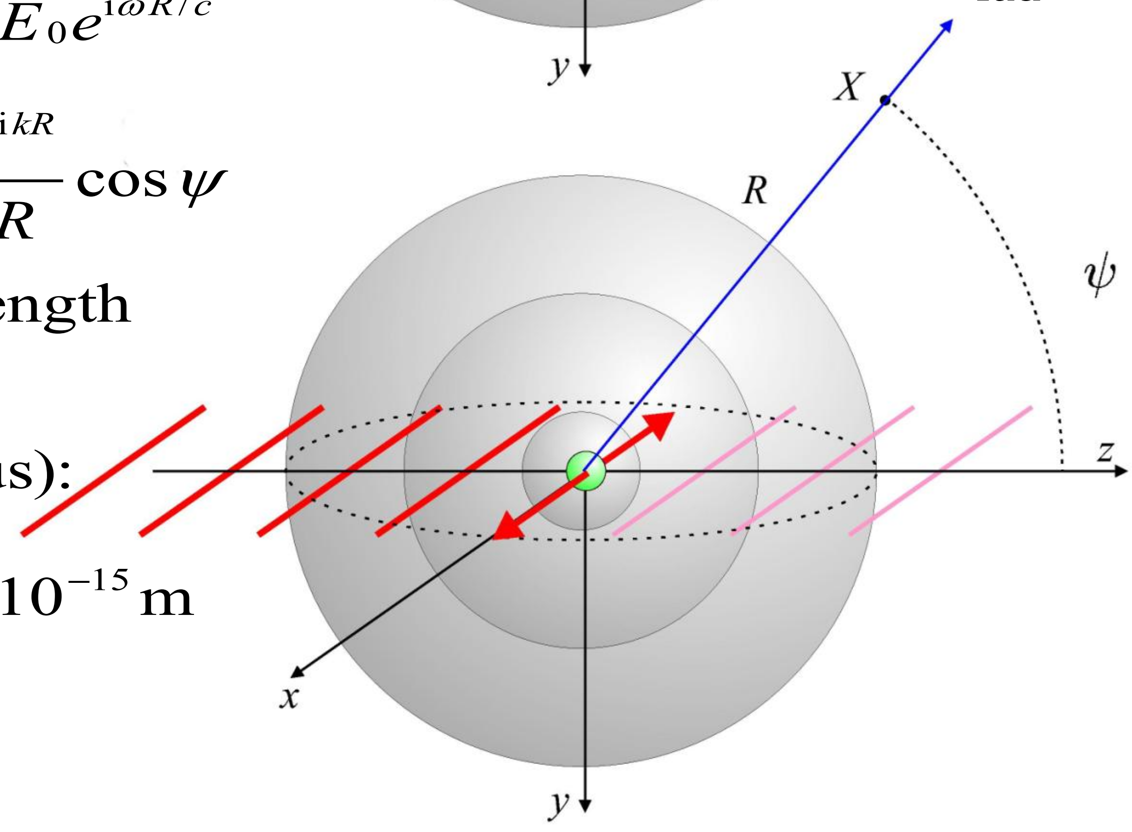
$$\vec{a}(t - R/c) = -\frac{e}{m}\alpha(\omega)\vec{E}_0 e^{\mathrm{i}\omega R/c}$$

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

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

$$r_0 = \frac{e^2}{4\pi\varepsilon_0 mc^2} = 2.82\times 10^{-15}\,\text{m}$$



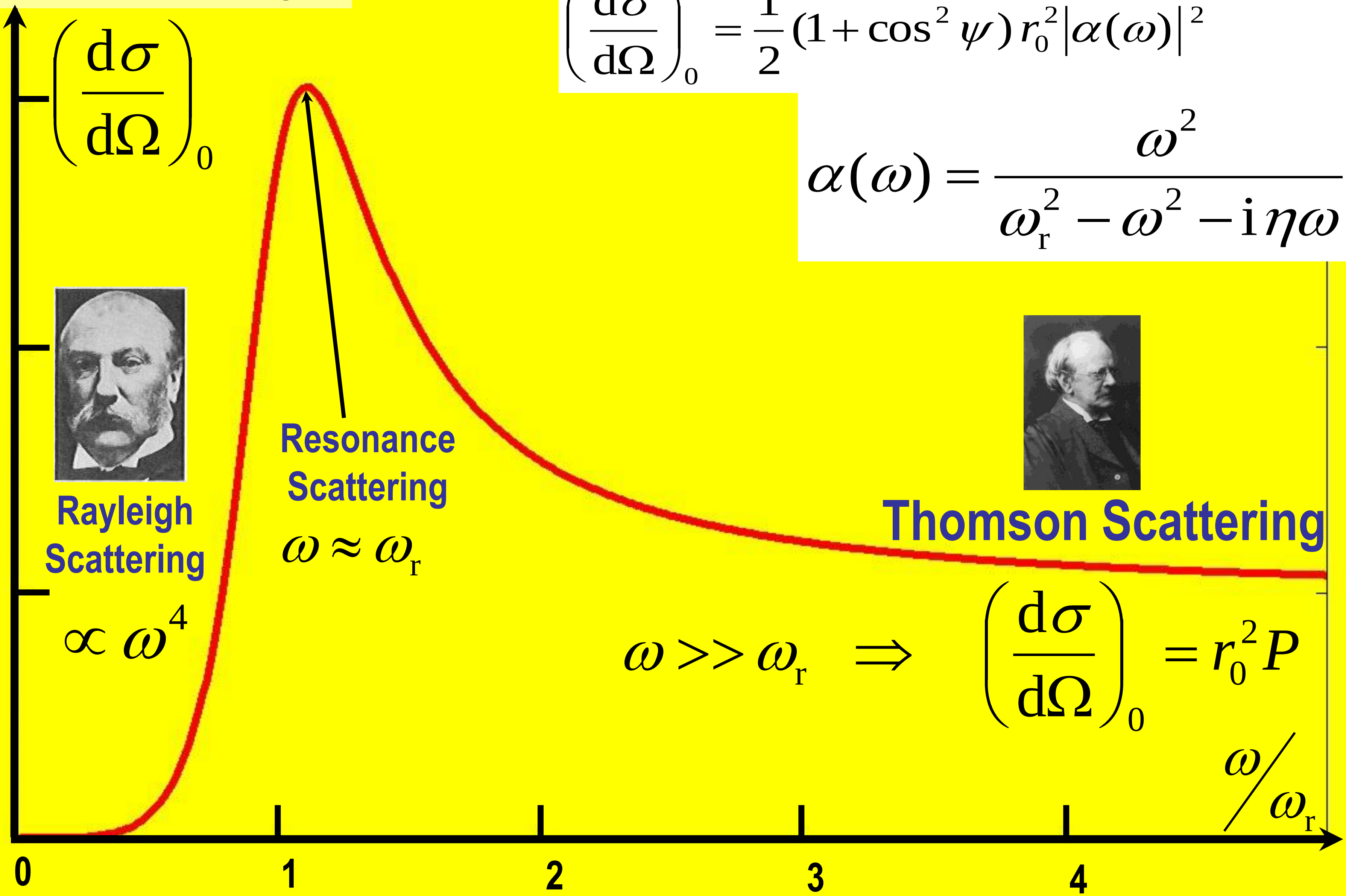


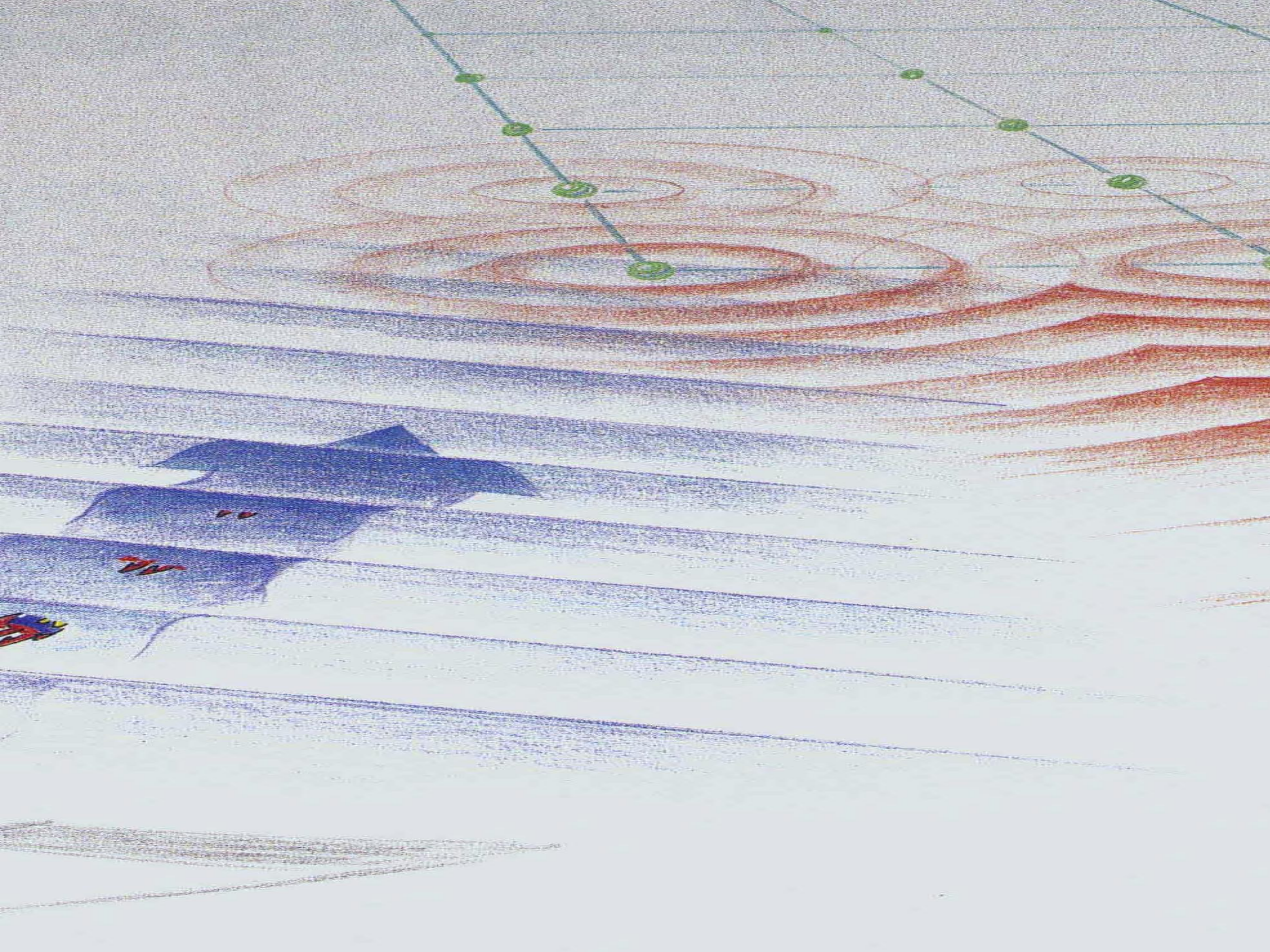
Intrinsic Cross Section: X-Rays

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

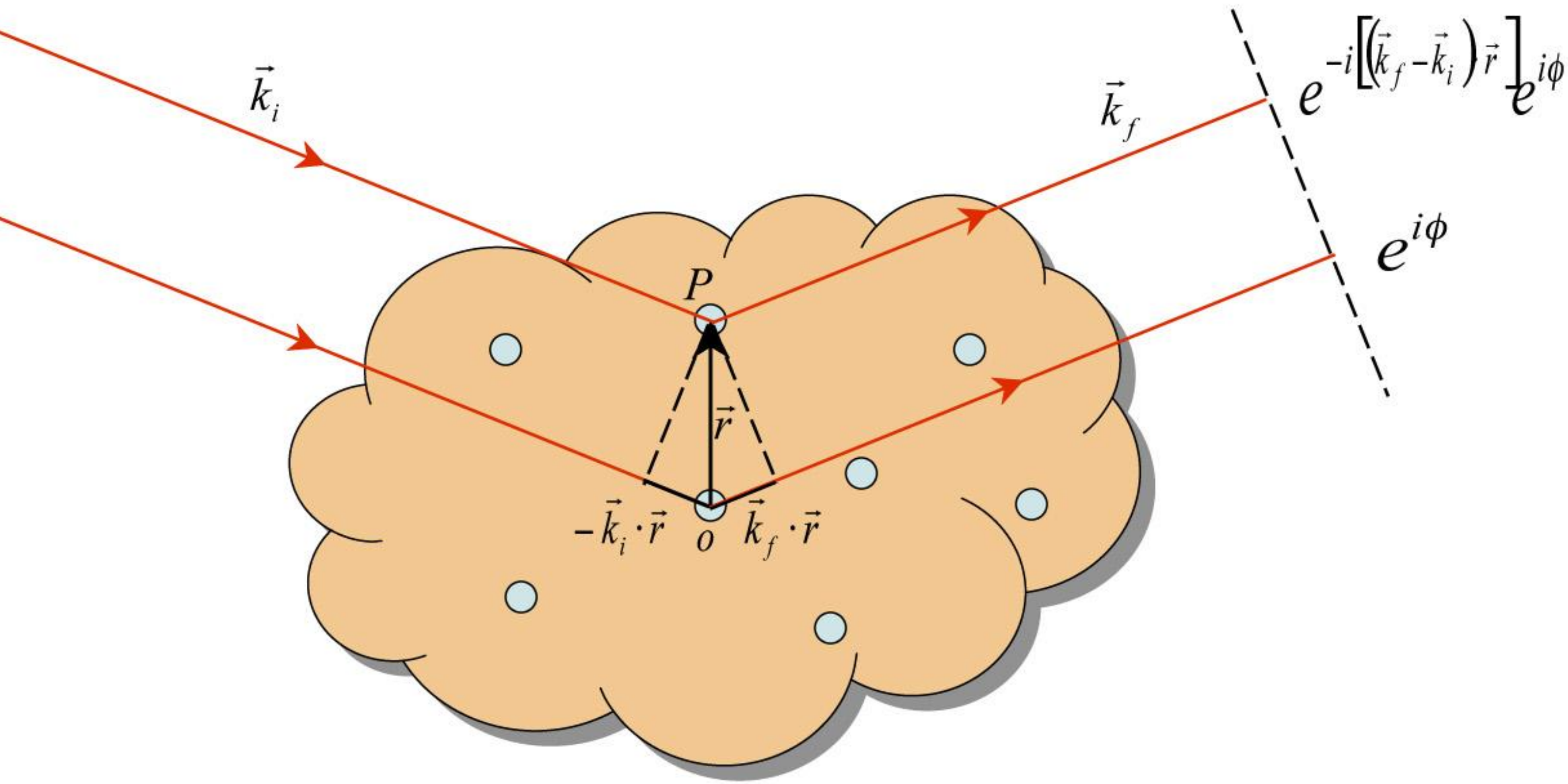
$$\left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\right)_0 = \frac{1}{2}(1+\cos^2\psi)\, r_0^2 \left|\alpha(\omega)\right|^2$$

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





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



Wave vector transfer is defined as

$$\mathbf{q} = \mathbf{k}_f - \mathbf{k}_i$$

Neutrons

Sum of scattered waves on plane II:

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

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

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

X-rays

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

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

For neutrons, b_i depends on nucleus (isotope, spin relative to neutron (↑↑ or ↓↑)), etc. Even for one type of atom,

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

$$b_i b_j = \langle b \rangle^2 + \langle b \rangle \left[\delta b_i + \delta b_j \right] + \delta b_i \, \delta b_j$$

zero (the bracketed term) — zero unless $i = j$ (the term $\delta b_i \, \delta b_j$)

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

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

$\langle b \rangle^2 \to \sigma_{coh}/4\pi$; $\left[\left\langle b^2 \right\rangle - \langle b \rangle^2 \right] \to \sigma_{inc}/4\pi$

"coherent" "incoherent"

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

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

$\{R_i\}$ = nuclear posns

X-rays

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

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

$\{\mathbf{r}_i\}$ == 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, $S(\mathbf{q}) = \langle \rho_{el}(\mathbf{q}) \, \rho_{el}^*(\mathbf{q}) \rangle$

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

but small coherent σ (1.8×10^{-24} cm^2)

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

and small incoherent σ (2.0×10^{-24} cm^2)

C, O have completely coherent σ's

V is almost completely incoherent (σ_{coh} ~ 0.02×10^{-24} cm^2 ; σ_{incoh} ~ 5.0×10^{-24} cm^2)

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 $\vec{R}_i$

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

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

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

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

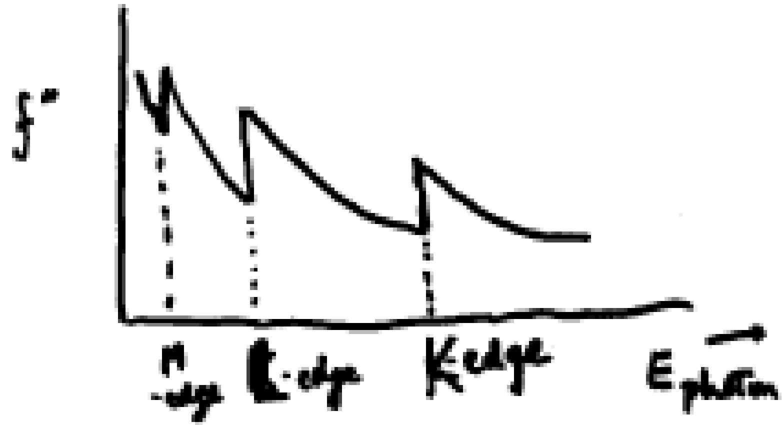
↙ atomic form factor

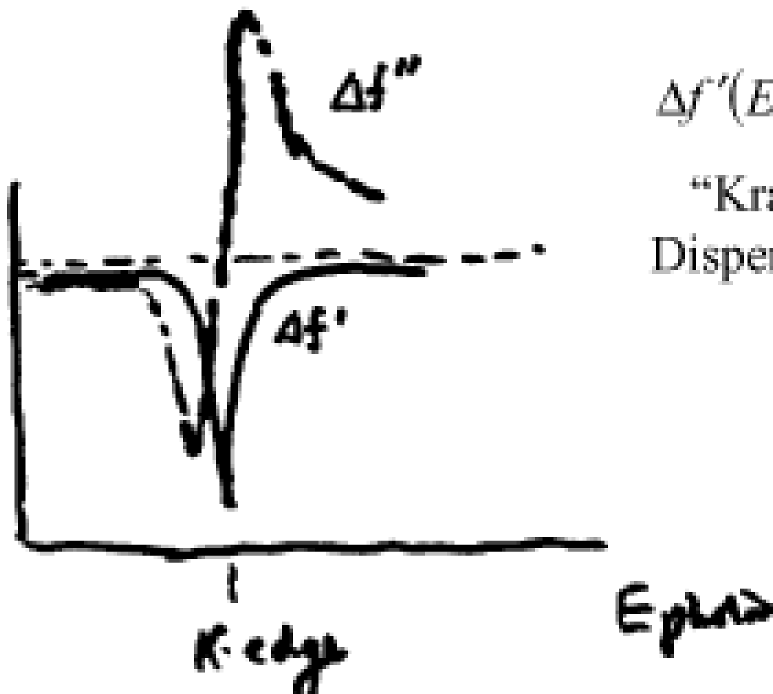
X-rays

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

"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

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

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

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

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

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

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

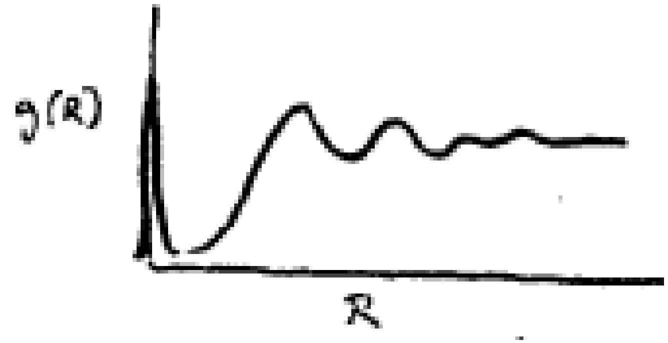
$g(\vec{R})$ = Pair-distribution function

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

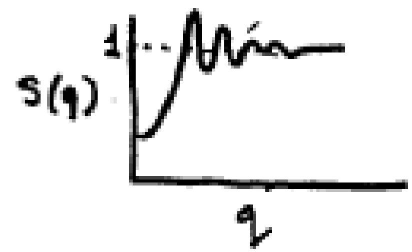
$\Rightarrow$ Probability that given a particle at $\vec{r}$, there is distance $\vec{R}$ from it (per unit volume)

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

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



Liquids and Glasses



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

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

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

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)

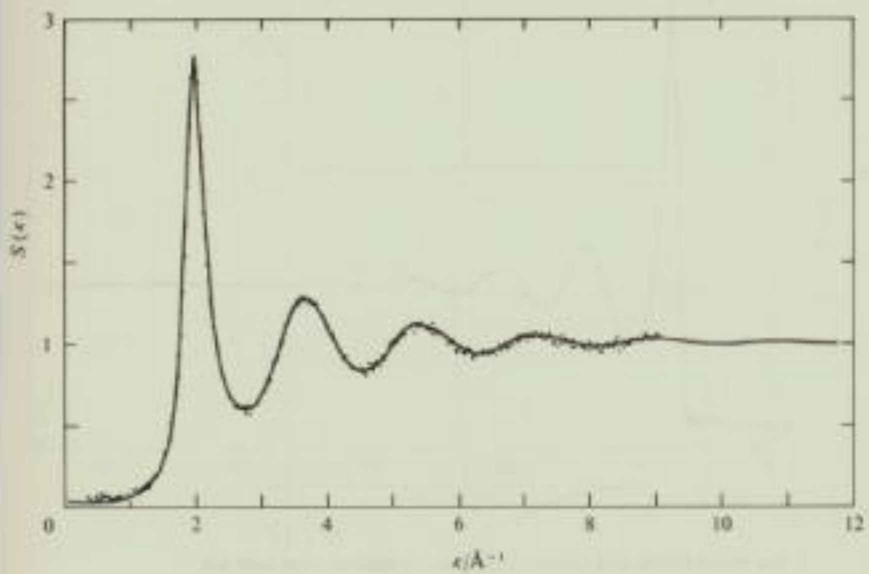


Fig. 5.1 The structure factor $S(\kappa)$ for ^{36}Ar at 85 K. The curve through the experimental points is obtained from a molecular dynamics calculation of Verlet based on a Lennard-Jones potential. (After Yarnell *et al.*, 1973.)

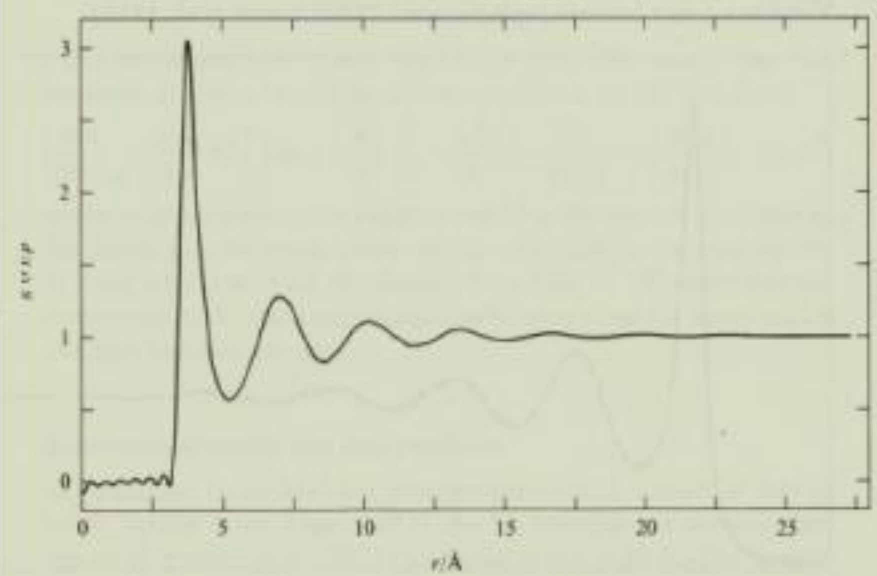


Fig. 5.2 The pair-distribution function $g(r)$ obtained from the experimental results in Fig. 5.1. The mean number density is $\rho = 2.13 \times 10^{28}$ atoms m^{-3}. (After Yarnell *et al.*, 1973.)

