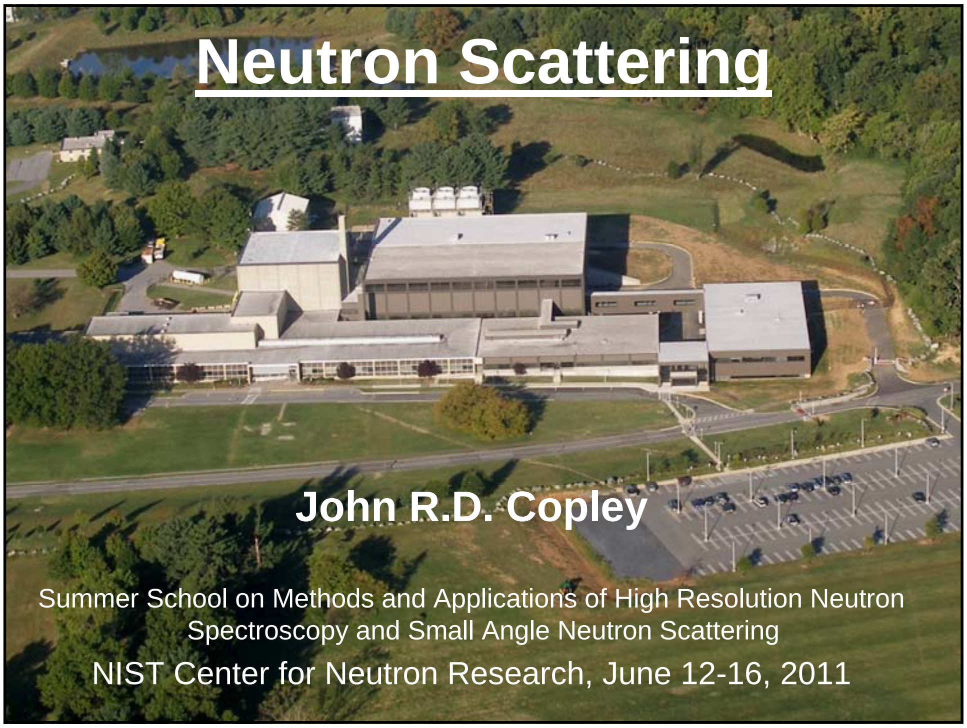

# Neutron Scattering

John R.D. Copley

Summer School on Methods and Applications of High Resolution Neutron Spectroscopy and Small Angle Neutron Scattering

NIST Center for Neutron Research, June 12-16, 2011

## Acknowledgements

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Center for High Resolution Neutron Scattering (CHRNS)

# (Slow) neutron interactions

**Scattering** plus **Absorption**

Total scattering (diffraction) = Elastic scattering + Inelastic scattering (spectroscopy)

Total scattering (diffraction) → Structure

Elastic scattering → Structure

Inelastic scattering (spectroscopy) → Dynamics

Inelastic scattering includes "Quasielastic neutron scattering" (QENS)



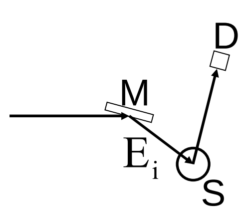
# Total, elastic, and inelastic scattering

Incident energy $E_i$

$\boxed{E = E_i - E_f}$
("energy transfer")

Scattered energy $E_f$

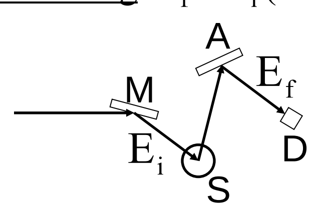
Total scattering:
all $E_f$ (i.e., all E)




Diffractometer

Elastic scattering: $E_f = E_i$ (i.e., $E = 0$)

Inelastic scattering: $E_f \neq E_i$ (i.e., $E \neq 0$)




Spectrometer

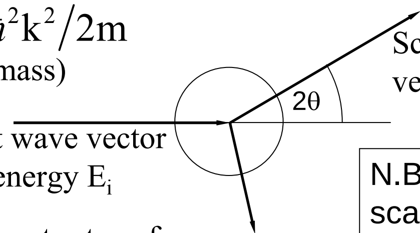
(Some write $E = E_f - E_i$)

