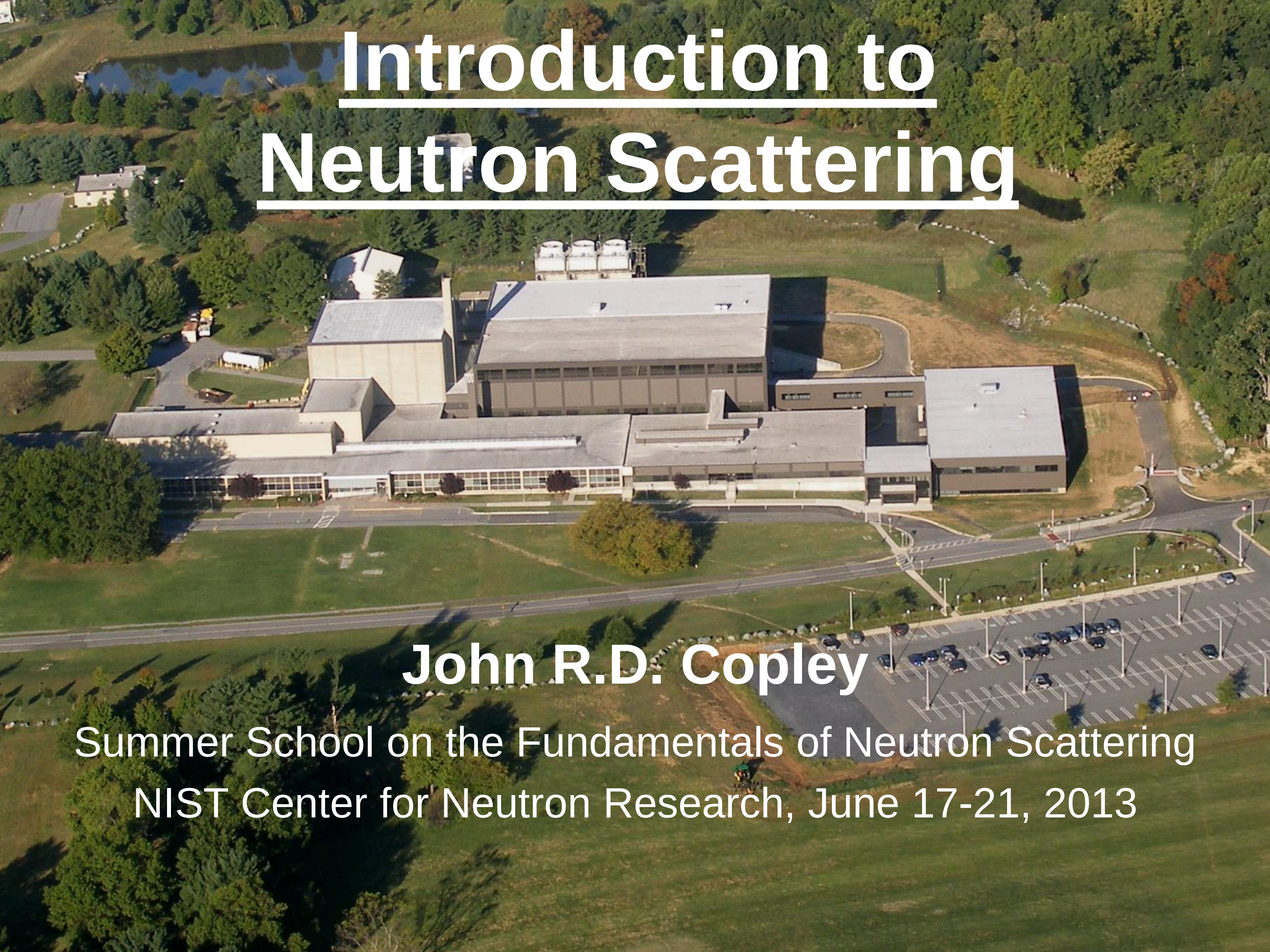


Introduction to Neutron Scattering

John R.D. Copley

Summer School on the Fundamentals of Neutron Scattering

NIST Center for Neutron Research, June 17-21, 2013

Acknowledgement

National Science Foundation (DMR-0944772)

NIST Center for Neutron Research (NCNR)

Center for High Resolution Neutron Scattering (CHRNS)

Outline

Introductory remarks
Neutron kinematics
Aspects of structure and dynamics
Intensities and total cross sections
Differential cross sections and
single particle scattering
Concluding remarks

<u>Supplementary materials</u>
Bibliography
Correlation functions

So what is neutron scattering?

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 it may or may not also change its kinetic energy.

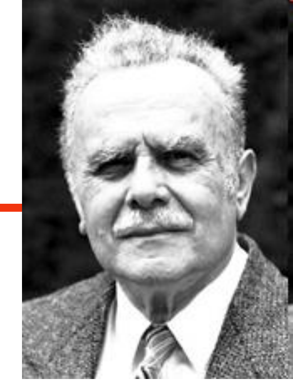
In a neutron scattering experiment a sample is placed in a beam and some of the scattered neutrons are counted.

Neutron scattering experiments are designed to reveal information about the structure and dynamics of materials.
Neutron diffraction yields structural information.
Neutron spectroscopy yields information about dynamics.