Neutrons

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

X-Rays

$I(q) = \sum_{K,K'} (r_0)^2 Z_K Z_{K'} f_K(q) f^*_{K'}(q) [(1 + \cos^2(\theta))/2] S_{K K'}(q)$

(K, K′ = Different Atomic Species)

$S_{K K'}(q) = \langle \sum_{l(K),m(K')} \exp\{-i\, q.[R_{l(K)} - R_{m(K')}]\} \rangle$ ---> Partial

Structure Factor

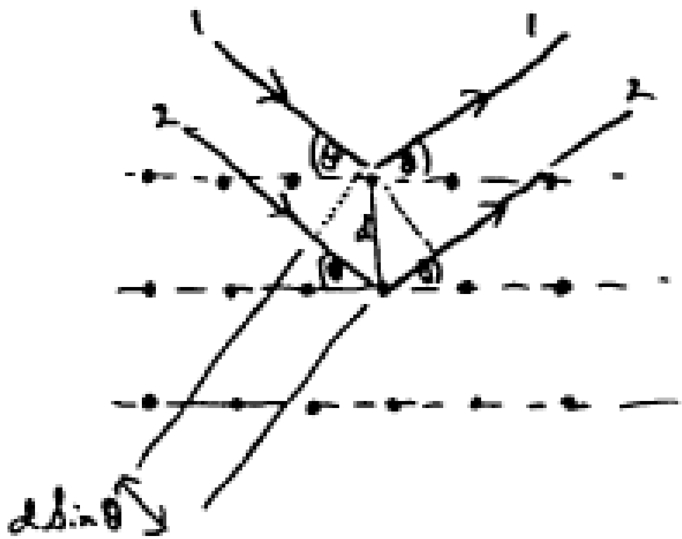
These can be unscrambled by simultaneous measurement of

$d\sigma/d\Omega$ for neutrons with different isotopes and/or X-rays.

Diffraction from Crystals

In general, in a scattering experiment

$$\left|\vec{q}\right| = 2k \, \text{Sin}\,\theta = \frac{4\pi}{\lambda} \text{Sin}\,\theta$$

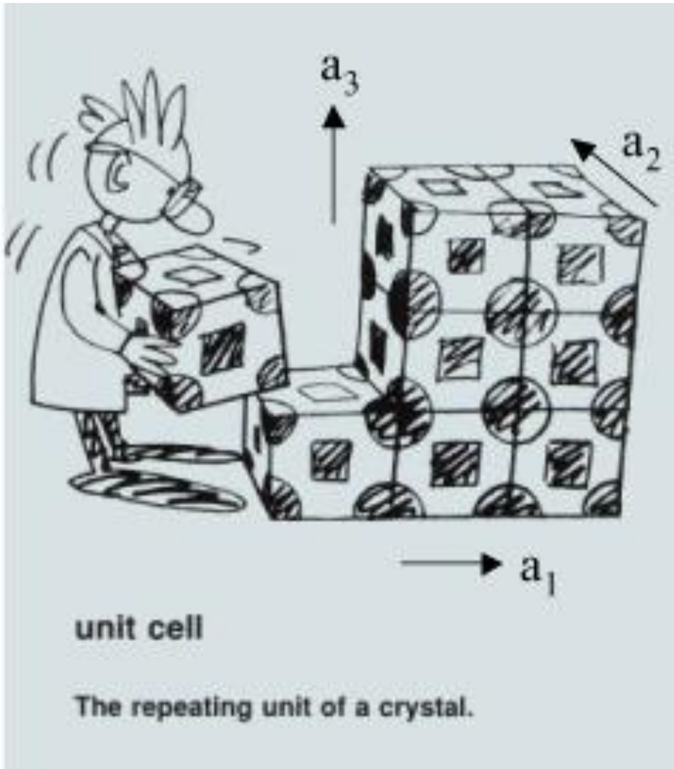


A simple way to see Bragg's Law:

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

$\therefore$ Constructive interference when

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



Reciprocal Lattice

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

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

S.K. Sinha

Define 3 other vectors:

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

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

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

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

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

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

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

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

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

OR

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

Crystals (Bravais or Monotonic)

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

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

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

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

[Property of reciprocal lattices and direct lattices:

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

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

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

Similarly,

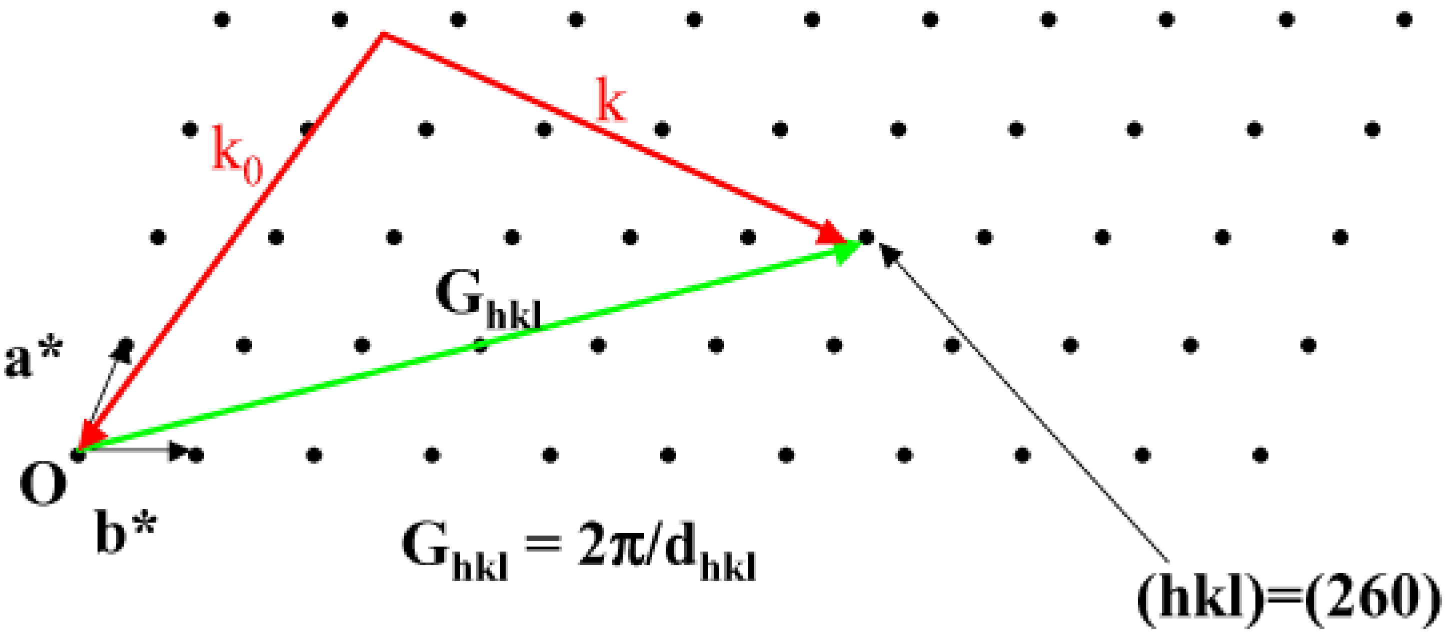
$$\left(\frac{d\sigma}{d\Omega}\right)_{x-rays} = Z^2 r_0^2 \left(\frac{1+\mathrm{Cos}^2(2\theta)}{2}\right) f^2(\vec{q}) e^{-2W} \quad N \cdot \frac{(2\pi)^3}{v_0} \sum_{\vec{G}} \delta(\vec{q}-\vec{G})$$

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

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

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

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



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

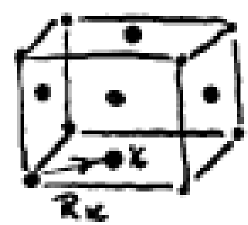
A single crystal has to be aligned precisely to record Bragg scattering

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

Generalization

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

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



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

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

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

→ "Phase Problem" → Special Methods

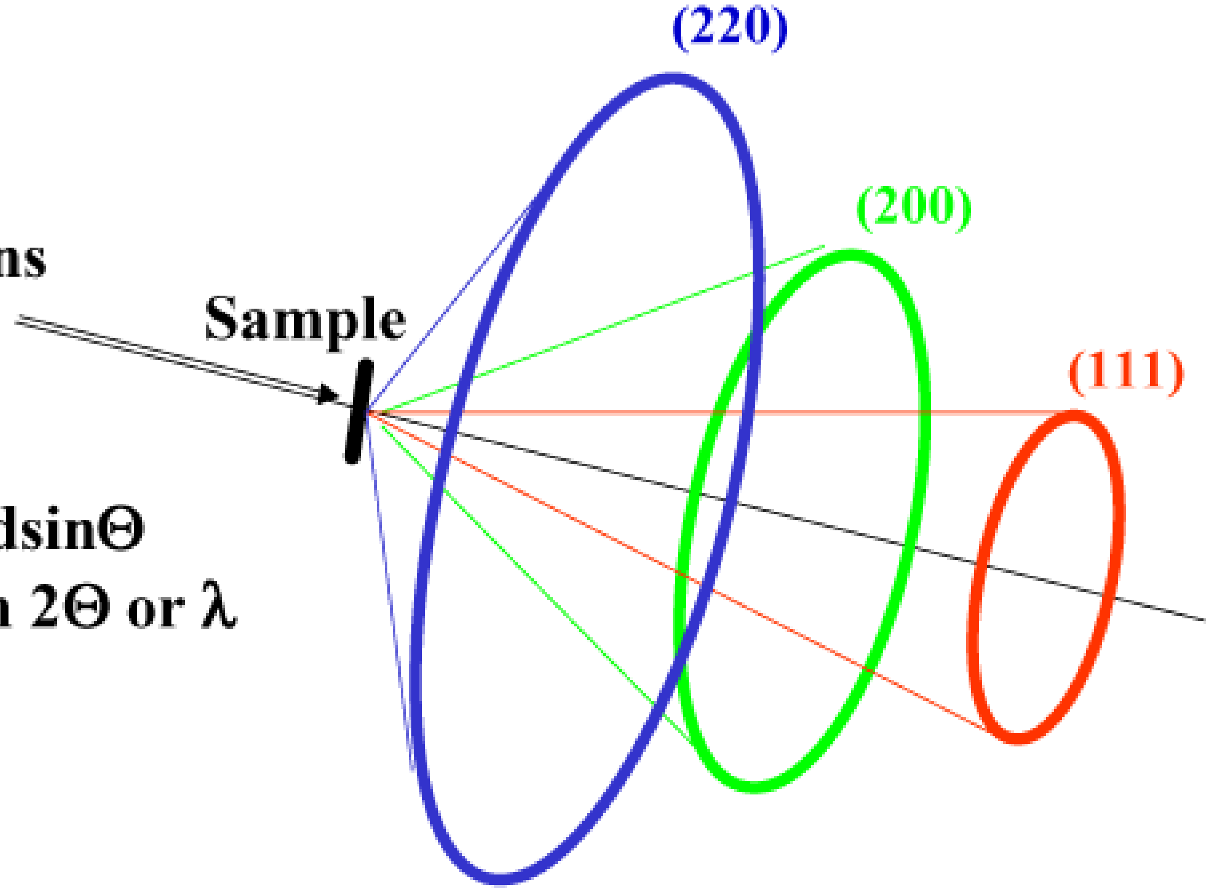
Note that $|F_G|^2$ can be written $\sum_{KK'} \mu_K \mu_{K'}\, e^{-i\vec{G}\cdot(\vec{R}_K-\vec{R}_{K'})}$

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

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

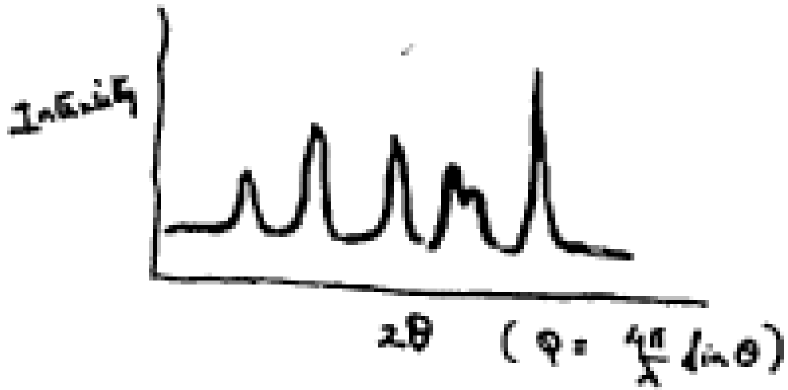
Powder Diffraction gives Scattering on Debye-Scherrer Cones

Incident beam
x-rays or neutrons



Bragg's Law $\lambda = 2d\sin\Theta$
Powder pattern – scan 2Θ **or** λ

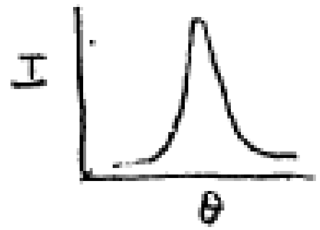
For a given $\vec{k}$, $\vec{k}'$ will lie on a cone (Debye-Scherrer cone) traced out by a $\vec{G}$ on the Ewald sphere as it is oriented randomly about the origin of reciprocal space.



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

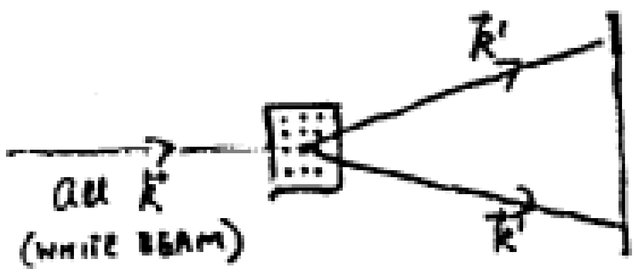
B. Single Crystal Bragg Methods



Integrated Intensity under Bragg Peak

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

C. Laue Method

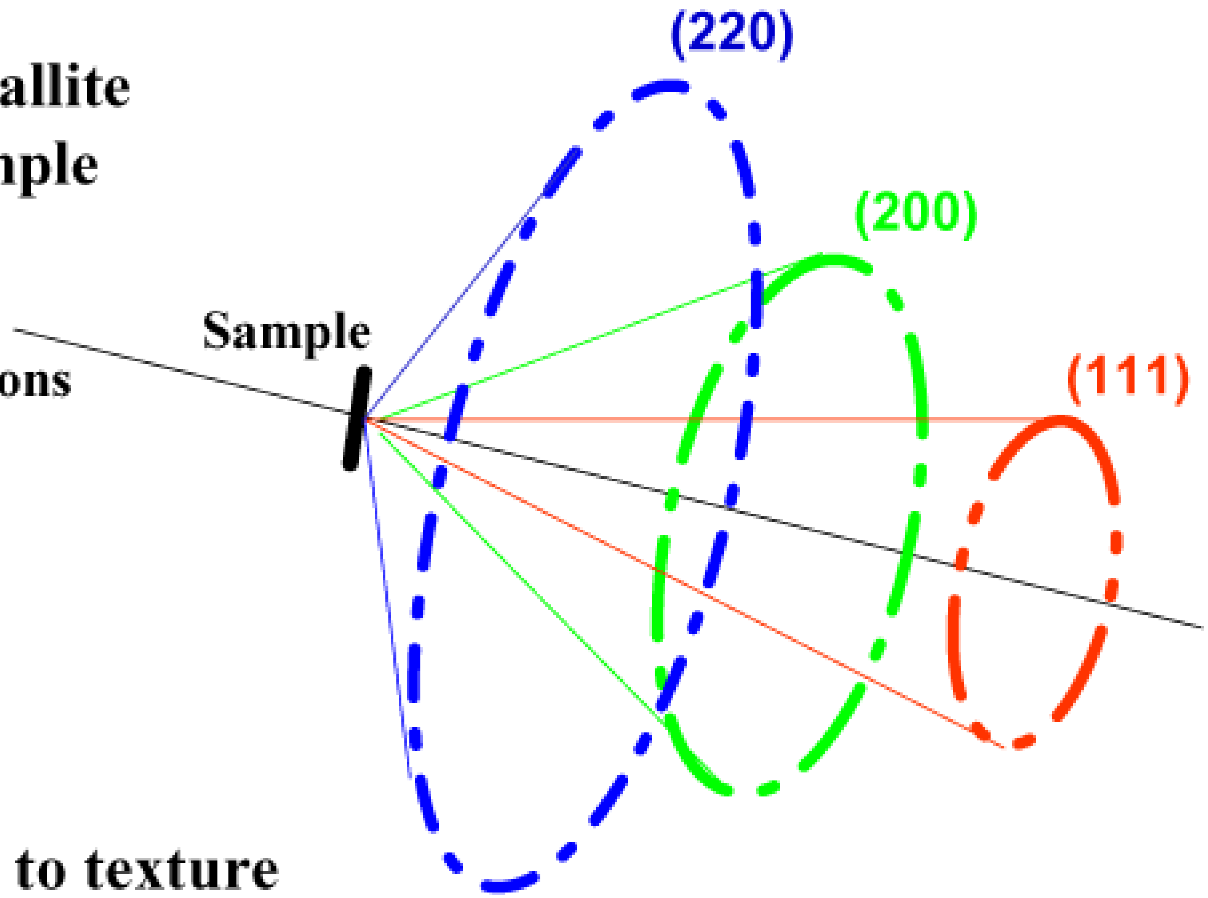


$$I_{hk\ell} - \phi(\lambda) \frac{V}{v_0^2} \frac{\lambda^4}{2\mathrm{Sin}^2\theta} |F_{hk\ell}|^2$$

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

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

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

which is thus independent of q_z.

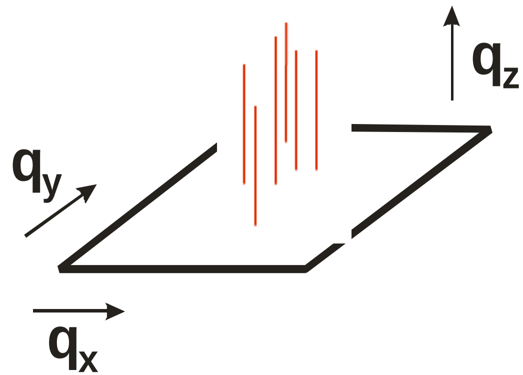
$$S(q) \propto \sum_{G_{||}} \delta\left(\vec{q}_{||} - \vec{G}_{||}\right)$$

where

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

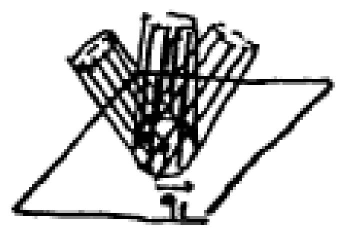
$\vec{q}_{||}$ is (x,y) plane component of $\vec{q}$

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



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

Powders of 2-D Crystals



asymmetric (saw-tooth) powder peak shape

(Warren)

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

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

[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

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

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

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.

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

where

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

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

2nd term → 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 ~ $\boxed{\left(\frac{2\pi}{q}\right)}$ (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

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

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

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

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

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

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,

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

V_0 = Particle Volume

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

Expanding exponential,

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

(the term $-i\bar{q}\cdot\int_V \bar{r}\, d\bar{r}$ is struck out)

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

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

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

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

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

↓ 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 :

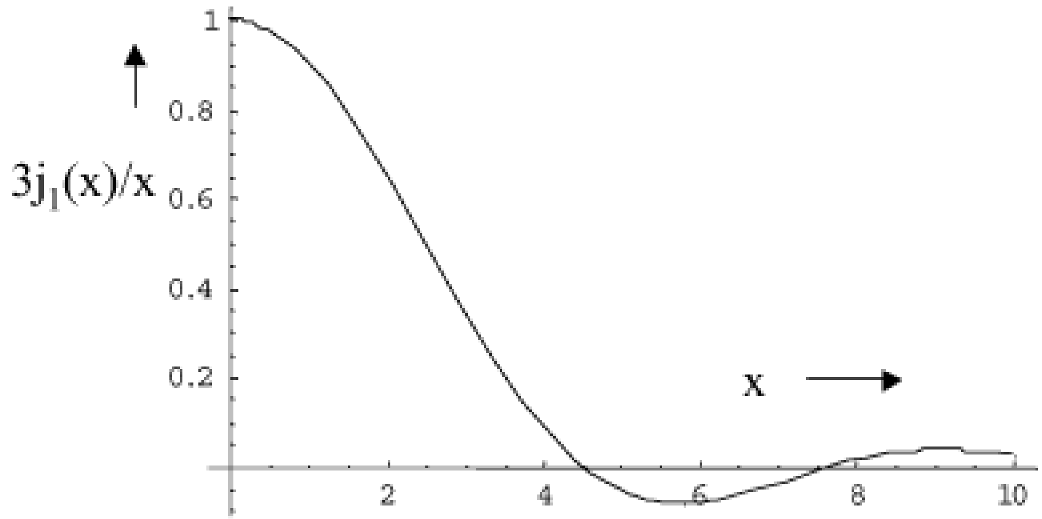
$$F_{sphere}(Q) = 3V_0\left[\frac{\sin QR - QR\cos QR}{(QR)^3}\right] \equiv \frac{3V_0}{QR} j_1(QR) \rightarrow V_0 \text{ at } Q = 0$$

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

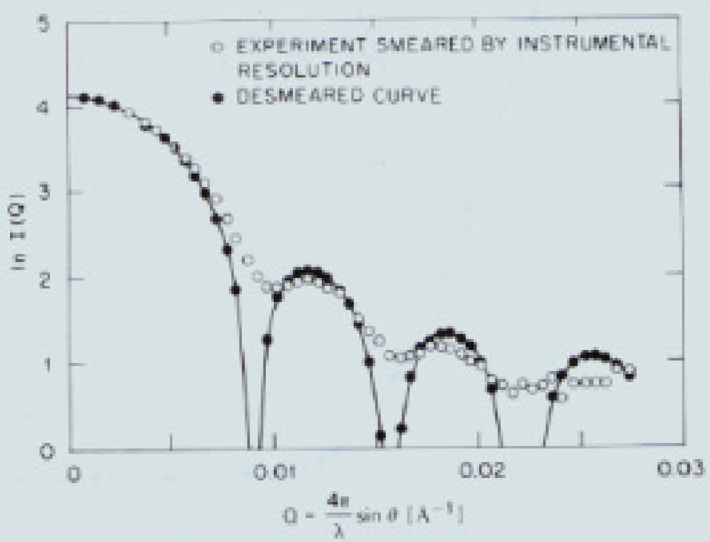
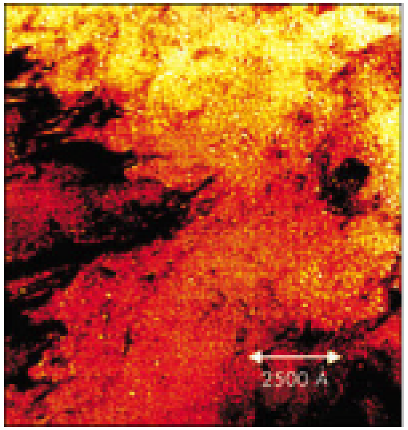
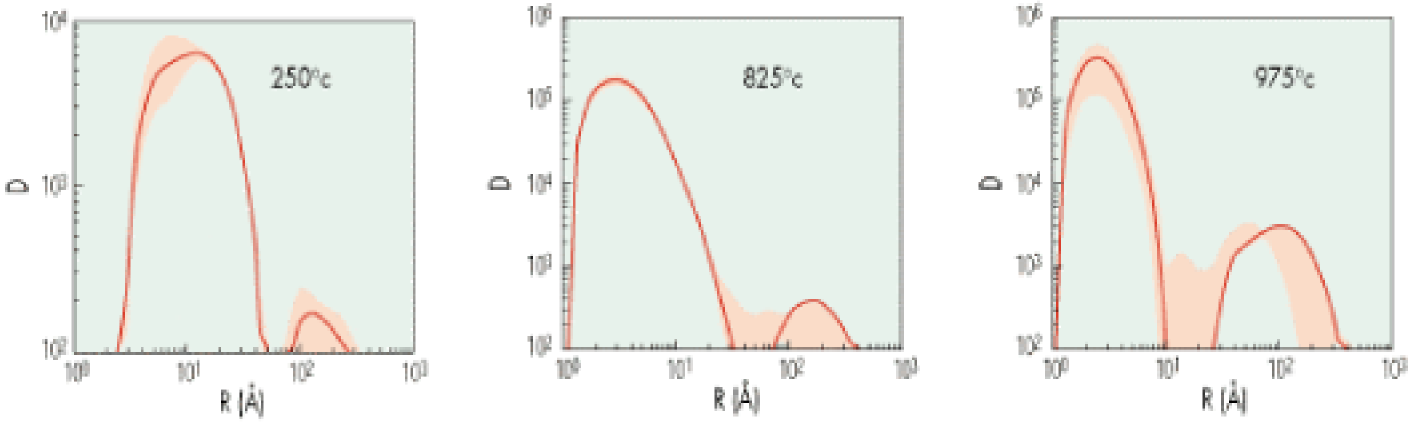


Fig. 4. Plot of ln $I(Q)$ *vs* Q for 3·98 vol.% monodisperse PMMA-H spheres (core $C1$) in D_2O/H_2O mixtures.

