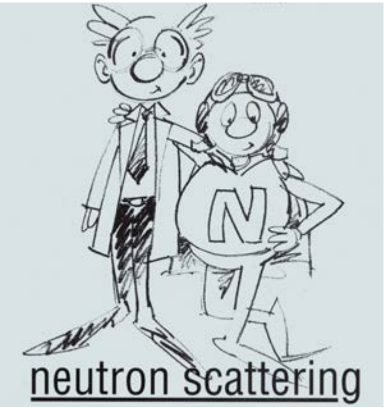


An Introduction to Neutron and X-Ray Scattering

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

Our culture depends on materials

- Material properties depend on structure at multiple length scales and time scales
- Designing new & better materials depends on mastering complex synthesis & understanding the relationship between structure/dynamics and material properties
- X-rays and neutrons provide two important tools for probing materials structure.

Wilhelm Conrad Röntgen 1845-1923

Dr W. C. Röntgen

EINE NEUE ART

VON

STRAHLEN.

VON

DR W. RÖNTGEN,

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

WÜRZBURG.

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

BUCH- UND KUNSTHANDLUNG.

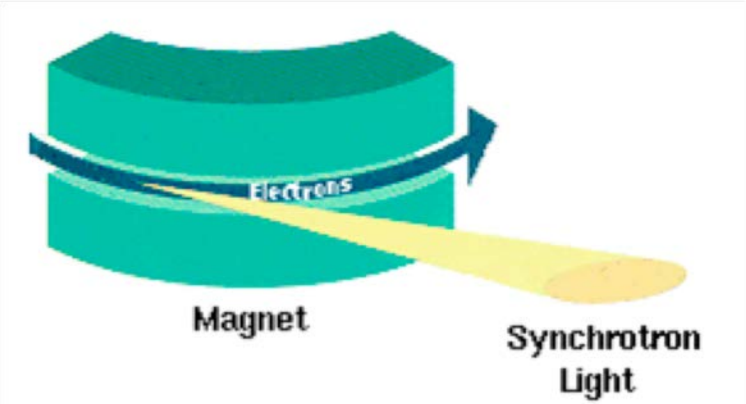
Ende 1895.

60 ₰.

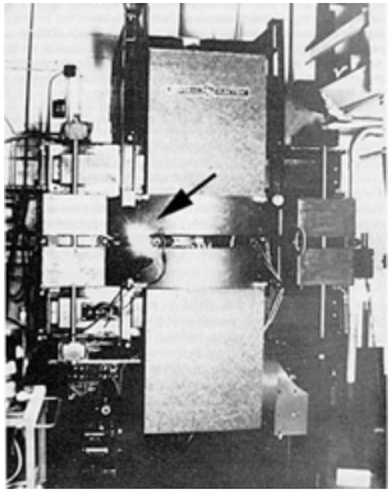
1895: Discovery of X-Rays

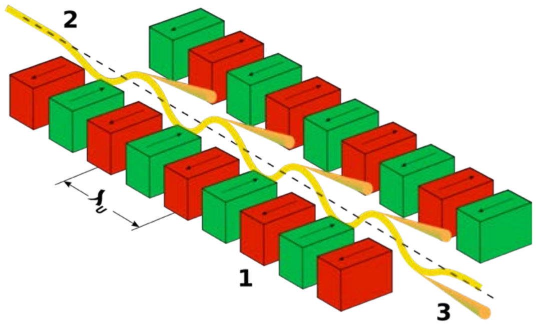
Synchrotron Radiation

- Produced when charged particles (electrons, positrons) accelerate perpendicular to their velocity



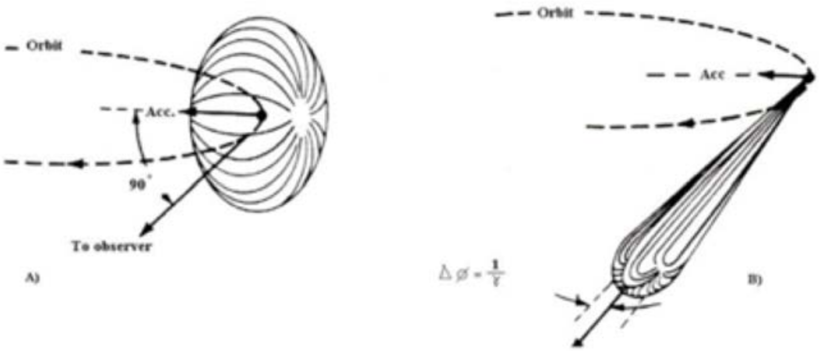
Bending magnet





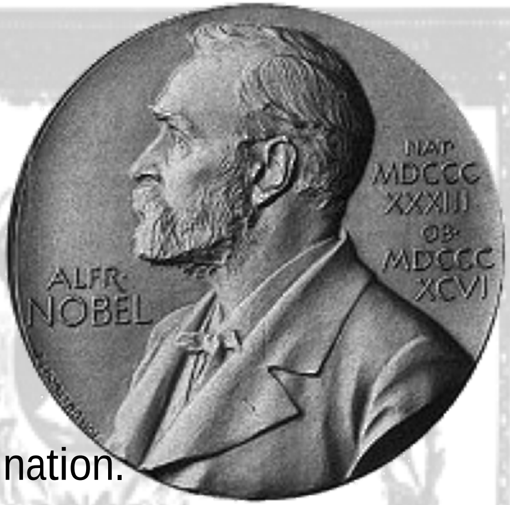
Undulator or Wiggler

- Discovered in 1946 using GE synchrotron. Emitted in forward cone with small divergence. Polarized



- Watson and Perlman;Science 1978 Mar 24;199(4335):1295-302: Seeing with a new light: synchrotron radiation

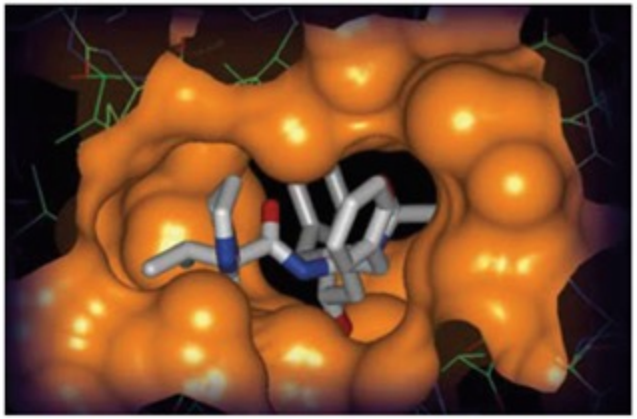
Nobel Prizes for Research with X-Rays



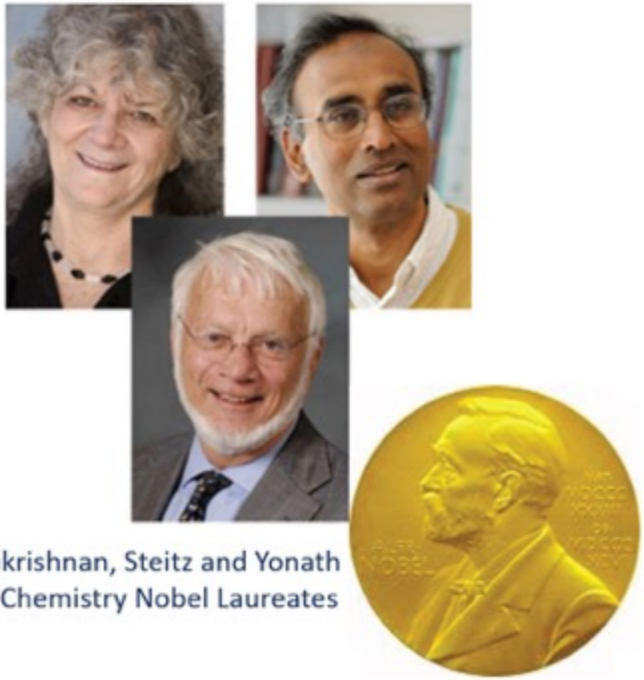
1901 W. C. Röntgen in Physics for the discovery of x-rays.
1914 M. von Laue in Physics for x-ray diffraction from crystals.
1915 W. H. Bragg and W. L. Bragg in Physics for crystal structure determination.
1917 C. G. Barkla in Physics for characteristic radiation of elements.
1924 K. M. G. Siegbahn in 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.
2010 A. Geim & K. Novoselov for graphene

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

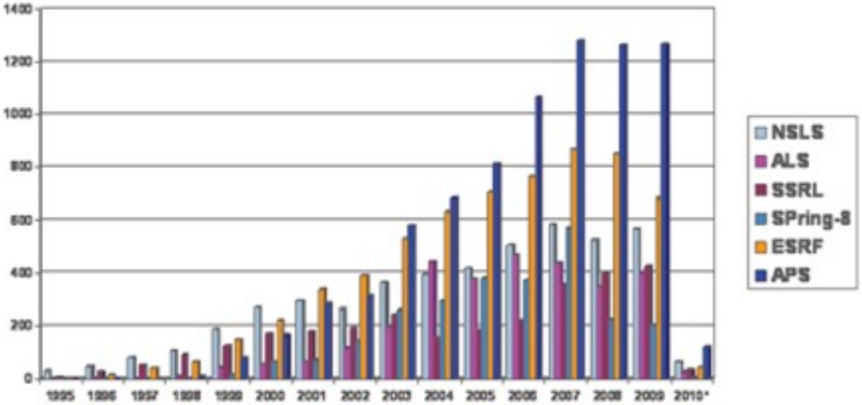
Renal cancer drug pazopanib™ developed in part based on APS research (GlaxoSmithKline)



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



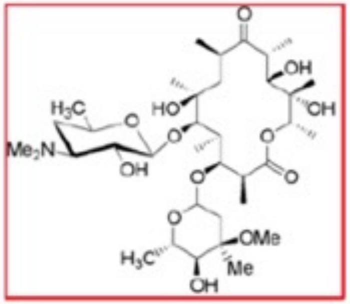
Ramakrishnan, Steitz and Yonath
2009 Chemistry Nobel Laureates