# Kinematics

$$mv = \hbar k$$

$$E = \tfrac{1}{2}mv^2 = \hbar^2 k^2 / 2m$$

(m is neutron's mass)




**Q** is wave vector transfer, or "scattering vector"
$\hbar$**Q** is momentum transfer

N.B. The symbol for scattering angle in SANS experiments is θ, not 2θ.

$$\boxed{\mathbf{Q} = \mathbf{k}_i - \mathbf{k}_f}$$

("wave vector transfer")

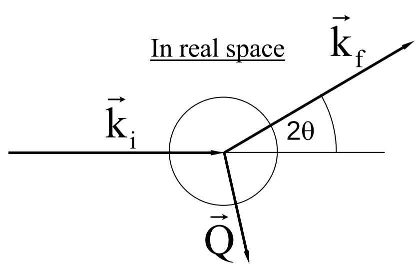
$\boxed{(\text{For x-rays}, E = \hbar c k)}$



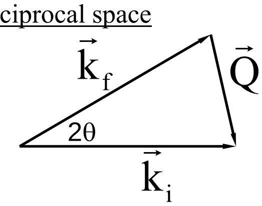
# Elastic scattering

$$\boxed{\mathbf{Q} = \mathbf{k}_i - \mathbf{k}_f}$$

In real space



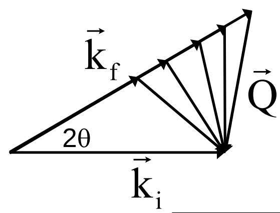

In reciprocal space




$$\boxed{E = 0 \qquad k_i = k_f \qquad Q = 2k_i \sin\theta}$$

# Total scattering, inelastic scattering

$$\boxed{\mathbf{Q} = \mathbf{k}_i - \mathbf{k}_f}$$




$$Q^2 = k_i^2 + k_f^2 - 2k_i k_f \cos 2\theta$$

At fixed scattering angle 2θ, the magnitude (and the direction) of **Q** varies with the energy transfer E.



# Structure and Neutron Diffraction

Neutron diffraction measures **structure**. The scattered intensity, I(2θ), is measured – hence S(Q).

The structure of a solid is determined from ***elastic scattering*** (Bragg reflection) intensities which are generally measured using a diffractometer (no energy analysis).

The structure of a fluid is related to the ***total scattering*** and is measured using a diffractometer; there is no elastic scattering from a fluid.

# Dynamics and Neutron Spectroscopy

Neutron spectroscopy (inelastic scattering) measures **dynamics**. The measured intensity yields S(Q,E).

Scattering with nonzero E, e.g. to study vibrational excitations, is called ***inelastic scattering***.

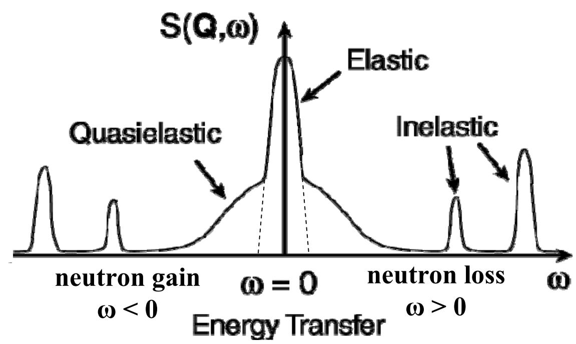
Inelastic scattering that is centered at E = 0 and associated with diffusional behavior, is called ***quasielastic neutron scattering (QENS).***

N.B. In an alternative notation the energy transfer is written $\hbar\omega = \mathrm{E}$ and the scattering function $\mathrm{S}(\mathrm{Q},\omega) = \hbar\mathrm{S}(\mathrm{Q},\mathrm{E})$



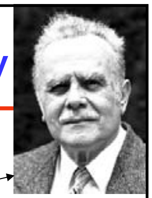
# Elastic, inelastic, quasielastic, …

The schematic spectrum shown below is resolution-broadened.