Size Distributions Have Been Measured for Helium Bubbles in Steel

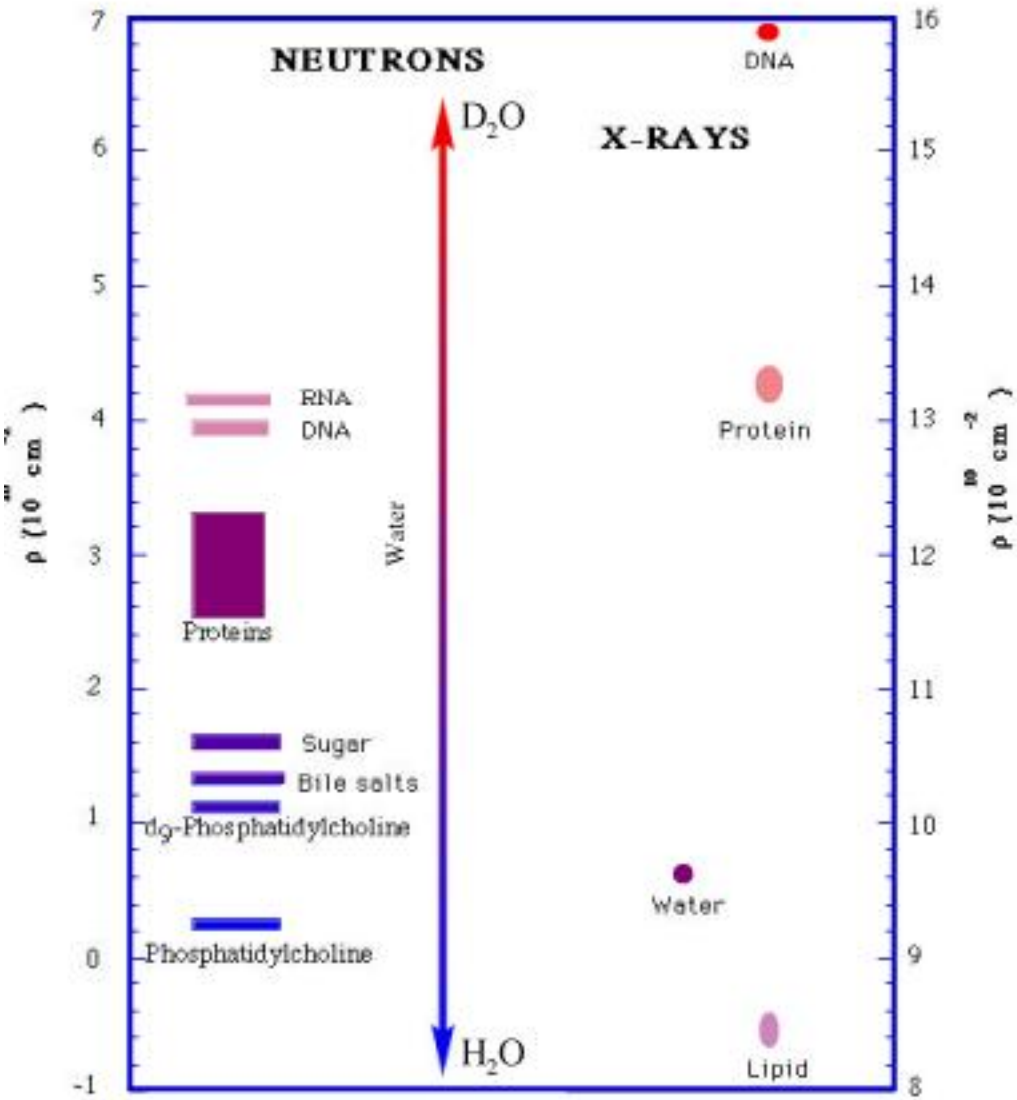
- The growth of He bubbles under neutron irradiation is a key factor limiting the lifetime of steel for fusion reactor walls
  - Simulate by bombarding steel with alpha particles
- TEM is difficult to use because bubble are small
- SANS shows that larger bubbles grow as the steel is annealed, as a result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



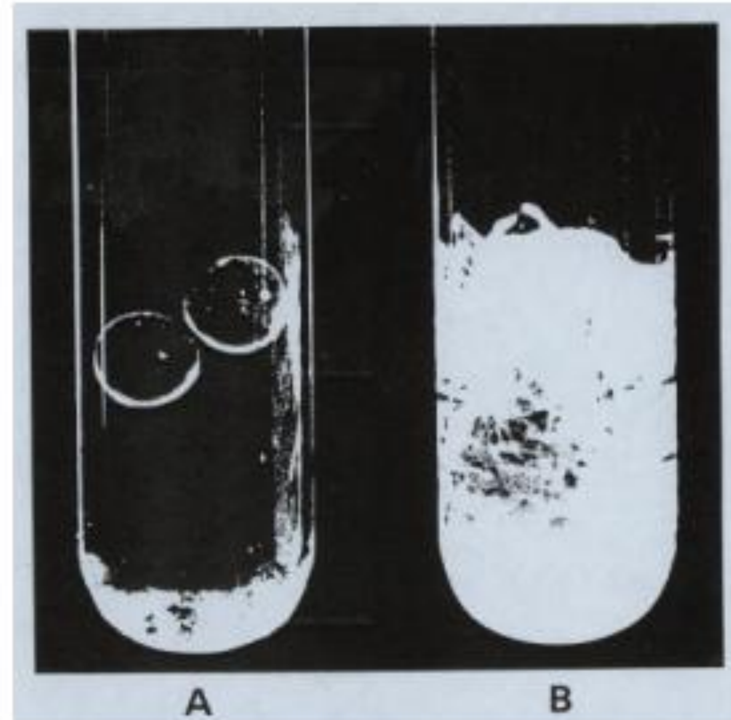


SANS gives bubble volume (arbitrary units on the plots) as a function of bubble size at different temperatures. Red shading is 80% confidence interval.

Contrast & Contrast Matching



* Chart courtesy of Rex Hjelm

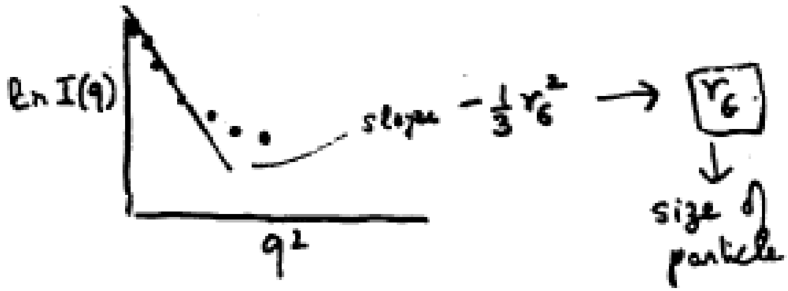


Both tubes contain borosilicate beads + pyrex fibers + solvent. (A) solvent refractive index matched to pyrex;. (B) solvent index different from both beads and fibers – scattering from fibers dominates

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:

- $\left\{\begin{matrix}\text{Sizes} \\ \text{Shapes}\end{matrix}\right\}$ 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 → $|f_\ell(\bar{q})|^2$ ← Structure Factor $S_0(\bar{q})$

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

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

→ Liquid- or glass-like

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

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

$$n(R) \sim R^D$$

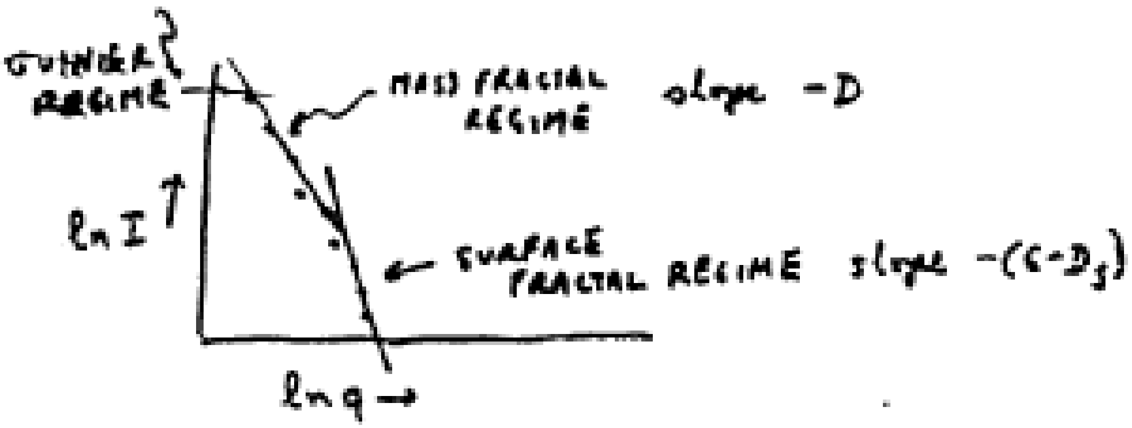
D = Fractal (Hausdorff) Dimension

It follows that

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

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

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



:**

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

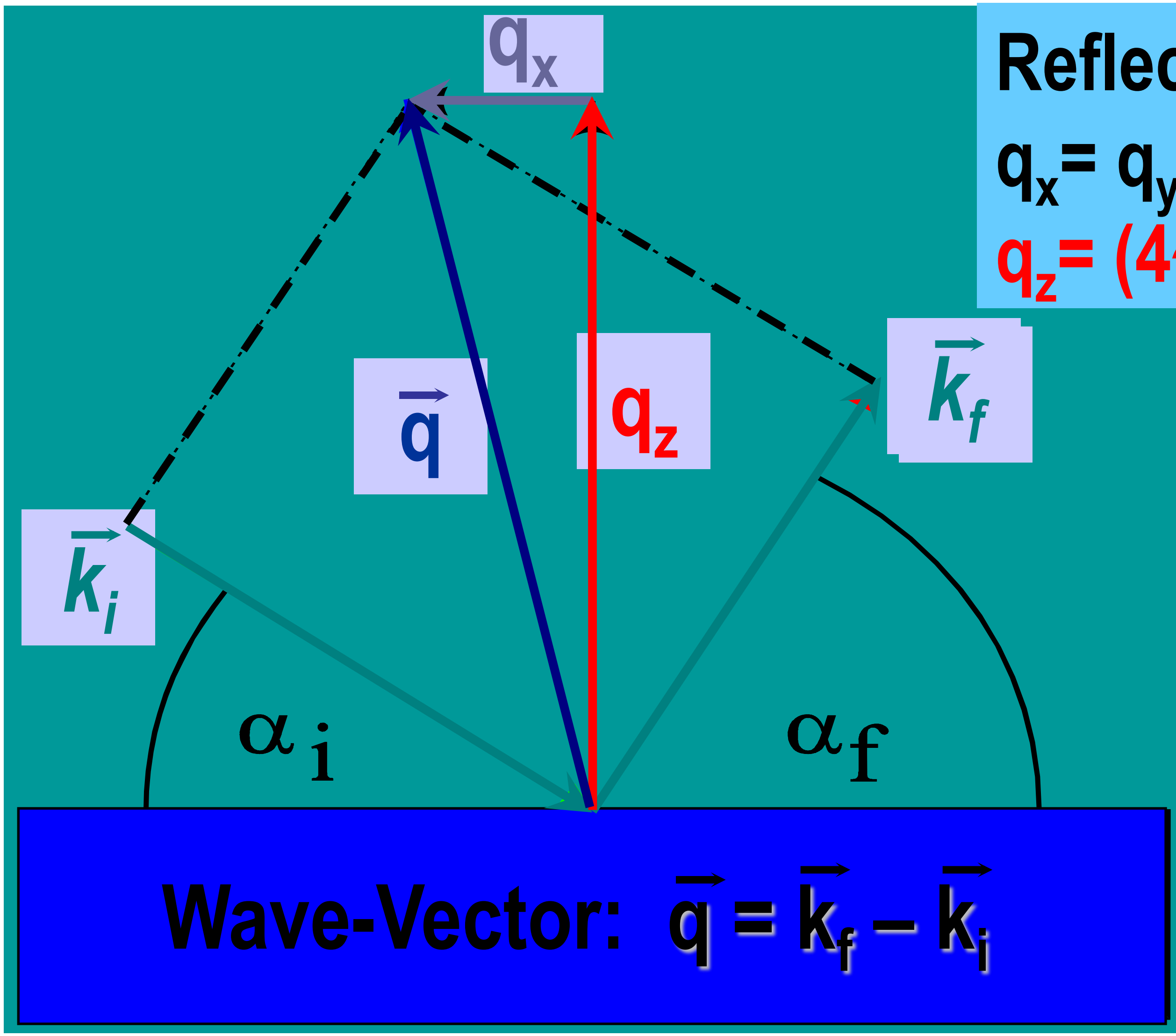
Surface fractals $S(q) \sim \dfrac{1}{q^{S-D_S}}$

(S = 6) D_s = Surface fractal dimension.

If $D_s = 2$, $S(q) \sim 1/q^4$ (Porod's Law for smooth internal surfaces)

If $2 < D_s < 3$, $S(q) \sim 1/q^n$ where $3 < n < 4$

Scattering Geometry & Notation



Reflectivity:

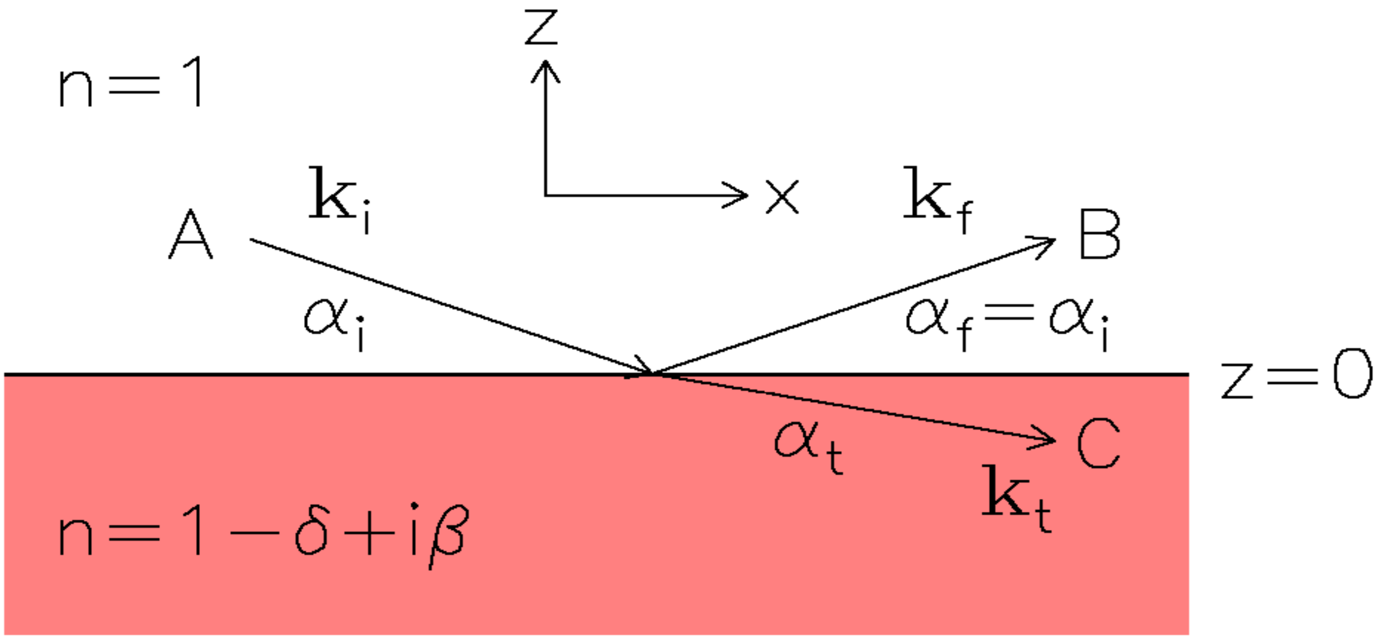
$q_x = q_y = 0$

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

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.

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

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

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

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

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

Single Interface: Vacuum/Matter

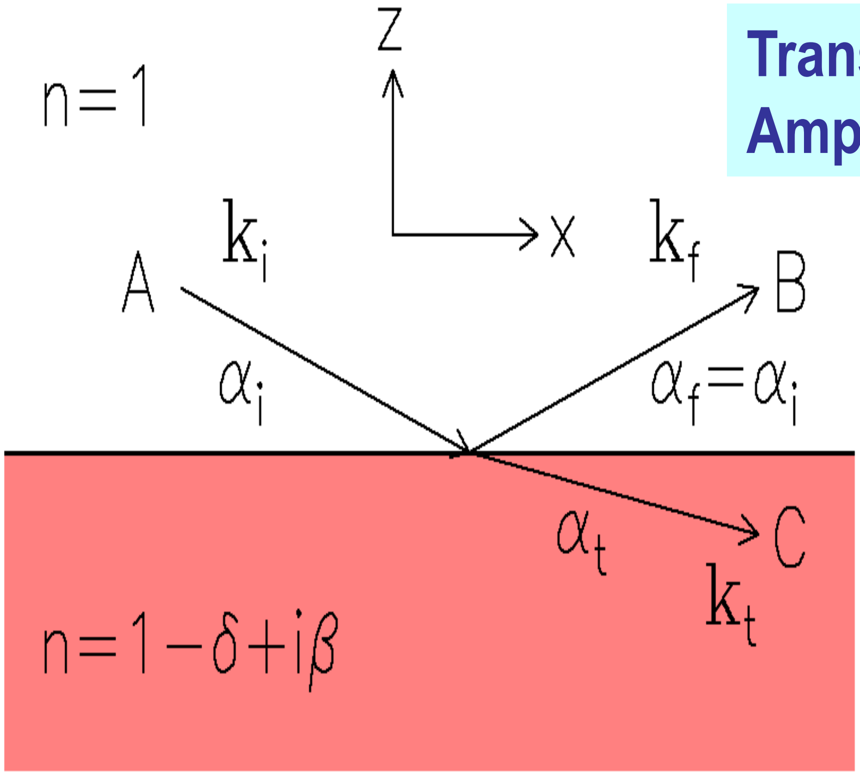
Fresnel-Formulae

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

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

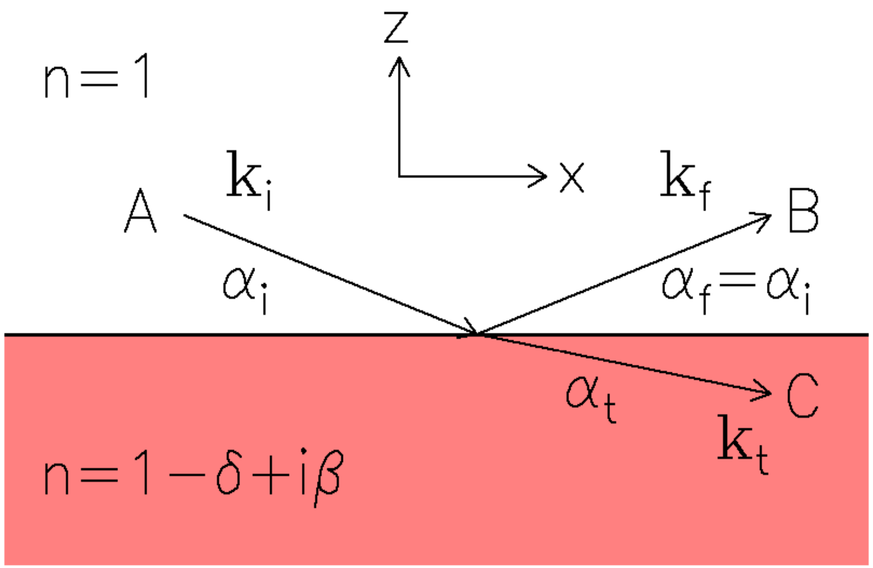


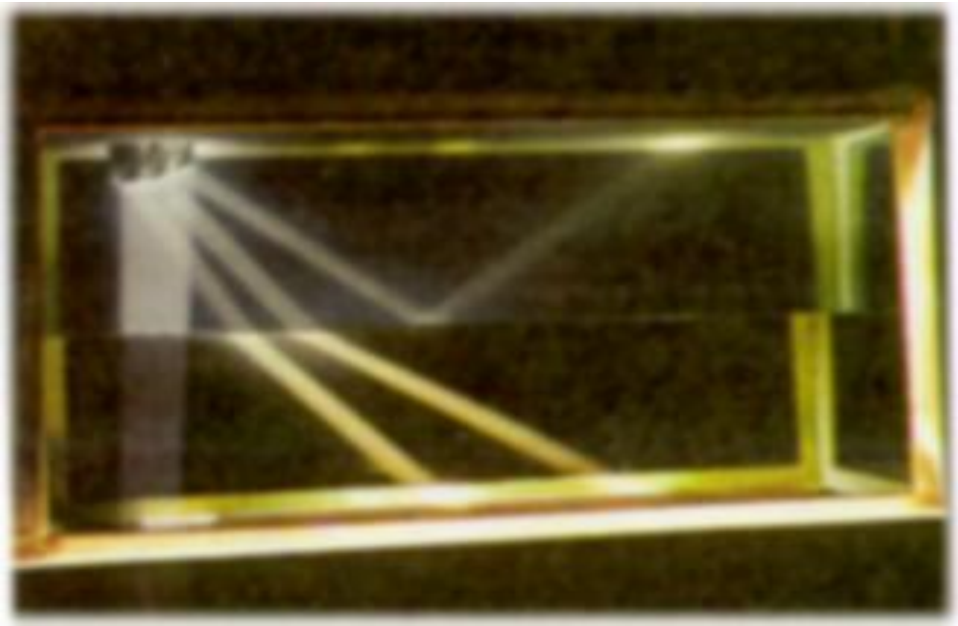
Wave-Vectors

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

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

Total External Reflection





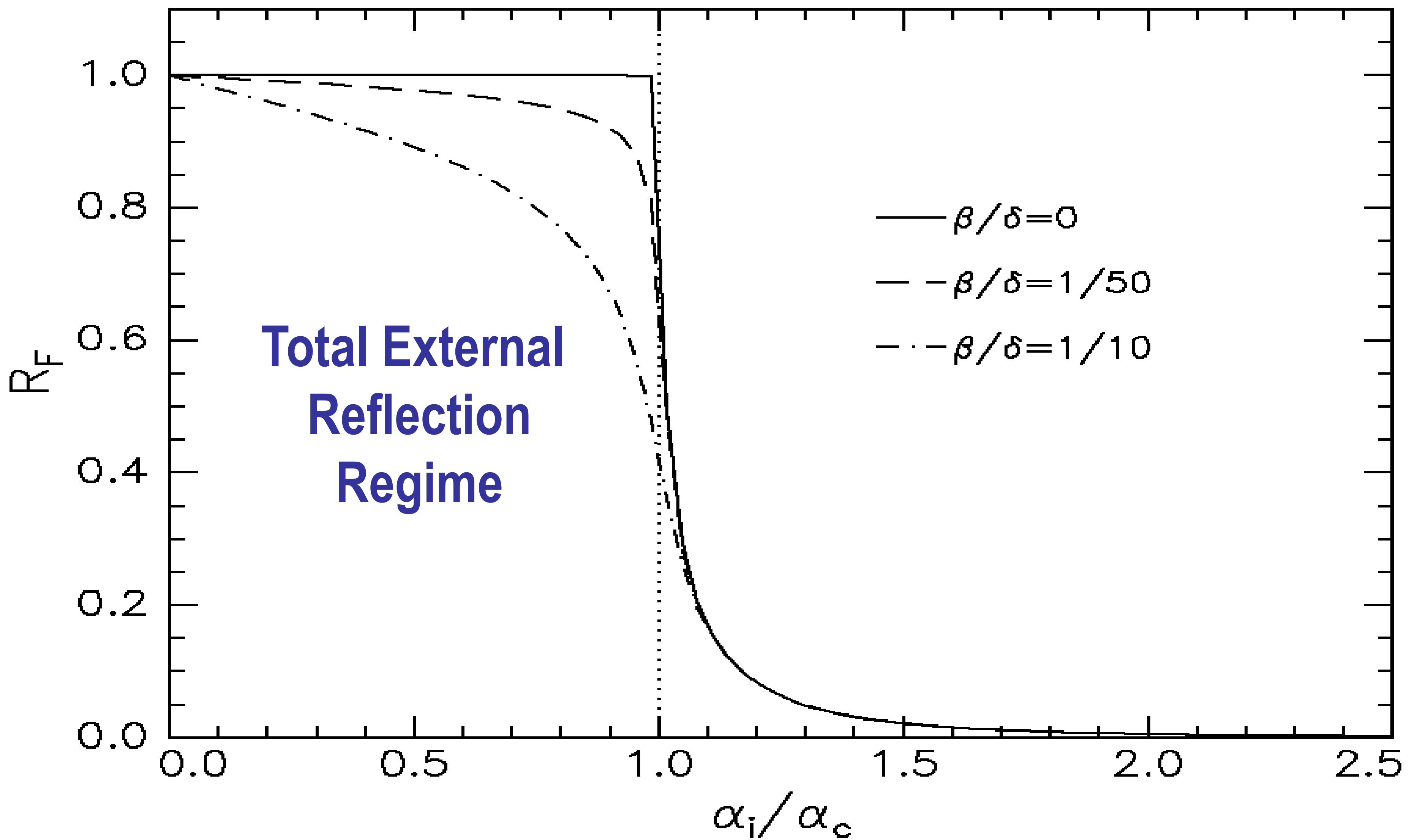
$\cos\alpha_i = (1-\delta)\cos\alpha_t$

$\alpha_t=0$

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

GRAZING ANGLES !!!