Recognition

Clifford G. Shull

Bertram N. Brockhouse



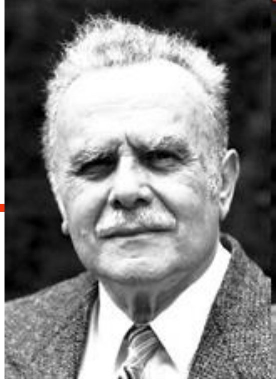
The importance of these techniques was recognized by the Royal Swedish Academy of Sciences who in 1994 awarded the Nobel Prize in Physics “for pioneering contributions to the development of neutron scattering techniques for studies of condensed matter”.

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

"Changes in the neutrons' *velocity* give information on the atoms' movements, e.g. their individual and collective oscillations, that is their **dynamics**." "Bertram N. Brockhouse has helped answer the question of **what the atoms 'do'**."

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

Neutron interactions - summary

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

Scattered neutrons are scattered **elastically** (with no change in energy) or **inelastically**, in which case they lose or gain energy.

Structures can be studied using a neutron diffractometer, in which total scattered intensity is measured as a function of scattering angle*. This is known as **diffraction**.

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 **spectroscopy**.

* (at a reactor)

Neutron kinematics

Energy, momentum, velocity

$$p = mv = h/\lambda = \hbar k$$

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

(m is neutron's mass)

$$\tau = 1/v$$

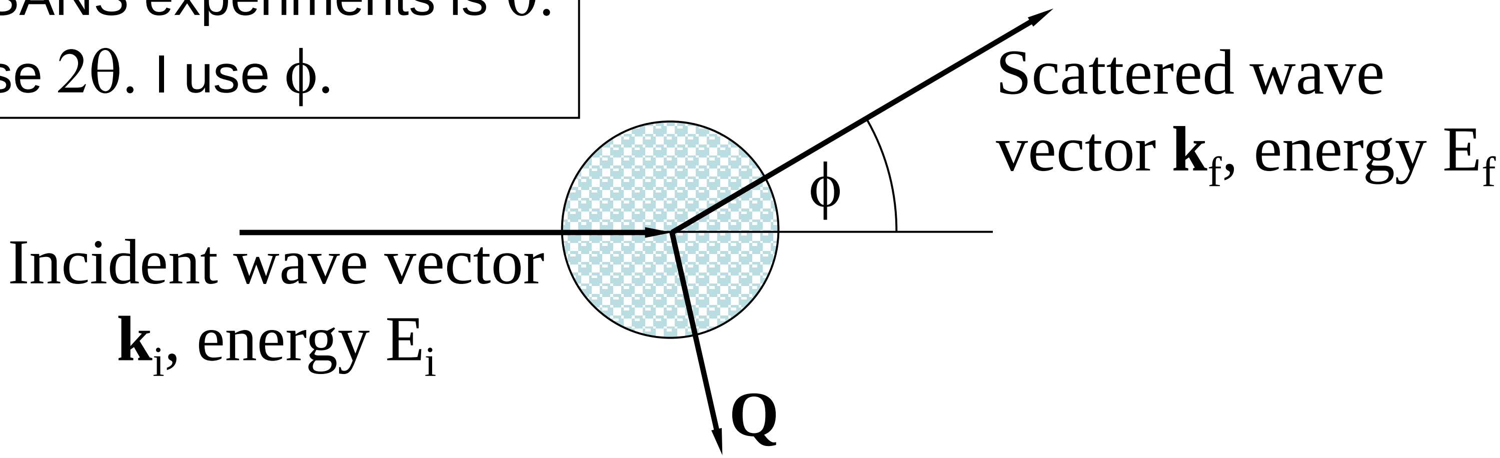
λ	E	v	τ
Å	meV	km/s	μs/mm
1	82	4	0.25
2	20.5	2	0.5
4	5.1	1	1
8	1.3	0.5	2

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

(1Å=0.1nm)

