Neutron Scattering and Dynamics

John R.D. Copley

NCNR Neutron Spectroscopy Tutorial

December 4, 2007

Acknowledgments

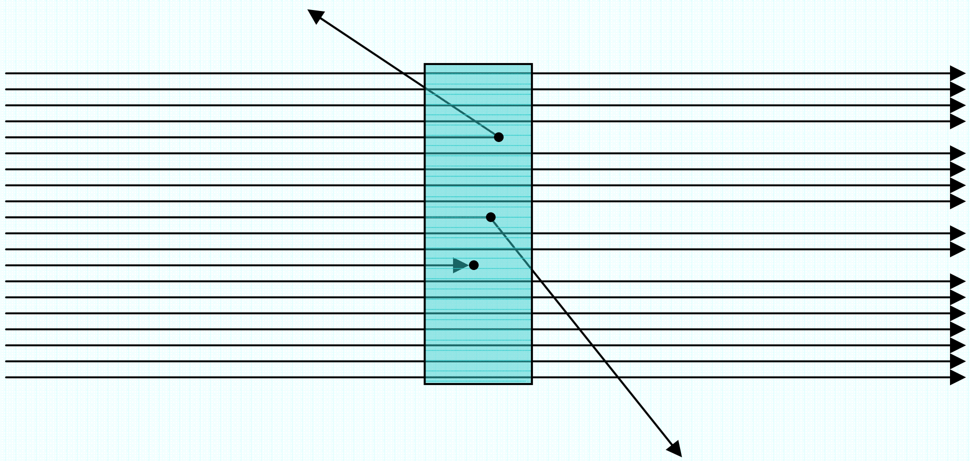
Center for High Resolution Neutron Scattering (CHRNS)
NSF DMR-0454672

NIST Center for Neutron Research (NCNR)

Yamali Hernandez

Fates of a neutron

Consider a sample placed in a neutron beam.
What happens to the neutrons?

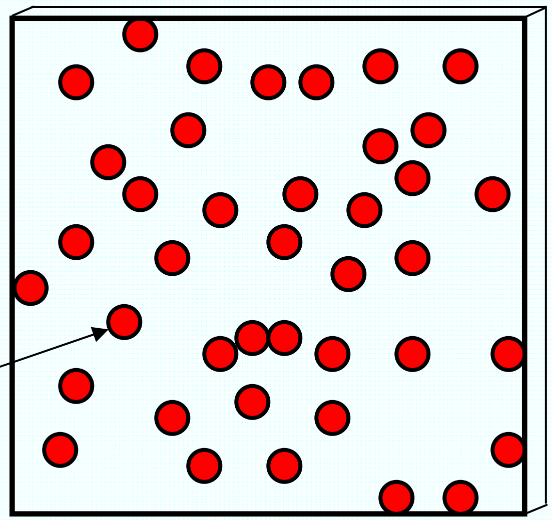


They are transmitted, absorbed, or scattered.

$$p_T + p_A + p_S = 1, \quad \text{but what are } p_T,\ p_A \text{ and } p_S\,?$$

Absorption probability p_A (one type of atom)

We consider a "thin" sample (no shadowing)



effective absorption area σ_A

- N atoms
- area A
- thickness t
- volume V=At
- number density ρ=N/V

$$p_A = \frac{N\sigma_A}{A} = \frac{N\sigma_A t}{V} = \Sigma_A t$$

σ_A is the *microscopic* absorption cross section (barn/atom)

$\Sigma_A = \rho\sigma_A$ is the *macroscopic* cross section (cm^{-1})

1 barn = 10^{-24} cm^2

Absorption and scattering rates

Our "thin" sample is placed in a beam whose current density (or "flux") is Φ (n/cm^2/s). The current, i.e. the number of neutrons hitting the sample, is $I_0 = \Phi A$ n/s.

The absorption rate is as follows:

$$I_A = I_0 p_A = (\Phi A)(\Sigma_A t) = \Phi V \Sigma_A = \Phi N \sigma_A$$

Similarly the scattering rate is:

$$I_S = I_0 p_S = (\Phi A)(\Sigma_S t) = \Phi V \Sigma_S = \Phi N \sigma_S$$

Hence the transmission rate (n/s) is

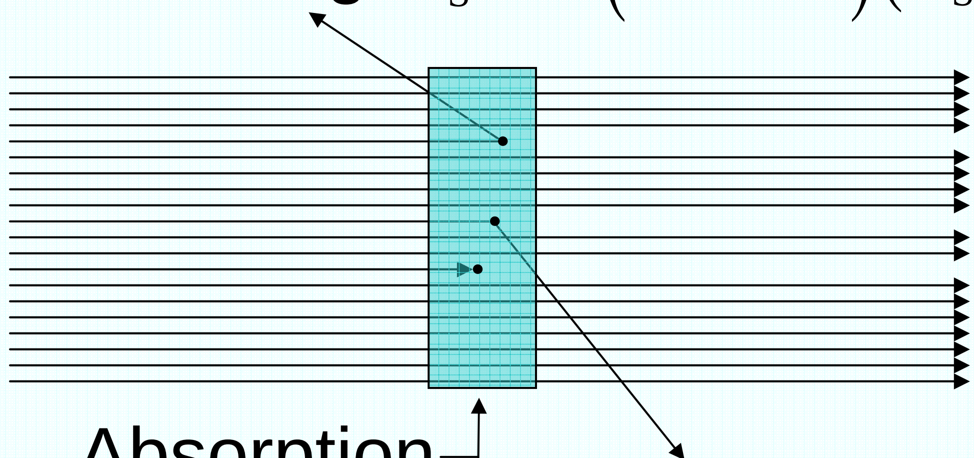
$$I_T = I_0 p_T = I_0 - I_A - I_S = (\Phi A)(1 - \Sigma_T t)$$

where $\Sigma_T = \Sigma_A + \Sigma_S$ is the <u>total removal cross section.</u>

“Thick” samples

Scattering, absorption and transmission probabilities for a sample that is not necessarily “thin”.

Scattering $\Sigma_S t \Leftrightarrow \left(1 - e^{-\Sigma_T t}\right)\left(\Sigma_S / \Sigma_T\right)$



Transmission

$\left(1 - \Sigma_S t - \Sigma_A t\right) \Leftrightarrow e^{-\Sigma_T t}$

Hence

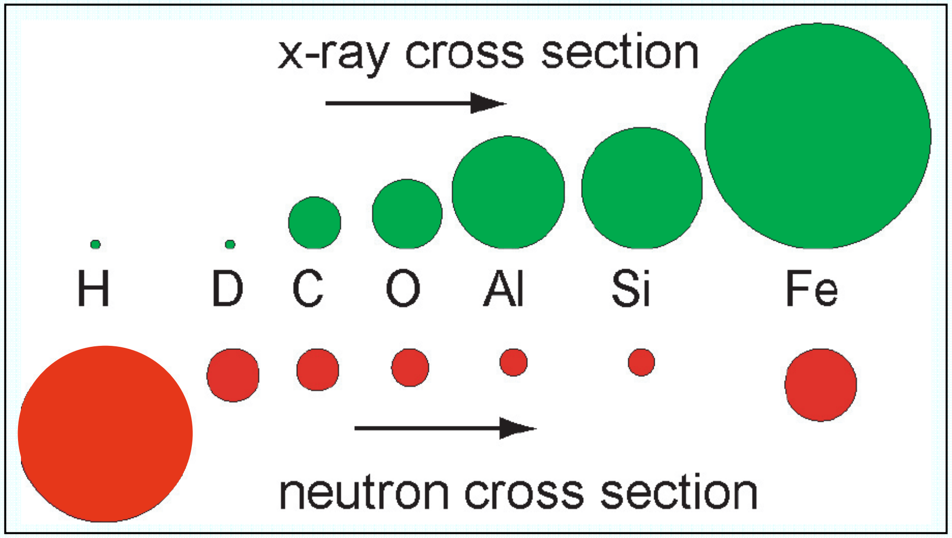
$I_T \Rightarrow I_0 e^{-\Sigma_T t}$ etc.

