Introduction to Neutron and X-Ray Scattering

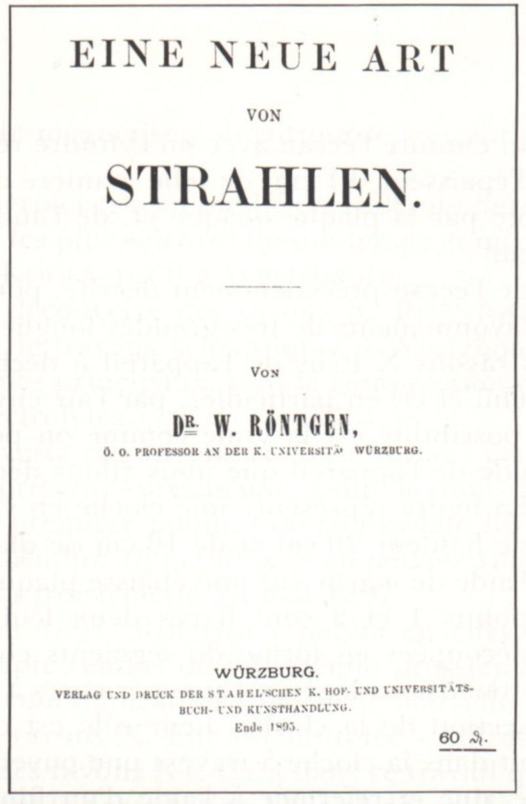
Sunil K. Sinha

UCSD/LANL

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

Wilhelm Conrad Röntgen 1845-1923

Dr. W. C. Röntgen



EINE NEUE ART

VON

STRAHLEN.

Von

Dr. W. RÖNTGEN,

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

WÜRZBURG.

VERLAG UND DRUCK DER STAHEL'SCHEN K. HOF- UND UNIVERSITÄTS-
BUCH- UND KUNSTHANDLUNG.
Ende 1895.

60 ₰.

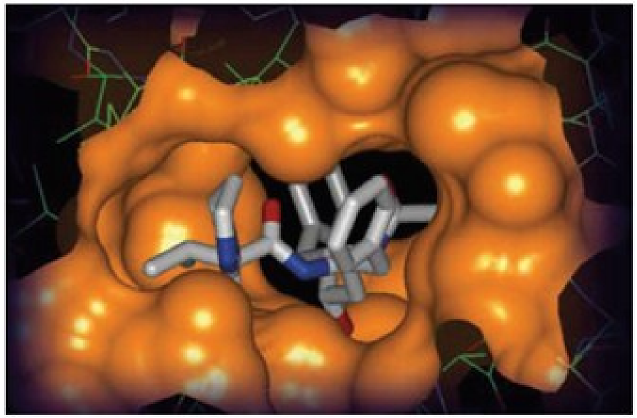
1895: Discovery of X-Rays

Nobel Prizes for Research with X-Rays

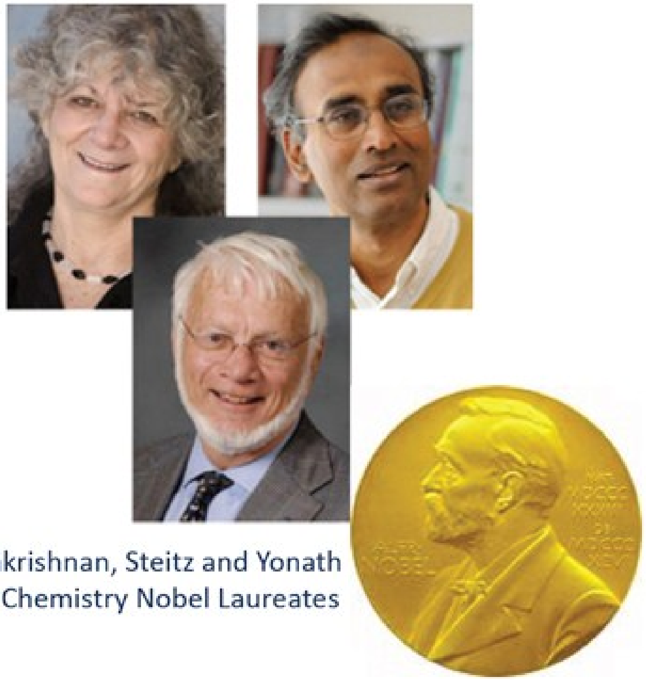
1901 W. C. Röntgen in Physics for the discovery of x-rays.
1914 M. von Laue in Physics for x-ray diffraction from crystals
1915 W. H. Bragg and W. L. Bragg in Physics for crystal structure determination.
1917 C. G. Barkla in Physics for characteristic radiation of elements.
1924 K. M. G. Siegbahn in Physics for x-ray spectroscopy.
1927 A. H. Compton in Physics for scattering of x-rays by electrons.
1936 P. Debye in Chemistry for diffraction of x-rays and electrons in gases.
1962 M. Perutz and J. Kendrew in Chemistry for the structure of hemoglobin.
1962 J. Watson, M. Wilkins, and F. Crick in Medicine for the structure of DNA.
1979 A. McLeod Cormack and G. Newbold Hounsfield in Medicine for computed axial tomography.
1981 K. M. Siegbahn in Physics for high resolution electron spectroscopy.
1985 H. Hauptman and J. Karle in Chemistry for direct methods to determine x-ray structures.
1988 J. Deisenhofer, R. Huber, and H. Michel in Chemistry for the structures of proteins that are crucial to photosynthesis.
2006 R. Kornberg in Chemistry for studies of the molecular basis of eukaryotic

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

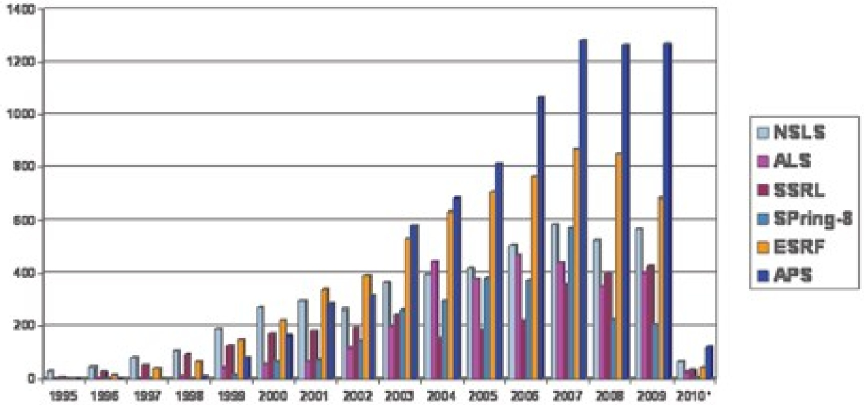
Renal cancer drug pazopanib™ developed in part based on APS research (GlaxoSmithKline)



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



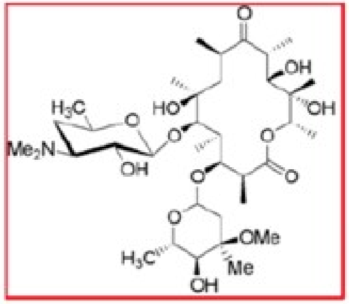
Ramakrishnan, Steitz and Yonath
2009 Chemistry Nobel Laureates



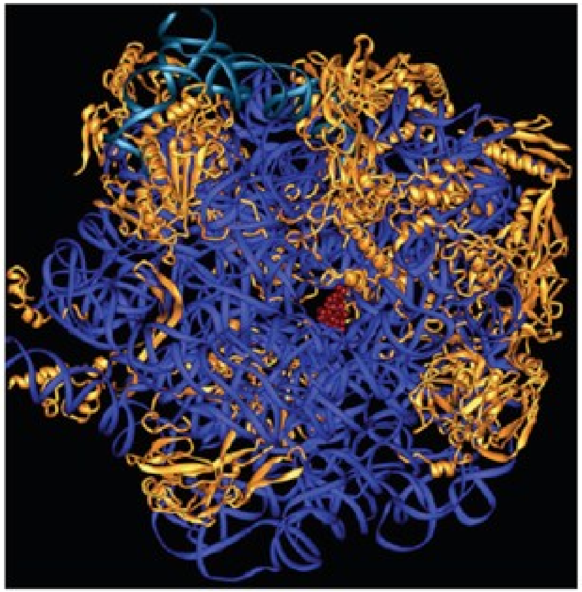
APS protein structure output is almost twice that of any other light source

Designing antibiotics -

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



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



www.molgen.mpg.de

Functional domain dynamics in proteins

NSE

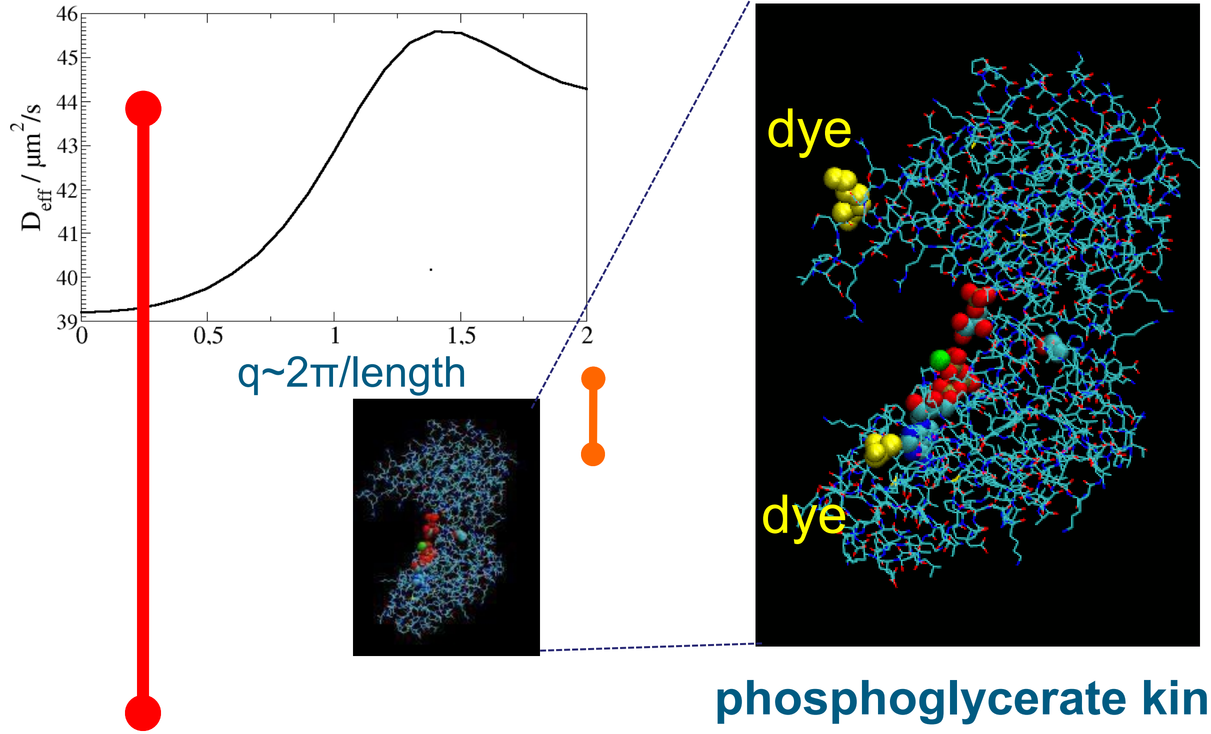
0.5-50 nm length scale
ps - μs time scale
orientational average

