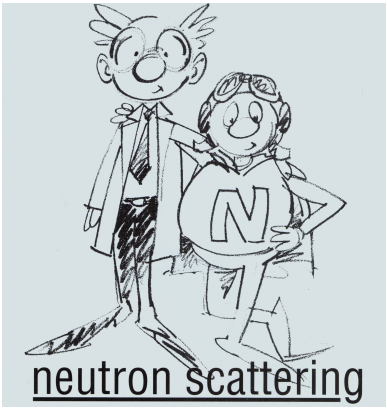


An Introduction to Neutron and X-Ray Scattering

by

Roger Pynn
Indiana University and Oak Ridge National Lab

With thanks to various friends for allowing me to use their materials: especially Jen Als- Nielsen, Mike Fitzsimmons & Sunhil Sinha

Wilhelm Conrad Röntgen 1845-1923

EINE NEUE ART

VON

STRAHLEN.

Von

Dr. W. RÖNTGEN,

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

WÜRZBURG.

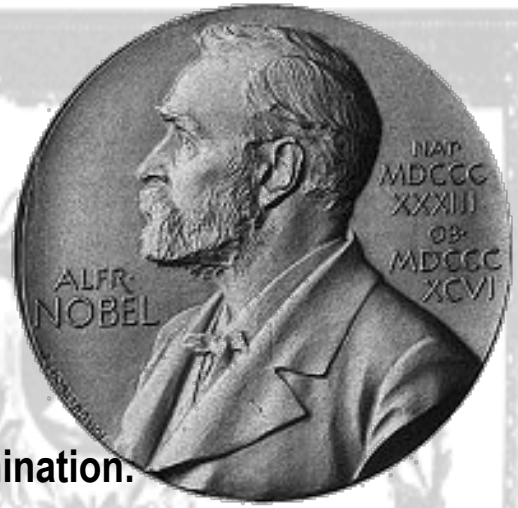
VERLAG UND DRUCK DER STAHEL'SCHEN K. HOF- UND UNIVERSITÄTS-BUCH- UND KUNSTHANDLUNG.

Ende 1895.

60 S.

1895: Discovery of X-Rays

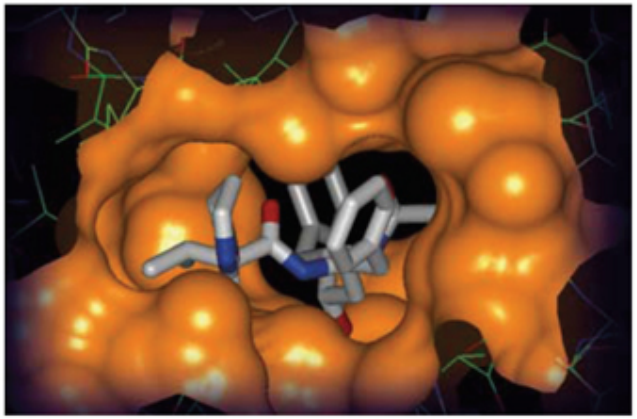
Nobel Prizes for Research with X-Rays



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 transcription.
2009 V.Ramakrishnan, T.A.Steitz and A.E.Yonath for studies of the structure and function of the ribosome.

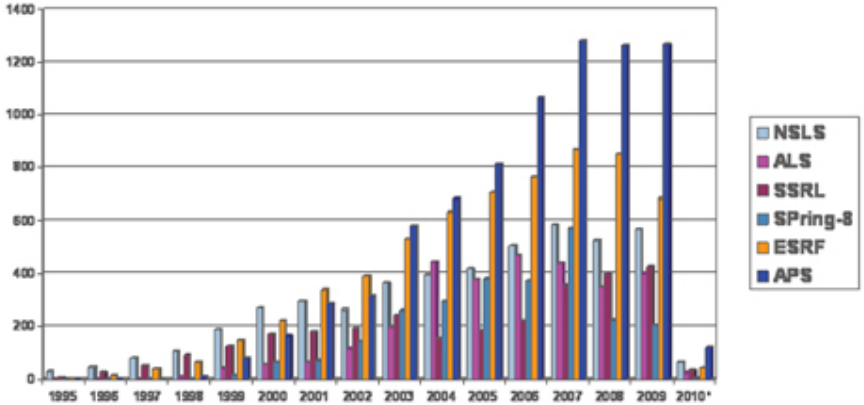
Synchrotron research on proteins has led to major advances in drugs to battle infection, HIV, cancer

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).

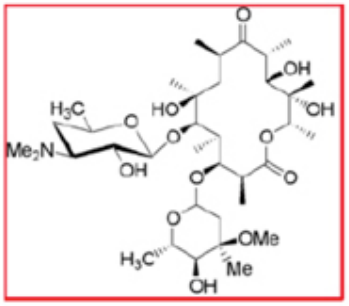
Ramakrishnan, Steitz and Yonath
2009 Chemistry Nobel Laureates



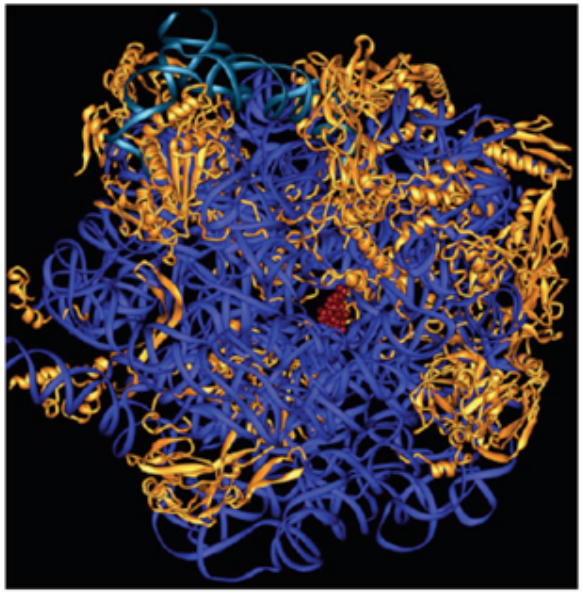
APS protein structure output is almost twice that of any other light source

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

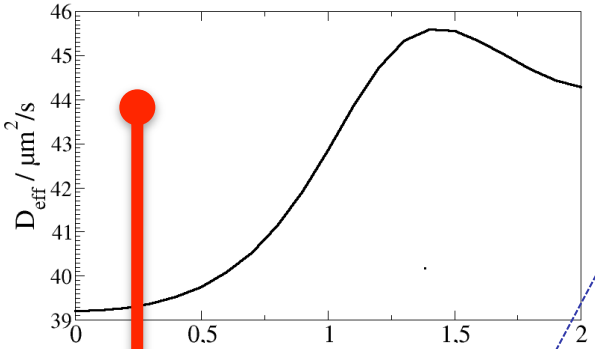


www.molgen.mpg.de

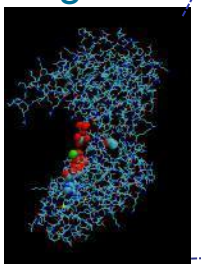
Functional domain dynamics in proteins

NSE

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

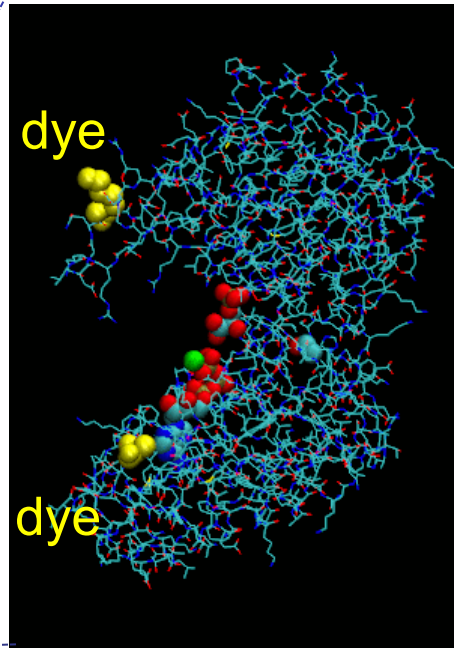


q~2π/length



FRET

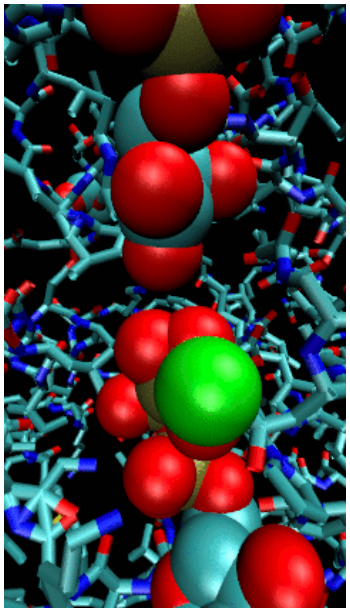
fixed defined position
> µs timescale



phosphoglycerate kinase

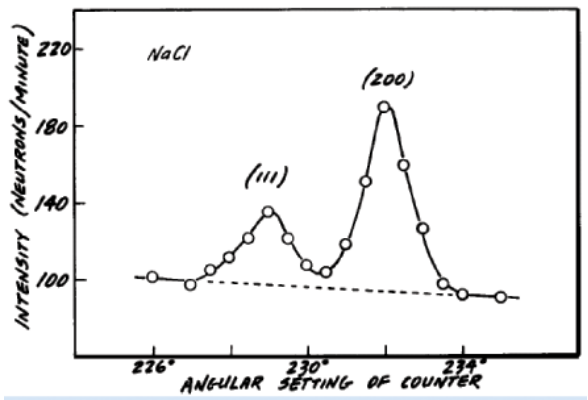
NMR

ps - ms timescale
small proteins



Some Neutron History

- 1932 – Chadwick discovers the neutron
- 1934 – thermalisation (Fermi)
- 1936 – scattering theory (Breit, Wigner)
- 1936 – wave interference (Mitchell, Powers)
- 1939 – fission



- 1945 – diffraction (Shull, Wollan), reflection, refraction
- 1948 – coherent & incoherent scattering (Shull, Wollan)
- 1948 – spallation
- 1949 – structure of AFM (Shull)

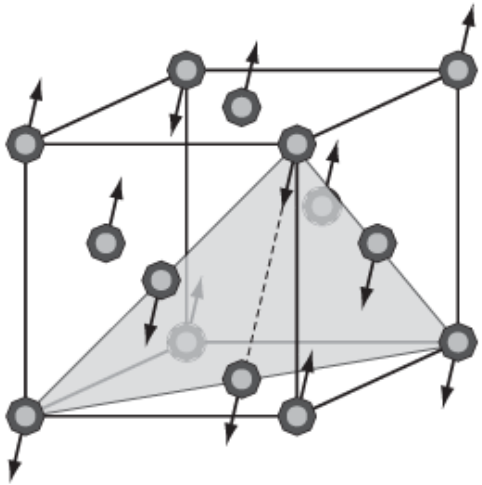
- 1951 – polarized neutrons (Shull & Wollan)
- 1955 – three axis spectrometer (Brockhouse)
- 1958 – rotons in helium (Palevsky, Otnes, Larsson)

- 1962 – Kohn anomalies
- 1960 – 79 – soft phonons & structural phase transitions
- 1969 – 79 – scaling and universality

- 1972 – conformation of polymers
-
- 1994 – Nobel Prize for Shull and Brockhouse

Cliff Shull (1915 – 2001)

First Study of an Antiferromagnetic Structure

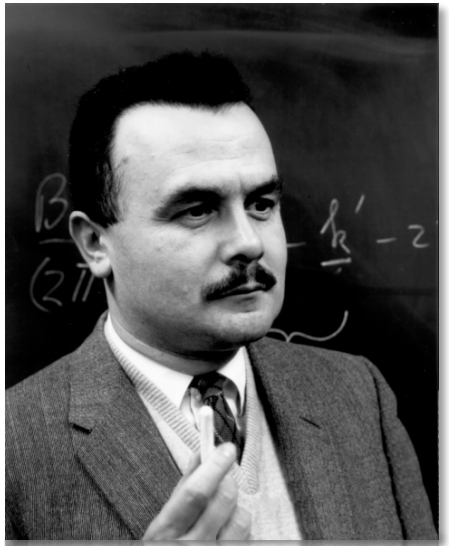


Antiferromagnetic Structure of MnO
(Shull and Wollan Phys. Rev. 83, 333 (1951)

Nobel Prize in Physics, 1994

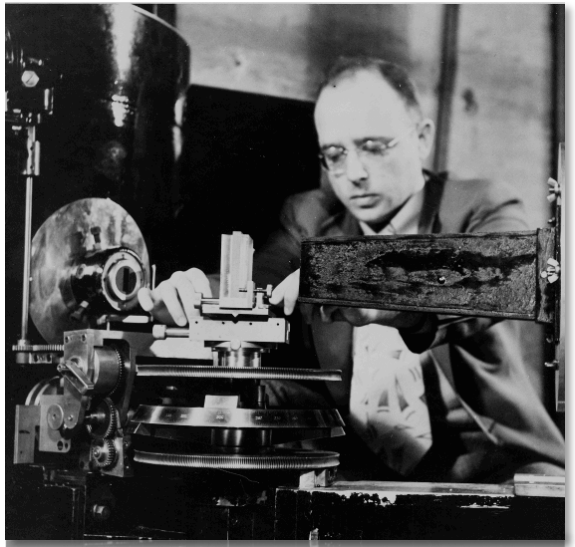
Awarded for "pioneering contributions to the development of neutron scattering techniques for studies of condensed matter"

Bertram N. Brockhouse



Development of neutron spectroscopy

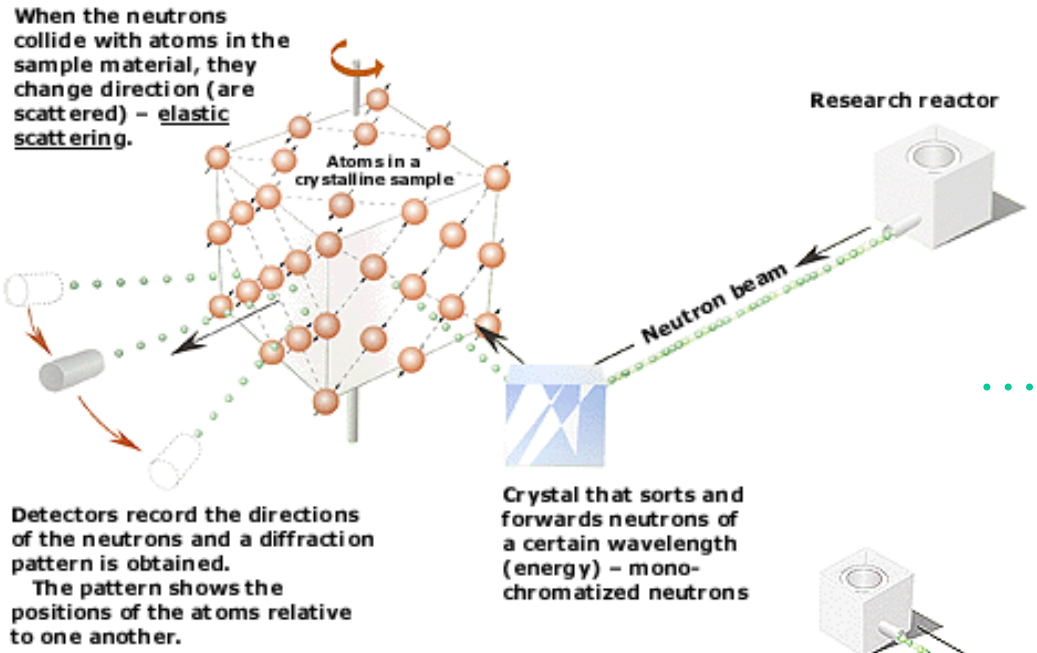
Clifford G. Shull

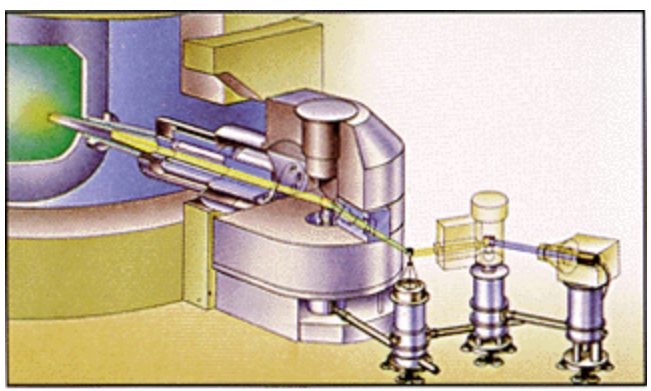


Development of the neutron diffraction technique

The 1994 Nobel Prize in Physics – Shull & Brockhouse

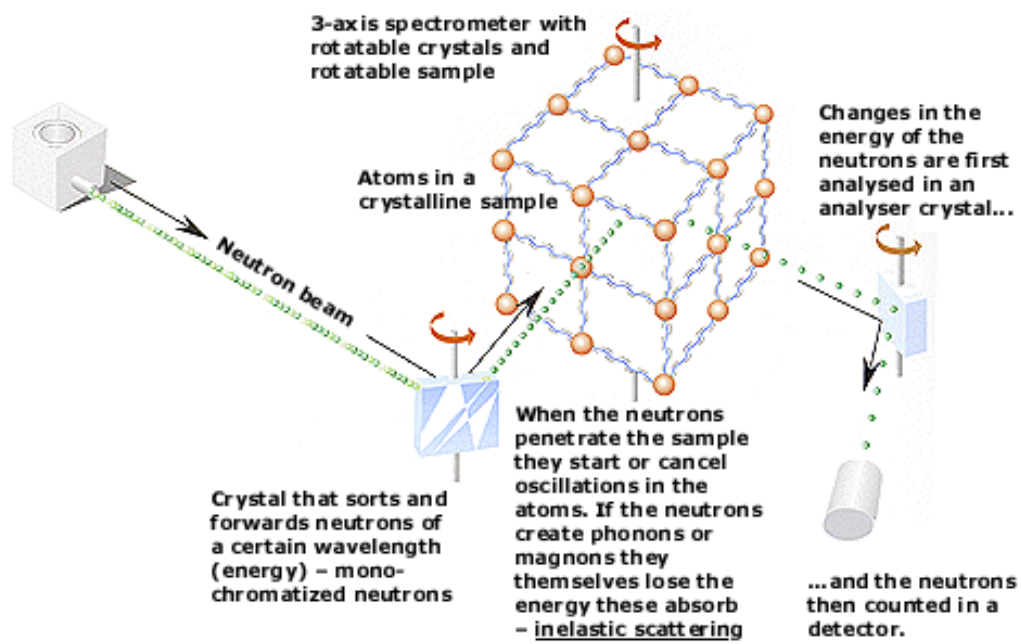
Neutrons show where the atoms are….





3-axis spectrometer

…and what the atoms do.



Why do Neutron Scattering?

- To determine the positions and motions of atoms in condensed matter
  - 1994 Nobel Prize to Shull and Brockhouse cited these areas
    (see http://www.nobel.se/physics/educational/poster/1994/neutrons.html)

- Neutron advantages:
  - Wavelength comparable with interatomic spacings
  - Kinetic energy comparable with that of atoms in a solid
  - Penetrating => bulk properties are measured & sample can be contained
  - Weak interaction with matter aids interpretation of scattering data
  - Isotopic sensitivity allows contrast variation
  - Neutron magnetic moment couples to ***B*** **=>** neutron "sees" unpaired electron spins

- Neutron Disadvantages
  - Neutron sources are weak => low signals, need for large samples etc
  - Some elements (e.g. Cd, B, Gd) absorb strongly
  - Kinematic restrictions (can't access all energy & momentum transfers)

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 of Neutrons

- 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

Recent Applications of Neutrons (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

Neutron 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.

Science with X-Rays

- Diffraction and crystal structures
- Structure Factors of liquids and glasses
- Surface and Interface structures
- 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

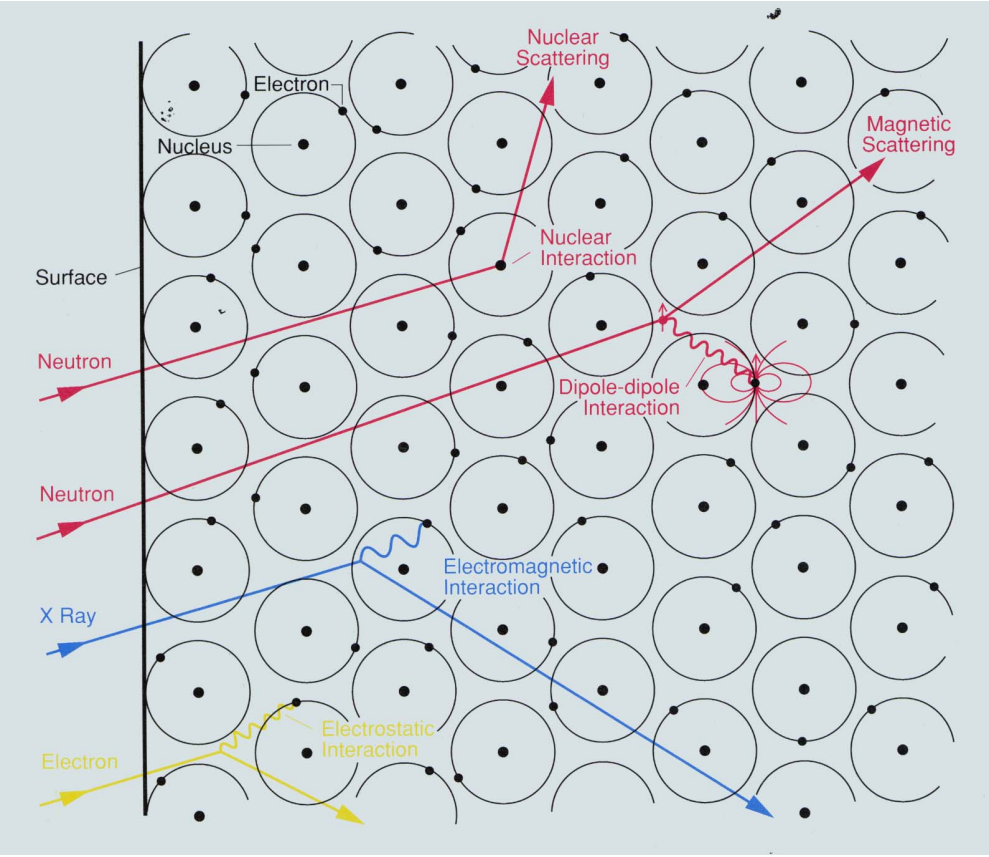
Applications of X-rays to Surface/ Interface Scattering

- 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

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

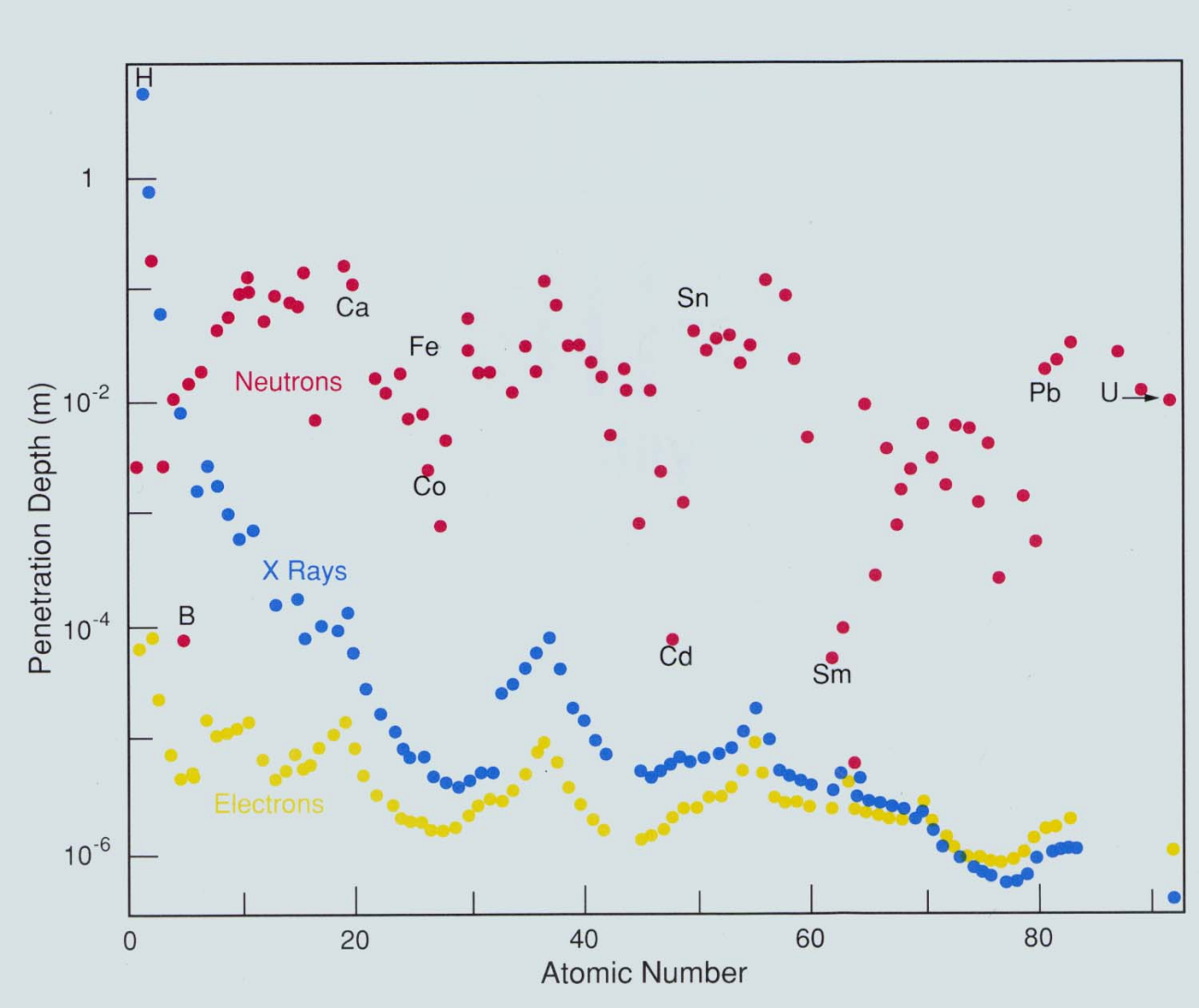
- How the constituent molecules self-assemble to form nanoparticles.
- How these self-organize into assemblies
- How structure and dynamics lead to function
- How emergent or collective properties arise

Interaction Mechanisms



- Neutrons interact with atomic nuclei via very short range (~fm) forces.
- Neutrons interact with unpaired electrons via magnetic dipole interaction.
- X-rays interact with electrons via an electromagnetic interaction

Thermal Neutrons, 8 keV X-Rays & Low Energy Electrons:- Penetration in Matter



Note for neutrons:

- H/D difference
- Cd, B, Sm
- no systematic Z dependence

For x-rays:

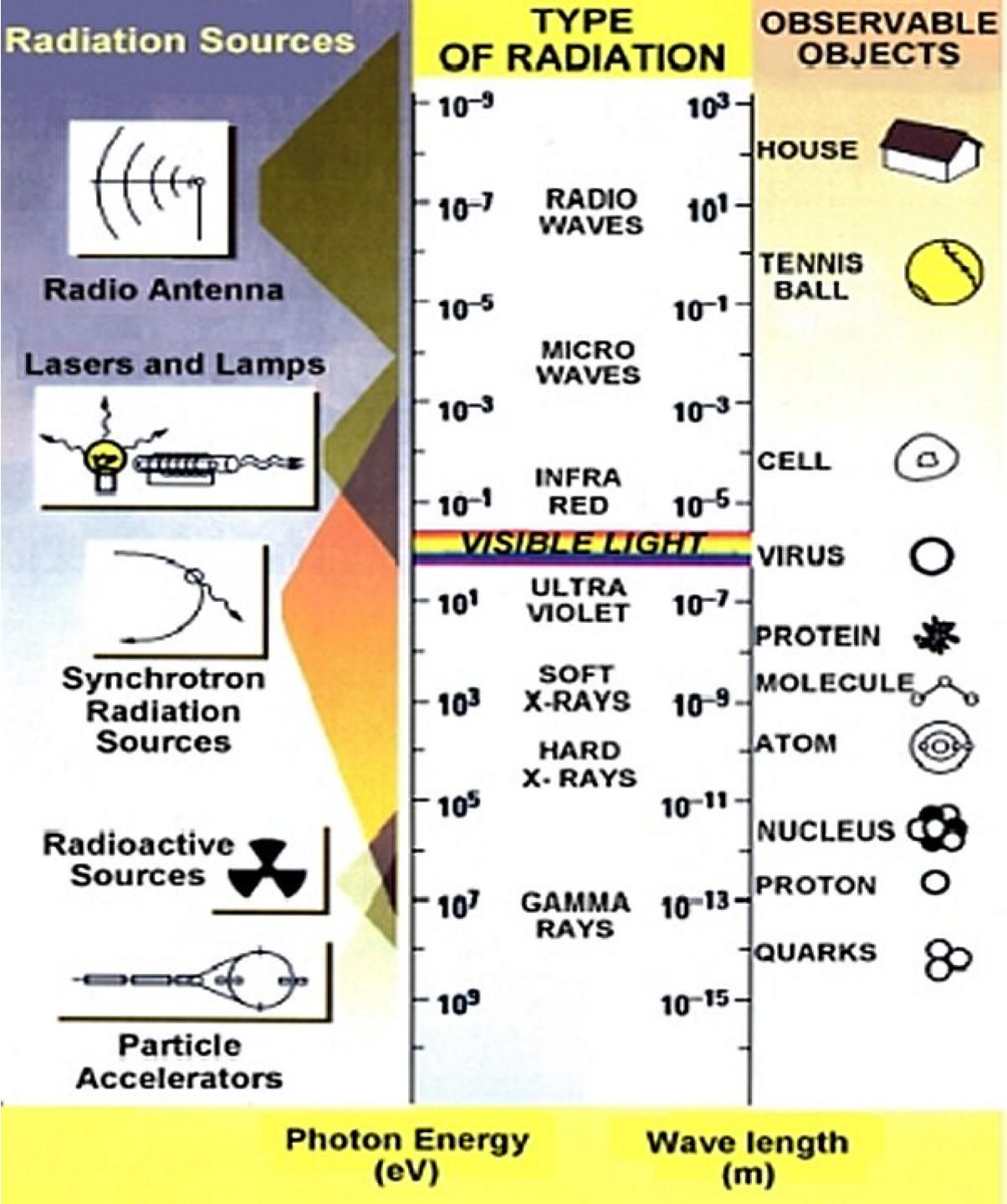
- decreasing penetration as Z increases

Types of Interaction

- Neutrons interacting with nuclei
  - Absorption by nuclei – cross section (i.e. absorption probability) for thermal neutrons usually ~1/v, resonances at high energy (> keV)
  - Coherent scattering – scattering from different nuclei add in phase
  - Incoherent scattering – random phases between scattering from different nuclei

- Neutrons interacting with magnetic fields
  - Magnetic dipolar interaction – scattering from magnetic field due to unpaired electrons – coherent

- X-rays interacting with electrons
  - Photoelectric absorption – x-rays kicks electron from shell to continuum
    - Leads to fluorescent X-ray emission when hole in shell is filled from outer shell
    - Goes as $1/E^3$ but with sharp steps at shell energies when new channel opens
  - Thomson scattering – elastic and coherent
  - Compton scattering – inelastic and incoherent



Wavelength

≈

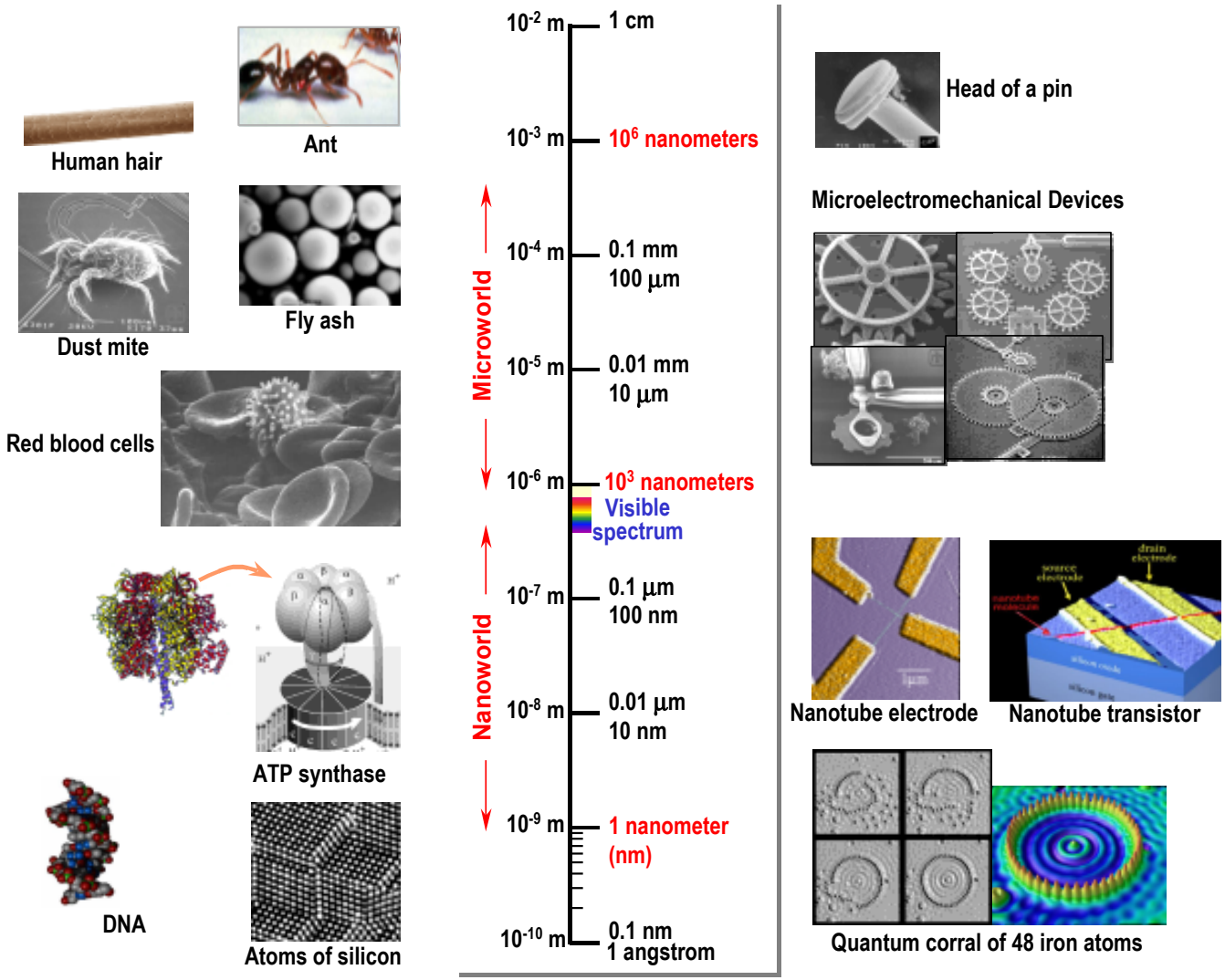
Object Size

≈

Angstroms for Condensed Matter Research

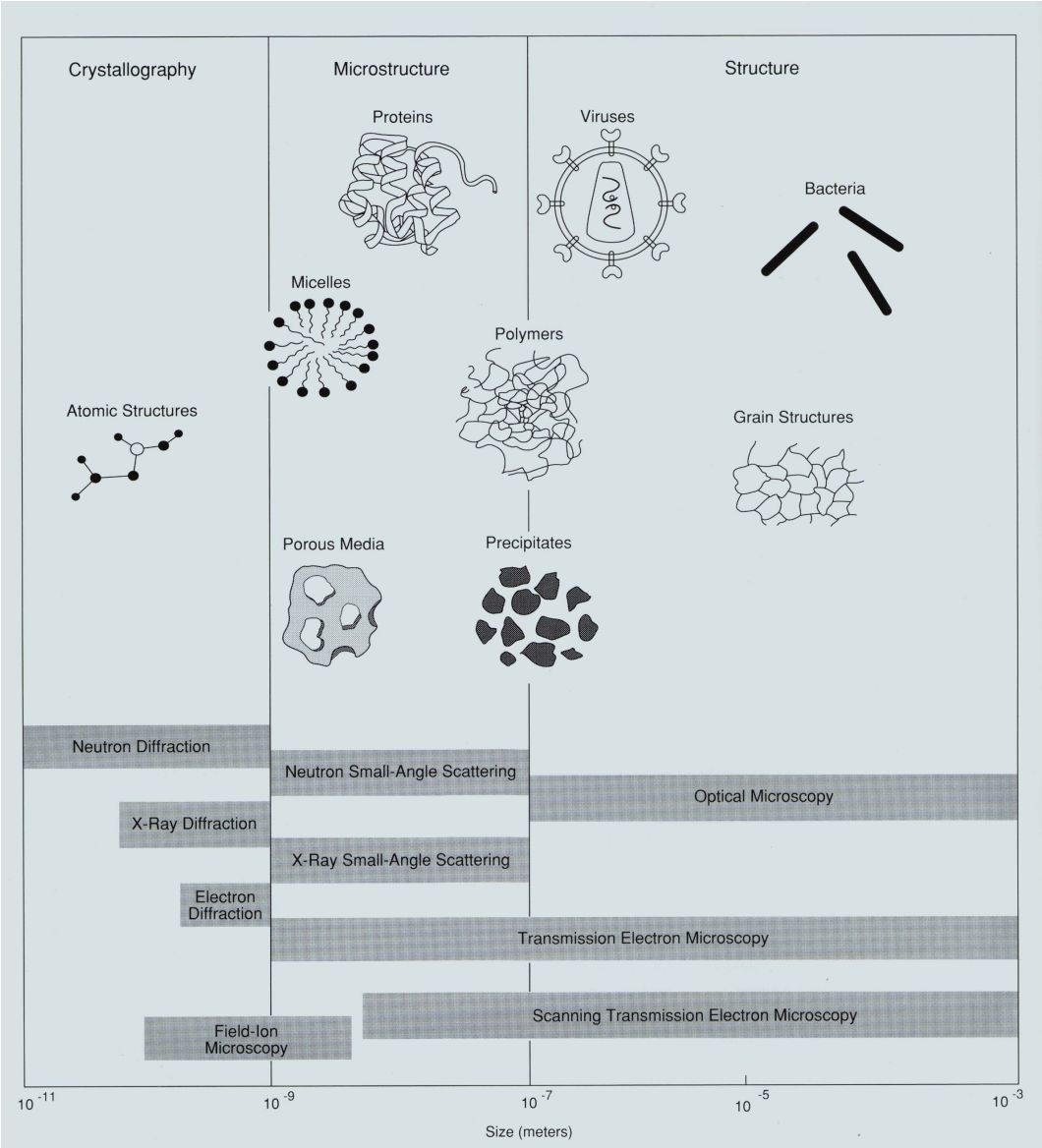
$$\lambda[\text{Å}] = \frac{12.398}{E_{\text{ph}}[\text{keV}]}$$

Neutron and X-Ray Scattering: Structure from Angstroms to Microns!