Fresnel Reflectivity: $R_F(\alpha_i)$



The „Master Formula“

Reformulation for Interfaces

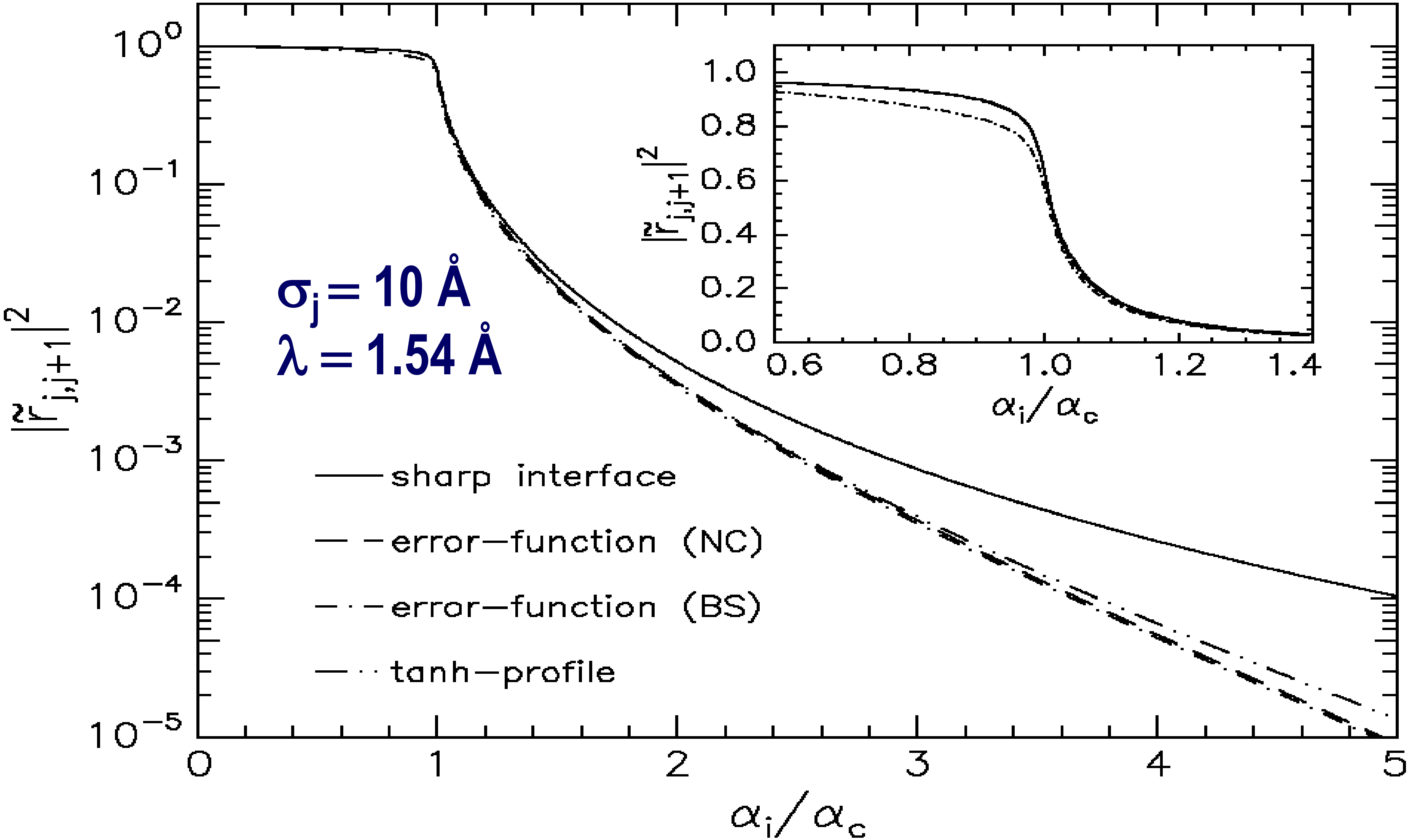
$$R(q_z) = R_{\mathrm{F}}(q_z) \left| \frac{1}{\varrho_\infty} \int \frac{\mathrm{d}\varrho(z)}{\mathrm{d}z} \exp(\mathrm{i}\, q_z z)\, \mathrm{d}z \right|^2$$

Fresnel-Reflectivity of the Substrate

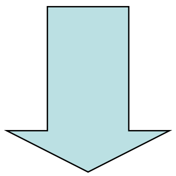
Electron Density Profile

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

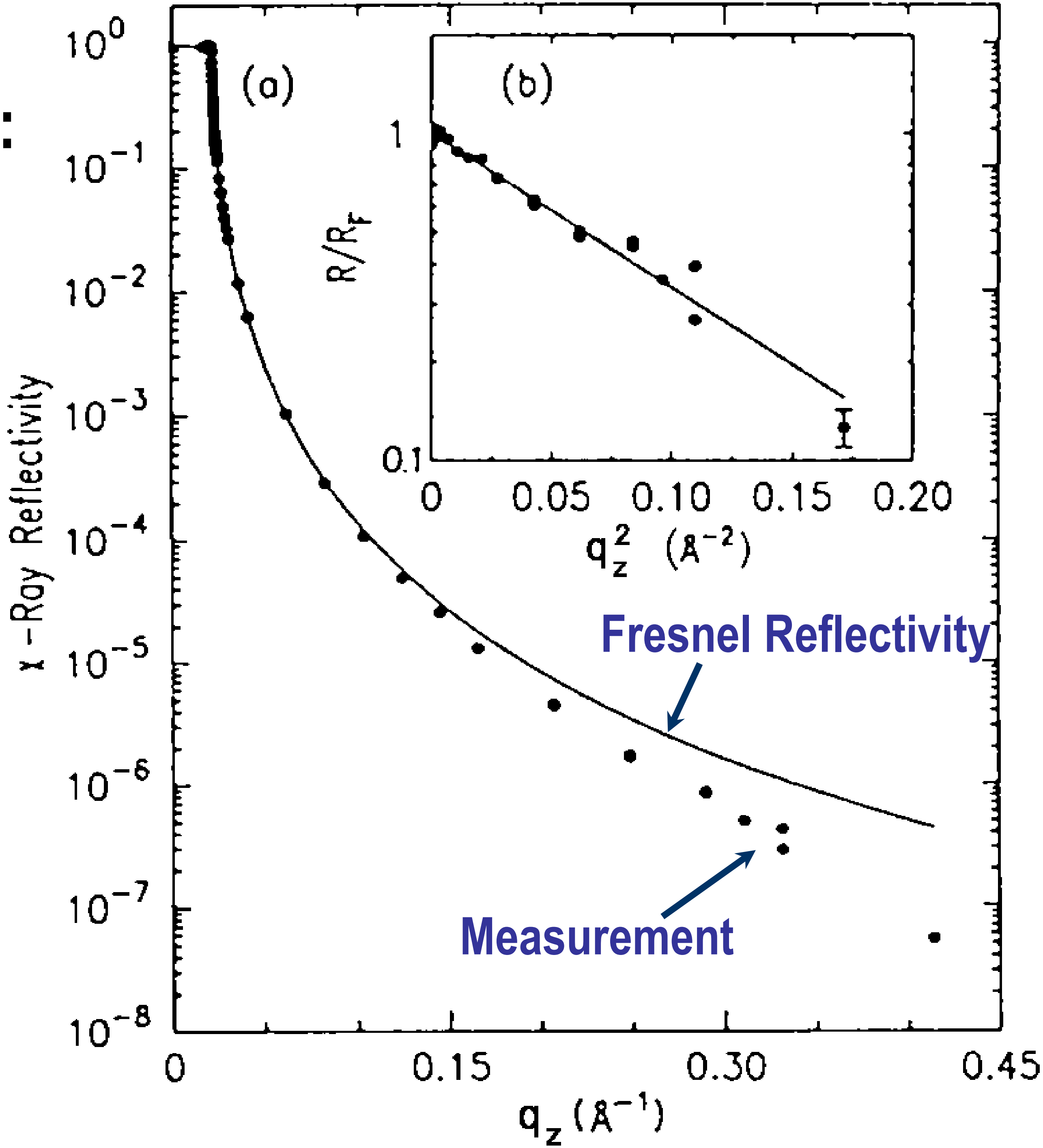
Roughness Damps Reflectivity



X-Ray Reflectivity: Water Surface



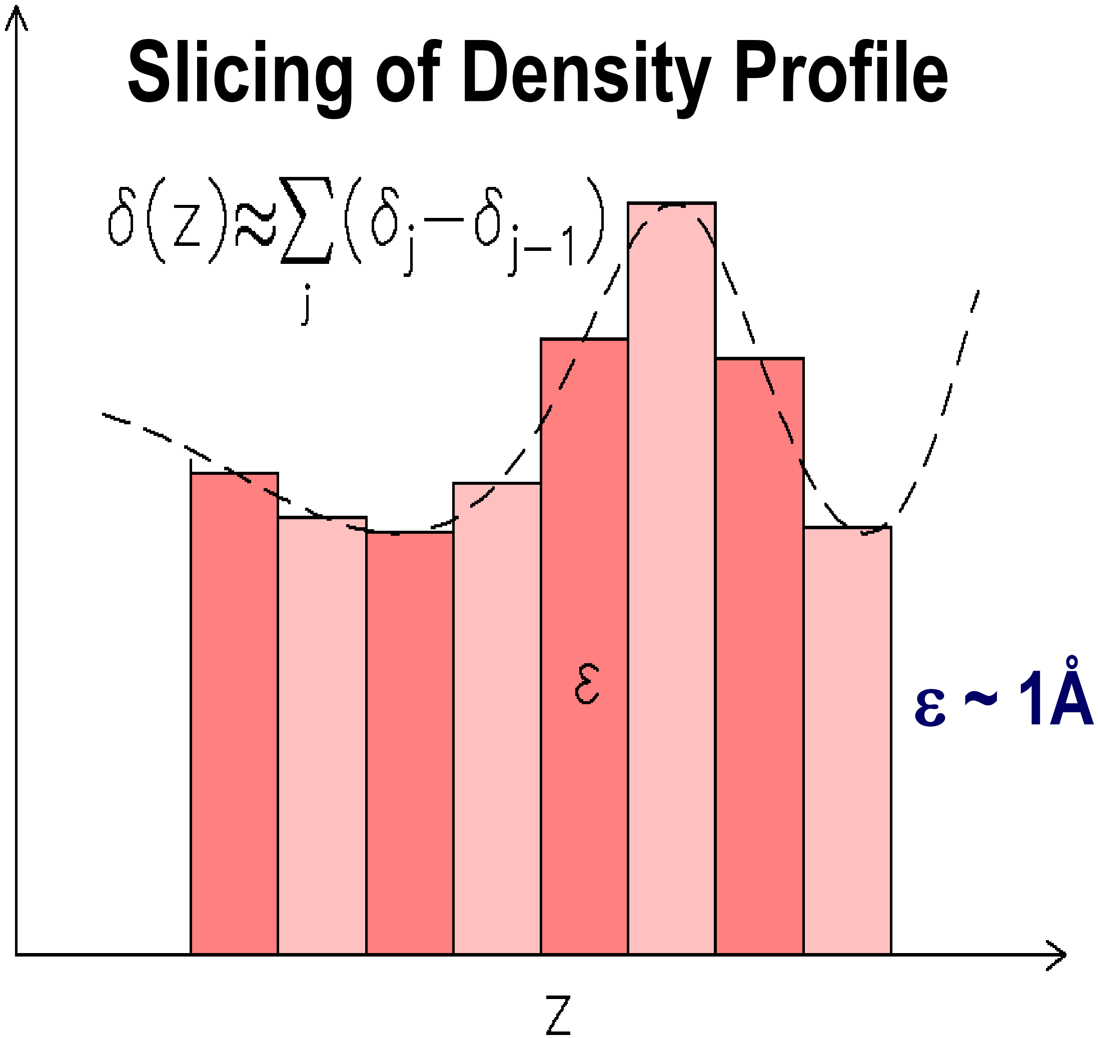
Difference Experiment-Theory: ***Roughness !!***



Braslau et al.
PRL 54, 114 (1985)

Calculation of Reflectivity

Slicing of Density Profile

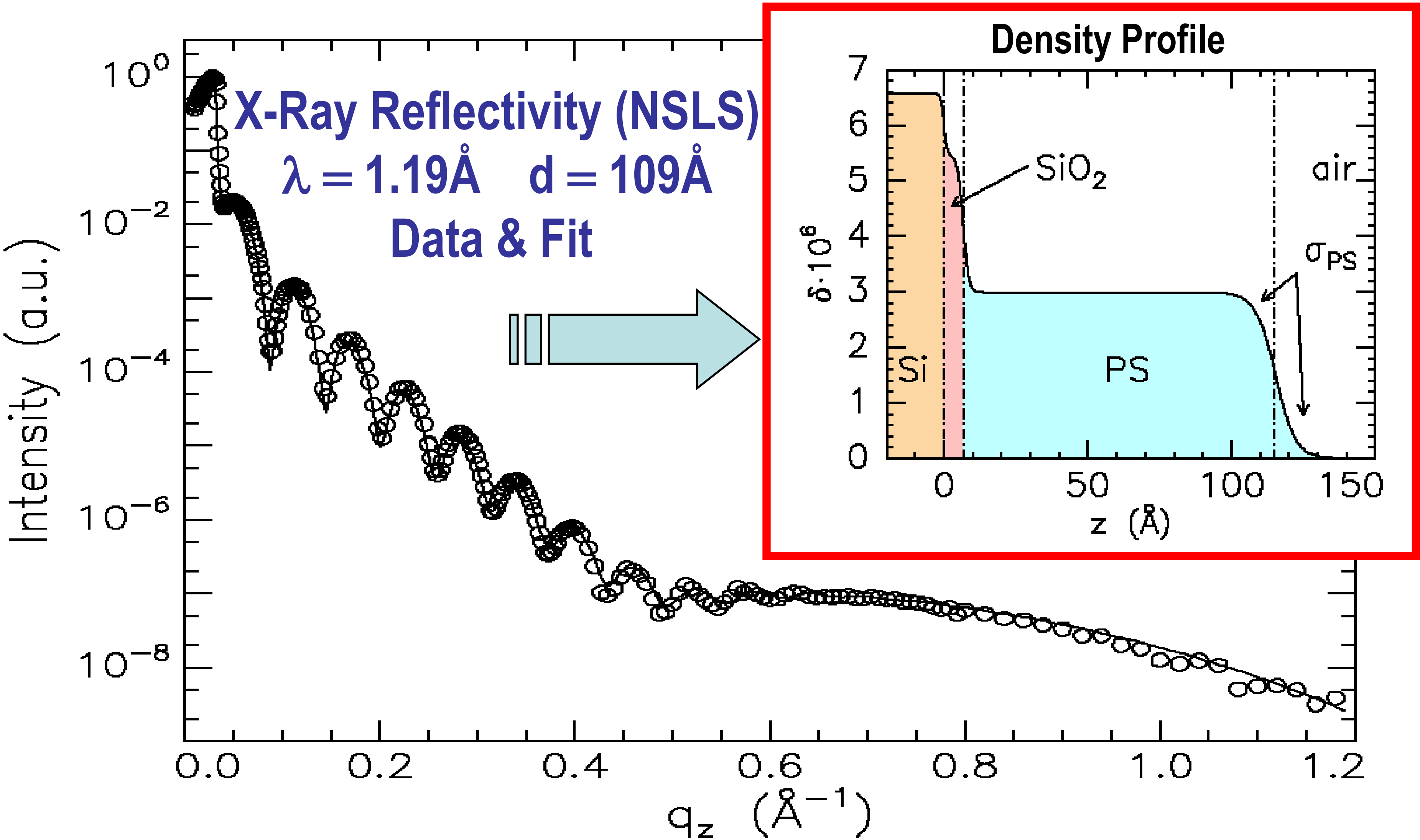


Slicing
&
Parratt-Iteration

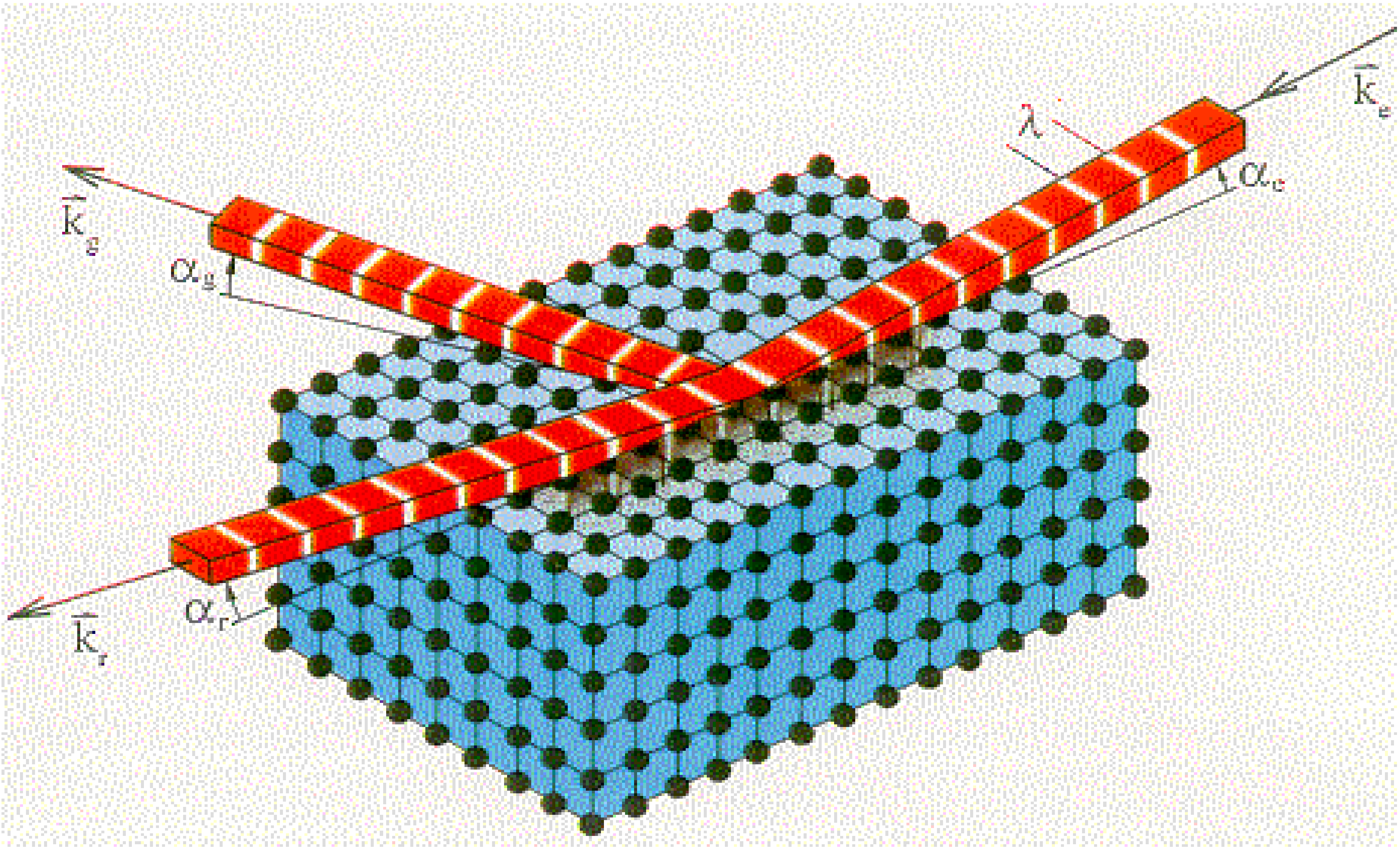
Reflectivity from Arbitrary Profiles !

- **Drawback: Numerical Effort !**

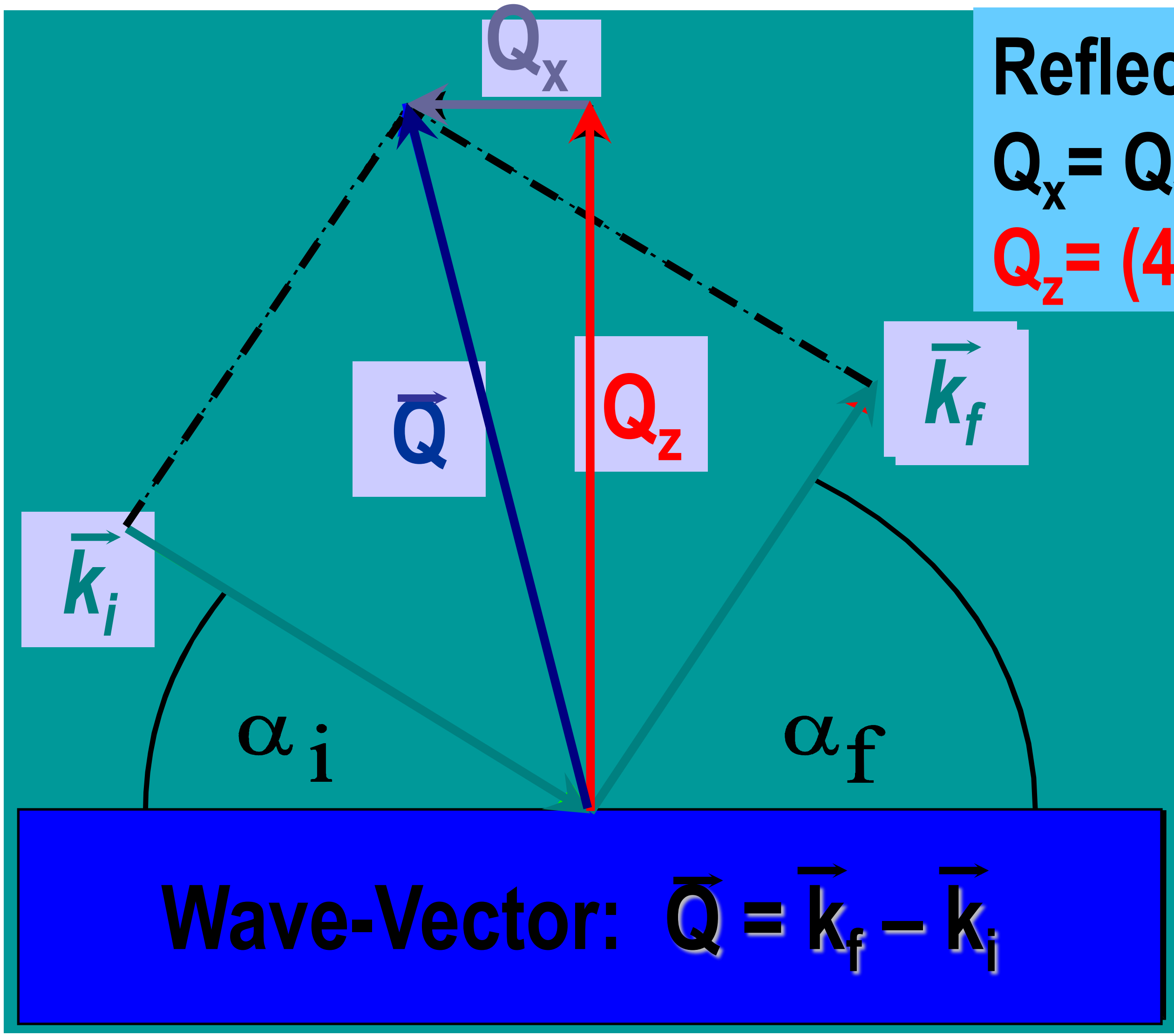
Example: PS Film on Si/SiO_2



Grazing-Incidence-Diffraction



Scattering Geometry & Notation



Reflectivity:

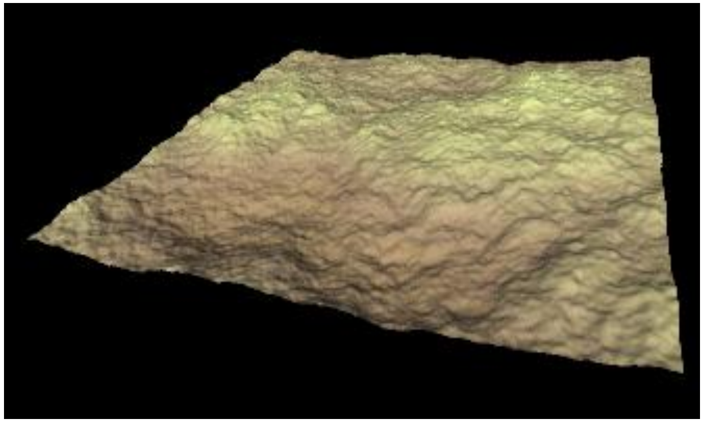
$Q_x = Q_y = 0$

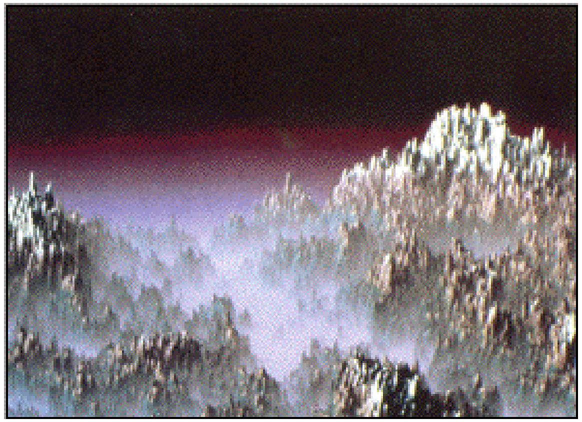
$Q_z = (4\pi/\lambda)\sin\alpha_i$

What do Specular and Off-specular scattering measure?