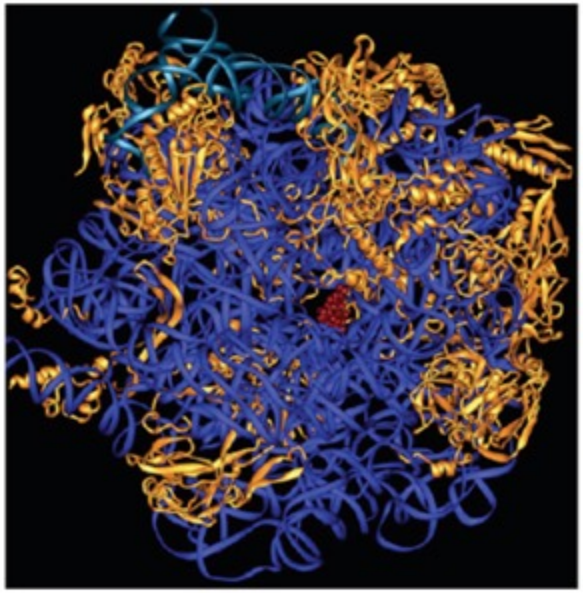
APS protein structure output is almost twice that of any other light source

Designing antibiotics –

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



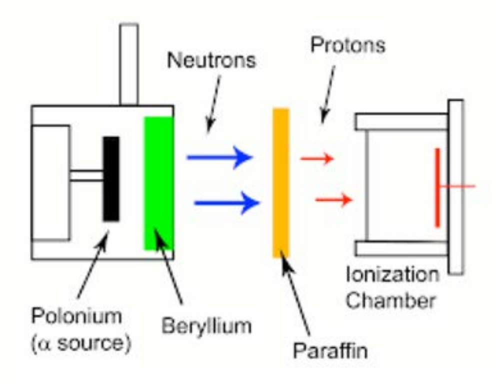
Erythromycin – a macrolide antibiotic that blocks protein synthesis by binding to bacterial ribosomes but not to eukaryotic ribosomes



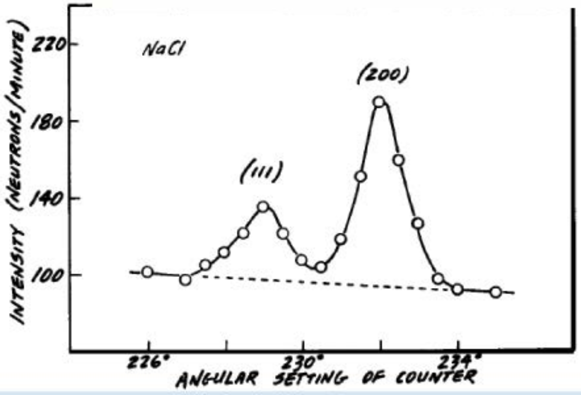
www.molgen.mpg.de

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

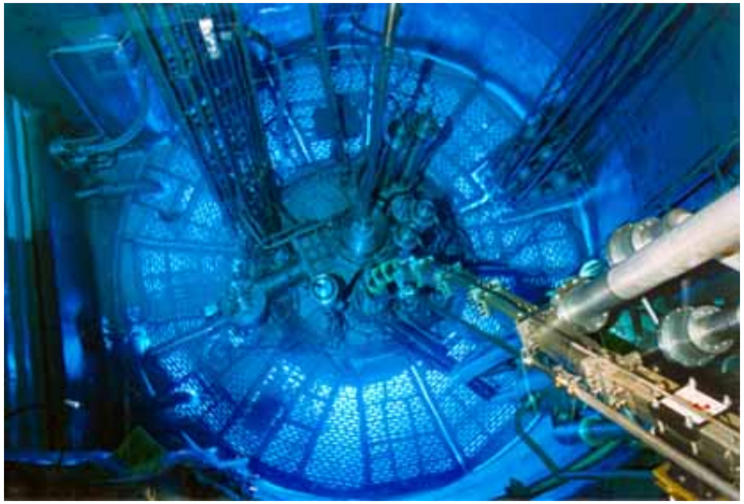
- 1972 – conformation of polymers
-
- 1994 – Nobel Prize for Shull and Brockhouse

Cliff Shull (1915 – 2001)

The Institut Laue Langevin Reactor

Cross section of reactor

1. Safety rod
2. Neutron guide pool
3. Reflector tank
4. Double neutron guide
5. Vertcial cold source
6. Reactor core
7. Horiz cold source
8. Control rod

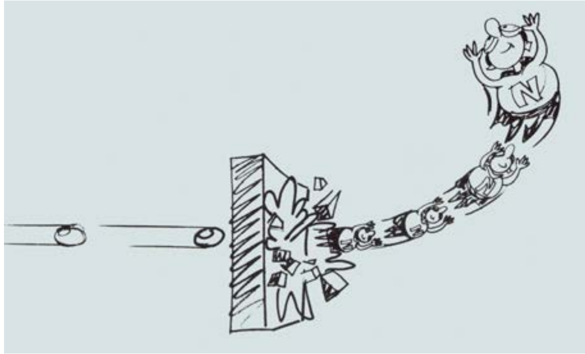


Reactor pool; light water

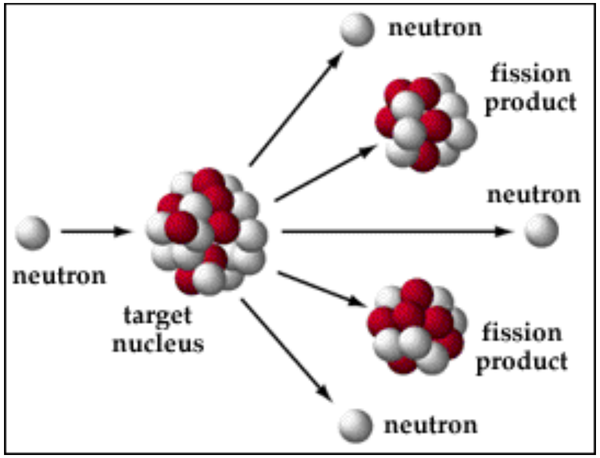
Fuel element: top view

Spent fuel pool →

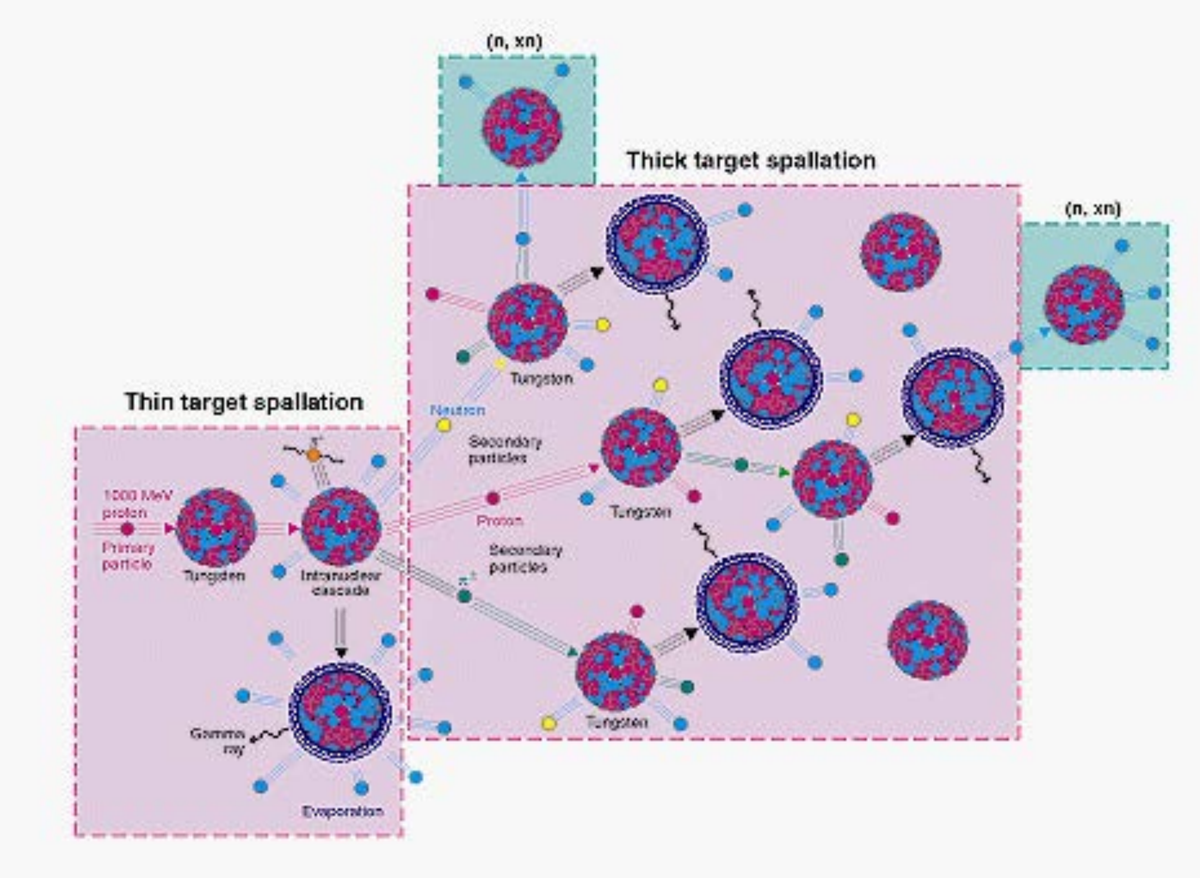
Nuclear Fission & Spallation are the Methods of Choice to Produce Neutrons for Scattering



Artist’s view of spallation



Nuclear Fission



Spallation

Fission: ~200 MeV per useful neutron
Spallation: ~20 MeV per useful neutron

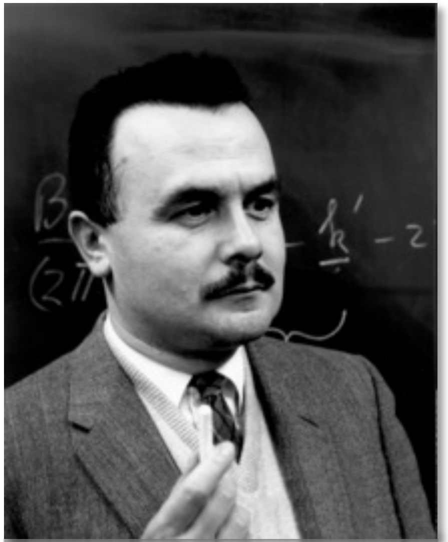
The ESRF* & ILL* With Grenoble & the Belledonne Mountains