FRET

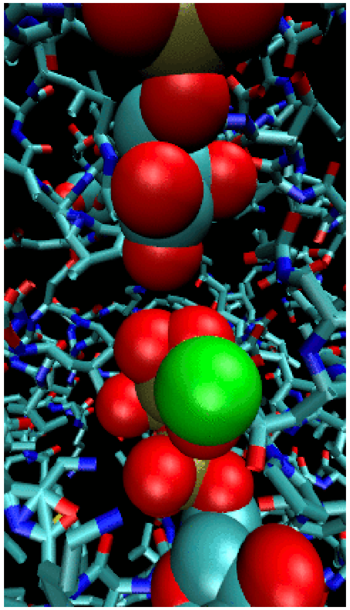
fixed defined position
> μs timescale

NMR

ps - ms timescale
small proteins



phosphoglycerate kinase



Neutron and X-ray Scattering:

“small” science at big facilities!

Advantages of Neutrons and X-Rays

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

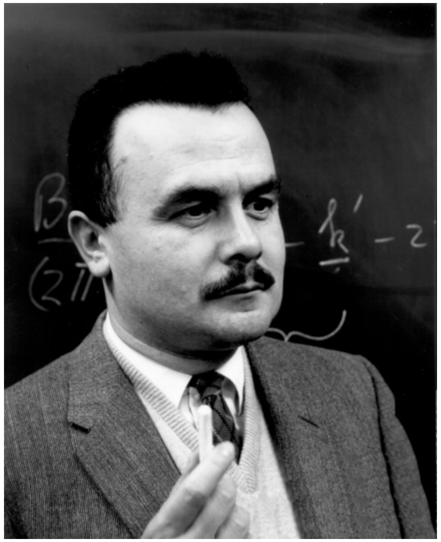
X-rays and neutrons are complementary to SPM’ s

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

Nobel Prize in Physics, 1994

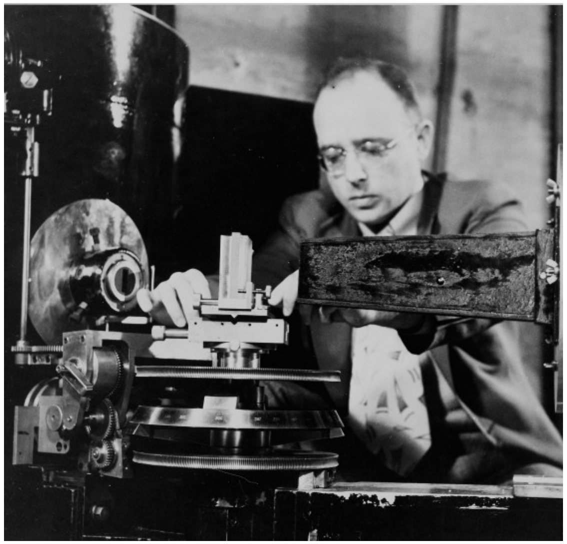
Awarded for “pioneering contributions to the development of neutron scattering techniques for studies of condensed matter”

Bertram N. Brockhouse



Development of
neutron spectroscopy

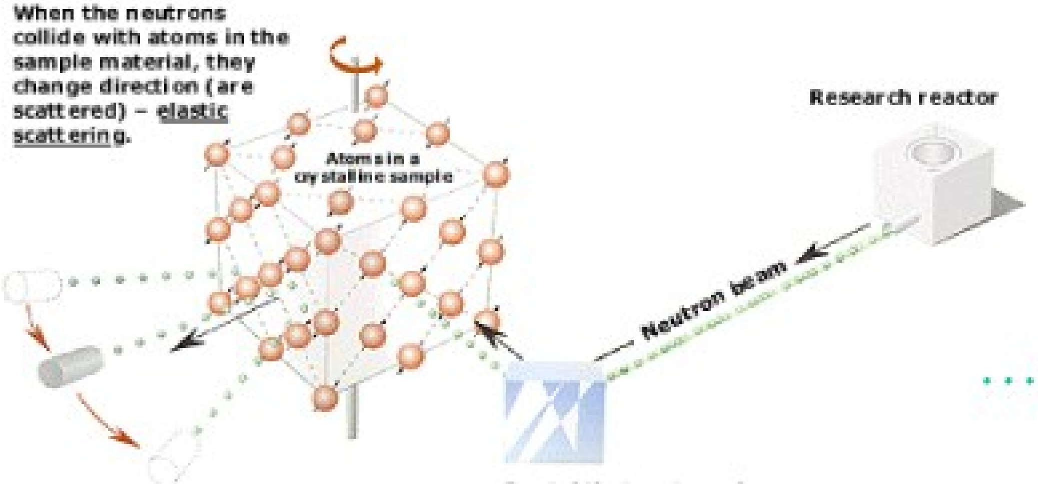
Clifford G. Shull



Development of the
neutron diffraction technique

The 1994 Nobel Prize in Physics – Shull & Brockhouse

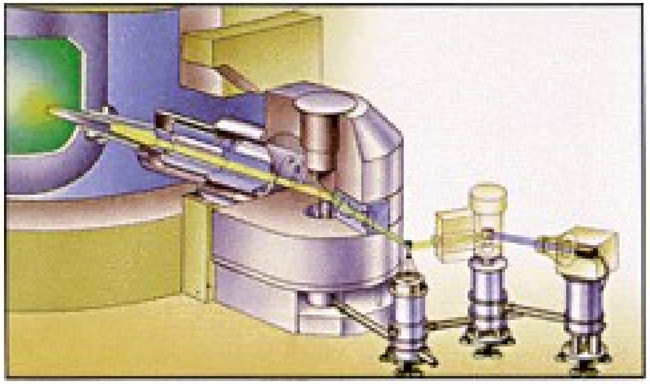
Neutrons show where the atoms are….



When the neutrons collide with atoms in the sample material, they change direction (are scattered) – elastic scattering.

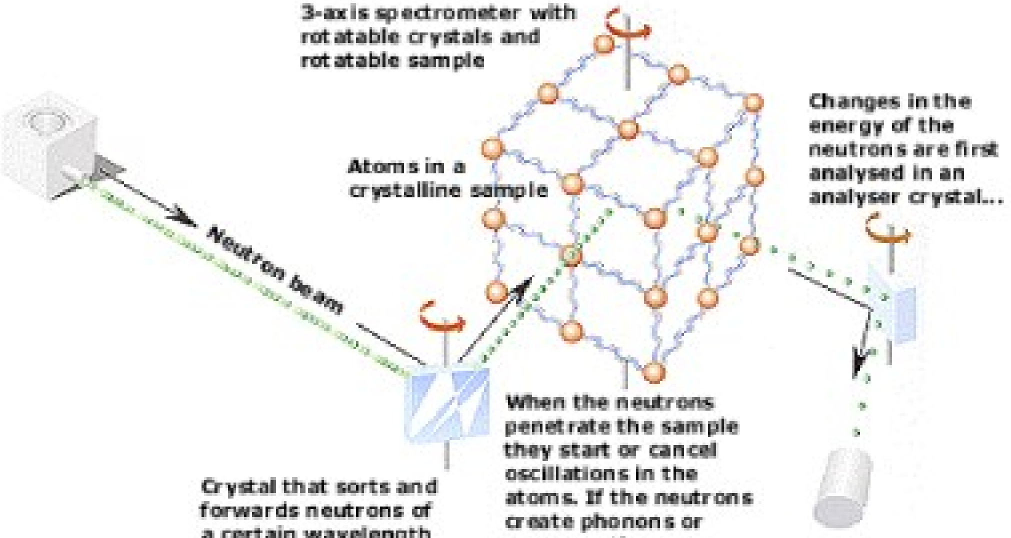
Detectors record the directions of the neutrons and a diffraction pattern is obtained.
The pattern shows the positions of the atoms relative to one another.

Crystal that sorts and forwards neutrons of a certain wavelength (energy) – monochromatized neutrons



3-axis spectrometer

…and what the atoms do.



3-axis spectrometer with rotatable crystals and rotatable sample

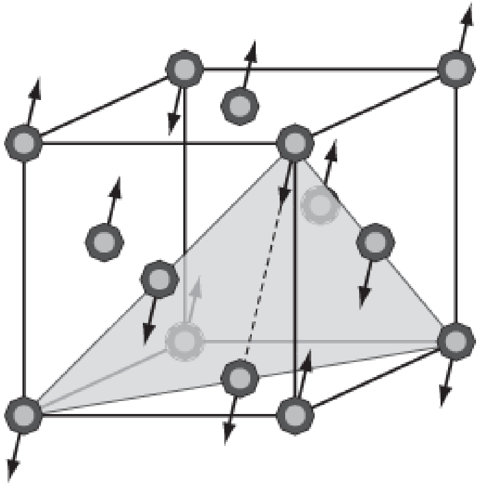
Changes in the energy of the neutrons are first analysed in an analyser crystal...