But in this size range we do not get real-space "pictures" directly

Comparison of Structural Probes



Note that scattering methods provide statistically averaged information on structure rather than real-space pictures of particular instances

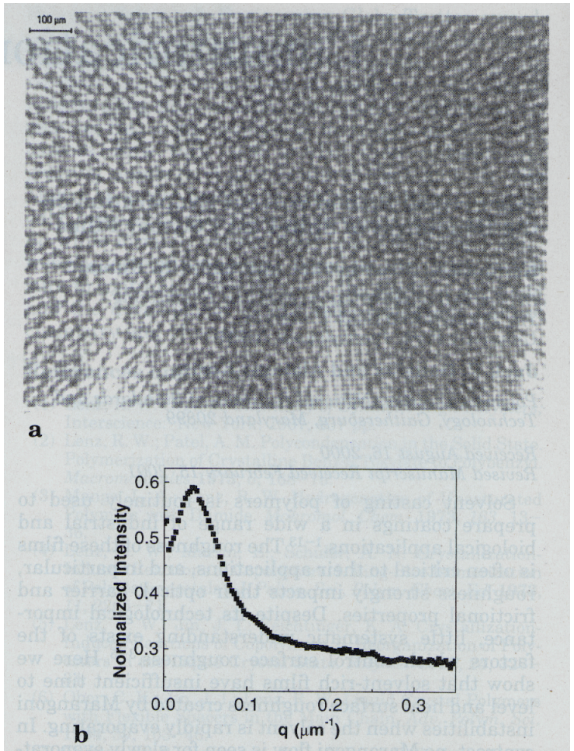
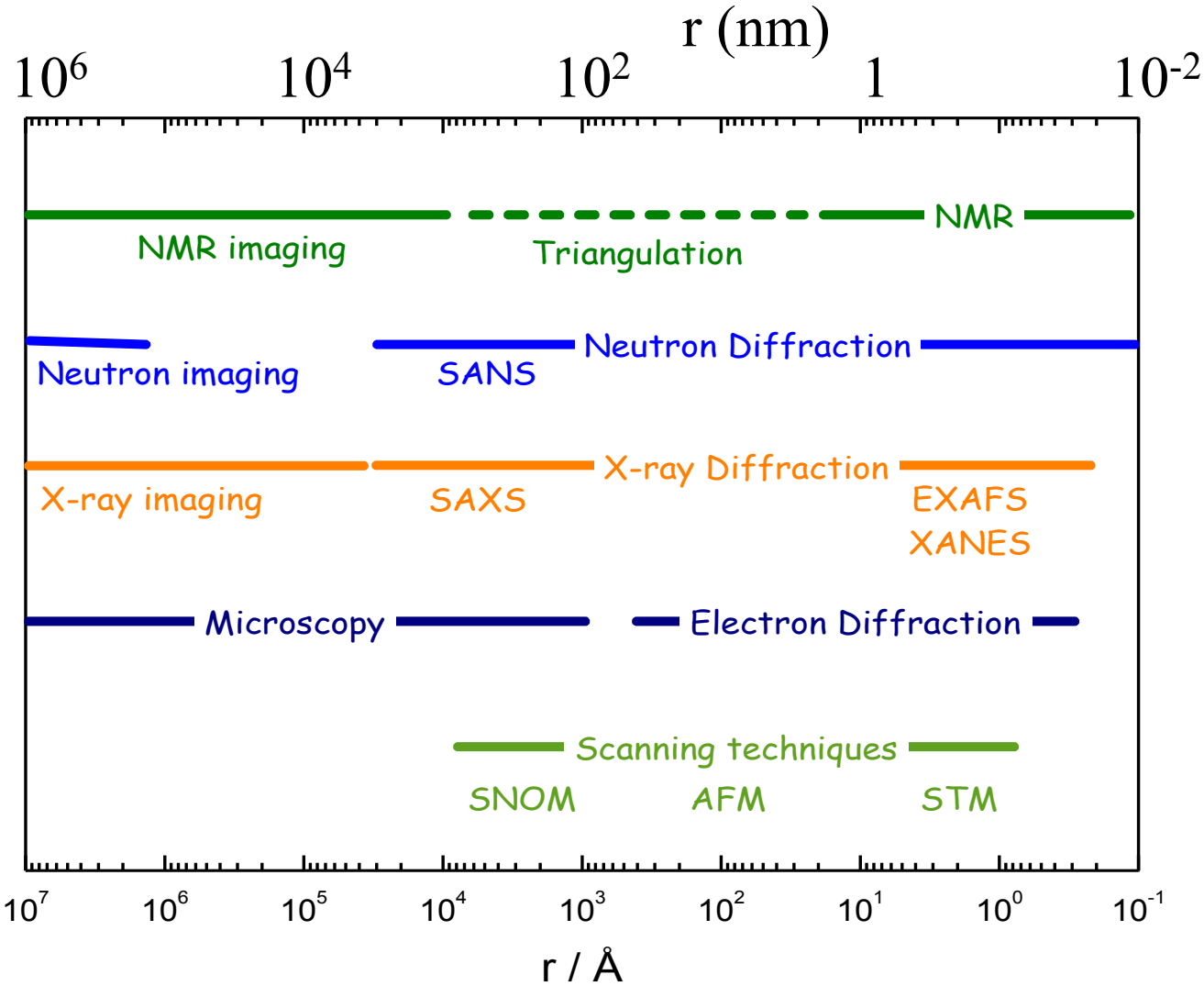


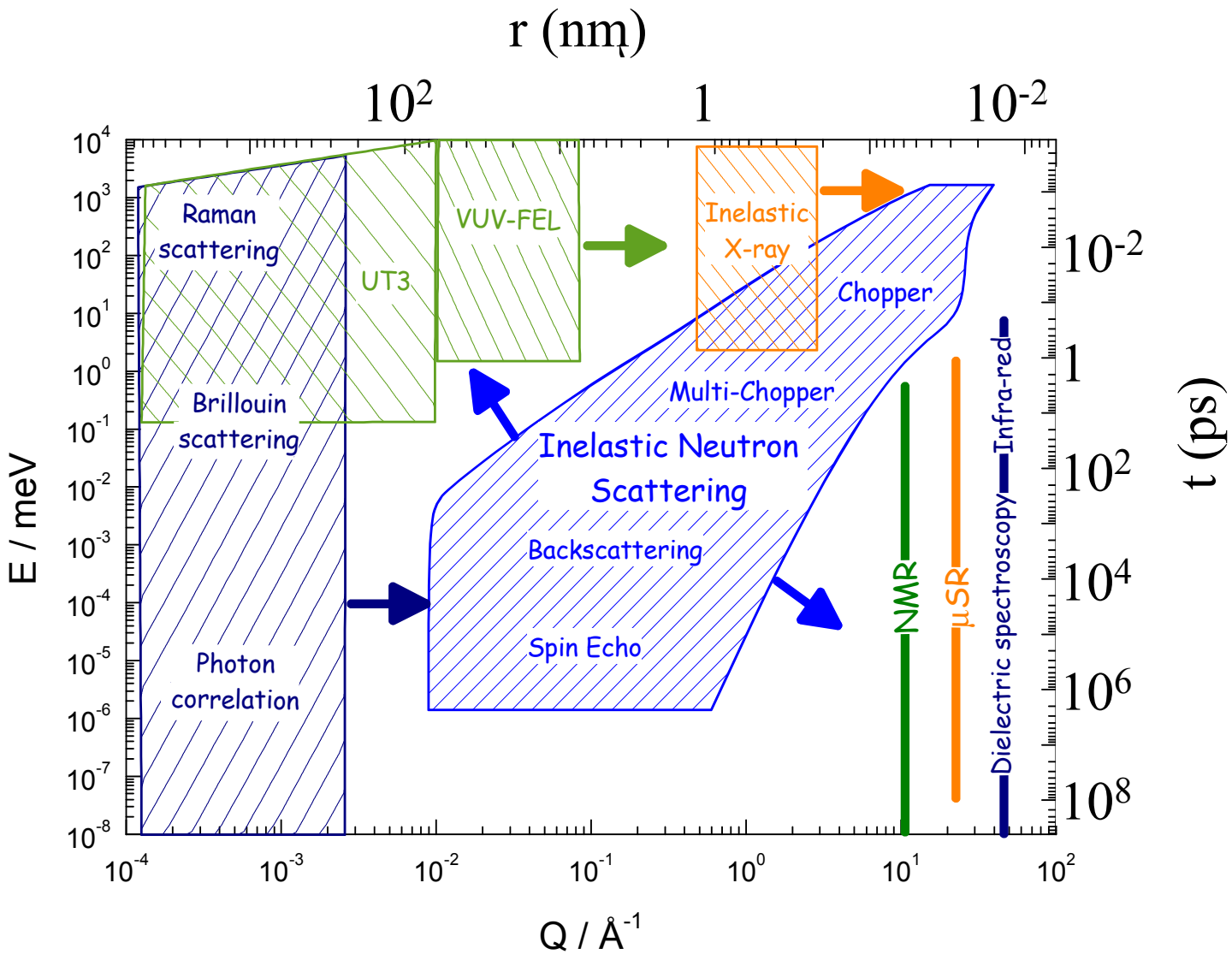
Figure 2. (a) Optical micrograph of PS-200 spin cast at 7500 rpm using THF (P_{vp} = 0.215 bar). (b) One-dimensional Fourier transform of central (isotropic) region of optical micrograph.

Macromolecules, 34, 4669 (2001)

Neutron & X-ray Scattering Complement Other Techniques in Length Scale….



……and Time Scale



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: $m_n = -1.913\ m_N$
- Nuclear magneton: $m_N = eh/4pm_p = 5.051 \times 10^{-27}$ J T^{-1}
- Velocity (v), kinetic energy (E), wavevector (k), wavelength (l), temperature (T).
- $E = m_n v^2/2 = k_B T = (hk/2p)^2/2m_n$; $k = 2\ p/l = m_n v/(h/2p)$

	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**

l (nm) = 395.6 / v (m/s)

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

X-Rays also have Wave-Like and Particle-Like Properties

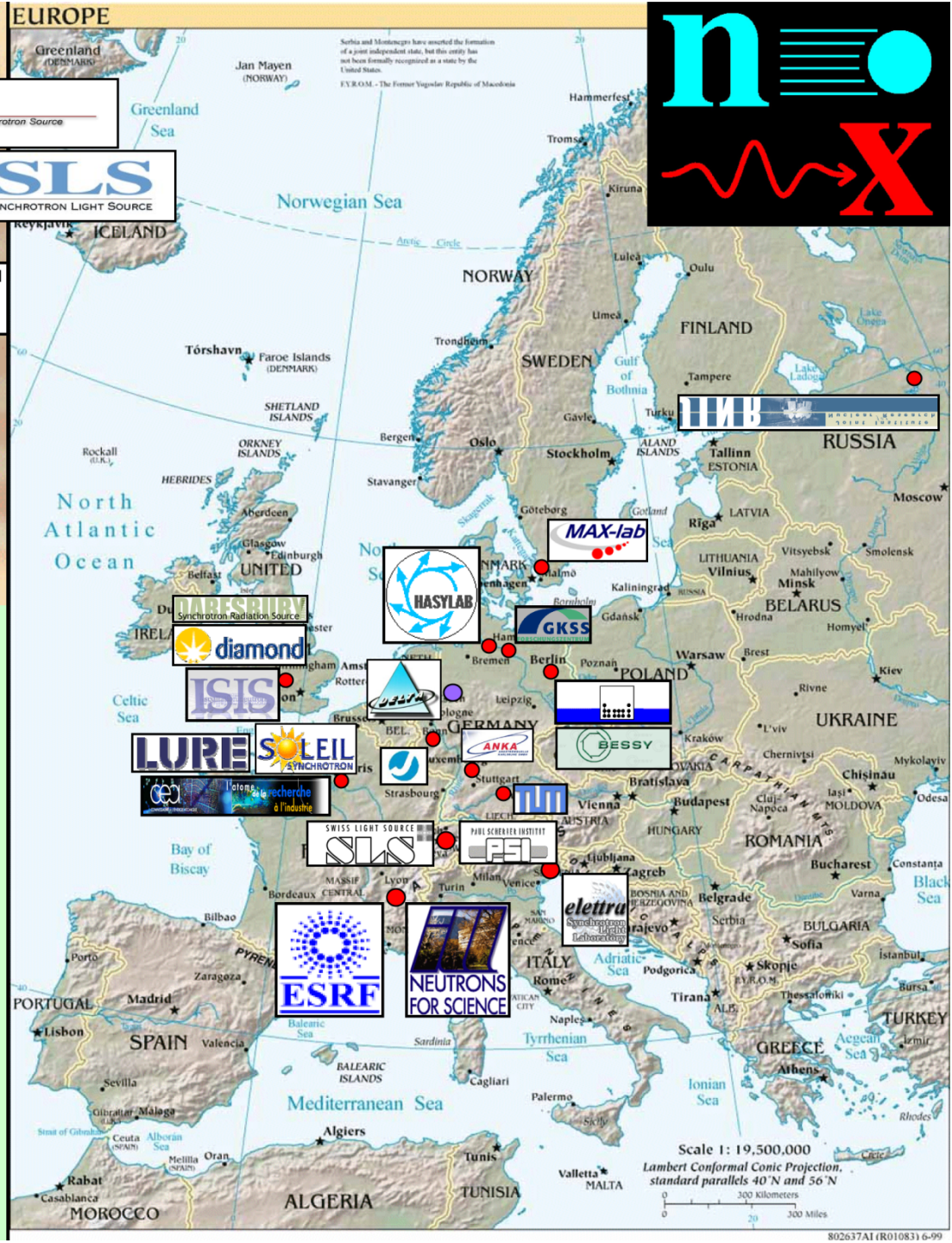
$$E = h\upsilon = hc/\lambda = (h/2\pi)c(2\pi/\lambda) = \hbar ck = pc$$

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

Typical interatomic distance in a crystal is 3.5 Å

Synchrotron- and Neutron Scattering Places



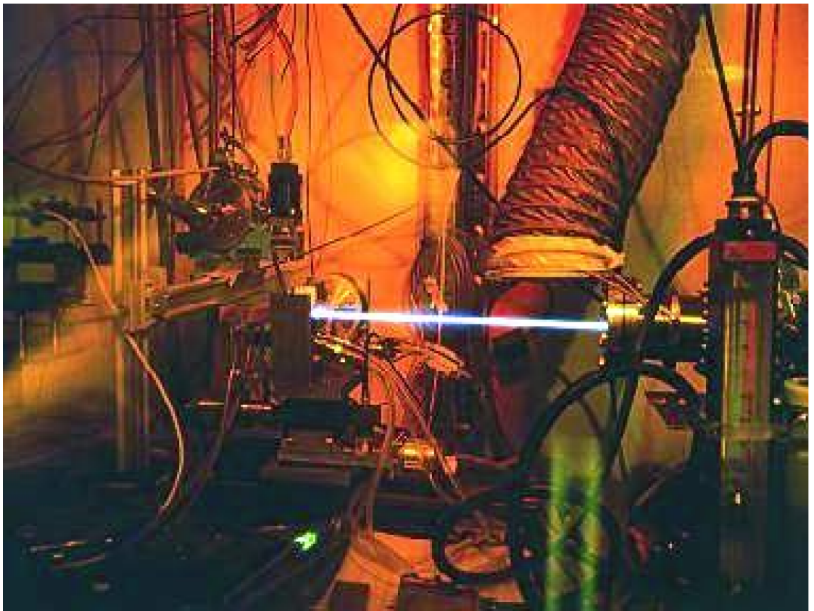
Brightness & Fluxes for Neutron & X-Ray Sources

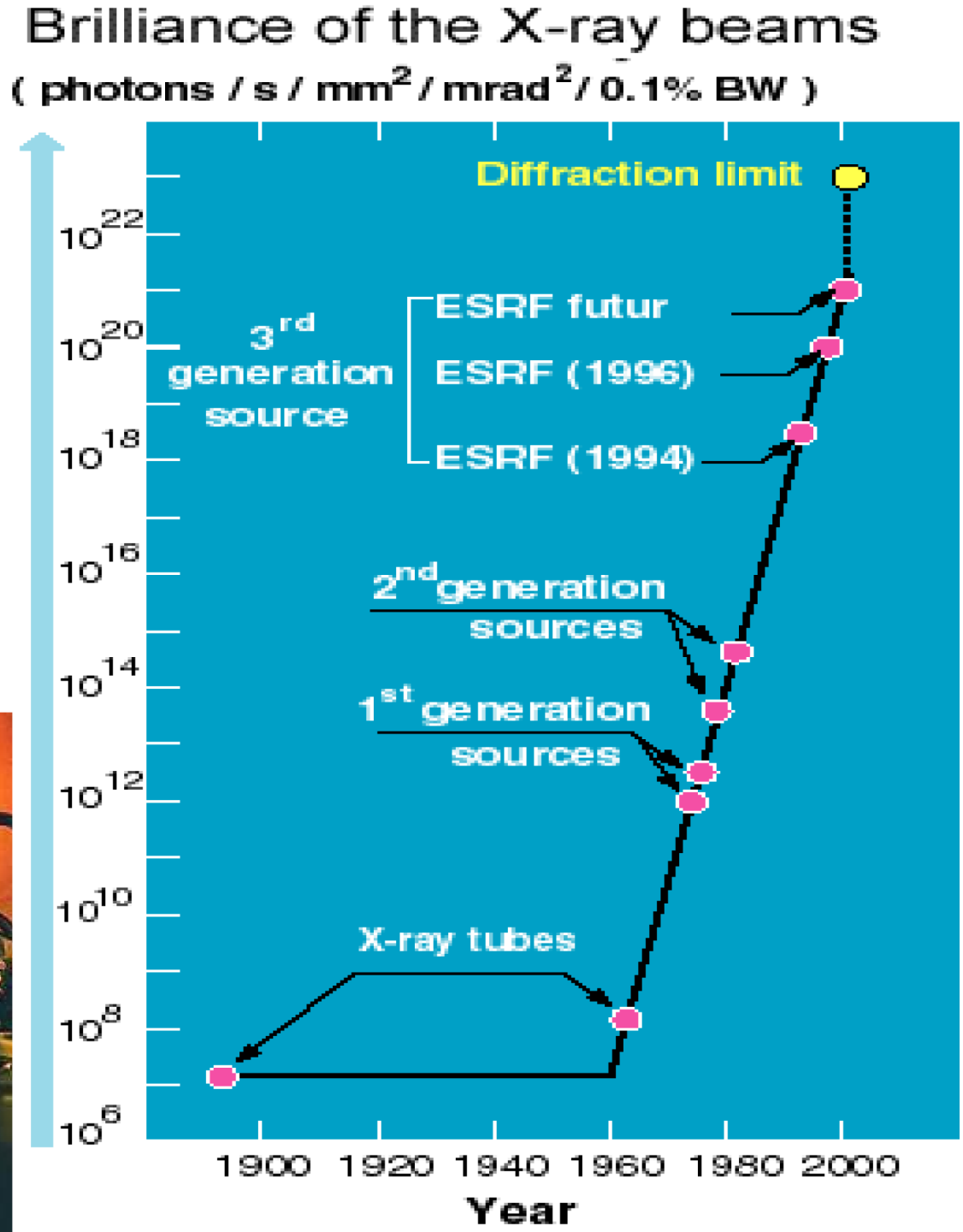
	Brightness (s^{-1} m^{-2} $ster^{-1}$)	*dE/E* (%)	*Divergence* ($mrad^2$)	*Flux* (s^{-1} m^{-2})
Neutrons	10^{15}	2	10 x 10	10^{11}
Rotating Anode	10^{16}	3	0.5 x 10	5×10^{10}
Bending Magnet	10^{24}	0.01	0.1 x 5	5×10^{17}
Wiggler	10^{26}	0.01	0.1 x 1	10^{19}
Undulator (APS)	10^{33}	0.01	0.01 x 0.1	10^{24}

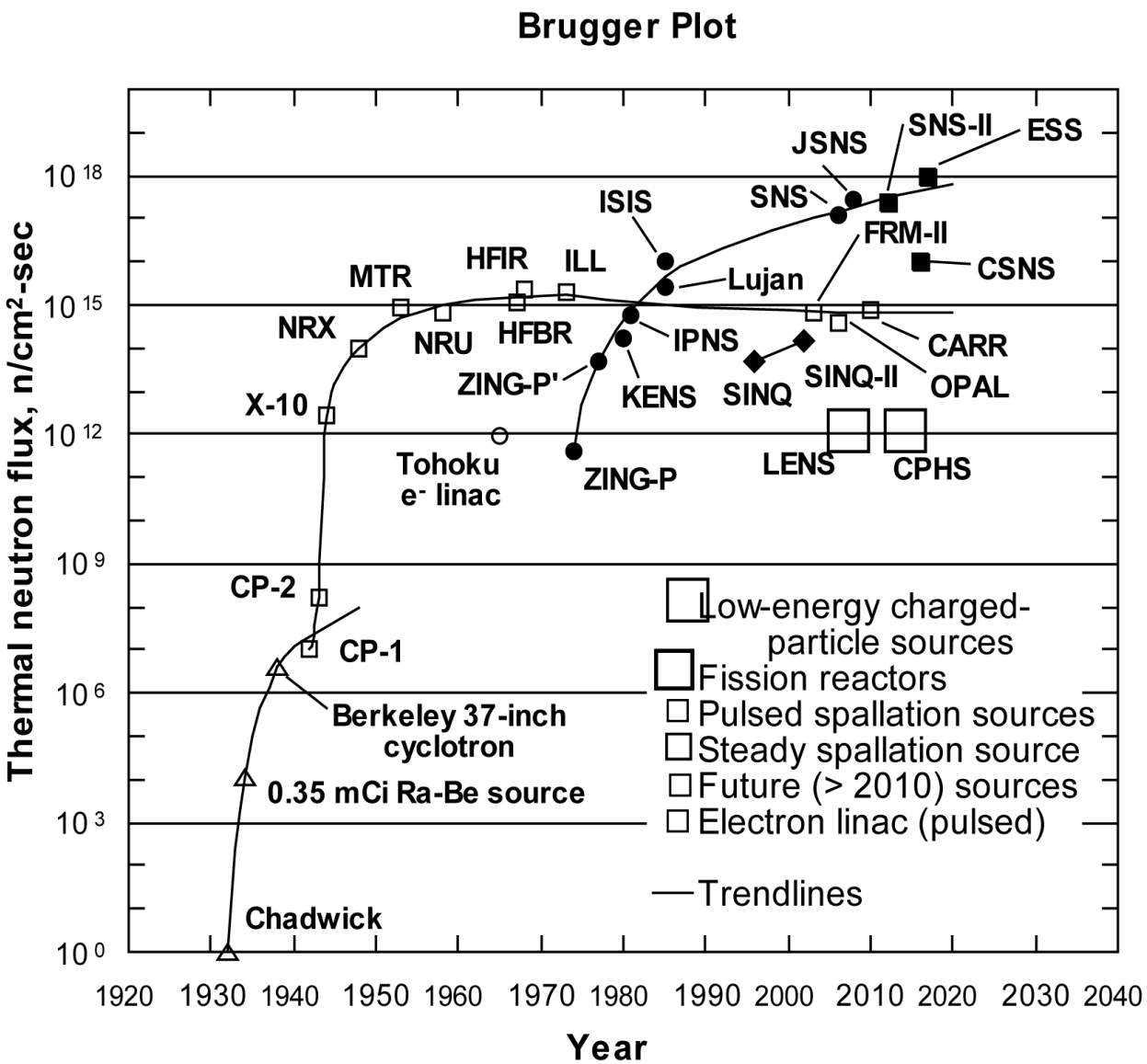
Flux = brightness * divergence; brilliance = brightness / energy bandwidth

Why Synchrotron-radiation ?

Intensity !!!







Redrawn 2009

Advantages & Disadvantages of Neutrons

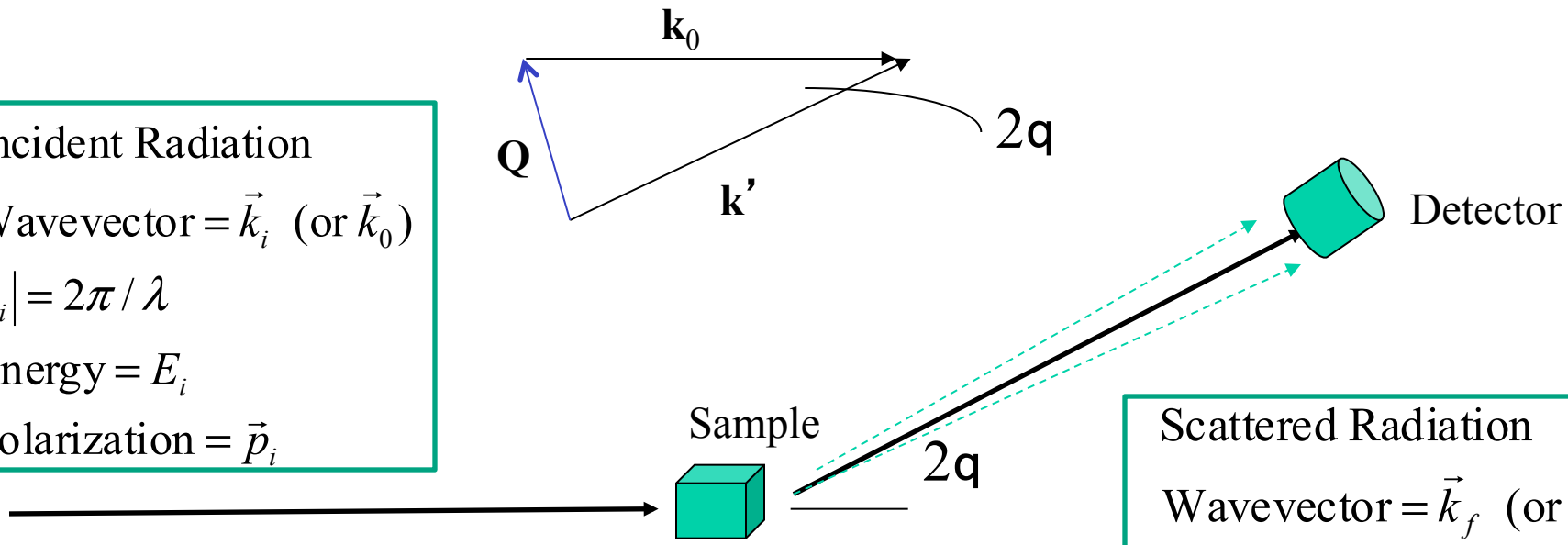
- Advantages
  - λ similar to interatomic spacings
  - Penetrates bulk matter
  - Strong contrast possible
  - Energy similar to that of elementary excitations (phonons, magnons etc)
  - Scattering strongly by magnetic fields
  - Data interpretation is direct
- Disadvantages
  - Low brilliance of neutron sources
  - Some elements absorb neutrons strongly
  - Kinematic restrictions on Q for large energy transfers
  - Difficult to study excitations at high (eV) energies
  - Provides statistical averages rather than real space pictures

Advantages and Disadvantages of X-Rays

- Advantages
  - λ similar to interatomic spacings
  - High brilliance x-ray sources (coherence, small beams etc)
  - No kinematic restrictions (Q and E not coupled)
  - No restriction on energy transfer that can be studied

- Disadvantages
  - Strong absorption of low energy photons
  - Contrast issues (low contrast for different hydrocarbons, scattering ~ Z^2)
  - Radiation damage to samples
  - Magnetic scattering not always easy to observe

A Typical Scattering Experiment



Incident Radiation

Wavevector $= \vec{k}_i$ (or $\vec{k}_0$)

$|k_i| = 2\pi / \lambda$

Energy $= E_i$

Polarization $= \vec{p}_i$

Scattered Radiation

Wavevector $= \vec{k}_f$ (or $\vec{k}'$)

Energy $= E_f$

Polarization $= \vec{p}_f$

Wavevector Transfer, $\vec{Q} = \vec{k}_f - \vec{k}_i$

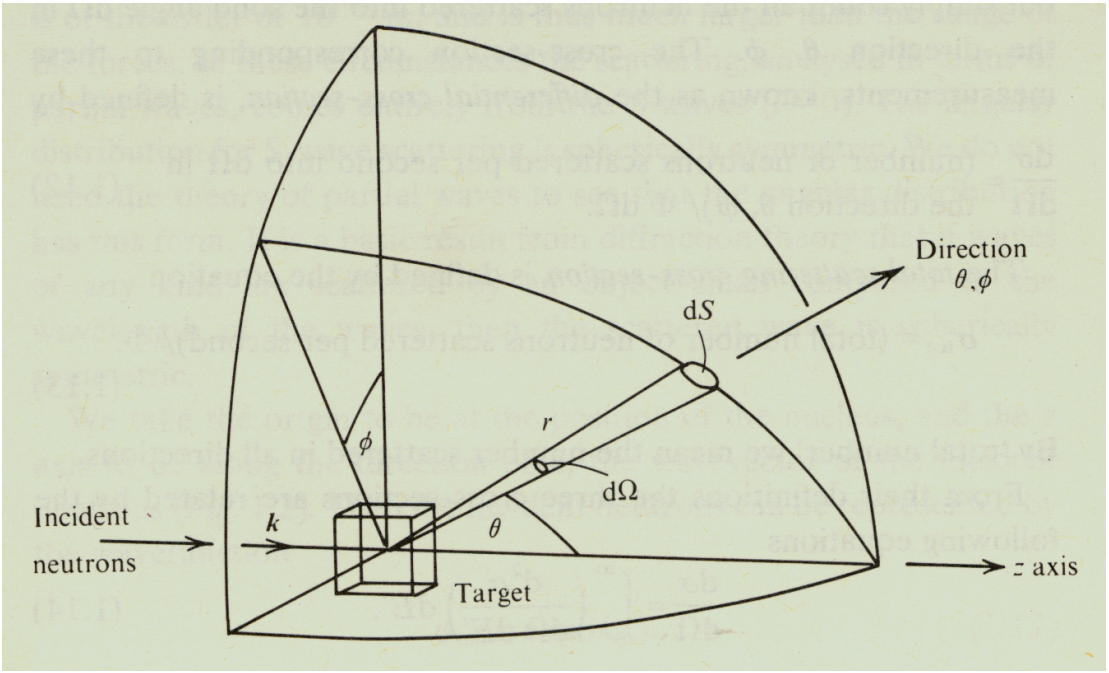
Energy Transfer, $\Delta E = h\upsilon = \hbar\omega = E_f - E_i$

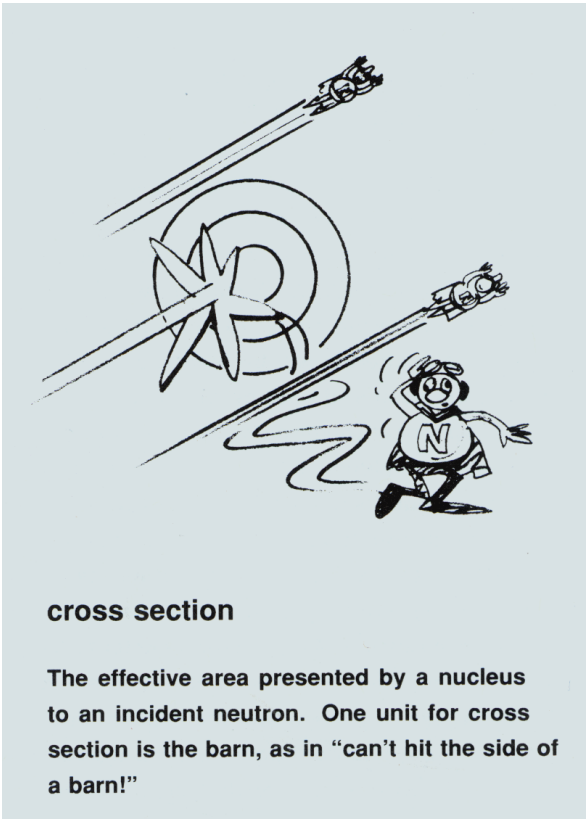
For x - rays : $\Delta E << E_f$ or E_i so $Q = 2k_i \sin\theta$

Polarization, $\vec{p}_i \rightarrow \vec{p}_f$

Notice that the finite size of the detector and sample imply uncertainty in the direction of the wavevectors

Cross Sections





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

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

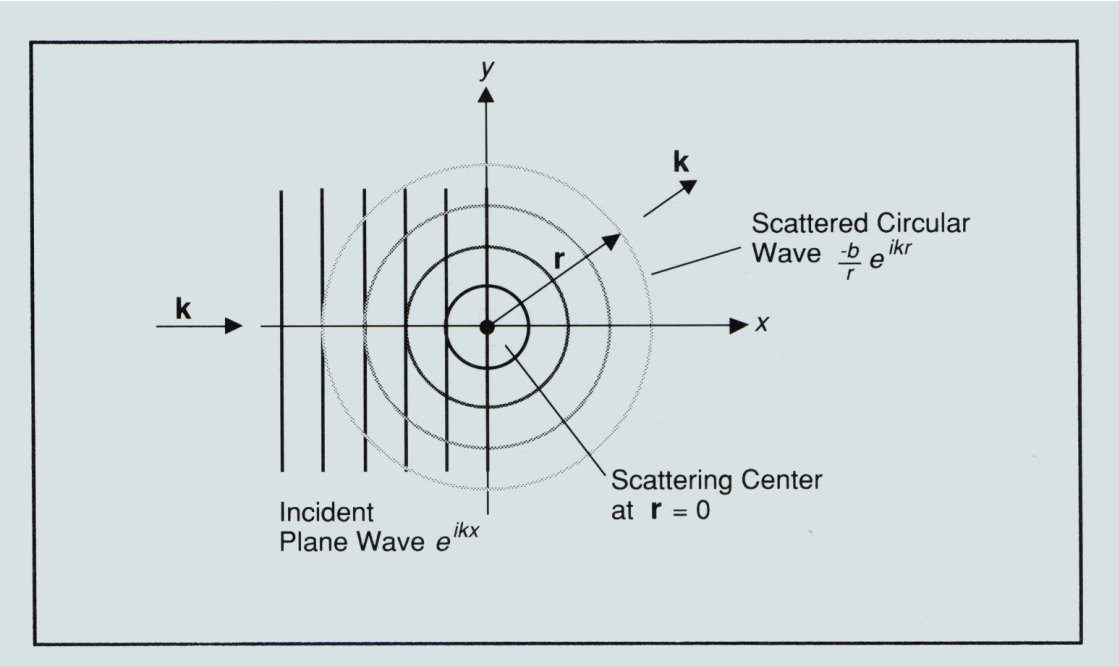
$$\frac{d\sigma}{d\Omega} = \frac{\text{number of neutrons scattered per second into d}\Omega}{\Phi \, \text{d}\Omega}$$

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

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

Attenuation = exp(-Nst)
N = # of atoms/unit volume
t = thickness

Neutron 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

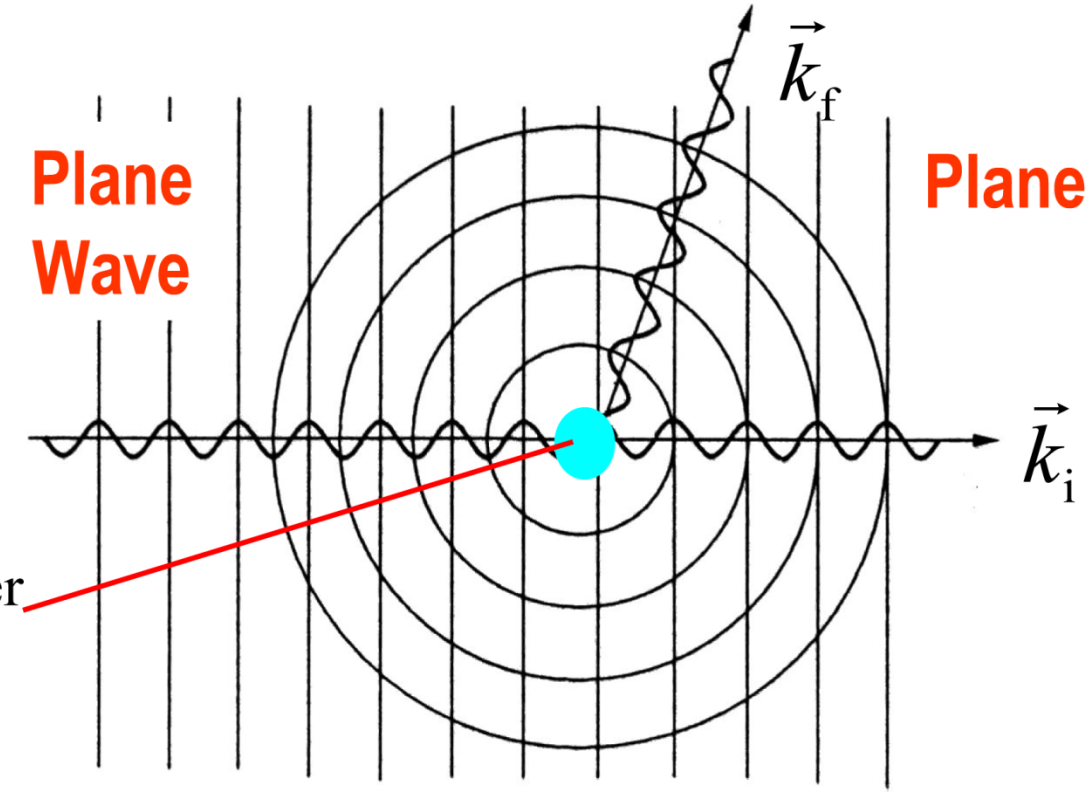
If v is the velocity of the neutron (same before and after scattering), the number of neutrons passing through an area dS per second after scattering is:

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

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

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

Intrinsic Cross Section



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 :

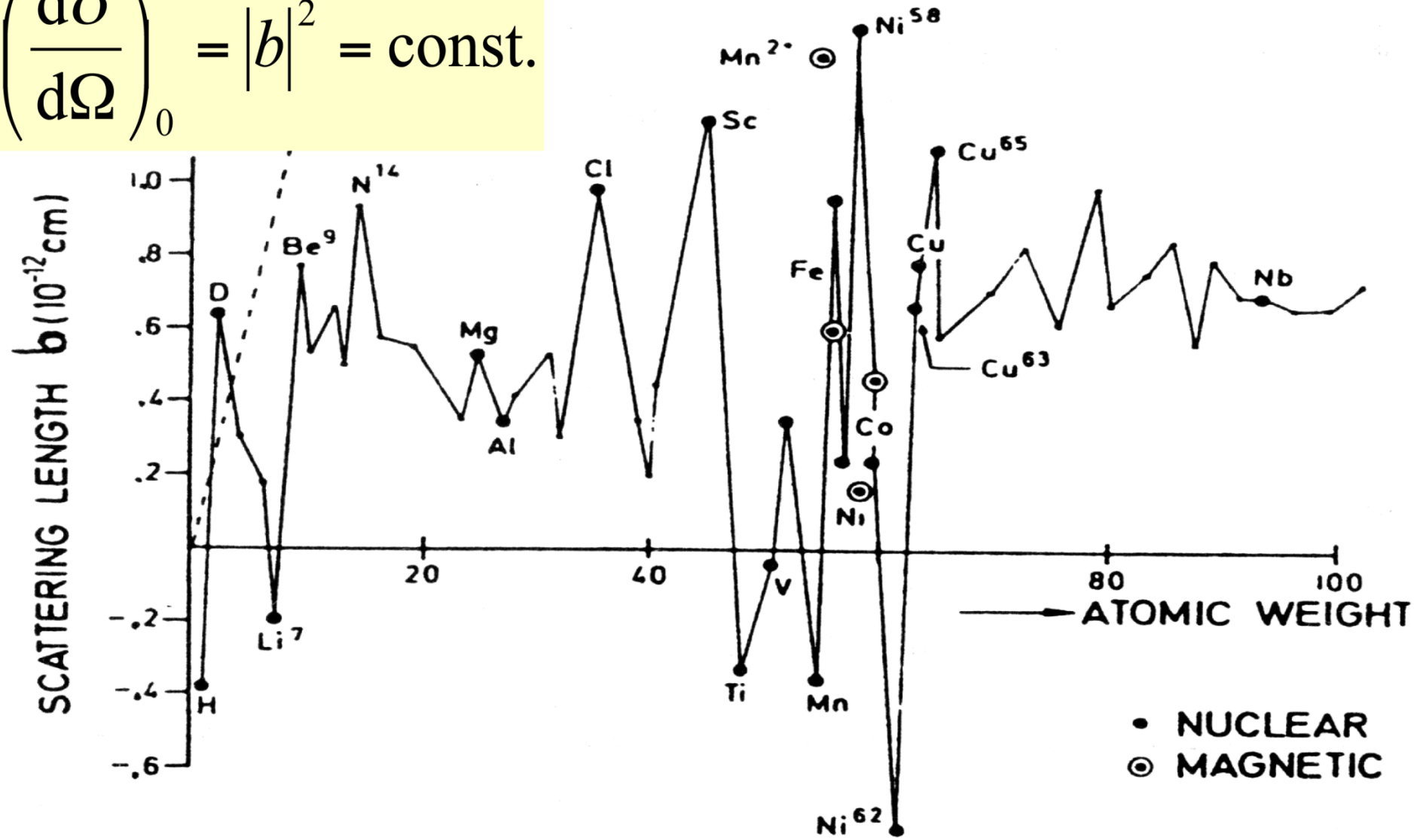
$$\sigma = \iint \left(\frac{d\sigma}{d\Omega}\right)_0 d\Omega$$

