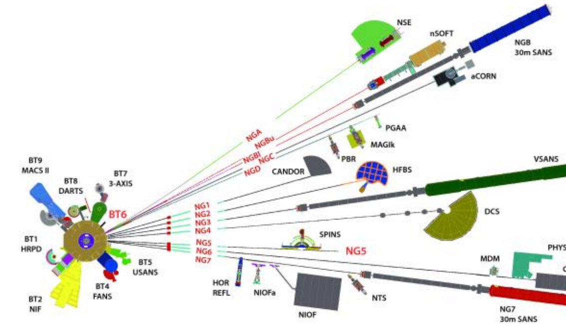
2022 NCNR CHRNS School on Methods and Applications of Neutron Spectroscopy




# Basic Elements of Neutron Inelastic Scattering

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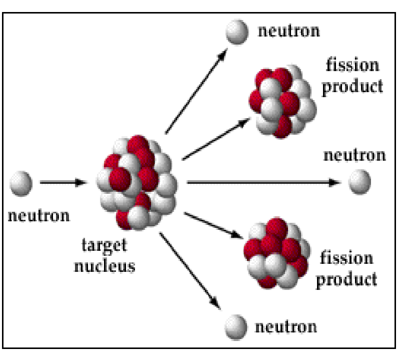
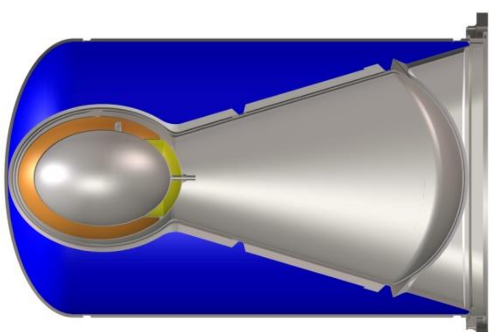
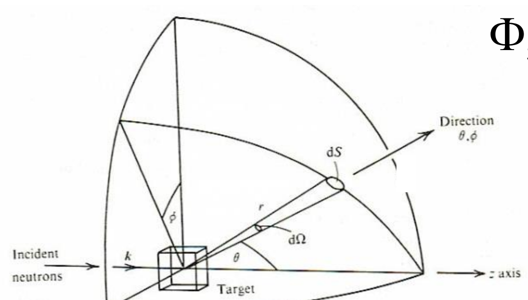
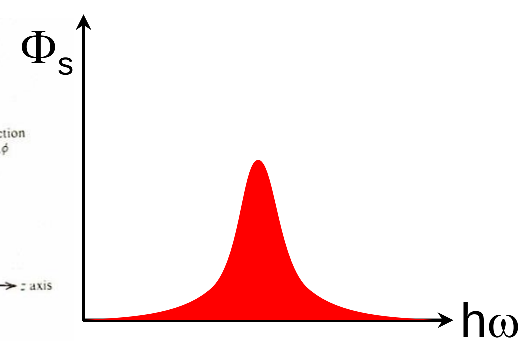


