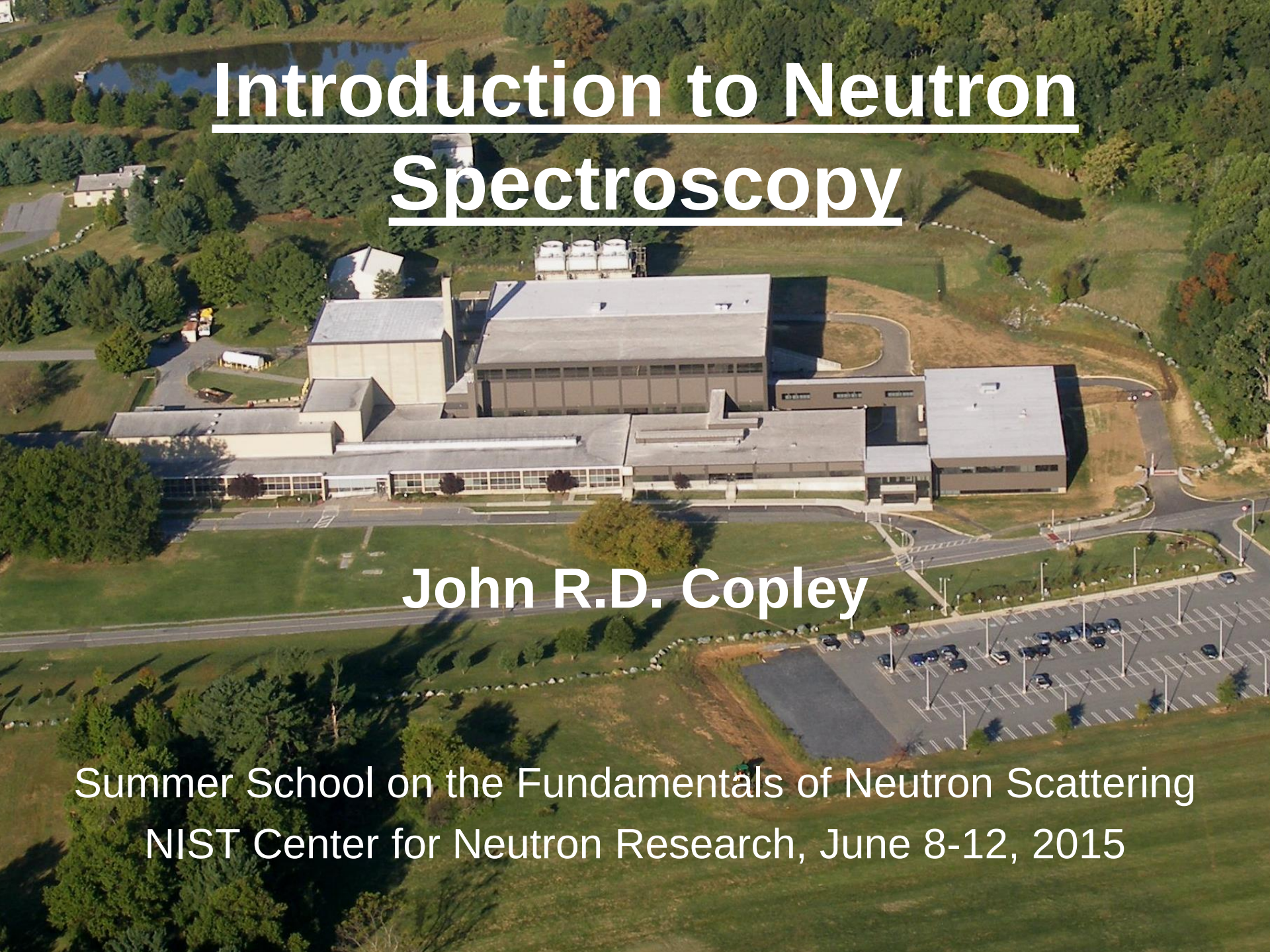
Introduction to Neutron Spectroscopy



John R.D. Copley

Summer School on the Fundamentals of Neutron Scattering

NIST Center for Neutron Research, June 8-12, 2015

Neutron scattering

Neutron scattering is an experimental technique that is used to reveal information about the structure and dynamics of materials.

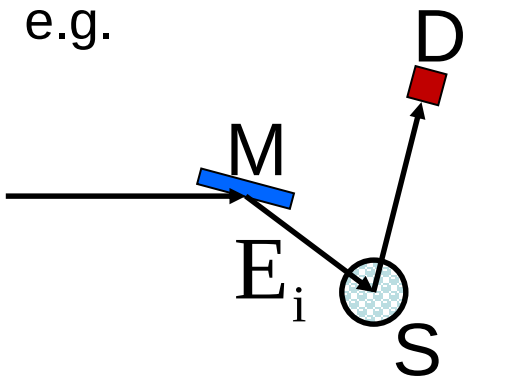
When a neutron strikes a material object and leaves in a new direction it is said to have been scattered. Its momentum is changed and there may also be a change in its kinetic energy.

In a neutron scattering experiment a sample is placed in a beam from a neutron source, and some of the scattered neutrons are counted.

Neutron scattering

There are two main types of neutron scattering experiments.

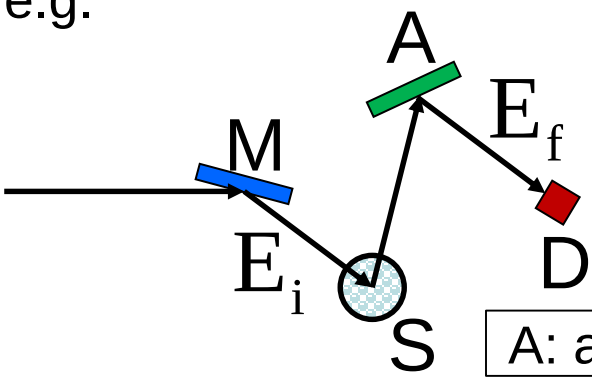
(1) Neutron diffraction experiments, which give structural information, e.g.