Crystal that sorts and forwards neutrons of a certain wavelength (energy) – monochromatized neutrons

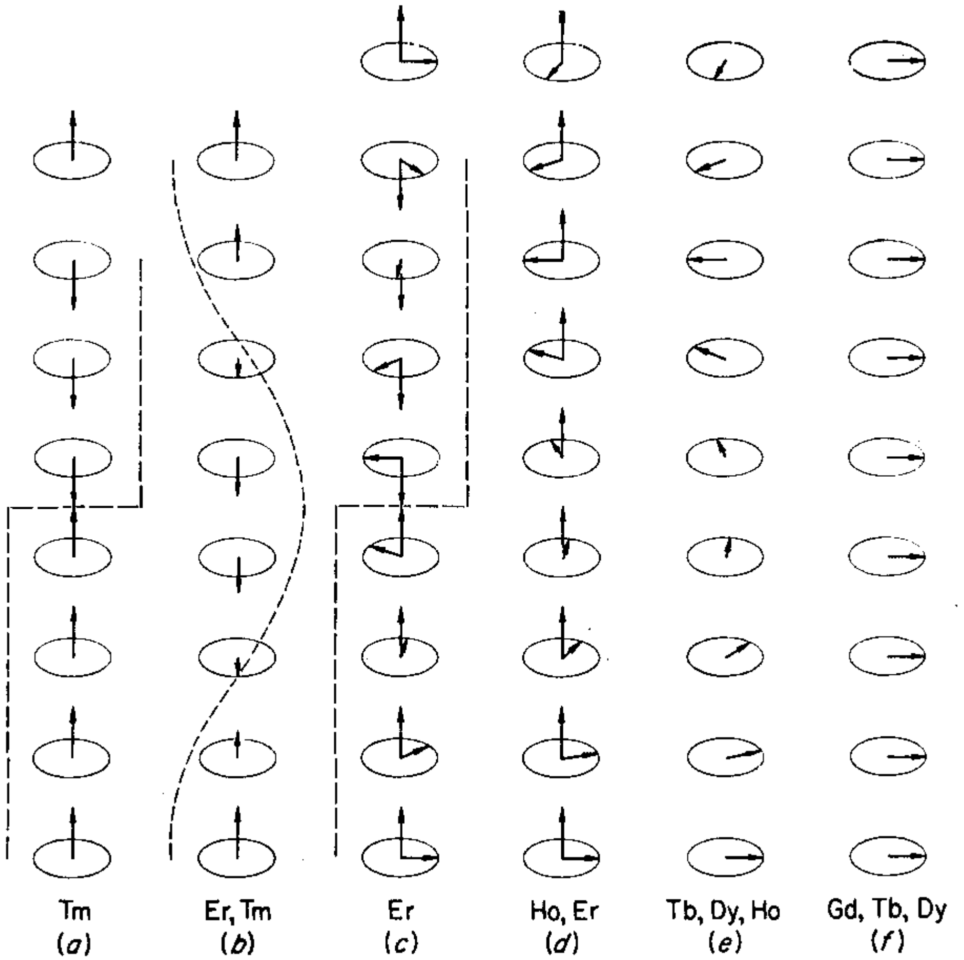
When the neutrons penetrate the sample they start or cancel oscillations in the atoms. If the neutrons create phonons or magnons they themselves lose the energy these absorb – inelastic scattering

...and the neutrons then counted in a detector.

First Study of an Antiferromagnetic Structure



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



Magnetic Structure of the Rare Earth Metals

(W.C. Koehler (1965))

Neutron Advantages

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

Historic accomplishments (Neutrons)

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

Recent Applications

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

Recent Applications (contd.)

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

Applications 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 Surface/Interface Scattering

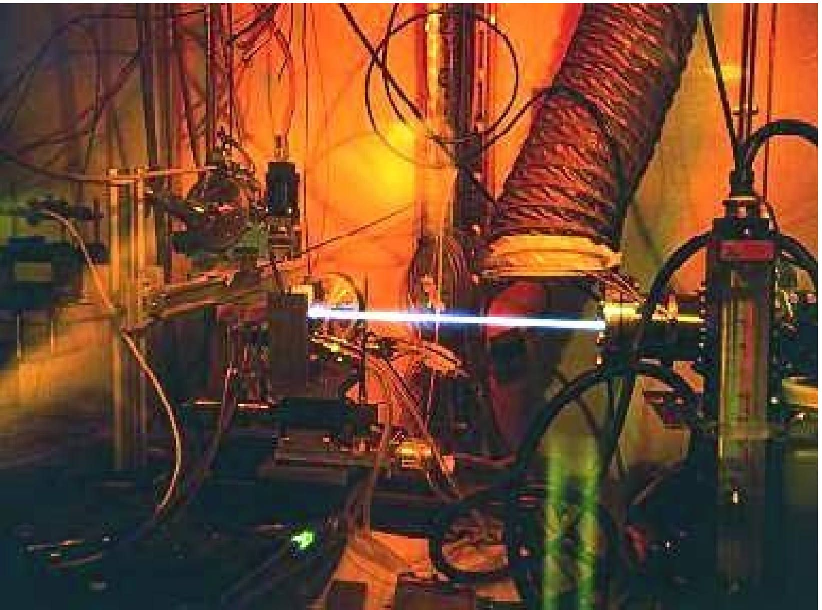
- study the morphology of surface and interface roughness
- wetting films
- film growth exponents
- capillary waves on liquid surfaces (polymers, microemulsions, liquid metals, etc.)
- islands on block copolymer films
- pitting corrosion
- magnetic roughness
- study the morphology of magnetic domains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

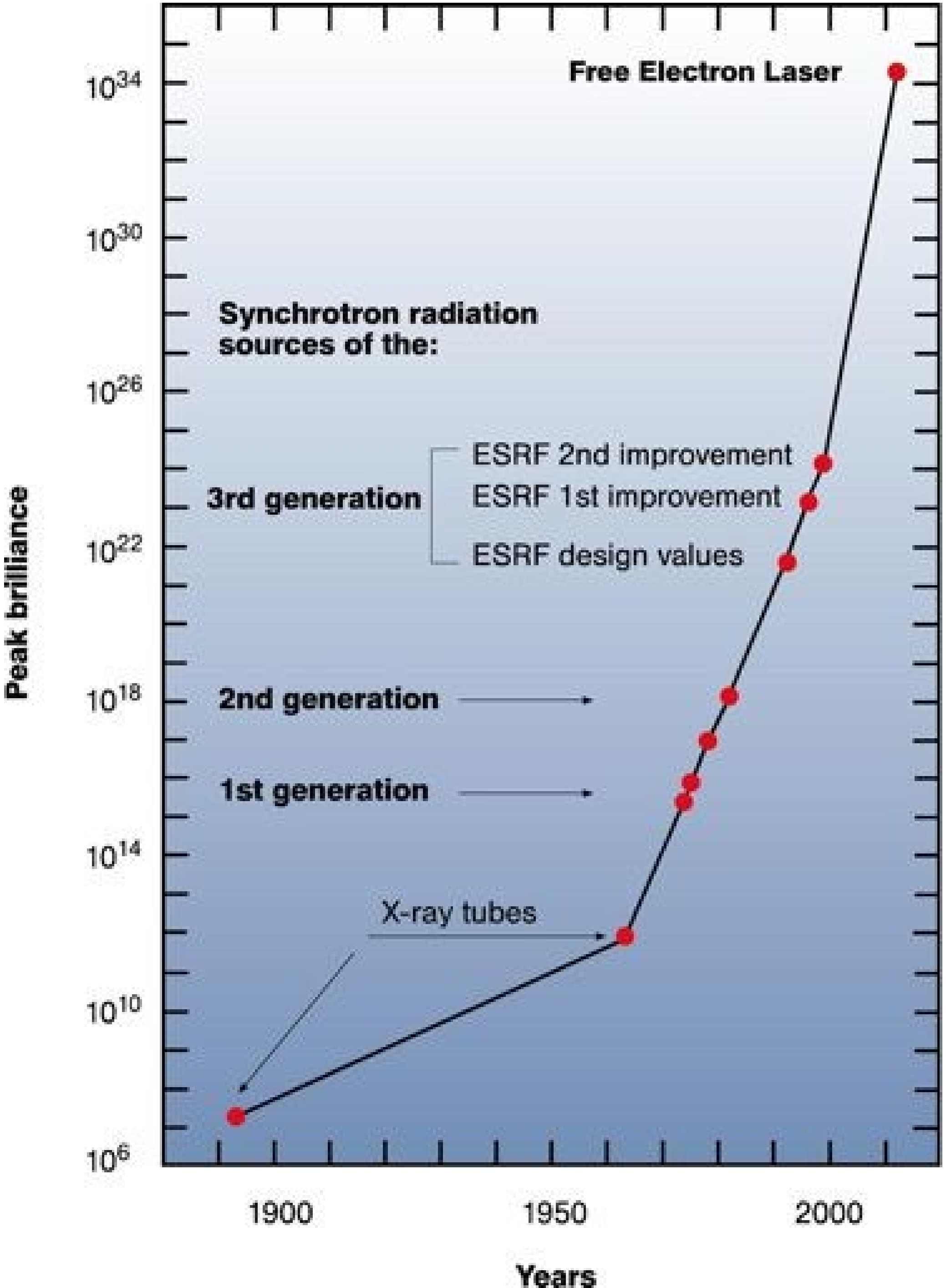
S.R. and neutron based research can help us to understand:

- 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

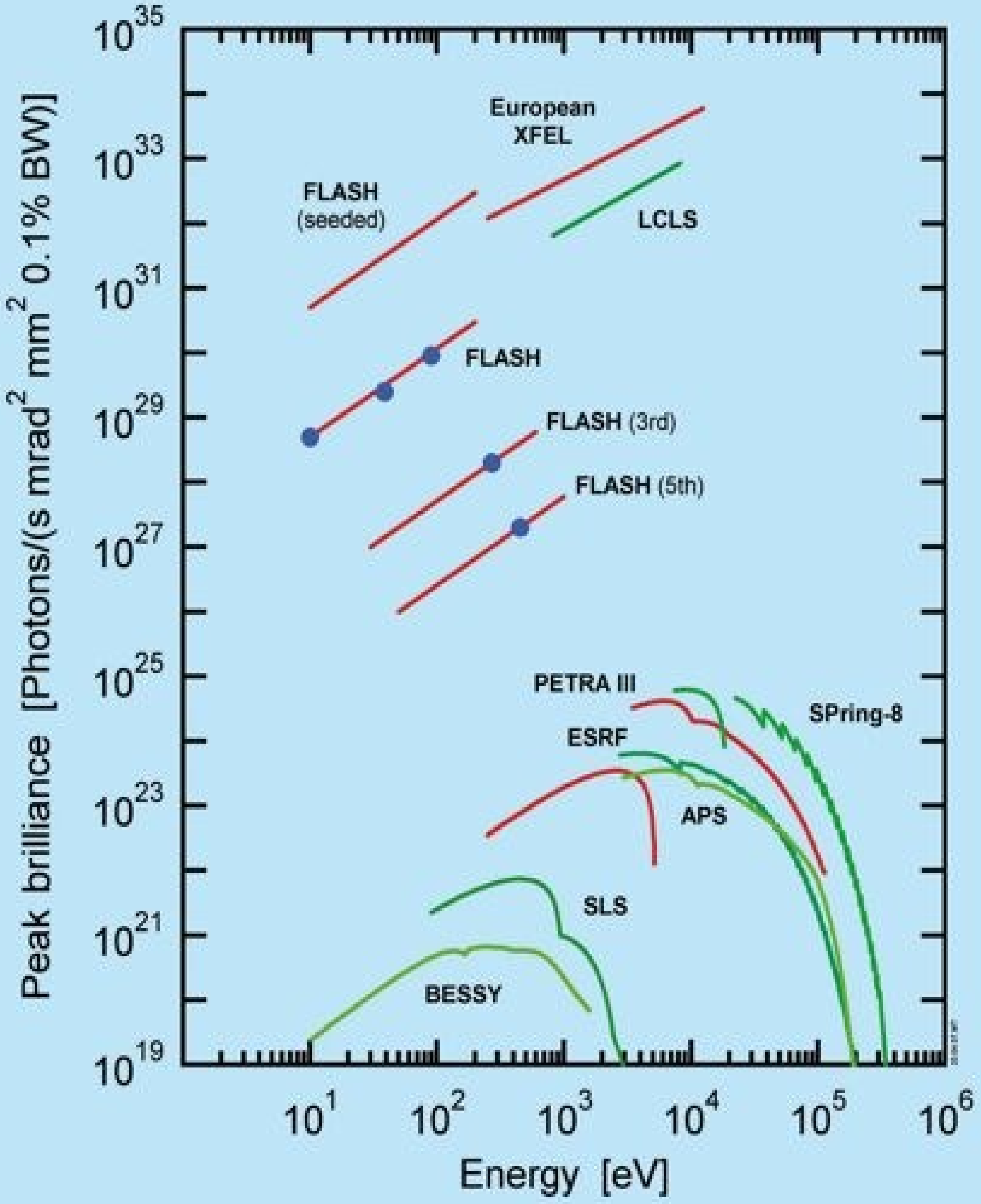
Why Synchrotron-radiation ?

Intensity !!!





		wavelength range (Å)	$\frac{\Delta\nu}{\nu}$	apparent source (mm)	Ω (sterad)	integrated flux (W)	Spectral brilliance (phot/sec/ /0.1% band/ /mrad^2/mm^2)
sealed-off X-ray tube	CuK	1.54	0.05%	1x1	0.1	0.01	$1.6\cdot10^8$
2 kW, 50 kV	Bremss.	0.25	white			0.02	10^5
V.H.power rot.-anode	CuK	1.54	0.05%	1x1	0.1	0.27	$4\cdot10^9$
tube 50 kW 50 kV	Bremss.	0.25	wh.			0.5	$3\cdot10^6$
µfocus rot.-anode tube	CuK	1.54	0.05%	0.1x0.1	0.1	0.02	$2.8\cdot10^{10}$
3.5 kW 50 kV	Bremss.	0.25	wh.			0.04	$2\cdot10^7$
ACO (Orsay) (operating)							
0.54 GeV, 150 mA, B=1.6T		λ_c=40 Å	wh.	0.5x0.6	$2\cdot10^{-6}$	0.16	$4.6\cdot10^{12}$
ADONE (Frascati) (operating)							
1.5 GeV 100 mA, B=1T		λ_c=8.3	wh.	1x0.4	$\frac{2}{3}\cdot10^{-6}$	1.4	$3.5\cdot10^{13}$
with 1.8T 5-pole wiggler		λ_c=4.6	"	1x0.1		2.5	$6.9\cdot10^{14}$
SRS (Daresbury) (under constr.)							
2 GeV 300 mA, B=1.2T		λ_c=3.9	"	5x0.2	$\frac{1}{2}\cdot10^{-6}$	12	$7.6\cdot10^{13}$
4.5T 1 pole wiggler		λ_c=1.1	"			45	"
ESRF (European S.R.Facility, proposal)							
5 GeV, 500 mA, B=0.7T		λ_c=1	"	1x0.1	$\frac{1}{5}\cdot10^{-6}$	185	$7.9\cdot10^{14}$
3T 1 pole wiggler		λ_c=0.23	"			790	"
undulator λ_0=5.6 cm, B=0.2T		λ_1 =5	7%	1x0.2	$2\cdot10^{-9}$	78	$7\cdot10^{18}$
5 m long (λ_5=5th harmonic)		λ_5=1	7%			26.4	$4.7\cdot10^{17}$


Peak brilliance [Photons/(s mrad^2 mm^2 0.1% BW)]
10^{35}
10^{33}
10^{31}
10^{29}
10^{27}
10^{25}
10^{23}
10^{21}
10^{19}
European XFEL
FLASH (seeded)
LCLS
FLASH
FLASH (3rd)
FLASH (5th)
PETRA III
SPring-8
ESRF
APS
SLS
BESSY
10^1
10^2
10^3
10^4
10^5
10^6
Energy [eV]

Example 1: X-Ray Diffraction & structural biology

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

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

Synchrotron Radiation - 8301 structures solved in 2009

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

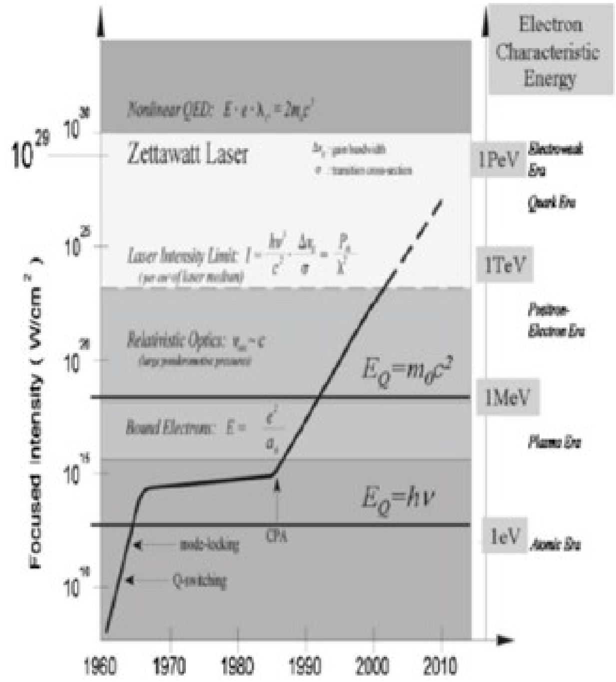
Hign-intensity at optical wavelengths
- high harmonic generation
- tabletop coherent x-ray radiation
- attosecond pulses

High-intensity at x-ray wavelengths

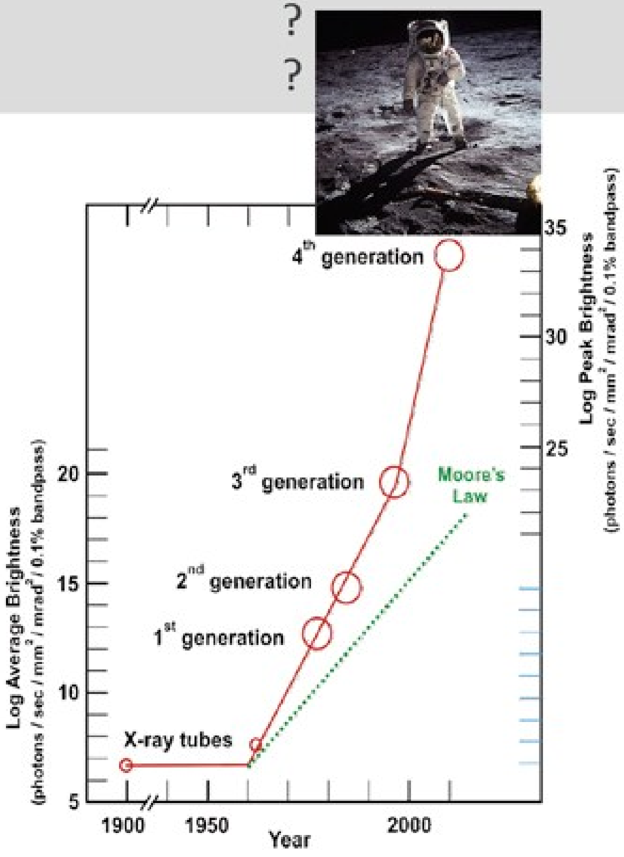
?

?

?