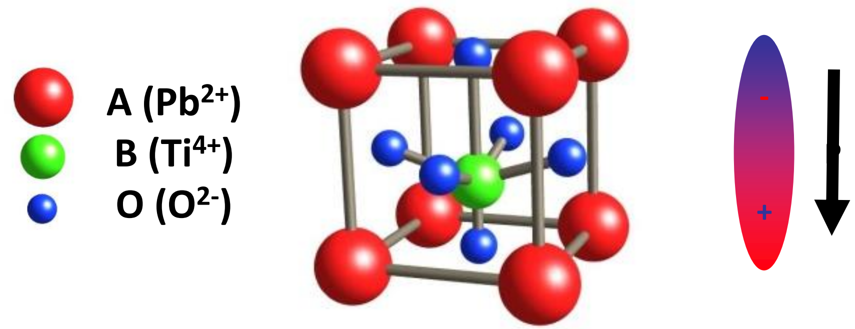


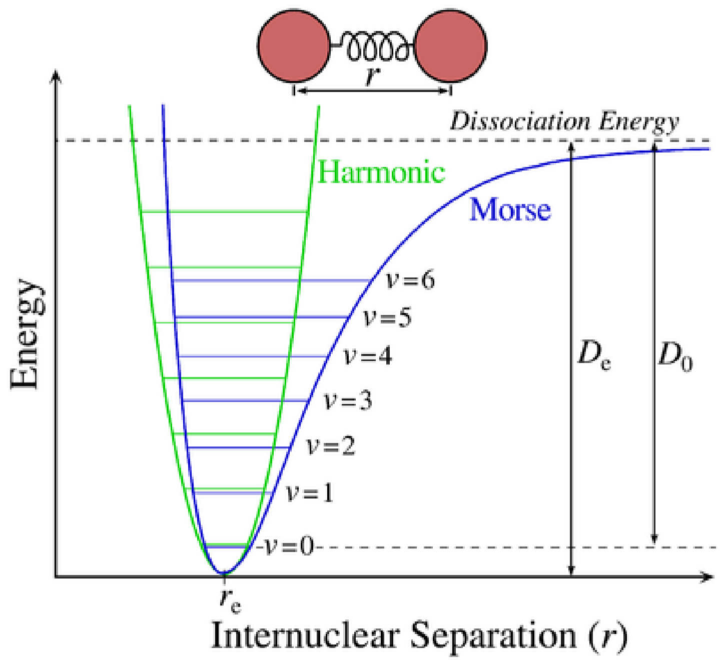



# Motivation

## Why Study Dynamics?

One of the most important properties of any material is its underlying structure.



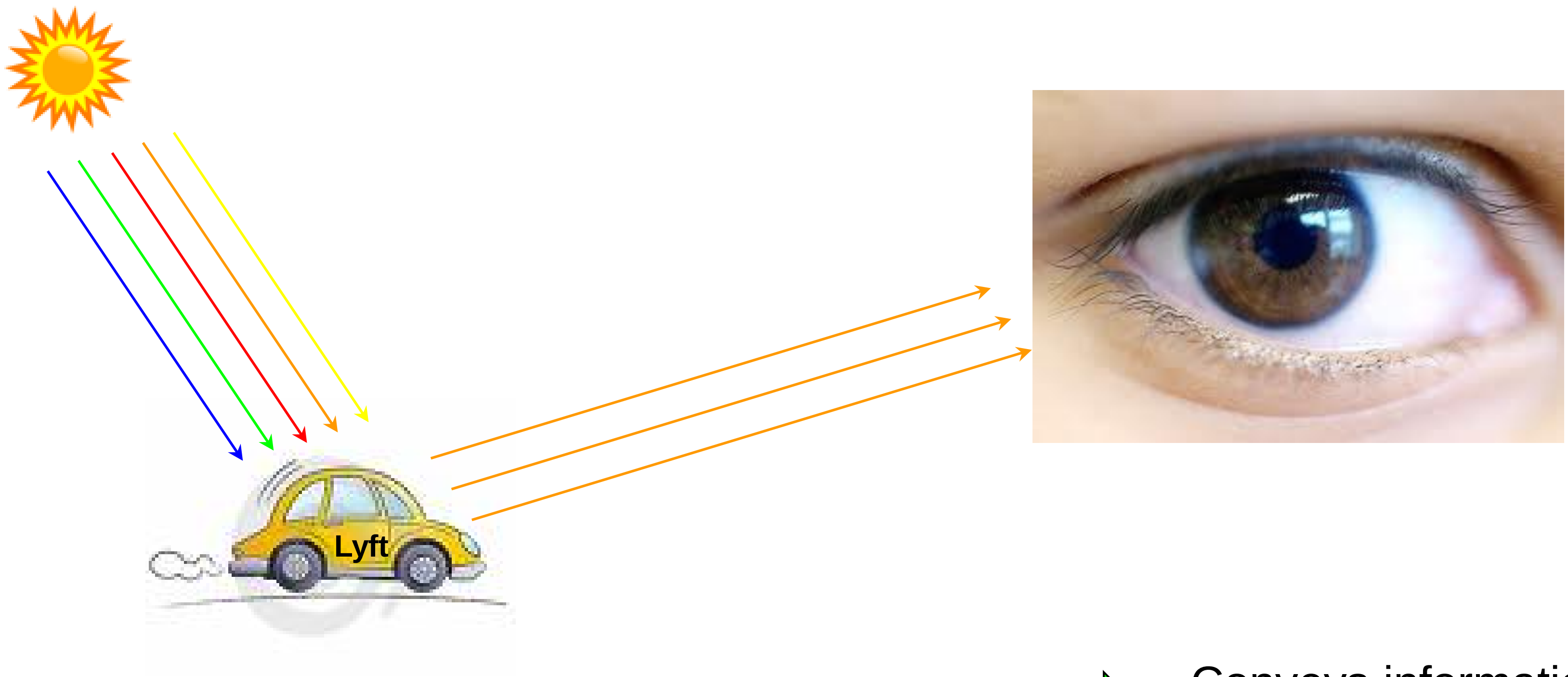




Characterizing the dynamics in solids is extremely important too, as it yields information about the interatomic potentials.