*ESRF = European Synchrotron Radiation Facility; ILL = Institut Laue-Langevin

Nobel Prize in Physics, 1994

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

Bertram N. Brockhouse



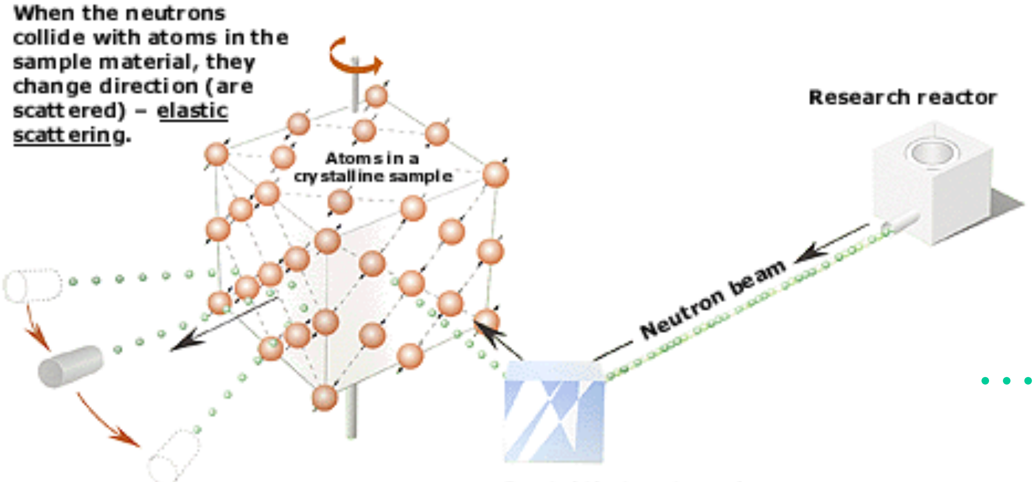
Development of
neutron spectroscopy

Clifford G. Shull

Development of the
neutron diffraction technique

The 1994 Nobel Prize in Physics – Shull & Brockhouse

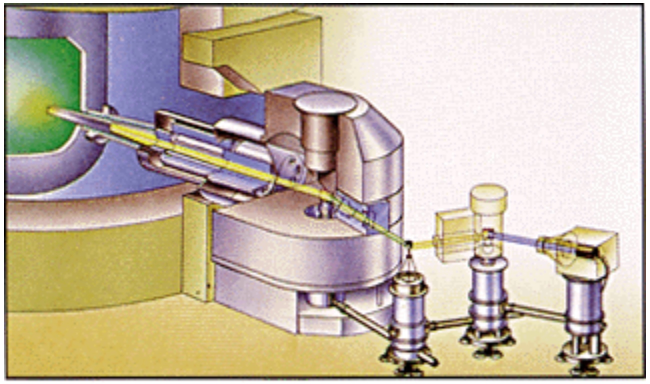
Neutrons show where the atoms are….



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

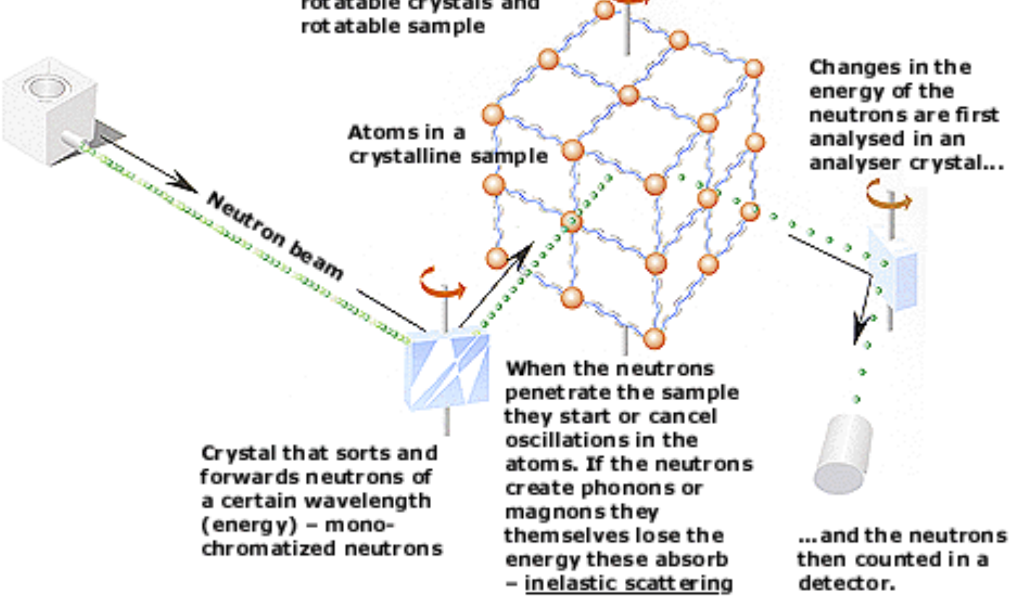
Crystal that sorts and forwards neutrons of a certain wavelength (energy) – monochromatized neutrons

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.



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.

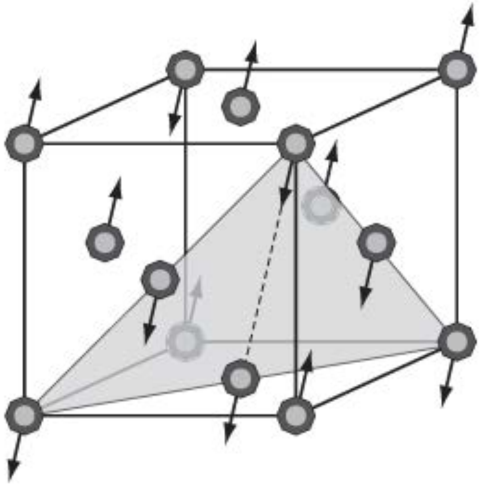
Why do Neutron Scattering?

- 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
  - Neutrons do not destroy samples

- Neutron Disadvantages/Issues
  - 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)
  - Many investigations that used to be the domain of neutrons (e.g. inelastic scattering, magnetic scattering) can now be done to some extent by x-rays because x-ray sources are so much more intense

First Study of an Antiferromagnetic Structure

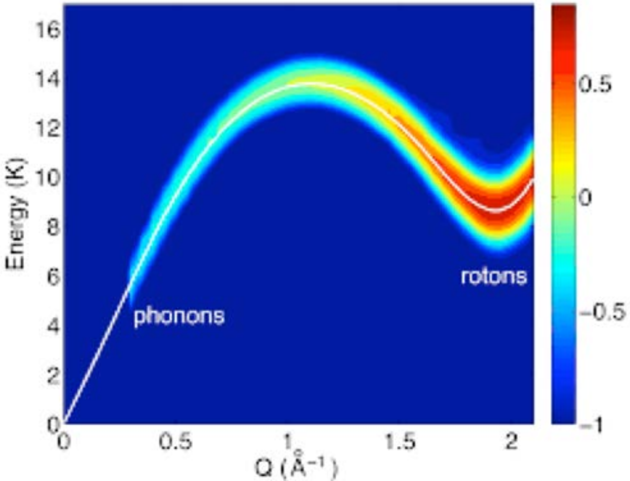


Antiferromagnetic Structure of MnO
(Shull and Wollan *Phys. Rev.* 83, 333 (1951))

1949, Shull & Smart: AF order exists
1951, Shull, Strauser & Wollan: FM order in (111) planes, noncollinear structure not excluded
1988, Shaked, Faber & Hitterman: collinear, spins oriented in (111) plane
2006, Goodwin & al.: oriented in <11-2> direction, slight out-of-plane component

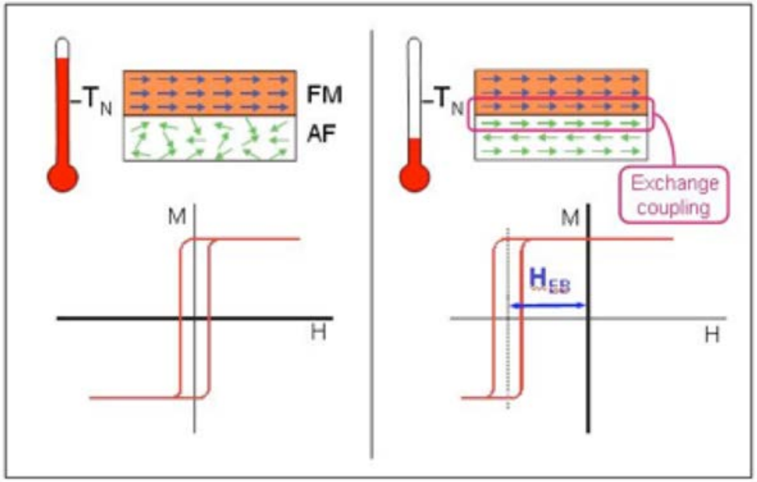
Historic accomplishments (Neutrons)

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



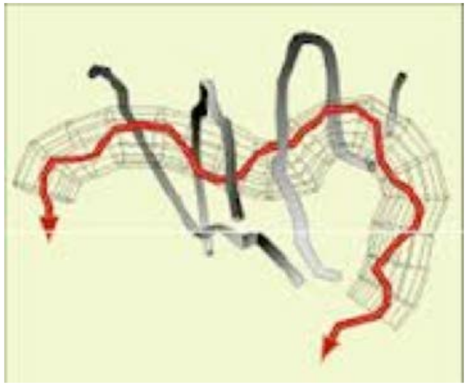
Recent Applications of Neutrons

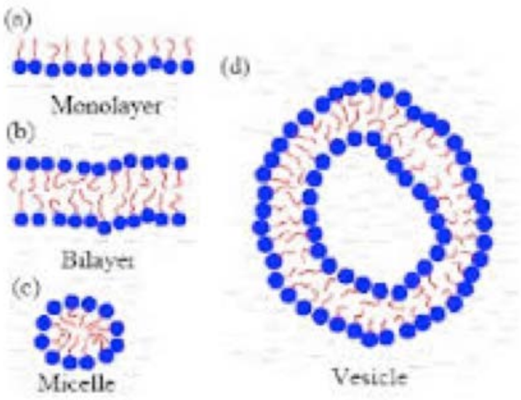
- Quantum Phase Transitions and Critical points
- Magnetic order and magnetic fluctuations in the high-Tc cuprates
- Gaps and low-lying excitations (including phonons) in High-Tc
- Magnetic Order and spin fluctuations in highly-correlated systems
- Manganites
- Magnetic nanodot/antidot arrays
- Exchange bias
- Protein dynamics
- Glass transition in polymer films
- Boson peaks in glasses
- Protonation states in biological macromolecules from nuclear density maps