M: monochromator
S: sample
D: detector

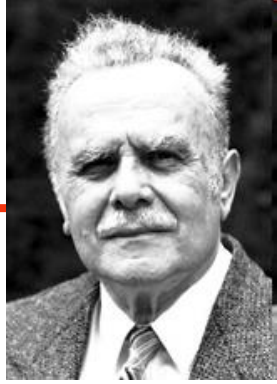
E_i is incident energy
E_f is scattered energy

(2) Neutron spectroscopy experiments, which give dynamical information, e.g.



A: analyzer

Recognition



Clifford G. Shull
(Neutron Diffraction)

Bertram N. Brockhouse
(Neutron Spectroscopy)

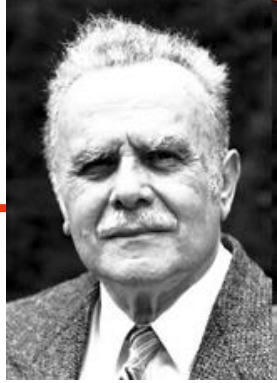
The importance of these techniques was recognized by the Royal Swedish Academy of Sciences who in 1994 awarded the Nobel Prize in Physics to two scientists "*for pioneering contributions to the development of neutron scattering techniques for studies of condensed matter*".

The Prize was shared between Professor Clifford G. Shull of MIT, "*for the development of the neutron diffraction technique*", and Professor Bertram N. Brockhouse of McMaster University (Canada), "*for the development of neutron spectroscopy*".

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

Recognition

"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* give information on the atoms' movements, e.g. their individual and collective oscillations, that is their **dynamics**."

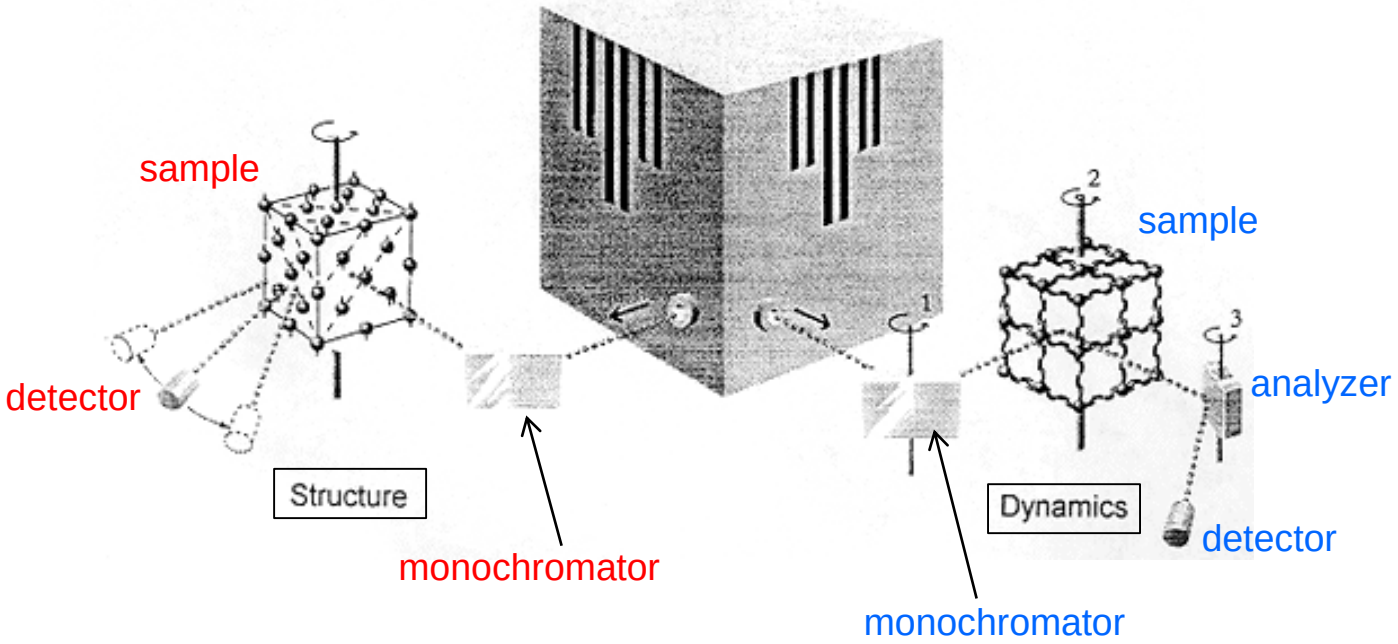
"Clifford G. Shull has helped answer the question of **where the atoms 'are'.**"

"Bertram N. Brockhouse has helped answer the question of **what the atoms 'do'**."

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

KUNGL. VETENSKAPSAKADEMIEN
THE ROYAL SWEDISH ACADEMY OF SCIENCES

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



"Through the studies of atomic structure and dynamics made possible by **Bertram N. Brockhouse** and **Clifford G. Shull** with their development of neutron scattering techniques, valuable information is being obtained for use in e.g. the development of new materials. An important example is the ceramic superconductors now being studied intensively, …"

Elastic and inelastic scattering

Neutrons that strike a sample may be transmitted, absorbed, or scattered.

The scattered neutrons may be scattered elastically (with no change in energy) or inelastically, in which case they lose or gain energy.