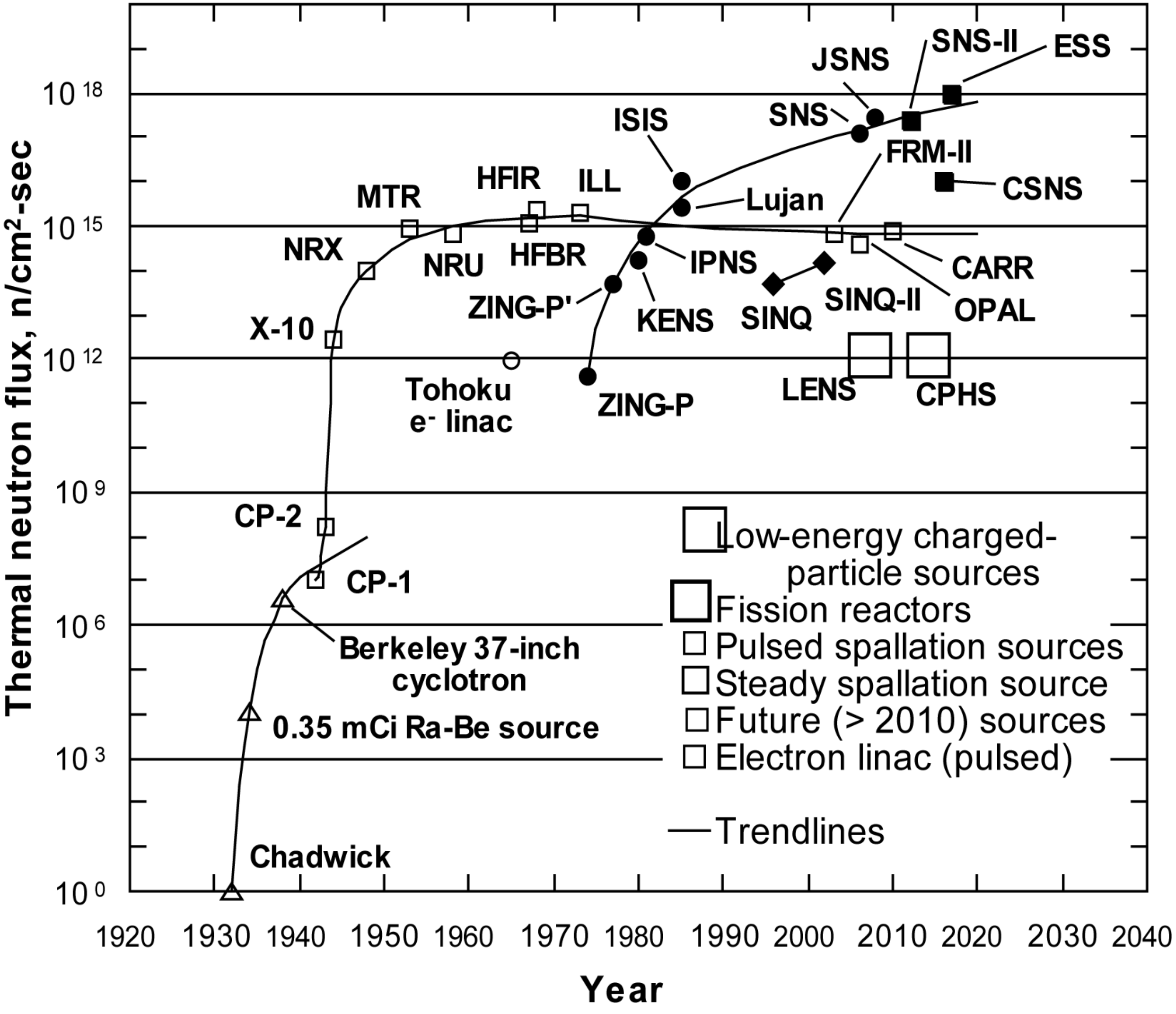


G. Mourou RMP 2006



D. Moncton, George Brown

Brugger Plot



Redrawn 2009

Neutron Fluxes

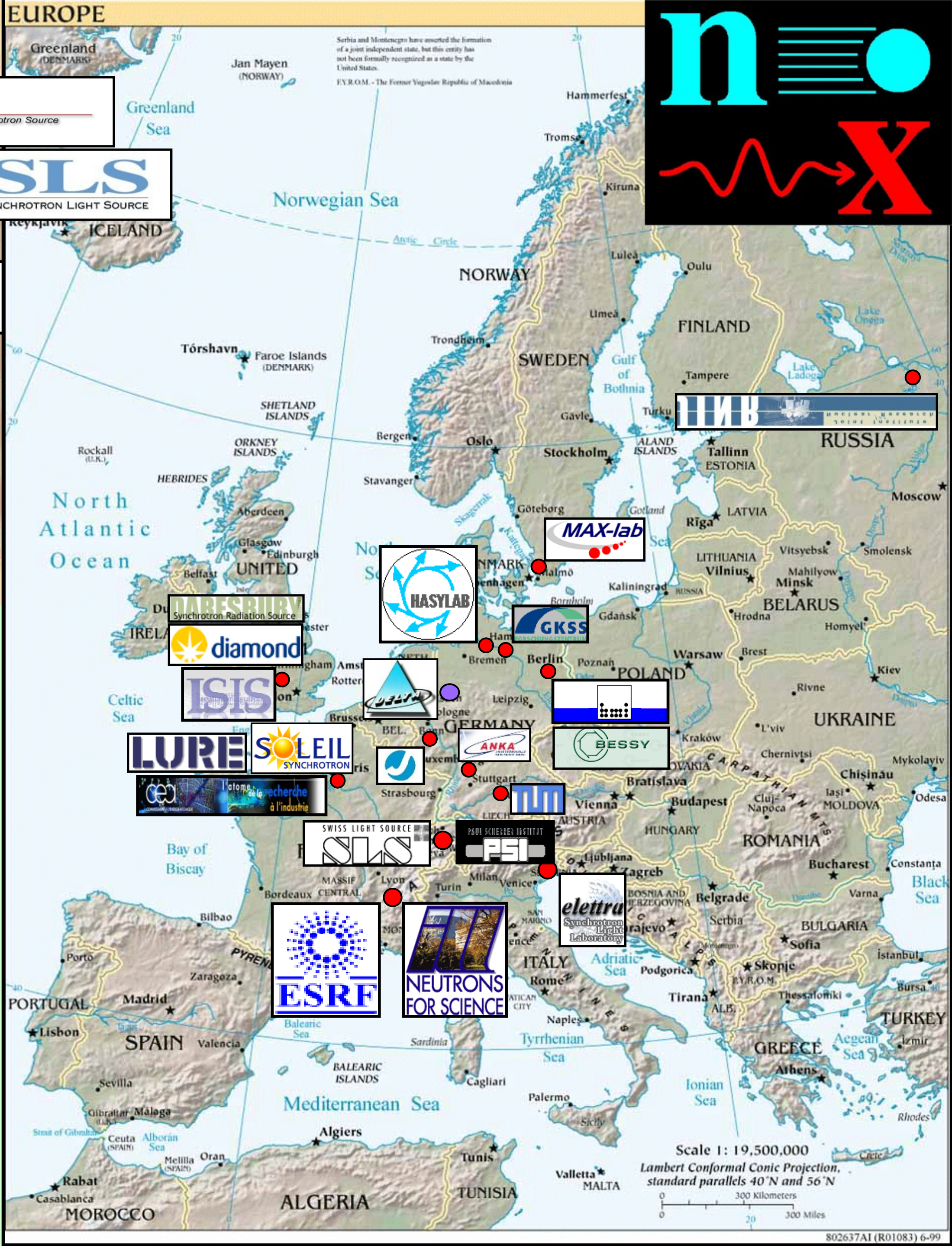
Inside a moderator (reactor source) $\Phi = 1.5 \cdot 10^{15}$ n/cm^2/s (steady state, e.g. ILL Grenoble, France)

Typical monochromatic flux at sample: $1.0.\ 10^{8}$ n/cm^2/s

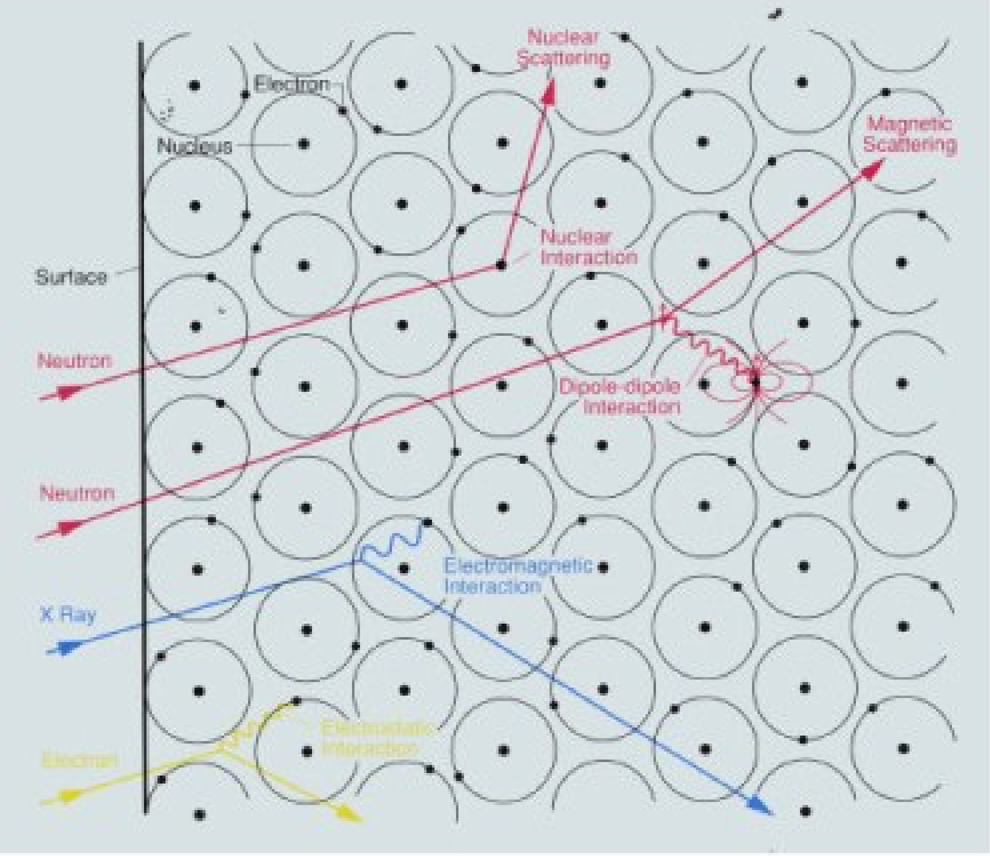
In moderator of Spallation Neutron Source (e.g. SNS @ 2 MW)

$\Phi = 3.0 \cdot 10^{16}$ n/cm^2/s (Peak) $\Phi = 4.0 \cdot 10^{13}$ n/cm^2/s (Average)