- **Specular reflectivity** measures variations in scattering density normal to surface (averaged over x,y plane)
- **Off-specular scattering** measures (x,y) variations of scattering density, e.g. due to roughness, magnetic domains, etc.

Almost all real surfaces are rough!





Self-Affine Fractal Surfaces

Let $\delta z(\mathbf{r})$ be height fluctuation about average surface at point $\mathbf{r}$ in 2D plane.

R.m.s. roughness σ is defined by

$$\sigma^2 = \langle\, [\delta z(\mathbf{r})]^2 \,\rangle$$

Consider quantity

$$G(\mathbf{R}) = \langle\, [\delta z(\mathbf{r}) - \delta z(\mathbf{r}+\mathbf{R})]^2 \,\rangle.$$

For self-affine surfaces,

$$G(\mathbf{R}) = AR^{2h} \qquad 0<h<1$$

h is called the roughness exponent.

For real surfaces, there must be a cutoff length ξ.

$$G(\mathbf{R}) = 2\sigma^2(1 - \exp(-[R/\,\xi]^{2h})$$

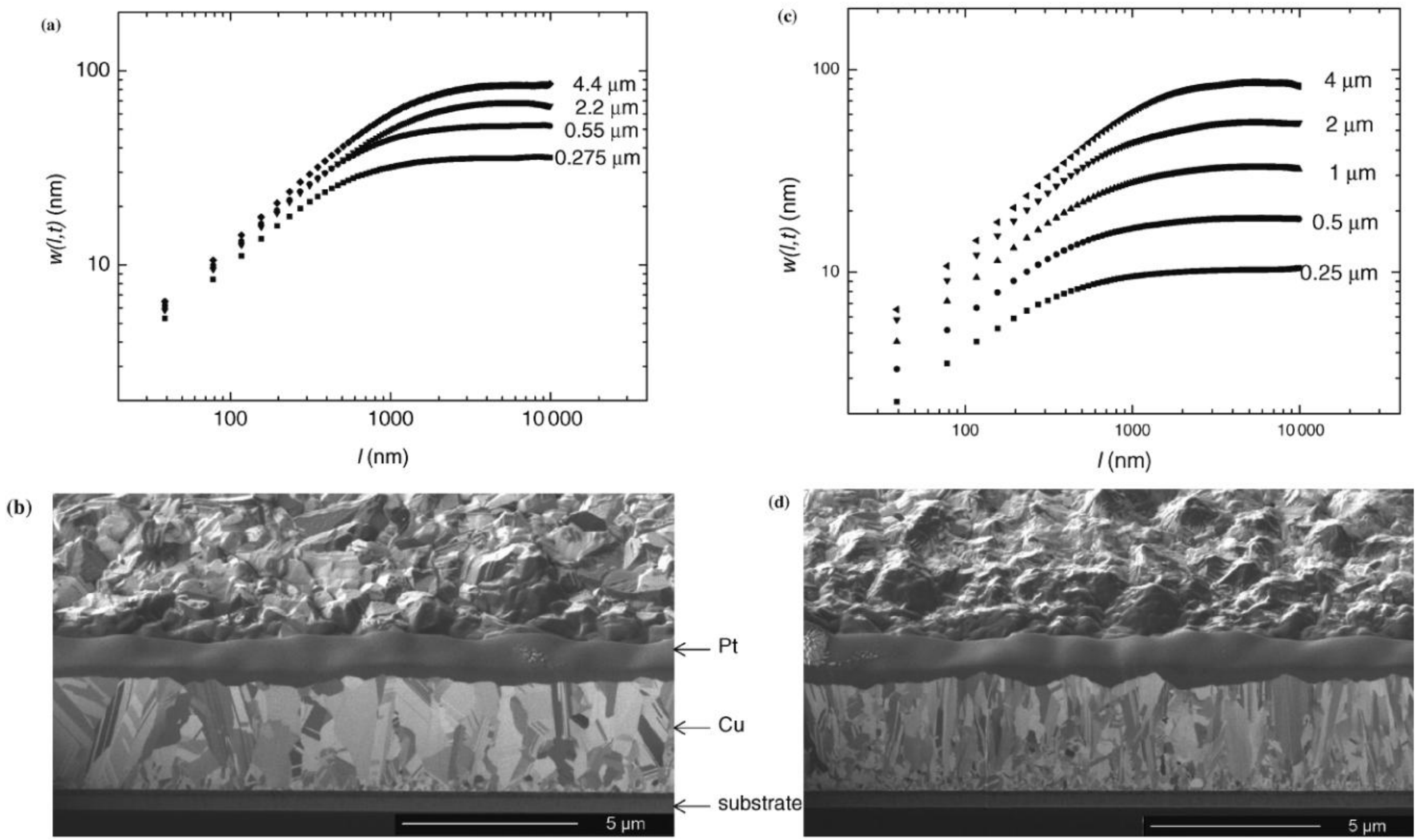
This implies that the **height-height correlation function**

$$C(\mathbf{R}) = \langle \delta z(\mathbf{r})\delta z(\mathbf{r}+\mathbf{R})\rangle = \sigma^2 \exp(-[R/\,\xi]^{2h}$$

AFM/FIB Studies-Electrodeposition

M.C. Lafouresse et al., PRL 98, 236101 (2007)

Cu Films



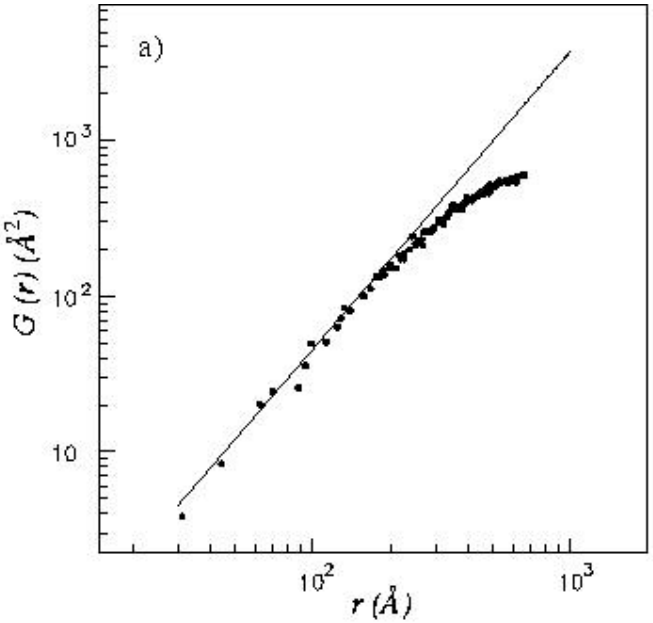
Scattering from a Self-Affine Fractal Surface

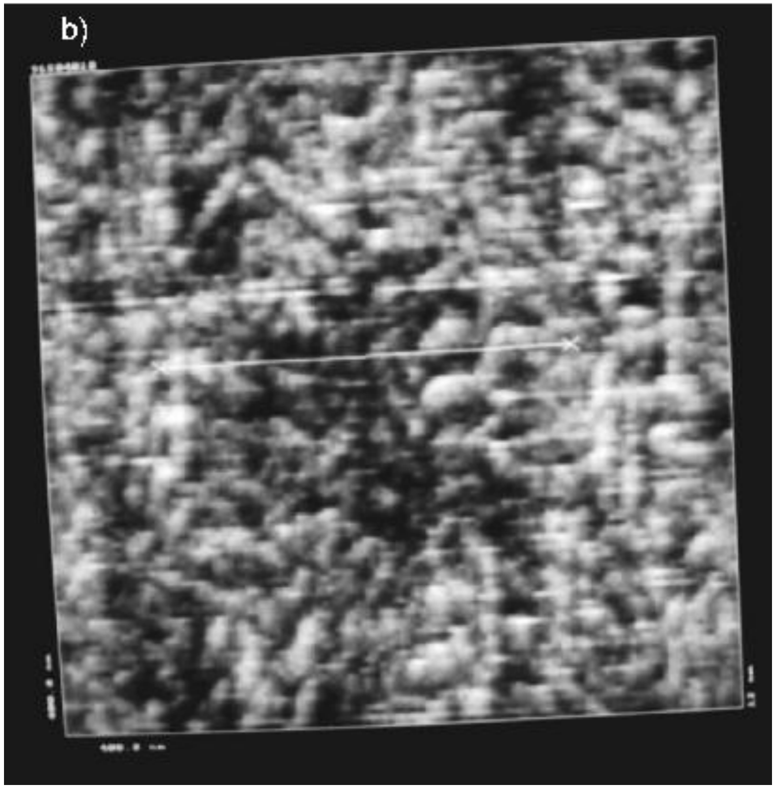
$$S(\vec{q}) = (Ar_0^2 / q_z^2) e^{-q_z^2 \sigma^2} \iint dX dY e^{q_z^2 C(R)} e^{-i(q_x X + q_y Y)}$$

SKS et al., Phys. Rev. B 38, 2297 (1988)

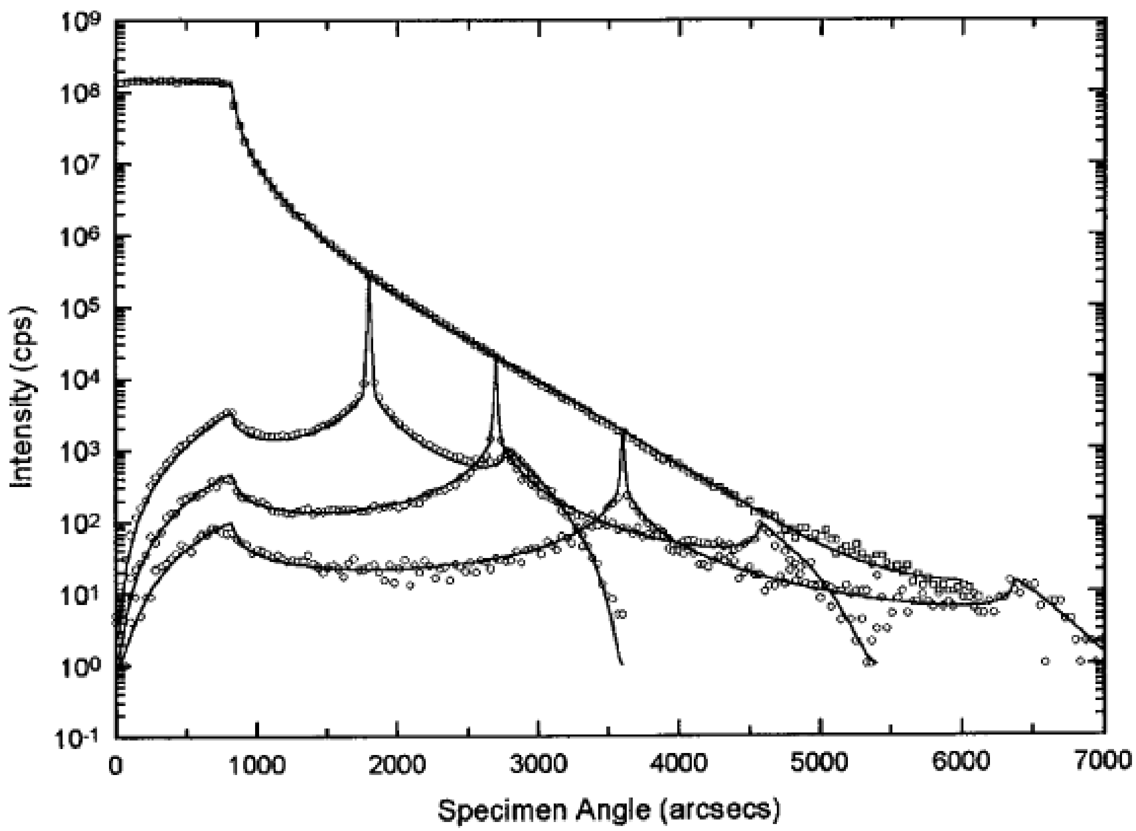
Jun Wang et al., Europhys. Lett, 42 283-288 (1998)

Mo layers

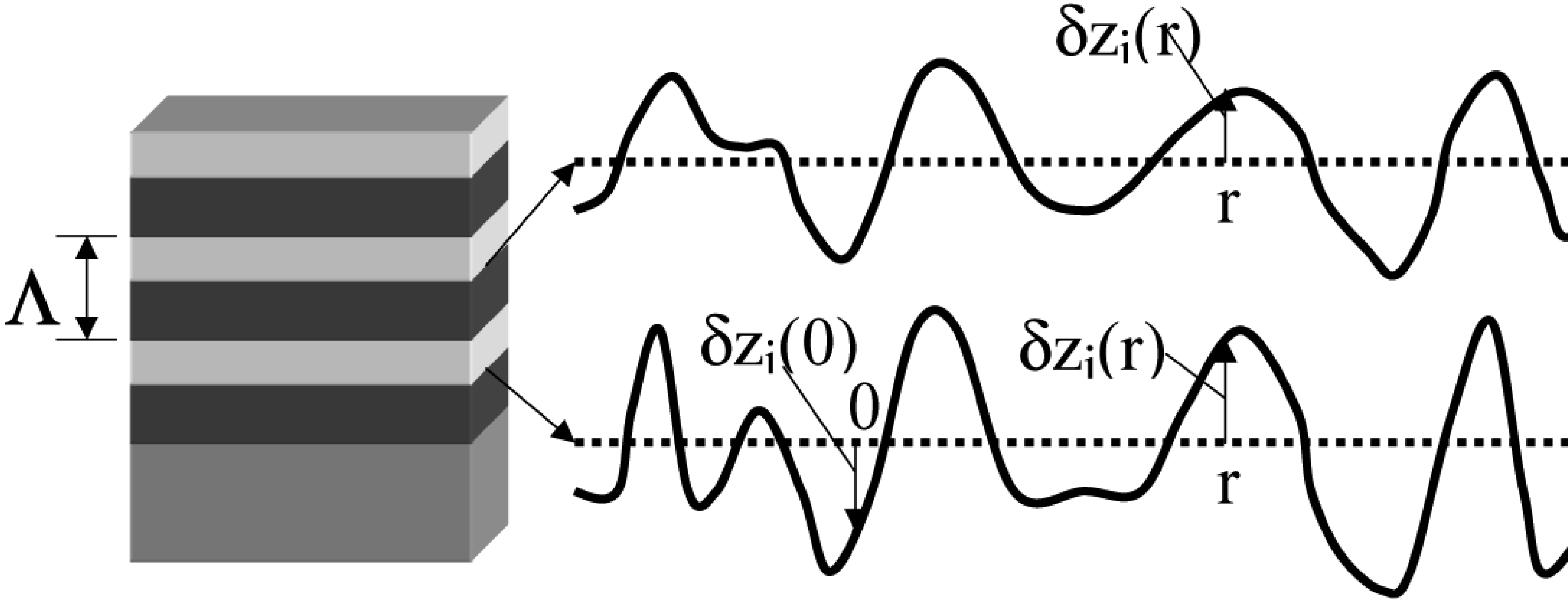




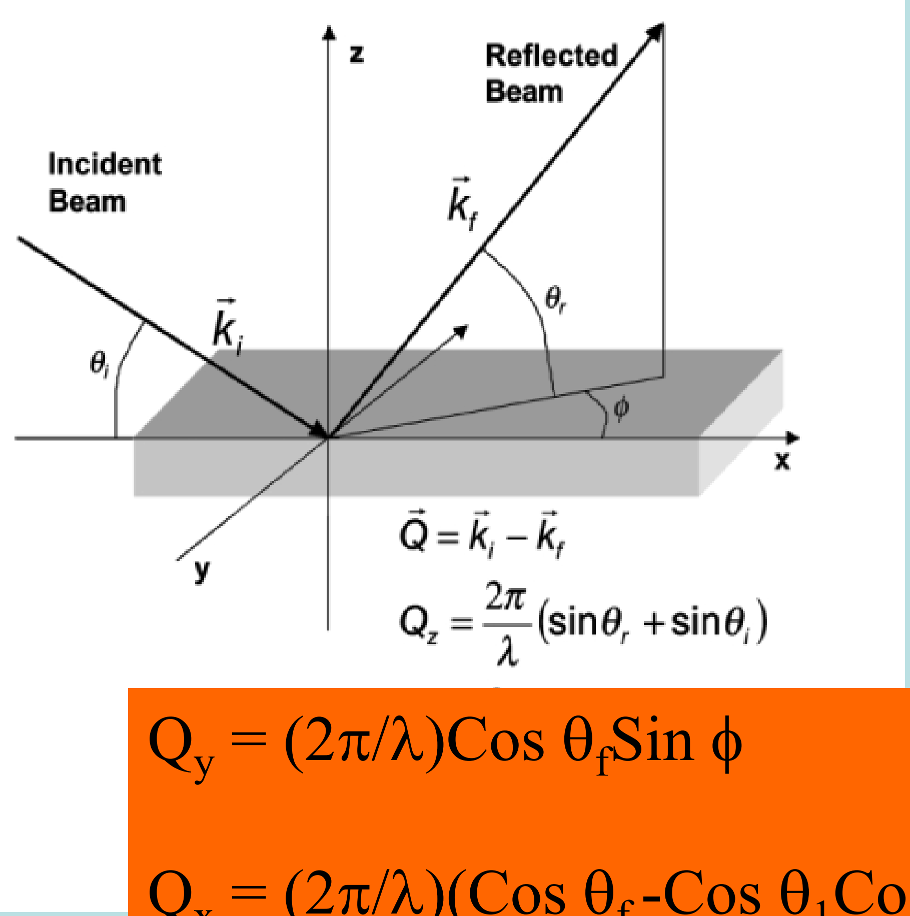
Example of Diffuse Scattering of X-Rays from a single rough surface



Multilayers



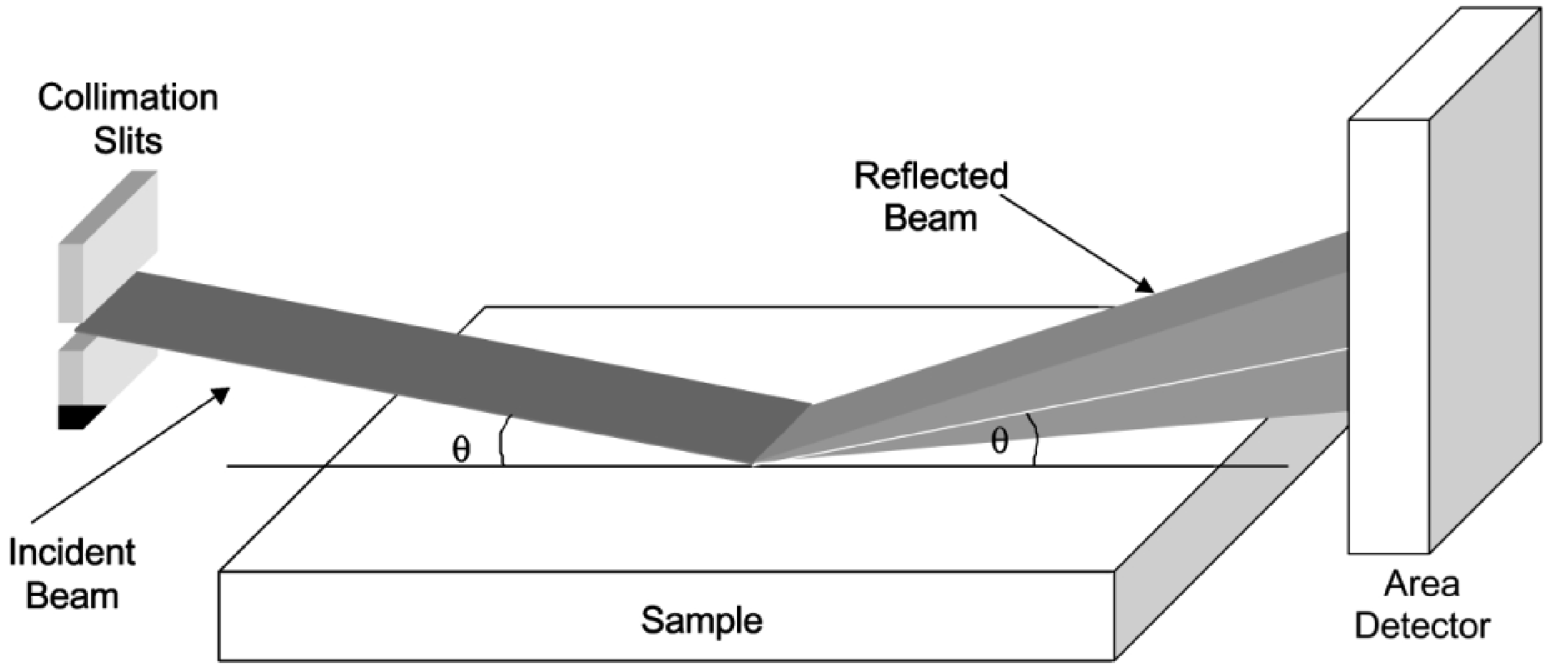
Vector Diagram for **Q** in GISAXS



$Q_y = (2\pi/\lambda)\mathrm{Cos}\ \theta_f \mathrm{Sin}\ \phi$

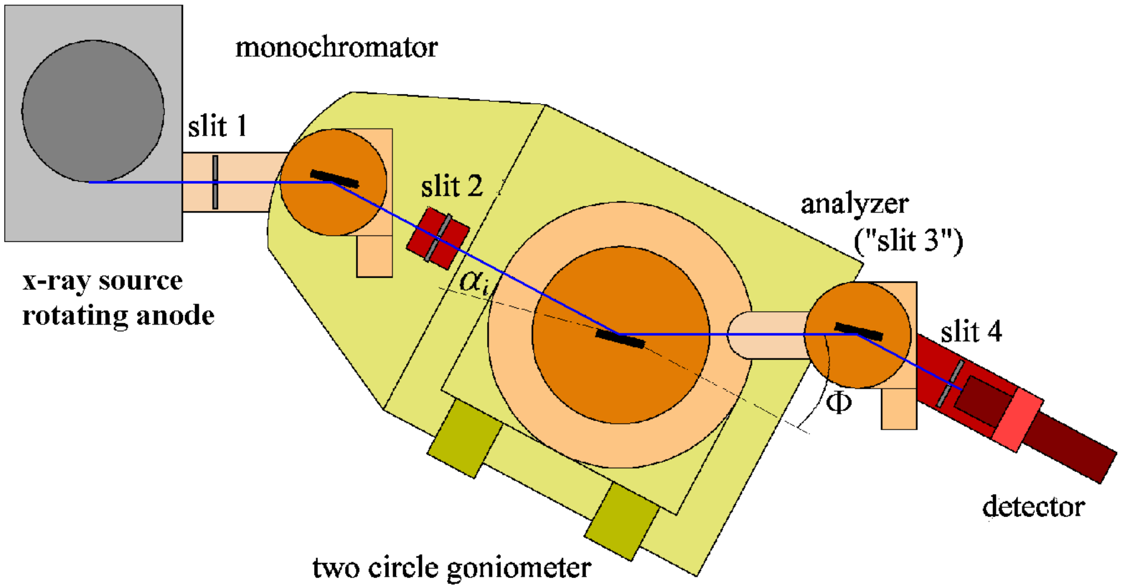
$Q_x = (2\pi/\lambda)(\mathrm{Cos}\ \theta_f - \mathrm{Cos}\ \theta_1 \mathrm{Cos}\ \phi)$

Measurement of GISAXS



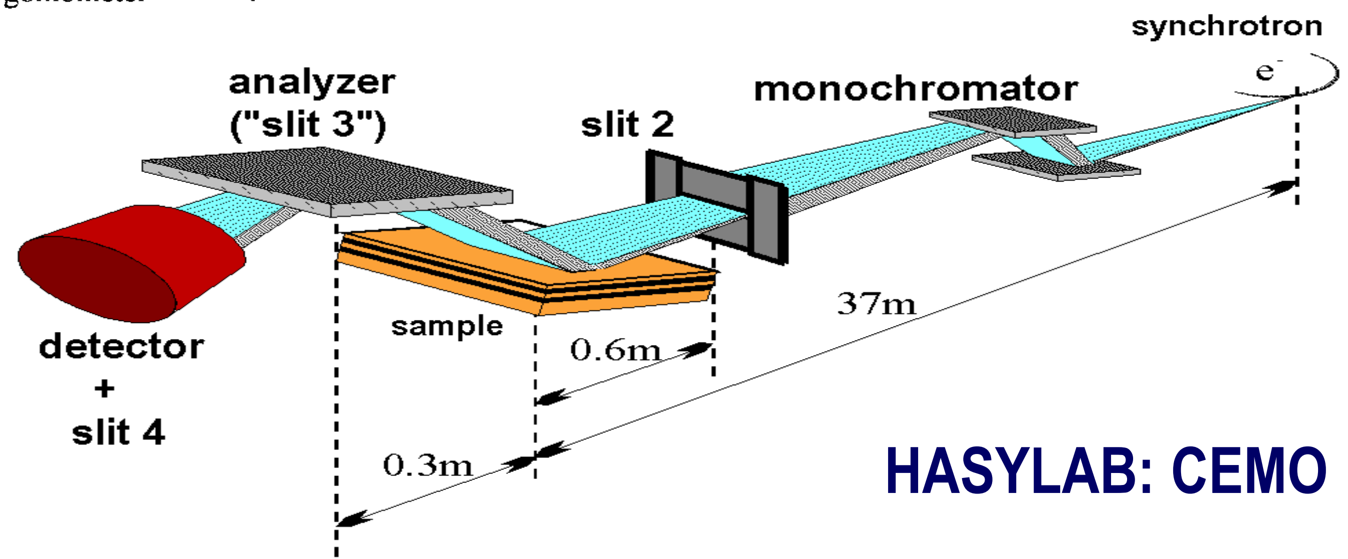
g. 2. A schematic diagram of an off-specular reflectivity experiment. A collimated polychromatic or monochromatic ribbon shaped beam is cident on the sample surface at angles of typically $\leq 2°$. The beam is reflected from the surface producing a diffuse signal about the specular rection. Multiwire or multielement detectors may be used as detectors or a single element detector may be scanned.