Absorption

$\Sigma_A t \Leftrightarrow \left(1 - e^{-\Sigma_T t}\right)\left(\Sigma_A / \Sigma_T\right)$

X-ray vs neutron scattering σ values

Compared with x-ray scattering cross sections, which vary as Z^2, neutron scattering cross sections show relatively little systematic variation with atomic number.

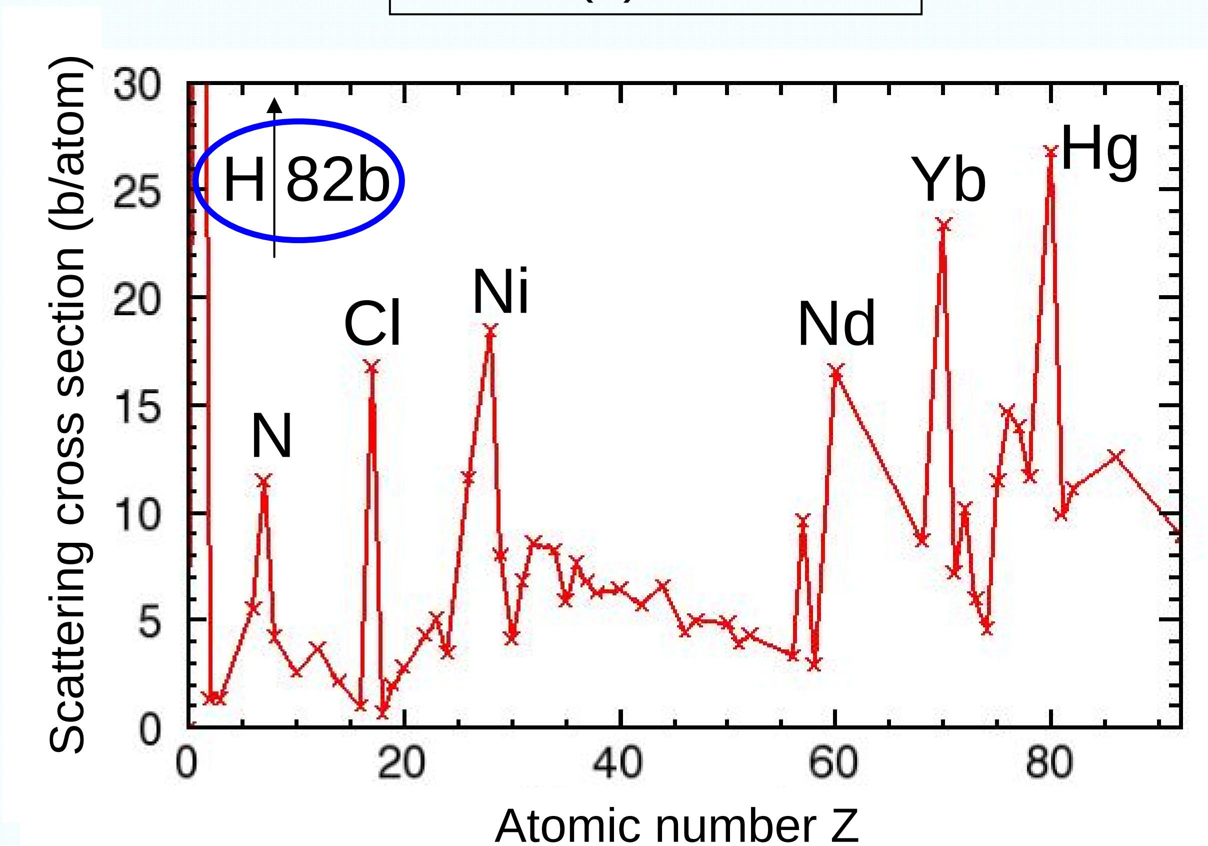


The x-ray scale has been reduced by a factor of ≈1.5 as compared with the neutron scale.

N.B. In this talk we only consider the interaction of neutrons with nuclei. We shall not discuss the magnetic interaction of neutrons with unpaired electrons.

Scattering cross sections, σ_S

1 barn (b) = 10^{-24}cm^2



Scattering lengths, b

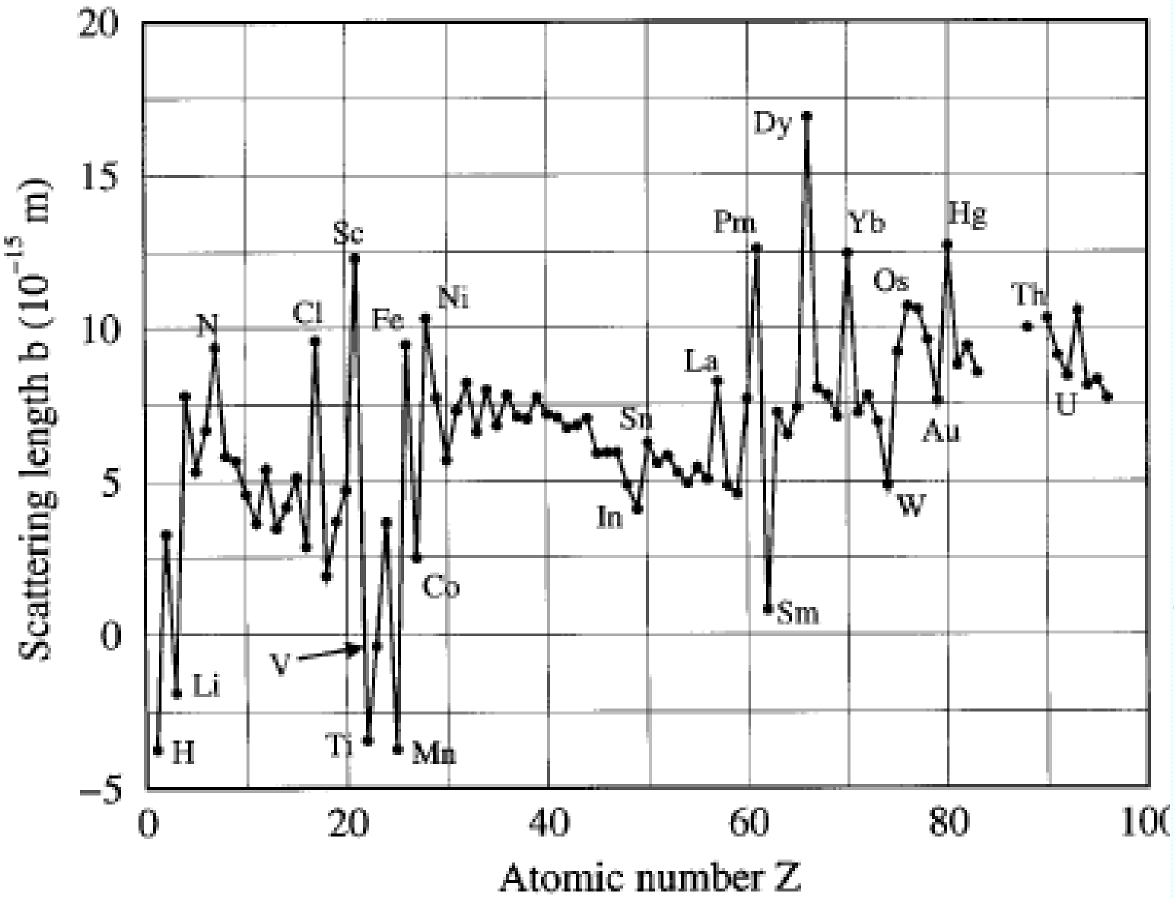


Fig. 7. The real part of the neutron scattering length b for the naturally occurring elements.

$$\sigma_S = 4\pi b^2$$

Absorption cross sections, σ_A

- As compared with x-ray absorption cross sections, neutron absorption cross sections are generally small.
- Strong absorbers include ^{3}He, ^{6}Li, ^{10}B, ^{113}Cd, $^{135}Xe^{*}$, ^{157}Gd.
- For most elements and isotopes the “1/v” law applies:

$$\sigma_A \propto \frac{1}{v} \propto \lambda$$

- The most important exceptions are Cd and Gd.