Synchrotron- and Neutron Scattering Places



Interaction Mechanisms



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

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

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

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

λ (nm) = 395.6 / v (m/s)
E (meV) = $0.02072\ k^2$ (k in nm^{-1})

The photon also has wave and particle properties

[redacted]

Charge = 0 Magnetic Moment = 0

Spin = 1

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

Thermal Neutrons

Advantages ☺

1) λ_n ~ Interatomic Spacing
2) Penetrates Bulk Matter (neutral particle)
3) Strong Contrasts Possible (e.g. H/D)
4) E_n ~ Elementary Excitations (phonons, magnons, etc.)
5) Scattered Strongly by Magnetic Moments

Disadvantages ☹

1) Low Brilliance of Neutron Sources-Low Resolution or Intensities; Large Samples; Low Coherence; Surfaces Difficult
2) Some Elements Strongly Absorb (e.g. Cd, Gd, B)
3) Kinematic Restriction on Q for Large E Transfers
4) Restricted to Excitations ≤ 100 meV

Synchrotron X-rays

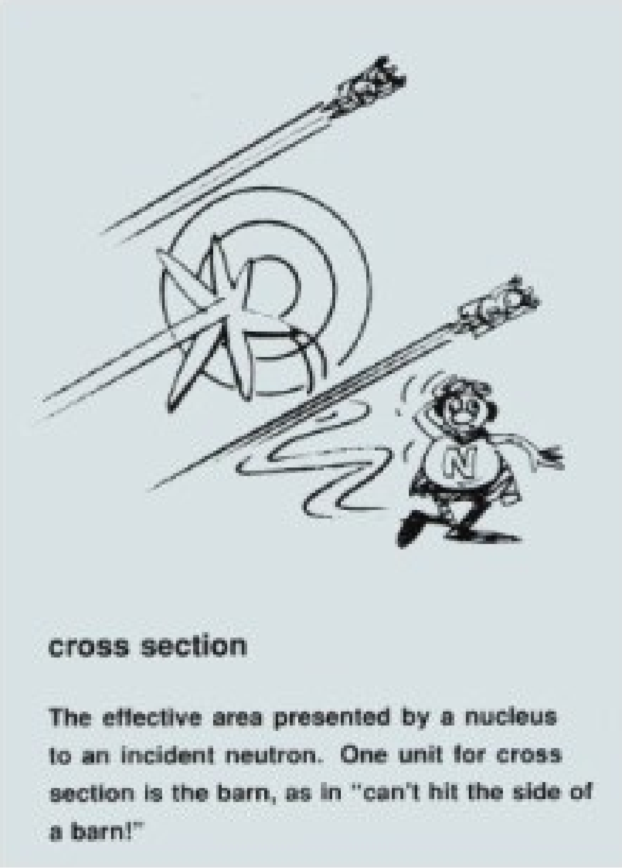
Advantages

1) λ_n - Interatomic Spacing
2) High Brilliance of X-ray Sources - High Resolution; Small Samples; High Degree of Coherence
3) No Kinematic Restrictions (E,Q uncoupled)
4) No Restriction on Energy Transfer that Can Be Studied

Disadvantages

1) Strong Absorption for Lower Energy Photons
2) Little Contrast for Hydrocarbons or Similar Elements
3) Weak Scattering from Light Elements
4) Radiation Damage to Samples

Cross Sections

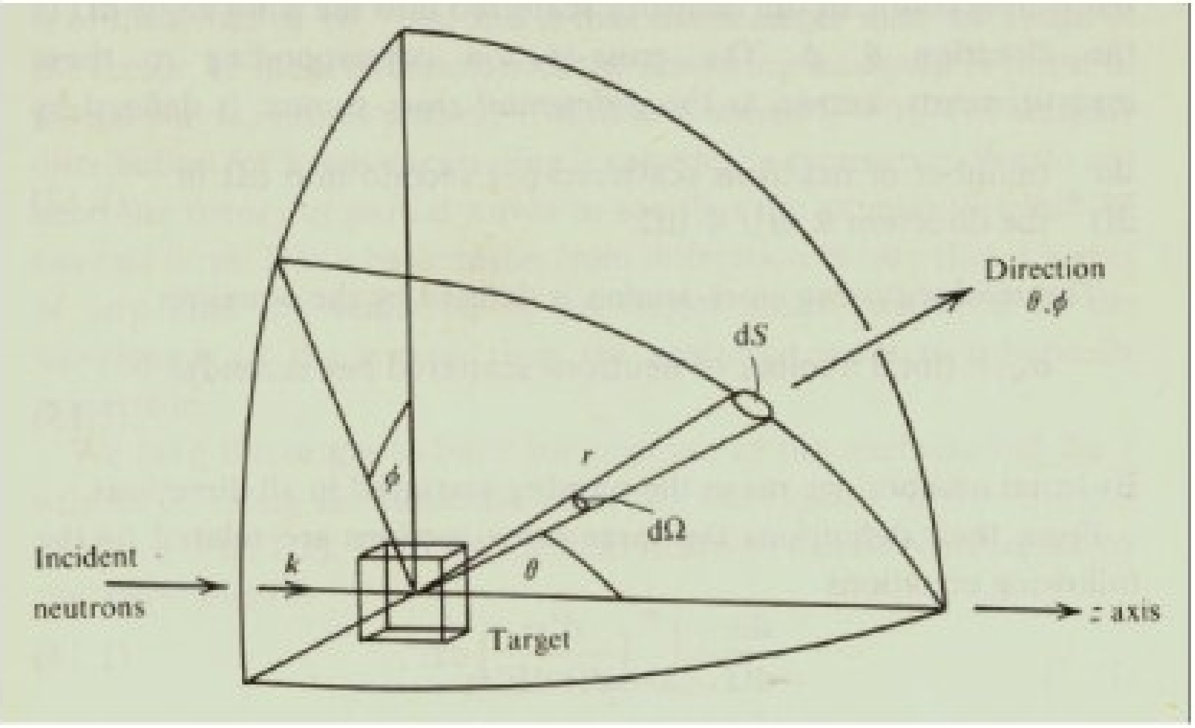


cross section

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

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

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



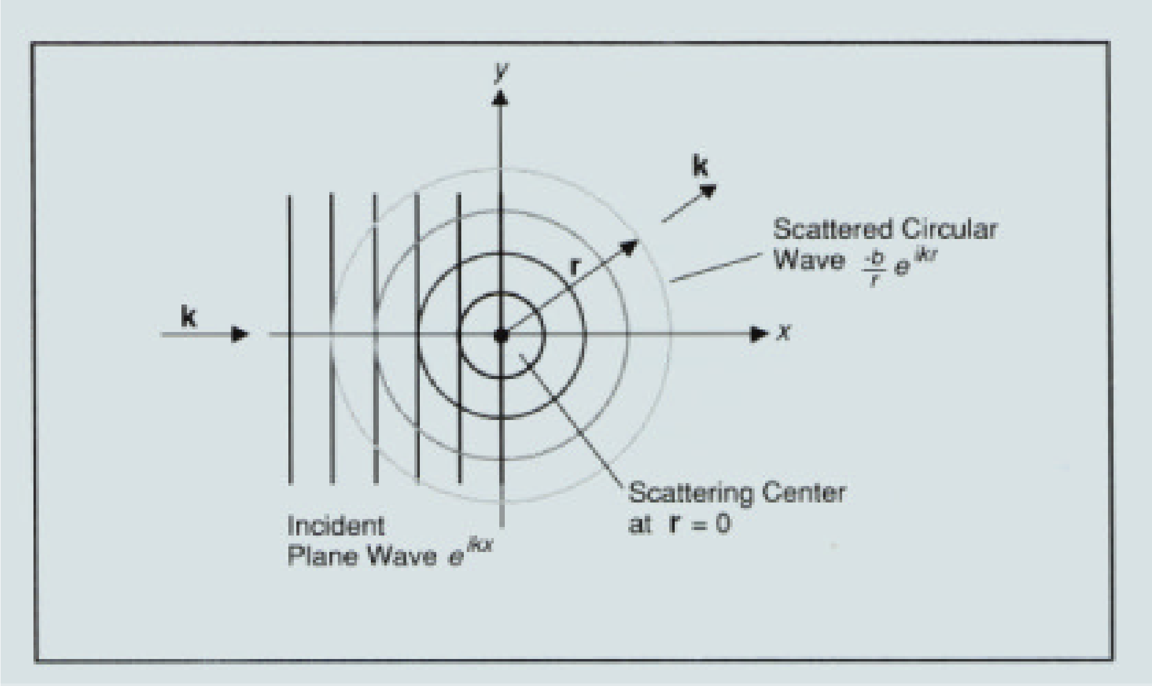
$$\Phi = \text{number of incident neutrons per cm}^2 \text{ per second}$$