A scattering event

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

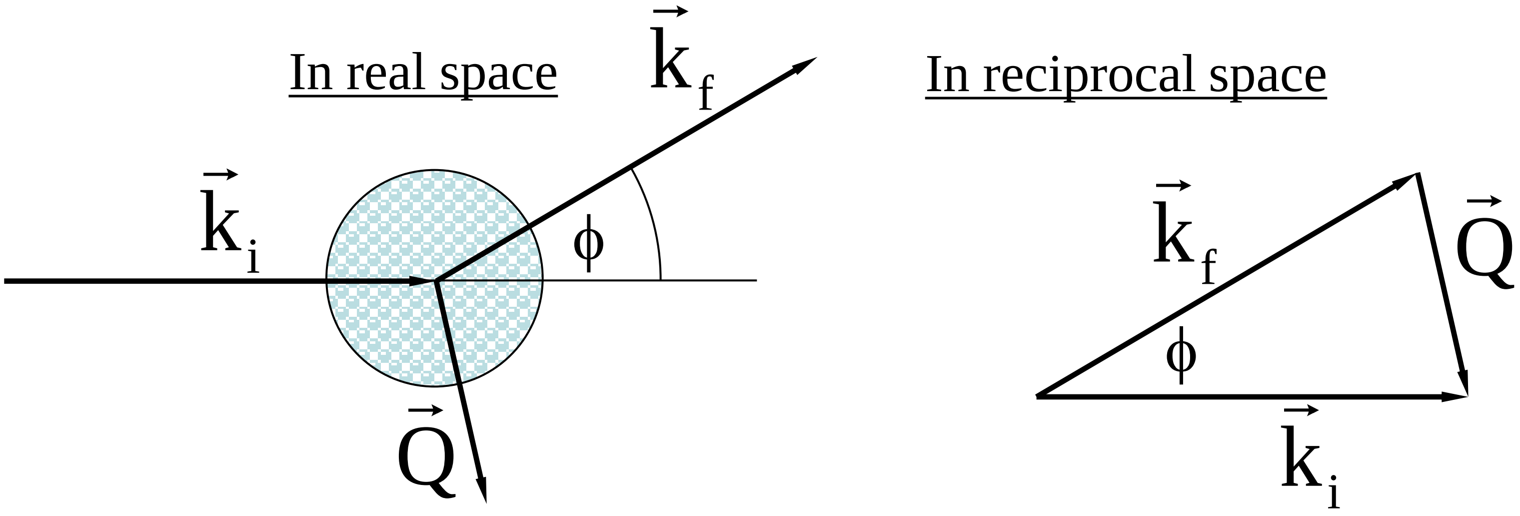


$$\boxed{E = E_i - E_f}$$
("energy transfer")

$$\boxed{\mathbf{Q} = \mathbf{k}_i - \mathbf{k}_f}$$
("wave vector transfer")

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

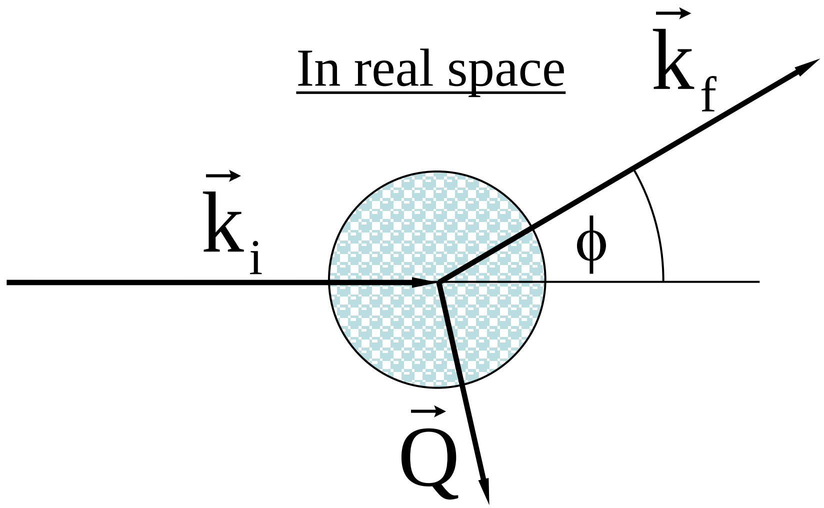
Elastic scattering



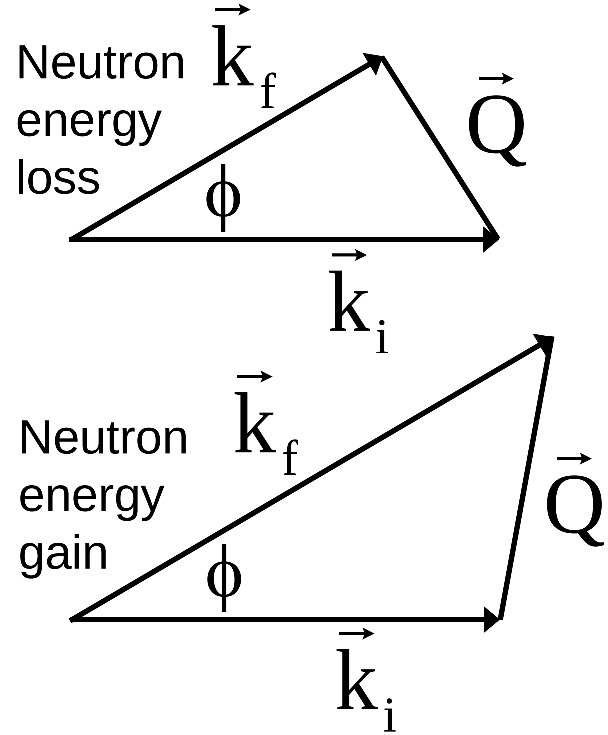
$$\boxed{E = 0 \qquad k_i = k_f \qquad Q = 2k_i \sin(\phi/2)}$$

Inelastic scattering

In real space



In reciprocal space



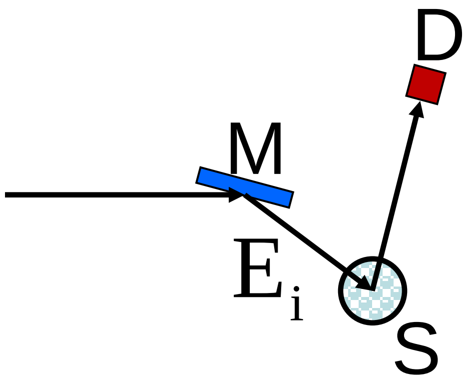
$$E \neq 0 \qquad k_i \neq k_f$$

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

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

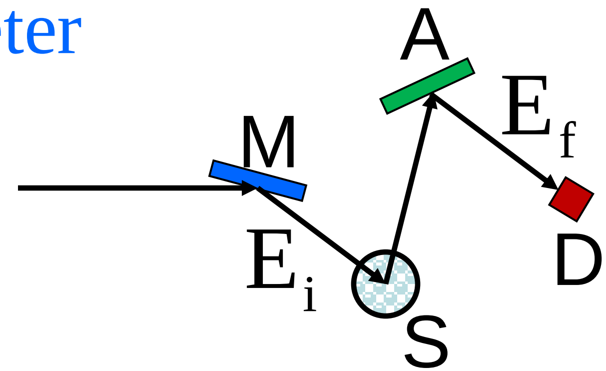
Total, elastic, and inelastic scattering