$$\int \mathrm{S}(\mathrm{Q},\omega)\, d\omega = \int \mathrm{S}(\mathrm{Q},\mathrm{E})\, d\mathrm{E} = \mathrm{S}(\mathrm{Q})$$

# 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 the atoms "are"**

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

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



# Advantages and disadvantages

- Neutrons have wavelengths comparable with interatomic spacings and energies comparable with material energies; the geometry of motions can be studied
- Little absorption → bulk probe: containment is simplified
- Weak interaction simplifies interpretation of data
- Sensitivity to isotope (esp. H/D) may be used to advantage
- Magnetic interaction enables studies of magnetic materials

BUT…

- Neutron sources are weak, intensities are low
- Some elements absorb strongly
- Kinematics restricts available (Q,E) space

# Neutron scattering intensities

$$\text{Intensity} \propto \left(\frac{k_f}{k_i}\right)\left(\frac{\sigma_S}{4\pi}\right)S(Q,E)$$

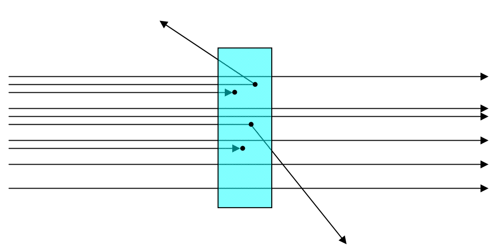
The measured intensity is proportional to the product of quantities that depend …

- on the method of measurement, e.g. the choice of $E_i$,
- on the strength of the interaction between neutrons and the sample (i.e. on the "scattering cross section"), and
- on the sample itself, through the scattering function $S(Q,E)$.

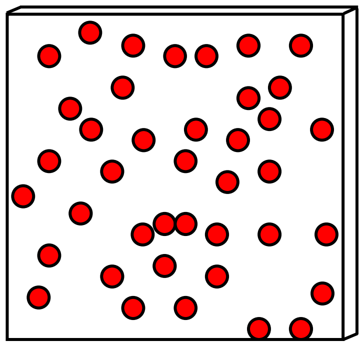


# Cross sections

Consider a "thin" sample placed in a neutron beam. The neutrons are transmitted, absorbed, or scattered, with probabilities $p_T$, $p_A$ and $p_S$ respectively.



# The scattering probability $p_S$



N atoms; area of sample = A

$$p_S = \frac{N\sigma_S}{A} = \frac{N\sigma_S t}{V} = \Sigma_S t$$

where $\sigma_S$ is the microscopic scattering cross section (barn/atom)

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

t is the sample thickness,
V is its volume,
$\rho$ = N/V is the number density,

$\Sigma_S = \rho\sigma_S$ is the macroscopic scattering cross section (cm$^{-1}$)



# Event rates

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

The scattering rate is:

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

The absorption rate is:

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

Hence the transmission rate is

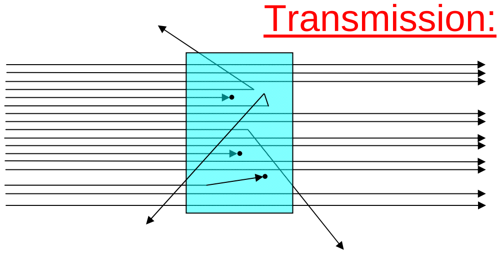
$$I_T = I_0 p_T = I_0 - I_A - I_S = (\Phi A)(1 - \Sigma_T t)$$

where $\Sigma_T = \Sigma_A + \Sigma_S$ is the total removal cross section.

# “Not necessarily thin” samples

The scattering, absorption and transmission probabilities for a sample that is “not necessarily thin” are as follows:

Transmission: $p_T = e^{-\Sigma_T t}$ (Beer’s law)



Absorption

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

Scattering

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

(N.B. Scattering may be followed by absorption, or by additional scattering)



# Absorption cross sections

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

N.B. log scale

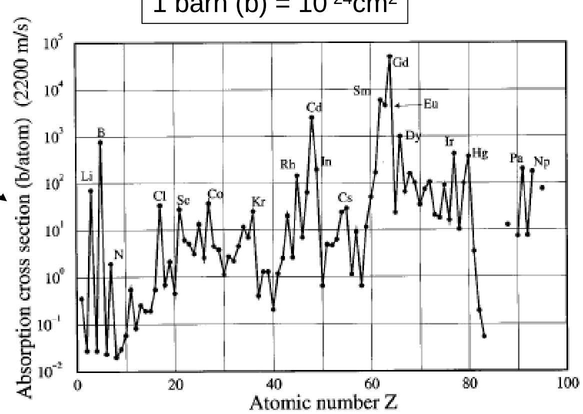



Fig. 8. The absorption cross section for 2200 m/s neutrons for the naturally occurring elements. Notice that the ordinate is plotted on a log scale.