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

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

Intrinsic Cross Section: Neutrons

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



Intrinsic Cross Section: X-Rays

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

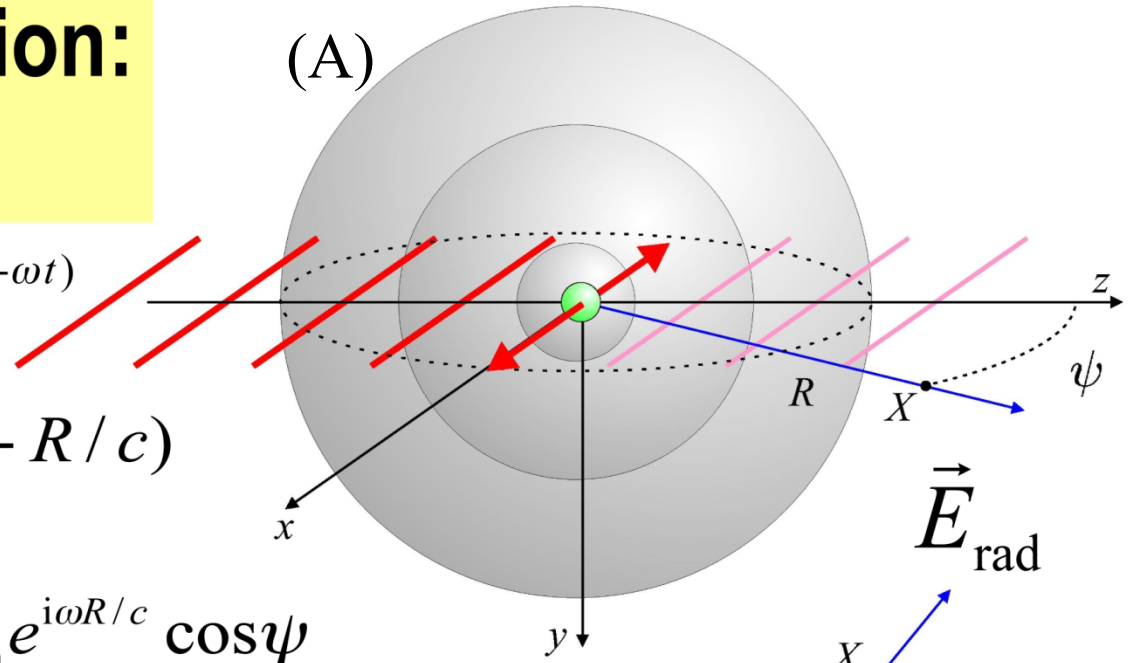
$$E_{\text{rad}}(R,t) = \frac{e}{4\pi\varepsilon_0 c^2 R}\,\ddot{x}(t-R/c)$$

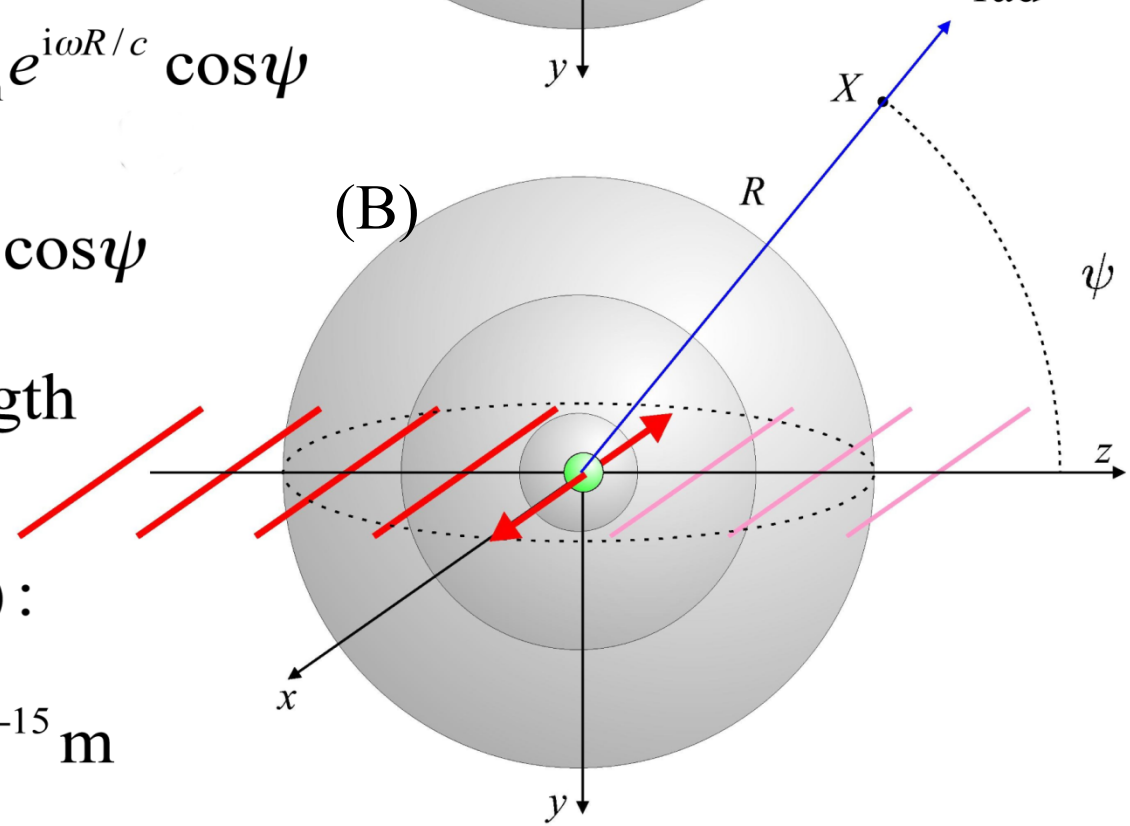
$$\ddot{x}(t-R/c) = -\frac{e}{m}\alpha(\omega)E_{\text{in}}e^{\mathrm{i}\omega R/c}\cos\psi$$

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

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

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





Single (free) Electron Scattering (cont'd)

$$\text{Measured intensity (i.e. number of x-ray photons)} \,\alpha\, \text{energy/sec}$$

$$\text{Energy per unit area of beam} \,\alpha\, E^2 \,;$$

$$\Rightarrow \frac{\text{intensity measured in detector}}{\text{incident intensity}} = \frac{I_{sc}}{I_0} = \frac{\left|E_{rad}\right|^2 R^2 \Delta\Omega}{\left|\mathrm{E}_{\mathrm{in}}\right|^2 A}$$

$$\text{differential cross section} = \frac{d\sigma}{d\Omega} = \frac{\text{number of xrays scattered per sec in } \Delta\Omega}{(\text{number of incident xrays per area}) * \Delta\Omega}$$

$$\frac{d\sigma}{d\Omega} = \frac{I_{sc}}{(I_0 / A)\Delta\Omega} = \frac{\left|E_{rad}\right|^2 R^2}{\left|\mathrm{E}_{\mathrm{in}}\right|^2} = r_0^2 \cos^2 \psi$$

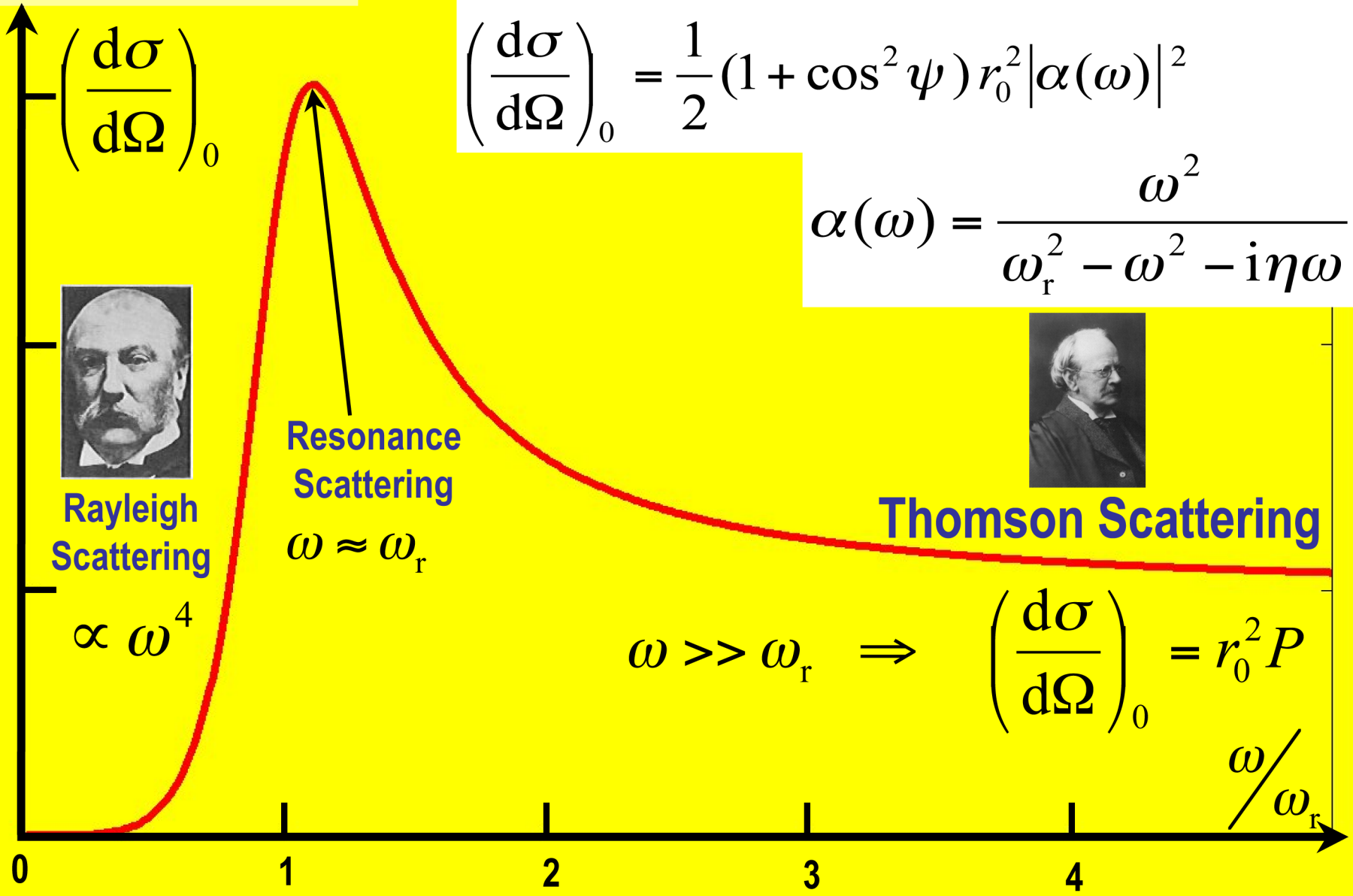
- Note that this form is for an incident beam polarized along x in part (A) of the previous viewgraph. If incident beam is polarized perpendicular to the scattering plane (Case B), $\cos^2 y \rightarrow 1$.
- For an unpolarized beam, averaging -> $(1+ \cos^2 y)/2$

Intrinsic Cross Section: X-Rays

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

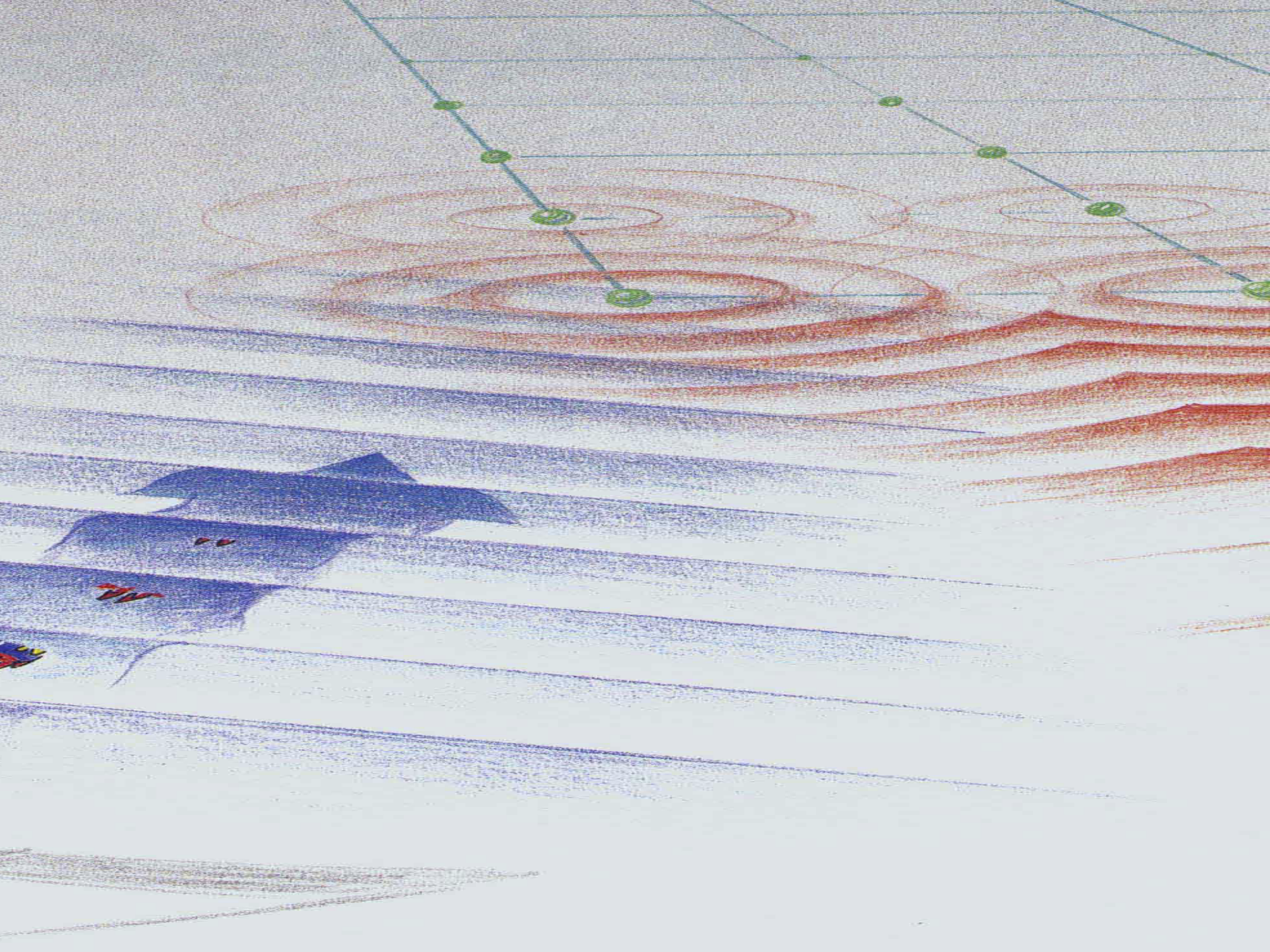
$$\left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\right)_0 = \frac{1}{2}(1+\cos^2\psi)\, r_0^2 \left|\alpha(\omega)\right|^2$$

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

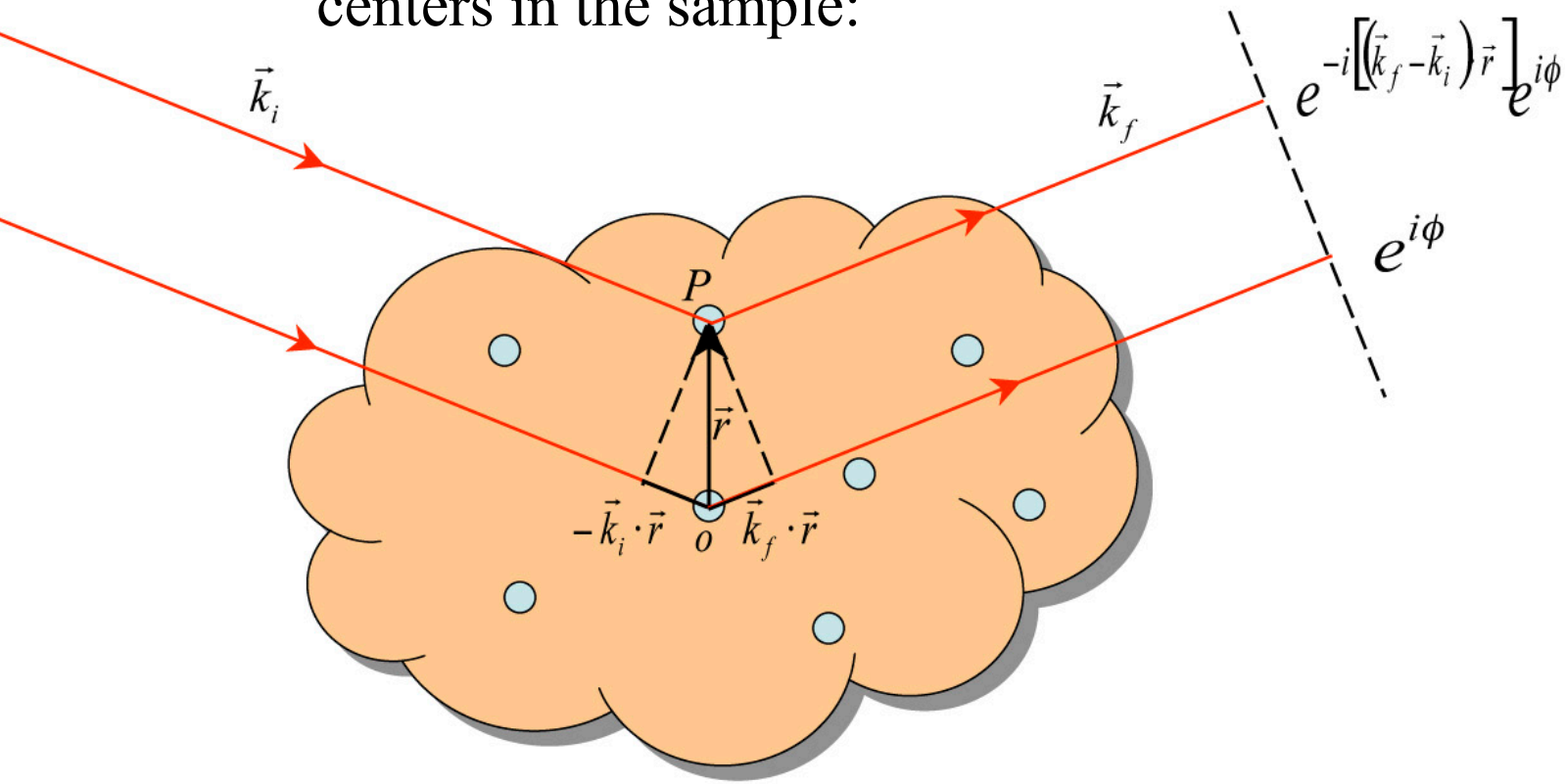


Magnetic Scattering of X-Rays

- If we include the magnetic field of the x-ray wave and the spin of the electron we get:
  - Terms in cross section that are sensitive to spin and orbital magnetic moments of the electrons
  - Very weak: scattering amplitude for magnetic x-ray scattering divided by the amplitude for charge scattering = (hn/mc^2) ~ 0.01 for 10 keV x-rays
  - => Bragg scattering intensity down by ~ 10^4
  - Magnetic scattering can be much enhanced at resonances i.e. when the x-ray energy is close to atomic absorption edges.



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



Adding up Neutrons Scattered by Many Nuclei

At a scattering center located at $\vec{R}_i$ the incident wave is $e^{i\vec{k}_0.\vec{R}_i}$

so the scattered wave at $\vec{r}$ is $\psi_{scat} = \sum e^{i\vec{k}_0.\vec{R}_i}\left[\frac{-b_i}{|\vec{r}-\vec{R}_i|}e^{i\vec{k}'.(\vec{r}-\vec{R}_i)}\right]$

$$\therefore \frac{d\sigma}{d\Omega} = \frac{v dS|\psi_{scat}|^2}{v d\Omega} = \frac{dS}{d\Omega}\left|b_i e^{i\vec{k}'.\vec{r}}\sum\frac{1}{|\vec{r}-\vec{R}_i|}e^{i(\vec{k}_0-\vec{k}').\vec{R}_i}\right|^2 \quad \text{(using defn. from earlier VG)}$$

If we measure far enough away so that $r >> R_i$ we can use $d\Omega = dS/r^2$ to get

$$\boxed{\frac{d\sigma}{d\Omega} = \sum_{i,j} b_i b_j e^{i(\vec{k}_0-\vec{k}').(\vec{R}_i-\vec{R}_j)} = \sum_{i,j} b_i b_j e^{-i\vec{Q}.(\vec{R}_i-\vec{R}_j)}}$$

where the wavevector transfer Q is defined by $\vec{Q} = \vec{k}' - \vec{k}$

$$\boxed{\text{For x-rays}: \frac{d\sigma}{d\Omega} = r_0^2 \sum_{i,j} e^{i(\vec{k}_0-\vec{k}').(\vec{R}_i-\vec{R}_j)}\left\{\frac{1-\cos^2 2\theta}{2}\right\}}$$

where $\vec{R}_i$ are electron positions

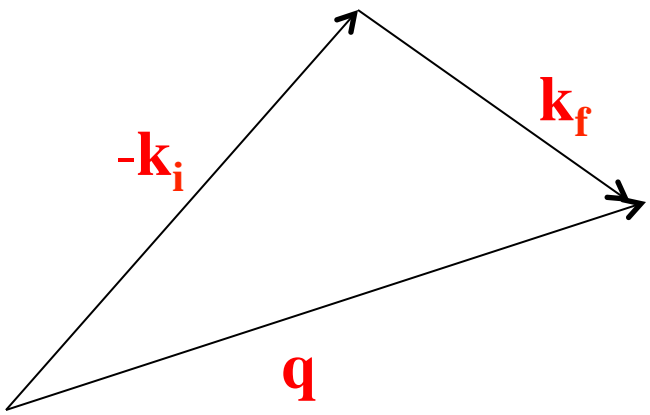
Note: we have assumed the scattering centers don't move

The Scattering Triangle

- The wavevector transfer, variously denoted Q or q, is defined by:

$$\vec{Q} = \vec{k}_i - \vec{k}_f$$

- The scattering triangle defines the vector realtionship between these quantities



Coherent and Incoherent Scattering of Neutrons

The scattering length, b_i , depends on the nuclear isotope, spin relative to the neutron & nuclear eigenstate. For a single nucleus:

$$b_i = \langle b \rangle + \delta b_i \quad \text{where } \delta b_i \text{ averages to zero}$$

$$b_i b_j = \langle b \rangle^2 + \langle b \rangle (\delta b_i + \delta b_j) + \delta b_i \delta b_j$$

$$\text{but } \langle \delta b \rangle = 0 \text{ and } \langle \delta b_i \delta b_j \rangle \text{ vanishes unless } i = j$$

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

$$\therefore \frac{d\sigma}{d\Omega} = \langle b \rangle^2 \sum_{i,j} e^{-i\vec{Q}.(\vec{R}_i - \vec{R}_j)} + (\langle b^2 \rangle - \langle b \rangle^2) N$$

Coherent Scattering
(scattering depends on the direction & magnitude of **Q**)

Incoherent Scattering
(scattering is uniform in all directions)

Note: N = number of atoms in scattering system

Nuclear Spin Incoherent Scattering

Consider a single isotope with spin I. The spin of the nucleus - neutron system can be $(I+1/2)$ or $(I-1/2)$.

The number of states with spin $(I+1/2)$ is $2(I+1/2)+1=2I+2$

The number of states with spin $(I-1/2)$ is $2(I-1/2)+1=2I$

If the neutrons and the nuclear spins are unpolarized, each spin state has the same *a priori* probability.

The frequency of occurence of b^+ state is $f^+ = (2\mathrm{I}+2)/(4\mathrm{I}+2)$

The frequency of occurence of b^- state is $f^- = (2\mathrm{I})/(4\mathrm{I}+2)$

Thus $\langle b \rangle = \dfrac{1}{2I+1}\left[(I+1)b^+ + Ib^-\right]$ and $\langle \mathrm{b}^2 \rangle = \dfrac{1}{2I+1}\left[(I+1)(b^+)^2 + I(b^-)^2\right]$

Values of s_{coh} and s_{inc}

Nuclide	s_{coh}	s_{inc}	Nuclide	s_{coh}	s_{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/

Coherent Elastic Scattering measures the Structure Factor S(Q) i.e. correlations of atomic positions

$$\frac{d\sigma}{d\Omega} = \langle b \rangle^2 N.S(\vec{Q})$$ for an assembly of similar atoms where $$S(\vec{Q}) = \frac{1}{N}\left\langle \sum_{i,j} e^{-i\vec{Q}.(\vec{R}_i - \vec{R}_j)} \right\rangle_{\text{ensemble}}$$

Now $\sum_i e^{-i\vec{Q}.\vec{R}_i} = \int d\vec{r}.e^{-i\vec{Q}.\vec{r}} \sum_i \delta(\vec{r} - \vec{R}_i) = \int d\vec{r}.e^{-i\vec{Q}.\vec{r}} \rho_N(\vec{r})$ where ρ_N is the nuclear number density

so $$\boxed{S(\vec{Q}) = \frac{1}{N}\left\langle \left| \int d\vec{r}.e^{-i\vec{Q}.\vec{r}} \rho_N(\vec{r}) \right|^2 \right\rangle}$$

or $$S(\vec{Q}) = \frac{1}{N}\int d\vec{r}' \int d\vec{r}.e^{-i\vec{Q}.(\vec{r}-\vec{r}')} \langle \rho_N(\vec{r})\rho_N(\vec{r}') \rangle = \frac{1}{N}\int d\vec{R} \int d\vec{r} e^{-i\vec{Q}.\vec{R}} \langle \rho_N(\vec{r})\rho_N(\vec{r} - \vec{R}) \rangle$$

ie $$\boxed{S(\vec{Q}) = 1 + \int d\vec{R}.\{g(\vec{R}) - \bar{\rho}\}.e^{-i\vec{Q}.\vec{R}}}$$

where $\boxed{g(\vec{R}) = \sum_{i \neq 0} \langle \delta(\vec{R} - \vec{R}_i + \vec{R}_0) \rangle}$ is a function of $\vec{R}$ only.

g(R) is known as the **static pair correlation function**. It gives the probability that there is an atom, i, at distance R from the origin of a coordinate system, given that there is also a (different) atom at the origin of the coordinate system at the same instant in time.

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

- Note that S(Q) and g(r)/r 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.)

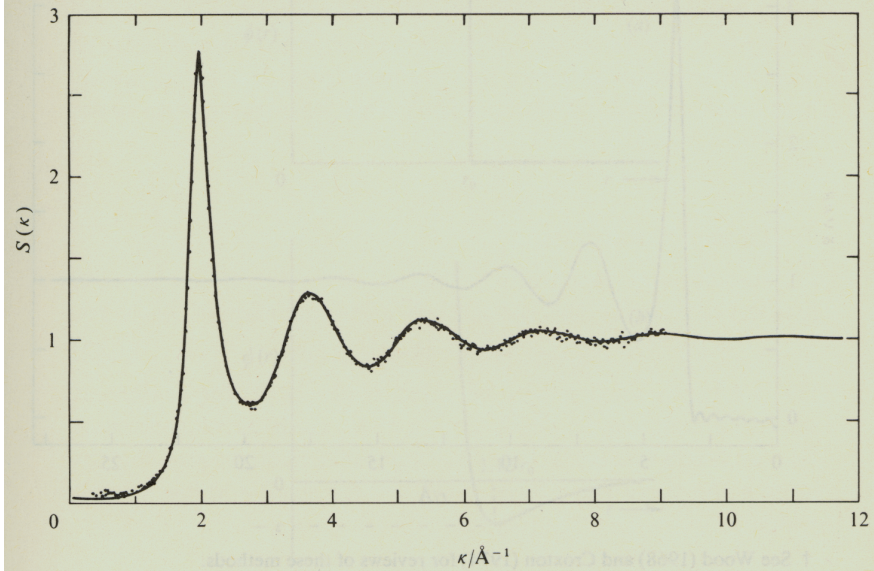
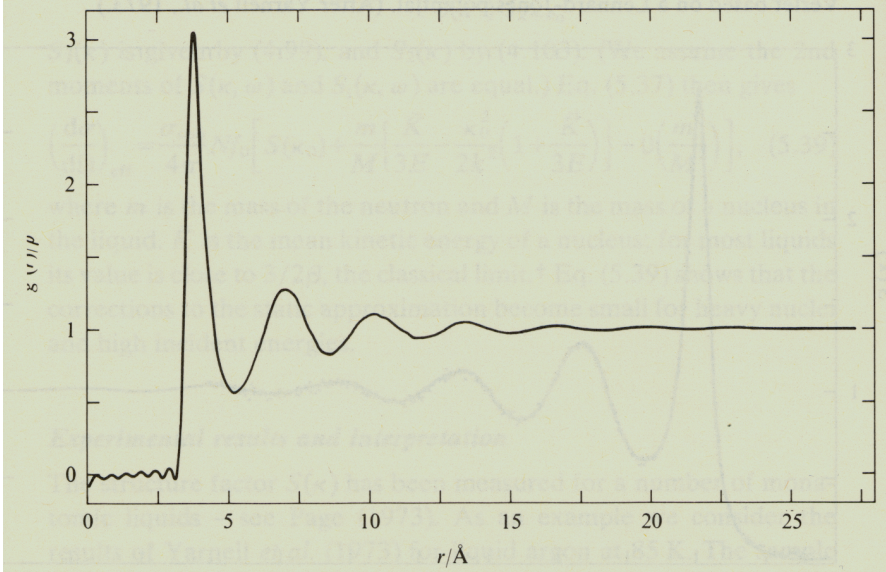


Fig. 5.2 The pair-distribution function $g(r)$ obtained from the experimental results in Fig. 5.1. The mean number density is $\rho = 2.13 \times 10^{28}$ atoms m^{-3}. (After Yarnell *et al.*, 1973.)



X-ray Scattering from an Atom

- We have to add up the Thomson scattering for all electrons in the atom.

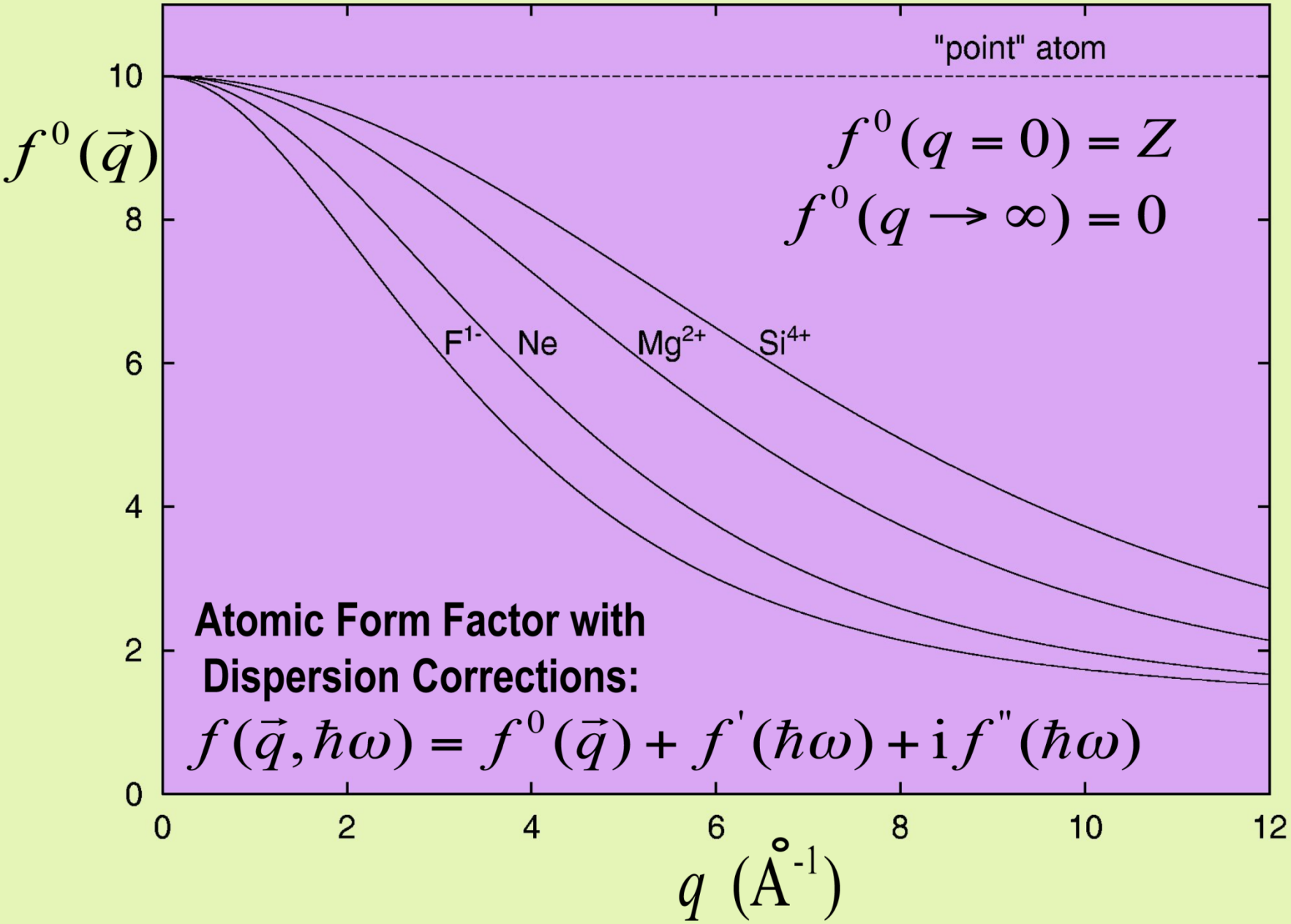
$$-r_0 f^0(\vec{Q}) = -r_0 \int \rho(\vec{r}) e^{i\vec{Q}.\vec{r}} d\vec{r} \qquad f^0(Q \to 0) = Z; \quad f^0(Q \to \infty) = 0$$

- f^0 is called the atomic form factor for a free electron
- We expect electrons that are more tightly bound to be able to respond less to the driving field. This will alter the real part of the scattering length. In addition, we also expect a forced electron to have a phase lag (c.f. forced oscillator)

$$f(\vec{Q},\omega) = f^0(\vec{Q}) + f'(\omega) + if''(\omega)$$

- f' and f'' are known as dispersion corrections
- Notice that we use *b* for neutrons and $r_0 f(Q,w)$ for x-rays in the scattering cross section

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



Atomic Form Factor with Dispersion Corrections:

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

The Fermi Pseudo-Potential for Neutrons

$$\frac{d\sigma}{d\Omega} = \frac{1}{\Phi}\frac{1}{d\Omega}\sum_{\vec{k}'\text{ in d}\Omega} W_{\vec{k}\to\vec{k}'}$$ where the sum is over probabilities of all transitions

By Fermi's Golden Rule : $$\sum_{\vec{k}'\text{ in d}\Omega} W_{\vec{k}\to\vec{k}'} = \frac{2\pi}{\hbar}\rho_{\vec{k}'}\left|\left\langle \vec{k}'\middle|V\middle|\vec{k}\right\rangle\right|^2 = \frac{2\pi}{\hbar}\rho_{\vec{k}'}\frac{1}{Y^2}\left|\int_Y V(\vec{r})e^{i(\vec{k}-\vec{k}').\vec{r}}d\vec{r}\right|^2$$

where $\rho_{\vec{k}'}$ is # of momentum states in dΩ, per unit energy, for neutrons in state $\vec{k}'$

Using standard "box normalization", the volume per k state is $(2\pi)^3/Y$ where Y = box volume

Final neutron energy is $E' = \frac{\hbar^2 k'^2}{2m} \Rightarrow dE' = \frac{\hbar^2 k' dk'}{m}$ so

$\rho_{k'} dE' =$ number of wavevector states in volume $k'^2 dk' d\Omega = \frac{Y}{(2\pi)^3} k'^2 dk' d\Omega$

i.e. $$\rho_{\vec{k}'} = \frac{\text{number of wavevector states}}{\text{dE}'} = \frac{Y}{(2\pi)^3} k' \frac{m}{\hbar^2} d\Omega$$

Further, $\Phi =$ incident flux = density x velocity $= \frac{1}{Y}\frac{\hbar}{m}k$

Fermi pseudopotential

So, $$\frac{d\sigma}{d\Omega} = \frac{Y}{k}\frac{m}{\hbar}\frac{1}{d\Omega}\frac{2\pi}{\hbar}\frac{Y}{(2\pi)^3}k'\frac{m}{\hbar^2}d\Omega\left|\left\langle \vec{k}'\middle|V\middle|\vec{k}\right\rangle\right|^2 = \left(\frac{m}{2\pi\hbar^2}\right)^2\left|\int V(\vec{r})e^{i(\vec{k}-\vec{k}').\vec{r}}d\vec{r}\right|^2$$ so $$\boxed{V(\vec{r}) = \frac{2\pi\hbar^2}{m} b\delta(\vec{r})}$$

Use V(r) to Calculate the Refractive Index for Neutrons

The nucleus - neutron potential is given by : $V(\vec{r}) = \frac{2\pi\hbar^2}{m} b\delta(\vec{r})$ for a single nucleus.

So the average potential inside the medium is : $\bar{V} = \frac{2\pi\hbar^2}{m}\rho$ where $\rho = \frac{1}{volume}\sum_i b_i$

ρ is called the nuclear Scattering Length Density (SLD) - used for SANS & reflectometry

The kinetic (and total) energy of neutron in vaccuum is $E = \frac{\hbar^2 k_0^2}{2m}$

Inside the medium the total energy is $\frac{\hbar^2 k^2}{2m} + \bar{V}$

Conservation of energy gives $\frac{\hbar^2 k_0^2}{2m} = \frac{\hbar^2 k^2}{2m} + \bar{V} = \frac{\hbar^2 k^2}{2m} + \frac{2\pi\hbar^2}{m}\rho$ or $k_0^2 - k^2 = 4\pi\rho$

Since $k/k_0 = n =$ refractive index (by definition), and ρ is very small ($\sim 10^{-6}$ A^{-2}) we get :

$$n = 1 - \lambda^2 \rho / 2\pi$$

Since generally n < 1, neutrons are externally reflected from most materials.

Why do we Care about the Refractive Index?