X-Ray Reflectometers



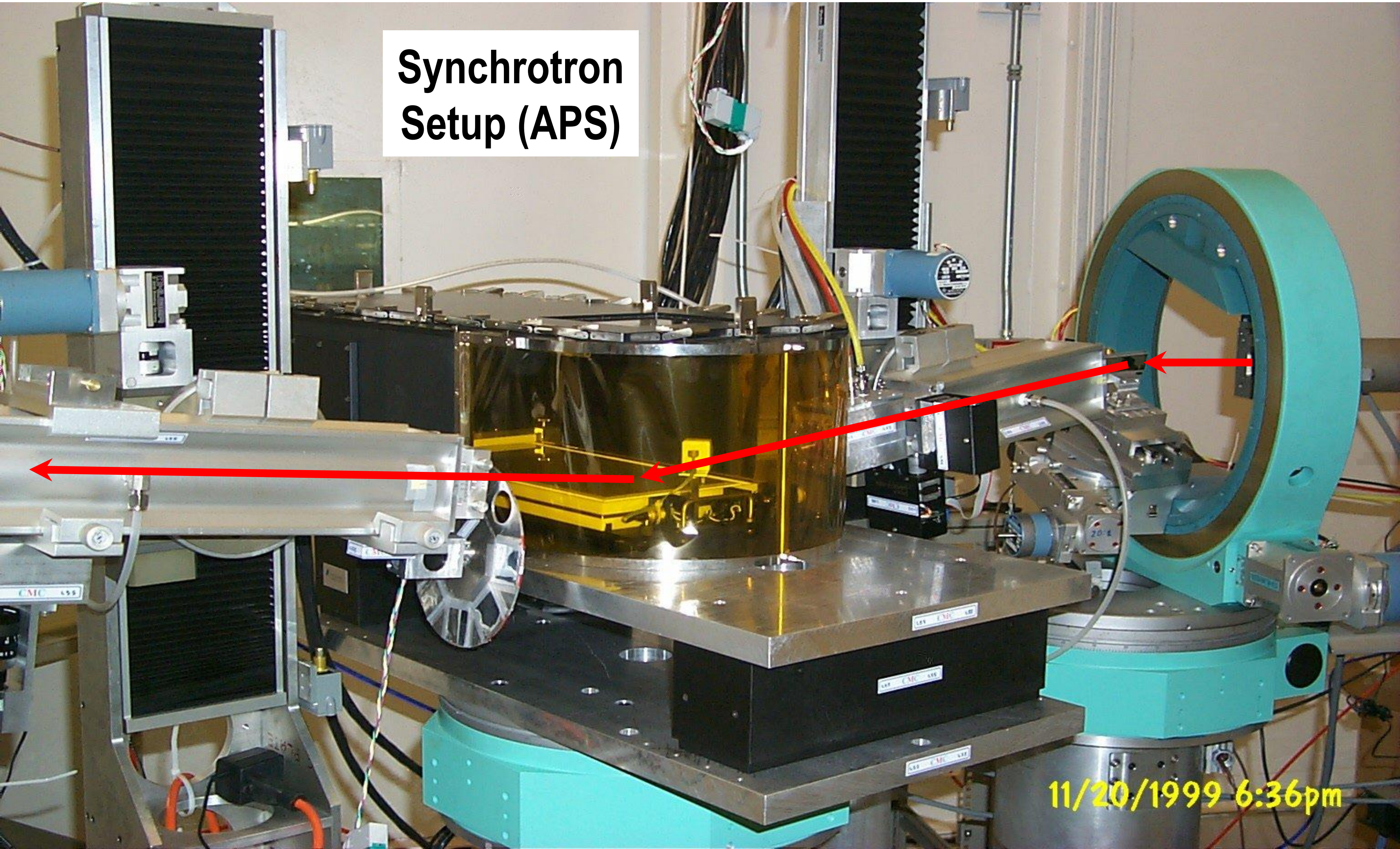
Laboratory Setup

Synchrotron Setup

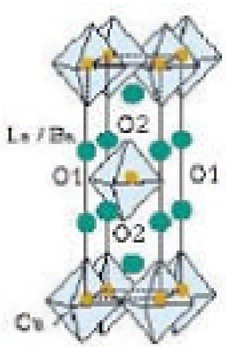


HASYLAB: CEMO

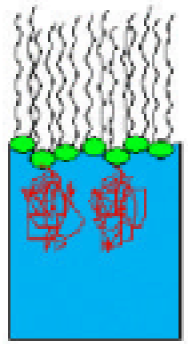
Reflectivity from Liquids I

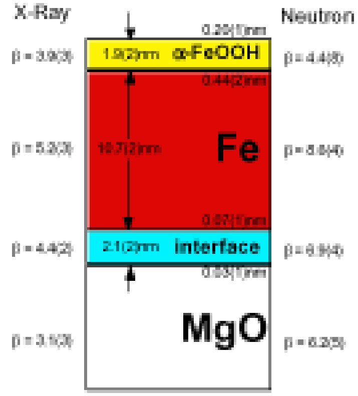


We Have Seen How Neutron Scattering Can Determine a Variety of Structures

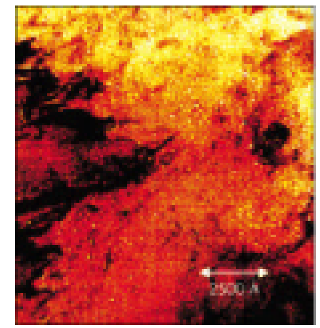


crystals

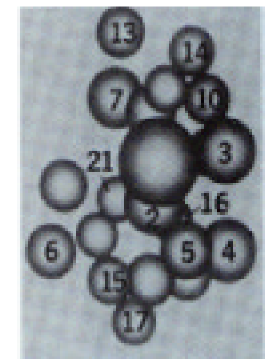




surfaces & interfaces

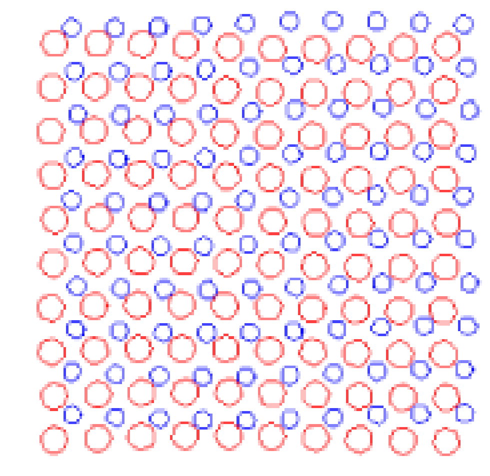


disordered/fractals



biomachines

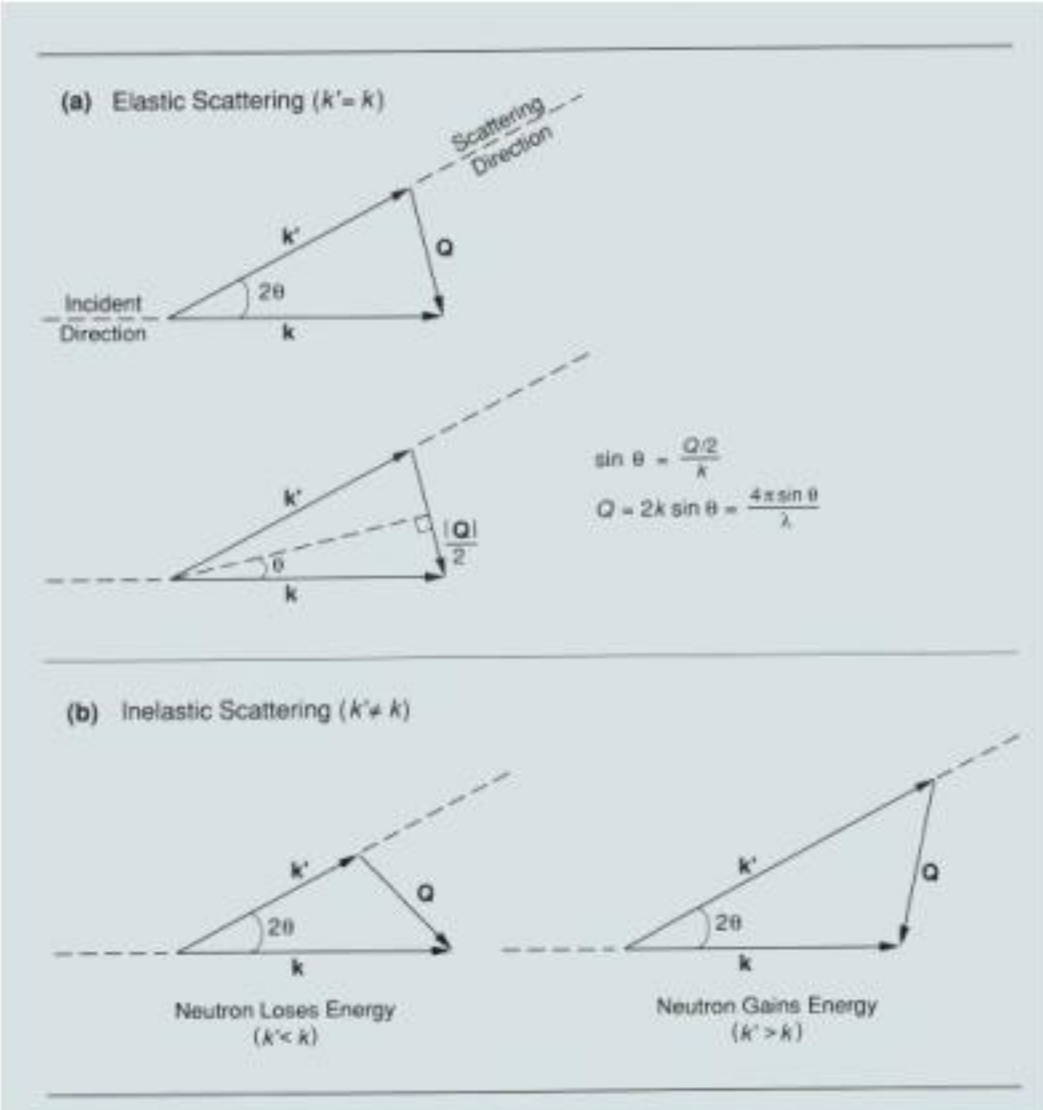
but what happens when the atoms are moving?

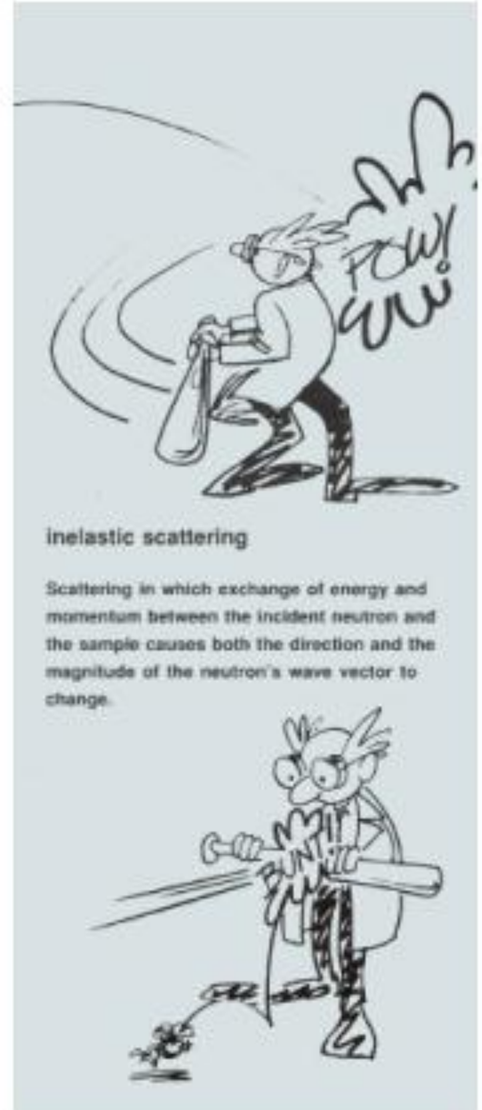


Can we determine the directions and time-dependence of atomic motions?
Can well tell whether motions are periodic?
Etc.

These are the types of questions answered by inelastic neutron scattering

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





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

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

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

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

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

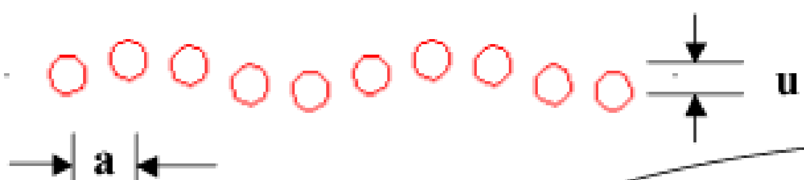
$$F_n = \alpha_0 u_n + \alpha_1 (u_{n-1} + u_{n+1}) + \alpha_2 (u_{n-2} + u_{n+2}) + \ldots$$

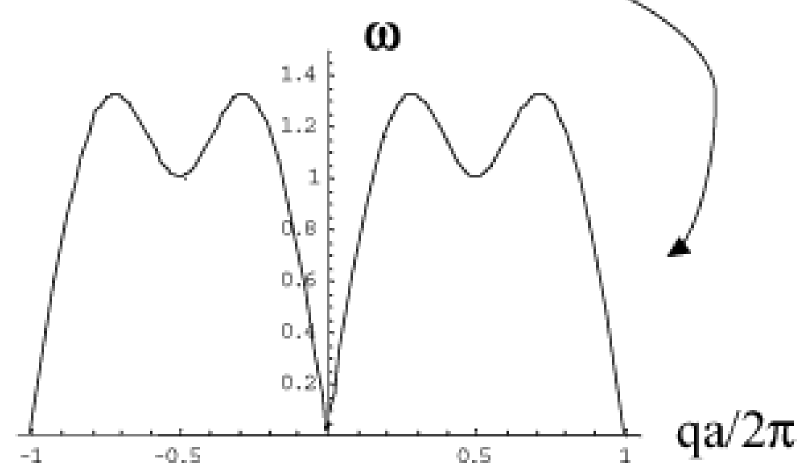
First neighbor force constant

displacements

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

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





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

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

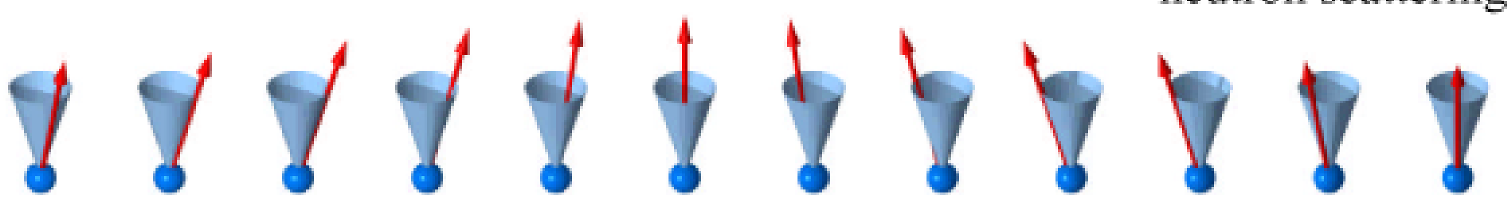
exchange coupling — ground state energy — spin waves (magnons)

with

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

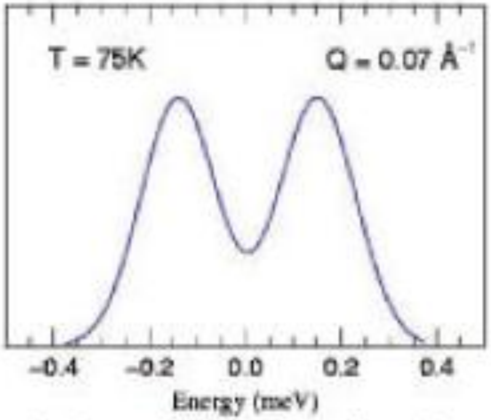
$\hbar\omega_q = Dq^2$ is the dispersion relation for a ferromagnet

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

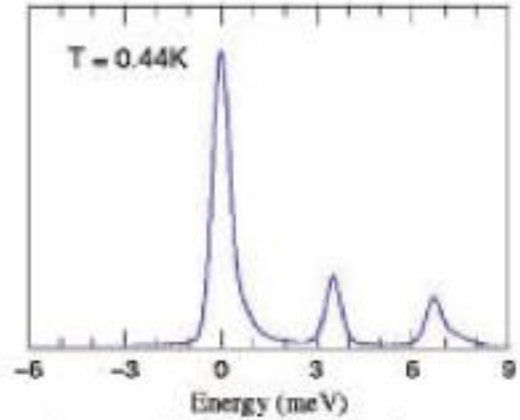


Spin wave animation courtesy of A. Zheludev (ORNL)

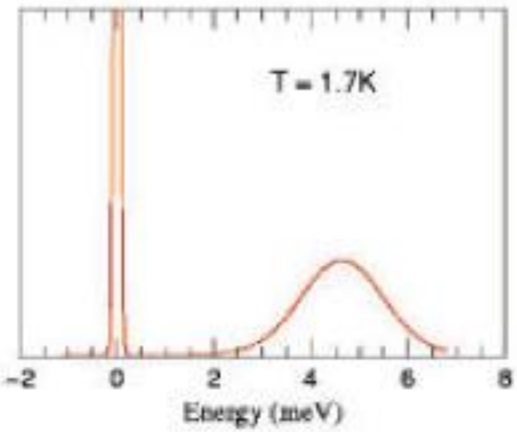
Measured Inelastic Neutron Scattering Signals in Crystalline Solids Show Both Collective & Local Fluctuations*



Spin waves – collective excitations



Crystal Field splittings ($HoPd_2Sn$) – local excitations

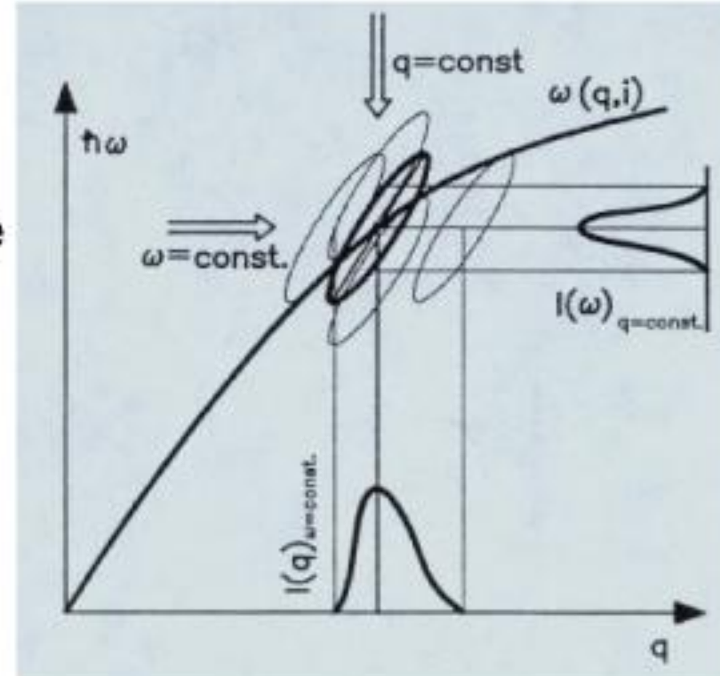


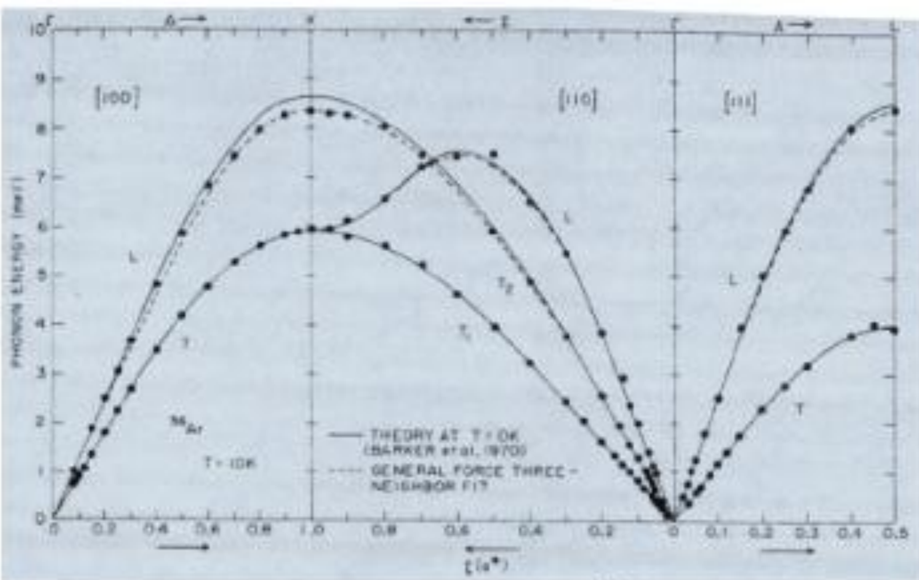
Local spin resonances (e.g. $ZnCr_2O_4$)

* Courtesy of Dan Neumann, NIST

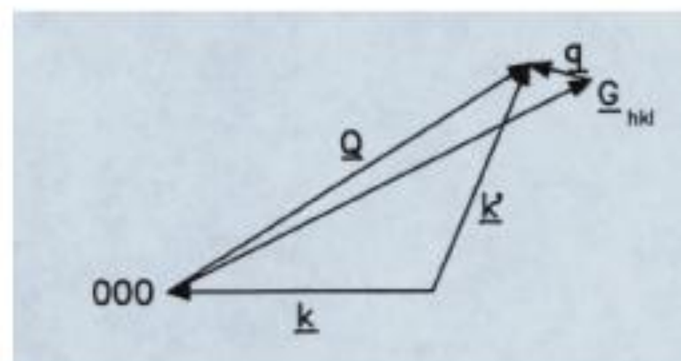
Triple Axis Spectrometers Have Mapped Phonons Dispersion Relations in Many Materials