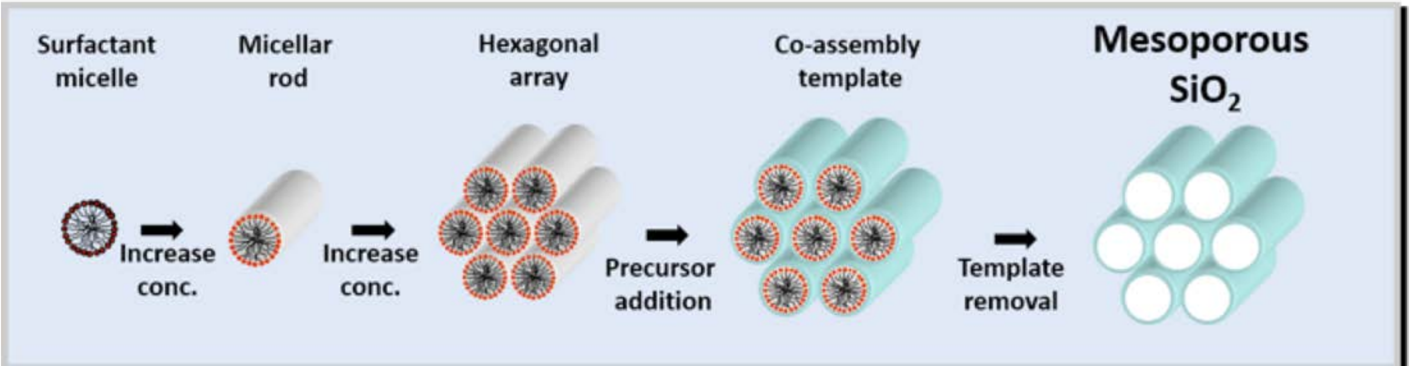


Neutron Applications to “large” structures

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



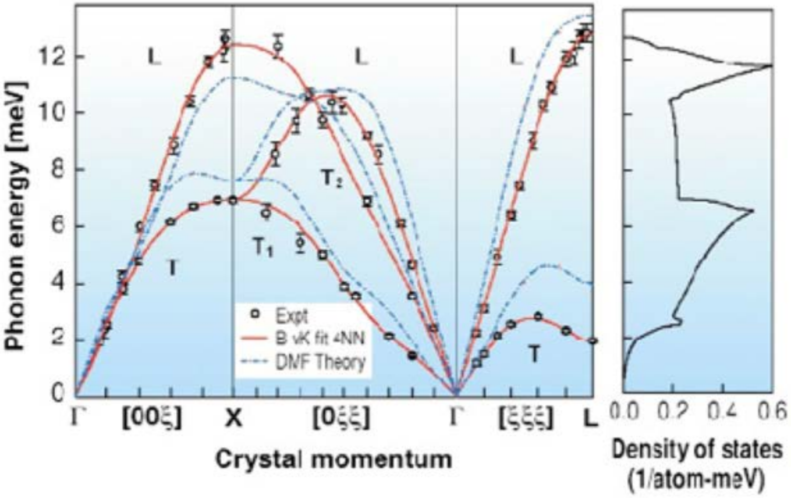




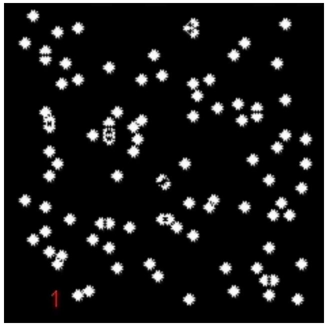
Science with X-Rays

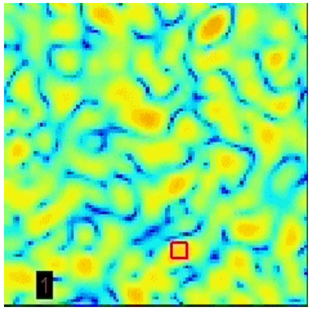
- Diffraction and crystal structures
- Structure Factors of liquids and glasses
- Surface and Interface structures
- Structures of Thin Films
- ARPES
- EXAFS, XANES
- Studies of Magnetism with resonant XM
- Inelastic X-ray scattering: phonons, electronic excitations
- Imaging/Tomography with very high spatial resolution
- Microscopy
- X-ray photon correlation spectroscopy