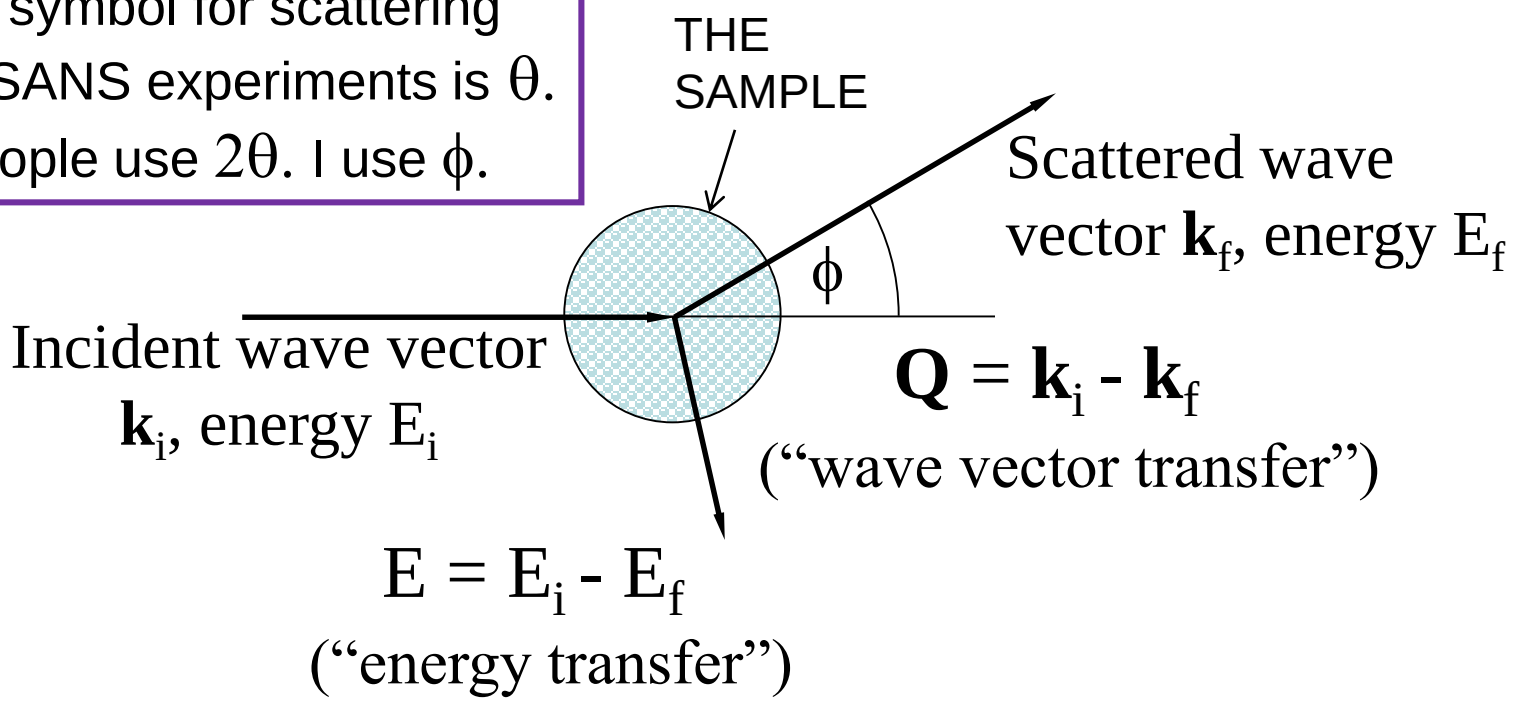
Structures are generally studied using a neutron **diffractometer**, in which total (integrated) scattered intensity is measured as a function of (for example) scattering angle. This is neutron diffraction, in which the dominant detected scattering is elastic. (The much weaker inelastic scattering is also counted.)

Dynamics is studied using a neutron **spectrometer**, in which scattered intensity is measured as a function of both scattering angle and energy transfer. This is neutron spectroscopy, in which the detected scattering is inelastic.

N.B. There is no elastic scattering from a liquid.

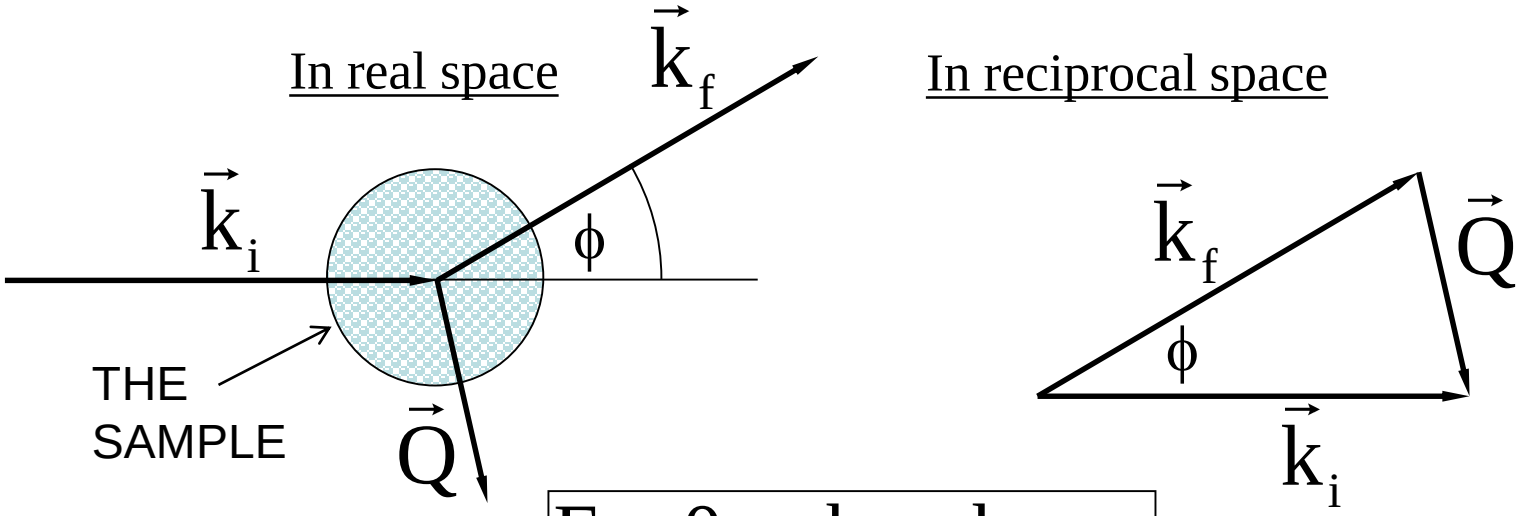
A scattering event

N.B. The symbol for scattering angle in SANS experiments is θ. Some people use 2θ. I use ϕ.