- When the wavevector transfer **Q** is small, the phase factors in the cross section do not vary much from nucleus to nucleus & we can use a continuum approximation

- We can use all of the apparatus of optics to calculate effects such as:
  - External reflection from single surfaces (for example from guide surfaces)
  - External reflection from multilayer stacks (including supermirrors)
  - Focusing by (normally) concave lenses or Fresnel lenses
  - The phase change of the neutron wave through a material for applications such as interferometry or phase radiography
  - Fresnel edge enhancement in radiography

Refractive Index for x-rays

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

where $\delta = \dfrac{2\pi\rho_a f^0(0) r_0}{k^2}$ and $\beta = \dfrac{\mu}{2k}$

ρ_a is the atomic number density; k is the x - ray wavevector

μ is the absorption coefficient (i.e. intensity decreases as $e^{-\mu z}$)

The wave outside the medium is e^{ikz}; inside the medium it is e^{inkz}

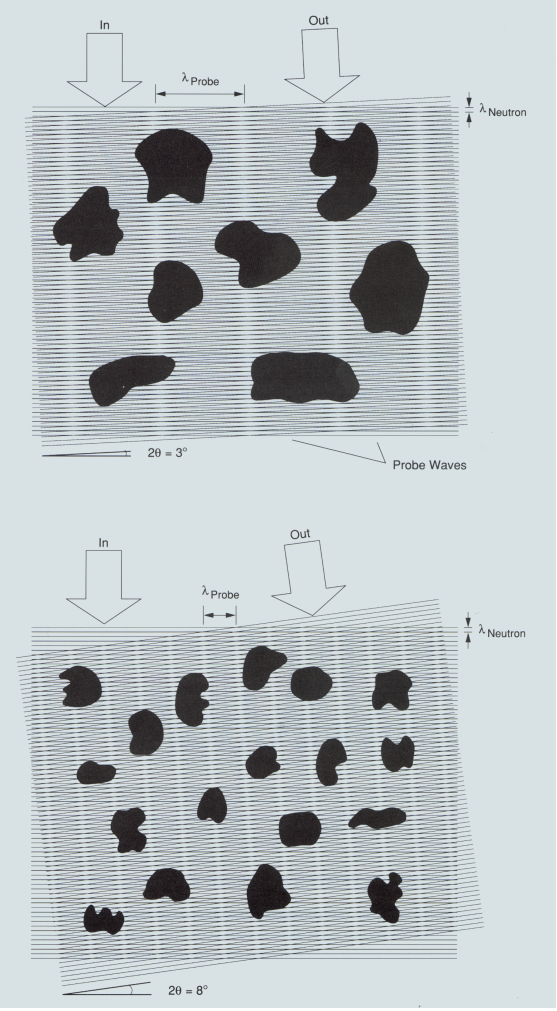
Note the we can also write :

$$n \equiv 1 - \frac{2\pi\rho_a r_0}{k^2}\left\{f^0(0) + f' + if''\right\} \quad \text{with} \quad \beta = -\left[\frac{2\pi\rho_a r_0}{k^2}\right] f''$$

so $f'' = -\left[\dfrac{k^2}{2\pi\rho_a r_0}\right]\beta = -\left[\dfrac{k^2}{2\pi\rho_a r_0}\right]\dfrac{\mu}{2k} = -\left(\dfrac{k}{4\pi r_0}\right)\sigma_a$ because $\mu = \rho_a \sigma_a$

Diffraction

- Neutron (or x-ray) diffraction is used to measure the differential cross section, ds/dW in the static approximation i.e. integrated over k' – measures G(r,0)
  - Crystalline solids (elastic scattering – G(r,∞))
    - Unit cell size; crystal symmetry; atomic arrangement and thermal motions (ellipsoids)
  - Liquids and amorphous materials
  - Large scale structures



- Depending on the scattering angle, structure on different length scales, d, is measured:

$$2\pi / Q = d = \lambda / 2\sin(\theta)$$

- For crystalline solids & liquids, use wide angle diffraction. For large structures, e.g. polymers, colloids, micelles, etc. use small-angle scattering

The Kinematic Approximation

- Note that the approximation we have just seen ignores
  - Depletion of the incident beam by scattering or absorption
  - Multiple scattering

  i.e. energy is not conserved

- This so-called "kinematic approximation" is OK for weak scattering, very small crystals or "bad" crystals

- It is usually used for interpreting diffraction experiments, though "extinction corrections" are often needed with single crystals
  - If it's not adequate, use dynamical theory

- In addition, we have so-far ignored thermal motion of atoms

Diffraction by a Lattice of Atoms

$$S(\vec{Q}) = \frac{1}{N}\left\langle \sum_{i,j} e^{-i\vec{Q}.(\vec{R}_i - \vec{R}_j)} \right\rangle$$ with $\vec{R}_i = \vec{i} + \vec{u}_i$ where $\vec{i}$ is the equilibrium position of atom i and $\vec{u}_i$ is any displacement (e.g. thermal) from the equilibrium position.

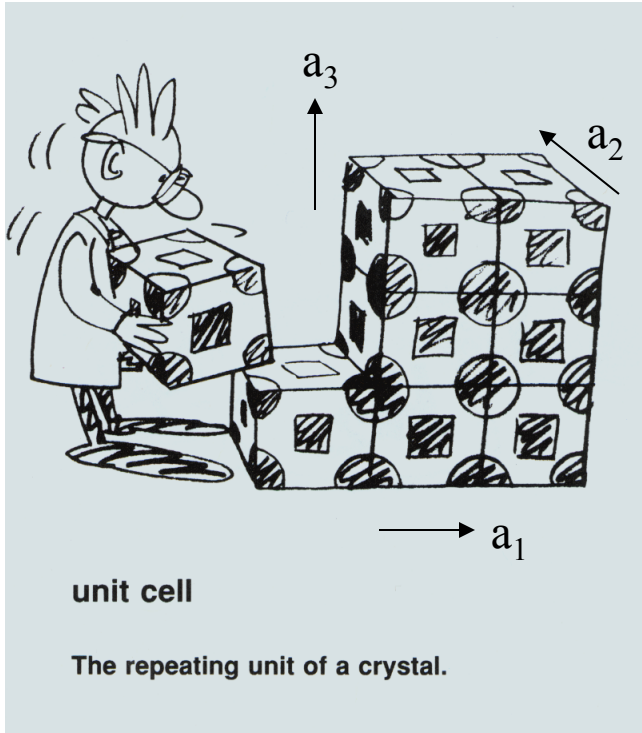
Ignoring thermal vibrations, S(Q) is only non-zero for Q's such that $\vec{Q}.(\vec{i} - \vec{j}) = 2M\pi$.

In a Bravais lattice, we can write $\vec{i} = m_{1i}\vec{a}_1 + m_{2i}\vec{a}_2 + m_{3i}\vec{a}_3$ where $\vec{a}_1, \vec{a}_2, \vec{a}_3$ are the primitive translation vectors of the unit cell.

Define $\vec{a}_1^* = \frac{2\pi}{V_0}\vec{a}_2 \wedge \vec{a}_3$ and cyclic permutations.

Then $\vec{a}_i^*.\vec{a}_j = 2\pi\delta_{ij}$.

If $\vec{Q} = \vec{G}_{hkl} = h\vec{a}_1^* + k\vec{a}_2^* + l\vec{a}_3^*$ then $\vec{Q}.(\vec{i} - \vec{j}) = 2M\pi$.



So scattering from a (frozen) lattice only occurs when the scattering wavevector, Q, is equal to a reciprocal lattice vector, G_{hkl}.

Direct and Reciprocal Lattices

In a Bravais lattice, we can write $\vec{R}_i = m_{1i}\vec{a}_1 + m_{2i}\vec{a}_2 + m_{3i}\vec{a}_3$ where $\vec{a}_1, \vec{a}_2, \vec{a}_3$ are the primitive translation vectors of the unit cell (see previous viewgraph).

Let's define $\vec{a}_1^* = \frac{2\pi}{V_0}\vec{a}_2 \times \vec{a}_3$; $\vec{a}_2^* = \frac{2\pi}{V_0}\vec{a}_3 \times \vec{a}_1$; $\vec{a}_3^* = \frac{2\pi}{V_0}\vec{a}_1 \times \vec{a}_2$

where $V_0 = \vec{a}_1.(\vec{a}_2 \times \vec{a}_3)$ = the volume of the unit cell.

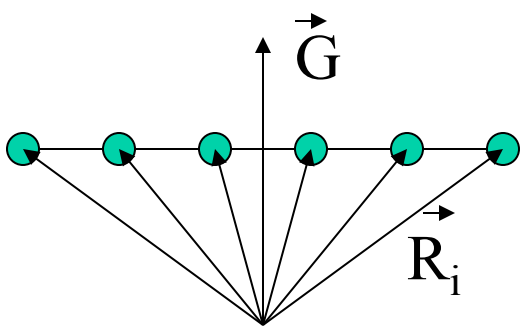
The $\vec{a}_i^*$ have the dimensions of (length)$^{-1}$ and the property that $\vec{a}_i^*.\vec{a}_j = 2\pi\delta_{ij}$, i.e. $\vec{a}_1^*$ is perpendicular to the plane defined by $\vec{a}_2$ and $\vec{a}_3$ etc.

If we choose a vector $\vec{G}_{hkl}$ defined by $\vec{G}_{hkl} = h\vec{a}_1^* + k\vec{a}_2^* + l\vec{a}_3^*$ then $\vec{G}_{hkl}.(\vec{R}_i - \vec{R}_j) = 2M\pi$.

i.e. $\vec{G}_{hkl}$ is normal to sets of planes of atoms spaced $2\pi / G_{hkl}$ apart

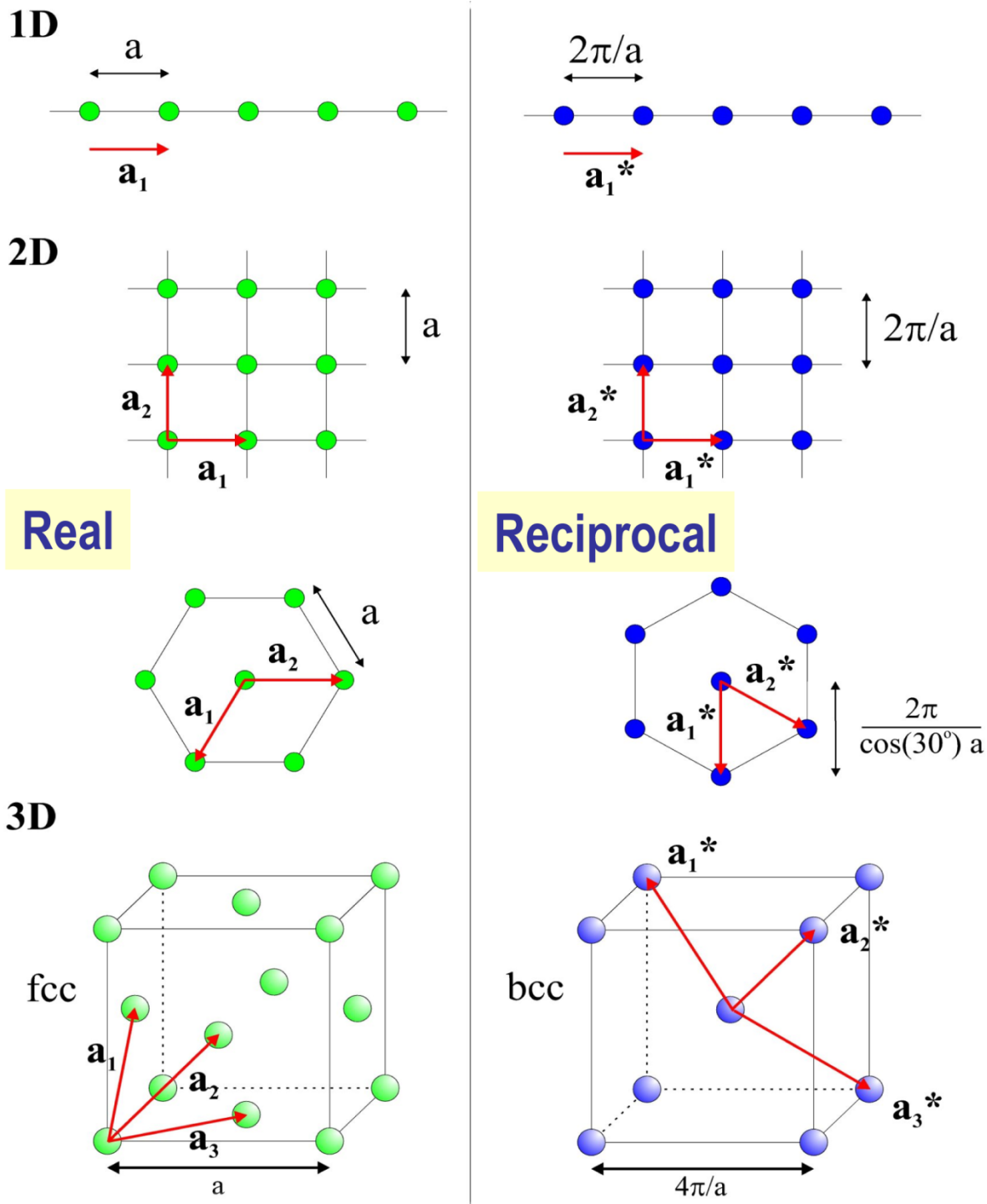
Scattering from a lattice of atoms occurs only when $\vec{Q} = \vec{G}_{hkl}$

The vectors $\vec{G}_{hkl}$ define a lattice of points called the reciprocal lattice



Homework: verify that Bragg's (l= 2 d sinq) follows from the above

Reciprocal Lattice:



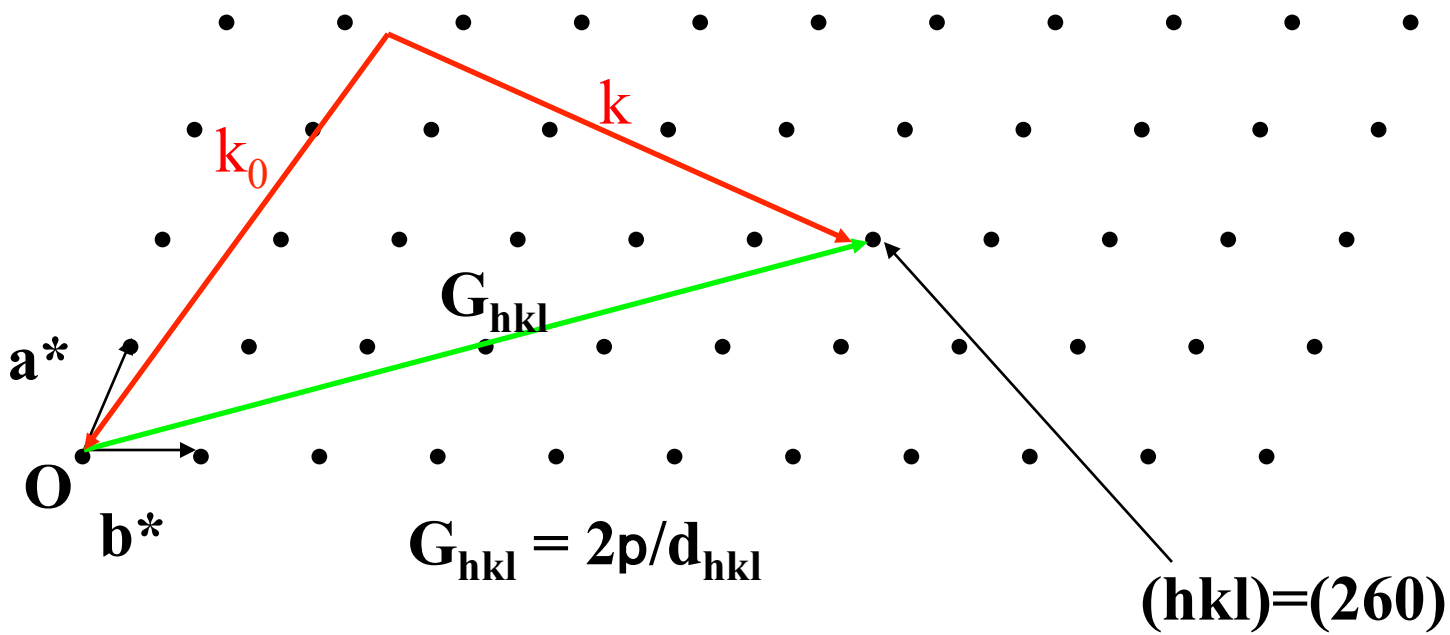
$$V_c = \vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)$$

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

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

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

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



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

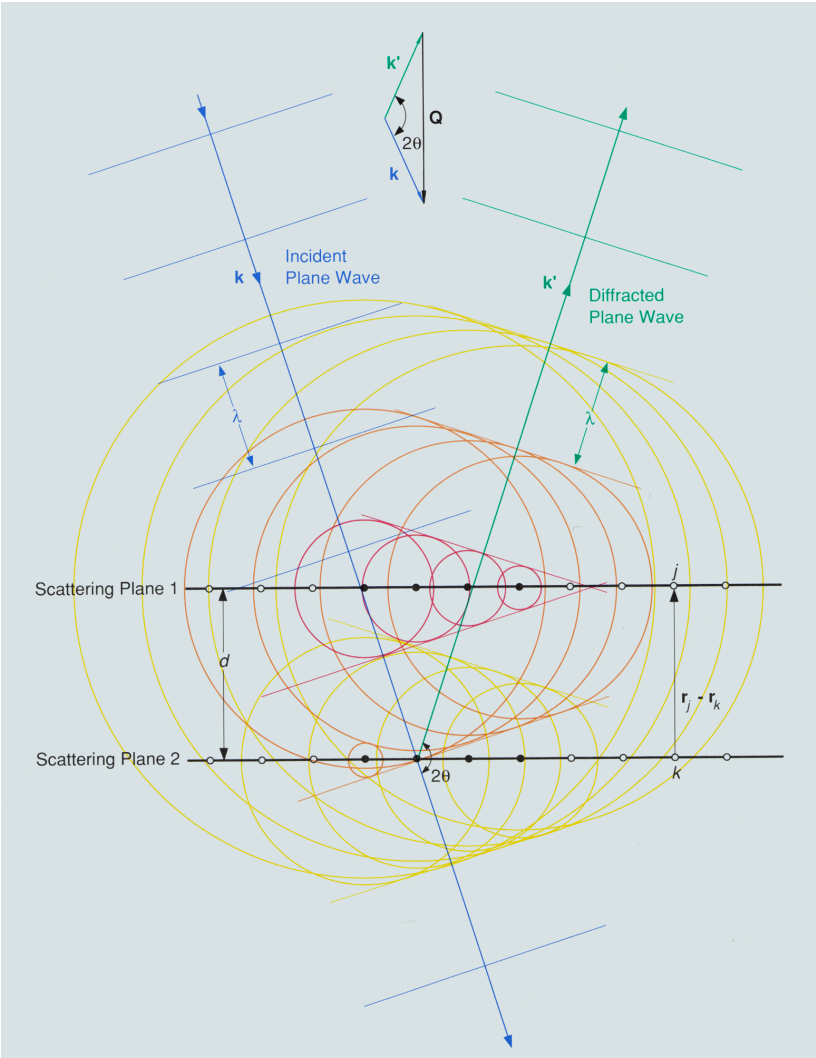
A single crystal has to be aligned precisely to record Bragg scattering

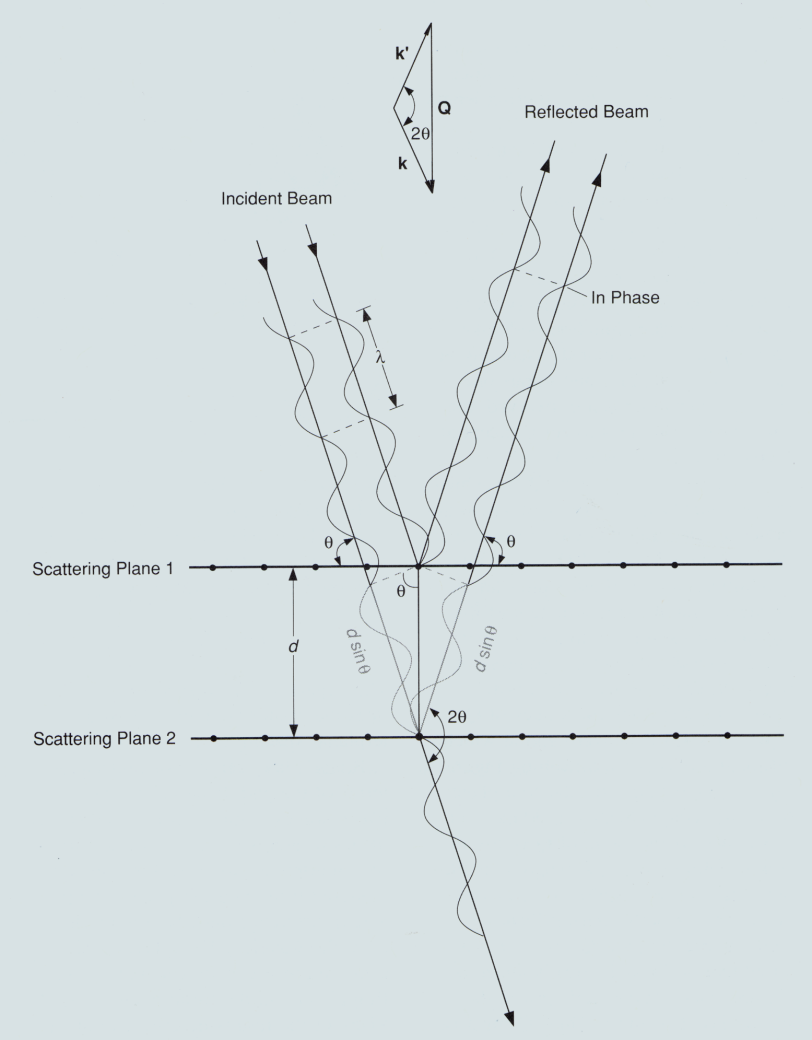
Notation

- $\vec{G}_{hkl}$ is called a reciprocal lattice vector (node denoted hkl)
- h, k and l are called Miller indices
- (hkl) describes a set of planes perpendicular to $\vec{G}_{hkl}$, separated by $2p/G_{hkl}$
- {hkl} represents a set of symmetry-related lattice planes
- [hkl] describes a crystallographic direction
- <hkl> describes a set of symmetry equivalent crystallographic directions

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

$l = 2\, d_{hkl} \sin(q)$ or $2\, k \sin(q) = G_{hkl}$ (where $G_{hkl} = 2p/d_{hkl}$)



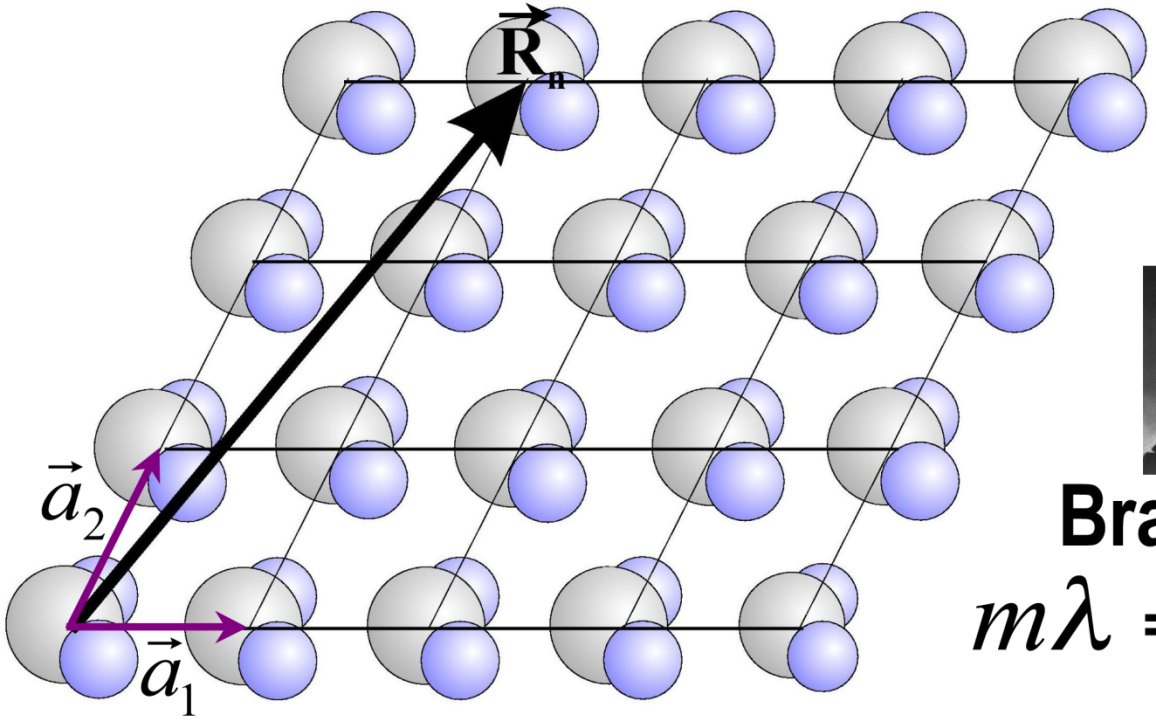


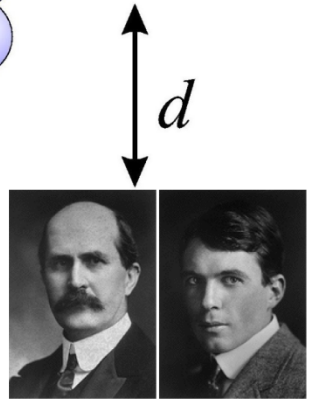
Atomic Vibrations

- **The formalism on the previous slide works fine if the atoms are stationary: in reality, they are not**
- **Remember that** $$S(\vec{Q}) = \frac{1}{N}\left\langle \sum_{i,j} e^{-i\vec{Q}.(\vec{R}_i - \vec{R}_j)} \right\rangle_{\text{ensemble}}$$
- **We average over the (fluctuating) atomic positions by introducing a probability that an atom will be at given position. Instead of the Fourier Transform of d functions, this gives the FT of the d functions *convolved* with a spread function. The result is that S(Q) is *multiplied* by the FT of the spread function i.e. by** $\exp - Q^2 \langle u^2 \rangle / 3$ **if we use a Gaussian spread function**

- **Atomic vibrations cause a decrease in the intensity of Bragg scattering. The "missing" scattering appears between Bragg peaks and results in inelastic scattering**

Diffraction from non-Bravais Crystals





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 $F_{uc}(\vec{q})$

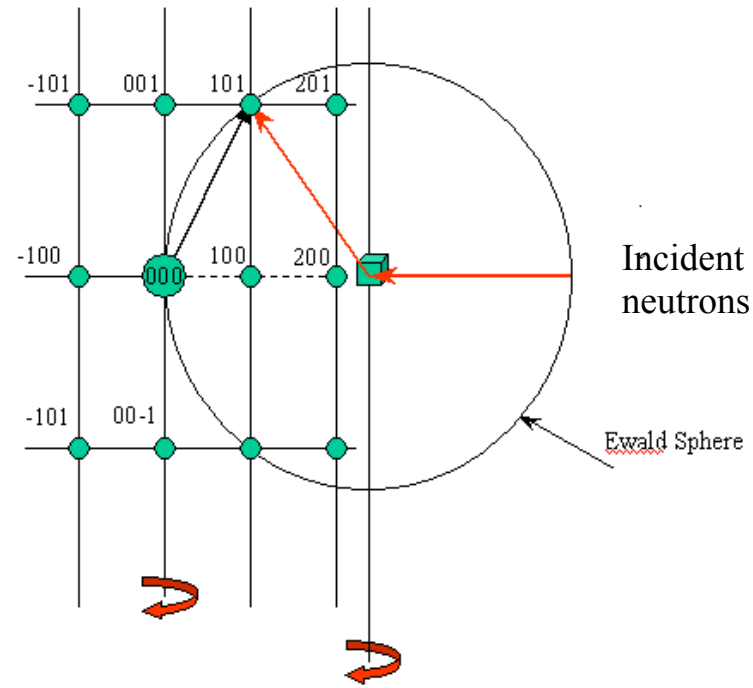
Lattice Sum

Key Points about Diffraction

- A monochromatic (single l) neutron beam is diffracted by a single crystal only if specific geometrical conditions are fulfilled

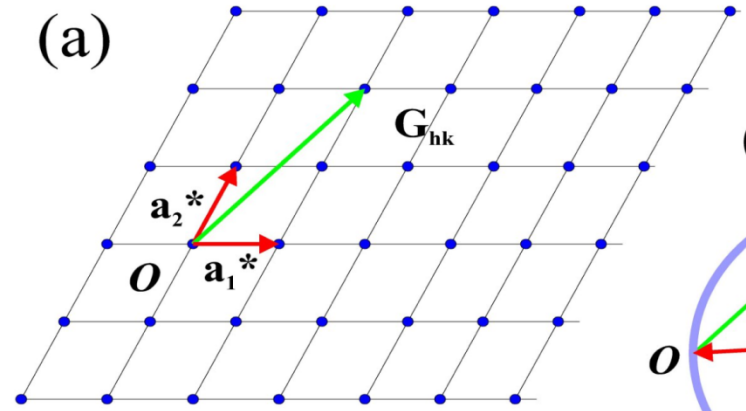
- These conditions can be expressed in several ways:
  - Laue's conditions: $\vec{Q}.\vec{a}_1 = h; \quad \vec{Q}.\vec{a}_2 = k; \quad \vec{Q}.\vec{a}_3 = l$ with h, k, and l as integers
  - Bragg's Law: $2d_{hkl}\sin\theta = \lambda$
  - Ewald's construction

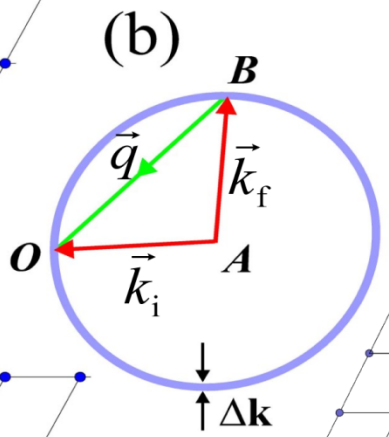
    see http://www.matter.org.uk/diffraction/geometry/default.htm

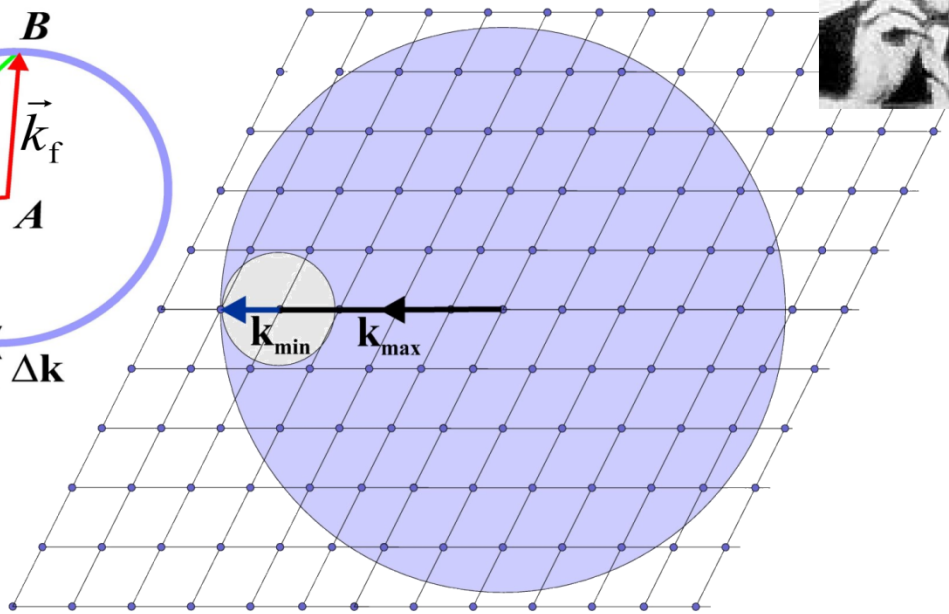


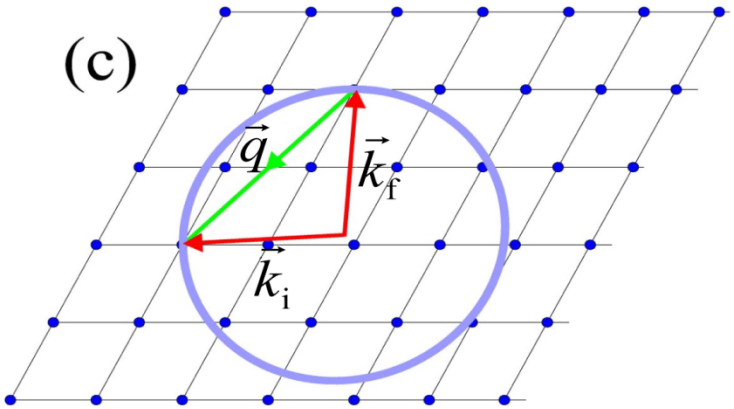
- Diffraction tells us about:
  - The dimensions of the unit cell
  - The symmetry of the crystal
  - The positions of atoms within the unit cell
  - The extent of thermal vibrations of atoms in various directions

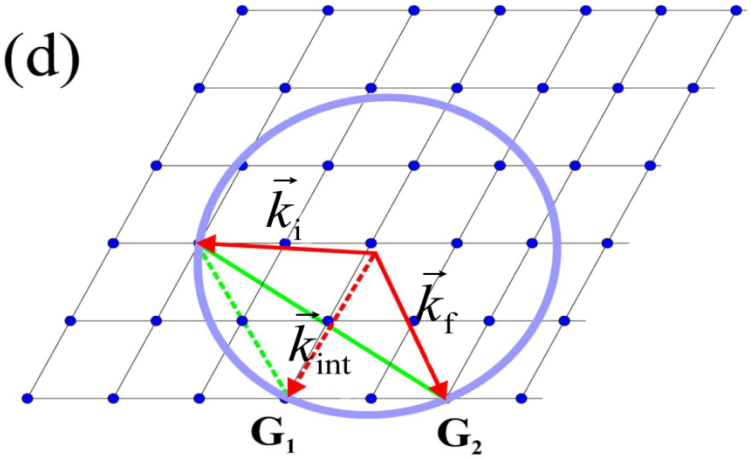
Ewald-Construction

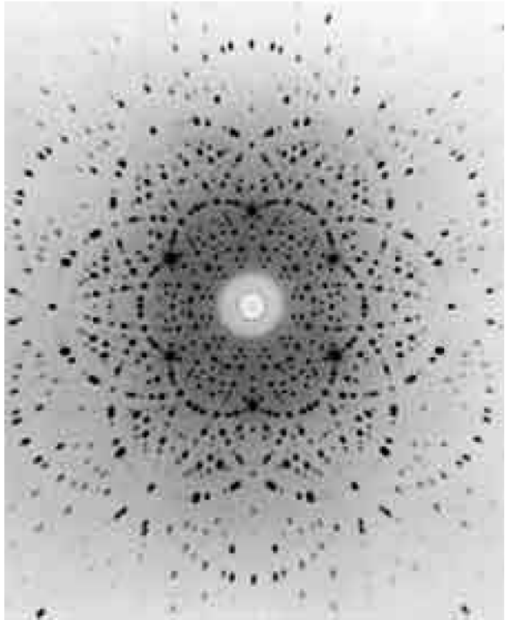












Laue Pattern of Beryllium-Aluminum-Silicate ("Beryl")

Bragg Scattering from Crystals

Working through the math (see, for example, Squires' book), we find:

$$\left(\frac{d\sigma}{d\Omega}\right)_{Bragg} = N\frac{(2\pi)^3}{V_0}\sum_{hkl}\delta(\vec{Q}-\vec{G}_{hkl})\left|F_{hkl}(\vec{Q})\right|^2$$

where the unit-cell structure factor is given by

$$F_{hkl}(\vec{Q}) = \sum_d \bar{b}_d e^{i\vec{Q}.\vec{d}} e^{-W_d}$$

and W_d is the Debye-Waller factor that accounts for thermal motions of atoms

- Using either single crystals or powders, neutron diffraction can be used to measure F^2 (which is proportional to the intensity of a Bragg peak) for various values of (hkl).
- Direct Fourier inversion of diffraction data to yield crystal structures is not possible because we only measure the magnitude of F, and not its phase => models must be fit to the data
- Neutron powder diffraction has been particularly successful at determining structures of new materials, e.g. high T_c materials

Comparison of X-ray and Neutron Cross Section for Crystal Diffraction

$$\left(\frac{d\sigma}{d\Omega}\right)_{Neutron} = N\frac{(2\pi)^3}{V_0}\sum_{hkl}\delta(\vec{Q}-\vec{G}_{hkl})\left|F_{hkl}(\vec{Q})\right|^2$$

where the unit - cell structure factor is given by

$$F_{hkl}(\vec{Q}) = \sum_d \bar{b}_d e^{i\vec{Q}.\vec{d}} e^{-W_d}$$

and W_d is the Debye - Waller factor that accounts for thermal motions of atoms

$$\left(\frac{d\sigma}{d\Omega}\right)_{x-ray} = r_0^2\left[\frac{1+\cos^2 2\theta}{2}\right]N\frac{(2\pi)^3}{V_0}\sum_{hkl}\delta(\vec{Q}-\vec{G}_{hkl})\left|F_{hkl}(\vec{Q})\right|^2$$

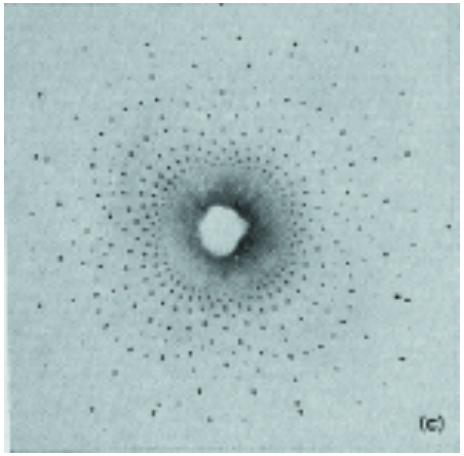
where the unit - cell structure factor is given by

$$F_{hkl}(\vec{Q}) = \sum_d f_d(\vec{Q},\omega) e^{i\vec{Q}.\vec{d}} e^{-W_d}$$

The Structure Factor

- The intensity of scattering at reciprocal lattice points is given by the square of the structure factor $F_{hkl}(\vec{Q}) = \sum_d \bar{b}_d e^{i\vec{Q}.\vec{d}} e^{-W_d}$

- Crystallography attempts to deduce atomic positions and thermal motions from measurements of a large number of such "reflections"
  - (Reciprocal) distance between diffraction "spots" => size of unit cell
  - Systematic absences and symmetry of reciprocal lattices => crystal symmetry (e.g. bcc h+k+l=2n)
  - Intensities of "spots" => atomic positions and thermal motions



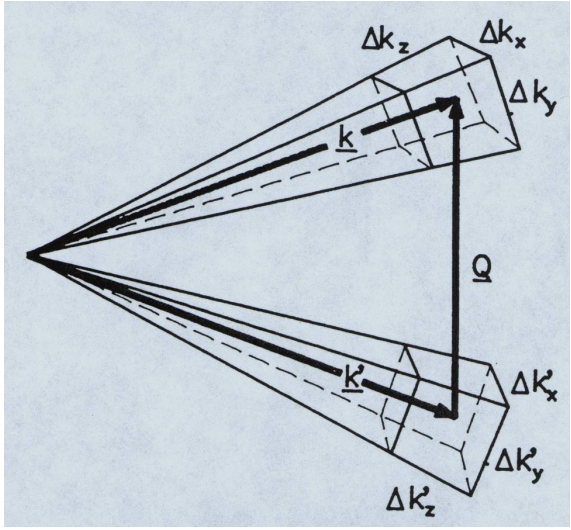
Laue diffraction pattern showing crystal symmetry

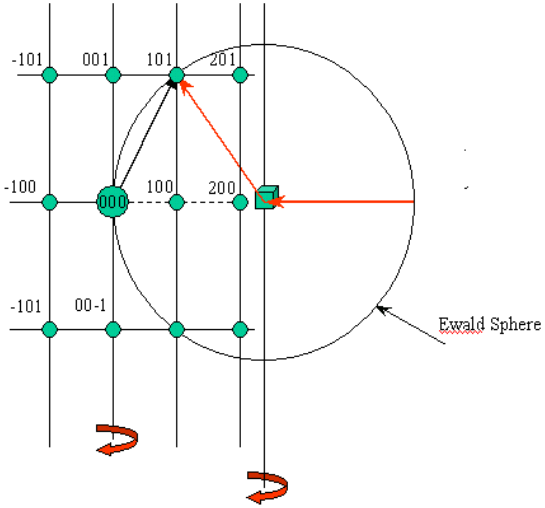
Resolution and Integrated Intensity

- Neutron beam is not perfectly collimated or monochromatic

- At a CW source, measure intensities of Bragg peaks either by rocking the crystal through the Ewald sphere or scanning 2q.
  - Width of rocking curve reflects instrumental resolution and (perhaps) crystallite size

- Integrated intensity of rocking curve is proportional to structure factor. Constant of proportionality depends on resolution function and scan direction
  – called the Lorentz factor





Useful Web Site

- The following site provides a tutorial on diffraction. It is a good idea to go through them and try the examples.

- http://www.matter.org.uk/diffraction/introduction/default.htm

If we could measure the complex quantity F_{hkl} we could figure out the positions of all atoms. But we only measure $|F_{hkl}|^2$. In fact, we would be better off if diffraction measured phase of scattering rather than amplitude! Unfortunately, nature did not oblige us.