- 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

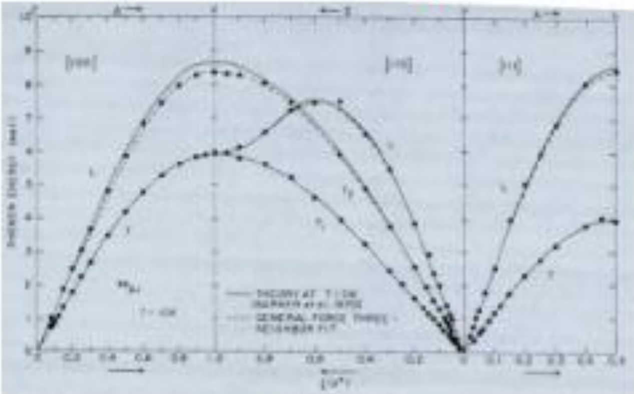




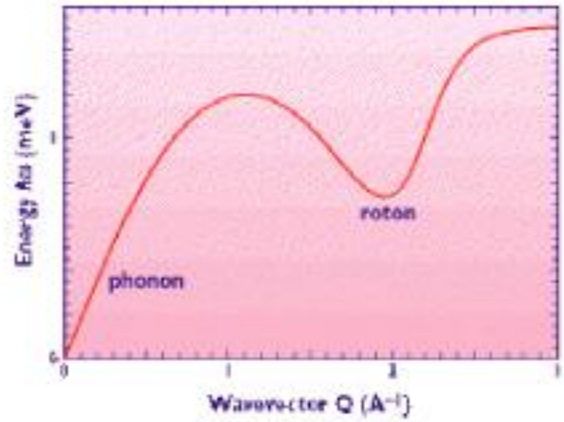
Phonon dispersion of ^{36}Ar



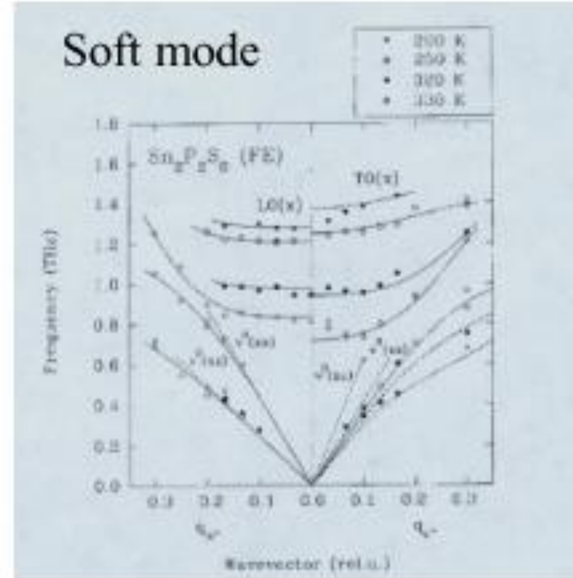
Examples of Phonon Measurements

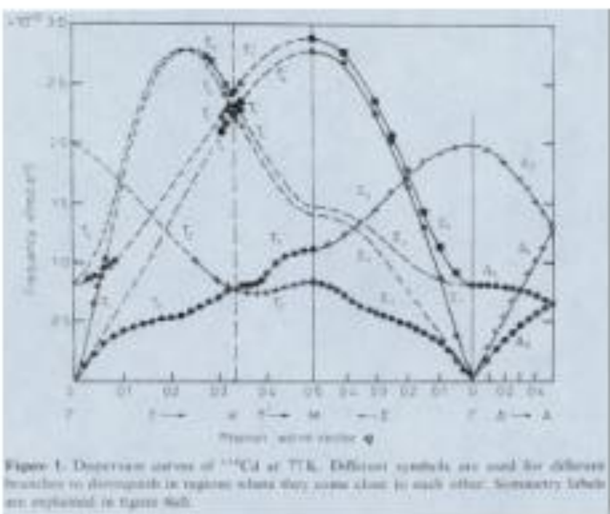


Phonons in ^{36}Ar – validation of LJ potential



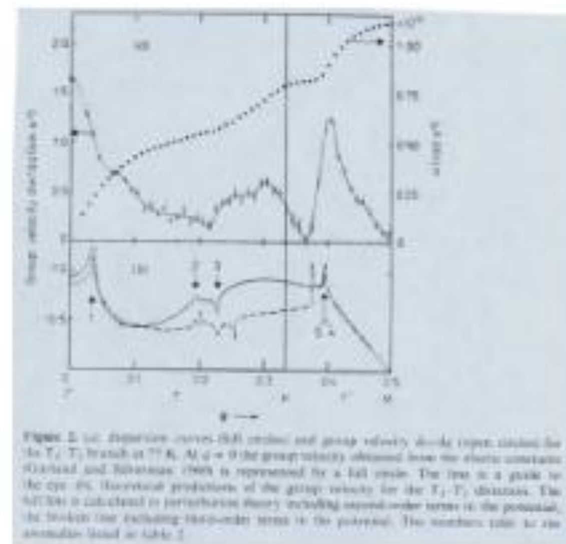
Roton dispersion in ^{4}He



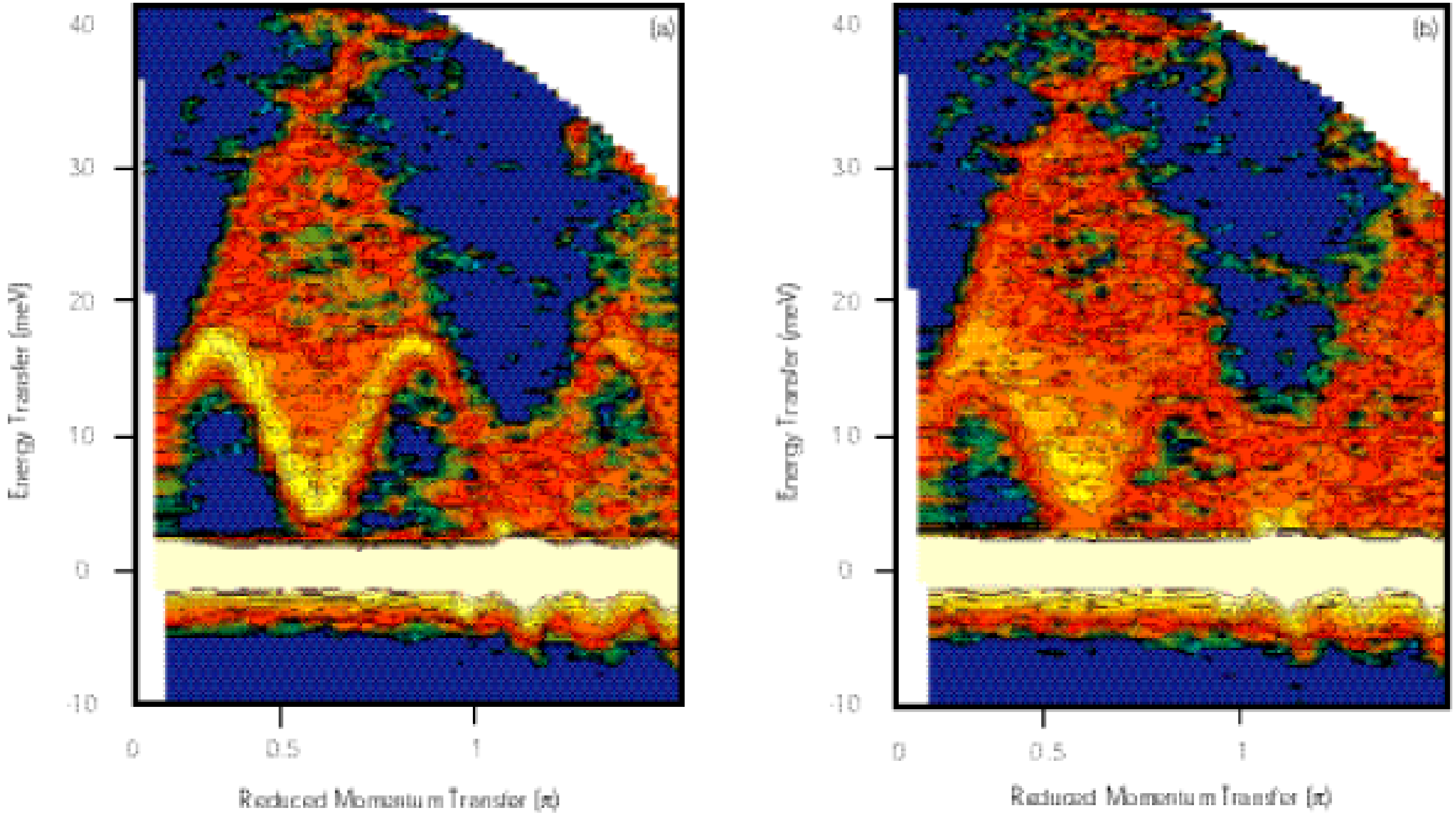


Phonons in ^{110}Cd

Kohn anomalies in ^{110}Cd

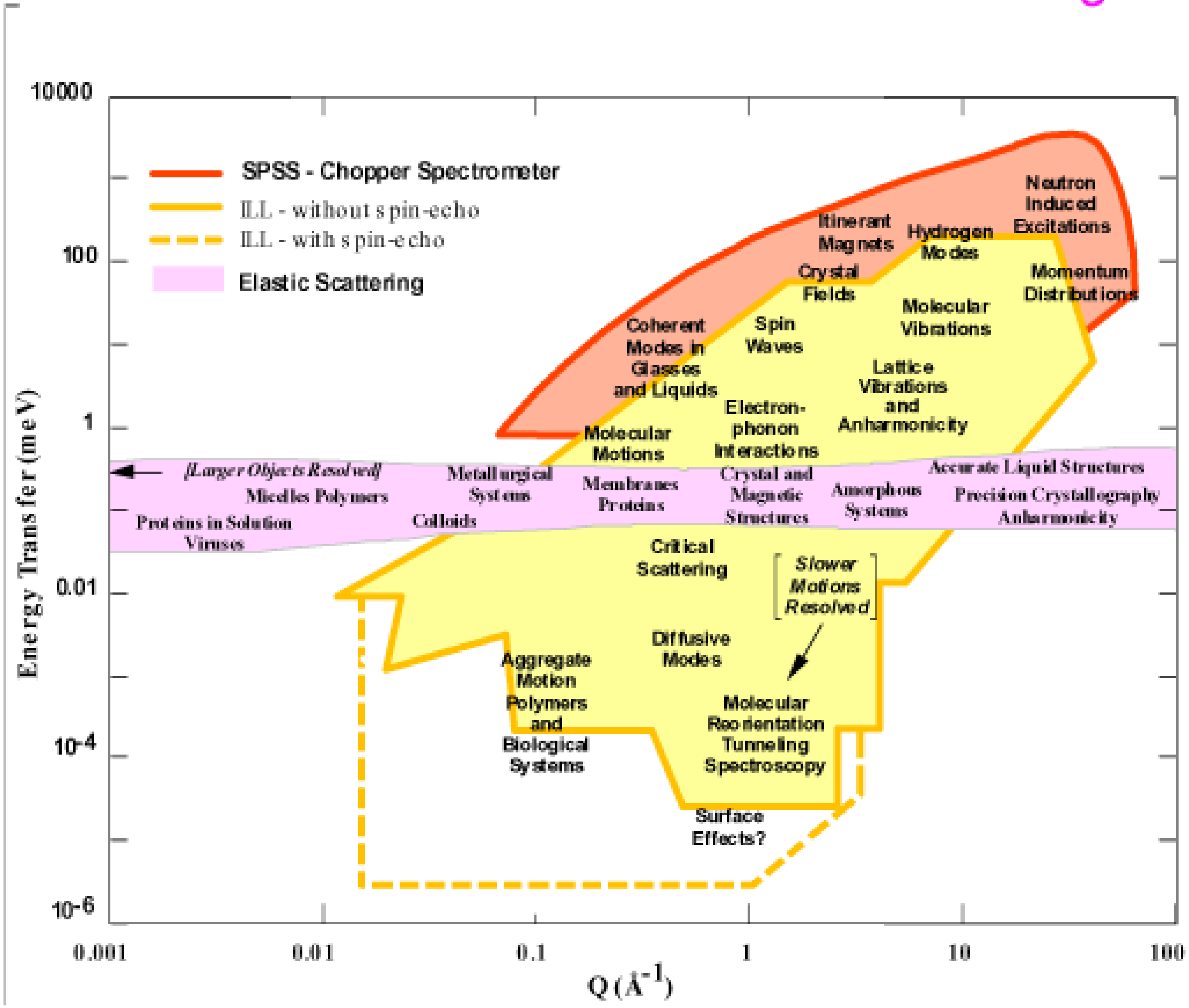


Time-of-flight Methods Can Give Complete Dispersion Curves at a Single Instrument Setting in Favorable Circumstances



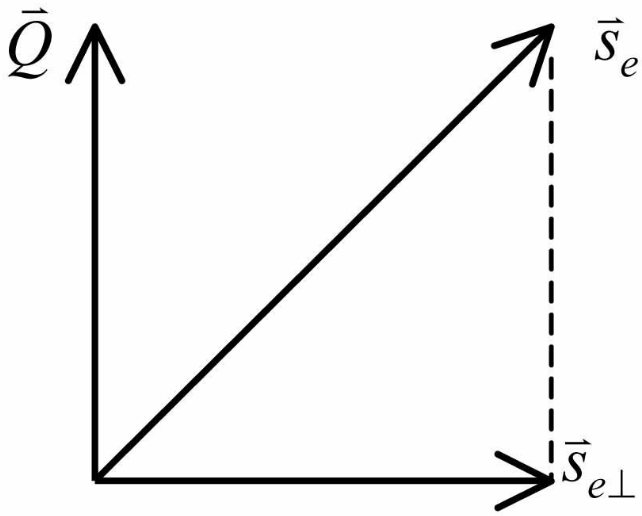
$CuGeO_3$ is a 1-d magnet. With the unique axis parallel to the incident neutron beam, the complete magnon dispersion can be obtained

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

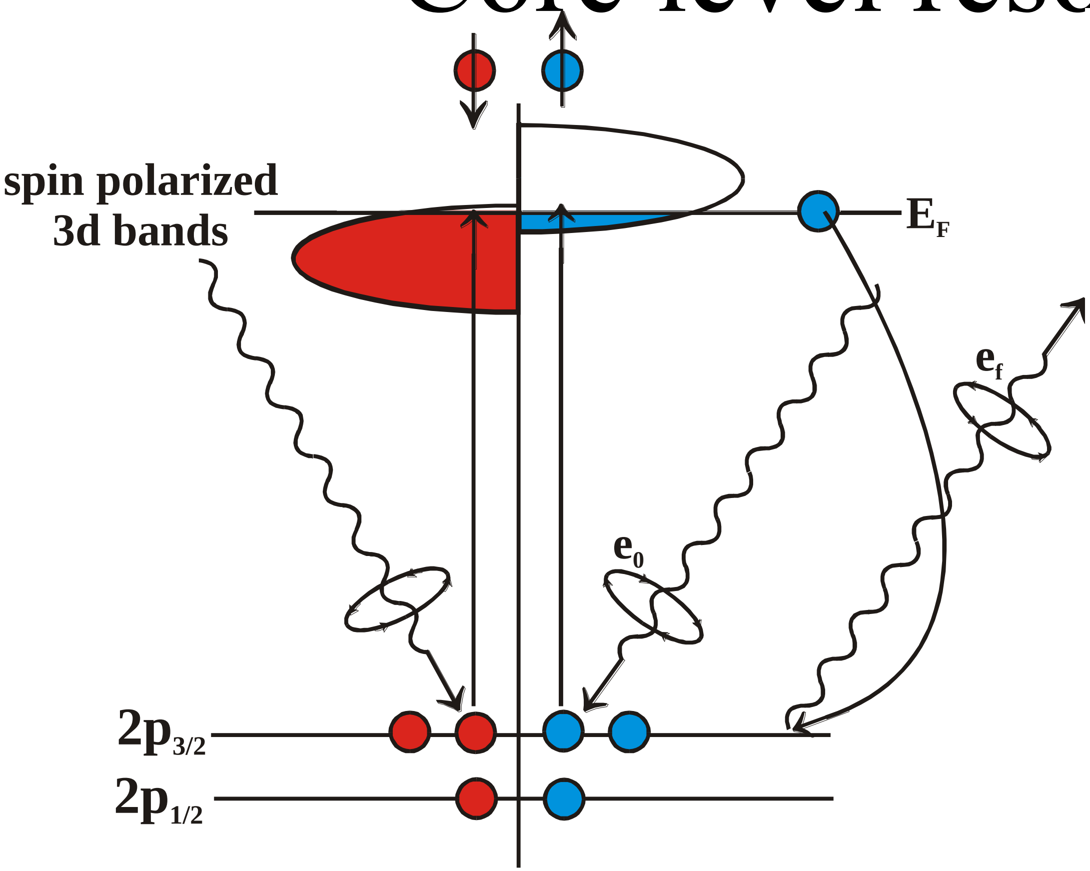


Energy & Wavevector Transfers accessible to Neutron Scattering

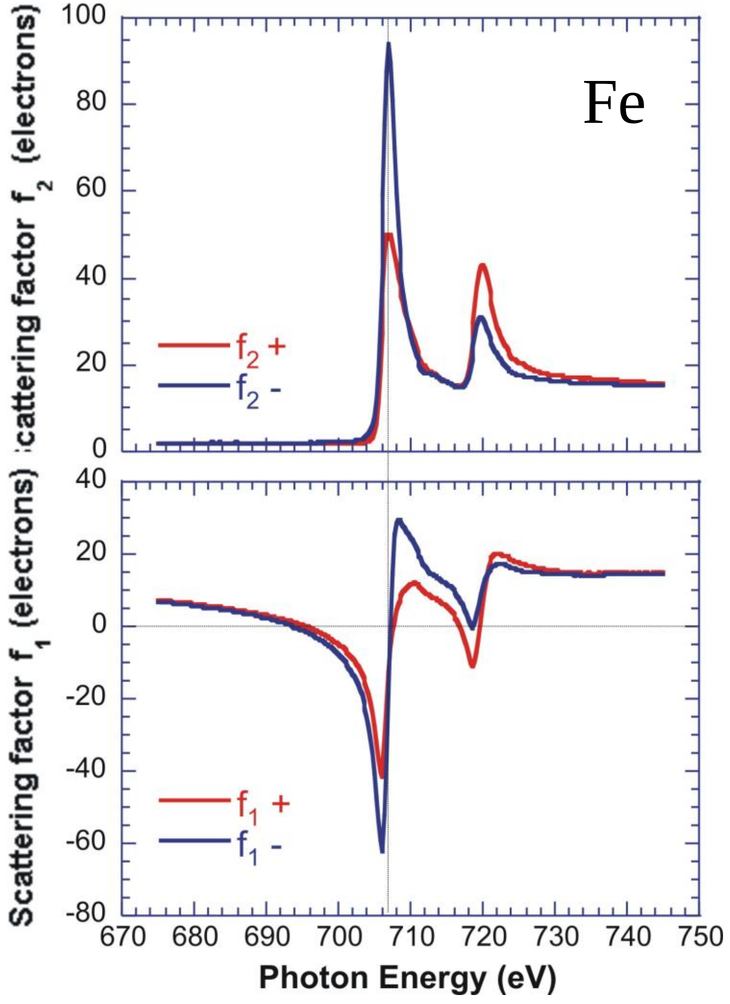
Magnetic Neutron Scattering



Core level resonances



$$f = f_1 + if_2$$



Kortright *et al.*, Phys. Rev. B **65**, 12216 (2000)

NEUTRONS:

$$R_{++}(Q_z) - R_{--}(Q_z) \sim M_{xy,||}(Q_z)\, n(Q_z)$$

$$R_{+-}(Q_z) = R_{-+}(Q_z) \sim |M_{xy,\perp}(Q_z)|^2$$

X-RAYS:

$$R_{+}(Q_z) - R_{-}(Q_z) \sim M_{||}(Q_z)\, n(Q_z)$$

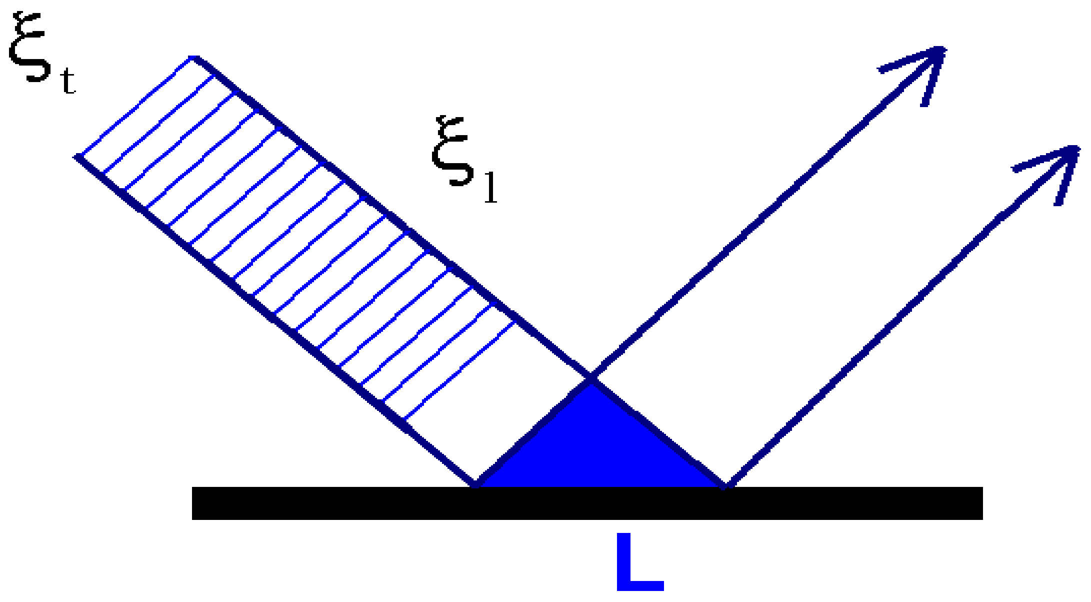
Coherence Lengths

$\xi_l = \lambda^2 / \Delta\lambda$

$= \lambda(\Delta\lambda / \lambda)^{-1}$

$\xi_t = \lambda\ R / s$

$(\xi_{hor.}, \xi_{vert.})$

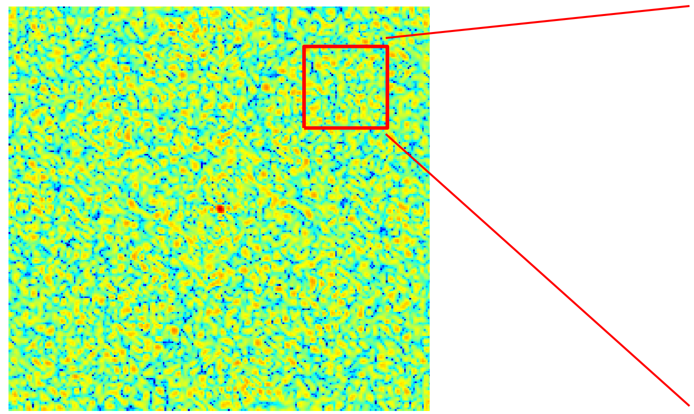


Photon Correlation Spectroscopy□

Brownian Motion of 100 particles

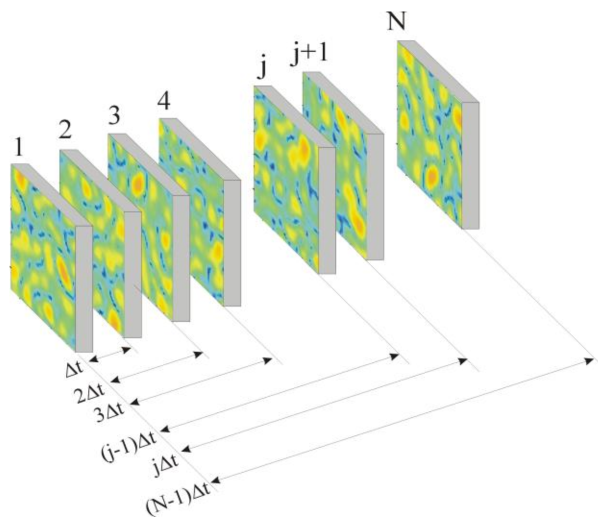
QuickTime™ and a
Video decompressor
are needed to see this picture.

Diffraction Pattern



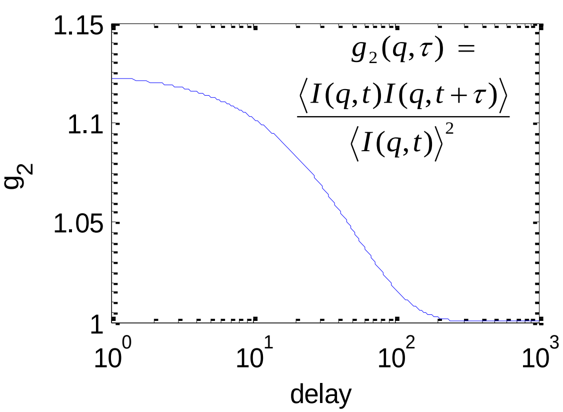
Speckles

QuickTime™ and a
Video decompressor
are needed to see this picture.