(N.B. Some people write $E = E_f - E_i$ and $\mathbf{Q} = \mathbf{k}_f - \mathbf{k}_i$)

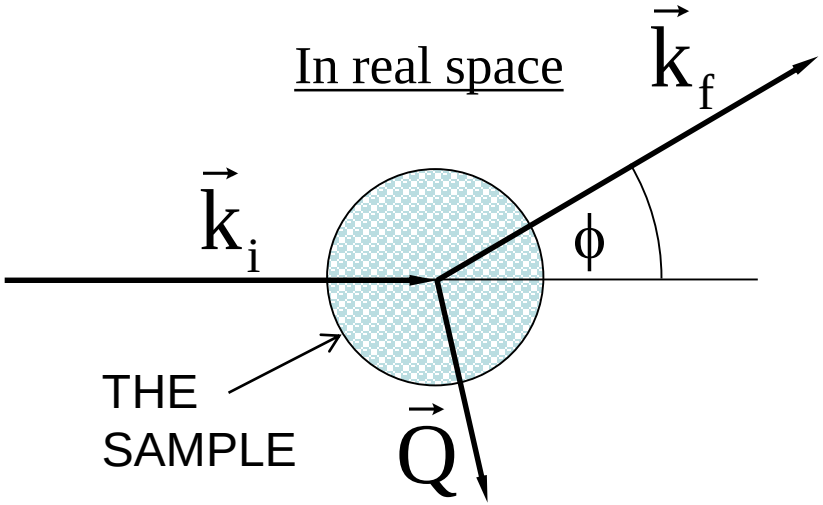
An elastic scattering event

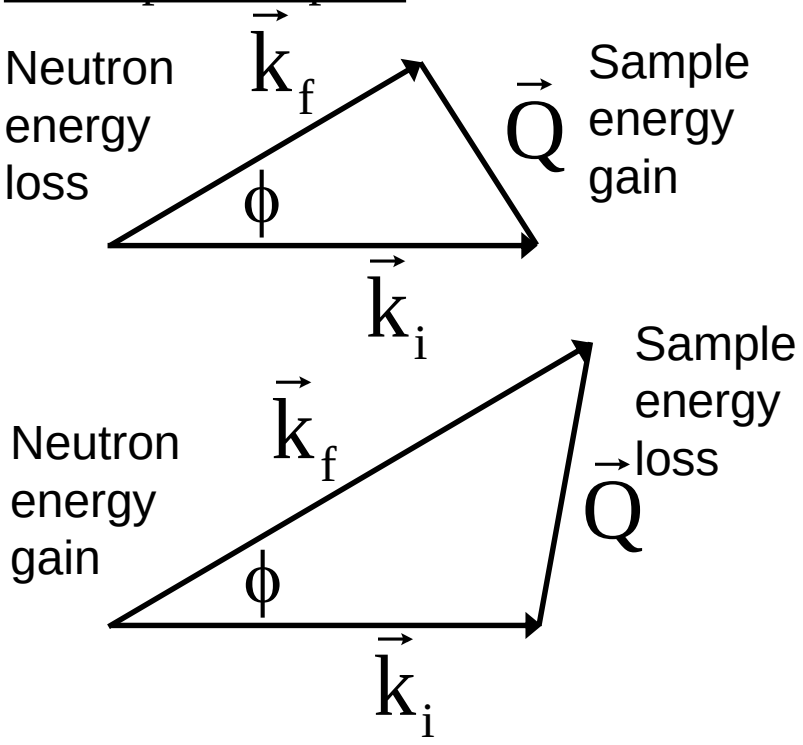


$$E = 0 \qquad k_i = k_f$$

$$Q = 2k_i \sin\left(\phi/2\right)$$

An inelastic scattering event





$$E \neq 0 \qquad k_i \neq k_f$$

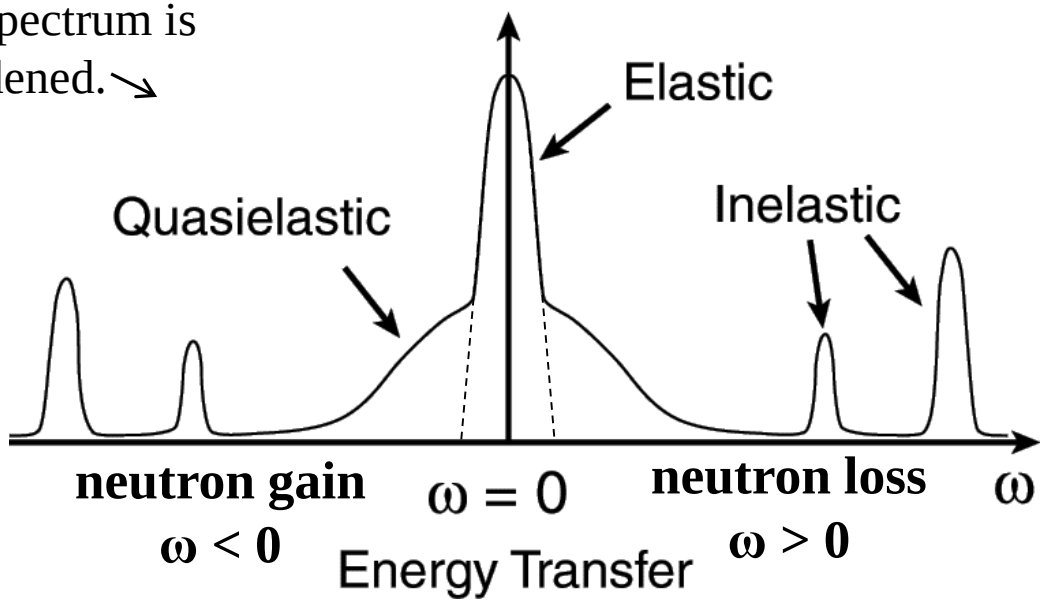
$$Q = \sqrt{k_i^2 + k_f^2 - 2k_i k_f \cos\phi}$$

At fixed scattering angle ϕ, and fixed incident energy E_i, both the magnitude and the direction of **Q** vary with the energy transfer E.