*http://en.wikipedia.org/wiki/Xenon#Isotopes

Absorption cross sections, σ_A

1 barn (b) = 10^{-24}cm^2

N.B. log scale

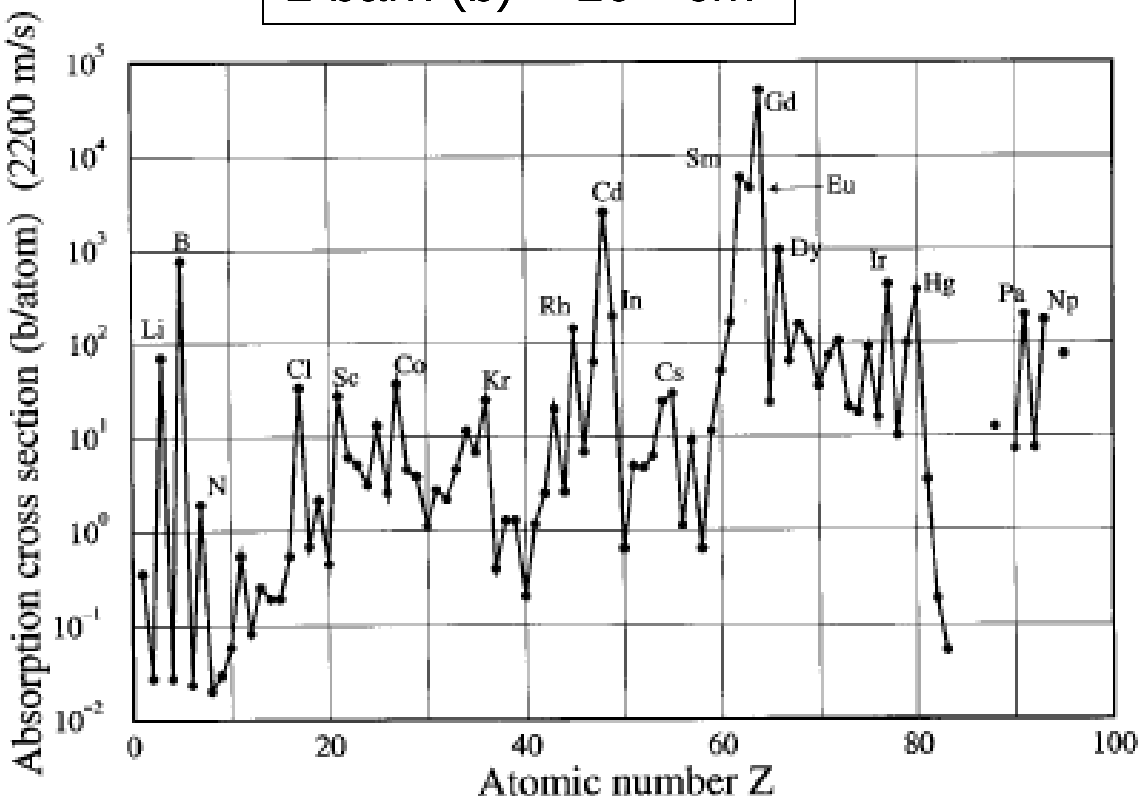


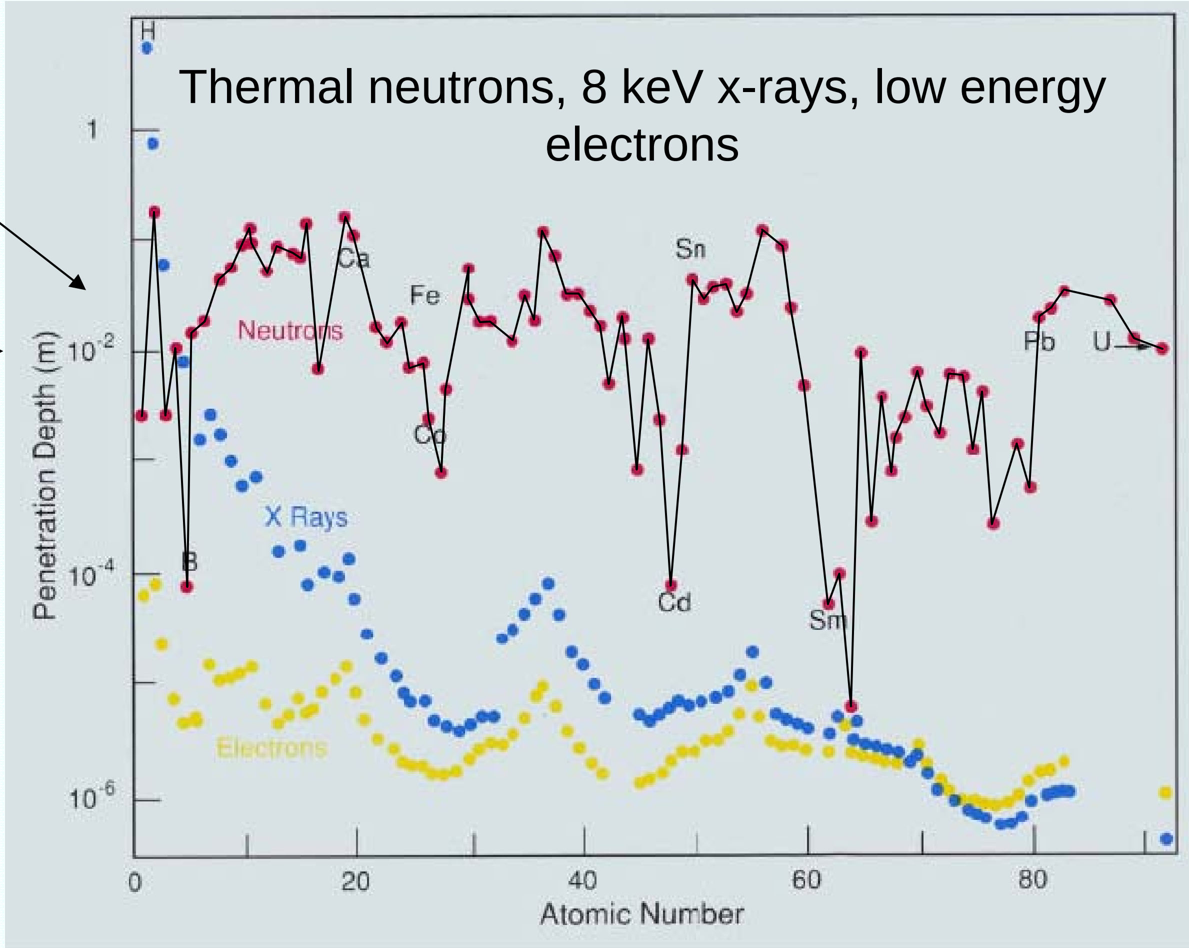
Fig. 8. The absorption cross section for 2200 m/s neutrons for the naturally occurring elements. Notice that the ordinate is plotted on a log scale.

Penetration depths, $1/\Sigma_T$

(Courtesy Roger Pynn)

log scale

$\Sigma_T = 1\mathrm{cm}^{-1}$



Cross section examples

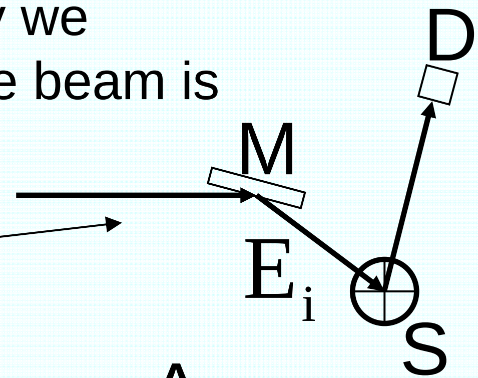
Calculations of scattering, absorption and transmission probabilities.