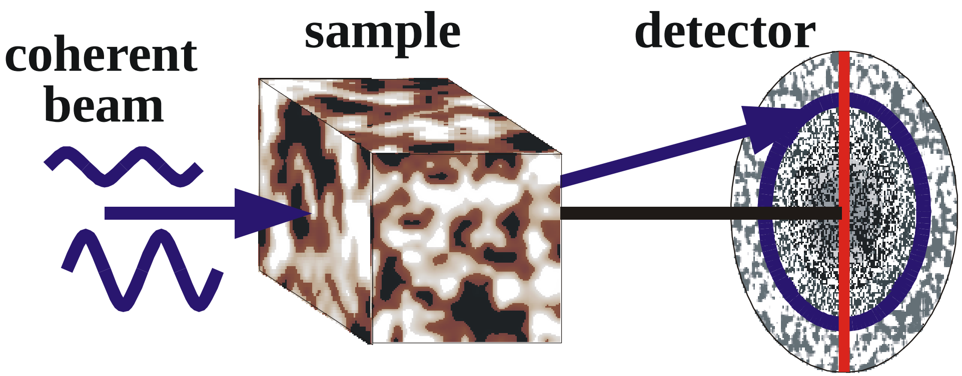


QuickTime™ and a
Video decompressor
are needed to see this picture.

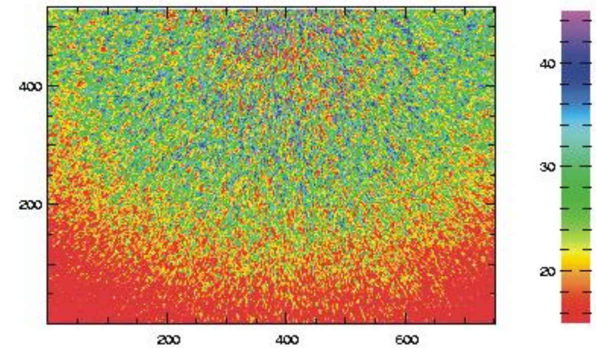
Intensity-intensity auto correlation

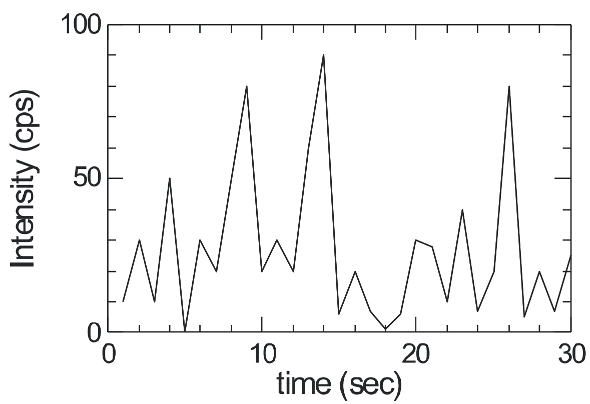


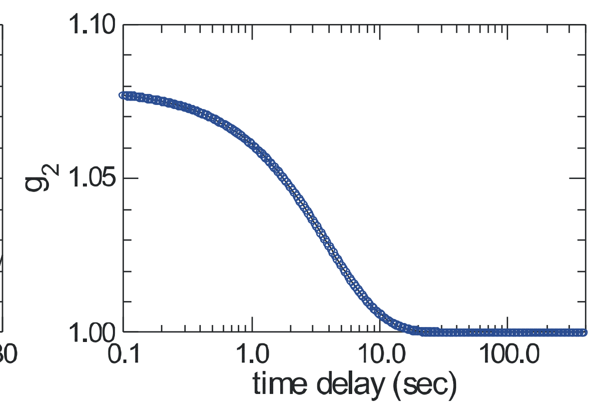
Photon Correlation Spectroscopy



X-ray speckle pattern from a static silica aerogel







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

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

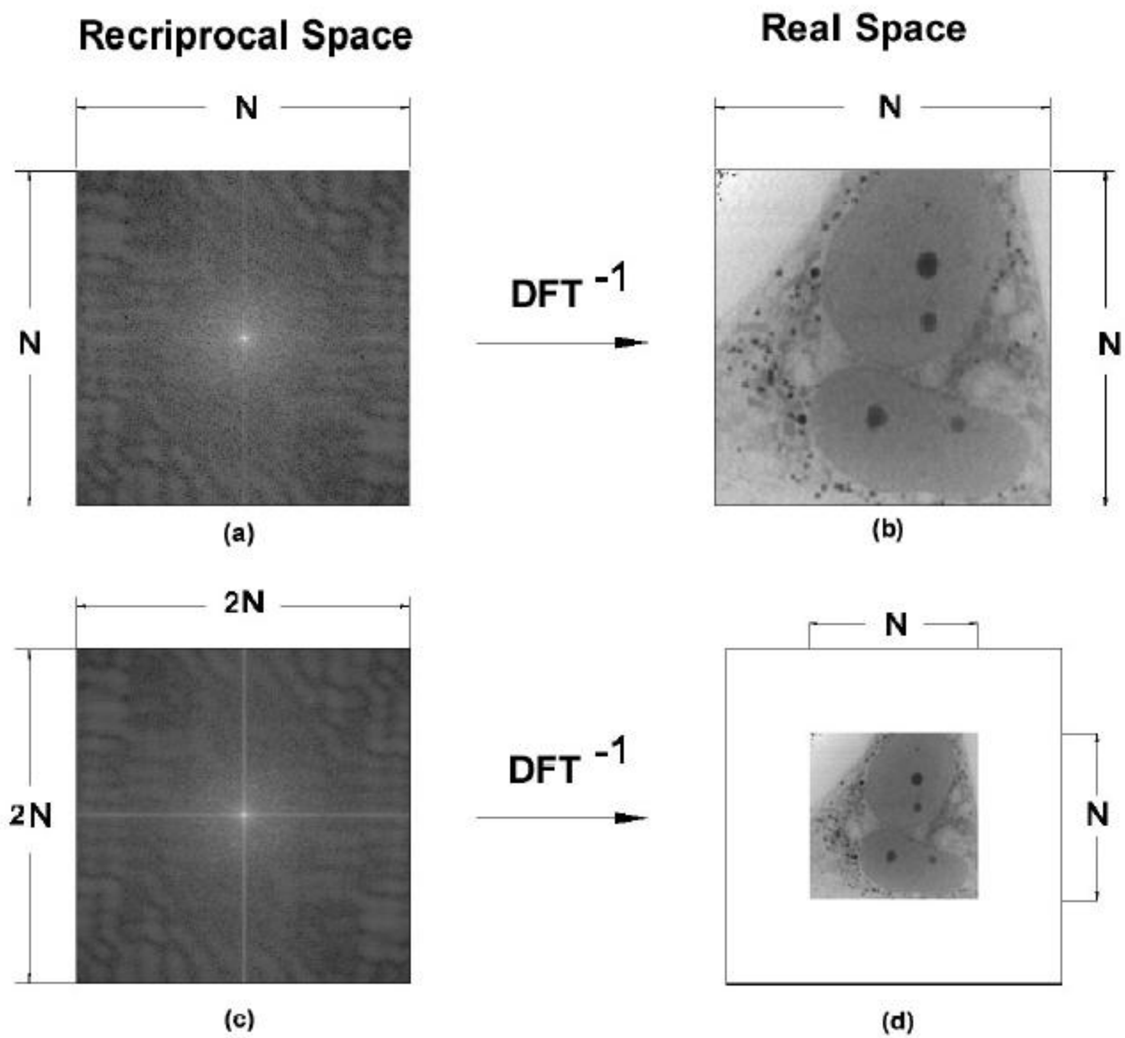
β: speckle contrast

"Oversampling":

Non-crystals:
pattern continuous,
can do finer sampling
of intensity

Finer sampling;
larger array;
smaller transform;
"finite support"

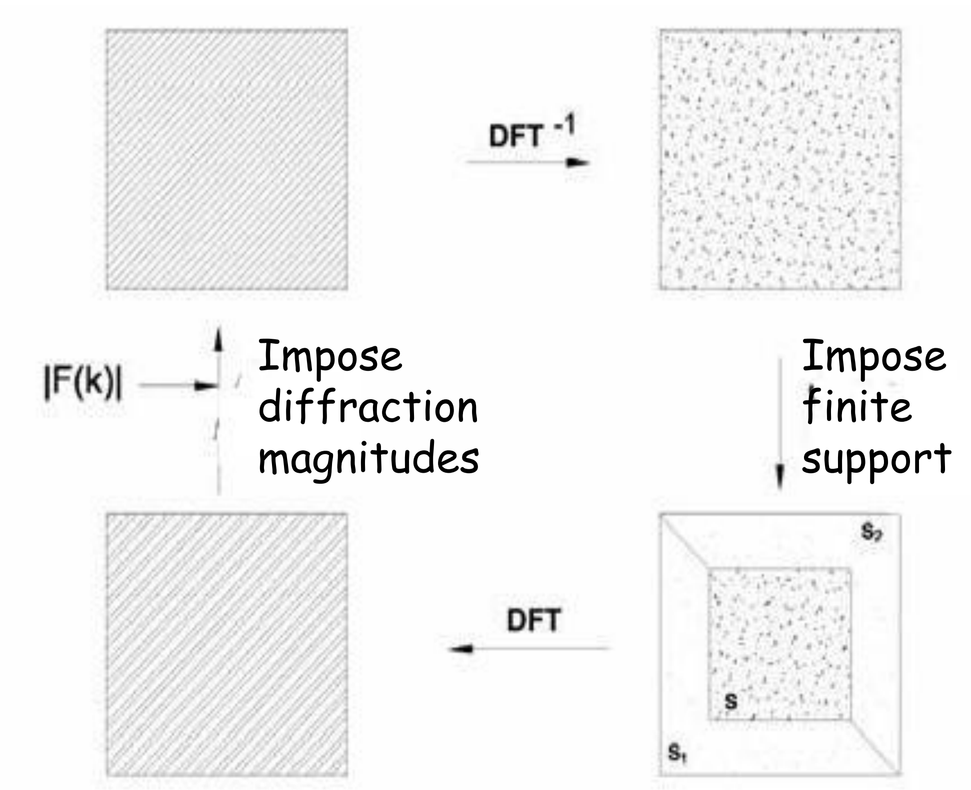
(area around specimen
must be clear!)



Reconstruction

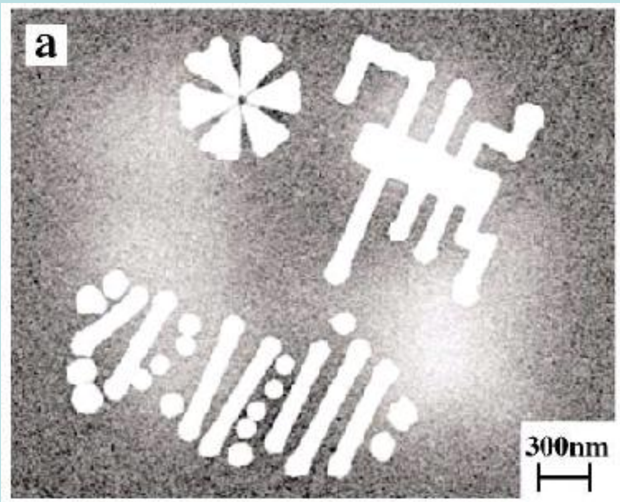
Equations can still not be solved analytically

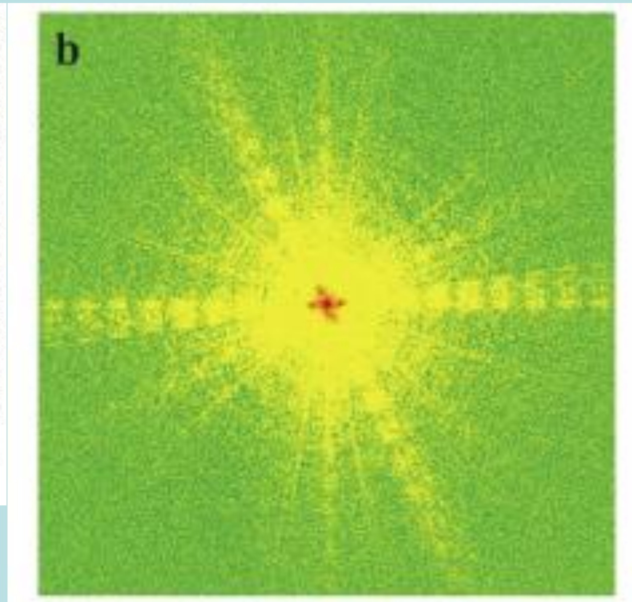
Fienup iterative algorithm

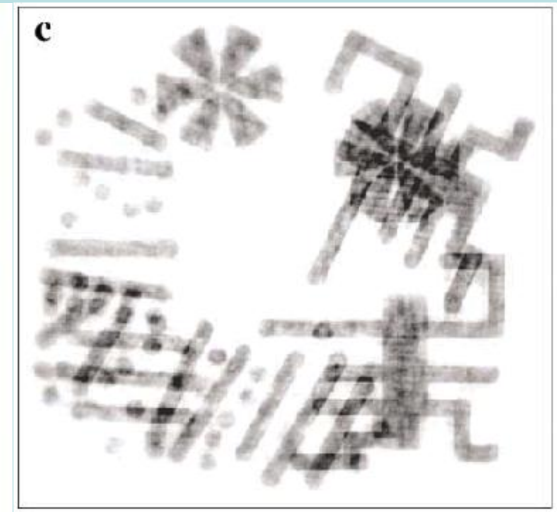


•Positivity of electron density helps!

DIFFRACTION IMAGING BY J. MIAO ET AL





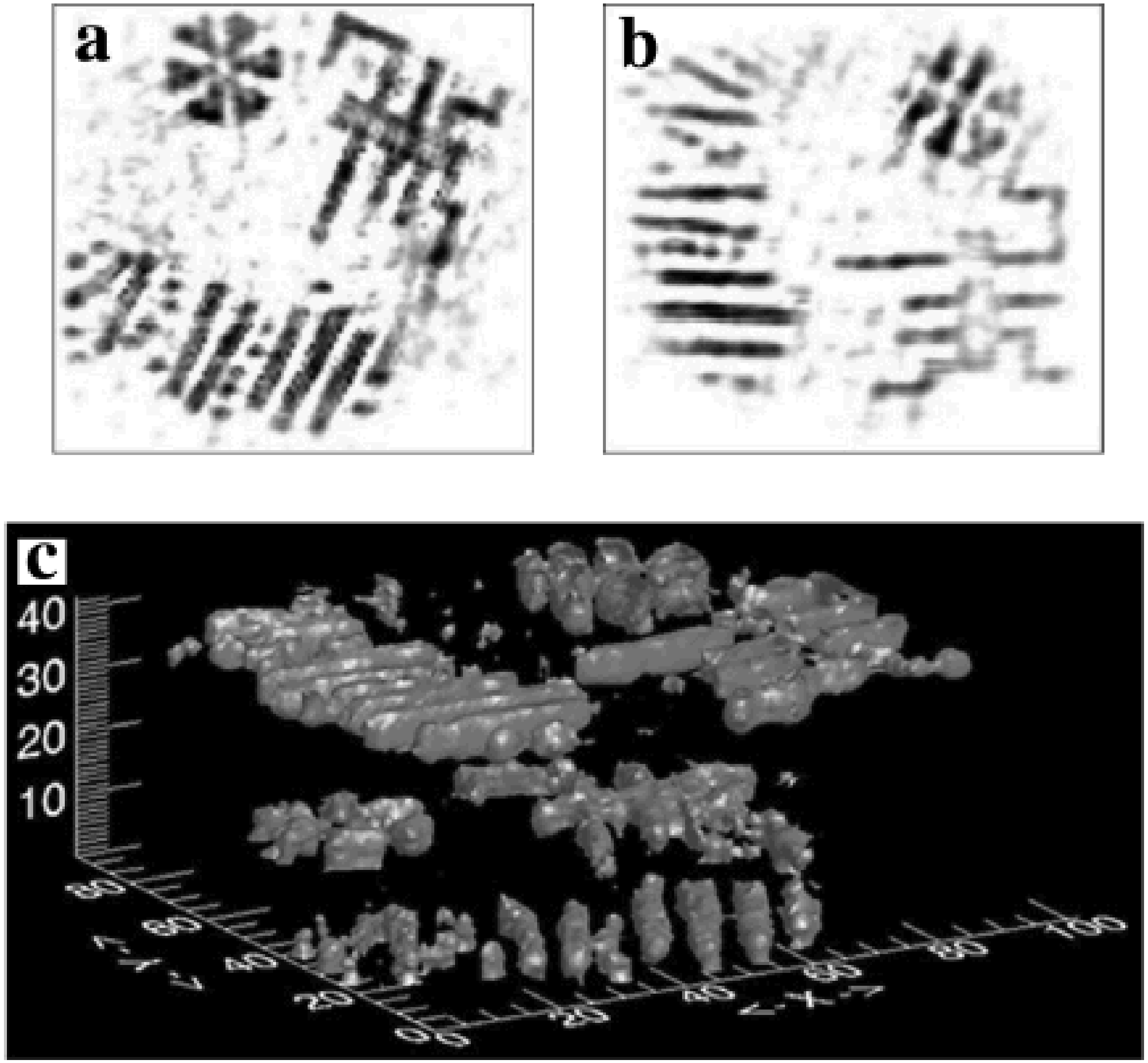


- From Miao, Ishikawa, Johnson, Anderson, Lai, Hodgson PRL Aug 2002
- SEM image of a 3-D Ni microfabricated object with two levels 1 μm apart
- Only top level shows to useful extent

- Diffraction pattern taken at 2 Å wavelength at SPring 8

- 2-D reconstruction with Fienup-type algorithm
- Both levels show because the depth of focus is sufficient
- <u>Resolution = 8 nm (new record)</u>

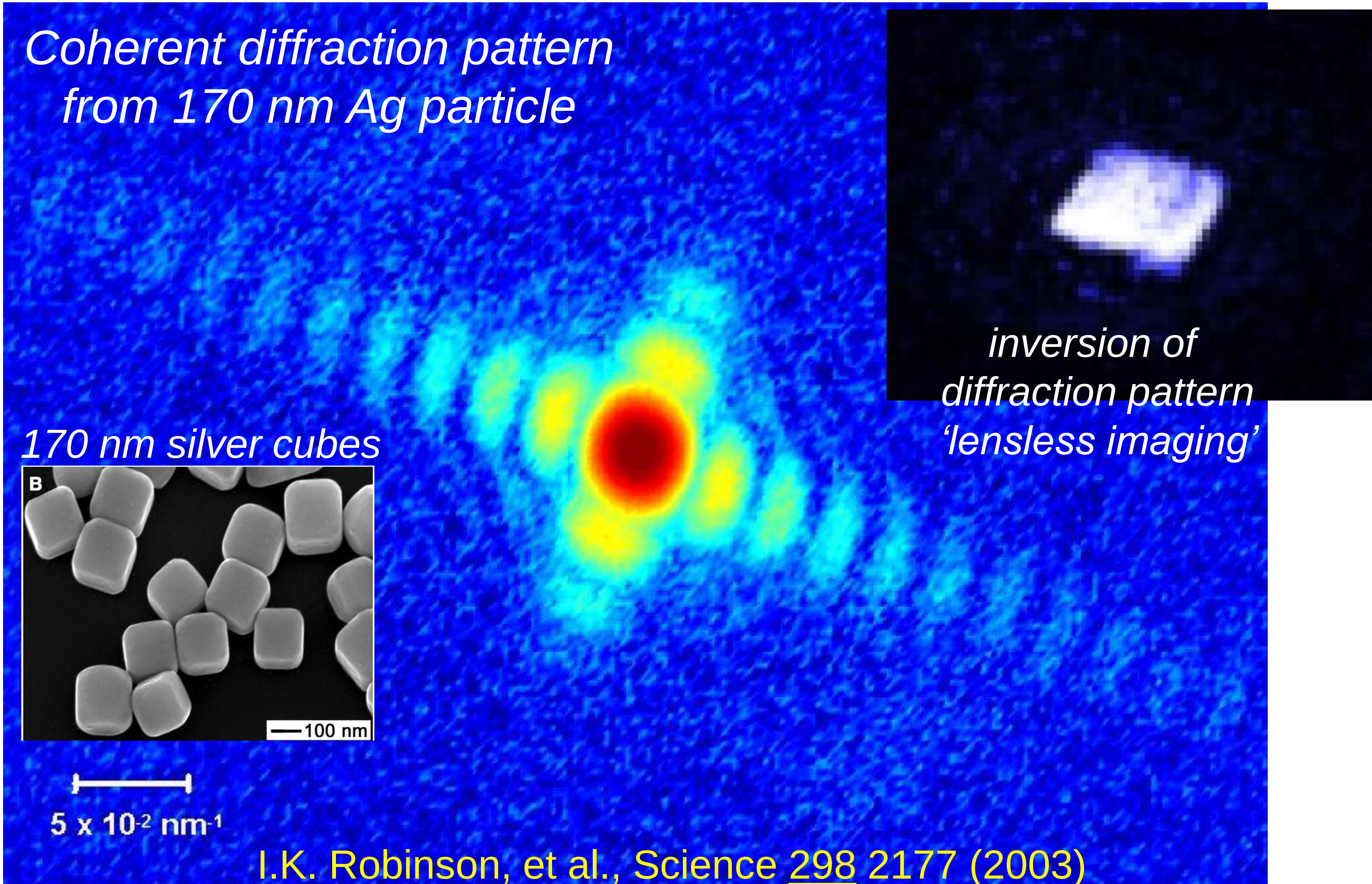
MIAO ET AL 3-D RECONSTRUCTIONS



- Miao et al 3-D reconstruction of the same object pair
- a and b are sections through the *image*
- c is 3-D density
- Resolution = 55 nm

Imaging of individual nanoparticles at the APS

Ross Harder, University of Illinois, Champaign



I.K. Robinson, et al., Science 298 2177 (2003)

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.

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

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

Use Fermi's Golden Rule:

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

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

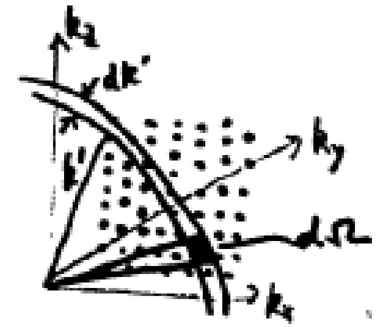
$V =$ Interaction potential of neutron with the sample.

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

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

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

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



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

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

Now $\nu_{k'}dE' =$ 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),

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

Use energy conservation law,

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

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

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

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 $\frac{d\sigma}{d\Omega} = b^2$

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

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

Scattering by an assembly of nuclei:

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

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

$$=\frac{1}{L^3}\left(\frac{2\pi\hbar^2}{m}\right)\sum_{j=1}^{N} b_j\left\langle\lambda'\left|e^{-i\vec{q}\cdot\vec{R}_j}\right|\lambda\right\rangle$$

Thus from Eq. (4)

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

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

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

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

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

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

$$b_i b_j=\langle b\rangle^2+\langle b\rangle[\delta b_i+\delta b_j]+\delta b_i\delta b_j$$

zero　　zero unless $i=j$

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

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

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

$\langle b\rangle^2 \rightarrow \sigma_{\text{coh}}/4\pi$

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

$\langle b^2\rangle - \langle b\rangle^2 \rightarrow \sigma_{\text{inc}}/4\pi$

Write it as

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

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

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

$$S_{\text{inc}}(\vec{q},\omega) = \frac{1}{N}\sum_{\lambda\lambda'} P_\lambda \sum_i \left\langle \lambda \middle| e^{-i\vec{q}\cdot\vec{R}_i} \middle| \lambda' \right\rangle \left\langle \lambda' \middle| e^{i\vec{q}\cdot\vec{R}_i} \middle| \lambda \right\rangle \delta(E_\lambda - E_{\lambda'} + \hbar\omega)$$

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

Then

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

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

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

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

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

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

Thus, by (6),

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

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

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

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

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,

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

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

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

$\Downarrow$

Van-Hove space-time correlation function of system

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

NOTE: $R_i(0)$, $R_j(t)$ are not commuting 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

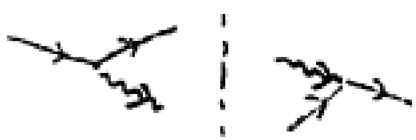
$$= \frac{1}{2m}\sum_i \left(P_i^2 + V(r_i)\right) + V_{\text{int}}^{e-e} \leftarrow H_{e\ell}$$

$$+ \frac{e}{2mc}\sum_i \left\{\vec{P}_i\cdot\vec{A}(\vec{r})\delta(\vec{r}-\vec{r}_i) + \vec{A}(\vec{r})\delta(r-r_i)\cdot\vec{P}_i\right\} \quad \swarrow H_{\text{int}}^{(1)}$$

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

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

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



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

In 2nd order $\rightarrow$ scattering

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

In 1st order $\rightarrow$ scattering

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

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

"Thomson" Scattering $\swarrow$ $\qquad \delta(E_\lambda - E_{\lambda'} + \hbar\omega)$

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

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

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

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

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

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

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

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

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

(Equal-Time Correlation Function)