Plutonium phonons

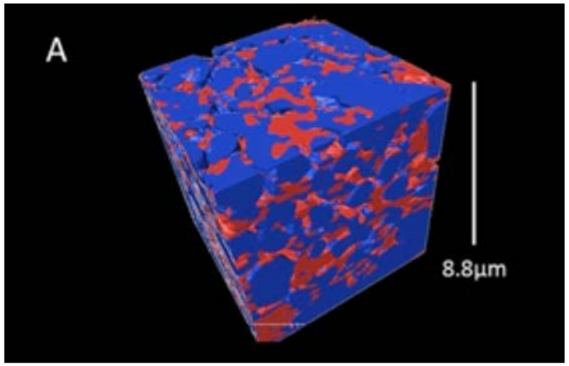


http://sinhagroup.ucsd.edu/Research_XPCS.htm

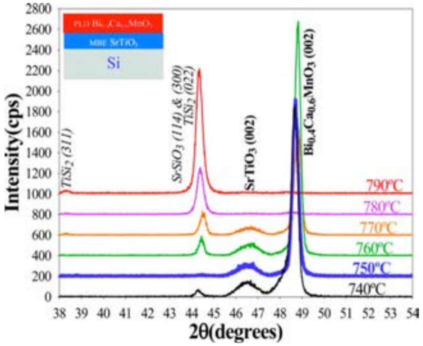




Microstructure of
battery electrodes

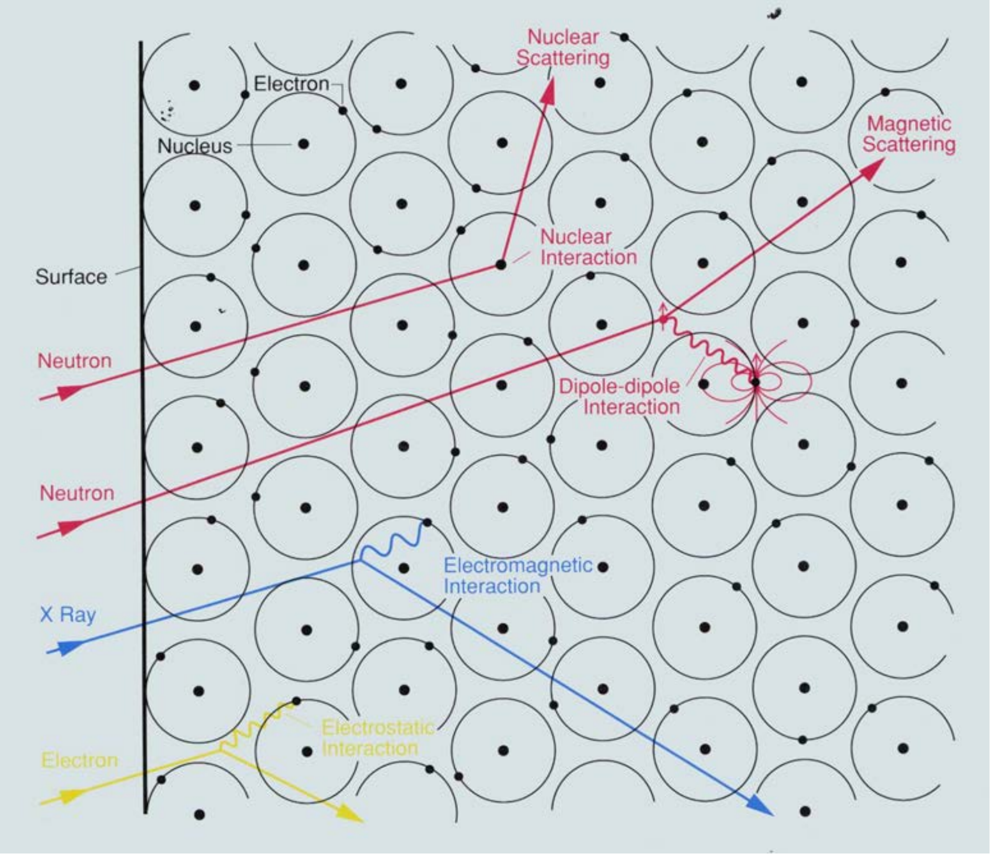


Applications of X-rays to Surface/Interface Scattering



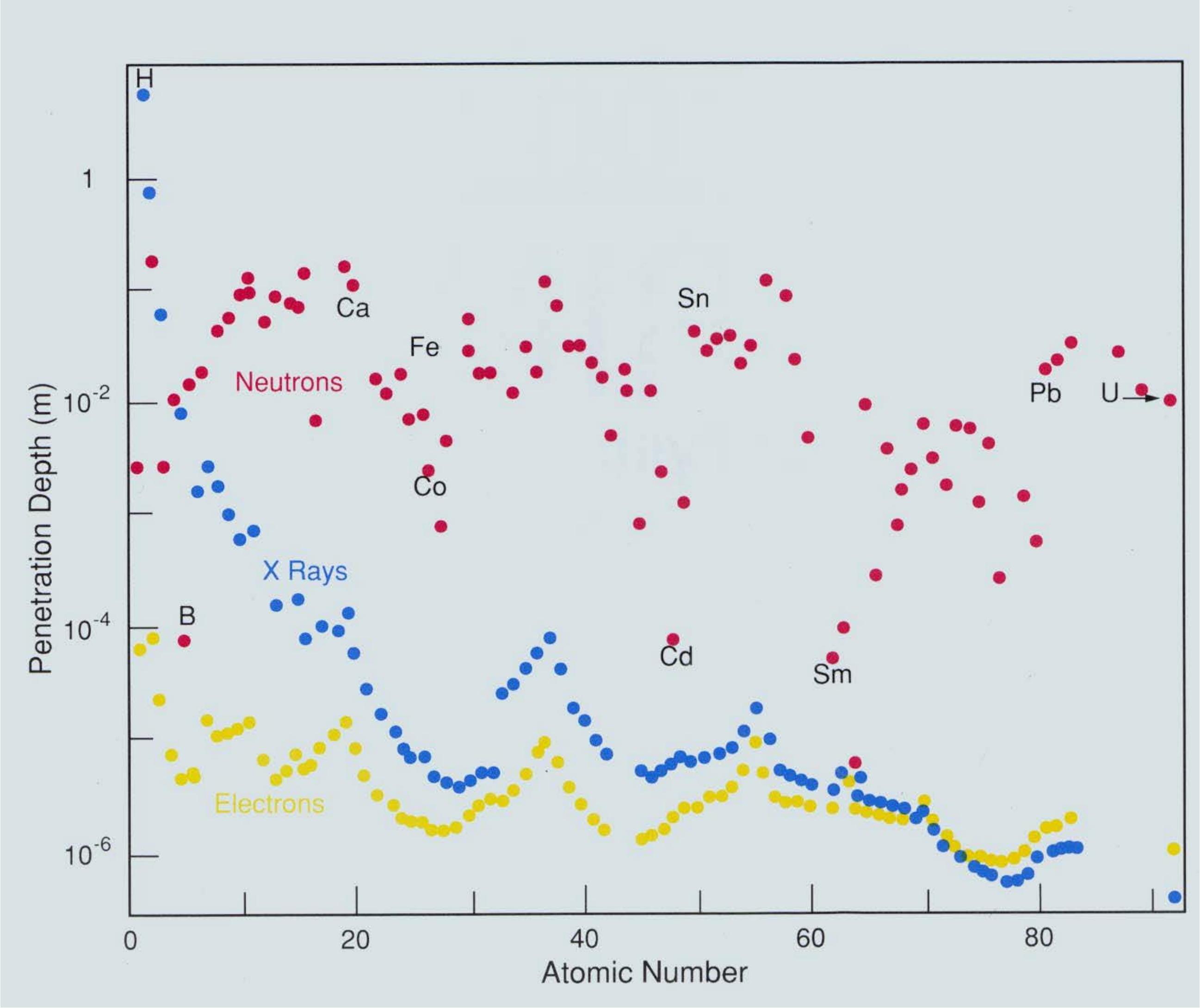
- study the morphology of surface and interface roughness
- wetting films
- film growth exponents
- capillary waves on liquid surfaces (polymers, microemulsions, liquid metals, etc.)
- islands on block copolymer films
- pitting corrosion
- magnetic roughness
- study the morphology of magnetic domains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

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:

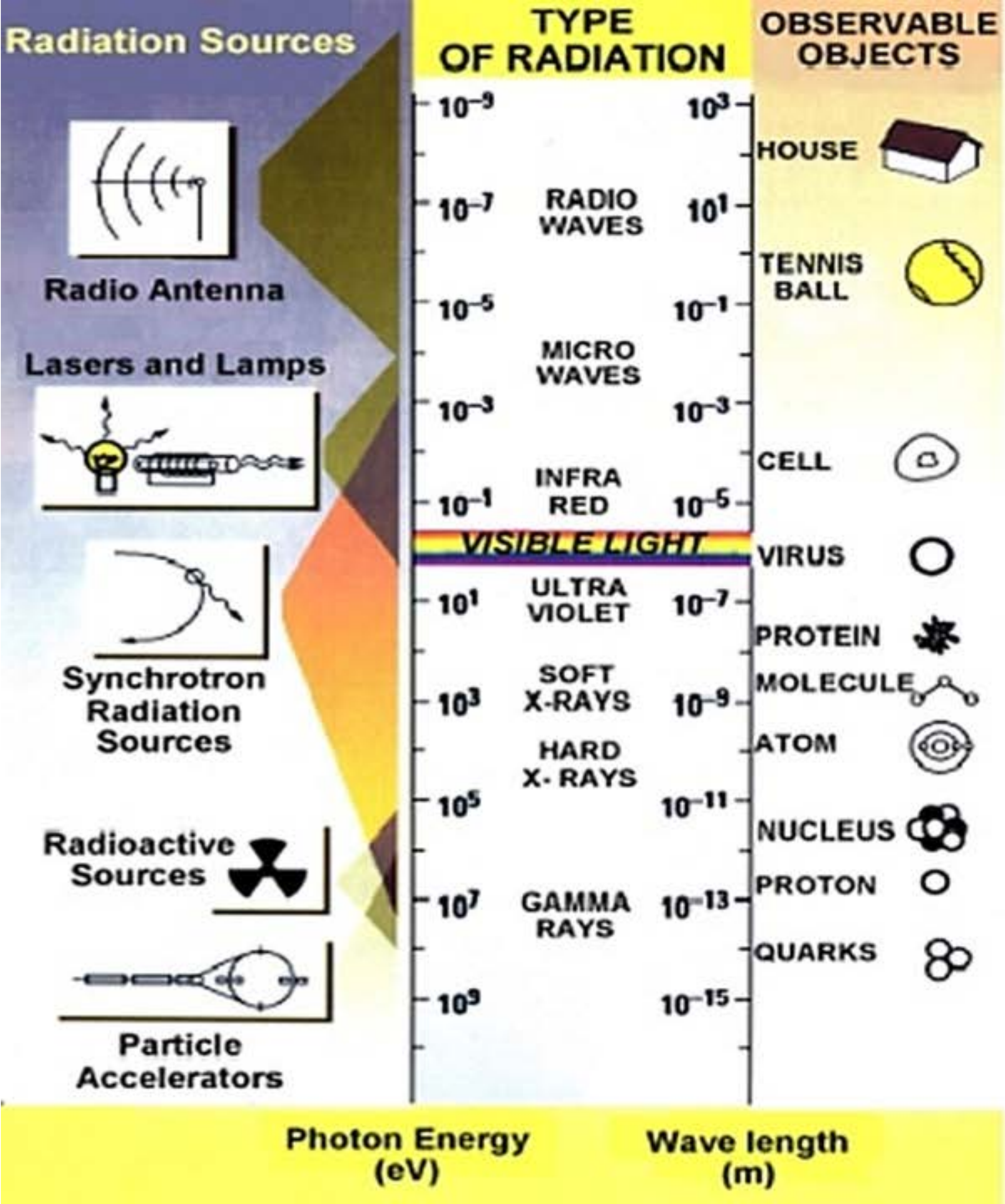
- decreasing penetration as Z increases

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



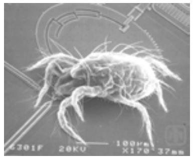
Wavelength
≈
Object Size
≈
Angstroms for Condensed Matter Research

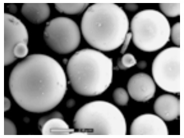
$$\lambda[\text{Å}] = \frac{12.398}{E_{\text{ph}}[\text{keV}]}$$

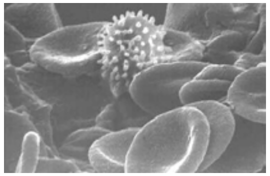
Neutron and X-Ray Scattering: Structure from Angstroms to Microns!

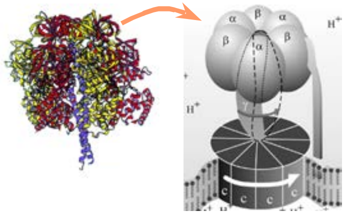

Human hair


Ant

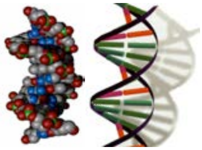

Dust mite

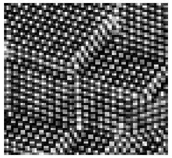

Fly ash

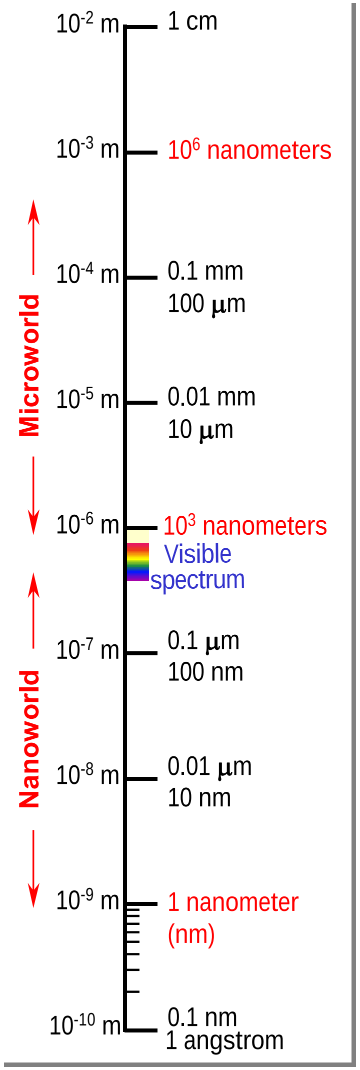

Red blood cells



ATP synthase


DNA


Atoms of silicon


10^{-2} m — 1 cm

10^{-3} m — 10^6 nanometers

10^{-4} m — 0.1 mm
100 μm

10^{-5} m — 0.01 mm
10 μm

10^{-6} m — 10^3 nanometers

Visible spectrum

10^{-7} m — 0.1 μm
100 nm

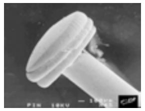
10^{-8} m — 0.01 μm
10 nm

10^{-9} m — 1 nanometer (nm)