Quasielastic scattering

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

The schematic spectrum is resolution-broadened.↘



Relationships among v, E, and λ

$$v = h / m\lambda$$

$$E = \tfrac{1}{2} m v^2$$

$$v\left[\text{mm}/\mu\text{s}\right] \approx 3.956 / \lambda\left[\text{Å}\right]$$

$$E\left[\text{meV}\right] \approx 81.8 / \left(\lambda\left[\text{Å}\right]\right)^2$$

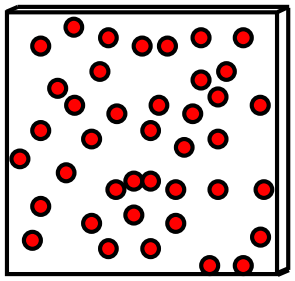
1 meV ≈
0.24 THz ≈
1.52 ps^{-1} ≈
8.1 cm^{-1} ≈
11.6K ≈
0.023 kcal/mol ≈
0.10 kJ/mol

m is neutron mass
h is Planck's constant

Cross sections

Consider a very thin sample placed in a neutron beam (no shadowing). Incident neutrons are transmitted, absorbed, or scattered, with probabilities p_T, p_A and p_S respectively; $p_T+p_A+p_S=1$.

N atoms
area A
thickness t
volume V



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

σ_S is the microscopic scattering cross section, (expressed in barns/atom) (1 barn = 10^{-24}cm^2)

ρ = N/V is the number density of atoms

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

$$p_A = \Sigma_A t \text{ and } p_T = 1 - \Sigma_T t$$

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

Unusual units…
1 shed = 10^{-24} b
1 outhouse = 10^{-6}b

Scattering rates

The sample is placed in a beam whose current density (or "flux") is Φ (n/cm^2/s). The number of neutrons hitting the sample per unit of time, is $I_0 = \Phi A$ n/s where A is the area.

The scattering rate (for a very thin sample) is

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

More generally, in the forward direction,

$$\left\{ \begin{aligned} I_S &= \Phi N \sigma_S f \\ I_A &= \Phi N \sigma_A f \\ I_T &= \Phi A e^{-\Sigma_T t} \end{aligned} \right\}$$

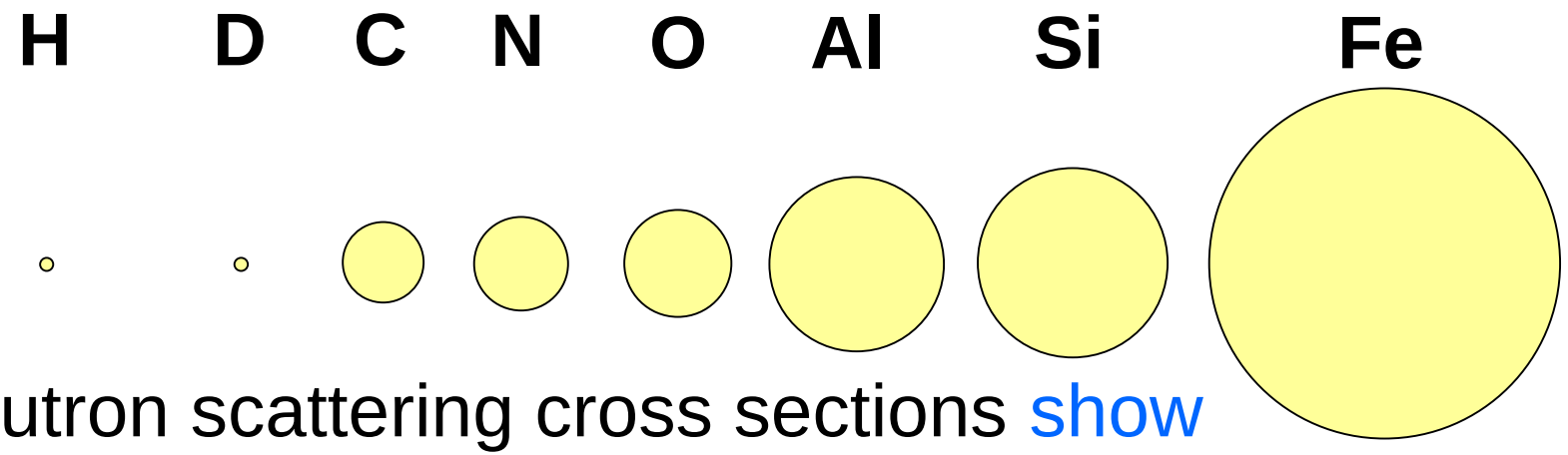
where

$$f = \frac{1 - e^{-\Sigma_T t}}{\Sigma_T t}$$

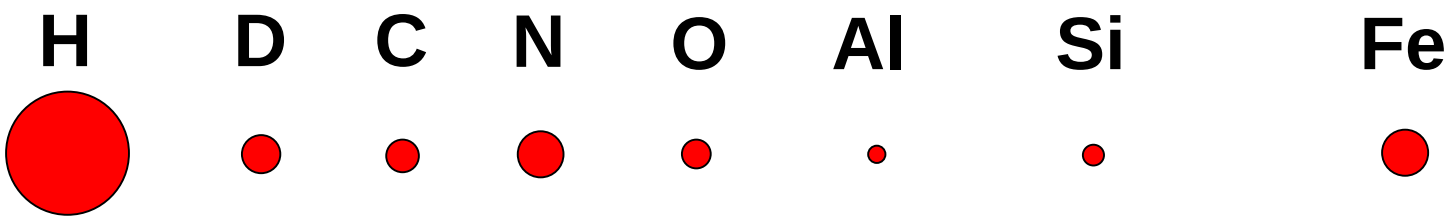
(N.B. The scattering may be followed by transmission, absorption, or additional scattering)