<u>Total scattering</u> is measured using a diffractometer (no analysis of energy transfer)



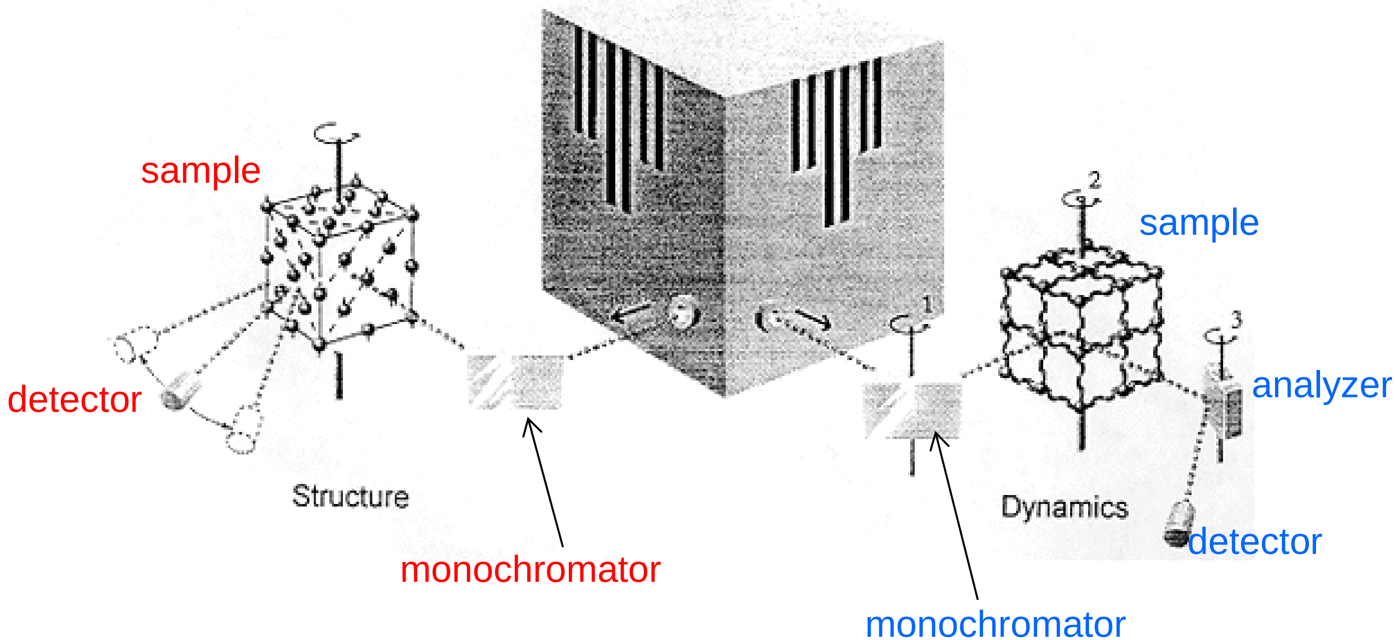
M: monochromator
S: sample
D: detector

<u>Elastic and inelastic scattering</u> are measured using a spectrometer



A: analyzer

(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, although these have not yet been developed for commercial use.”

Aspects of structure and dynamics

An aside: the concept of "structure"

The structure of a crystalline solid, i.e. the average positions of the atoms in the unit cell, is determined from ***elastic scattering*** (Bragg reflection) intensities which are generally measured using a diffractometer. Contaminant scattering such as diffuse scattering (sometimes called "background") is subtracted from the measured intensity, yielding the elastic structure factor $S_{EL}(Q)$.