The Phase Problem

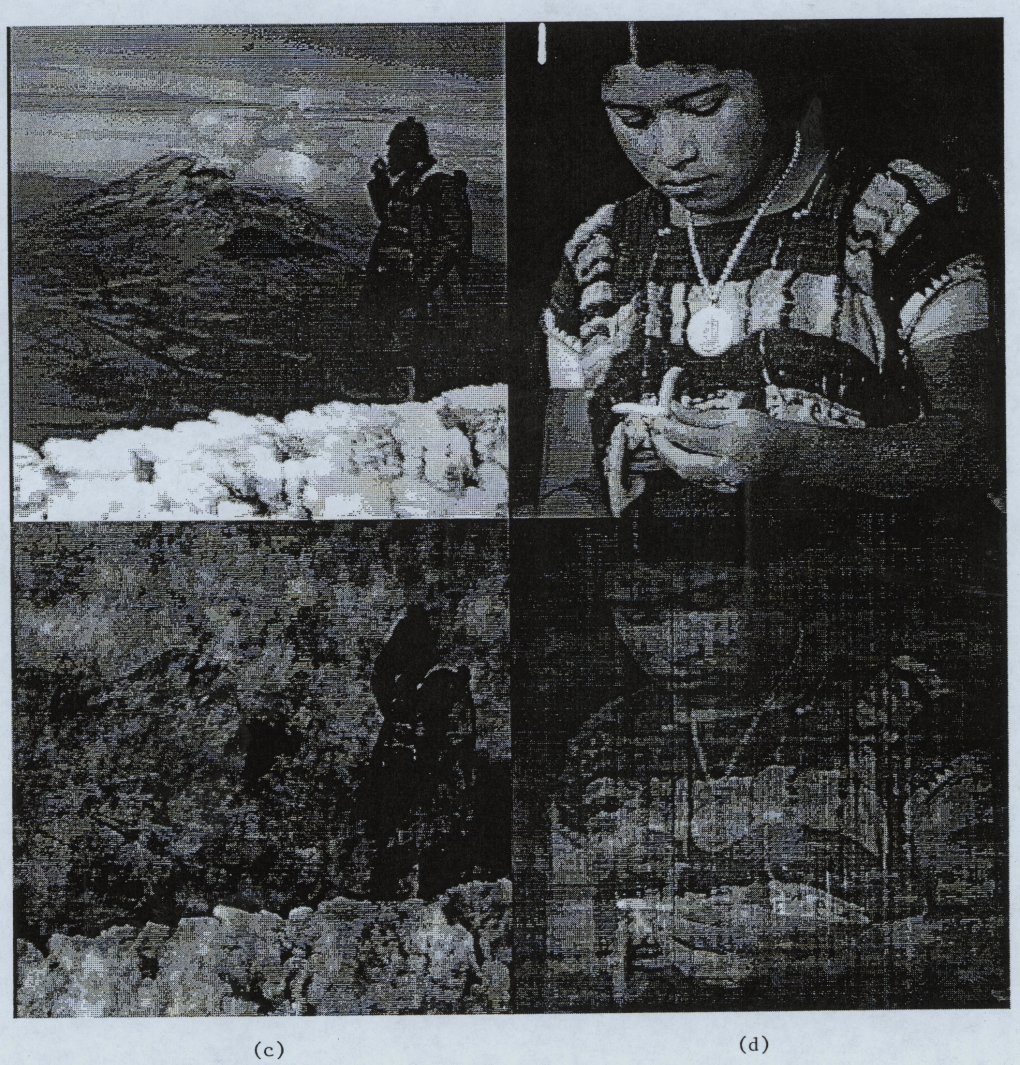
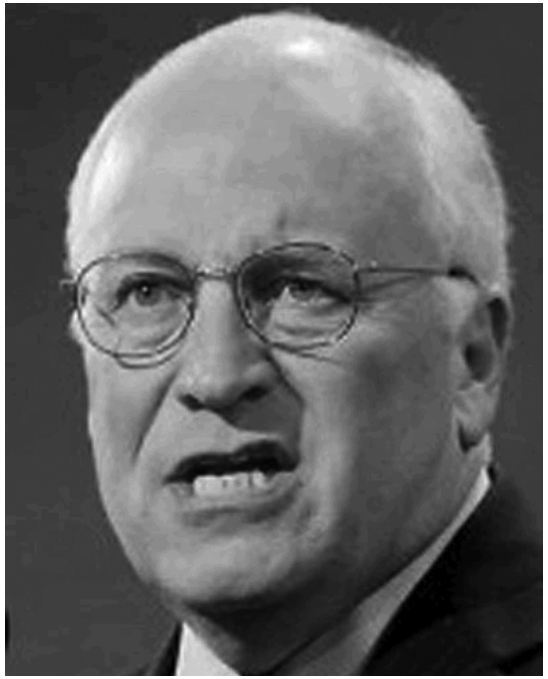


Figure 1.2

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

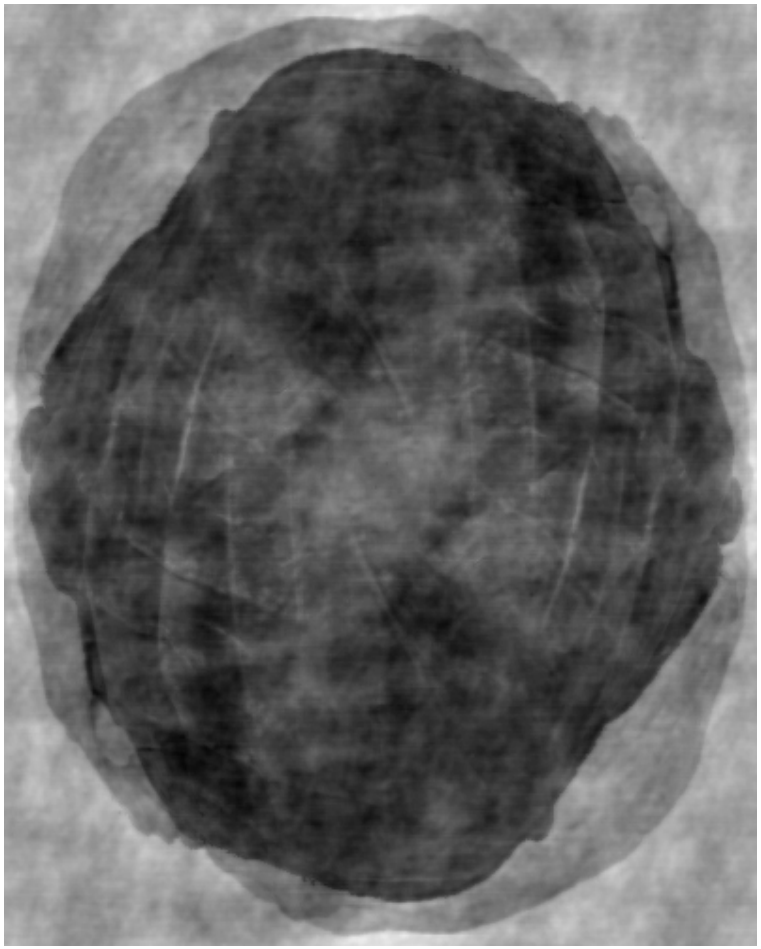
Object A



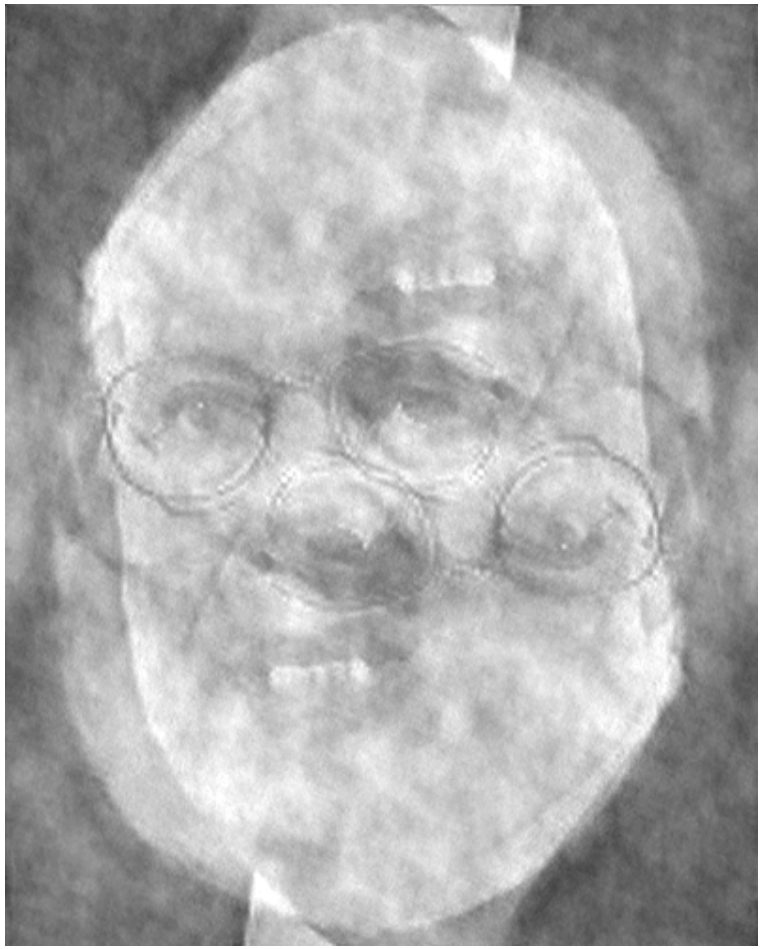
Object B

Professor Sinha's demonstration of the "Phase Problem" is much more memorable

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

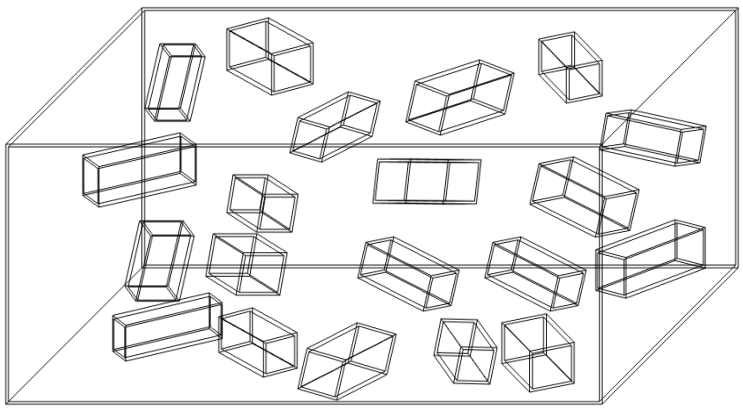


Fourier Reconstruction with phases of object B and amplitudes of Object A



PHASE tells us where the different parts of the object are located!

Powder – A Polycrystalline Mass



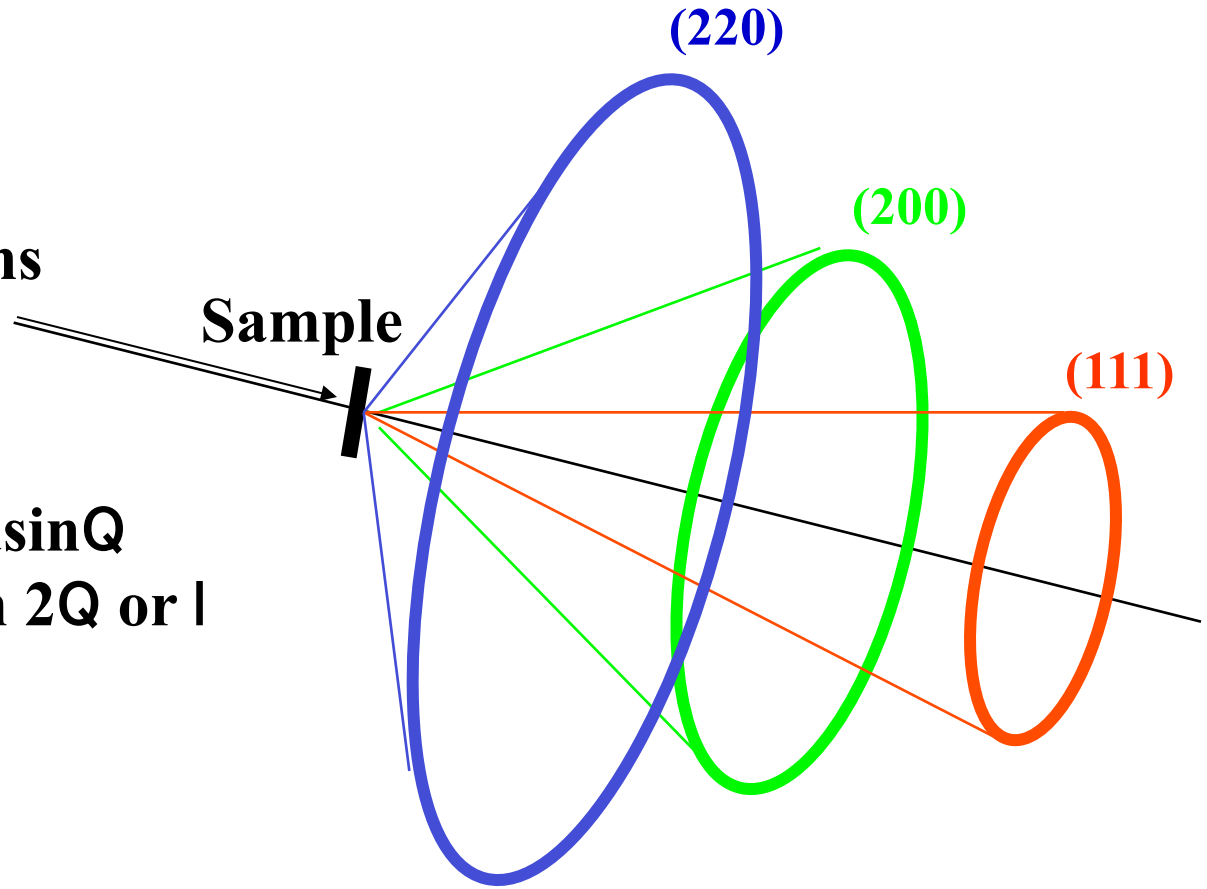
All orientations of crystallites possible

Typical Sample: 1cc powder of 10mm crystallites - 10^9 particles
if 1mm crystallites - 10^{12} particles

Single crystal reciprocal lattice
- smeared into spherical shells

Powder Diffraction gives Scattering on Debye-Scherrer Cones

Incident beam
x-rays or neutrons



Bragg's Law $l = 2d\sin Q$
Powder pattern – scan 2Q or l

Typical SANS/SAXS Applications

- Biology
  - Organization of biomolecular complexes in solution
  - Conformation changes affecting function of proteins, enzymes, protein/DNA complexes, membranes etc
  - Mechanisms and pathways for protein folding and DNA supercoiling
- Polymers
  - Conformation of polymer molecules in solution and in the bulk
  - Structure of microphase separated block copolymers
  - Factors affecting miscibility of polymer blends
- Chemistry
  - Structure and interactions in colloid suspensions, microemeulsions, surfactant phases etc
  - Mechanisms of molecular self-assembly in solutions

Biological Applications of SANS

- Studying Biological Macromolecules in Solution
  - Proteins
  - Nucleic Acids
  - Protein-nucleic acid complexes
  - Multi-subunit protein complexes
  - Membranes and membrane components
  - Protein-lipid complexes

- One of the issues with studying bio-molecules is that most contain H which gives a large, constant background of incoherent scattering. To avoid this:
  - Use D_2O instead of water as a fluid for suspension
  - May need to deuterate some molecular components

Instrumental Resolution for SANS/SAXS

$$Q = \frac{4\pi}{\lambda}\sin\theta \;\Rightarrow\; \left\langle \frac{\delta Q^2}{Q^2} \right\rangle = \left\langle \frac{\delta\lambda^2}{\lambda^2} \right\rangle + \left\langle \frac{\cos^2\theta.\delta\theta^2}{\sin^2\theta} \right\rangle$$

For SANS, $(\delta\lambda/\lambda)_{rms} \sim 5\%$ and θ is small, so $\left\langle \frac{\delta Q^2}{Q^2} \right\rangle = 0.0025 + \left\langle \frac{\delta\theta^2}{\theta^2} \right\rangle$

For equal source - sample & sample - detector distances of L and equal apertures at source and sample of h, $\delta\theta_{rms} = \sqrt{5/12}\,\mathrm{h/L}$.

The smallest value of θ is determined by the direct beam size: $2\theta_{\min} \sim 1.5h/L$

At this value of θ, angular resolution dominates and

$\delta Q_{\mathrm{rms}} \sim (\delta\theta_{\mathrm{rms}}/\theta_{\min})Q_{\min} \sim \delta\theta_{\mathrm{rms}}\,4\pi/\lambda \sim (2\pi/\lambda)h/L$

The largest observable object is $\sim 2\pi/\delta Q_{\mathrm{rms}} \sim \lambda L/h$.

This achieves a maximum of about 5 μm at the ILL 40 m SANS instrument using 15 Å neutrons.

Note that at the largest values of θ, set by the detector size and distance from the sample, wavelength resolution dominates.

Scattering Length Density

- Remember $\frac{d\sigma}{d\Omega} = b_{coh}^2 \left\langle \left| \int d\vec{r}.e^{-i\vec{Q}.\vec{r}} n_{nuc}(\vec{r}) \right|^2 \right\rangle$
- What happens if Q is very small?
  - The phase factor will not change significantly between neighboring atoms
  - We can average the nuclear scattering potential over length scales ~2p/10Q
  - This average is called the scattering length density and denoted $\rho(\vec{r})$
- How do we calculate the SLD?
  - Easiest method: go to www.ncnr.nist.gov/resources/sldcalc.html
  - By hand: let us calculate the scattering length density for quartz – SiO_2
  - Density is 2.66 gm.cm^{-3}; Molecular weight is 60.08 gm. mole^{-1}
  - Number of molecules per Å^3 = N = 10^{-24}(2.66/60.08)*$N_{avagadro}$ = 0.0267 molecules per Å^3
  - SLD=Sb/volume = N(b_{Si} + 2b_O) = 0.0267(4.15 + 11.6) 10^{-5} Å^{-2} = 4.21 x10^{-6} Å^{-2}
- A uniform SLD causes scattering only at Q=0; variations in the SLD cause scattering at finite values of Q

SLD Calculation

- www.ncnr.nist.gov/resources/sldcalc.html
- Need to know chemical formula and density

Enter → Compound: C6H12

Enter → Density (g/cm^3): 0.86

Not relevant for SLD → Wavelength (A): 6

Calculate

Neutron SLD	-3.07E-7 (A^-2)
Cu Ka SLD	8.34E-6 +9.36E-9i (A^-:
Mo Ka SLD	8.33E-6 +2.08E-9i (A^-:
Neutron Inc. XS	5.93; 33.4 (cm^-1)
Neutron Abs. XS	0.0823 (cm^-1)
Neutron 1/e length	0.166 (cm)

X-ray values → Cu Ka SLD, Mo Ka SLD

Background → Neutron Inc. XS

Determine best sample thickness → Neutron 1/e length

Note units of the cross section – this is cross section per unit volume of sample

SANS Measures Particle Shapes and Inter-particle Correlations

$$\frac{d\sigma}{d\Omega} = \langle b \rangle^2 \int_{space} d^3r \int_{space} d^3r' n_N(\vec{r}) n_N(\vec{r}') . e^{i\vec{Q}.(\vec{r}-\vec{r}')}$$

$$= \int_{space} d^3R \int_{space} d^3R' \langle n_P(\vec{R}) n_P(\vec{R}') \rangle e^{i\vec{Q}.(\vec{R}-\vec{R}')} \left\langle \left| (\rho - \rho_0) \int_{particle} d^3x . e^{i\vec{Q}.\vec{x}} \right|^2 \right\rangle_{orientation}$$

$$\boxed{\frac{d\sigma}{d\Omega} = (\rho - \rho_0)^2 \left| F(\vec{Q}) \right|^2 V_p^2 N_P \int_{space} d^3R . G_P(\vec{R}) . e^{i\vec{Q}.\vec{R}}}$$

where G_P is the particle - particle correlation function (the probability that there is a particle at $\vec{R}$ if there's one at the origin) and $\left|F(\vec{Q})\right|^2$ is the particle form factor :

$$\boxed{\left| F(\vec{Q}) \right|^2 = \frac{1}{V_p^2} \left\langle \left| \int_{particle} d^3x . e^{i\vec{Q}.\vec{x}} \right|^2 \right\rangle_{orientation}}$$

These expressions are the same as those for nuclear scattering except for the addition of a form factor that arises because the scattering is no longer from point-like particles

Scattering from Independent Particles

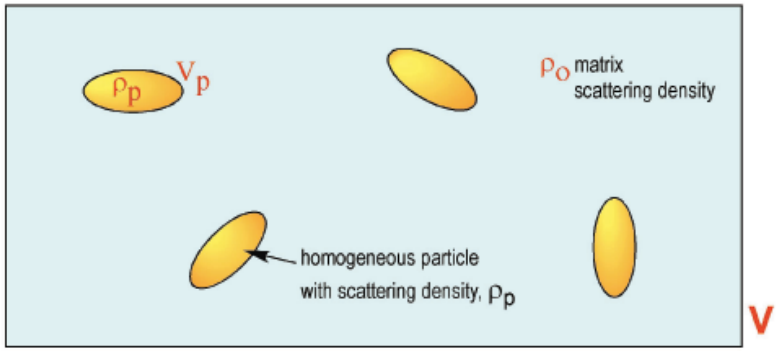
Scattered intensity per unit volume of sample = $I(\vec{Q}) = \frac{1}{V}\frac{d\sigma}{d\Omega} = \frac{1}{V}\left\langle \left| \int \rho(\vec{r}) e^{i\vec{Q}.\vec{r}} d\vec{r} \right|^2 \right\rangle$

For identical particles

$$I(Q) = \frac{N}{V}(\rho_p - \rho_0)^2 V_p^2 \left\langle \left| \frac{1}{V_p} \int_{particle} e^{i\vec{Q}.\vec{r}} d\vec{r} \right|^2 \right\rangle$$

contrast factor

particle form factor $|F(\vec{Q})|^2$



Note that $I(0) = \frac{N}{V}(\rho_p - \rho_0)^2 V_p^2$

Particle concentration $c = NV_p / V$ and particle molecular weight $M_w = \rho V_p N_A$

where ρ is the particle mass density and N_A is Avagadro's number

so $I(0) = \frac{cM_w}{\rho N_A}(\rho_p - \rho_0)^2$ provides a way to find the particle molecular weight

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:

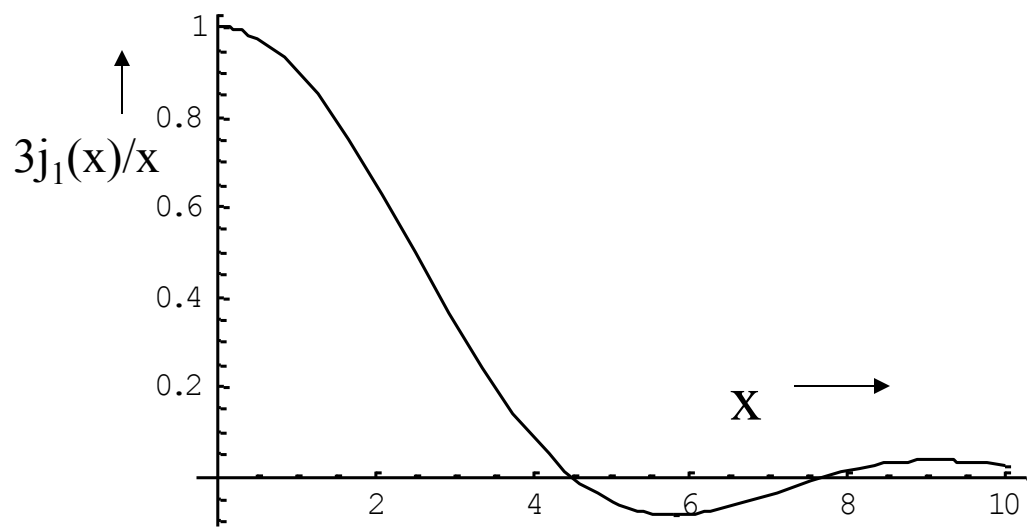
$$\boxed{F_{sphere}(Q) = 3V_0\left[\frac{\sin QR - QR\cos QR}{(QR)^3}\right] \equiv \frac{3V_0}{QR}\, j_1(QR) \;\rightarrow V_0 \text{ at } Q = 0}$$

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 $\vec{Q}$



Radius of Gyration Is the Particle "Size" Usually Deduced From SANS Measurements

If we measure $\vec{r}$ from the centroid of the particle and expand the exponential in the definition of the form factor at small Q:

$$F(Q) = \int_V d\vec{r} e^{i\vec{Q}.\vec{r}} \approx V_0 + \cancel{i\int_V \vec{Q}.\vec{r} d^3r} - \frac{1}{2}\int_V (\vec{Q}.\vec{r})^2 d^3r + \ldots.$$

$$= V_0\left[1 - \frac{Q^2}{2}\frac{\int_0^\pi \cos^2\theta \sin\theta.d\theta \int_{V_0} r^2 d^3r}{\int_0^\pi \sin\theta.d\theta \int_{V_0} d^3r} + \ldots\right] = V_0\left[1 - \frac{Q^2 r_g^2}{6} + \ldots\right] \approx V_0 e^{-\frac{Q^2 r_g^2}{6}}$$

where r_g is the radius of gyration is $r_g = \int_V R^2 d^3r / \int_V d^3r$. It is usually obtained from a fit to SANS data at low Q (in the so-called Guinier region) or by plotting ln(Intensity) v Q^2. The slope of the data at the lowest values of Q is $r_g^2/3$. It is easily verified that the expression for the form factor of a sphere is a special case of this general result.

Shape Determination for Dilute, Randomly Oriented, Uniform Particles

$$I(Q) = \frac{N}{V}(\rho_p - \rho_0)^2 \left\langle \left| \int_{V_p} e^{i\vec{Q}.\vec{r}} d\vec{r} \right|^2 \right\rangle = \frac{N}{V}(\rho_p - \rho_0)^2 \left\langle \int_{V_p} e^{i\vec{Q}.\vec{r}} d\vec{r} \int_{V_p} e^{-i\vec{Q}.\vec{r}'} d\vec{r}' \right\rangle$$

$$I(Q) = \frac{N}{V}(\rho_p - \rho_0)^2 \left\langle \int_{V_p} e^{i\vec{Q}.(\vec{r}-\vec{r}')} d(\vec{r}-\vec{r}')V_p \right\rangle = (\rho_p - \rho_0)^2 \left\langle \int_{V_p} \gamma(\vec{R}) e^{i\vec{Q}.\vec{R}} d\vec{R} \right\rangle_{orientation}$$

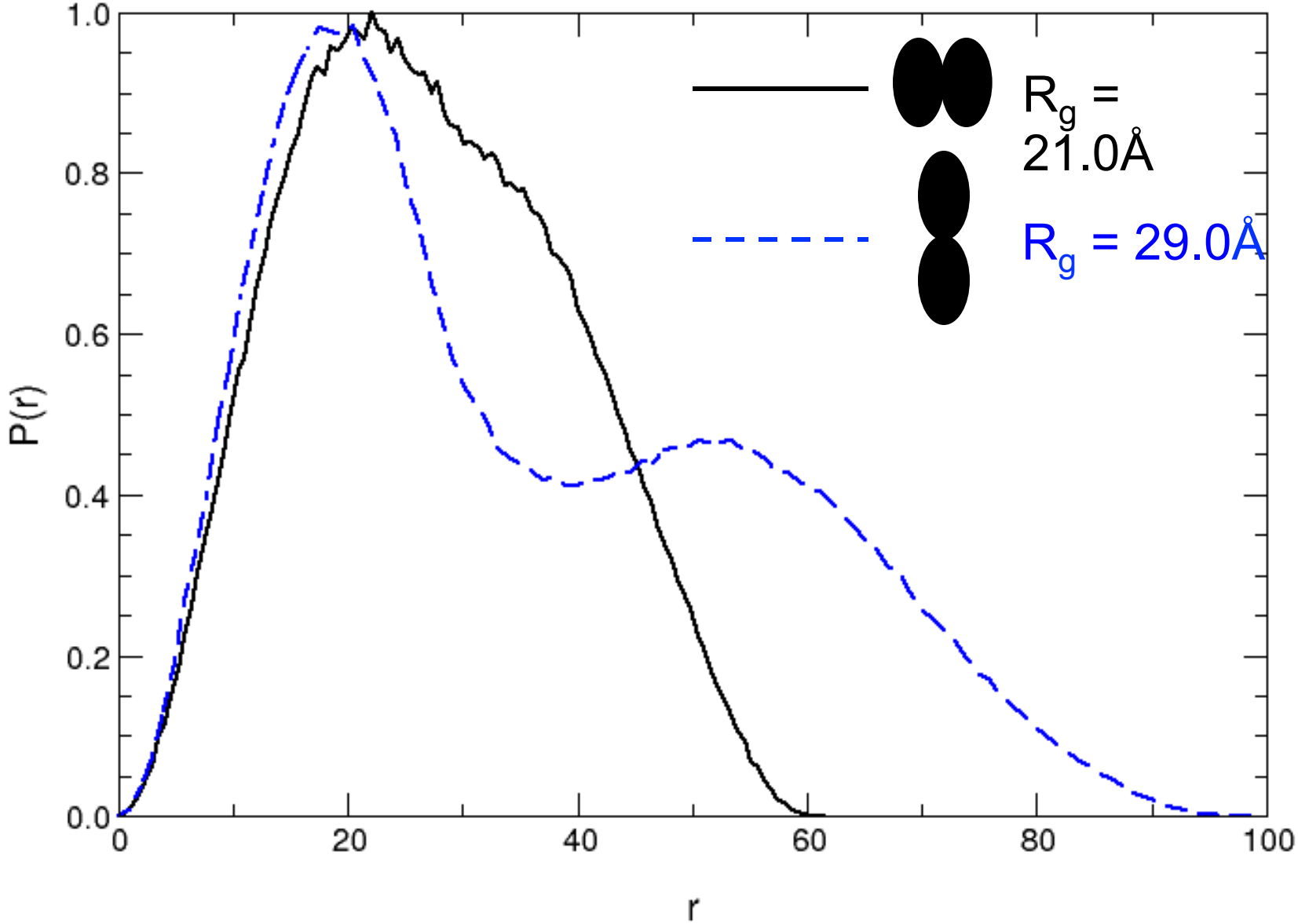
$$I(Q) = (\rho_p - \rho_0)^2 4\pi \int_0^{D_{max}} r^2 \gamma(r) \frac{\sin Qr}{Qr} dr$$

where $P(r) \equiv 4\pi r^2 \gamma(r)$ is the probability of finding two points in the particle separated by r

- If I(Q) is measured over a wide enough Q range then the inverse transform can be computed

$$P(r) \equiv 4\pi r^2 \gamma(r) = \frac{2}{\pi} \int Q I(Q) \sin(Qr) dQ$$

P(r) for Simple Models



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

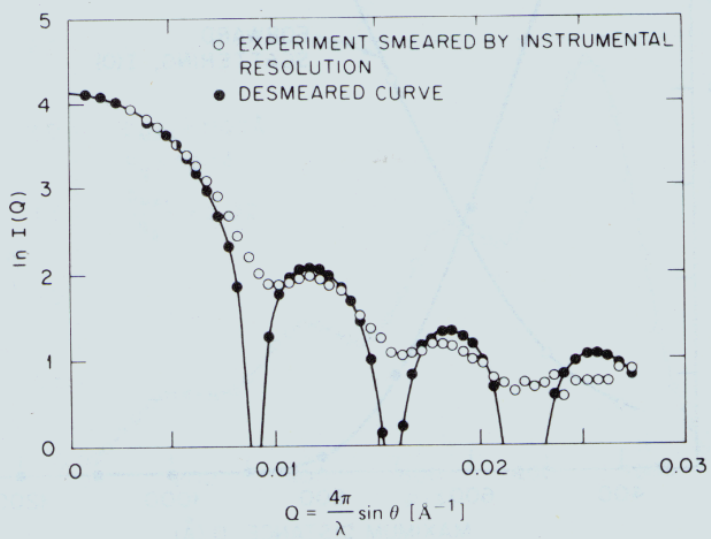


Fig. 4. Plot of ln $I(Q)$ *vs* Q for 3·98 vol.% monodisperse PMMA-H spheres (core $C1$) in D_2O/H_2O mixtures.

Correlations Can Be Measured in Concentrated Systems

- A series of experiments in the late 1980's by Hayter et al and Chen et al produced accurate measurements of S(Q) for colloidal and micellar systems
- To a large extent these data could be fit by S(Q) calculated from the mean spherical model using a Yukawa potential to yield surface charge and screening length

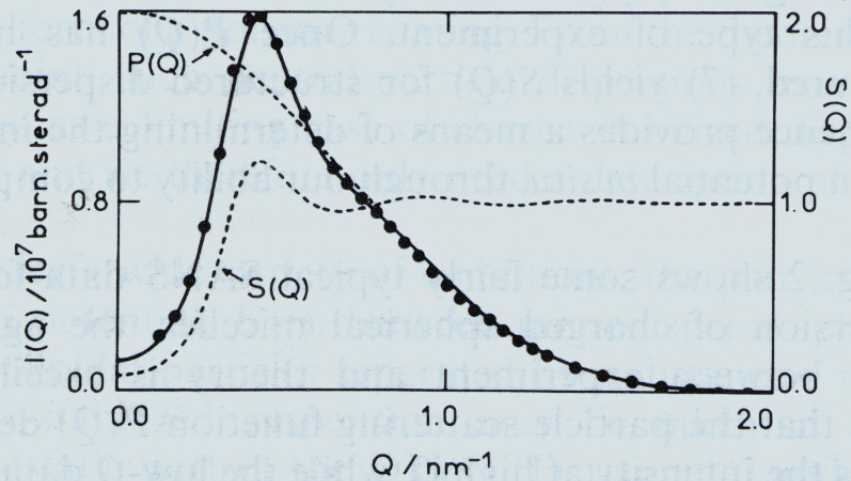
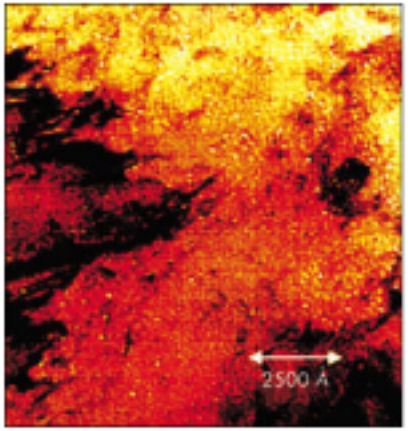
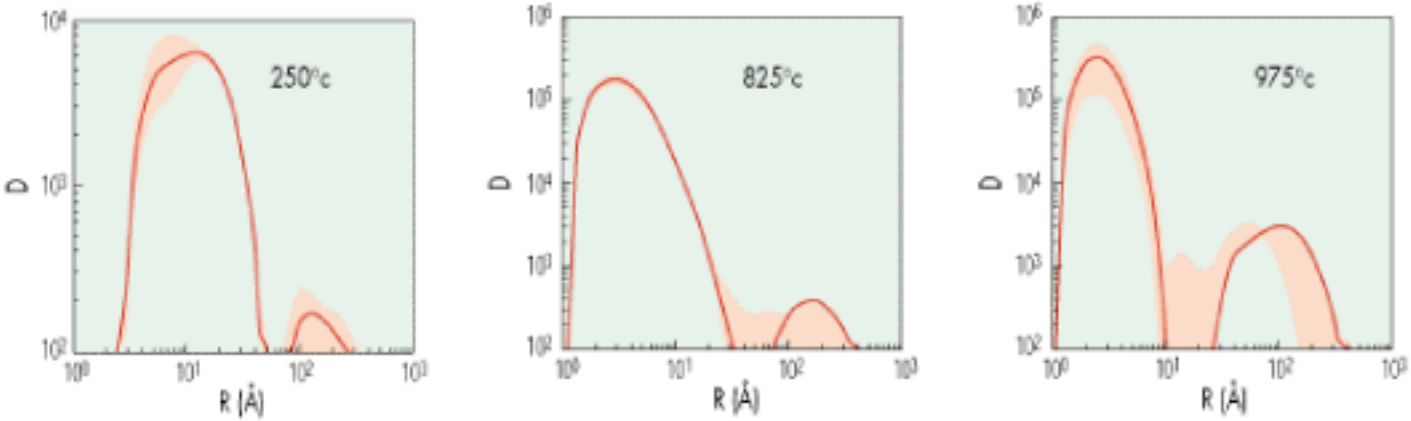


Fig. 2. Observed (●) and calculated (——) scattered intensity $I(Q)$ as a function of momentum transfer Q for a charged micellar dispersion: 0·03 mol dm^{-3} hexadecyltrimethylammonium chloride in D_2O at 313 K. The functions $P(Q)$ and $S(Q)$ are discussed in the text. (1 barn sterad^{-1} = 10^{-28} M^2 sterad^{-1}).

Size Distributions Have Been Measured for Helium Bubbles in Steel

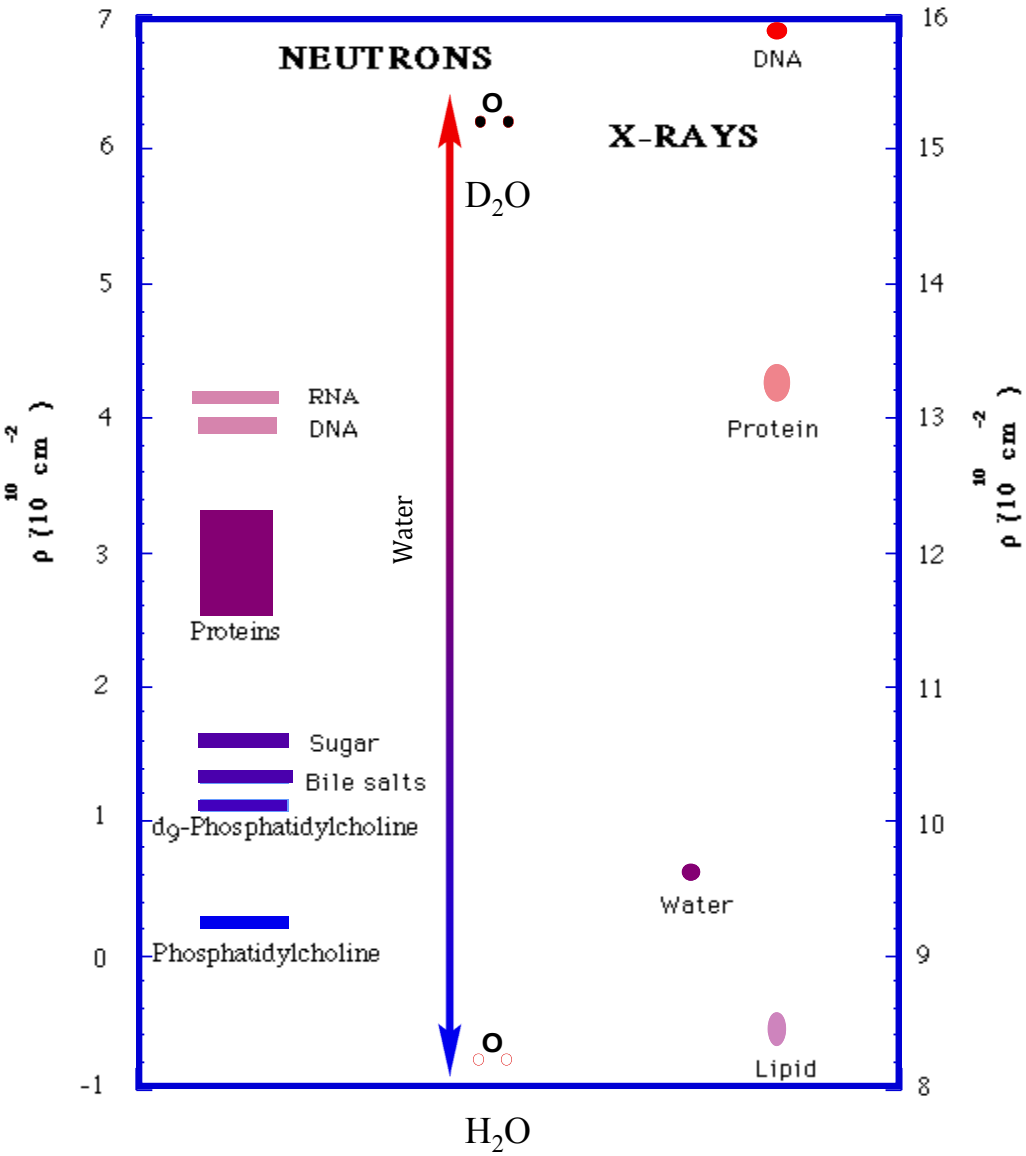
- The growth of He bubbles under neutron irradiation is a key factor limiting the lifetime of steel for fusion reactor walls
  - Simulate by bombarding steel with alpha particles
- TEM is difficult to use because bubble are small
- SANS shows that larger bubbles grow as the steel is annealed, as a result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

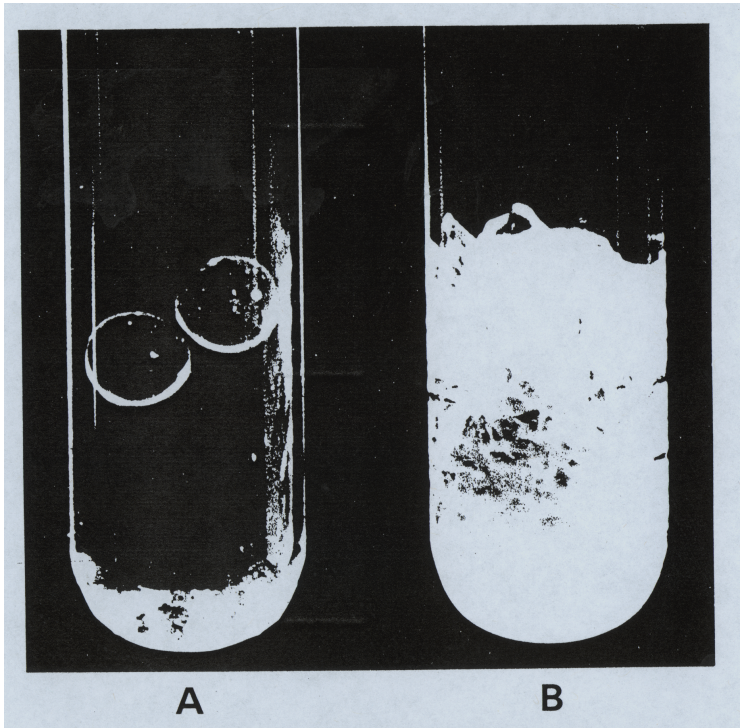




SANS gives bubble volume (arbitrary units on the plots) as a function of bubble size at different temperatures. Red shading is 80% confidence interval.