# Absorption

- ➢ As compared with x-ray absorption cross sections, neutron absorption cross sections are generally small.

- ➢ Exceptions include $^{3}$He, $^{6}$Li, $^{10}$B, $^{113}$Cd, $^{135}$Xe*, $^{157}$Gd.

  *($2.6 \times 10^{6}$ barns)
  Rhodes, Richard, 1986, “The Making of the Atomic Bomb”, Simon and Schuster, ISBN 0-671-44133-7.

- ➢ For most elements and isotopes the “1/v” law applies:

$$\boxed{\sigma_{abs} \propto 1/v \propto \lambda}$$

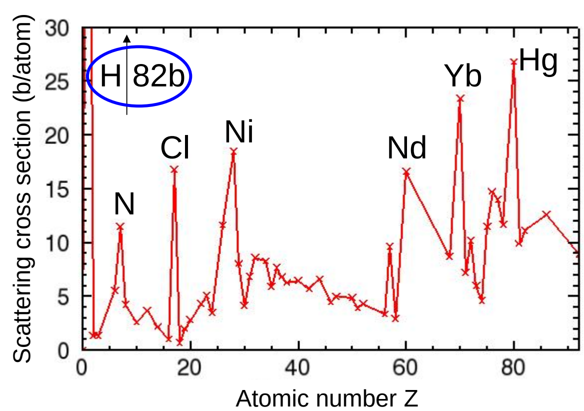
- ➢ Important exceptions to the “1/v” law include Cd and Gd.



# Scattering cross sections

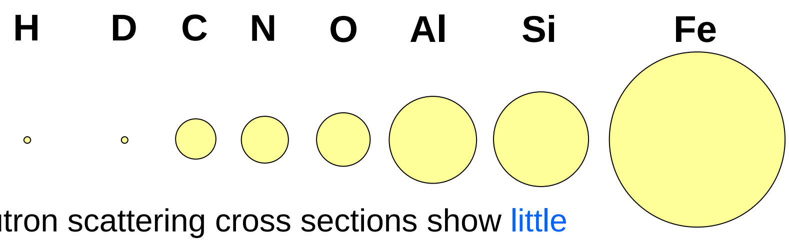
linear scale

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

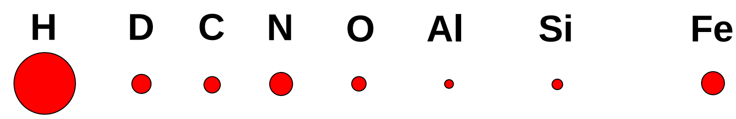


# Comparison with x-rays

As compared with x-ray (Q=0) cross sections, which vary as $Z^2$:




neutron scattering cross sections show little systematic variation with atomic number:




X-ray cross sections vary with Q; neutron cross sections do not.



# Cross section examples

1 mm of aluminum has 99% transmission

0.020” of cadmium has 0.3% transmission

1 m of dry air scatters 4.8%, absorbs 0.7%

0.1 mm of water scatters 5.5%

(These results were obtained using thermal neutron (2200 m/s, 1.8 Å) absorption cross sections.)

# The single differential cross section

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

$$I_S(E_i) = \phi N \sigma_S(E_i).$$

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

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

solid angle

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

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

$(Q = 4\pi \sin\theta / \lambda)$

ONLY DEPENDS ON THE SAMPLE

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

The measured intensity is proportional to S(Q).



# Correlation functions – S(Q)

Neutron diffractometers measure $S(\vec{Q})$.