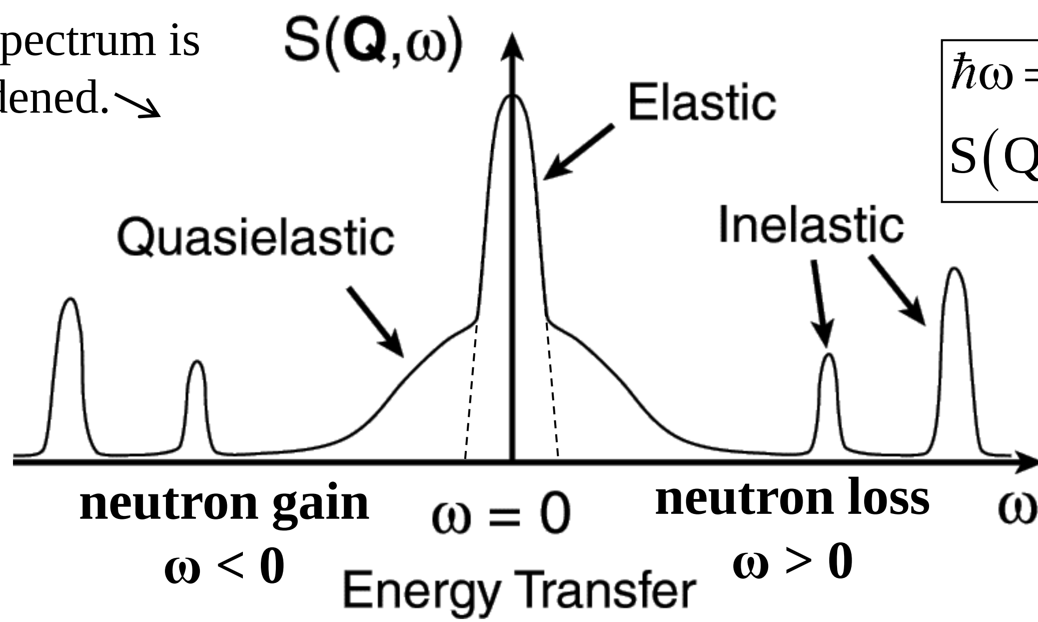
The structure of a fluid is related to the ***total scattering*** and measured using a diffractometer; there is no purely elastic scattering from a fluid. Inelasticity ("Placzek") corrections may be applied in order to obtain the measured total structure factor $S_{TOT}(Q)$.

Dynamics and Neutron Spectroscopy

Neutron spectroscopy (inelastic scattering) measures **dynamics**. The measured intensity yields the scattering function (or “scattering law”, or “dynamic structure factor”) S(Q,E).

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.



$$\hbar\omega = E$$

$$S(Q,\omega) = \hbar S(Q,E)$$

Intensities and total cross sections

So what is a cross section?

If there is just one type of atom the measured intensity in a diffraction experiment is proportional to the product of quantities σ_S and S(Q):

$$I_{DIFF} \propto \left(\frac{\sigma_S}{4\pi}\right) S(Q).$$

Similarly the measured intensity in a spectroscopy experiment is proportional to the product of quantities σ_S and S(Q,E):

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

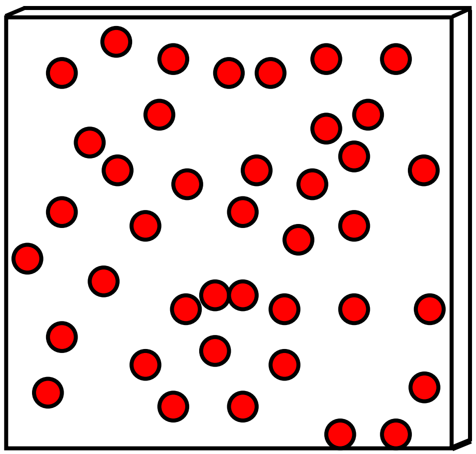
The scattering cross section σ_S depends (only) on the strength of the nuclear interaction between neutrons and the sample. (We ignore the magnetic interaction.)

The structure factors S(Q) and S(Q,E) depend on the sample (only).

If there is more than one type of atom we need to introduce concepts such as scattering length, scattering length density, and partial structure factors.

Cross sections

Consider an infinitely thin sample in a neutron beam (no shadowing). Incident neutrons are transmitted, absorbed, or scattered, with probabilities p_T, p_A and p_S respectively.



The sample contains N atoms spread over area A.

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

t = thickness, V = volume, ρ = N/V is number density

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

$\Sigma_S = \rho\sigma_S$ is the macroscopic scattering cross section (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.

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 beam area.

The scattering rate is

$$\boxed{I_S = I_0 p_S = \left(\Phi A\right)\left(\Sigma_S t\right) = \Phi V \Sigma_S = \Phi N \sigma_S}$$

(For a thick sample

$$I_S = \Phi N \sigma_S f,\ I_A = \Phi N \sigma_A f,\ \text{and}\ I_T = \Phi A e^{-\Sigma_T t}$$

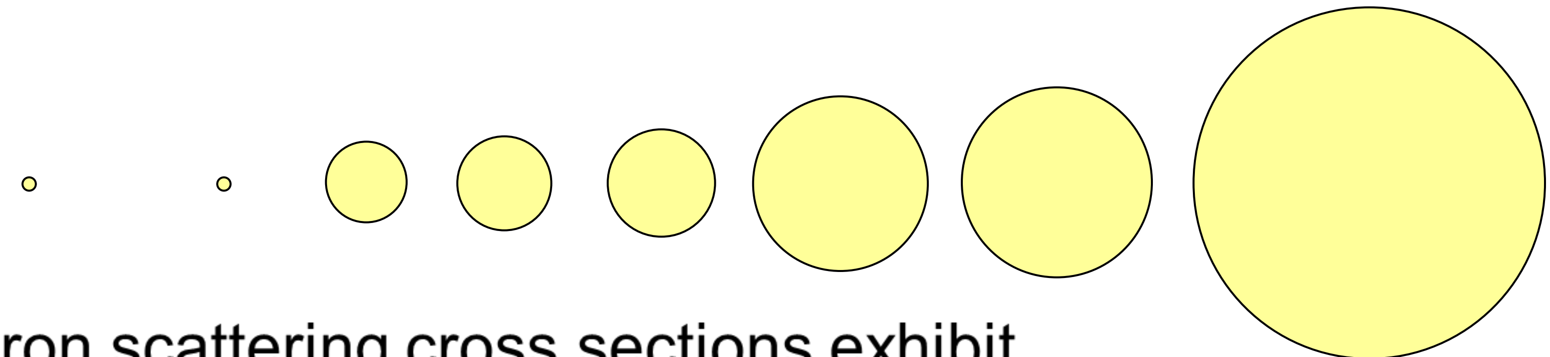
$$\text{where } f = \left(1 - e^{-\Sigma_T t}\right) \Big/ \Sigma_T t)$$