		0.1 mm water	1 m (dry) air	1 cm aluminum	10 thou cadmium
"Molecule"		H2O	(N2)0.8(O2)0.2	Al	Cd
sigma_s	barn	168.3	20.1	1.5	6.5
sigma_a	barn	0.67	3.04	0.23	2520
sigma_t	barn	168.97	23.14	1.73	2526.5
Density	g/cc	1	0.00117	2.7	8.65
Mol. Wt.		18	28.8	27	112.4
Number density	E24/cc	0.033333	0.000024	0.060000	0.046174
SIGMA_S	cm-1	5.610000	0.000490	0.090000	0.300133
SIGMA_A	cm-1	0.022333	0.000074	0.013800	116.359431
SIGMA_T	cm-1	5.632333	0.000564	0.103800	116.659564
Thickness	cm	0.01	100	1	0.0254
Scattering		5.5%	4.8%	8.5%	0.2%
Absorption		0.0%	0.7%	1.3%	94.6%
Transmission		94.5%	94.5%	90.1%	5.2%

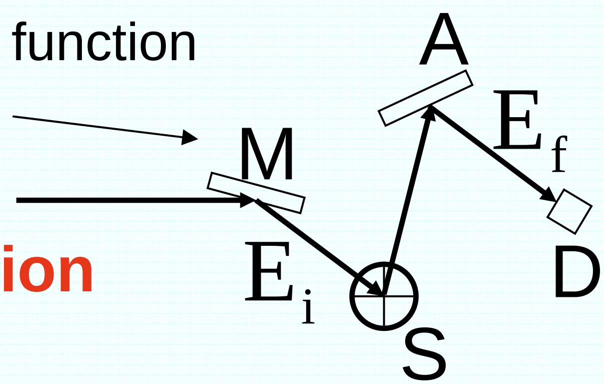
The scattered neutrons

How we study the scattered neutrons depends on several factors including the type of source. For simplicity we assume that the source is continuous and that the beam is ***monochromatic*** (single incident energy $\mathbf{E_i}$).

(a) We could study the intensity as a function of **scattering angle 2θ**.



(b) We could study the intensity as a function of both **scattering angle 2θ and scattered energy E_f**.

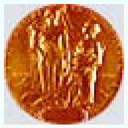


These are examples of **diffraction (no energy analysis)** and **spectroscopy (energy analysis)**.

Elastic scattering: $E_i = E_f$.

Inelastic scattering: $E_i \neq E_f$.

Diffraction and Spectroscopy



The Nobel Prize in Physics 1994

"to Professor Clifford G. Shull .. for the development of the neutron diffraction technique"

"to Professor Bertram N. Brockhouse .. for the development of neutron spectroscopy"

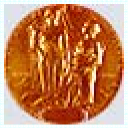
"Both methods are based on the use of neutrons flowing out from a nuclear reactor. When the neutrons bounce against (are scattered by) atoms in the sample being investigated, their *directions* change, depending on the atoms' relative positions. This shows how the atoms are arranged in relation to each other, that is, the structure of the sample. Changes in the neutrons' *velocity,* however, give information on the atoms' movements, e.g. their individual and collective oscillations, that is their dynamics.

.. Clifford G. Shull has helped answer the question of where atoms "are"

.. Bertram N. Brockhouse [has helped with] the question of what atoms "do"."

http://nobelprize.org/nobel_prizes/physics/laureates/1994/press.html

Diffraction and Spectroscopy



The Nobel Prize in Physics 1994

"to Professor Clifford G. Shull .. for the development of the neutron diffraction technique"

"to Professor Bertram N. Brockhouse .. for the development of neutron spectroscopy"

"Both methods are based on the use of neutrons flowing out from a nuclear reactor. When the neutrons bounce against (are scattered by) atoms in the sample being investigated, their *directions* change, depending on the atoms' relative positions. This shows how the atoms are arranged in relation to each other, that is, the structure of the sample. Changes in the neutrons' *velocity,* however, give information on the atoms' movements, e.g. their individual and collective oscillations, that is their dynamics.

.. Clifford G. Shull has helped answer the question of where atoms "are"

.. Bertram N. Brockhouse [has helped with] the question of what atoms "do"."

http://nobelprize.org/nobel_prizes/physics/laureates/1994/press.html

Single differential cross section

For a "thin" sample, the total integrated scattering is:

$$I_S = \phi N \sigma_S .$$

The measured intensity in a diffraction experiment (on a "thin" sample) is related to the single differential cross section:

$$I_S(E_i, 2\theta) = \phi N \left(\frac{d\sigma}{d\Omega} \right) \Delta\Omega$$

solid angle

The single differential cross section is related to the "structure factor" $S(Q)$.

When there is one type of atom we obtain, in the static approximation,

$$\frac{d\sigma}{d\Omega}(E_i, 2\theta) = \frac{\sigma_S}{4\pi} S(Q)$$

ONLY DEPENDS ON THE SAMPLE

Double differential cross section

The measured intensity in a spectroscopy experiment is related to the double differential cross section:

$$I_S(E_i, 2\theta, E_f) = \phi N \left(\frac{d^2\sigma}{d\Omega dE_f} \right) \Delta\Omega \Delta E_f .$$

energy window

The double differential cross section is related to the "scattering function"

$$S(Q, \omega)$$

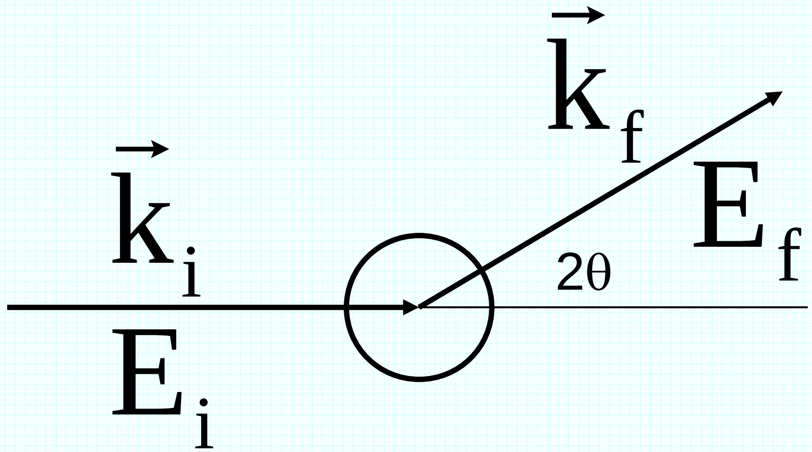
When there is one type of atom,

$$\frac{d^2\sigma}{d\Omega dE_f}(E_i, 2\theta, E_f) = \frac{\sigma}{4\pi\hbar} \frac{k_f}{k_i} S(Q, \omega),$$

ONLY DEPENDS ON THE SAMPLE

… but what are Q, ω, 2θ, k_i, k_f, E_i, and E_f?

Q, ω, 2θ, k_i, k_f, E_i, and E_f



$\vec{k}_i$ is the incident neutron wave vector

$\vec{k}_f$ is the scattered neutron wave vector

E_i is the incident neutron energy

E_f is the scattered neutron energy

$\vec{Q}$ is the wave vector transfer $\quad \vec{Q} = \vec{k}_i - \vec{k}_f$

$\hbar\omega$ is the energy transfer $\quad \hbar\omega = E_i - E_f$

2θ is the scattering angle

Alternative notations

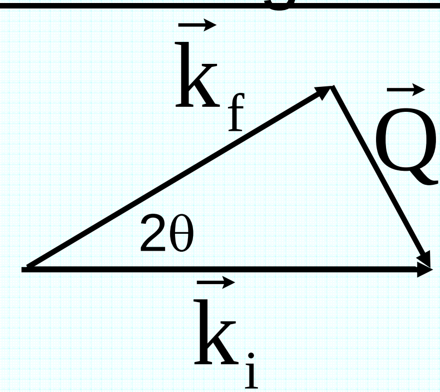
2θ or θ or ϕ

k_i or k_0 or k

E_i or E_0 or E

k_f or k', etc.

Scattering triangle



Exact and approximate relationships

$$(1)\quad \lambda = \frac{h}{mv} = \frac{2\pi}{k} \longrightarrow \boxed{\lambda(\text{Å}) \approx \frac{4}{v(\text{mm}/\mu\text{s})}}$$

$$(2)\quad E = \frac{1}{2}mv^2 = \frac{\hbar^2 k^2}{2m} = \frac{h^2}{2m\lambda^2}$$

$$\boxed{E(\text{meV}) \approx 2\left[k\left(\text{Å}^{-1}\right)\right]^2 \approx \frac{82}{\left[\lambda(\text{Å})\right]^2}}$$

Wavelength, energy, velocity, …

A thermal neutron with wavelength 2 Å has energy ≈20 meV and velocity ≈2000 ms^{-1}.