Contrast & Contrast Matching

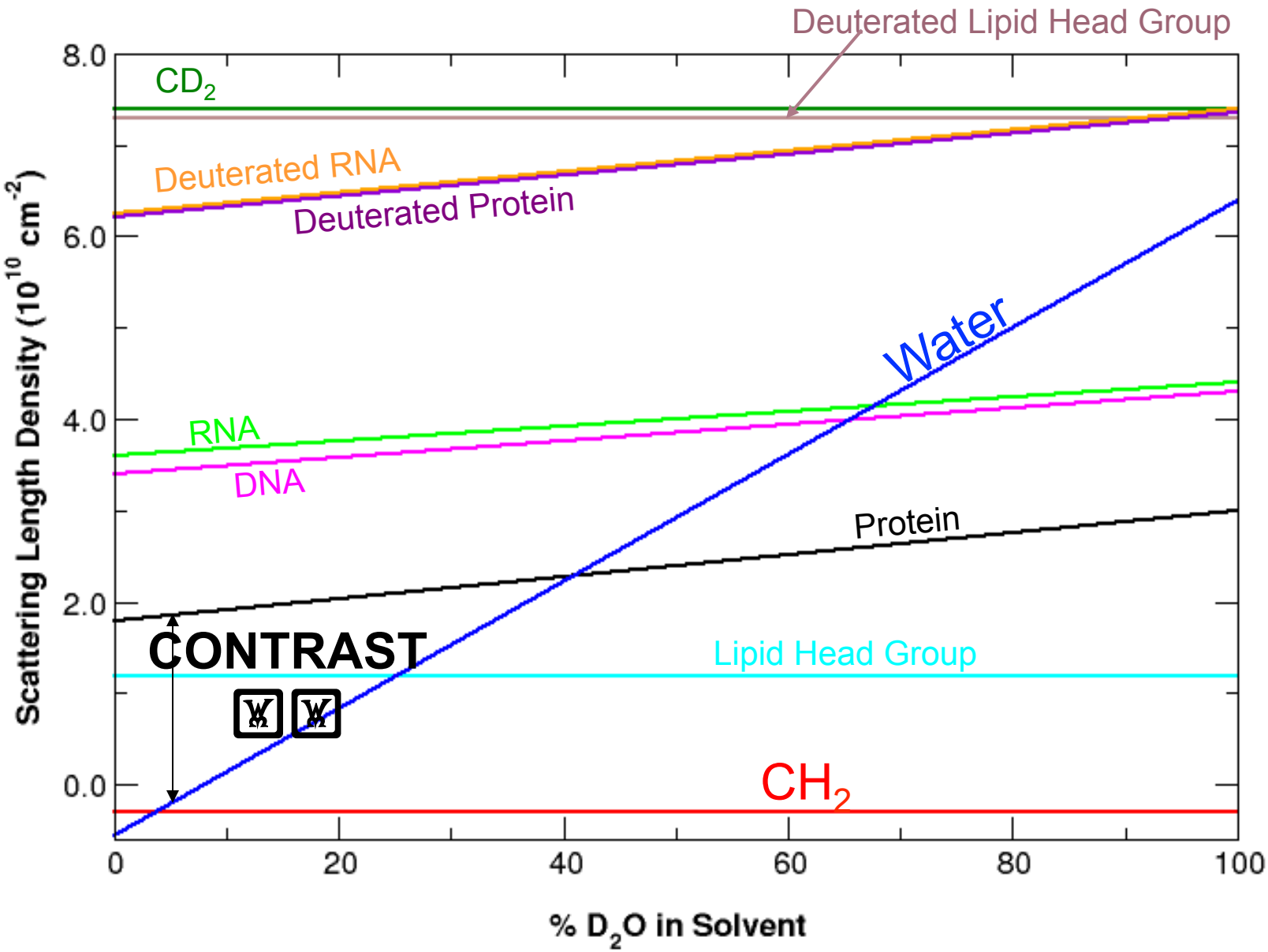




Both tubes contain borosilicate beads + pyrex fibers + solvent. (A) solvent refractive index matched to pyrex;. (B) solvent index different from both beads and fibers – scattering from fibers dominates

* Chart courtesy of Rex Hjelm

Contrast Variation

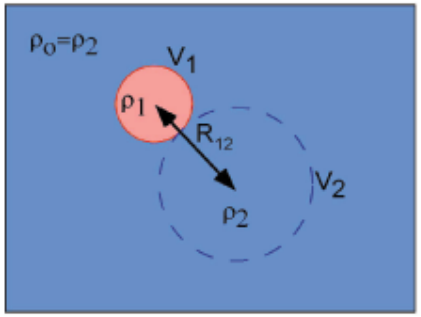


Isotopic Contrast for Neutrons

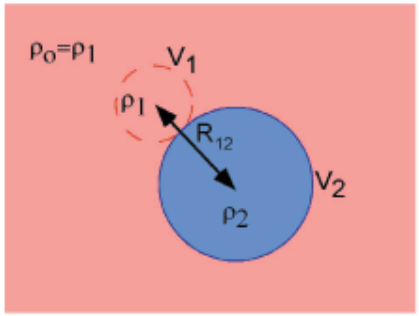
Hydrogen Isotope	Scattering Length b (fm)
^{1}H	-3.7409 (11)
^{2}D	6.674 (6)
^{3}T	4.792 (27)

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)

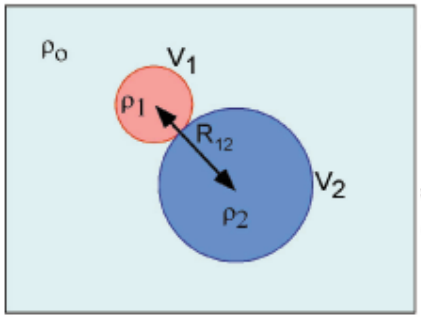
Using Contrast Variation to Study Compound Particles



$$I_1(Q) = (\rho_1 - \rho_2)^2 F_1^2$$



$$I_2(Q) = (\rho_2 - \rho_1)^2 F_2^2$$



$$I_3(Q) - \frac{(\rho_1 - \rho_o)^2}{(\rho_1 - \rho_2)^2} I_1(Q) - \frac{(\rho_2 - \rho_o)^2}{(\rho_1 - \rho_2)^2} I_2(Q)$$

$$= 2(\rho_1 - \rho_o)(\rho_2 - \rho_o) F_1 F_2 \frac{\sin(QR_{12})}{QR_{12}}$$

=0 at $Q = \pi/R_{12}$

Examples include nucleosomes (protein/DNA) and ribosomes (poteins/RNA)

$$I(Q) = \frac{N}{V} \left\langle \left| \Delta\rho_1 \int_{V_1} e^{i\vec{Q}.\vec{r}} d\vec{r}_1 + \Delta\rho_2 \int_{V_2} e^{i\vec{Q}.\vec{r}} d\vec{r}_2 \right|^2 \right\rangle$$

$$I(Q) = \Delta\rho_1^2 \left\langle |F_1(Q)|^2 \right\rangle + \Delta\rho_2^2 \left\langle |F_2(Q)|^2 \right\rangle +$$

$$\Delta\rho_1 \Delta\rho_2 |F_1(Q)||F_2(Q)| \frac{\sin(QR_{12})}{QR_{12}}$$

Viewgraph from Charles Glinka (NIST)

Porod Scattering

Let us examine the behavior of $|F(Q)|^2 (QR)^4$ at large values of Q for a spherical particle (i.e. Q >> 1/R where R is the sphere radius)

$$|F(Q)|^2 (QR)^4 = 9V^2 \left[\frac{\sin QR - QR.\cos QR}{(QR)^3} \right]^2 (QR)^4 = 9V^2 \left[\frac{\sin QR}{QR} - \cos QR \right]^2$$

$$\rightarrow 9V^2 \cos^2 QR \text{ as } Q \rightarrow \infty$$

$$= 9V^2 / 2 \text{ on average (the oscillations will be smeared out by resolution)}$$

Thus $\boxed{|F(Q)|^2 \rightarrow \frac{9V^2}{2(QR)^4} = \frac{2\pi A}{Q^4}}$ where A is the area of the sphere's surface.

This is Porod's law and holds as $Q \rightarrow \infty$ for any particle shape provided the particle surface is smooth.

Another way to obtain it is to expand $G(r) = 1 - ar + br^2 + ..$ [with $a = A/(2\pi V)$] at small r and to evaluate the form factor with this (Debye) form for the correlation function.

Scattering From Fractal Systems

- Fractals are systems that are "self-similar" under a change of scale I.e. R -> CR
- For a mass fractal the number of particles within a sphere of radius R is proportional to R^D where D is the fractal dimension

Thus

$$4\pi R^2 dR.G(R) = \text{number of particles between distance R and R} + \text{dR} = cR^{D-1}dR$$

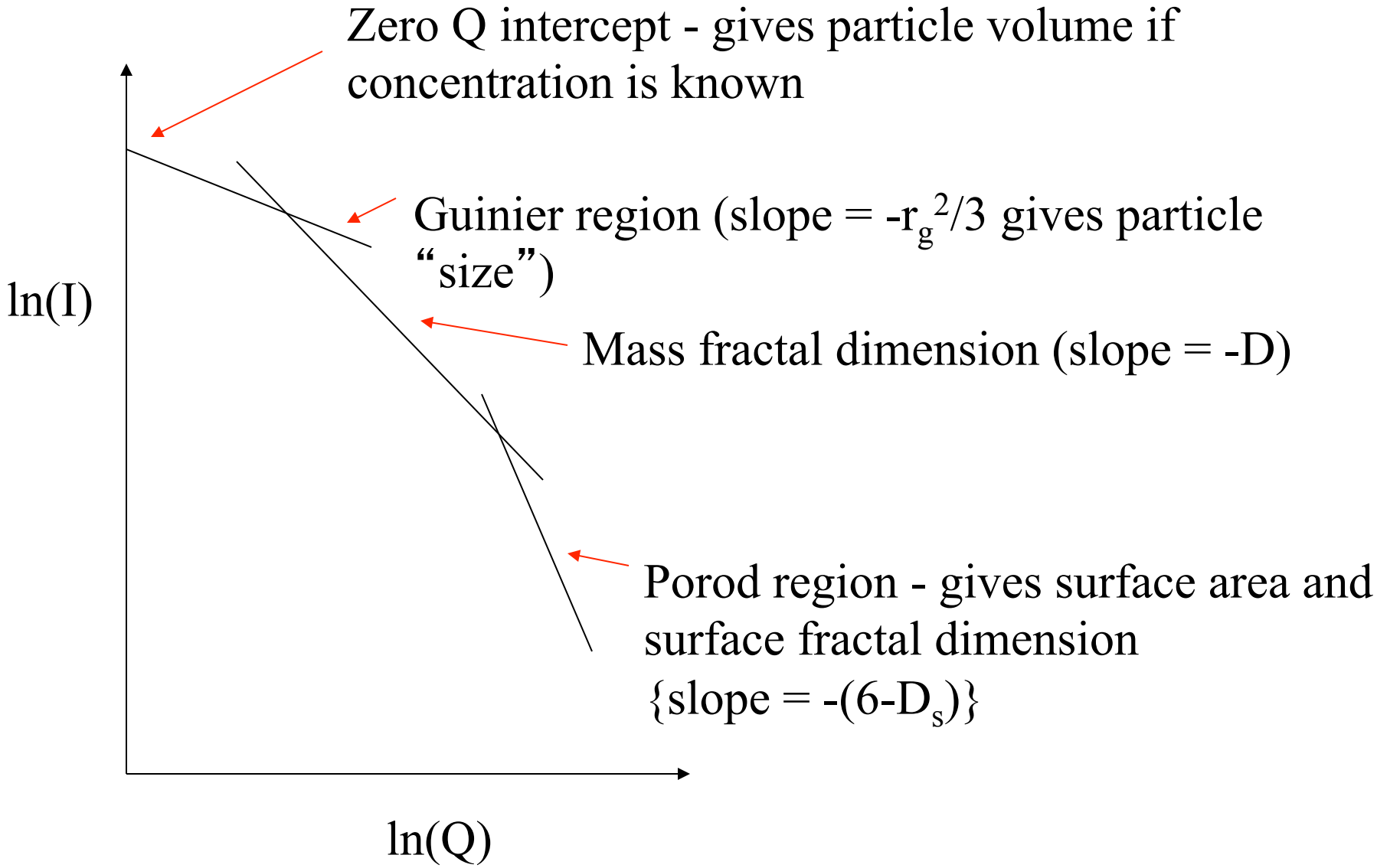
$$\therefore\ G(R) = (c/4\pi)R^{D-3}$$

$$\text{and}\ \ S(\vec{Q}) = \int d\vec{R}.e^{i\vec{Q}.\vec{R}}G(R) = \frac{2\pi}{Q}\int dR.R.\sin QR.(c/4\pi)R^{D-3}$$

$$= \frac{c}{2}\frac{1}{Q^D}\int dx.x^{D-2}.\sin x = \frac{const}{Q^D}$$

For a surface fractal, one can prove that $S(Q) \propto \dfrac{const}{Q^{6-D_s}}$ which reduces to the Porod form for smooth surfaces of dimension 2.

Typical Intensity Plot for SANS From Disordered Systems

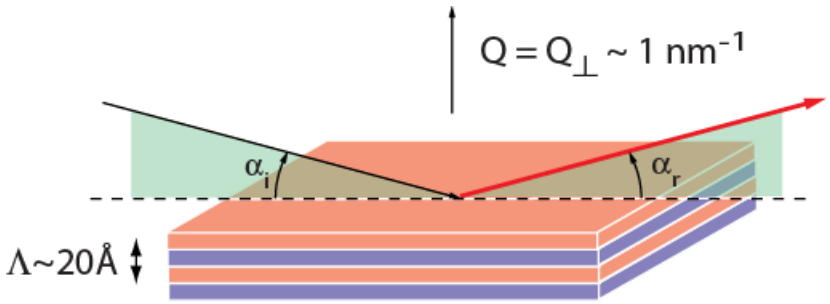


Surface Reflection Is Very Different From Most Neutron and X-ray Scattering

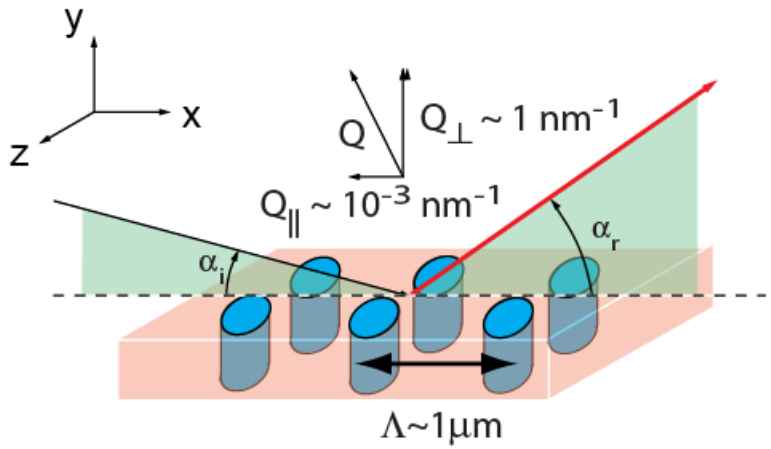
- We worked out the cross section by adding scattering from different scattering centers
  - We ignored double scattering processes because these are usually very weak
- This approximation is called the Born Approximation

- Below an angle of incidence called the critical angle, neutrons and x-rays are perfectly reflected from a smooth surface
  - This is NOT weak scattering and the Born Approximation is not applicable to this case
- Specular reflection is used:
  - In neutron guides and x-ray mirrors
  - In multilayer monochromators and neutron polarizers
  - To probe surface and interface structure in layered systems

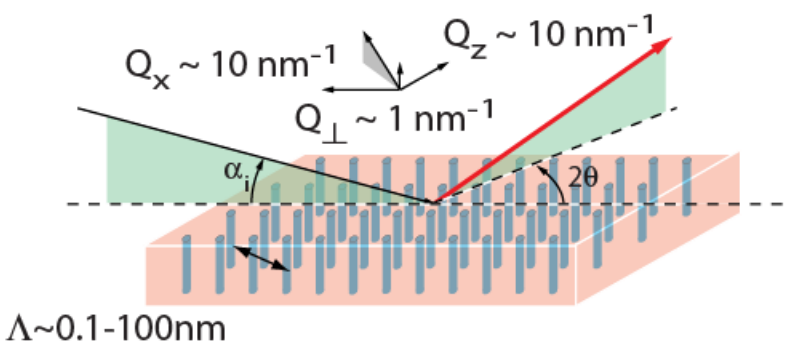
Various forms of small (glancing) angle neutron reflection



Specular reflectometry
Depth profiles
(nuclear and/or magnetic)



Off-specular (diffuse) scattering
In-plane correlated roughness
Magnetic stripes
Phase separation (polymers)



Glancing incidence diffraction
Ordering in liquid crystals
Atomic structures near surfaces
Interactions among nanodots

Viewgraph from M. R. Fitzsimmons

Only Neutrons With Very Low Velocities Perpendicular to a Surface Are Reflected

$k / k_0 = n$

The surface cannot change the neutron velocity parallel to the surface so:

$k_0 \cos\alpha = k \cos\alpha' = k_0 n \cos\alpha'$ i.e $n = \cos\alpha / \cos\alpha'$

Neutrons obey Snell's Law

Since $k^2 = k_0^2 - 4\pi\rho$ $k^2(\cos^2\alpha' + \sin^2\alpha') = k_0^2(\cos^2\alpha + \sin^2\alpha) - 4\pi\rho$

i.e. $k^2 \sin^2\alpha' = k_0^2 \sin^2\alpha - 4\pi\rho$ or $k_z^2 = k_{0z}^2 - 4\pi\rho$

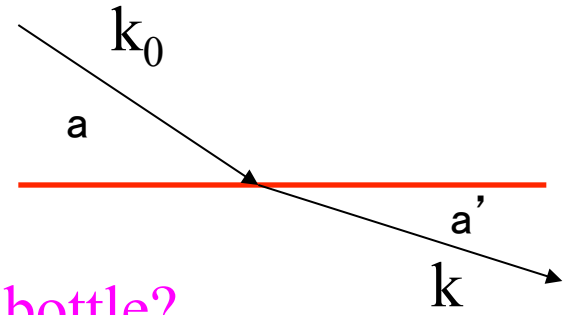
The critical value of k_{0z} for total external reflection is $k_{0z} = \sqrt{4\pi\rho}$

For quartz $k_{0z}^{critical} = 2.05x10^{-3}$ A^{-1}

$(2\pi/\lambda)\sin\alpha_{\text{critical}} = k_{0z}^{critical} \Rightarrow$

$\alpha_{\text{critical}}(^o) \approx 0.02\lambda(A)$ for quartz

Note: $\alpha_{\text{critical}}(^o) \approx 0.1\lambda(A)$ for nickel



How do we make a neutron bottle?

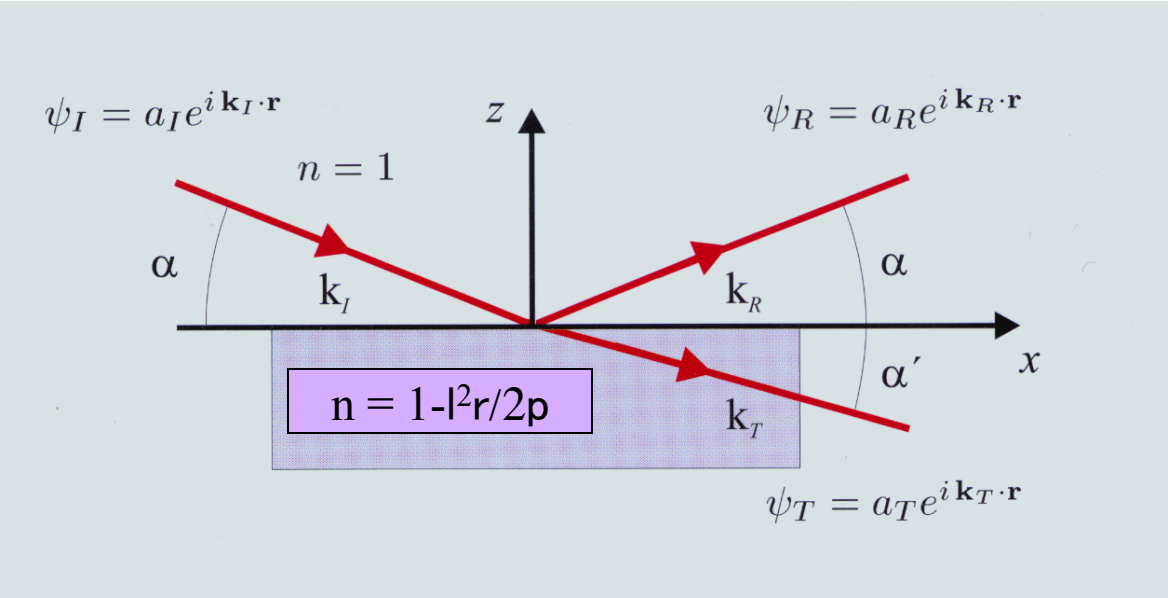
Reflection of Neutrons by a Smooth Surface: Fresnel's Law

continuity

of ψ & $\dot{\psi}$ at $z = 0 \Rightarrow$

$$a_I + a_R = a_T \qquad (1)$$

$$a_I \vec{k}_I + a_R \vec{k}_R = a_T \vec{k}_T$$



components perpendicular and parallel to the surface:

$$a_I k \cos\alpha + a_R k \cos\alpha = a_T n k \cos\alpha' \qquad (2)$$

$$-(a_I - a_R) k \sin\alpha = -a_T n k \sin\alpha' \qquad (3)$$

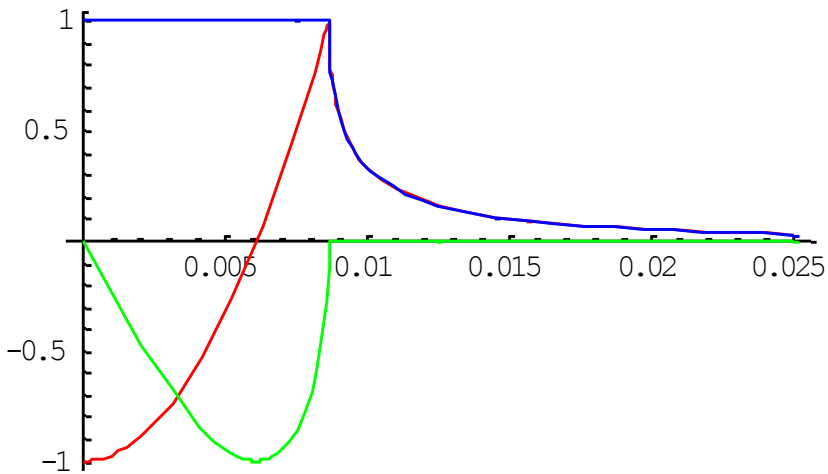
(1) & (2) => Snell's Law: $\boxed{\cos\alpha = n \cos\alpha'}$

$$(1)\ \&\ (3) \Rightarrow \frac{(a_I - a_R)}{(a_I + a_R)} = n \frac{\sin\alpha'}{\sin\alpha} \approx \frac{\sin\alpha'}{\sin\alpha} = \frac{k_{Tz}}{k_{Iz}}$$

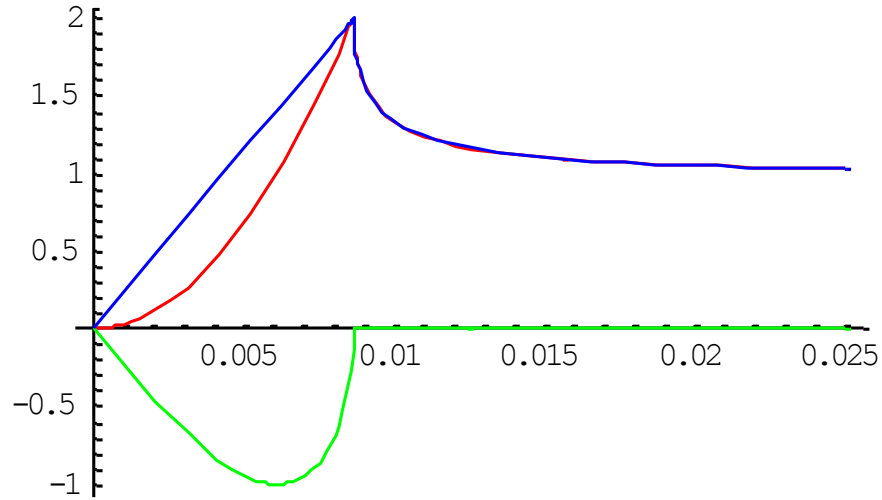
so reflectance is given by $\boxed{r = a_R / a_I = (k_{Iz} - k_{Tz})/(k_{Iz} + k_{Tz})}$

What do the Amplitudes a_R and a_T Look Like?

- For reflection from a flat substrate, both a_R and a_T are complex when $k_0 < 4pr$ I.e. below the critical edge. For $a_I = 1$, we find:



Real (red) & imaginary (green) parts of a_R plotted against k_0. The modulus of a_R is plotted in blue. The critical edge is at $k_0 \sim 0.009$ A^{-1} . Note that the reflected wave is completely out of phase with the incident wave at $k_0 = 0$



Real (red) and imaginary (green) parts of a_T. The modulus of a_T is plotted in blue. Note that a_T tends to unity at large values of k_0 as one would expect and that the transmitted intensity peaks at the critical edge.

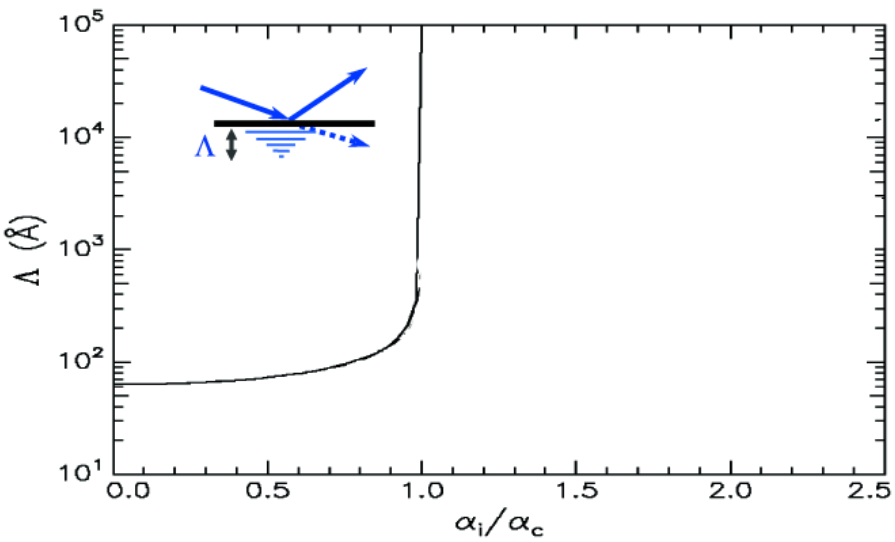
Penetration Depth

- In the absence of absorption, the penetration depth becomes infinite at large enough angles

- Because k_z is imaginary below the critical edge (recall that $k_z^2 = k_{0z}^2 - 4\pi\rho$), the transmitted wave is evanescent

- The penetration depth $\Lambda = 1/\mathrm{Im}(k)$

- Around the critical edge, one may tune the penetration depth to probe different depths in the sample



Measured Reflectivity

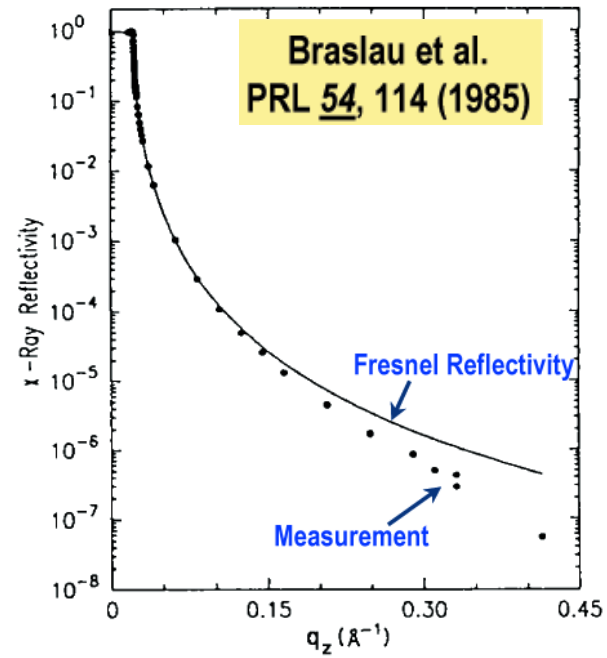
- We do not measure the reflectance, r, but the reflectivity, R given by:

  R = <u># of neutrons reflected at Qz</u> = r.r*
  # of incident neutrons

  i.e., just as in diffraction, we lose phase information

- Notice, also, that the measurement averages the reflectivity over the surface of the sample: i.e. measured reflectivity depends on

$$\bar{\rho}(z) = \frac{1}{S}\int dx \int dy \rho(x,y,z)$$



Measured and Fresnel reflectivities for water – difference is due to surface roughness

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

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

Minus!!

Dispersion

Absorption

Refractive Index: X-Rays

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

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

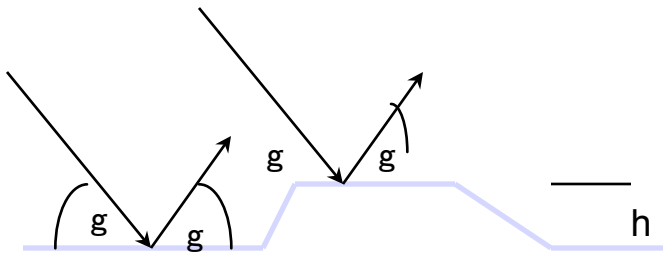
	$r_e\varrho\,(10^{10}\mathrm{cm}^{-2})$	$\delta(10^{-6})$	$\mu\,(\mathrm{cm}^{-1})$	$\alpha_c(^\circ)$
Vacuum	0	0	0	0
PS $(C_8H_8)_n$	9.5	3.5	4	0.153
PMMA $(C_5H_8O_2)_n$	10.6	4.0	7	0.162
PVC $(C_2H_3Cl)_n$	12.1	4.6	86	0.174
PBrS $(C_8H_7Br)_n$	13.2	5.0	97	0.181
Quartz (SiO_2)	18.0–19.7	6.8–7.4	85	0.21–0.22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

Electron Density *Profile* !

E = 8 keV λ = 1.54 Å

When Does a "Rough" Surface Scatter Diffusely?

- Rayleigh criterion

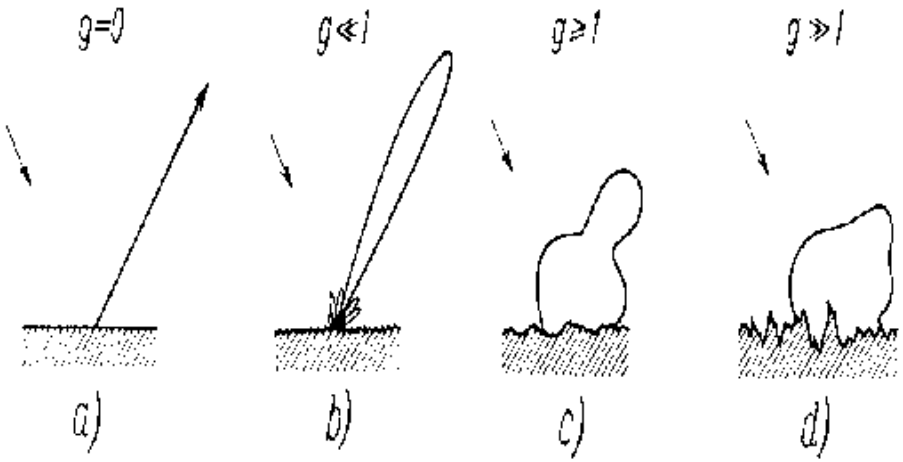


path difference: $\Delta r = 2\,h \sin g$

phase difference: $\Delta f = (4ph/l) \sin g$

boundary between rough and smooth: $\Delta f = p/2$

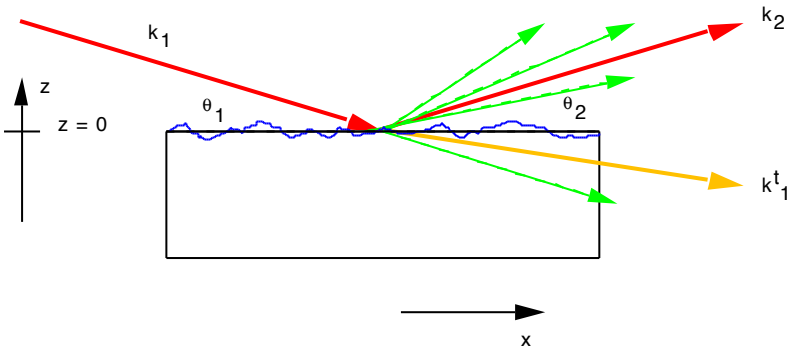
that is $h < l/(8 \sin g)$ **for a smooth surface**



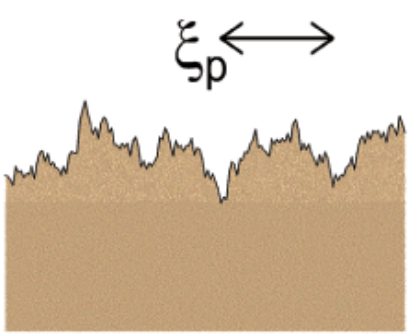
where $g = 4\,p\,h \sin g / l = Q_z\,h$

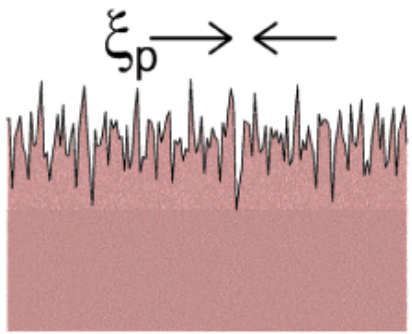
Surface Roughness

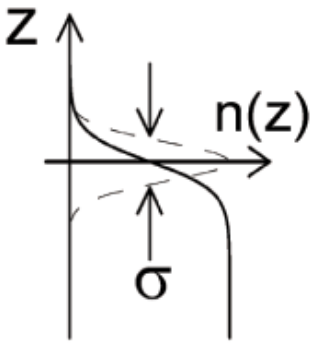
- Surface roughness causes diffuse (non-specular) scattering and so reduces the magnitude of the specular reflectivity



- The way in which the specular reflection is damped depends on the length scale of the roughness in the surface as well as on the magnitude and distribution of roughness







Note that roughness introduces a SLD profile averaged over the sample surface

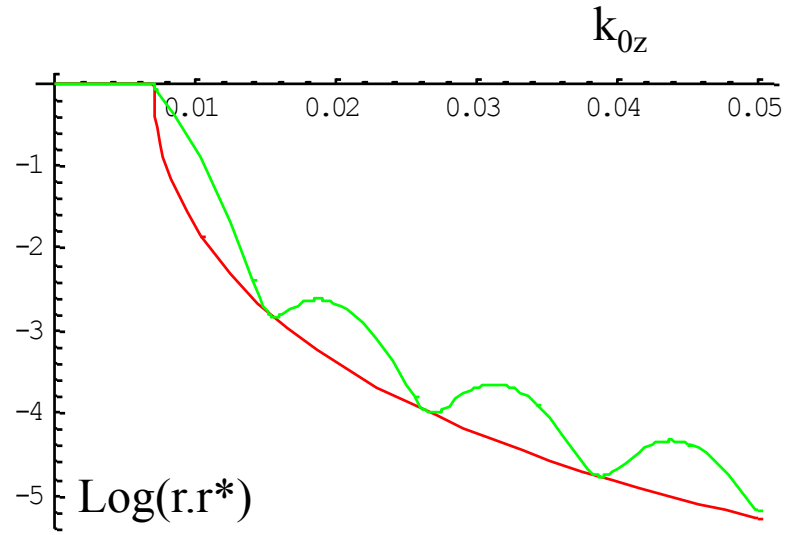
"sparkling sea" model -- specular from many facets

each piece of surface scatters indepedently -- Nevot Croce model

$$R = R_F e^{-2k_{Iz}k_{1z}^{t}\sigma^2}$$

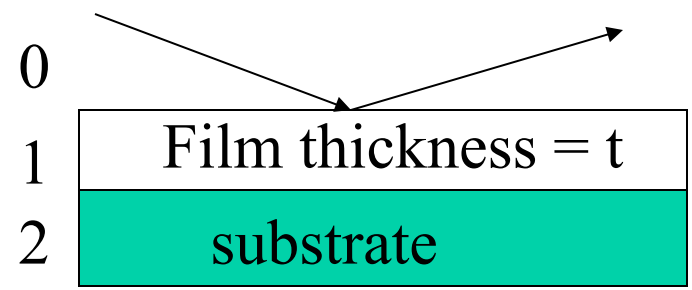
Fresnel's Law for a Thin Film

- $r=(k_{0z}-k_{1z})/(k_{1z}+k_{0z})$ is Fresnel's law
- Evaluate with $r=4.10^{-6}$ A^{-2} gives the red curve with critical wavevector given by $k_{0z} = (4pr)^{1/2}$
- If we add a thin layer on top of the substrate we get interference fringes & the reflectance is given by:



$$r = \frac{r_{01} + r_{12} e^{i2k_{1z}t}}{1 + r_{01} r_{12} e^{i2k_{1z}t}}$$

and we measure the reflectivity R = r.r*



- If the film has a higher scattering length density than the substrate we get the green curve (if the film scattering is weaker than the substance, the green curve is below the red one)
- The fringe spacing at large k_{0z} is ~ p/t (a 250 A film was used for the figure)

Multiple Layers – Parratt Iteration (1954)

- The same method of matching wavefunctions and derivatives at interfaces can be used to obtain an expression for the reflectivity of multiple layers

$$X_j = \frac{R_j}{T_j} = e^{-2ik_{z,j}z_j} \frac{r_{j,j+1} + X_{j+1} e^{2ik_{z,j+1}z_j}}{1 + r_{j,j+1} X_{j+1} e^{2ik_{z,j+1}z_j}}$$

where $r_{j,j+1} = \dfrac{k_{z,j} - k_{z,j+1}}{k_{z,j} + k_{z,j+1}}$

Start iteration with

$R_{N+1} = X_{N+1} = 0$ and $T_1 = 1$

(i.e. nothing coming back from inside substrate & unit amplitude incident wave)

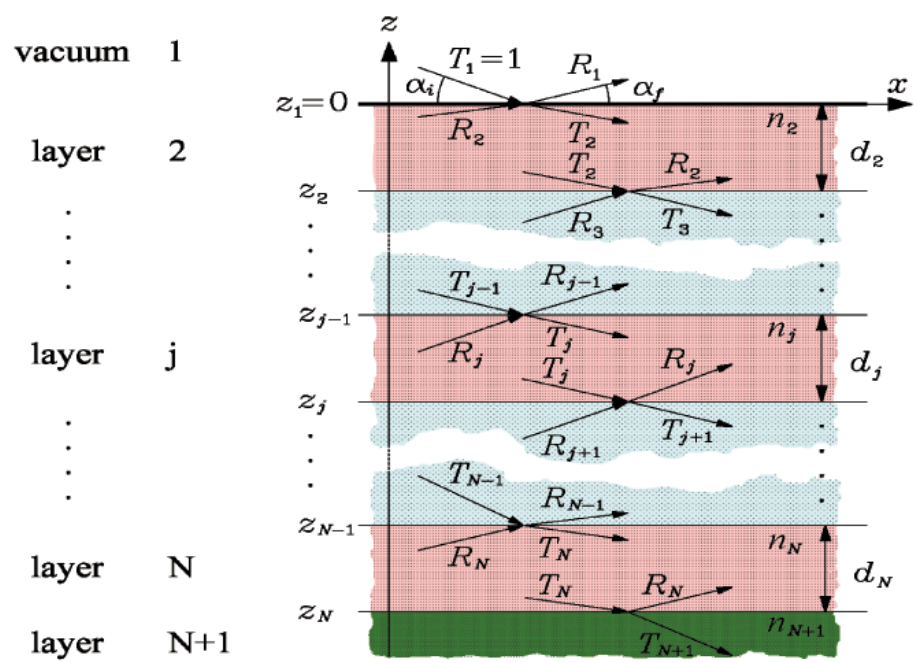


Image from M. Tolan

Dealing with Complex Density Profiles

- Any SLD depth profile can be "chopped" into slices
- The Parratt formalism allows the reflectivity to be calculated
- A thickness resolution of 1 Å is adequate – this corresponds to a value of Q_z where the reflectivity has dropped below what neutrons can normally measure
- Computationally intensive!!