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

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

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

Scattering by a Single (fixed) Nucleus



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

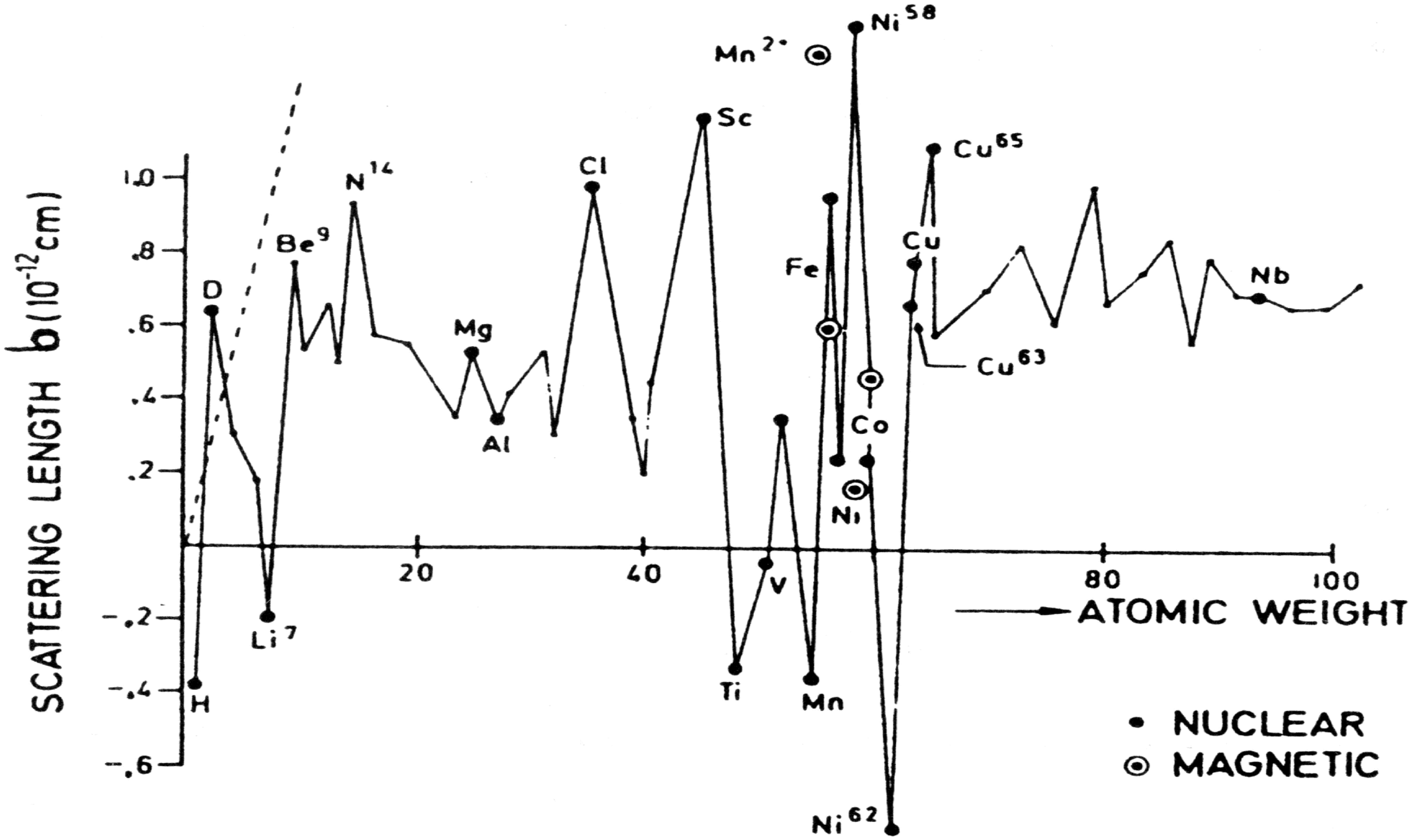
If v is the velocity of the neutron (same before and after scattering), the number of neutrons passing through an area dS per second after scattering is :

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

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

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

Intrinsic Cross Section: Neutrons



Intrinsic Cross Section: X-Rays

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

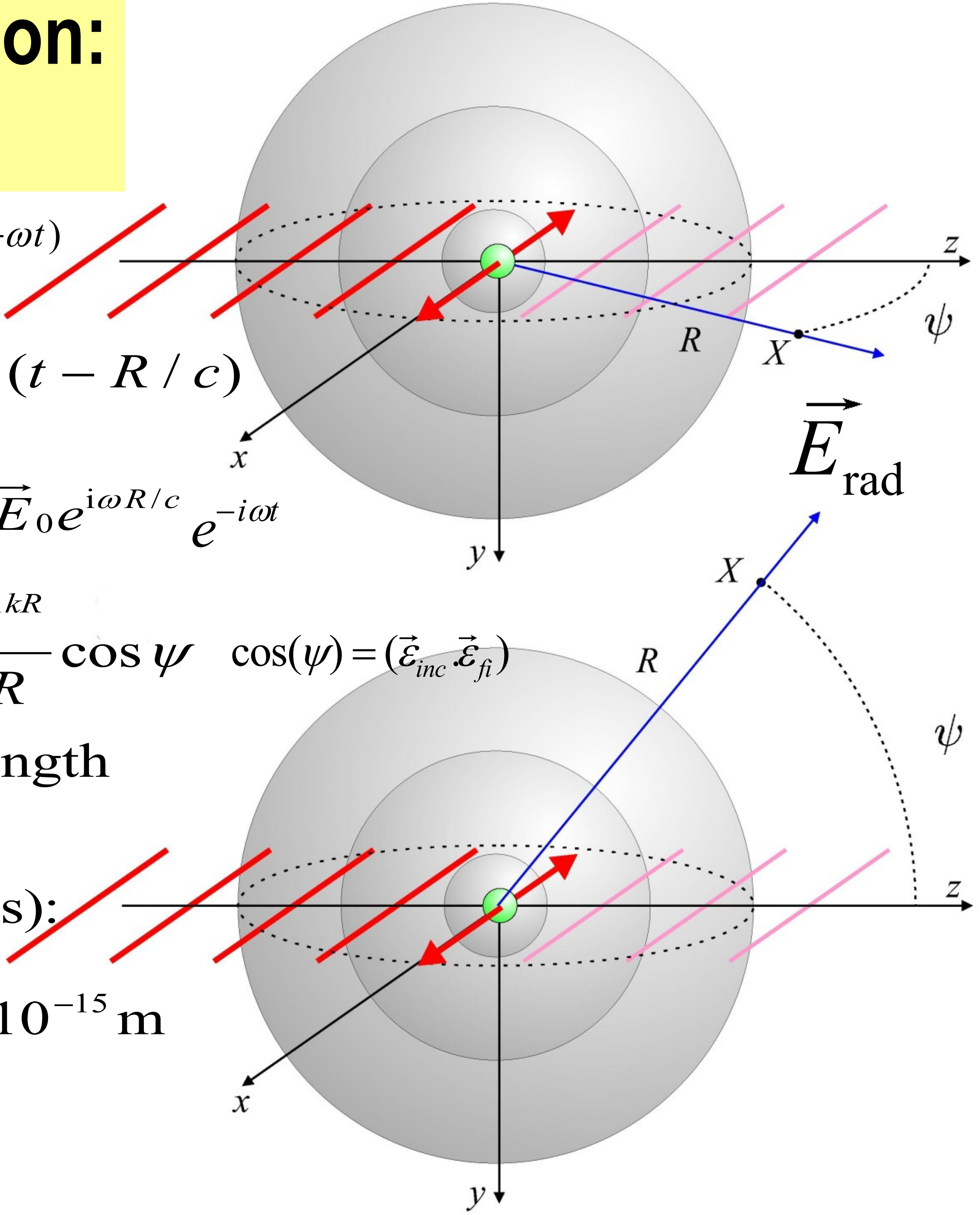
$$E_{i,\text{rad}}(R,t) = \frac{e}{4\pi\varepsilon_0 c^2 R}\, a_i(t-R/c)$$

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

$$\frac{E_{i,\text{rad}}(R,t)}{E_{\text{in}}} = -r_0\,\alpha(\omega)\,\frac{e^{\mathrm{i}kR}}{R}\cos\psi \qquad \cos(\psi) = (\vec{\varepsilon}_{inc}\cdot\vec{\varepsilon}_{fi})$$