The presence of anharmonicity affects thermal expansion, thermal conductivity, phase transitions, SC, ferroelectricity, phonon lifetimes …

# Motivation

## Why Should We Scatter?




- We see something when light scatters from it. → Conveys information: location, speed, shape
- Light is composed of electromagnetic waves. → $4000\ \text{Å} < \lambda < 7000\ \text{Å}$
- **However**, the details of what we can see are ultimately limited by the wavelength.

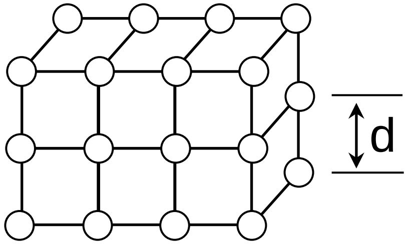
# Motivation

## Why Should We Scatter?

The tracks of a compact disk act as a diffraction grating, producing a separation of the colors of white light when it scatters from the surface.

From this one can determine the nominal distance between tracks on a CD, which is 1.6 x $10^{-6}$ meters = 16,000 Angstroms.

To characterize materials we must determine the underlying structure. We do this by using the material as a diffraction grating.



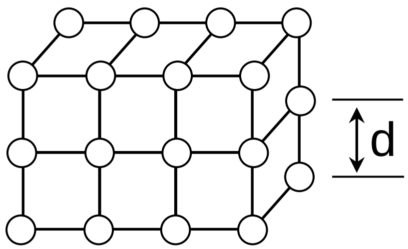

Problem: Distances between atoms in materials are of order Angstroms → light is inadequate. Moreover, most materials are opaque to light.

$\lambda_{Light} >> d \sim 4$ Å

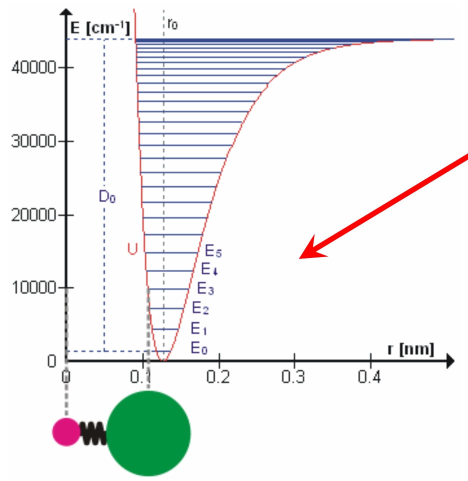
# Motivation

## Why Should We Scatter?

To characterize structure requires a probe with wavelengths $\lambda$ that are comparable to the length scales of interest.




To characterize dynamics requires a probe with energies $h\omega$ that are comparable to the energy scales of interest.



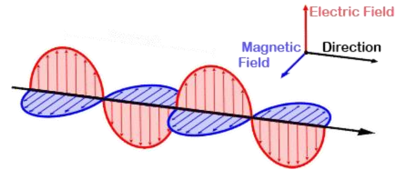

An ideal method of characterization should provide detailed information about structure and dynamics at the same time …

# Scattering Probes

To measure atomic structure requires a probe with a $\lambda$ ~ length scale of interest.

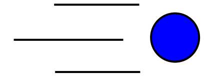
Two main candidates …

X rays




EM - wave

Neutrons



Neutral particle

1929 Nobel Laureate in Physics

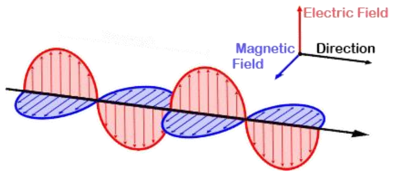
From Louis de Broglie:

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

Particles have wave properties too.

Scattering Probes

# X rays: Pros and Cons




If we wish only to determine relative atomic positions, then we should choose x rays almost every time.