λ	E	v	τ
Å	meV	m/s	ms/mm
1	82	4000	0.25
2	20.5	2000	0.5
4	5.1	1000	1
8	1.3	500	2

1 meV ≈ 0.24×10^{12} c/s

8.1 cm^{-1}

11.6K

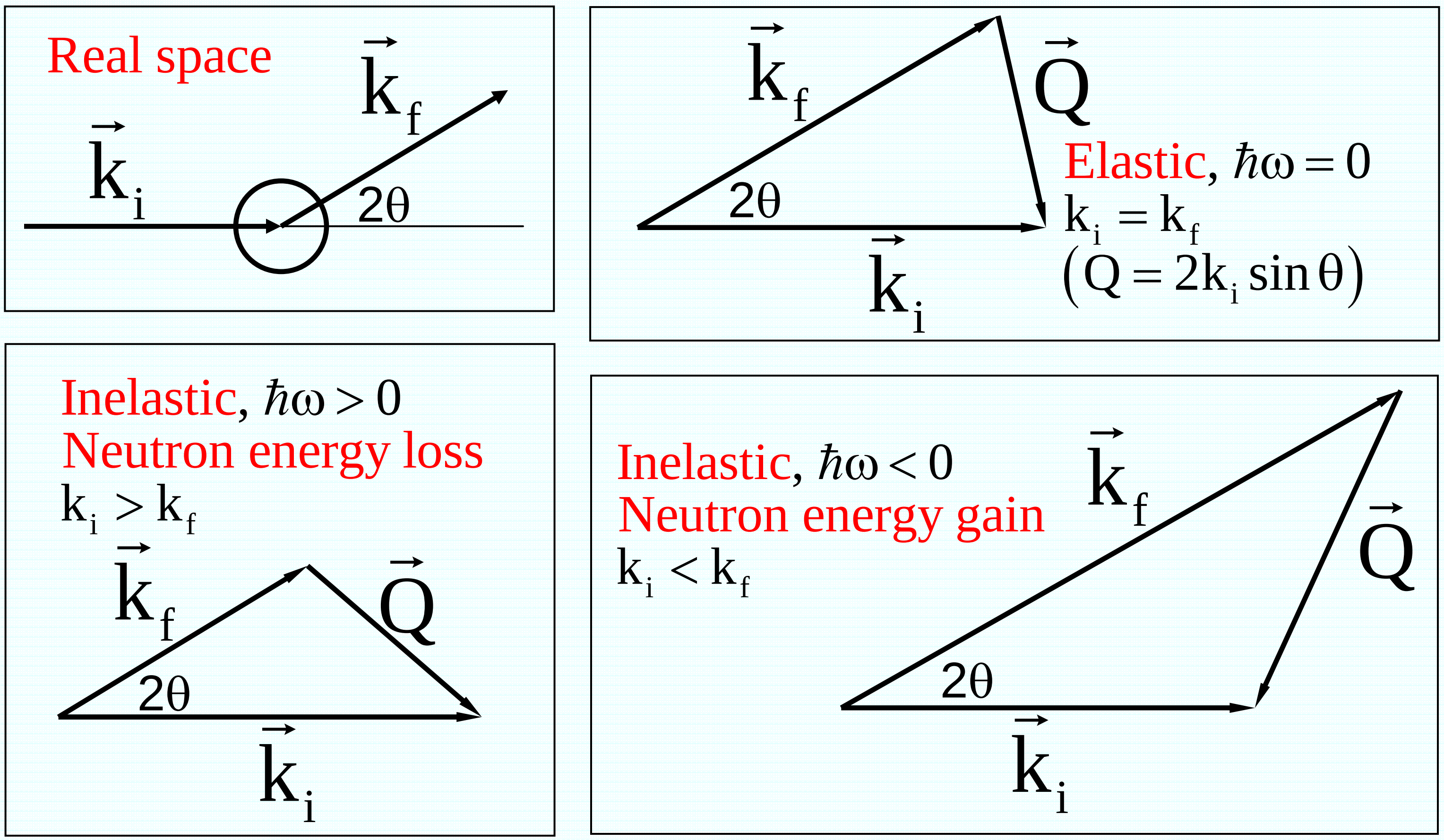
0.023 kcal/mol

0.10 kJ/mol

1Å=0.1nm

Elastic and inelastic scattering

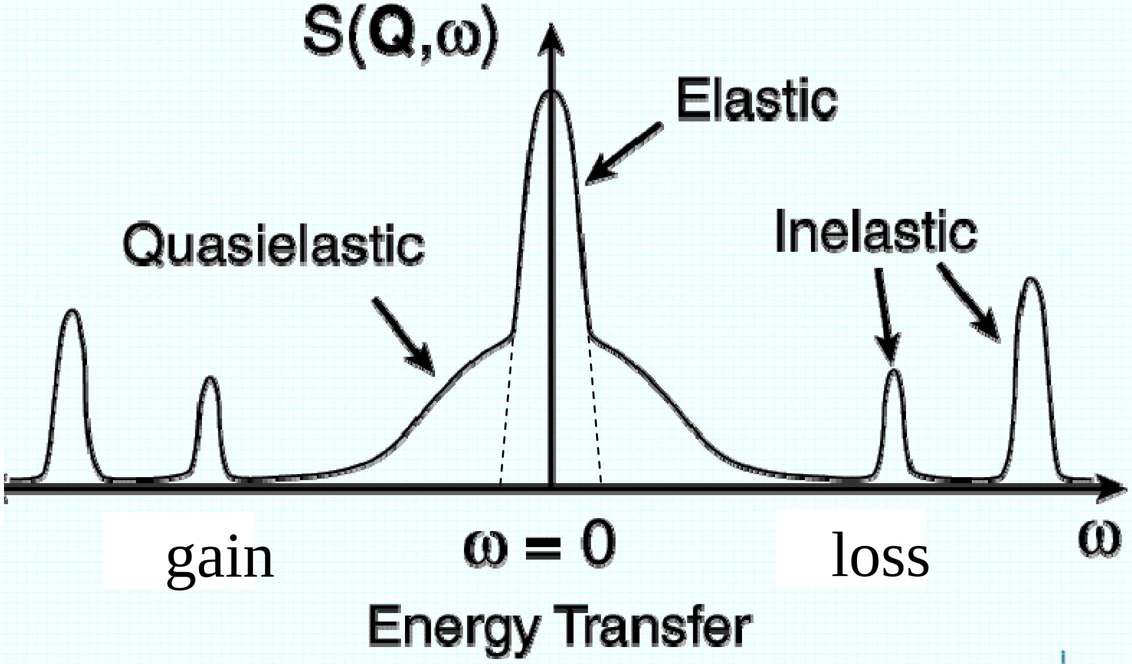
$$\hbar\omega = E_i - E_f \qquad \vec{Q} = \vec{k}_i - \vec{k}_f$$



Quasielastic scattering

Quasielastic scattering is a type of inelastic scattering that is centered at ω = 0, typically associated with diffusive motion, whereas inelastic peaks are typically associated with lattice or localized excitations.

The schematic spectrum shown below is resolution-broadened.



The double differential cross section

$$\frac{d^2\sigma}{d\Omega dE_f}\left(E_i, 2\theta, E_f\right)\Delta\Omega\Delta E_f,$$

is proportional to the probability of scattering at scattering angle 2θ into solid angle $\Delta\Omega$, with scattered energy E_f and scattered energy window ΔE_f; it is directly related to the scattering function $S(Q,\omega)$.

$$\frac{d^2\sigma}{d\Omega dE_f} = \frac{\sigma_S}{4\pi\hbar}\frac{k_f}{k_i}S\left(Q,\omega\right)$$

ONLY DEPENDS ON THE SAMPLE

The scattering function $S(Q,\omega)$ only depends on the energy and wave vector transfers Q and ω (rather than on the incident and scattered energies and wave vectors).