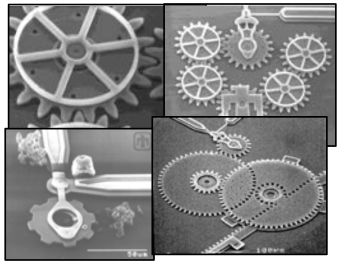
10^{-10} m — 0.1 nm
1 angstrom

Microworld

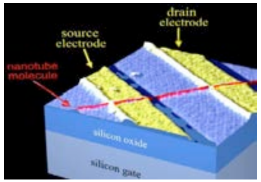
Nanoworld


Head of a pin

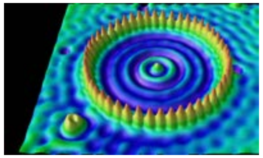
Microelectromechanical Devices



Nanotube electrode

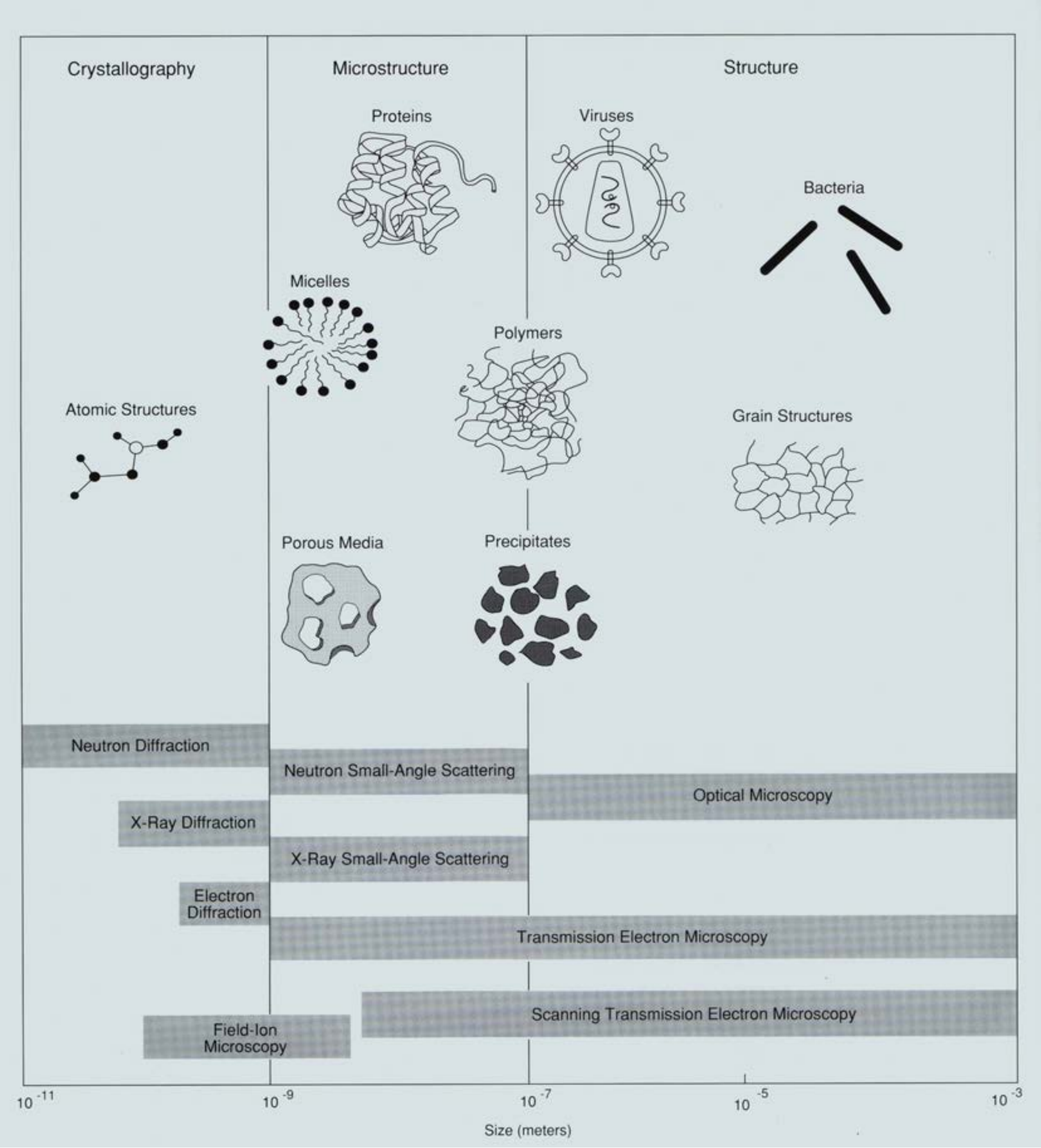


Nanotube transistor


Quantum corral of 48 iron atoms

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

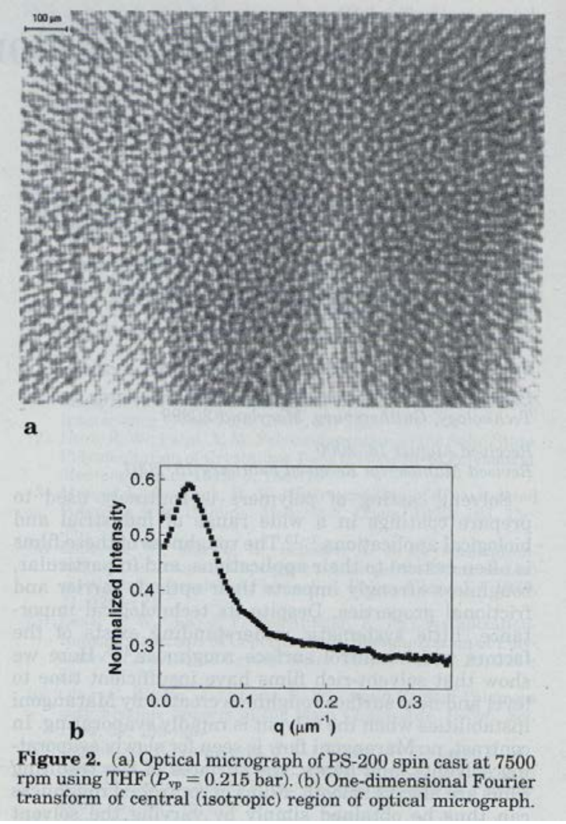


Figure 2. (a) Optical micrograph of PS-200 spin cast at 7500 rpm using THF (P_{vp} = 0.215 bar). (b) One-dimensional Fourier transform of central (isotropic) region of optical micrograph.

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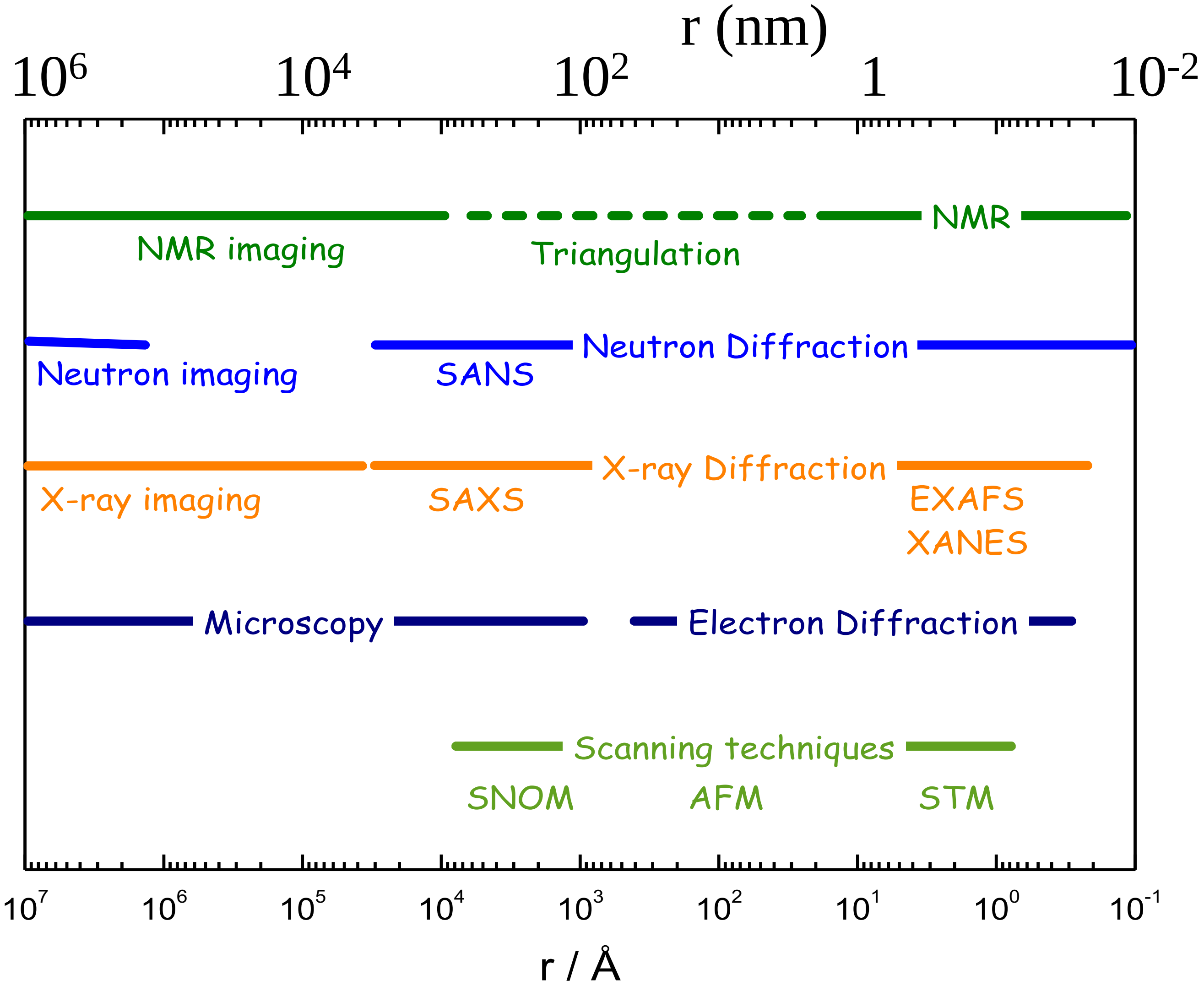
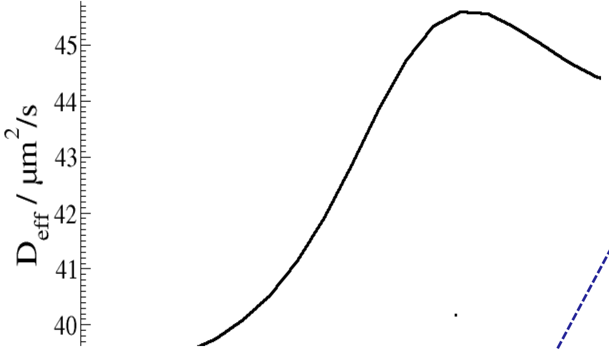
Neutron & X-ray Scattering Complement Other Techniques in Length Scale….