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

Comparison with x-ray cross sections

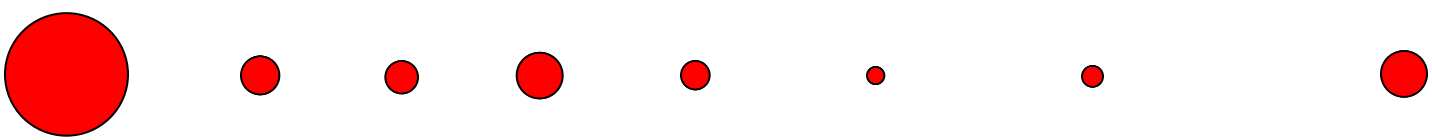
As compared with x-ray (Q=0) cross sections, which vary as Z^2,

H D C N O Al Si Fe



neutron scattering cross sections exhibit little systematic variation with Z:

H D C N O Al Si Fe

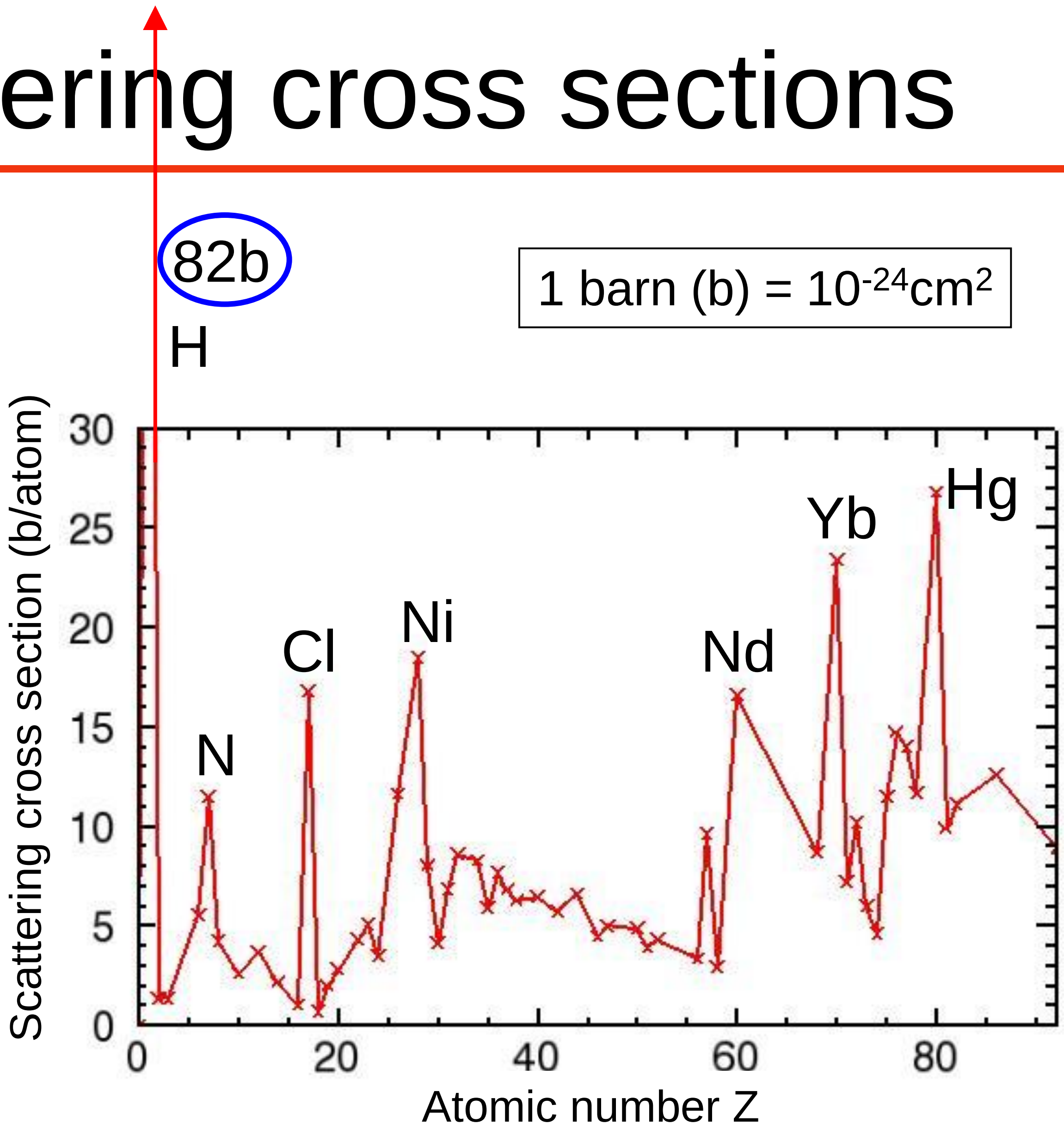


X-ray cross sections vary with Q; neutron cross sections do not.