Notice that there is no equivalent of the Q-dependent x-ray atomic scattering factor since the neutron interacts with the nucleus.
*(In magnetic neutron scattering there **is** a Q-dependent form factor.)*

The functions S (Q,ω), I (Q,t), G (r,t)

Most neutron spectrometers measure S(Q,ω).

The quantity I(Q,t), known as the "intermediate scattering function", is the frequency Fourier transform of S(Q,ω):

$$I(\vec{Q},t) = \hbar\int S(\vec{Q},\omega)\exp(i\omega t)d\omega$$

This quantity is typically computed, e.g. in molecular dynamics simulations, for comparison with experiment.
The neutron spin echo technique measures this quantity.

The quantity G(r,t), known as the "time-dependent pair correlation function", is the reciprocal space Fourier transform of I(Q,t):

$$G(\vec{r},t) = \frac{1}{(2\pi)^3}\int I(\vec{Q},t)\exp\left(-i\vec{Q}.\vec{r}\right)d\vec{Q}$$

These functions contain detailed information about the collective (pair) dynamics of materials.

Single particle motion

So far we have implicitly assumed that all atoms of a given element have the same scattering cross section (which is true in the x-ray case).

But what if they don't? This can happen if there is more than one isotope and/or nonzero nuclear spins. In that case there is a second contribution to the double differential cross section. In the simplest case it reads as follows:

$$\frac{d^2\sigma}{d\Omega dE_f} = \frac{\sigma_{coh}}{4\pi\hbar}\frac{k_f}{k_i}S(Q,\omega) + \frac{\sigma_{inc}}{4\pi\hbar}\frac{k_f}{k_i}S_S(Q,\omega)$$

where

- $S(Q,\omega)$ reflects the collective behavior of the particles (e.g. phonons)
- $S_S(Q,\omega)$ reflects the single particle behavior (e.g. diffusion)
- σ_{coh} and σ_{inc} are "coherent" and "incoherent" scattering cross sections respectively.

Coherent and incoherent scattering

The scattering cross section of an atom is proportional to the square of the strength of its interaction with neutrons (its scattering length), denoted “b”:

$$\sigma = 4\pi b^2.$$

For an element with more than one isotope, b depends on the isotope. If the nucleus has nonzero spin, b depends on the compound nucleus spin state.

The coherent cross section σ_{coh} reflects the mean scattering length. The incoherent cross section σ_{inc} reflects the variance of the distribution of scattering lengths:

$$\sigma_{coh} = 4\pi\left(\overline{b}\right)^2$$

$$\sigma_{inc} = 4\pi\left[\overline{b^2} - \left(\overline{b}\right)^2\right].$$

The underlying assumption (which is justified) is that there is no correlation between an atom’s position and its isotope and/or spin state.

Coherent and incoherent scattering

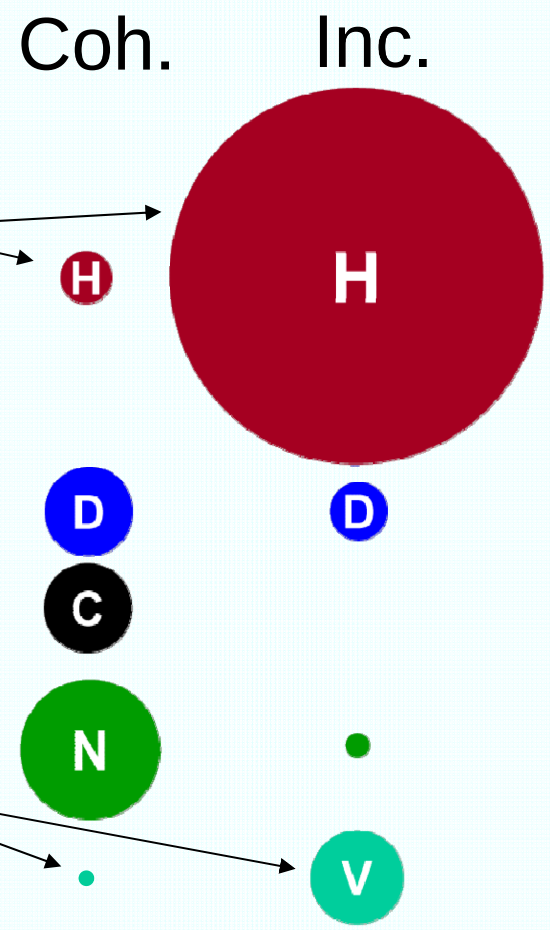
For most elements the coherent cross section dominates.

Hydrogen is a very important exception:

The huge incoherent cross section enables studies of hydrogen diffusion in candidate storage materials, ...

Selective deuteration enables detailed studies of the dynamics of polymers and biomolecules, ...

Vanadium has a significant incoherent cross section and a very small coherent cross section. It is used for instrument calibration/normalization.



The single particle functions

We need to modify some of our earlier statements:

Most neutron spectrometers measure $S(Q,\omega)$ and $S_S(Q,\omega)$.

The quantity $I_S(Q,t)$, is the frequency Fourier transform of $S_S(Q,\omega)$:

$$I_S(\vec{Q},t) = \hbar \int S_S(\vec{Q},\omega)\exp(i\omega t)\,d\omega$$

This quantity is typically computed, e.g. in molecular dynamics simulations, for comparison with experiment.
The neutron spin echo technique measures $I(Q,t)$ and $I_S(Q,t)$.

The quantity $G_S(r,t)$, known as the "time-dependent self correlation function", is the reciprocal space Fourier transform of $I_S(Q,t)$:

$$G_S(\vec{r},t) = \frac{1}{(2\pi)^3}\int I_S(\vec{Q},t)\exp\left(-i\vec{Q}.\vec{r}\right)d\vec{Q}$$

The self functions contain detailed information about the single particle (self) dynamics of materials.

What can one study using n.s.?

Single particle and/or collective motions in all sorts of materials

such as metals, insulators, semiconductors, glasses, magnetic materials, heavy fermions, superconductors, solid and liquid helium, plastic crystals, molecular solids, liquid metals, molten salts, biomolecules, water in confined geometries, polymer systems, micelles, microemulsions, etc., etc.,

under all sorts of conditions

such as (at the NCNR) T ≈50 mK to ≈1900K, P to ≈2.5 GPa, B to ≈11.5T, also strong electric fields, controlled humidity, etc., etc.,

provided that

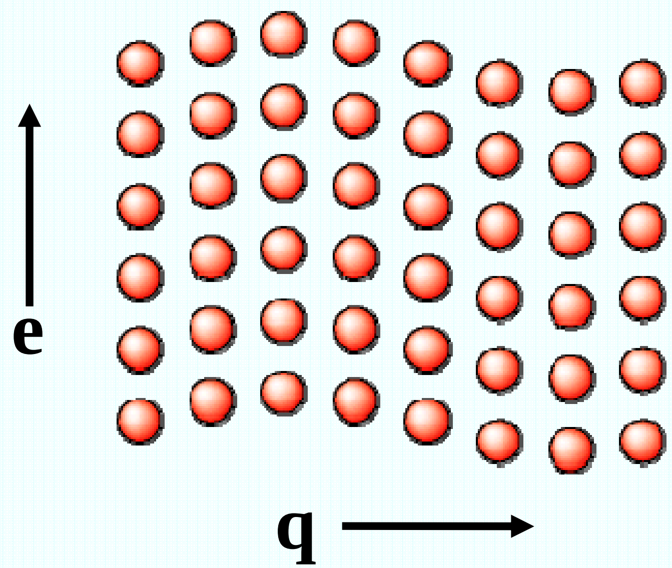
- the length and time scales (Q and ω ranges) are consistent with instrument capabilities
- the scattering (and absorption) cross sections are acceptable
- the quantity of material is acceptable

See the NCNR annual reports for examples.