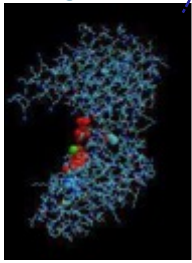
Functional domain dynamics in proteins

NSE

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

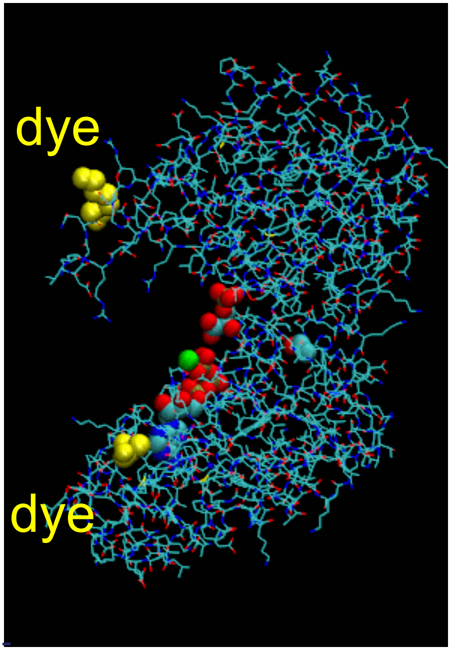


q~2π/length



FRET

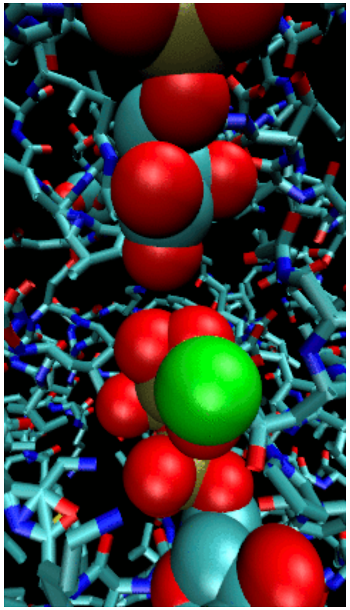
fixed defined position
> µs timescale



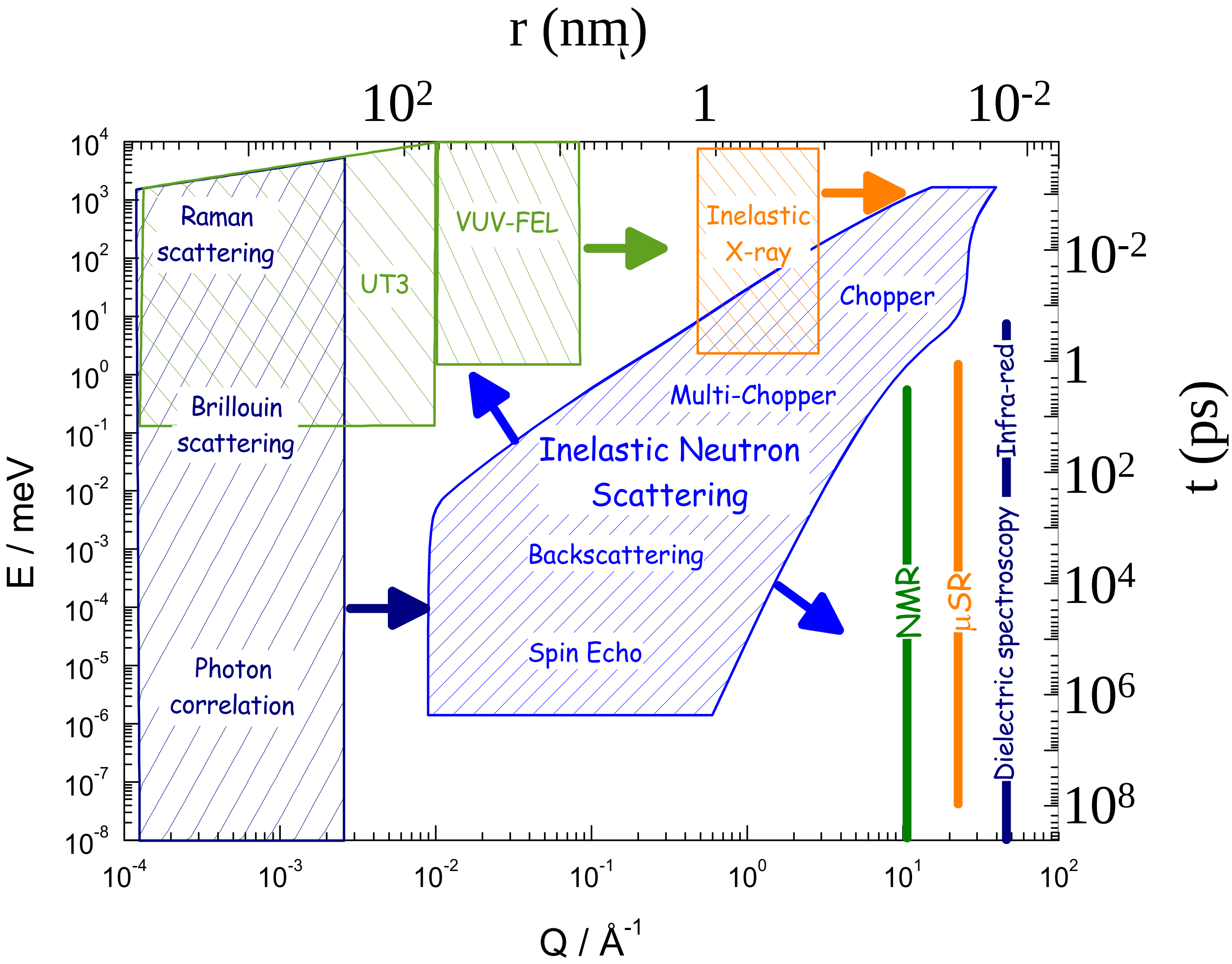
phosphoglycerate kinase

NMR

ps - ms timescale
small proteins



……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: $\mu_n = - 1.913\ \mu_N$
- 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})

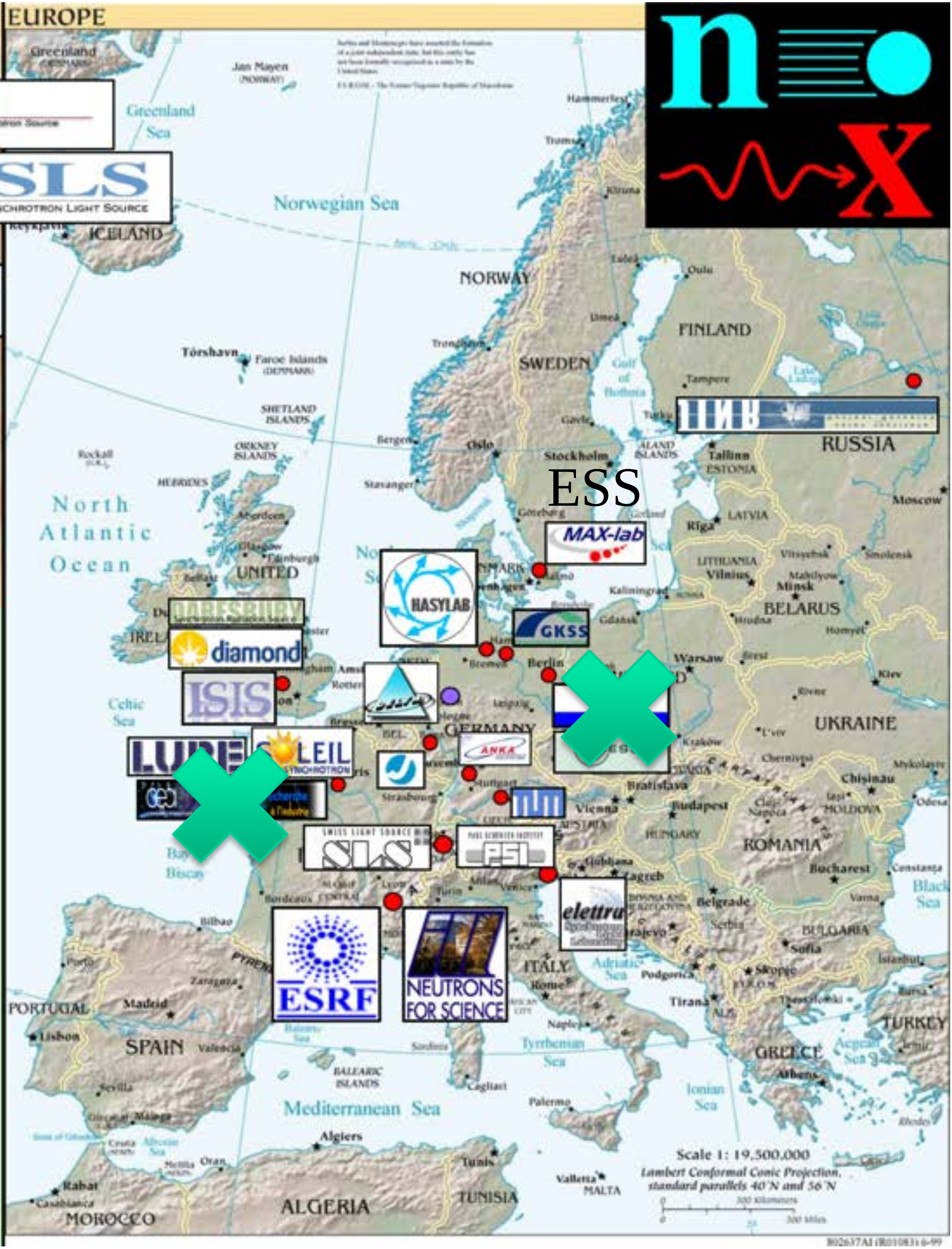
X-Rays also have Wave-Like and Particle-Like Properties