Comparison with x-ray cross sections

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



neutron scattering cross sections show little systematic variation with Z:

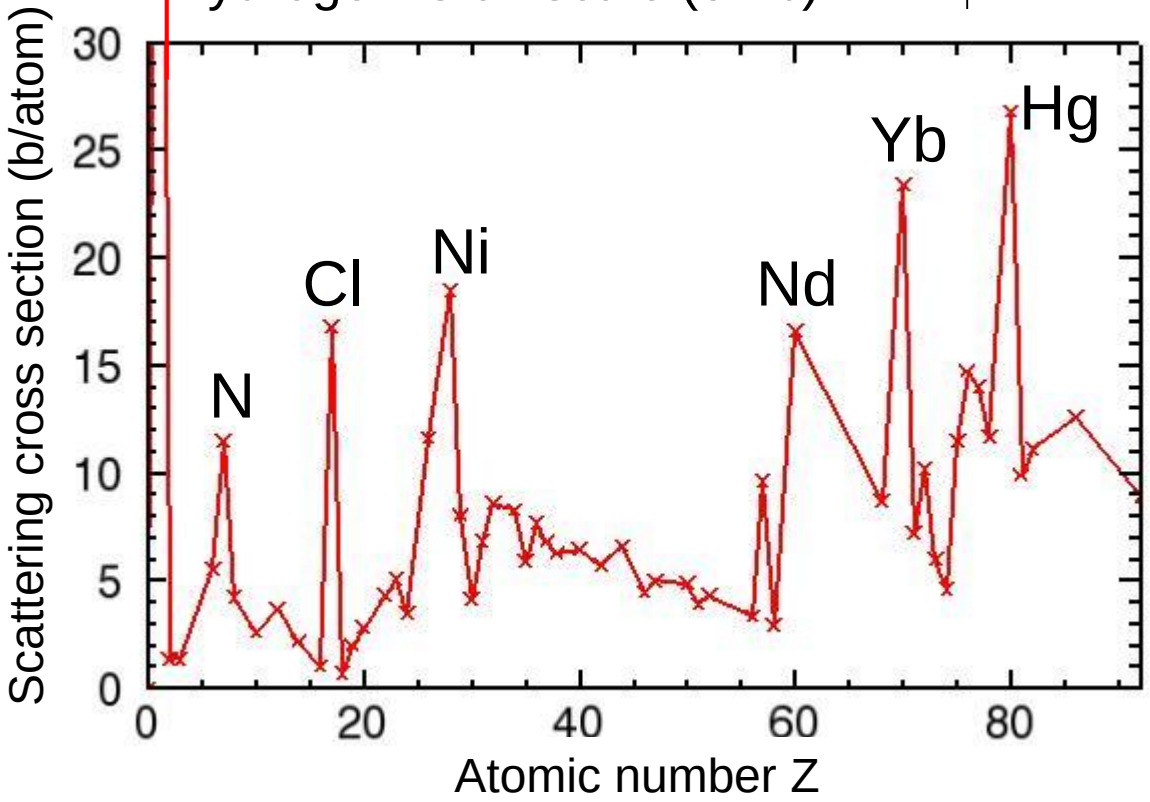


Scattering cross sections

linear scale

Hydrogen is off scale (82 b)

1 barn (b) = $10^{-28} m^2$



Absorption cross sections

As compared with x-ray absorption cross sections, neutron absorption cross sections are for the most part small.

Important exceptions include ^{3}He, ^{6}Li, ^{10}B, ^{113}Cd, and ^{157}Gd.

For most elements and isotopes the "1/v" law applies: $\sigma_{abs} \propto 1/v \propto \lambda$

^{113}Cd and ^{157}Gd are important exceptions.

For ^{135}Xe, σ_{abs} = 2.6 megabarns!!!
Fortunately it decays (half-life 9 h).

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

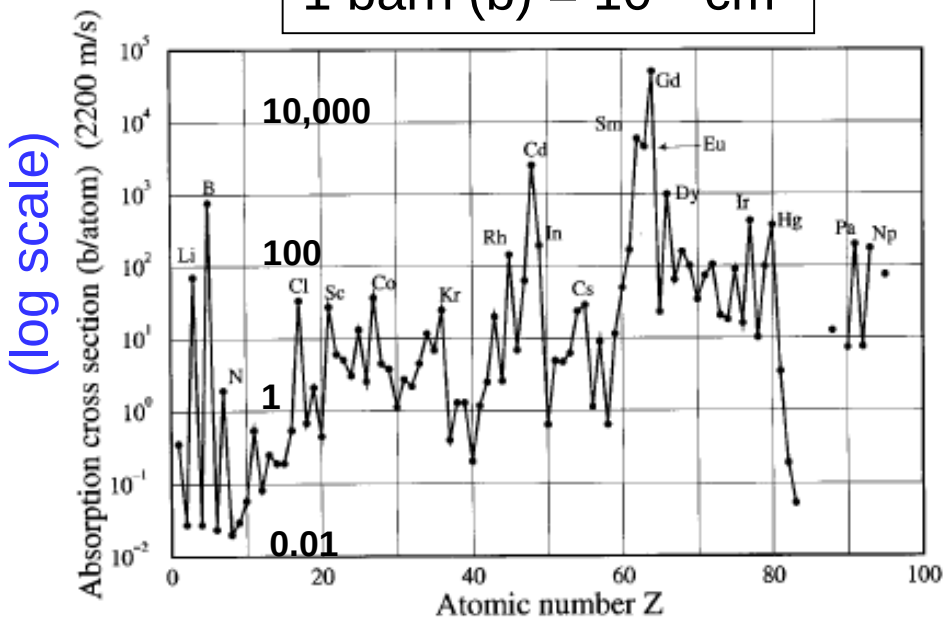


Fig. 8. The absorption cross section for 2200 m/s neutrons for the naturally occurring elements. Notice that the ordinate is plotted on a log scale.