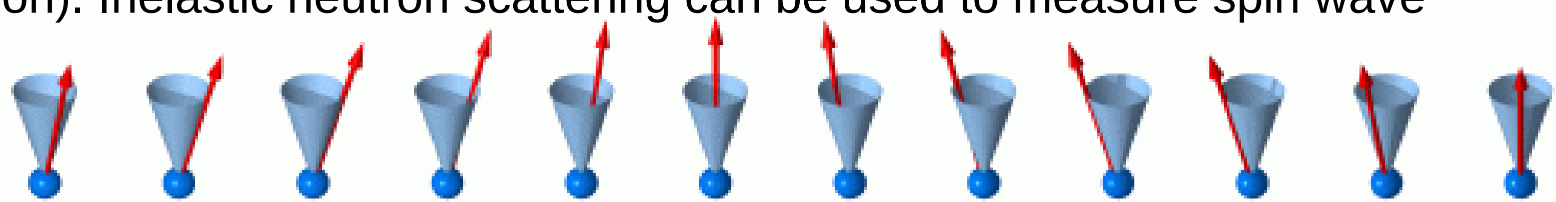
http://www.ncnr.nist.gov/AnnualReport/

Collective dynamics

Phonons are quantized lattice vibrations, characterized by their wave vector **q**, eigenvector **e** and frequency ω(**q**,**e**). Inelastic neutron scattering can be used to measure phonons.



In magnetically ordered systems the magnetic moments are coupled. Rotating one spin from its equilibrium orientation exerts torque on neighboring spins. The result is a spin wave (magnon). Inelastic neutron scattering can be used to measure spin wave dispersion.

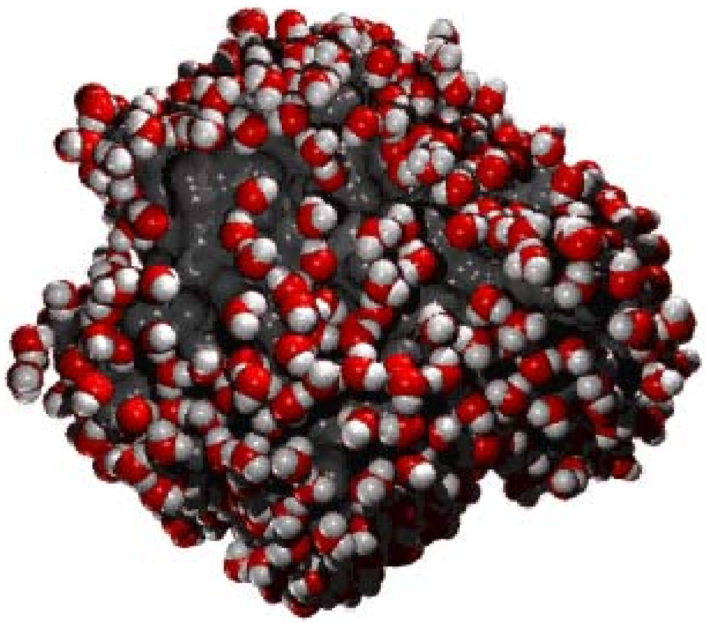


Animation courtesy of A. Zheludev (ORNL)

Single particle dynamics

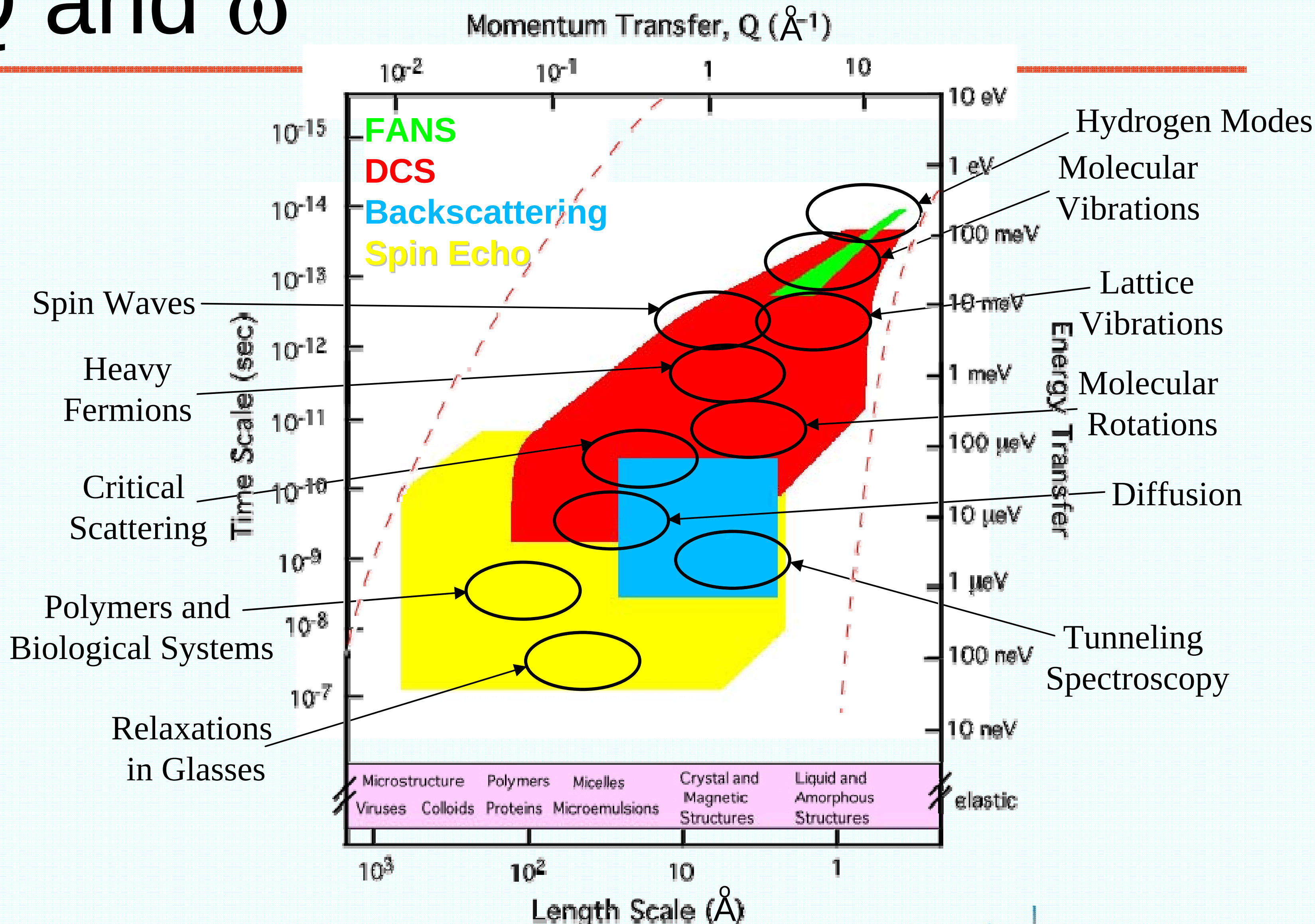
Water plays a vital role in determining the structures and dynamics, *hence the function*, of globular soluble proteins. The movie is from a molecular dynamics simulation of a myoglobin molecule in solution. Only water molecules in the first hydration shell (d < 4 Å) are shown.

Duration is 50 ps.