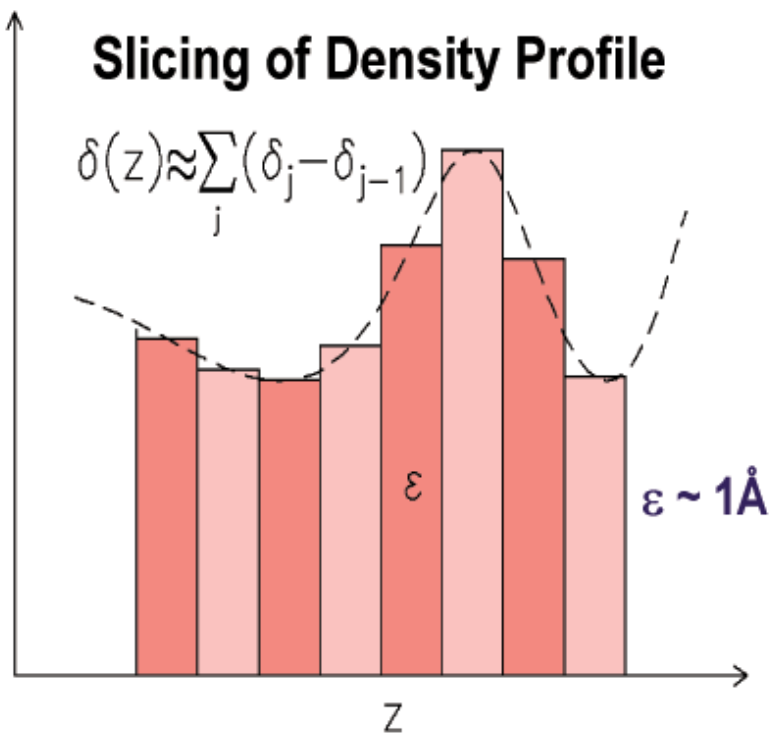


Image from M. Tolan

Kinematic (Born) Approximation

- We defined the scattering cross section in terms of an incident plane wave & a **weakly** scattered spherical wave (called the Born Approximation)
- This picture is not correct for surface reflection, except at large values of Q_z
- For large Q_z, one may use the definition of the scattering cross section to calculate R for a flat surface (in the Born Approximation) as follows:

$$R = \frac{\text{number of neutrons reflected by a sample of size } L_x L_y}{\text{number of neutrons incident on sample } (= \Phi L_x L_y \sin\alpha)}$$

$$= \frac{\sigma}{L_x L_y \sin\alpha} = \frac{1}{L_x L_y \sin\alpha}\int \frac{d\sigma}{d\Omega} d\Omega = \frac{1}{L_x L_y \sin\alpha}\int \frac{d\sigma}{d\Omega}\frac{dk_x dk_y}{k_0^2 \sin\alpha}$$

because $k_x = k_0 \cos\alpha$ so $dk_x = -k_0 \sin\alpha \, d\alpha.$

From the definition of a cross section we get for a smooth substrate:

$$\frac{d\sigma}{d\Omega} = \rho^2 \int d\vec{r} \int d\vec{r}\,' e^{i\vec{Q}.(\vec{r}-\vec{r}\,')} = \rho^2 \frac{4\pi^2}{Q_z^2} L_x L_y \delta(Q_x)\delta(Q_y) \text{ so } \boxed{R = 16\pi^2 \rho^2 / Q_z^4}$$

It is easy to show that this is the same as the Fresnel form at large Q_z

Reflection by a Graded Interface

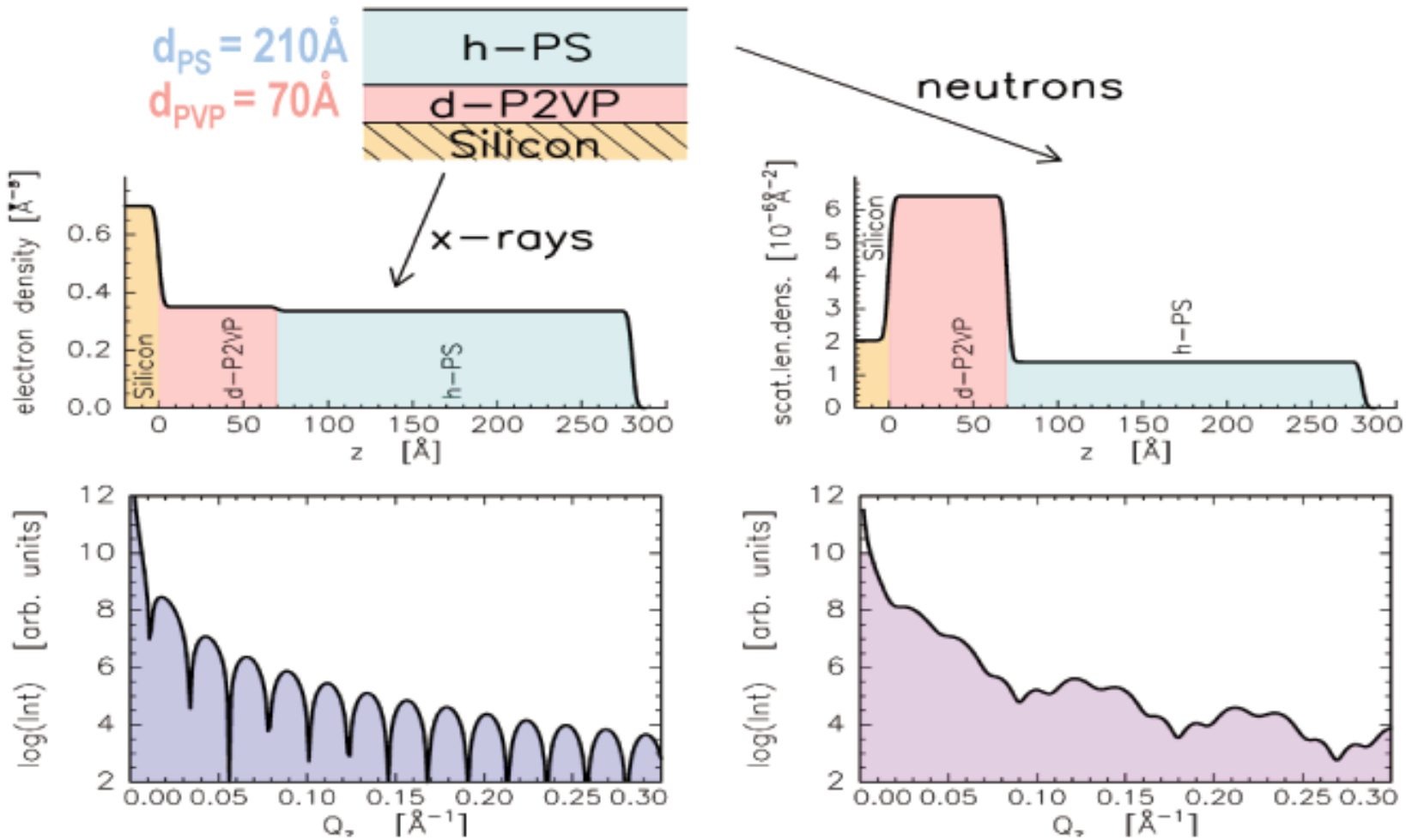
Repeating the bottom line of the previous viewgraph but keeping the z-dependence of ρ gives: $R = \frac{16\pi^2}{Q_z^2}\left|\int \rho(z)e^{iQ_z z}dz\right|^2 = \frac{16\pi^2}{Q_z^4}\left|\int \frac{d\rho(z)}{dz}e^{iQ_z z}dz\right|^2$ where the second equality follows after intergrating by parts.

If we replace the prefactor by the Fresnel reflectivity R_F, we get the right answer for a smooth interface, as well as the correct form at large Q_z

$$\boxed{R = R_F\left|\int \frac{d\rho(z)}{dz}e^{iQ_z z}dz\right|^2}$$

This can be solved analytically for several convenient forms of $d\rho/dz$ such as $1/\cosh^2(z)$. This approximate equation illustrates an important point: reflectivity data cannot be inverted uniquely to obtain $\rho(z)$, because we generally lack important phase information. This means that models refined to fit reflectivity data must have good physical justification.

Comparison of Neutron and X-Ray Reflectivity



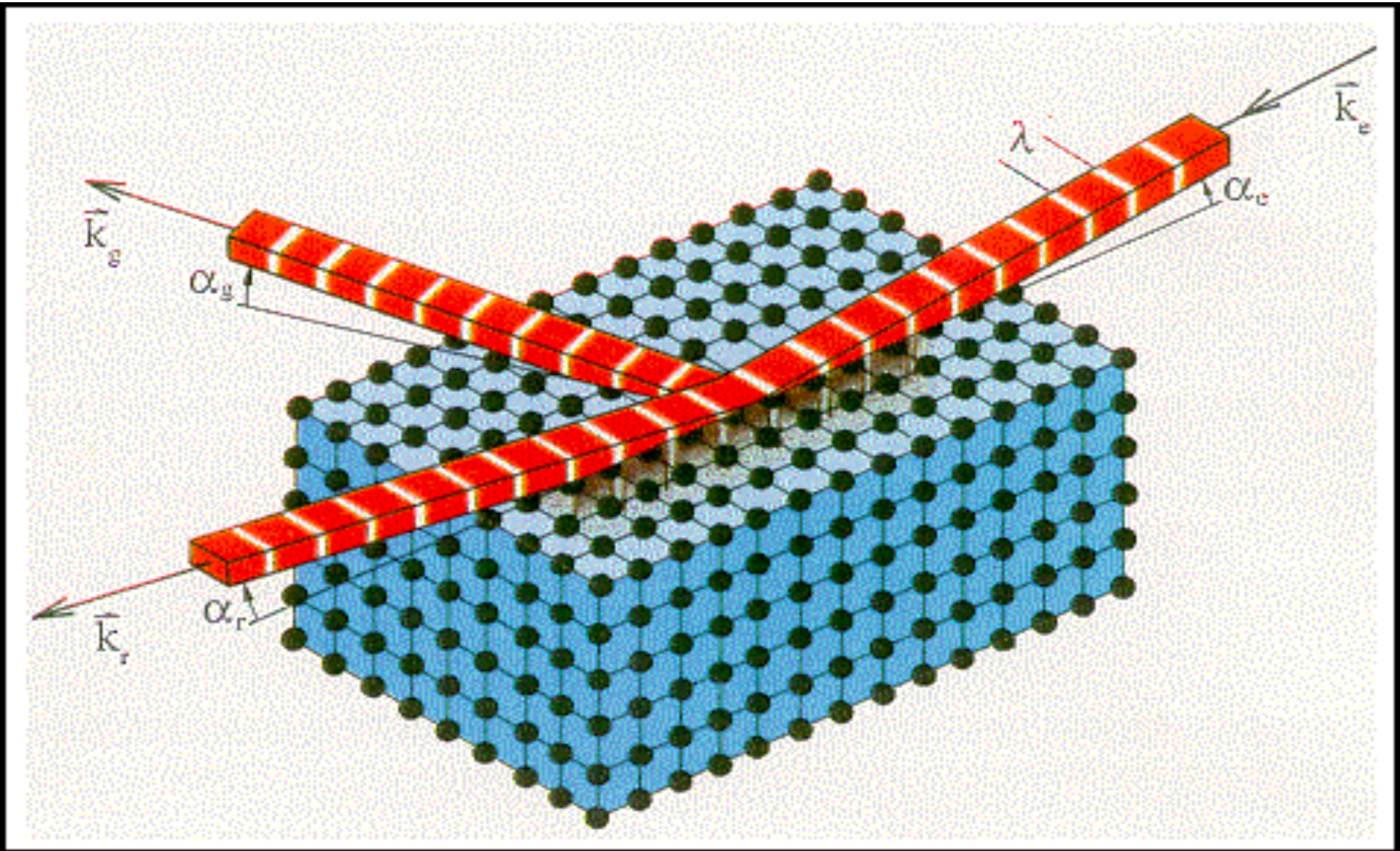
Neutrons often provide better contrast and don't damage samples
X-rays provide better Q resolution and higher Q values

Viewgraph courtesy of M. Tolan

The Goal of Reflectivity Measurements Is to Infer a Density Profile Perpendicular to a Flat Interface

- In general the results are not unique, but independent knowledge of the system often makes them very reliable
- Frequently, layer models are used to fit the data
- Advantages of neutrons include:
  - Contrast variation (using H and D, for example)
  - Low absorption – probe buried interfaces, solid/liquid interfaces etc
  - Non-destructive
  - Sensitive to magnetism
  - Thickness length scale 10 – 5000 Å
- Issues include
  - Generally no unique solution for the SLD profile (use prior knowledge)
  - Large samples (~10 cm^2) with good scattering contrast are needed

Grazing-Incidence-Diffraction

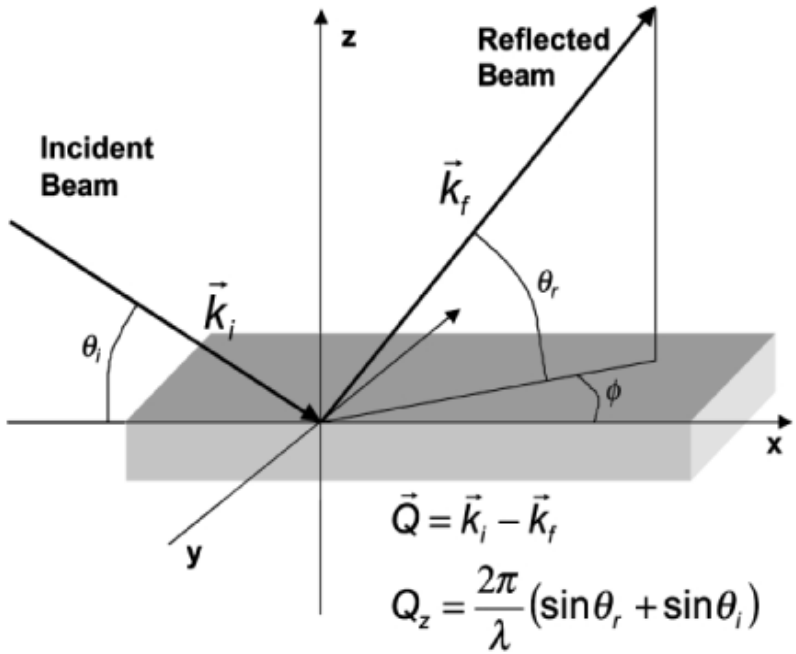


What do Specular and Off-specular scattering measure?

- **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.

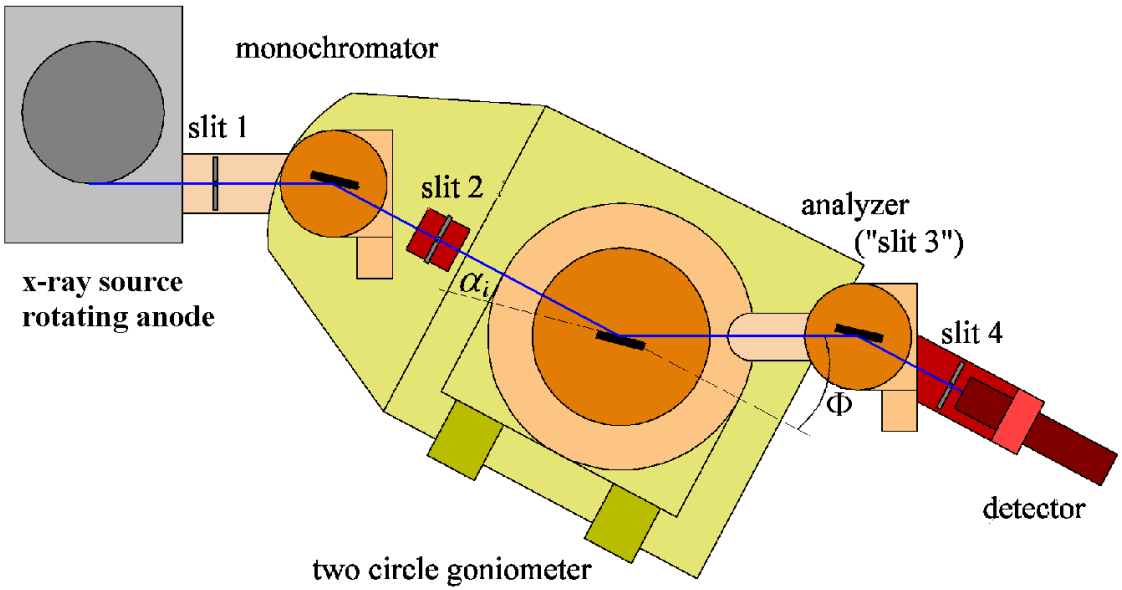
Vector Diagram for Q in GISAXS



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

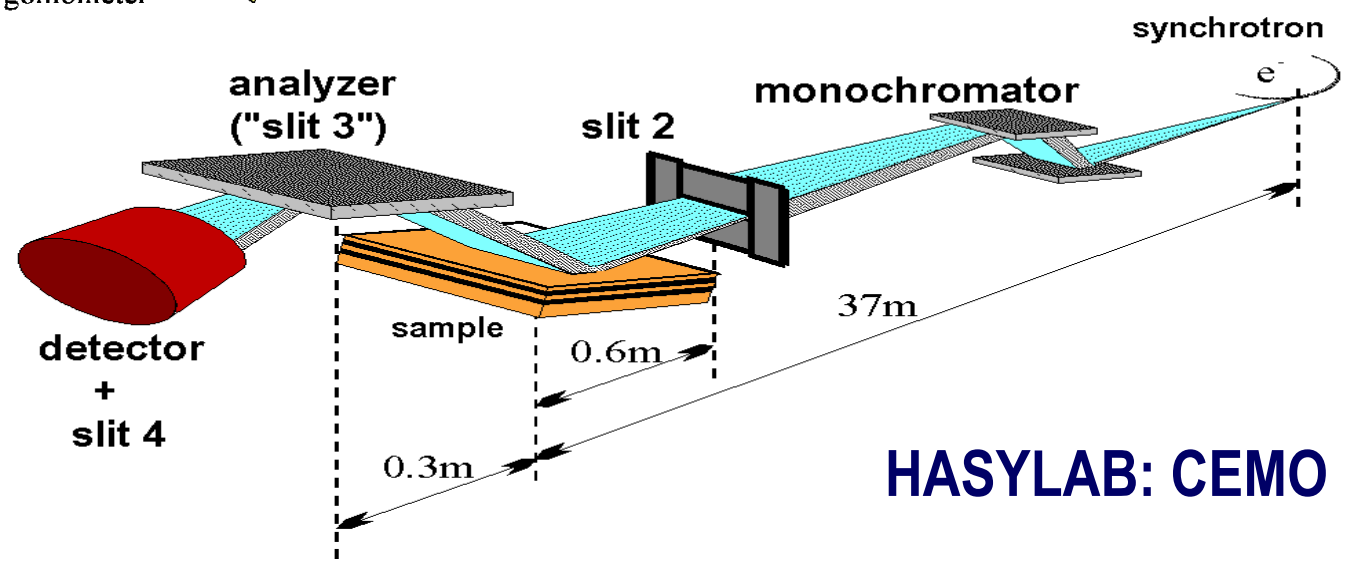
$Q_x = (2\pi/\lambda)(\mathrm{Cos}\ \theta_f \mathrm{Cos}\phi - \mathrm{Cos}\ \theta_i)$

X-Ray Reflectometers



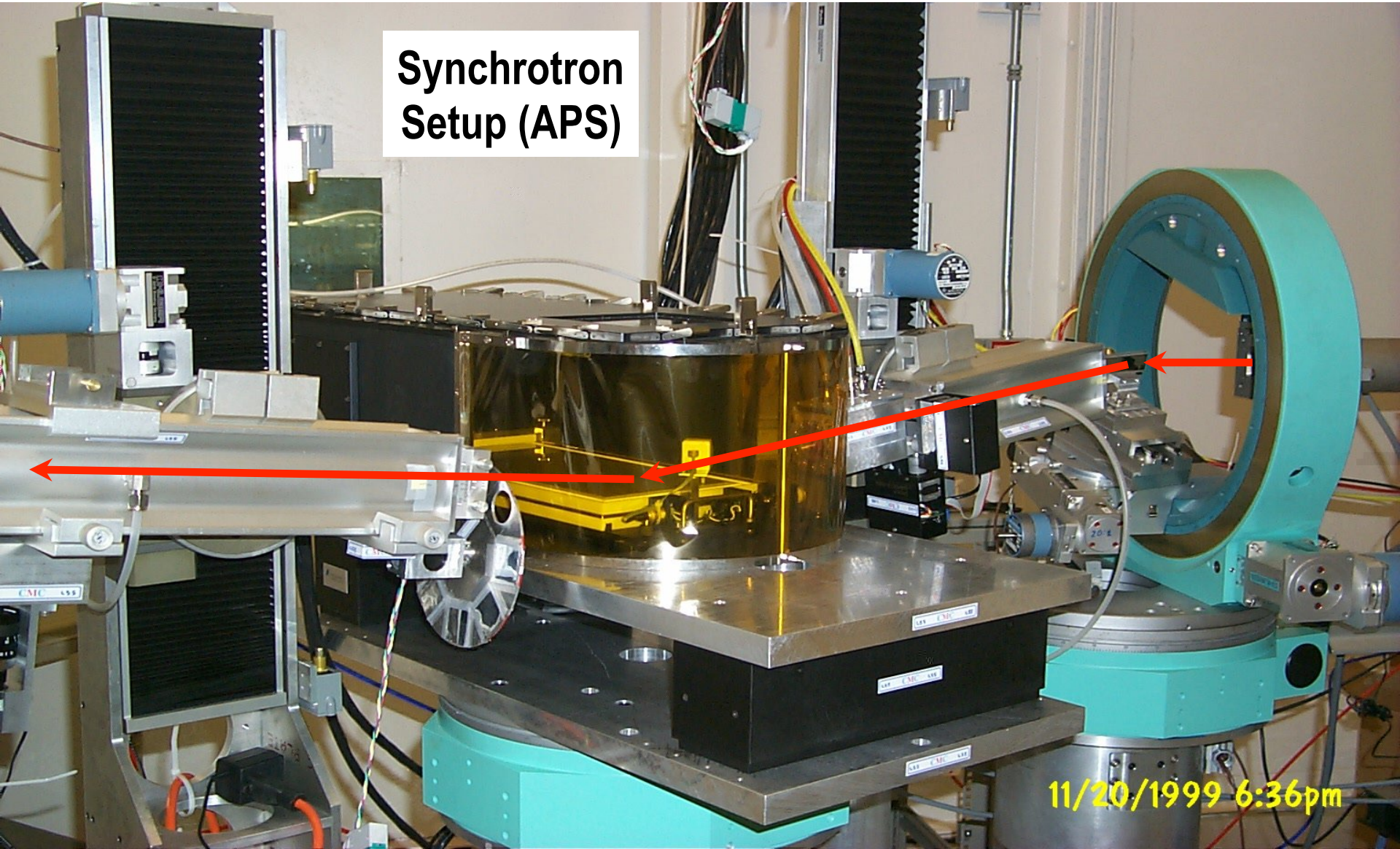
Laboratory Setup

Synchrotron Setup

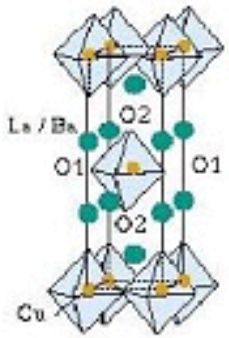


HASYLAB: CEMO

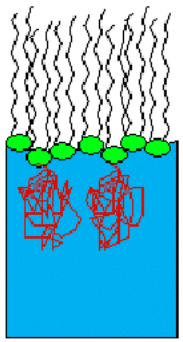
Reflectivity from Liquids I

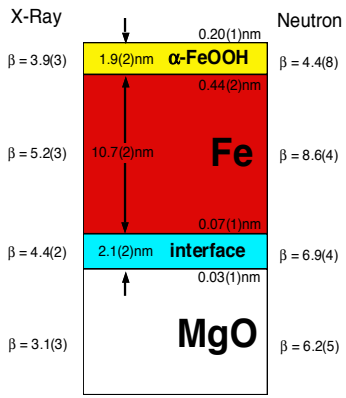


We Have Seen How Neutron Scattering Can Determine a Variety of Structures

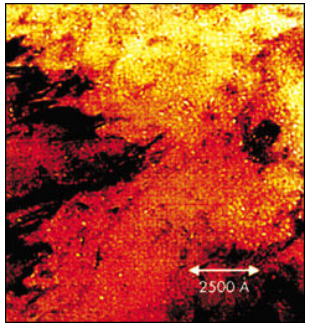


crystals

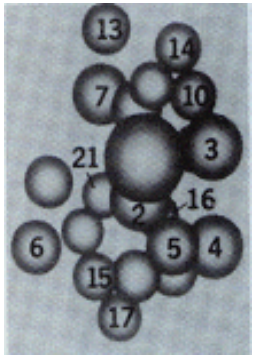




surfaces & interfaces

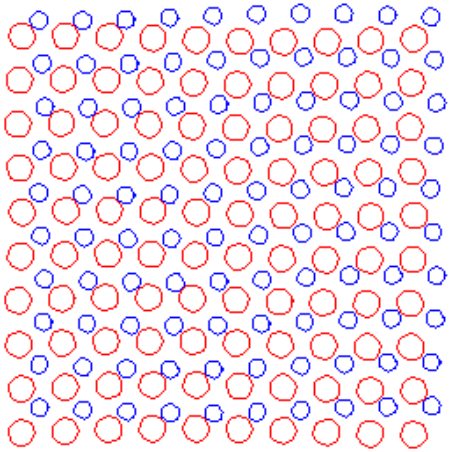


disordered/fractals



biomachines

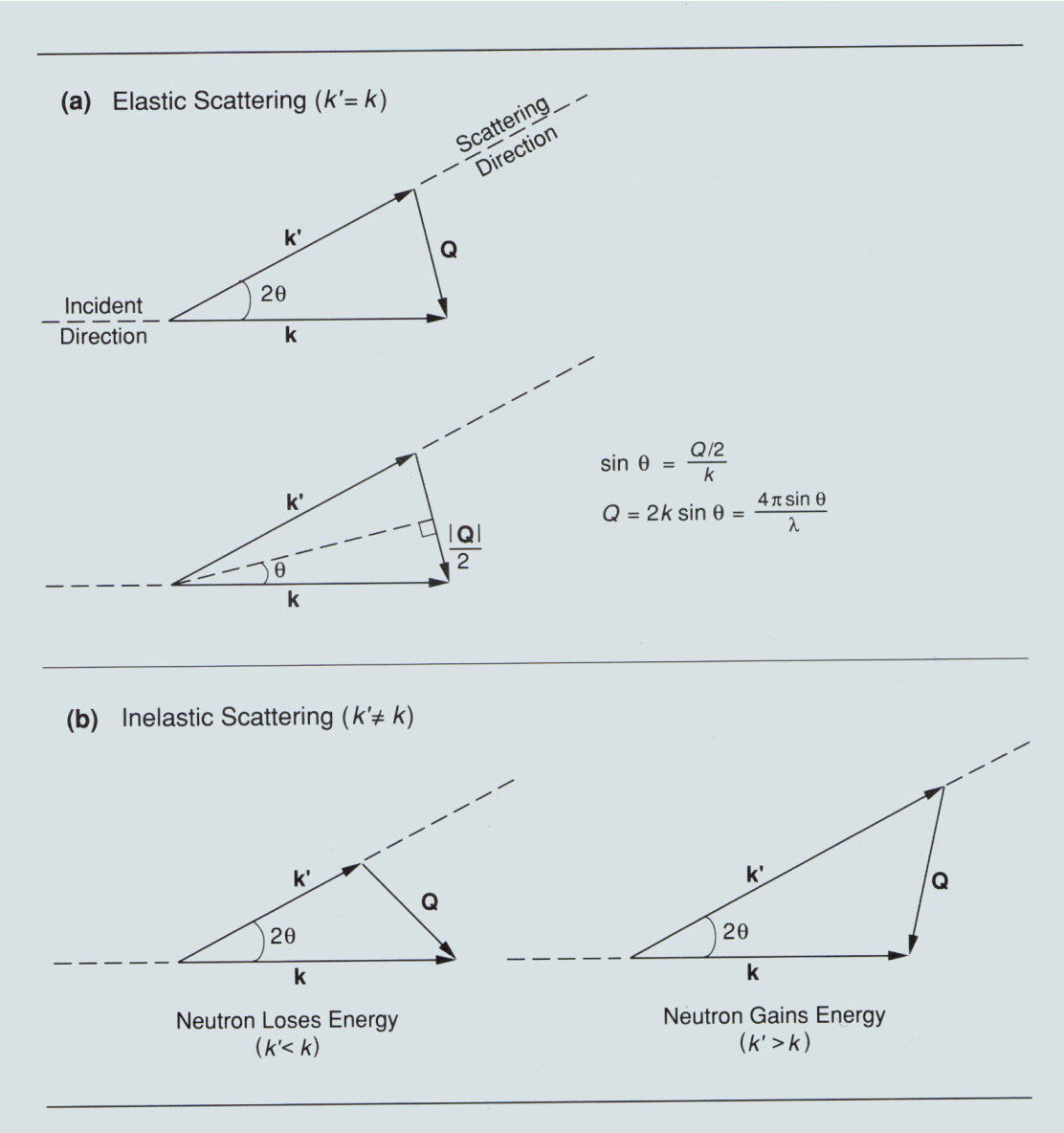
but what happens when the atoms are moving?



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

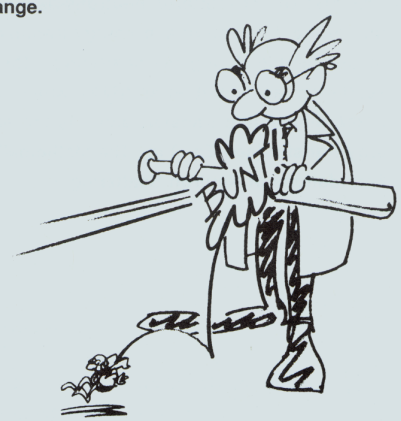
These are the types of questions answered by inelastic neutron scattering

Neutrons can also gain or lose energy in the scattering process: this is called inelastic scattering



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

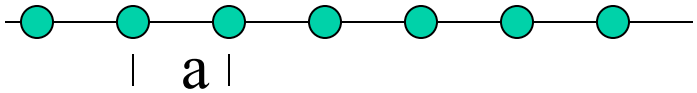
- The intensity of elastic, coherent neutron scattering is proportional to the spatial Fourier Transform of the Pair Correlation Function, G(r) I.e. the probability of finding a particle at position r if there is simultaneously a particle at r=0

- 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

Diffraction from a Frozen Wave

- Recall that $S(\vec{Q}) = \frac{1}{N}\left|\sum_k e^{i\vec{Q}.\vec{r}_k}\right|^2$

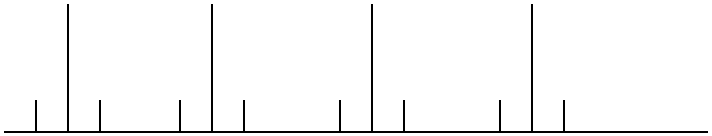


- We know that for a linear chain of "atoms" along the x axis, $S(Q_x)$ is just a series of delta function reciprocal lattice planes at $Q_x = n2p/a$, where a is the separation of atoms

What happens if we put a "frozen" wave in the chain of atoms so that the atomic positions are $x_p = pa + u\cos kpa$ where p is an integer and u is small?

$$S(Q) = \left|\sum_p e^{iQpa} e^{iQu\cos kpa}\right|^2 \approx \left|\sum_p e^{iQpa}(1 + iQu[e^{ikpa} + e^{-ikpa}])\right|^2$$

$$\approx \left|\sum_p e^{iQpa} + iQu[e^{i(Q+k)pa} + e^{i(Q-k)pa}]\right|^2$$



so that in addition to the Bragg peaks we get weak satellites at $Q = G \pm k$

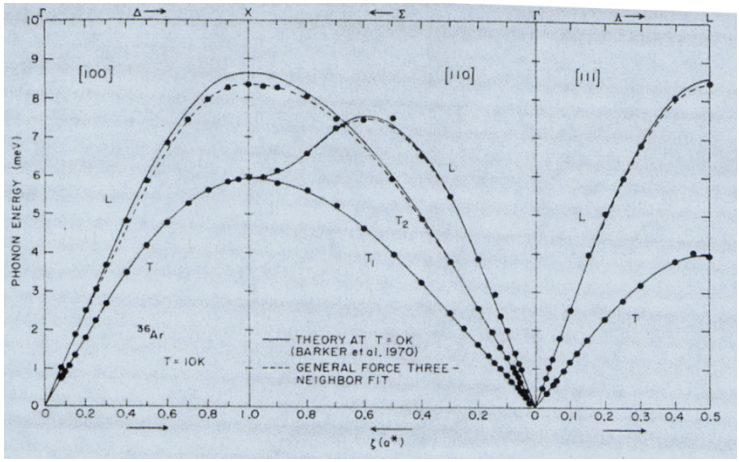
What Happens if the Wave Moves?

- If the wave moves through the chain, the scattering still occurs at wavevectors G + k and G – k but now the scattering is inelastic

- For quantized lattice vibrations, called phonons, the energy change of the neutron is $\hbar\omega$ where w is the vibration frequency.

- In a crystal, the vibration frequency at a given value of k (called the phonon wavevector) is determined by interatomic forces. These frequencies map out the so-called phonon dispersion curves.