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%

$$0.945^{40} \approx 0.1$$

N.B. These numbers were obtained using thermal neutron absorption cross sections (2200 m/s).

For any given element the scattering and absorption cross sections generally depend on the isotope and the nuclear spin state.

The single differential cross section

For a “thin” sample, the intensity in a total scattering measurement is:

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

By extension the measured intensity in a diffraction experiment is related to the ***single differential scattering cross section (sdscs)*** $d\sigma/d\Omega$:

$$I_S(E_i, \phi) = \Phi N \left[\frac{d\sigma}{d\Omega}(E_i, \phi) \right] \Delta\Omega$$

← solid angle subtended by detector

When there is only one type of atom

$$\frac{d\sigma}{d\Omega}(E_i, \phi) = \frac{\sigma_B}{4\pi} S(Q)$$

so that the intensity I_S, is proportional to the structure factor S(Q), (“S-of-Q”), which is the Fourier transform of the pair distribution function g(r).

The double differential cross section

Similarly the measured intensity in a spectroscopy experiment is related to the ***double differential scattering cross section (ddscs)*** $d^2\sigma/d\Omega dE_f$:

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

Energy window

The ddscs is related to the "scattering function", or "dynamic structure factor", S(Q,E).

When there is one type of atom,

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

Thus the ddscs, and the measured intensity, are proportional to S(Q,E) (which is often called "S-Q-Omega").

Incoherent scattering

So far we have implicitly assumed that all atoms of a given element have the same scattering cross section.

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, **incoherent**, contribution to I(Q).

Consider first an elementary diffraction experiment.

In general, $I(\mathbf{Q}) = \left| \sum_i^N b_i \exp(i\mathbf{Q}.\mathbf{r}_i) \right|^2$

If there's only one isotope/compound spin state, $I(\mathbf{Q}) = \langle b \rangle^2 \left| \sum_i^N \exp(i\mathbf{Q}.\mathbf{r}_i) \right|^2$

If there's more than one isotope/compound spin state,

$$I(\mathbf{Q}) = \langle b \rangle^2 \left| \sum_i^N \exp(i\mathbf{Q}.\mathbf{r}_i) \right|^2 + N\left(\langle b^2 \rangle - \langle b \rangle^2 \right) = \frac{N\sigma_{COH}}{4\pi} S(\mathbf{Q}) + \frac{N\sigma_{INC}}{4\pi}$$

Single particle motion

Similarly there is a second contribution to the double differential scattering cross section. In the simplest case we have:

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

$$\frac{\sigma_{COH}}{4\pi} = \langle b \rangle^2$$

$$\frac{\sigma_{INC}}{4\pi} = \langle b^2 \rangle - \langle b \rangle^2$$

$$\frac{\sigma_{TOT}}{4\pi} = \langle b^2 \rangle$$

where

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

Coherent and incoherent scattering

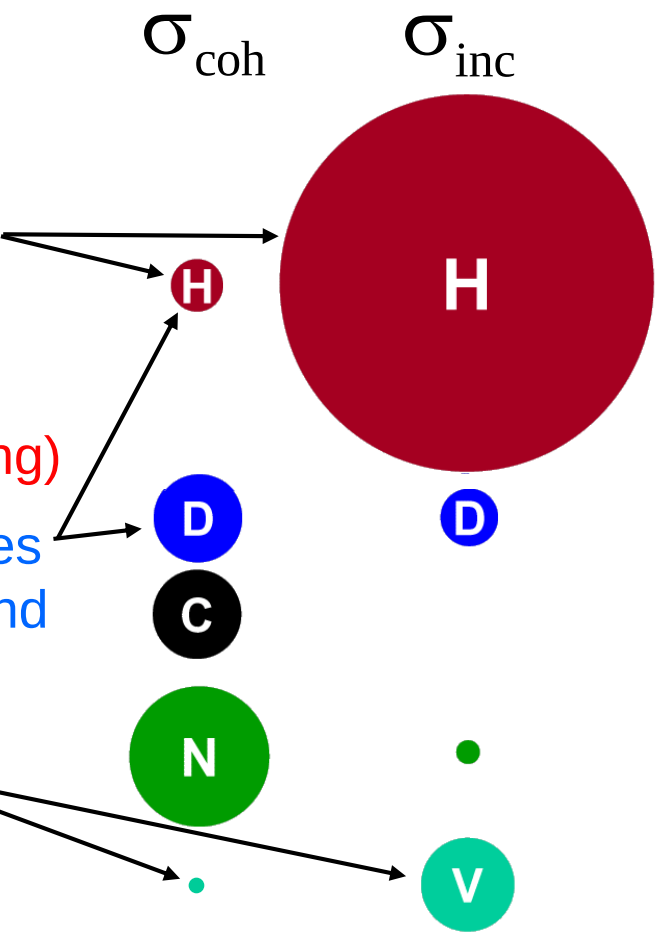
In most elements the coherent cross section dominates.

Hydrogen is a very important exception:

Its huge incoherent cross section enables studies of hydrogen diffusion in a variety of materials (quasielastic and inelastic scattering)

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 sample cans).



Correlation functions

- ✓ The FT of $S(Q,\omega)$ is the intermediate scattering function $I(Q,t)$ which is directly measured by Neutron Spin Echo.
- ✓ Similarly the FT of $S_S(Q,\omega)$ is the self-intermediate scattering function $I_S(Q,t)$.
- ✓ Theory and simulations typically evaluate $I(Q,t)$ and/or $I_S(Q,t)$.
- ✓ The coherent functions $S(Q,\omega)$ and $I(Q,t)$ contain information about the collective (pair) dynamics of materials.
- ✓ The corresponding incoherent functions $S_S(Q,\omega)$ and $I_S(Q,t)$ contain information about single particle dynamics.