Animation courtesy of D. Tobias, UC Irvine

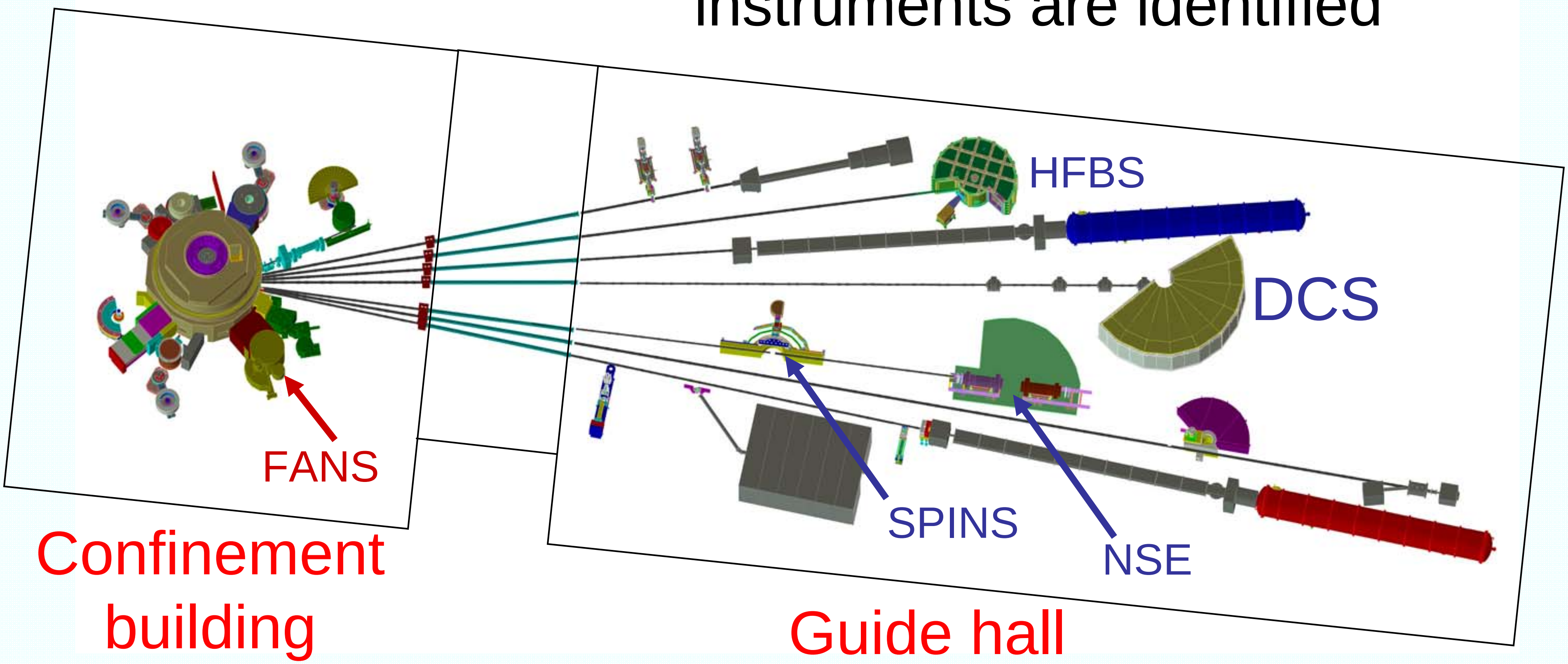
Q and ω



Momentum Transfer, Q (Å⁻¹)
10⁻²
10⁻¹
1
10
FANS
DCS
Backscattering
Spin Echo
Time Scale (sec)
10⁻¹⁵
10⁻¹⁴
10⁻¹³
10⁻¹²
10⁻¹¹
10⁻¹⁰
10⁻⁹
10⁻⁸
10⁻⁷
Energy Transfer
10 eV
1 eV
100 meV
10 meV
1 meV
100 μeV
10 μeV
1 μeV
100 neV
10 neV
elastic
Hydrogen Modes
Molecular Vibrations
Lattice Vibrations
Molecular Rotations
Diffusion
Tunneling Spectroscopy
Spin Waves
Heavy Fermions
Critical Scattering
Polymers and Biological Systems
Relaxations in Glasses
Microstructure
Viruses
Colloids
Polymers
Proteins
Micelles
Microemulsions
Crystal and Magnetic Structures
Liquid and Amorphous Structures
10³
10²
10
1
Length Scale (Å)

NCNR Instruments

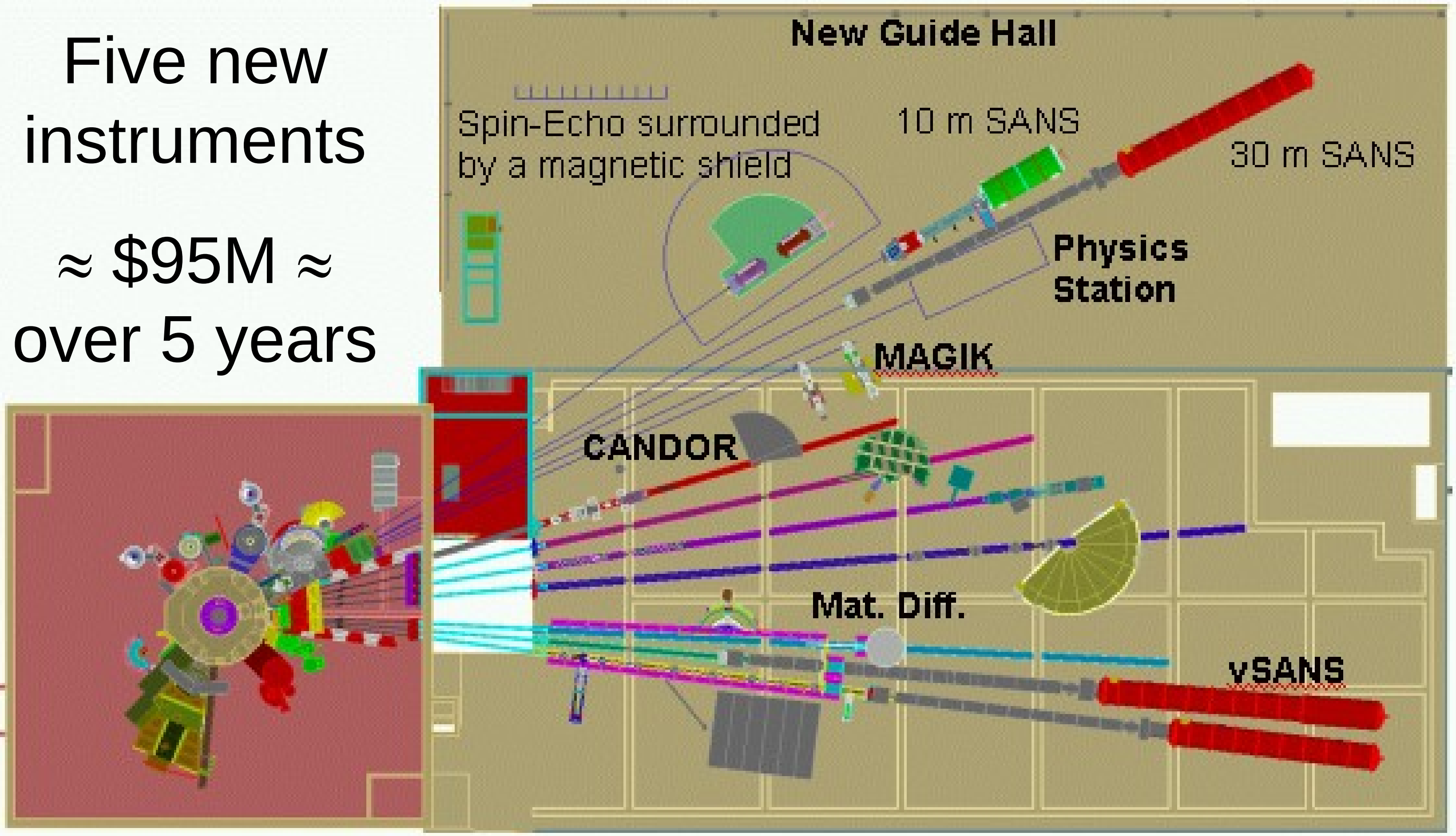
The principal neutron spectroscopy instruments are identified



The NCNR Expansion Project

Five new instruments

≈ $95M ≈ over 5 years



http://www.ncnr.nist.gov/expansion/

Useful references

R. Pynn, “An Introduction to Neutron Scattering” and “Neutron Scattering for Biomolecular Science” (lecture notes), also “Neutron Scattering: A Primer” (www.mrl.ucsb.edu/~pynn).

G. L. Squires, “Introduction to the Theory of Thermal Neutron Scattering”, Dover Publications (1996) (ISBN 048669447), and references therein.

S. W. Lovesey, “Theory of Thermal Neutron Scattering from Condensed Matter”, Clarendon Press, Oxford (1984).

For detailed information about scattering and absorption cross sections, see:

V.F. Sears, Neut. News 3 (3) 26 (1992); http://www.ncnr.nist.gov/resources/n-lengths/.

The bottom line

"Neutron Scattering is an excellent way to study dynamics."

(D.A. Neumann)