$S(\vec{Q})$ is the Fourier transform of the pair distribution function $g(\vec{r})$:

$$S(\vec{Q}) = 1 + \rho \int [g(\vec{r}) - 1] \exp\left(i\vec{Q}.\vec{r}\right) d\vec{r}$$

$$g(\vec{r}) = 1 + \frac{1}{\rho(2\pi)^3} \int \left[S(\vec{Q}) - 1\right] \exp\left(-i\vec{Q}.\vec{r}\right) d\vec{Q}$$

Averaging over directions within the sample we obtain:

$$S(Q) = 1 + \frac{4\pi\rho}{Q} \int r \left[g(r) - 1\right] \sin Qr \, dr$$

$$g(r) = 1 + \frac{1}{2\pi^2 \rho} \int Q^2 [S(Q) - 1] \frac{\sin(Qr)}{Qr} dQ$$

**Pair distribution functions contain detailed information about structure.**

# The double differential cross section

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

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

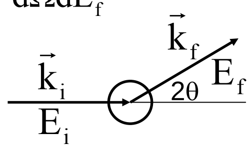
energy window

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

$$S(Q,E)$$

When there is one type of atom, we obtain

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




ONLY DEPENDS ON THE SAMPLE

The measured intensity is proportional to

$$(k_f/k_i)S(Q,E).$$



# Correlation functions – S(Q,ω)

Most neutron spectrometers measure S(**Q**,ω).

The quantity I(**Q**,t) is known as the "intermediate scattering function".

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

$$S(\vec{Q},\omega) = \frac{1}{2\pi\hbar} \int I(\vec{Q},t) \exp(-i\omega t) dt$$

Neutron spin echo measures I(**Q**,t) directly.

The quantity G(**r**,t) is the "time-dependent pair correlation function":

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

$$I(\vec{Q},t) = \int G(\vec{r},t) \exp\left(i\vec{Q}.\vec{r}\right) d\vec{r}$$

**The functions I and G 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 we have:

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

where

– $S(Q,\omega)$ reflects the collective behavior of the particles (e.g. phonons)

– $S_S(Q,\omega)$ reflects the single particle (self) behavior (e.g. diffusion)

– $\sigma_{coh}$ and $\sigma_{inc}$ are **coherent** and **incoherent** scattering cross sections respectively



# Coherent and incoherent scattering

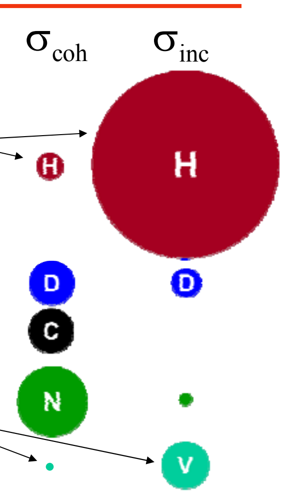
For most elements the coherent cross section dominates.

**Hydrogen is a very important exception:**

Its huge incoherent cross section enables studies of hydrogen diffusion in a variety of materials.

Selective deuteration enables detailed studies of the structure and 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 (and for neutron diffraction sample cans).



# Self correlation functions

Most neutron spectrometers measure S(**Q**,ω) and $S_S$(**Q**,ω).

$$I_S(\vec{Q},t) = \hbar \int S_S(\vec{Q},\omega)\exp(i\omega t)d\omega$$
$$S_S(\vec{Q},\omega) = \frac{1}{2\pi\hbar}\int I_S(\vec{Q},t)\exp(-i\omega t)dt$$

The quantity $G_S$(**r**,t) is the "self time-dependent pair correlation function":

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

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



# What can one study using neutrons?

Structure and dynamics in all sorts of materials

such as metals, insulators, semiconductors, glasses, magnetic materials, superconductors, helium, plastic crystals, molecular solids, molten salts, biomolecules, water, polymers, micelles, microemulsions, …

under all sorts of conditions

such as (at the NCNR) T from ≈50 mK to ≈1600C; P to ≈2.5 GPa; B to ≈11.5T; E to 6 kV; controlled humidity, etc.,