1. Relatively cheap

2. Sources are ubiquitous → easy access

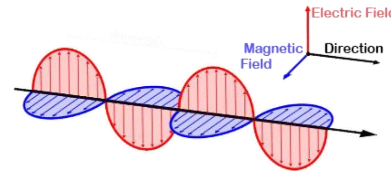
3. High flux → can study small samples

4. Can obtain extremely good spatial resolution

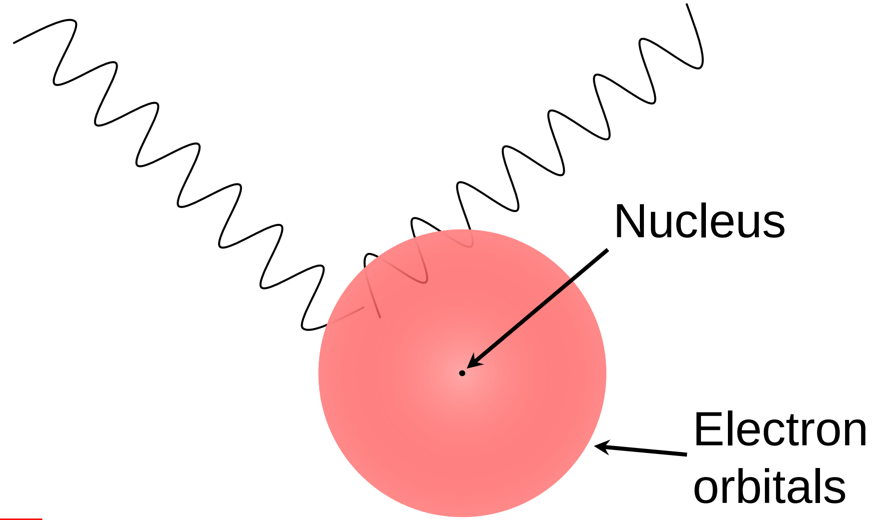
5. High energies (keV) → less constrained by kinematics

# Scattering Probes

## X rays:  Pros and Cons




X rays scatter from the charge density.



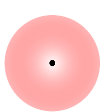

### Consequences:

Low-Z elements are hard to see.

Elements with similar atomic numbers have very little contrast.

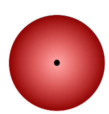
X rays are strongly attenuated when passing through furnaces, cryostats, and samples too.

Hydrogen



(Z = 1)

Cobalt



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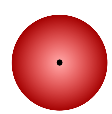
Nickel

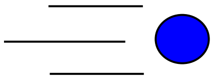


(Z = 27)

(Z = 28)

Scattering Probes

# Neutrons: Pros and Cons



1. Zero charge → not strongly attenuated by furnaces, etc.

2. Magnetic dipole moment → can study magnetic structures

3. Nuclear interaction → see low-Z elements easily (H) → good for the study of biomolecules/polymers

4. Nuclear interaction is simple → scattering is easy to model

5. Low energies (meV) → non-destructive probe

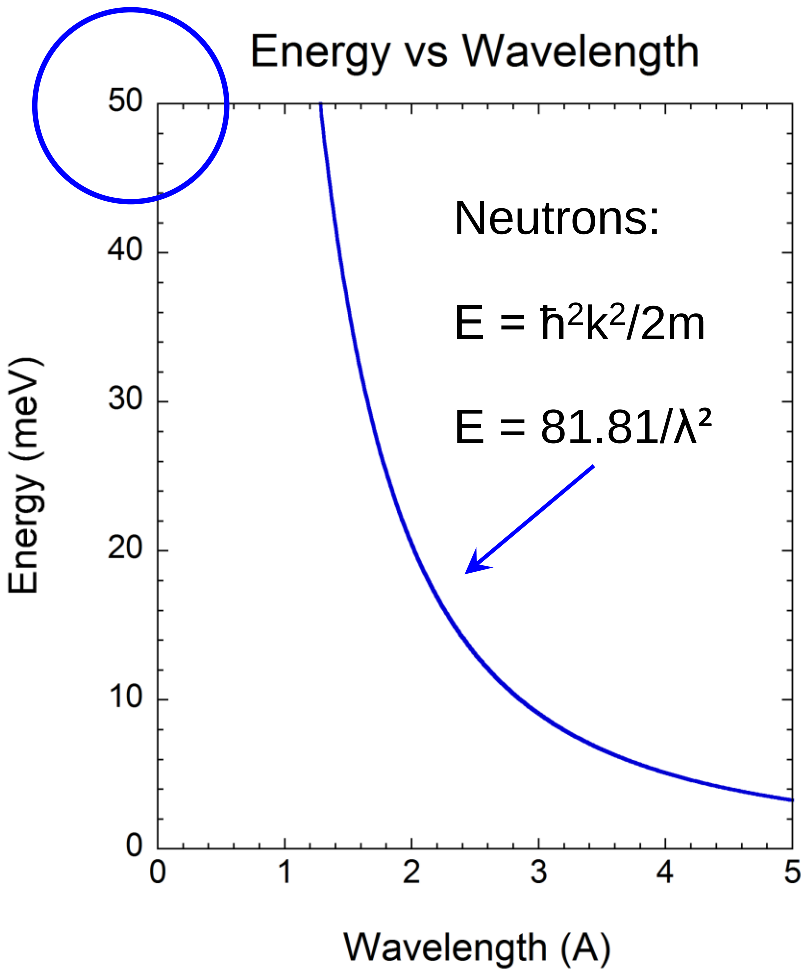
Expensive to produce → access not as easy