Scattering cross sections

linear scale

1 barn (b) = 10^{-24}cm^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: $\boxed{\sigma_{abs} \propto 1/v \propto \lambda}$

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

For ^{135}Xe, $\sigma_{abs} = 2.6 \times 10^{6}$ barns. To learn about this discovery see Richard Rhodes, "The Making of the Atomic Bomb", Simon and Schuster (1986).

(log scale)

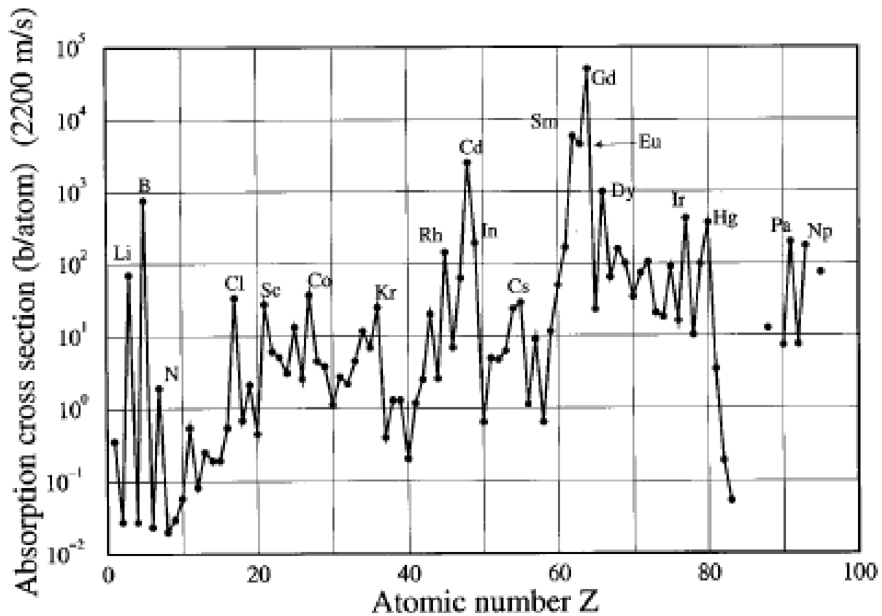


Fig. 8. The absorption cross section for 2200 m/s neutrons for the naturally occurring elements. Notice that the ordinate is plotted on a log scale.

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%

N.B. These results were obtained using thermal neutron absorption cross sections.

Differential cross sections
and
single particle scattering

The single differential cross section

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

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

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

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

solid angle subtended by detector

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

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

Thus the sdscs, and therefore I_S, is proportional to the structure factor S(Q), which is the Fourier transform of the pair distribution function g(r).

The double differential cross section

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

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

energy window

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

When there is one type of atom we obtain

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

Thus the ddscs, and the measured intensity, are proportional to S(Q,E).

Single particle motion

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 contribution to the ddscs. 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 individual (self) behavior (e.g. diffusion)
- σ_{coh} and σ_{inc} are **coherent** and **incoherent** scattering cross sections respectively

Coherent and incoherent scattering

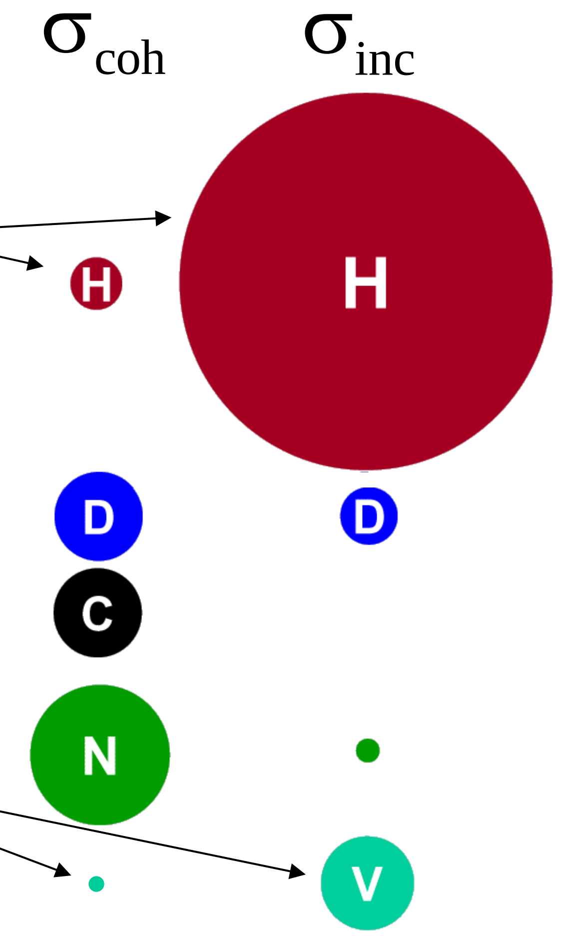
In most elements the coherent cross section dominates.

<ins>**Hydrogen is a very important exception:**</ins>

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

Selective deuteration enables detailed studies of structure and dynamics in 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

Neutron spectrometers (other than spin echo) generally yield some combination of **$S(Q,E)$** and **$S_S(Q,E)$**.