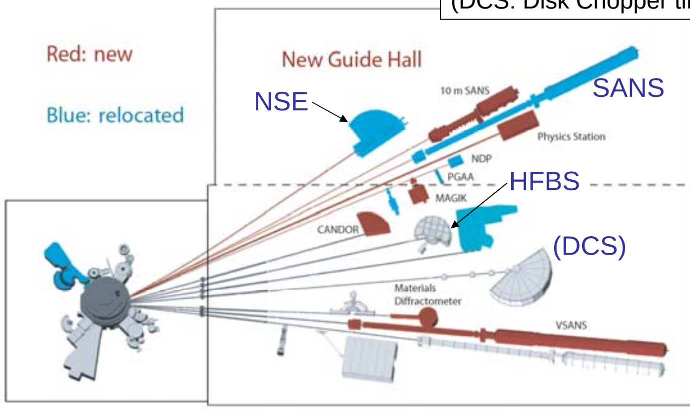
provided that

– the length and time scales (Q and ω ranges) and the desired instrumental resolution (in Q and ω) are consistent with instrumental capabilities
– the scattering (and absorption) cross sections are acceptable
– the quantity of material is sufficient

See the NCNR annual reports (on the Web) for examples.

# NCNR spectrometers

SANS: Small Angle Neutron Scattering
HFBS: Backscattering
NSE: Neutron Spin Echo
(DCS: Disk Chopper time-of-flight)




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



# Which instrument to use (dynamics)?

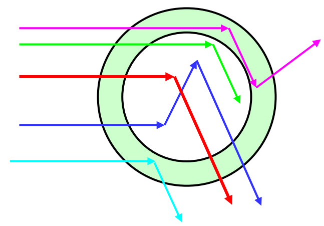
← (slow) ——— S(Q,ω) ——— (fast) →

Instrument Resolution

| | delta-function peak | Narrow peak | Medium width peak | Broad peak | Flat back-ground |
|---|---|---|---|---|---|
| **Low resn. (broad)** | (Elastic) | **Elastic** | **Elastic** | **Match** | (Flat) |
| **Med. resn. (medium)** | (Elastic) | **Elastic** | **Match** | **Flat** | (Flat) |
| **High resn. (narrow)** | (Elastic) | **Match** | **Flat** | **Flat** | (Flat) |

# Caveats and approximations

- Self-shielding
- Scattering from sample environment/container
- Resolution
- Backgrounds
- Spurions



- Static approximation: ignore variation of Q with E.
- One type of atom: assume one element dominates
- Multiple scattering: argue that it can be neglected



# Units and conversion factors

A 2 Å thermal neutron has energy ≈20 meV and velocity ≈2000 $ms^{-1}$.
(A 2Å *photon* has energy ≈6 keV )

| $\lambda$ | E | v | $\tau$ |
|---|---|---|---|
| Å | meV | m/s | μs/mm |
| 1 | 82 | 4000 | 0.25 |
| 2 | 20.5 | 2000 | 0.5 |
| 4 | 5.1 | 1000 | 1 |
| 8 | 1.3 | 500 | 2 |

1 meV ≈ $0.24\times10^{12}$ c/s (THz)
1.52 $ps^{-1}$
8.1 $cm^{-1}$
11.6K
0.023 kcal/mol
0.10 kJ/mol

(1Å=0.1nm)

## Concluding remarks

Neutron scattering is a powerful technique with applications in a variety of fields, but available fluxes are relatively low.

Selective deuteration allows the experimenter to highlight interesting fragments of molecules.

The magnetic interaction provides unique information about magnetic materials.

The NCNR has spectrometers that collectively cover wide ranges in distance and time.

COME AND SEE FOR YOURSELVES!!!



## The bottom line

"Neutron Scattering
is an excellent way
to study dynamics"
(D.A. Neumann, 2001)
"and structure."

# Useful references (1)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# Useful references (2)


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• R. Pynn, "Neutron Scattering: A Primer", Los Alamos Science (1990)

• R. Pynn, "Neutron Scattering—A Non-destructive Microscope for Seeing Inside Matter"; go to www.springer.com/materials/characterization+%26+evaluation/book/978-0-387-09415-1?detailsPage=samplePages, scroll down, and download "Sample pages 2".


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/).