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

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

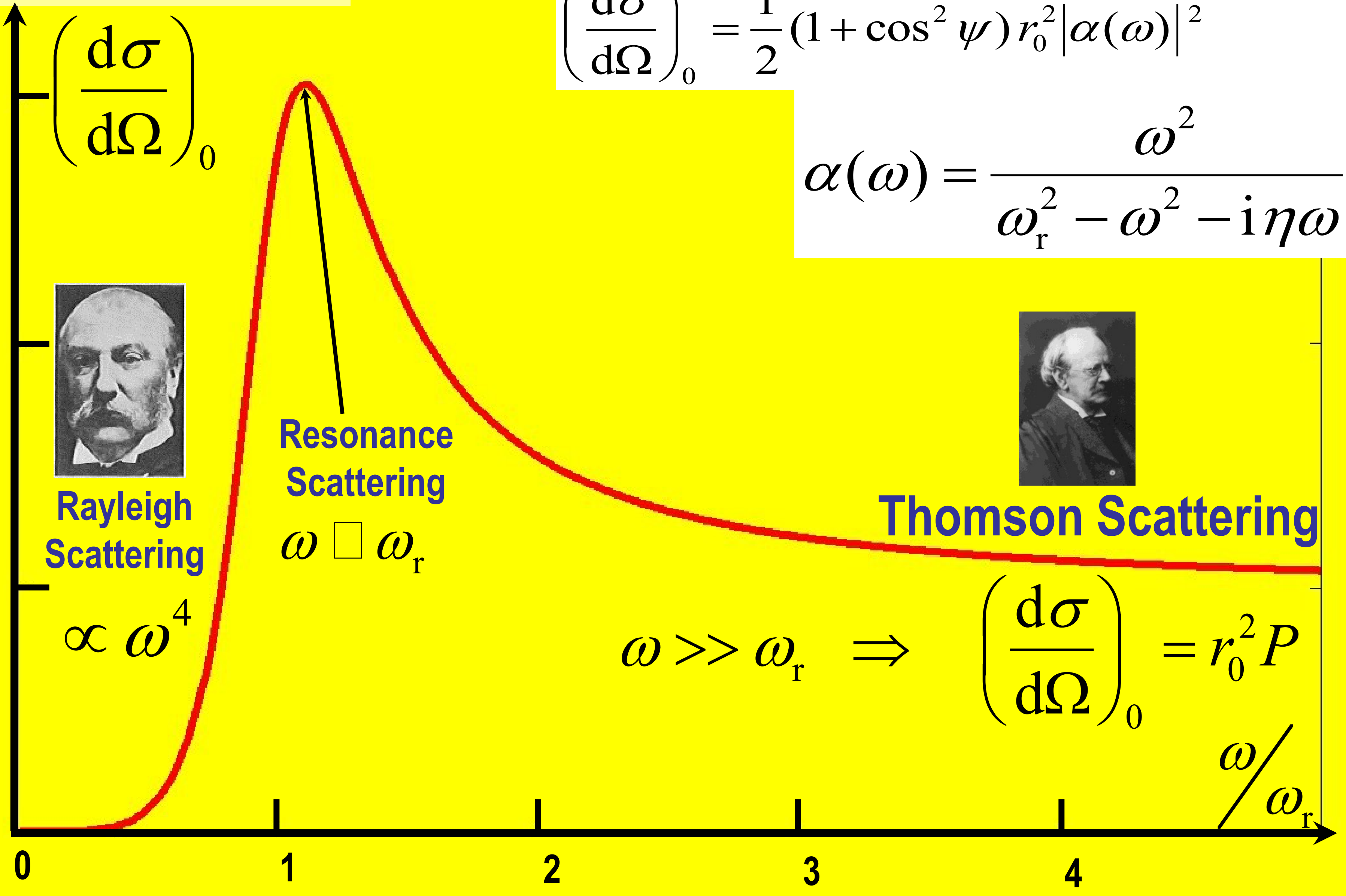


Intrinsic Cross Section: X-Rays

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

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

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



Rayleigh Scattering

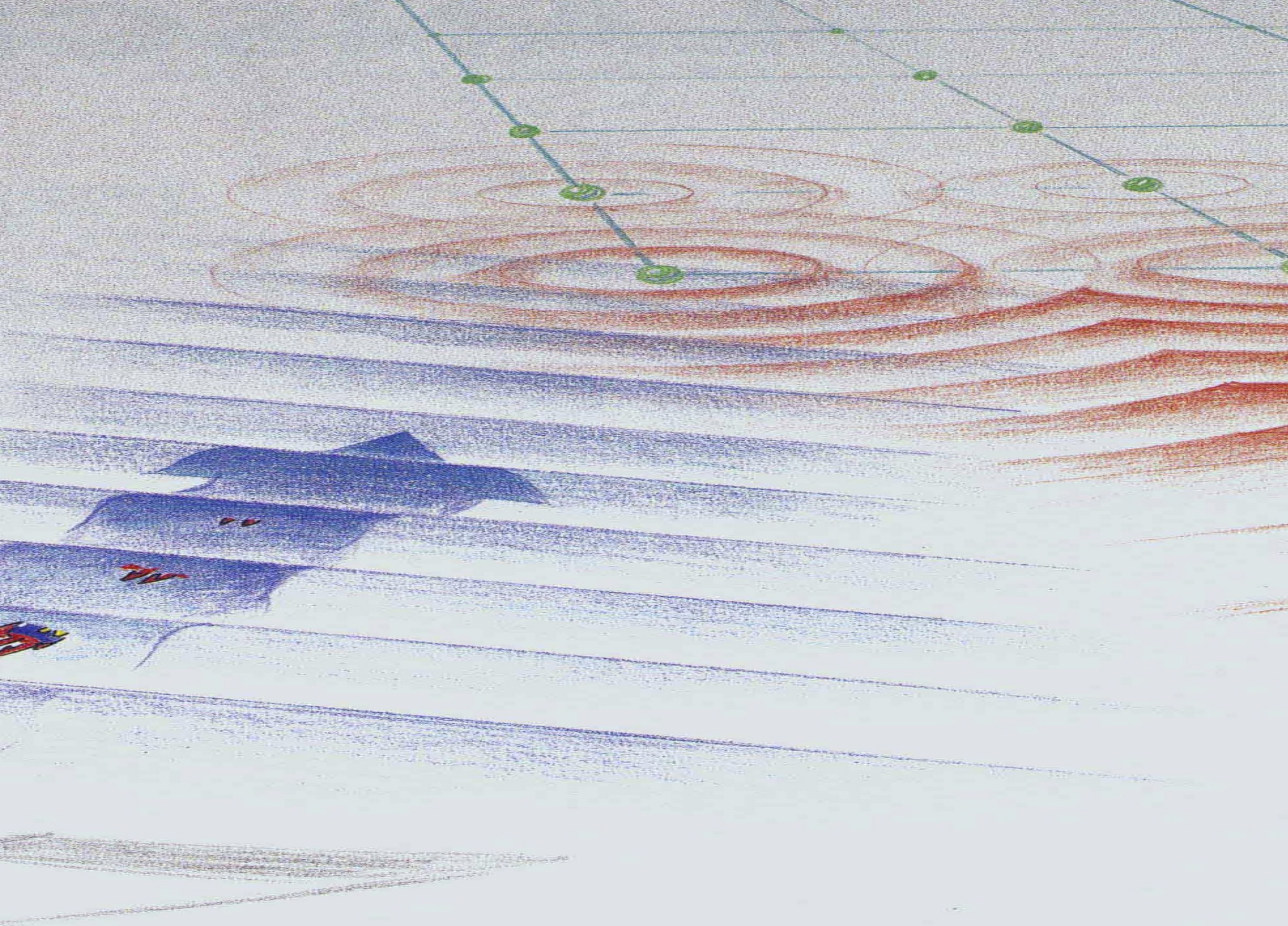
$\propto \omega^4$

Resonance Scattering

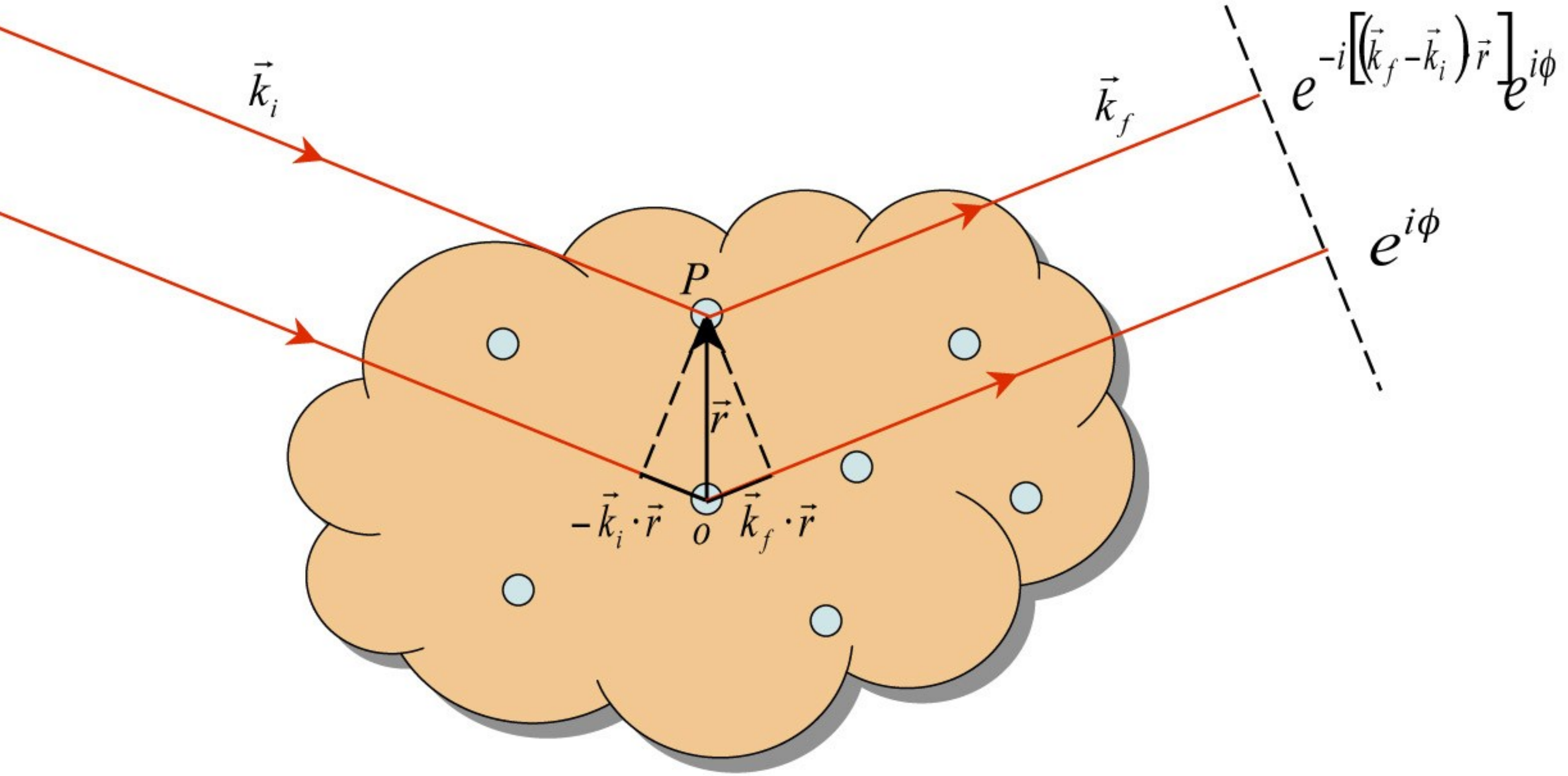
$\omega \,\square\, \omega_{\mathrm{r}}$

Thomson Scattering

$$\omega \gg \omega_{\mathrm{r}} \Rightarrow \left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\right)_0 = r_0^2 P$$

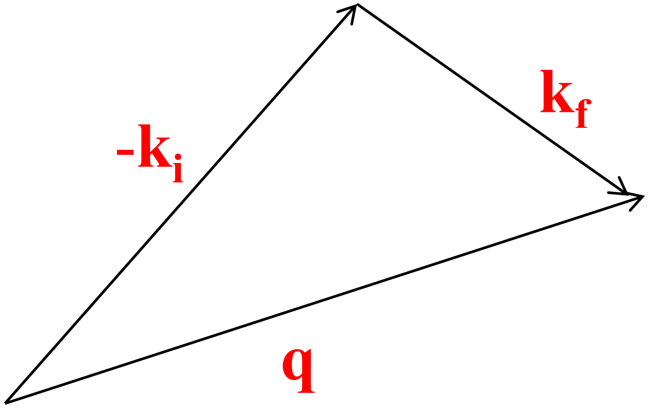


Adding up phases at the detector of the wavelets scattered from all the scattering centers in the sample:



Wave vector transfer is defined as

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



Neutrons

Sum of scattered waves on plane II:

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

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

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

X-rays

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

$\vec{r}_i$ → electron coordinates

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

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

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

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

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

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

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

$\{R_i\}$ = nuclear posns

x-rays

Now [redacted] = Fourier Transform of particle density

Proof: [redacted]

So

[redacted]

So [redacted]

Values of σ_{coh} and σ_{inc}

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

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

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