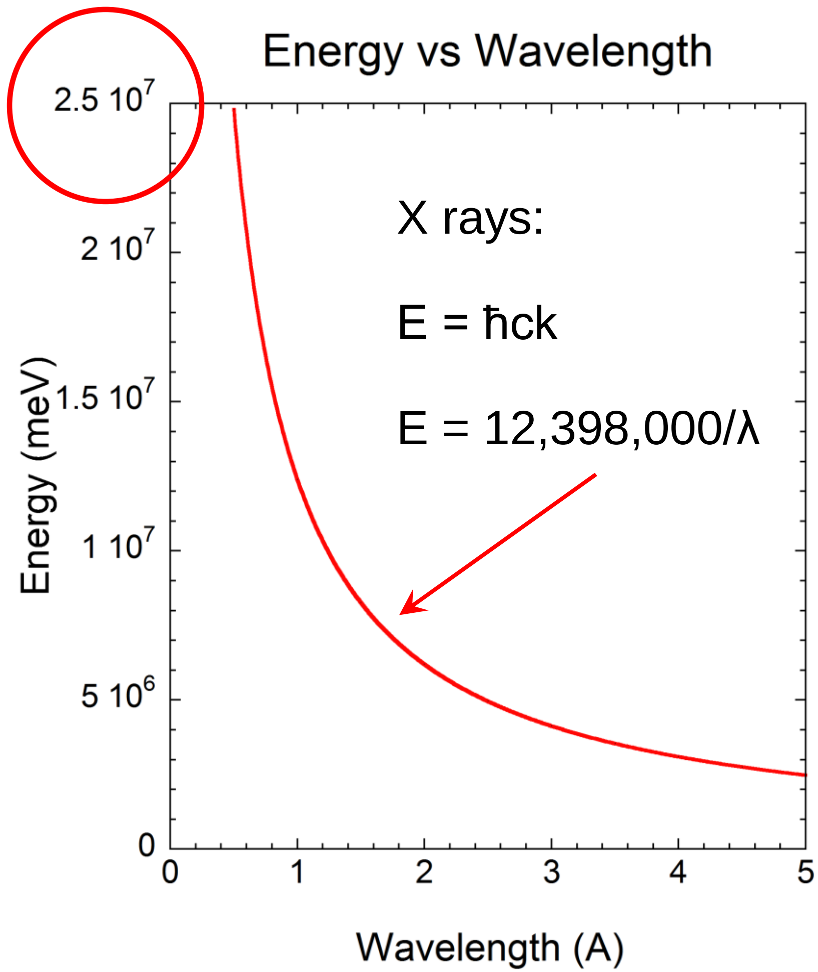
Interact weakly with matter → often need large samples