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

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

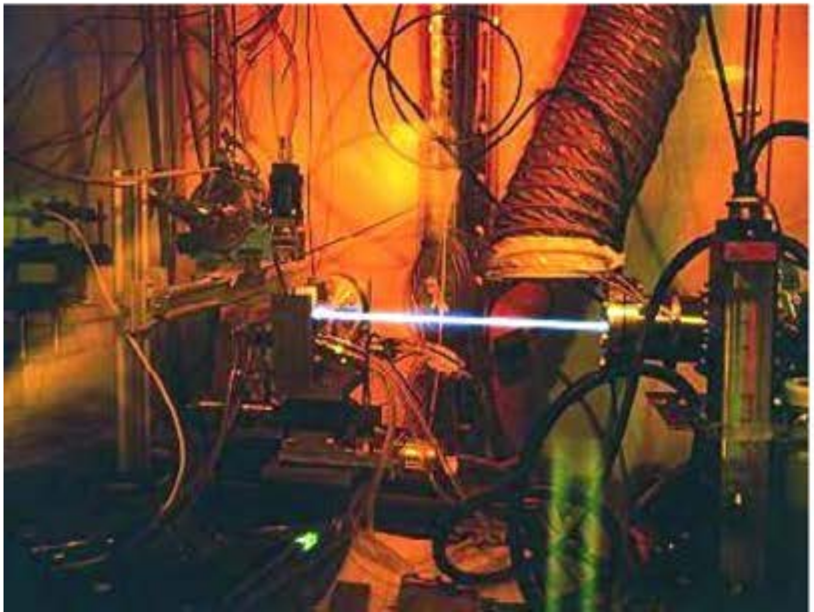
Brightness & Fluxes for Neutron & X-Ray Sources

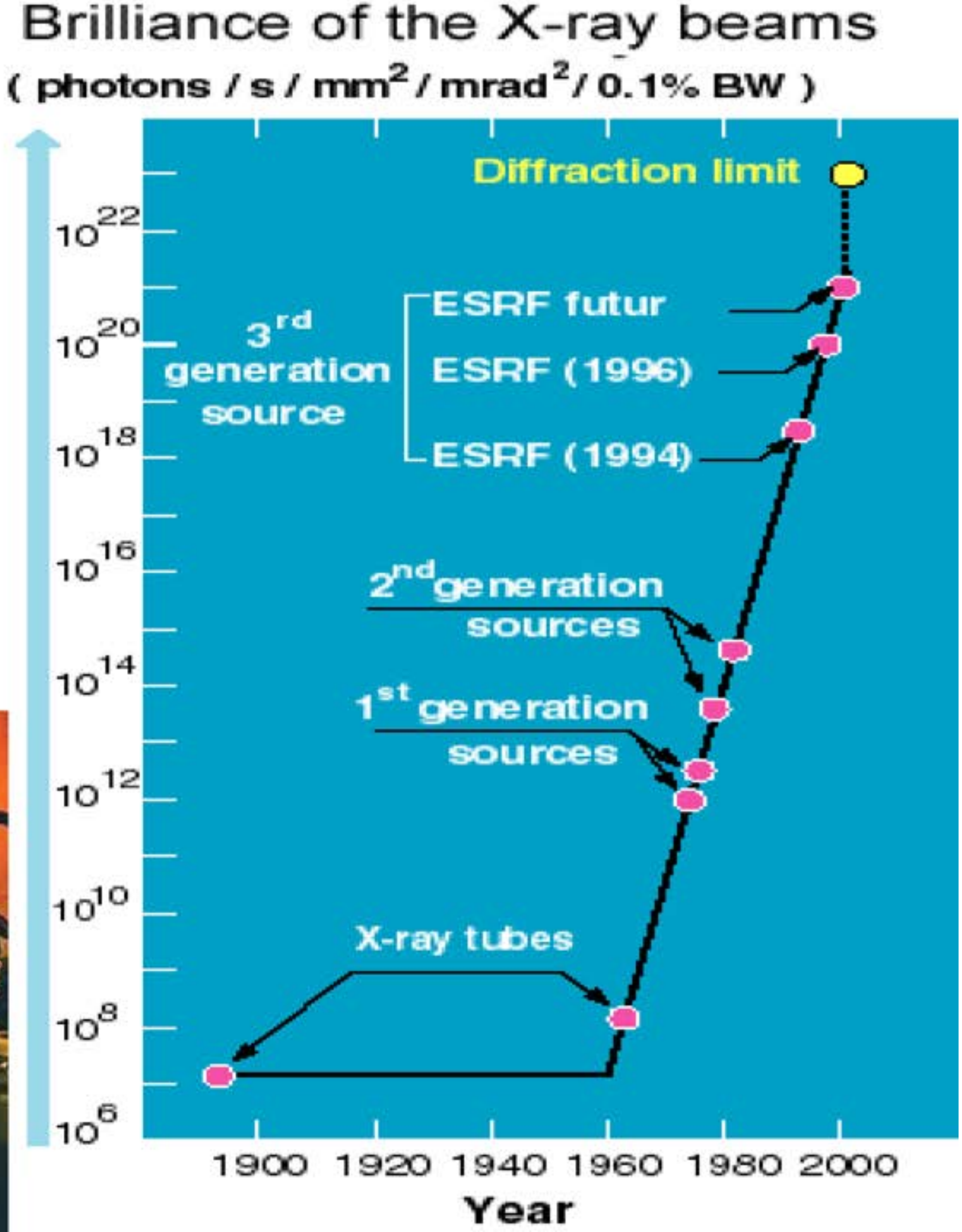
	Brightness *(s^{-1} m^{-2} $ster^{-1}$)*	*dE/E* *(%)*	*Divergence* *($mrad^2$)*	*Flux* *(s^{-1} m^{-2})*
Neutrons	10^{15}	2	10 x 10	10^{11}
Rotating Anode	10^{16}	3	0.5 x 10	5 x 10^{10}
Bending Magnet	10^{24}	0.01	0.1 x 5	5 x 10^{17}
Wiggler	10^{26}	0.01	0.1 x 1	10^{19}
Undulator (APS)	10^{33}	0.01	0.01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

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

Why Synchrotron-radiation ?

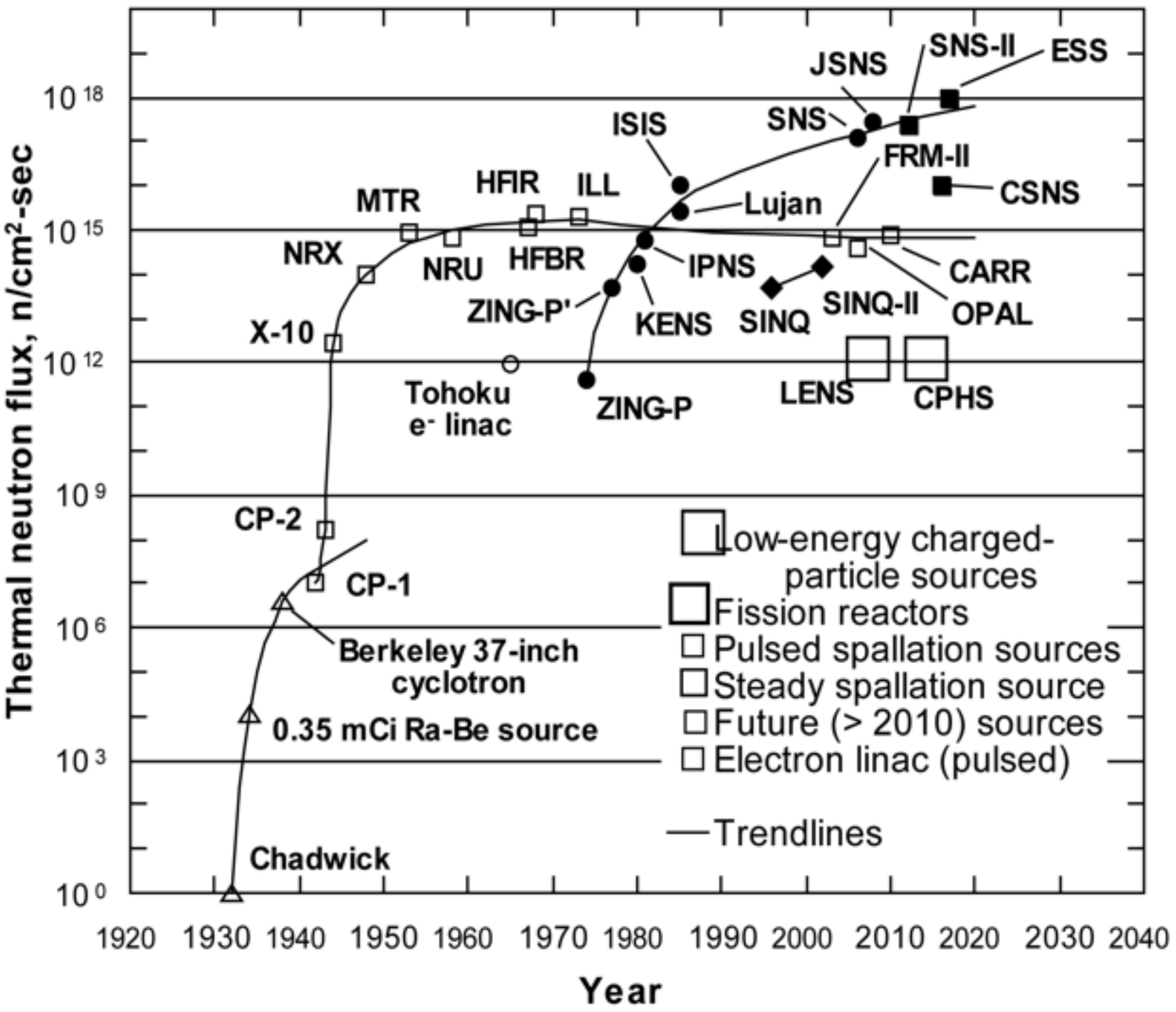
Intensity !!!





Brilliance of the X-ray beams

Brugger Plot



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 by nuclear potential and magnetic fields comparable
  - 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
  - Orbital and spin components of magnetic scattering can be separated

- Disadvantages ☹
  - Strong absorption of low energy photons
  - Contrast issues (low contrast for different hydrocarbons, scattering ~ Z^2)
  - Radiation damage to samples
  - Magnetic scattering is weak except at resonances resonances
  - Energy resolution limited for inelastic scattering