The good news and the bad news

- Neutrons have **wavelengths comparable with interatomic spacings**, **and energies comparable with material energies**; both temporal and spatial aspects of atomic and molecular motions can be explored
- **Little absorption** → bulk probe: containment is simplified
- The ≈80 barn cross section of H facilitates proton dynamics studies
- **Sensitivity to isotope** (esp. H/D), and irregular behavior of scattering cross sections with Z, can be used to advantage
- The **magnetic interaction** enables studies of magnetic materials

BUT…

- Neutron sources are weak, intensities low, large samples needed
- Some elements/isotopes absorb strongly (and activate)
- Kinematics restricts available (Q,E) space

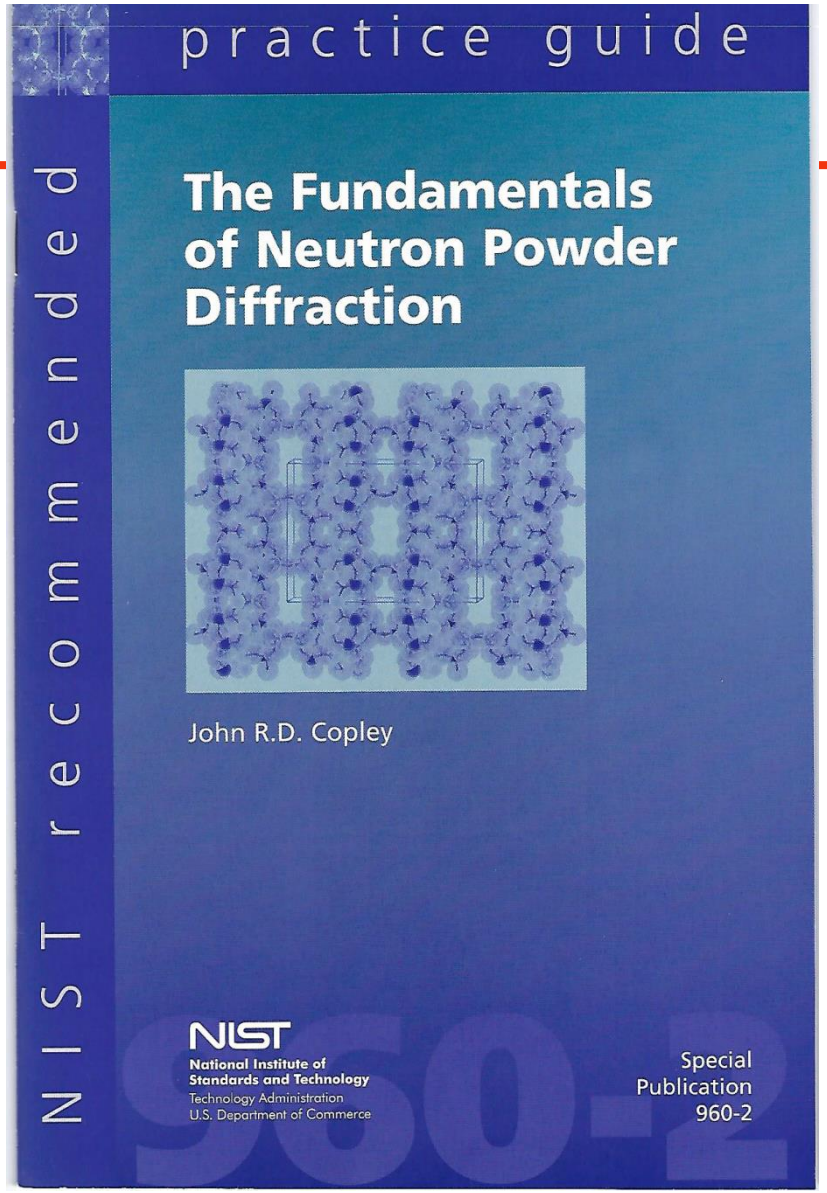
The bottom line

"Neutron Scattering
is an excellent way
to study dynamics"

(Dan Neumann, 2001)

and structure.

COME AND SEE FOR YOURSELVES!!!



These are free. I have lots. Take as many as you would like.

Useful references

• 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).

• G. Shirane, S. M. Shapiro, and J. M. Tranquada, “Neutron Scattering With a Triple-Axis Spectrometer”, Cambridge University Press, Cambridge (2002).

• M. Bée, “Quasielastic neutron scattering”, Adam Hilger, Bristol and Philadelphia (1988).

• R. Hempelmann, “Quasielastic Neutron Scattering and Solid State Diffusion”, Clarendon Press, Oxford (2000).

• B. T. M. Willis and C. J. Carlile, “Experimental Neutron Scattering”, Oxford University Press (2009).

• D. S. Divia, “Elementary Scattering Theory”, Oxford University Press (2011).

More useful references

- R. Pynn, “An Introduction to Neutron Scattering” and “Neutron Scattering for Biomolecular Science” (lecture notes, possibly “out of print”)
- 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, click on “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/).

Correlation functions – S(Q)

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

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

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

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

Averaging over directions within the sample we obtain:

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

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

Pair distribution functions contain information about structure.

Correlation functions – S(Q,ω)

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

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

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

The quantity I(**Q**,t) is known as the "intermediate scattering function".
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 information about the collective (pair) dynamics of materials.

Correlation functions – $S_S(Q,\omega)$

Most neutron spectrometers measure both $S(\mathbf{Q},\omega)$ and $S_S(\mathbf{Q},\omega)$.

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

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

The quantity $G_S(\mathbf{r},t)$ is the "time-dependent self 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 information about the single particle (self) dynamics of materials.