Comparisons with theory and/or computer simulations are commonly accomplished in terms of the so-called coherent and incoherent intermediate scattering functions **$I(Q,t)$** and **$I_S(Q,t)$**, which are frequency Fourier transforms of $S(Q,E)$ and $S_S(Q,E)$ respectively. These functions contain information about the collective and single particle dynamics of materials.

The quantities **$G(r,t)$** and **$G_S(r,t)$**, known as the "time-dependent pair correlation function" and the "time-dependent self correlation function" respectively, are space Fourier transforms of $I(Q,t)$ and $I_S(Q,t)$.

Note that $S(Q) = I(Q,0)$ and $g(r) \propto G(r,0)$.

Concluding remarks

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 interesting 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.

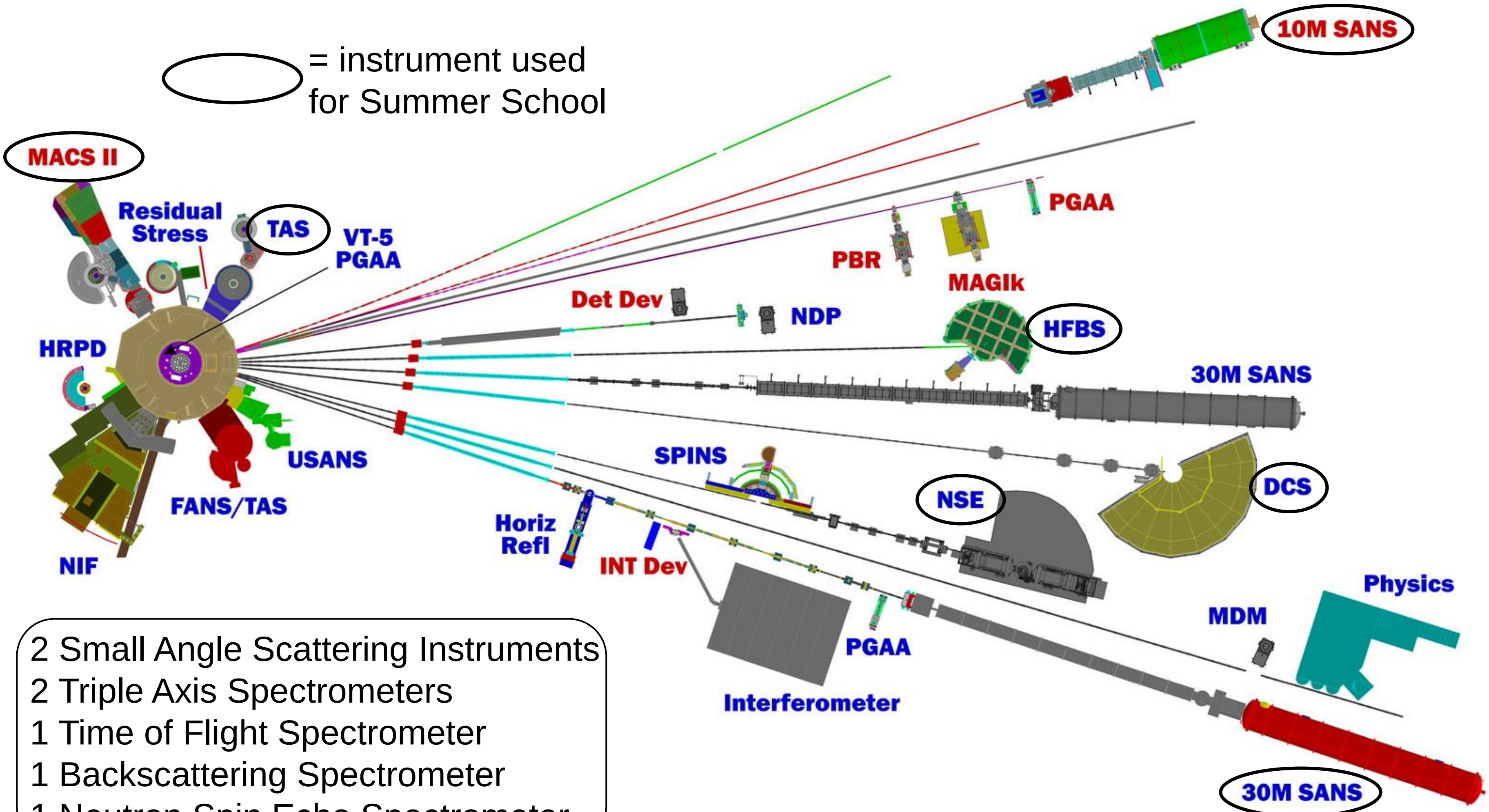
Advantages and disadvantages

- 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 studied
- Little absorption $\rightarrow$ bulk probe: containment is simplified
- Weak neutron-nucleus interaction simplifies interpretation of data
- Sensitivity to isotope (esp. H/D), and irregular behavior of scattering lengths with Z, can be used to advantage
- Magnetic interaction enables studies of magnetic materials

BUT…

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

NCNR spectrometers



2 Small Angle Scattering Instruments
2 Triple Axis Spectrometers
1 Time of Flight Spectrometer
1 Backscattering Spectrometer
1 Neutron Spin Echo Spectrometer

The bottom line

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

COME AND SEE FOR YOURSELVES!!!

Bibliography

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

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:

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

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

Pair distribution functions contain 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 <u>collective</u> (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 <u>single particle</u> (self) dynamics of materials.