- Different branches of the dispersion curves correspond to different types of motion



phonon dispersion in ^{36}Ar

A Phonon is a Quantized Lattice Vibration

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

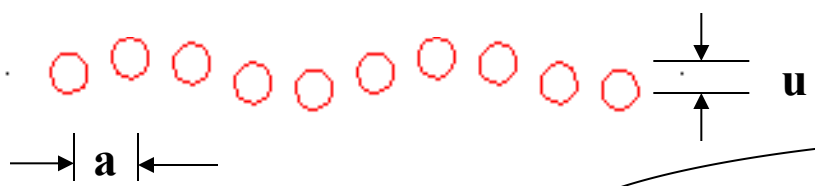
$$F_n = \alpha_0 u_n + \alpha_1 (u_{n-1} + u_{n+1}) + \alpha_2 (u_{n-2} + u_{n+2}) + \ldots$$

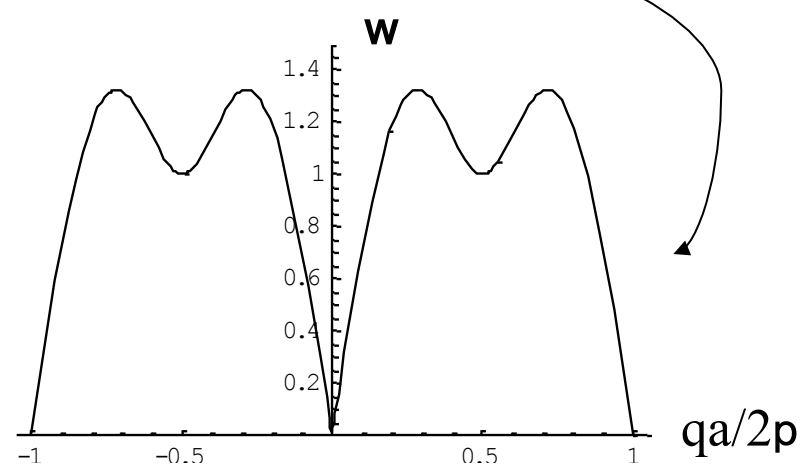
First neighbor force constant

displacements

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

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

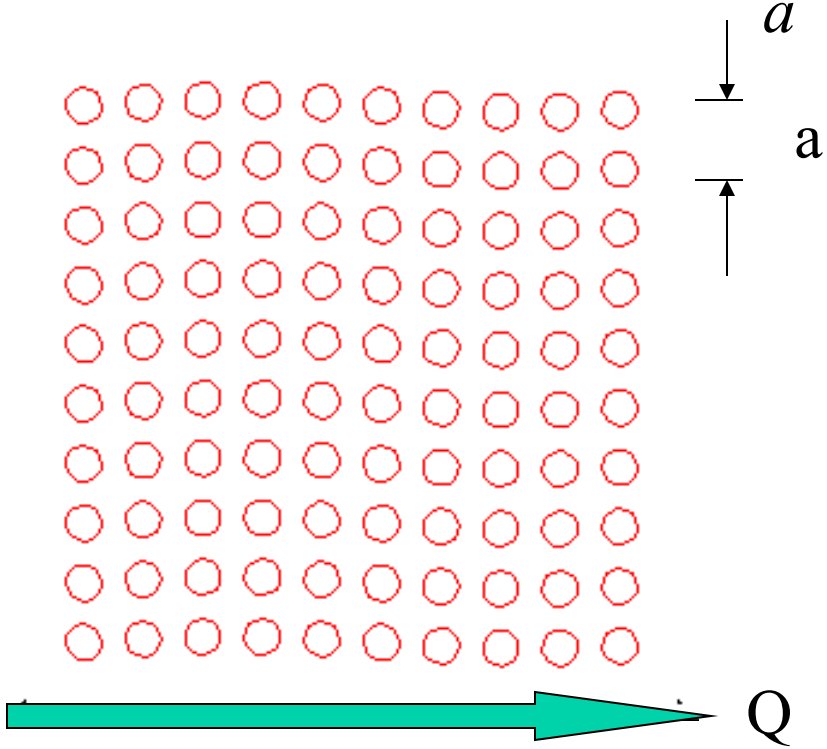


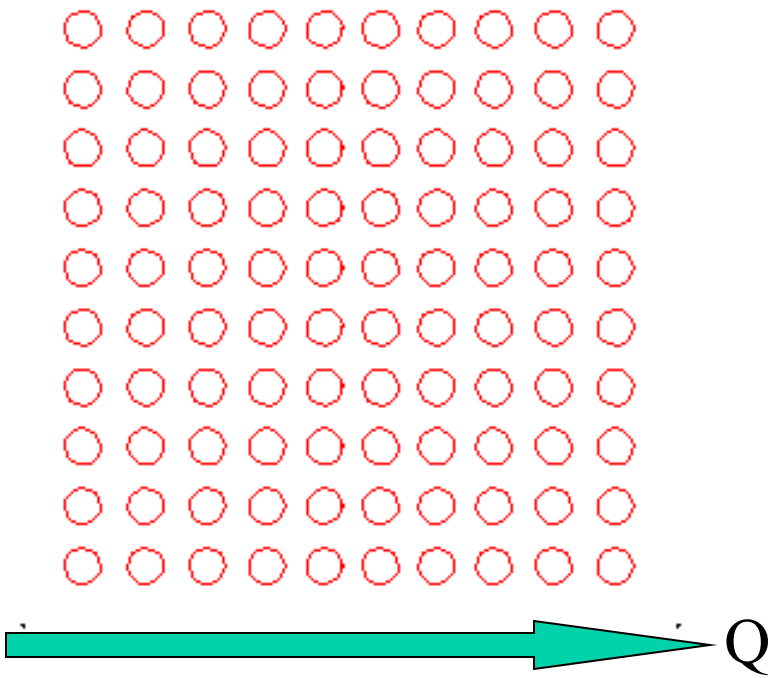


Phonon Dispersion Relation:
Measurable by inelastic neutron scattering

Atomic Motions for Longitudinal & Transverse Phonons

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





Transverse phonon

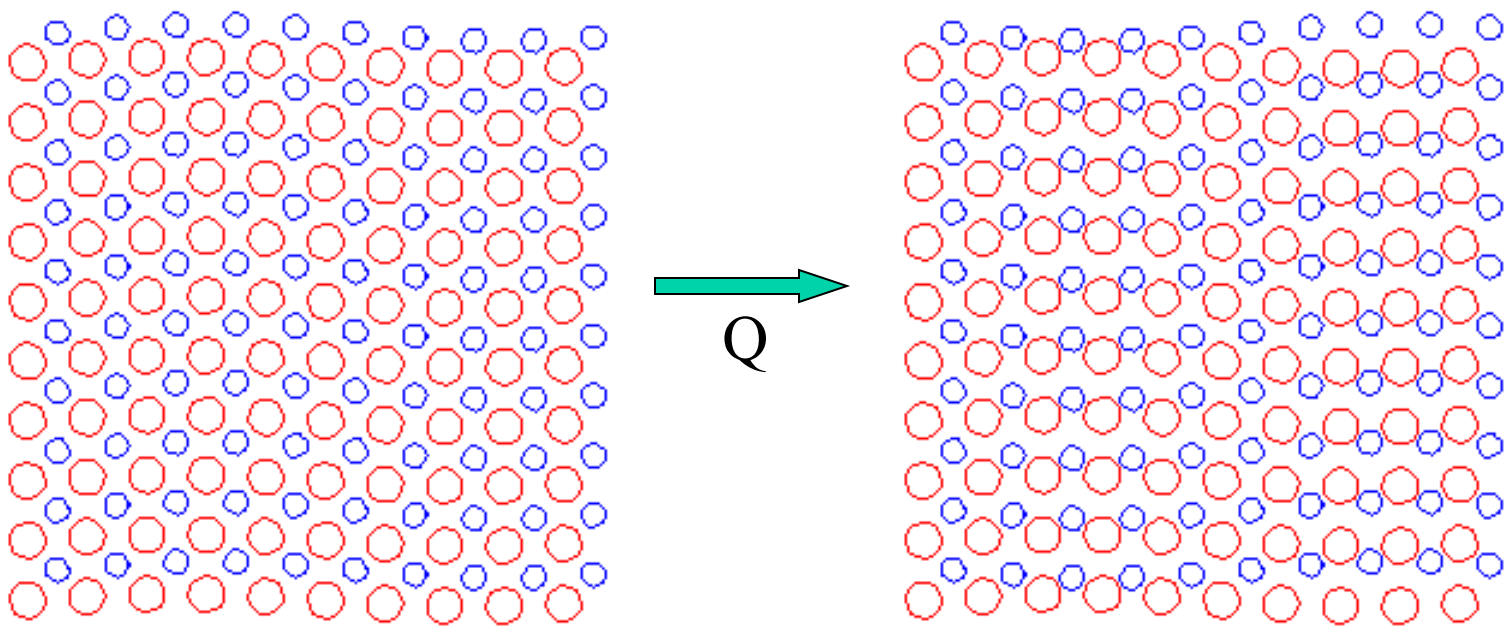
$$\vec{e}_T = (0,0.1,0)a$$

Longitudinal phonon

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

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

Transverse Optic and Acoustic Phonons



Acoustic

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

$$\vec{e}_{blue} = (0,0.14,0)a$$

Optic

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

$$\vec{e}_{blue} = (0,-0.14,0)a$$

$$\vec{R}_{lk} = \vec{R}^{0}_{lk} + \vec{e}_s e^{i(\vec{Q}.\vec{R}_l - \omega t)}$$

General Expression for $d^2s/dWdE$

- Squires (eqn 2.59) derives the following expression:

$$\boxed{\frac{d^2\sigma}{d\Omega dE'} = \frac{k'}{k}\frac{1}{2\pi\hbar}\sum_{i,i'} b_i b'_{i'} \int_{-\infty}^{\infty} \left\langle e^{-i\vec{Q}.\vec{R}_{i'}(0)} e^{i\vec{Q}.\vec{R}_i(t)} \right\rangle e^{-i\omega t} dt}$$

where $\vec{R}_i(t)$ is a Heisenberg operator i.e.

$e^{-i\vec{Q}.\vec{R}_i(t)} = e^{iHt/\hbar} e^{-i\vec{Q}.\vec{R}_i} e^{-iHt/\hbar}$ where H is the Hamiltonian of the scatterer

and $\langle\ \rangle$ denotes a thermal average over the possible states, λ, of the scatterer -- i.e. for any operator, $\langle \mathrm{A} \rangle = \sum_{\lambda} p_{\lambda} \langle \lambda | A | \lambda \rangle$

- Note that, because of the operators and the average over the states of the system, this expression is not easy to evaluate in the general case

- Note also that the exponential operators do not commute – each contains H and therefore p, and p and R do not commute.

Correlation Functions

Suppose we define : $G(\vec{r},t) = \frac{1}{(2\pi)^3}\frac{1}{N}\int e^{-i\vec{Q}'.\vec{r}}\sum_{j,j'}\left\langle e^{-i\vec{Q}'.\vec{R}_{j'}(0)}e^{i\vec{Q}'.\vec{R}_j(t)}\right\rangle d\vec{Q}'$

and $S(\vec{Q},\omega) = \frac{1}{2\pi\hbar}\int G(\vec{r},t)e^{i(\vec{Q}.\vec{r}-\omega t)}d\vec{r}.dt$ then we find

$\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{coh} = b_{coh}^2\frac{k'}{k}NS(\vec{Q},\omega)$ provided there is only one type of atom

Squires (eqn 4.14 to 4.17) shows that

$$G(\vec{r},t) = \frac{1}{N}\sum_{j,j'}\int\left\langle\delta\{\vec{r}'-\vec{R}_{j'}(0)\}\delta\{\vec{r}'+\vec{r}-\vec{R}_j(t)\}\right\rangle d\vec{r}'$$

- Note again that the operators do not commute. If we ignore this fact, we can do the integration and obtain

$$G_{classical}(\vec{r},t) = \frac{1}{N}\sum_{j,j'}\left\langle\delta\{\vec{r}-\vec{R}_j(t)+\vec{R}_{j'}(0)\}\right\rangle$$

Correlation Functions (cont'd)

$$G_{classical}(\vec{r},t) = \frac{1}{N}\sum_{j,j'}\left\langle \delta\{\vec{r} - \vec{R}_j(t) + \vec{R}_{j'}(0)\}\right\rangle$$

- We expressed the coherent scattering cross section in terms of G(**r**,t)

- If we use the classical variant given above, there is a clear physical meaning – G(**r**,t) is the probability that if particle j' is at the origin at time zero, particle j will be at position **r** at time t.

- We can do the same thing with the incoherent scattering and express it in terms of a self-correlation function whose classical version is

$$G^{self}_{classical}(\vec{r},t) = \left\langle \delta\{\vec{r} - R_j(t) + R_j(0)\}\right\rangle$$

- This says that the incoherent scattering is related to the probability that if a particle is at the origin at time zero, *the same* particle will be at position **r** at time t.

Inelastic Neutron Scattering Measures Atomic Motions

In term of the pair correlation functions, one finds

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

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

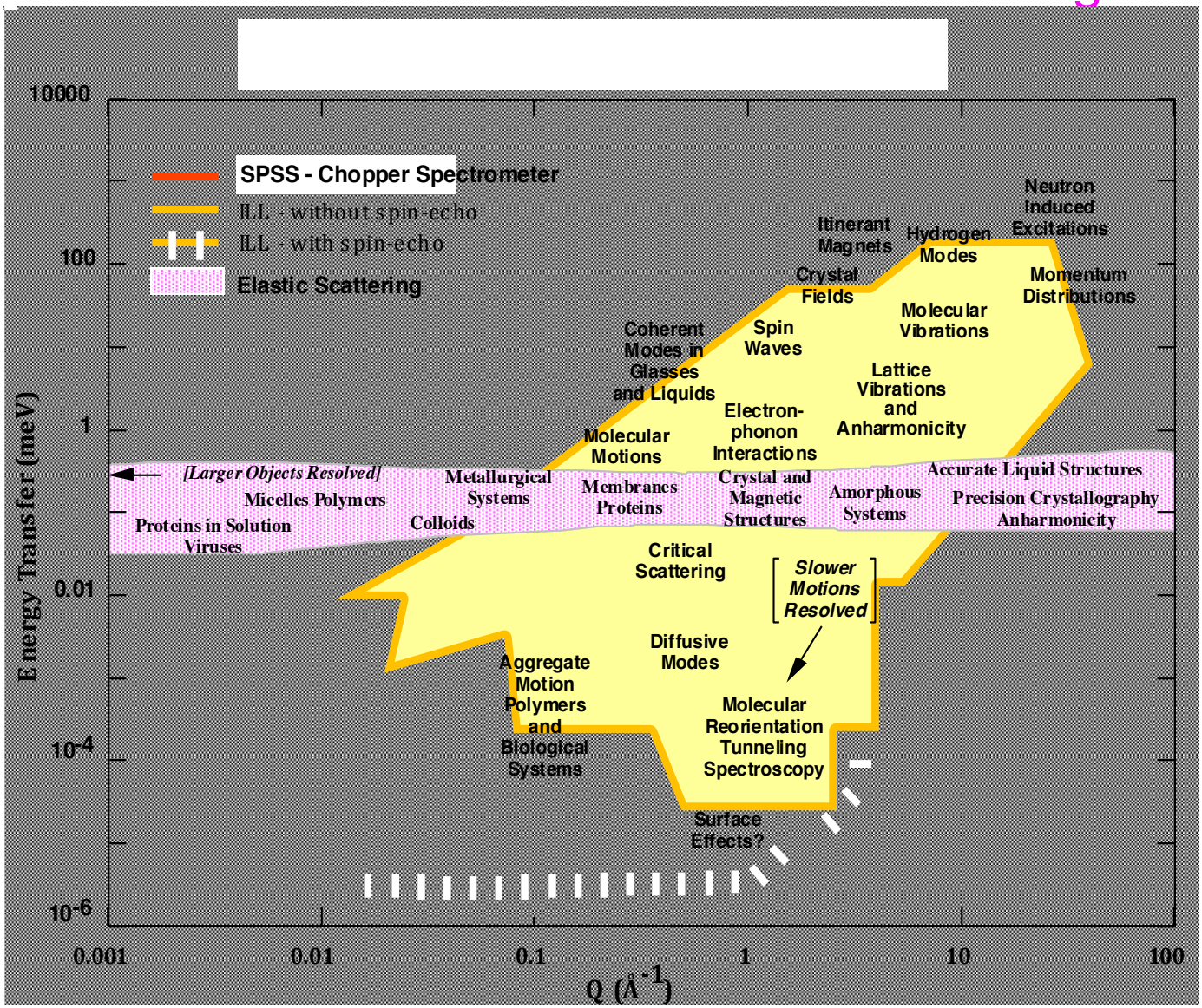
(h/2p)**Q** & (h/2p)w are the momentum & energy transferred to the neutron during the scattering process

where

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

- Inelastic coherent scattering measures *correlated* motions of different atoms
- Inelastic incoherent scattering measures *self-correlations* e.g. diffusion

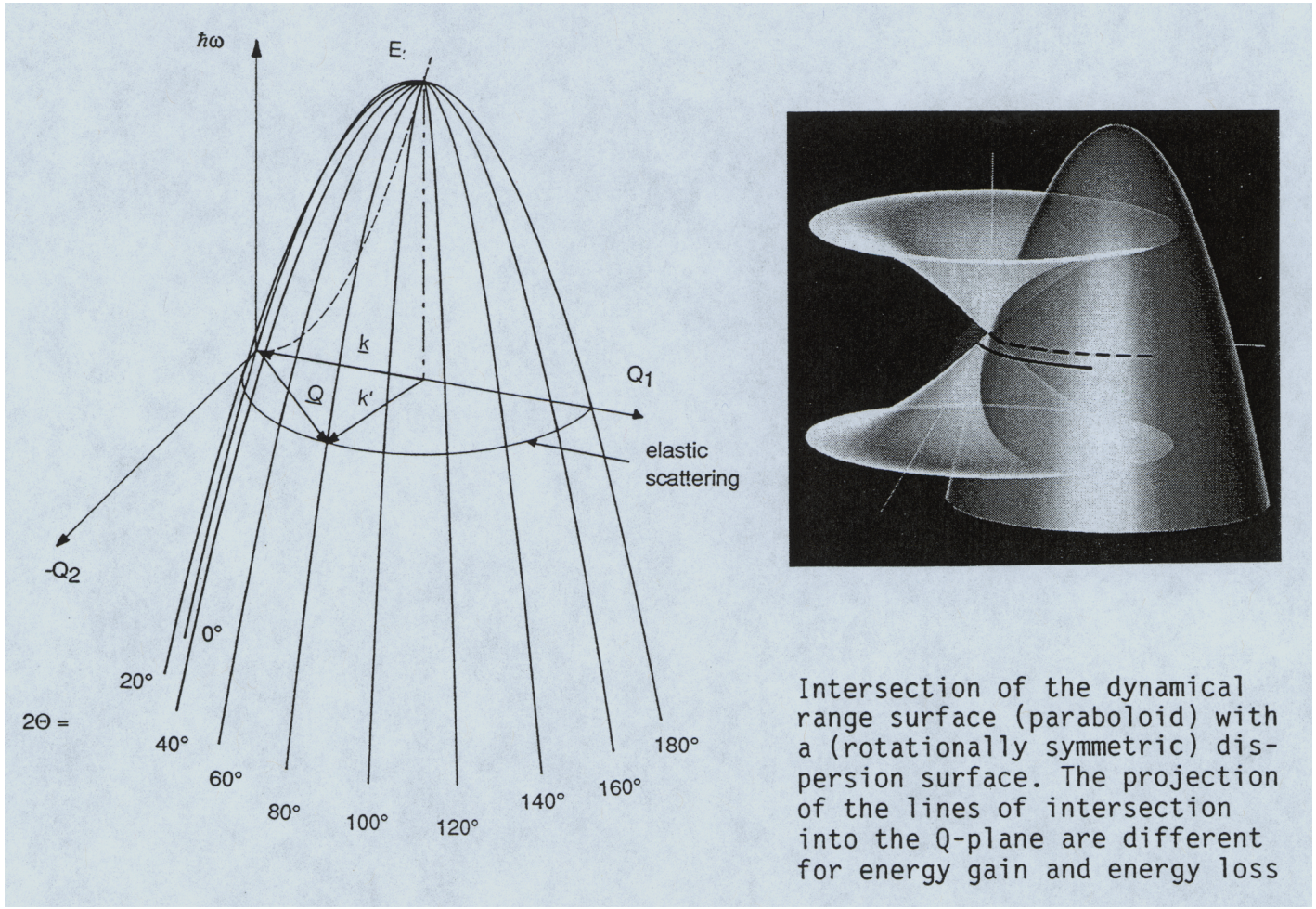
Much of the Scientific Impact of Neutron Scattering Has Involved the Measurement of Inelastic Scattering



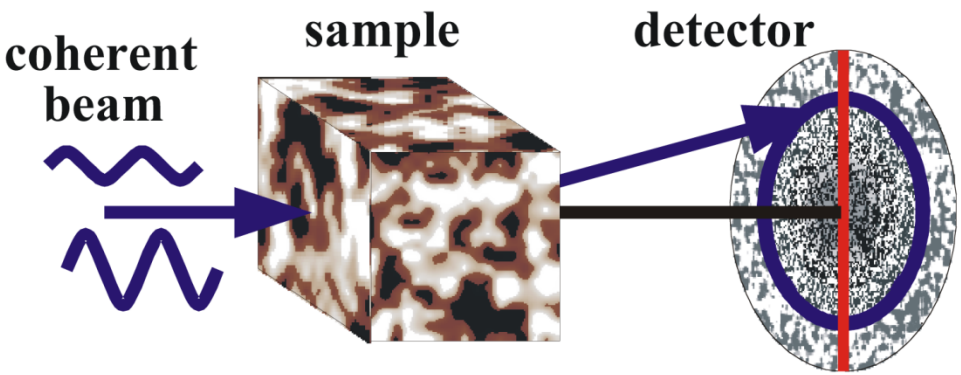
Energy & Wavevector Transfers accessible to Neutron Scattering

The Accessible Energy and Wavevector Transfers Are Limited by Conservation Laws

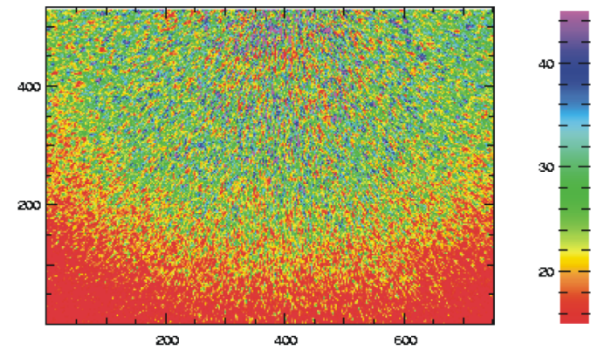
- Neutron cannot lose more than its initial kinetic energy & momentum must be conserved

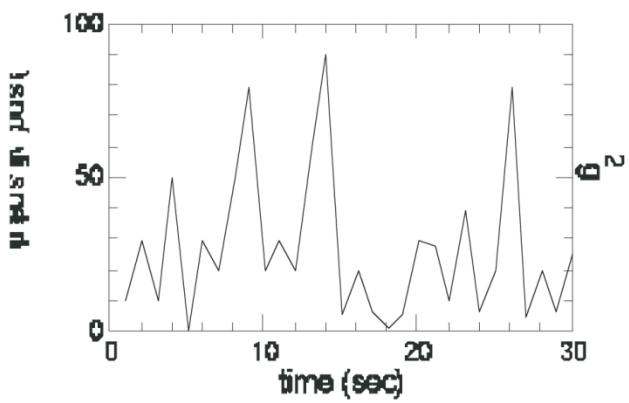


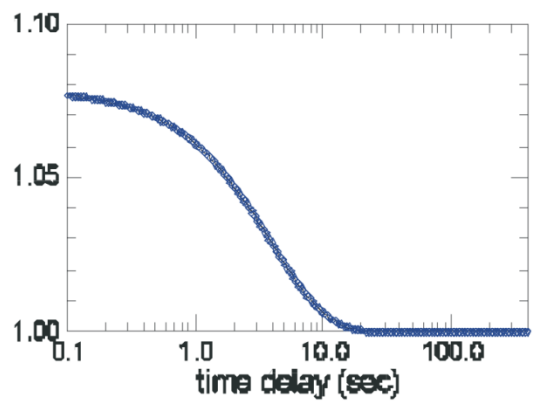
Photon Correlation Spectroscopy



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

Elastic Scattering as the t-> ∞ Limit of G(**r**,t)

- Elastic scattering occurs at w = 0. Since it involves a d(w), only the part of G(**r**,t) which is constant contributes
- G(**r**,t) decays as t increases, so the constant part is G(**r**,∞)
- Since we only need the part of the correlation that is time-independent, we can write (noting that the correlation between the positions of j and j' are independent of t as t-> ∞)

$$G(\vec{r},t) = \frac{1}{N}\sum_{j,j'}\int\left\langle \delta\{\vec{r}'-\vec{R}_{j'}(0)\}\delta\{\vec{r}'+\vec{r}-\vec{R}_j(t)\}\right\rangle d\vec{r}'$$

$$G(\vec{r},\infty) = \frac{1}{N}\sum_{j,j'}\int\left\langle \delta\{\vec{r}'-\vec{R}_{j'}\}\right\rangle\left\langle \delta\{\vec{r}'+\vec{r}-\vec{R}_j\}\right\rangle d\vec{r}'$$

$$= \frac{1}{N}\int\left\langle \rho(\vec{r}')\right\rangle\left\langle \rho(\vec{r}'+\vec{r})\right\rangle d\vec{r}'$$

where $\rho(\vec{r}')$ is the particle density operator at any time

Note – no truly elastic scattering for a liquid

G(**r**,∞) is called the Patterson function

The Static Approximation

Earlier we had :

$$\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{coh} = b_{coh}^2 \frac{k'}{k} N \frac{1}{2\pi\hbar} \int G(\vec{r},t) e^{i(\vec{Q}.\vec{r}-\omega t)} d\vec{r}.dt$$

$$\text{where } G(\vec{r},t) = \frac{1}{(2\pi)^3} \frac{1}{N} \int e^{-i\vec{Q}.\vec{r}} \sum_{j,j'} \left\langle e^{-i\vec{Q}.\vec{R}_{j'}(0)} e^{i\vec{Q}.\vec{R}_j(t)} \right\rangle$$

- In diffraction measurements, we measure scattered neutron intensity in a particular direction, independent of the change in neutron energy – i.e. we integrate the cross section over E = hw/2p. This is the Static Approximation.

Because $\hbar\delta(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\omega t} d(\hbar\omega)$

the integral over w picks out the t = 0 value of G to give

$$\left(\frac{d\sigma}{d\Omega}\right)_{coh}^{static} = b_{coh}^2 N \int G(\vec{r},t) e^{i(\vec{Q}.\vec{r}-\omega t)} d\vec{r}.dt.d\omega$$

$$= b_{coh}^2 N \int G(\vec{r},0) e^{i\vec{Q}.\vec{r}} d\vec{r}$$

Comparison of Elastic Scattering and the Static Approximation

$$\left(\frac{d\sigma}{d\Omega}\right)_{coh}^{static} = b_{coh}^2 N \int G(\vec{r},0) e^{i\vec{Q}.\vec{r}} d\vec{r}$$

$$\left(\frac{d\sigma}{d\Omega}\right)_{coh}^{elastic} = b_{coh}^2 N \int G(\vec{r},\infty) e^{i\vec{Q}.\vec{r}} d\vec{r}$$

- These are not the same, except in an (unreal) system with no motion
- The elastic scattering cross section gives the *true* elastic scattering that results when the positions of different atoms are correlated for all times, as they are in a crystalline solid, even when phonons are present
- The static approximation, as its name suggests, gives the scattering for a system that is frozen in time

The Intermediate Scattering Function

- Another function that is often useful is the Intermediate Scattering Function defined as

$$\boxed{I(\vec{Q},t) = \int G(\vec{r},t) e^{i\vec{Q}.\vec{r}} d\vec{r}}$$

This is the quantity measured with Neutron Spin Echo (NSE)

- It is not possible to derive exact expressions for I, G or S except for simple models. It is therefore useful to know the various analytical properties of these functions to ensure that models preserve them. Squires shows:

$$I(\vec{Q},t) = I^*(\vec{Q},-t); \qquad I(\vec{Q},t) = I(-\vec{Q},-t+i\hbar/k_B T)$$

$$G(\vec{r},t) = G^*(-\vec{r},-t); \qquad G(\vec{r},t) = G(-\vec{r},-t+i\hbar/k_B T)$$

$$S(\vec{Q},\omega) = S^*(\vec{Q},\omega); \qquad S(\vec{Q},\omega) = e^{\hbar\omega/k_B T} S(-\vec{Q},-\omega)$$

- There are also various sum & moment rules on these quantities that are sometimes useful (see Squires for details)

Magnetic Properties of the Neutron

- The neutron has a magnetic moment of -9.649 x 10^{-27} JT^{-1}

$$\vec{\mu}_n = -\gamma \mu_N \vec{\sigma}$$

where $\mu_N = e\hbar / 2m_p$ is the nuclear magneton,

$m_p =$ proton mass, $e =$ proton charge and $\gamma = 1.913$

$\vec{\sigma}$ is the Pauli spin operator for the neutron. Its eignevalues are ± 1

- Note that the neutron's spin and magnetic moment are antiparallel
- Because of its magnetic moment, the neutron feels a potential given by:

$$V_m(\vec{r}) = -\vec{\mu}_n . \vec{B}(\vec{r}) \quad \text{where } \vec{B}(\vec{r}) = \mu_0 \mu \vec{H}(\vec{r}) = \mu_0 [\vec{H}(\vec{r}) + \vec{M}(\vec{r})]$$

- Thus the neutron senses the distribution of magnetization in a material
- Homework problems: What is the Zeeman energy in meV of a neutron in a 1 Tesla field? At what temperature is the Boltzmann energy equal to this Zeeman energy? What is the effective scattering length of a "point" magnetic moment of one Bohr magneton?

Magnetic Scattering of the Neutron

- For nuclear scattering, the matrix element that appears in the expression for the scattering cross section is: $\sum_j b_j e^{i\vec{Q}.\vec{R}_j}$

- The equivalent matrix element for magnetic scattering is:

$$\gamma r_0 \frac{1}{2\mu_B} \vec{\sigma}.\vec{M}_\perp(\vec{Q}) \quad \text{where } \mu_B = \frac{e\hbar}{2m_e} \text{ is the Bohr magneton } (9.27 \text{ x } 10^{-24} \text{ JT}^{-1})$$

$$\text{and } r_0 = \frac{\mu_0}{4\pi}\frac{e^2}{m_e} \text{ is classical radius of the electron } (2.818 \text{ x } 10^{-6} \text{ nm})$$

- Here $\vec{M}_\perp(\vec{Q})$ is the component of the Fourier transform of the magnetization that is perpendicular to the scattering vector $\vec{Q}$. This form arises directly from the dipolar nature of the magnetic interaction.

- Unlike the neutron-nucleus interaction, the magnetic interaction of the neutron with a scattering system specifically depends on neutron spin

Derivation

The $\vec{B}$ field at distance $\vec{R}$ from a magnetic moment $\vec{M}$ is $\frac{\mu_0}{4\pi}\vec{\nabla}\Lambda\left(\frac{\vec{M}\Lambda\vec{R}}{R^3}\right) = -\frac{\mu_0}{4\pi}\vec{\nabla}\Lambda\left(\vec{M}\Lambda\nabla(1/R)\right)$

Since $\int \frac{1}{q^2}\exp(i\vec{q}.\vec{R})d\vec{q} = 2\pi\int_0^\infty dq\int_{-1}^{1}\exp(iqR\cos\theta)d(\cos\theta) = 4\pi\int_0^\infty \frac{\sin(qR)}{qR}dq = \frac{2\pi^2}{R}$

$$\vec{\nabla}\Lambda\left(\frac{\vec{M}\Lambda\vec{R}}{R^3}\right) = -\frac{1}{2\pi^2}\int\frac{1}{q^2}\vec{\nabla}\Lambda\left(\vec{M}\Lambda\nabla\{\exp i\vec{q}.\vec{R}\}\right)d\vec{q}$$

But $\vec{M}\Lambda\nabla\{\exp i\vec{q}.\vec{R}\} = i\vec{M}\Lambda\vec{q}\exp i\vec{q}.\vec{R}$ and $\vec{\nabla}\Lambda\vec{M}\Lambda\vec{q}\exp i\vec{q}.\vec{R} = i\vec{q}\Lambda\vec{M}\Lambda\vec{q}\exp i\vec{q}.\vec{R}$

so $\vec{\nabla}\Lambda\left(\frac{\vec{M}\Lambda\vec{R}}{R^3}\right) = \frac{1}{2\pi^2}\int\frac{1}{q^2}\vec{q}\Lambda\left(\vec{M}\Lambda\vec{q}\right)\{\exp i\vec{q}.\vec{R}\}d\vec{q} = \frac{1}{2\pi^2}\int\vec{M}_\perp(\vec{q})\{\exp i\vec{q}.\vec{R}\}d\vec{q}$

The Magnetic Scattering Cross Section

- Development of the magnetic scattering cross section follows the same formalism as for the nuclear cross section, with nuclear matrix element replaced by the magnetic interaction matrix element given above

- Need to keep the explicit dependence on neutron spin (or average over neutron spin states for an unpolarized neutron beam).
  - Magnetic scattering may cause a change in the neutron's spin state

- General expressions tend to be complicated, so specific expressions are obtained for various contributions to sample magnetization e.g. unpaired electron spins

- The form of the magnetic cross section implies that neutrons are only sensitive to components of the magnetization that are perpendicular to **Q**.

Scattering by Ions with Unpaired Electrons

- Including only magnetization due to unpaired electron spins and assuming an unpolarized incident neutron beam:

$$\frac{d^2\sigma}{d\Omega.dE} = \frac{(\gamma r_0)^2}{2\pi\hbar}\frac{k'}{k}\sum_{\alpha,\beta}(\delta_{\alpha\beta} - \hat{Q}_\alpha\hat{Q}_\beta)\sum_{ldl'd'}F^*_{d'}(\vec{Q})F_d(\vec{Q})$$

$$\text{x}\int_{-\infty}^{\infty} dt\left\langle \exp\{-i\vec{Q}.\vec{R}_{l'd'}(0)\}\exp\{i\vec{Q}.\vec{R}_{ld}(t)\}\right\rangle.\left\langle S^{\alpha}_{l'd'}(0)S^{\beta}_{ld}(t)\right\rangle e^{-i\omega t}$$

where $F_d(Q)$ is the Fourier transform of the electron spin density around atom *d,* often called the atomic form factor; S^a is the *a* component of the electron spin and *l,d* labels an atom *d* in unit cell *l*

- This expression can be manipulated to give the scattering cross sections for elastic magnetic scattering inelastic magnetic scattering and magneto-vibrational scattering

What Happens to a Neutron's Spin When the Neutron is Scattered?

- The cross section for magnetic scattering that takes the neutron spin state from s->s' and the scattering system from l->l' is:

$$\left(\frac{d^2\sigma}{d\Omega.dE}\right)_{\sigma\lambda\to\sigma'\lambda'} = \left(\frac{\gamma r_0}{2\mu_B}\right)^2 \frac{k'}{k}\left|\langle\sigma'\lambda'|\vec{\sigma}.\vec{M}_\perp|\sigma\lambda\rangle\right|^2 \delta(E_\lambda - E\lambda' + \hbar\omega)$$

- One can show (see Squires) that if $|u\rangle, |v\rangle$ are the neutron spin eigenstates:

$$\langle u|\vec{\sigma}.\vec{M}_\perp|u\rangle = M_{\perp z};\ \langle v|\vec{\sigma}.\vec{M}_\perp|v\rangle = -M_{\perp z};\ \langle v|\vec{\sigma}.\vec{M}_\perp|u\rangle = M_{\perp x} + iM_{\perp y};\quad \langle u|\vec{\sigma}.\vec{M}_\perp|v\rangle = M_{\perp x} - iM_{\perp y}$$

  so, sample magnetization parallel to the neutron's magnetic moment (z) does not change the neutron spin, whereas perpendicular components of magnetization 'flip' the neutron's spin

- Homework: show that for a paramagnet (where $\langle S_i^\alpha S_j^\beta\rangle = \frac{1}{3}\delta_{ij}\delta_{\alpha\beta}S(S+1)$ for spins i and j)
  - If z is parallel to **Q**, the scattering is entirely spin flip
  - If z is perpendicular to **Q**, half the scattering is spin flip

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

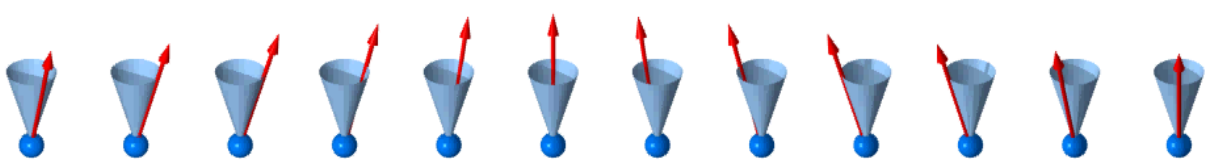
spin waves (magnons)

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

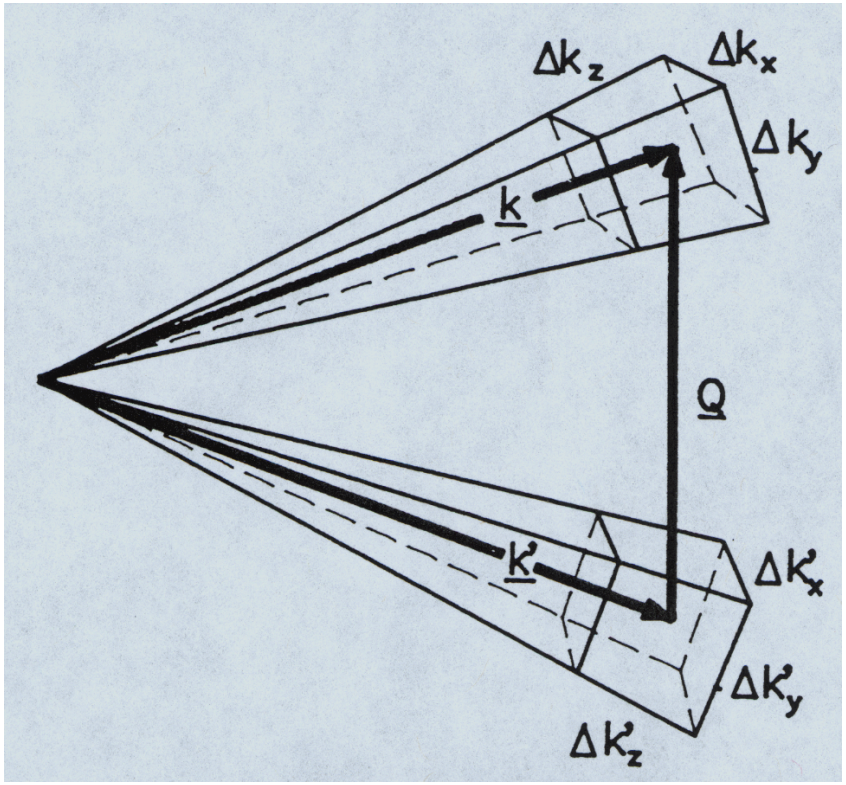


Spin wave animation courtesy of A. Zheludev (ORNL)

Instrumental Resolution

- Uncertainties in the neutron wavelength & direction of travel imply that Q and E can only be defined with a certain precision

- When the box-like resolution volumes in the figure are convolved, the overall resolution width is the quadrature sum of the box sizes. Small “boxes” give good resolution.

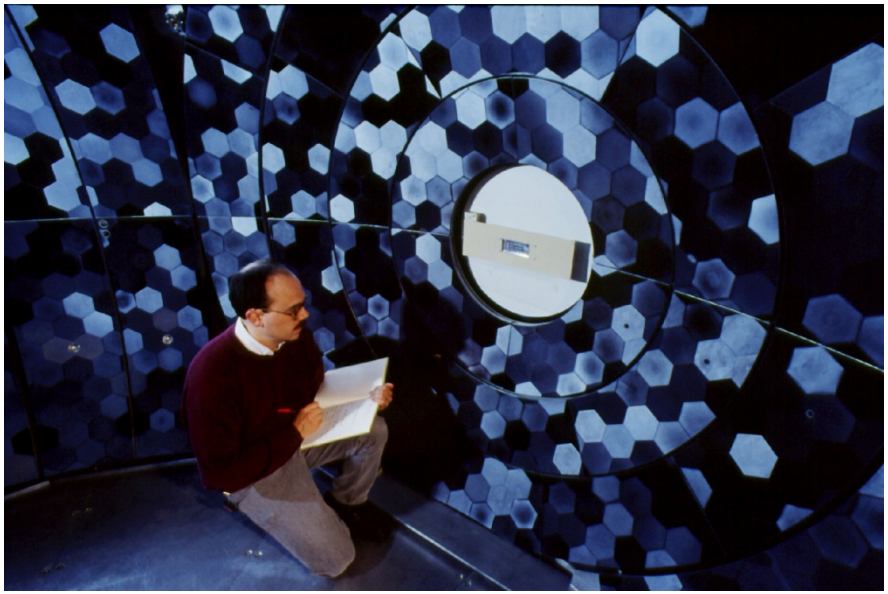


- The total signal in a scattering experiment is proportional to the product of the “box” sizes

The better the resolution, the lower the count rate

Examples of Specialization of Spectrometers: Optimizing the Signal for the Science

- Small angle scattering [$Q = 4p \sin q/l$; $(dQ/Q)^2 = (dl/l)^2 + (\cot q\, dq)^2$]
  - Small diffraction angles to observe large objects => long (20 m) instrument
  - poor monochromatization ($dl/l \sim 10\%$) sufficient to match obtainable angular resolution (1 cm^2 pixels on 1 m^2 detector at 10 m => $dq \sim 10^{-3}$ at $q \sim 10^{-2}$))
- Back scattering [$q = p/2$; $l = 2\, d \sin q$; $dl/l = \cot q + \ldots$]
  - very good energy resolution (~neV) => perfect crystal analyzer at $q \sim p/2$
  - poor Q resolution => analyzer crystal is very large (several m^2)



Neutron Scattering Instrumentation is Designed to Compromise between Intensity & Resolution

- Maxwellian distribution of neutron velocities $P(v) \sim \frac{1}{T^{3/2}} e^{-\frac{1}{2}mv^2/kT}$
- Liouville's theorem – the (6-dimensional) phase space density of non-interacting particles cannot be increased by conservative forces
  - Brighter sources => colder moderators or non-equilibrium neutron production
- We can only increase scattered intensity at a given ($\vec{Q}$,E) by increasing the phase space volume
- Design instruments to have good resolution in the direction of ($\vec{Q}$,E) space that is important for the science
- Neutron optics & instrumentation is designed to:
  - Maintain neutron brightness
  - Provide good resolution in a chosen direction in ($\vec{Q}$,E) space
  - Simultaneously measure as many resolution elements [i.e. ($\vec{Q}$,E) points] as is useful

General References

- Introduction to the Theory of Thermal Neutron Scattering
  by G. L. Squires

- Neutron Scattering: A Non-Destructive Microscope for Seeing Inside Matter
  by Roger Pynn
  Available on-line at http://www.springerlink.com/content/978-0-387-09415-1

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- International Neutron Scattering Instrumentation School (INSIS)
  http://neutrons.ornl.gov/conf/insis2012/

SANS References

- Viewgraphs describing the NIST 30-m SANS instrument
  - www.ncnr.nist.gov/programs/sans/tutorials/30mSANS_desc.pdf
- SANS data can be simulated for various particle shapes using the programs available at:
  - www.ncnr.nist.gov/resources/simulator.html
- To choose instrument parameters for a SANS experiment at NIST go to:
  - www.ncnr.nist.gov/resources/sansplan.html
- A very good description of SANS experiments can be found at:
  http://www.strubi.ox.ac.uk/people/gilbert/sans.html

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