Fluxes are low compared to x-ray sources → long counting times

# Scattering Probes

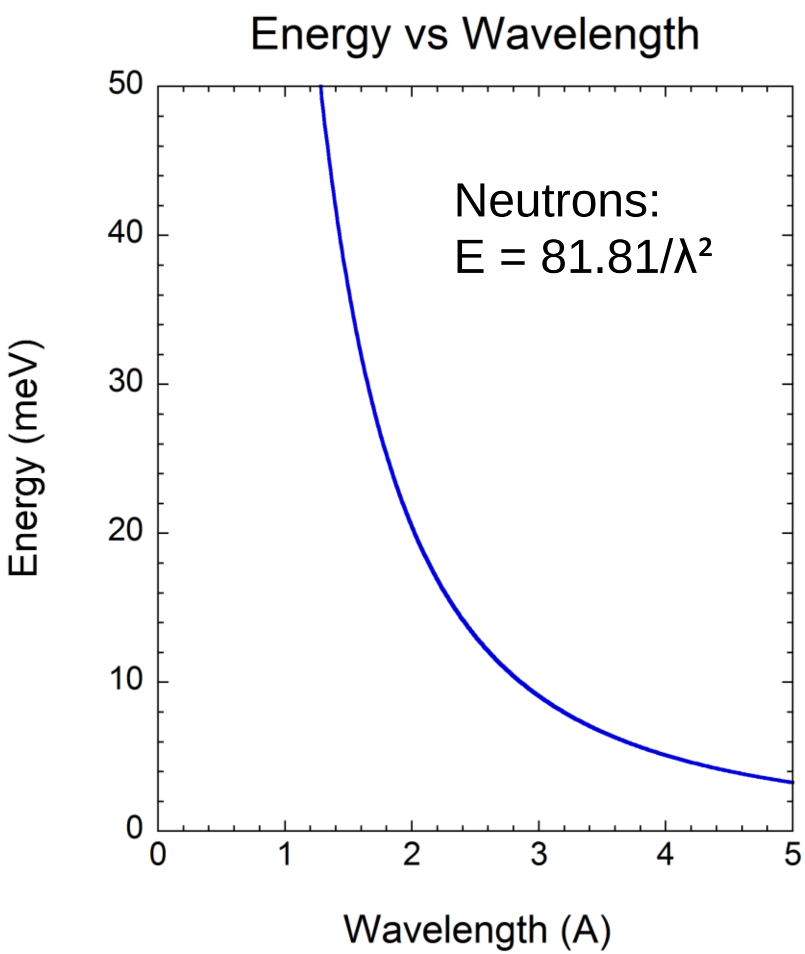
To characterize atomic **dynamics** requires a probe with $\hbar\omega$ ~ **energy scale** of interest.

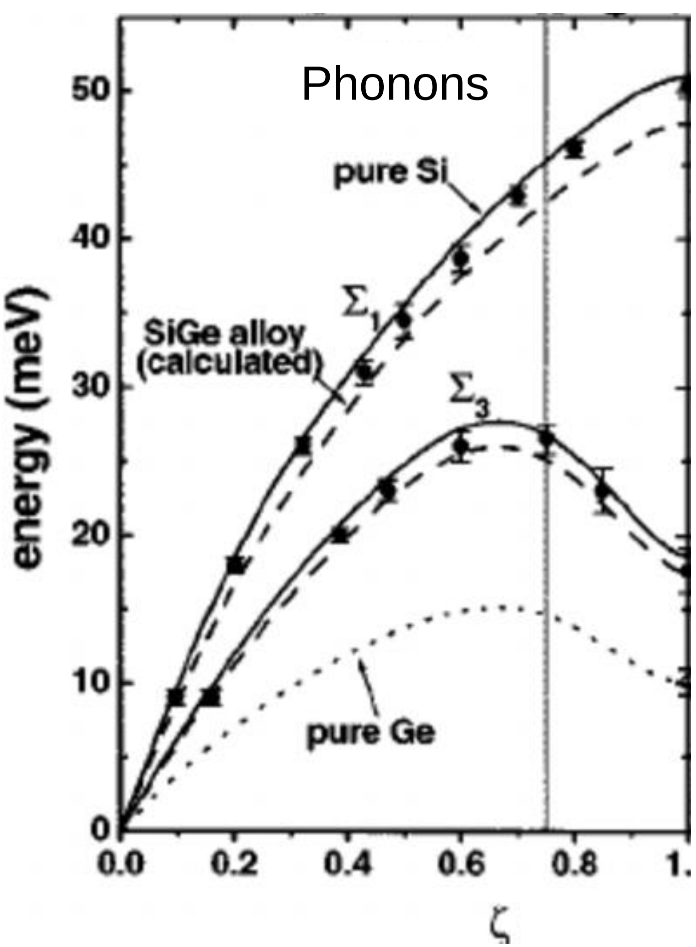


# Scattering Probes

To characterize atomic dynamics requires a probe with hω ~ energy scale of interest.



Scattering Probes

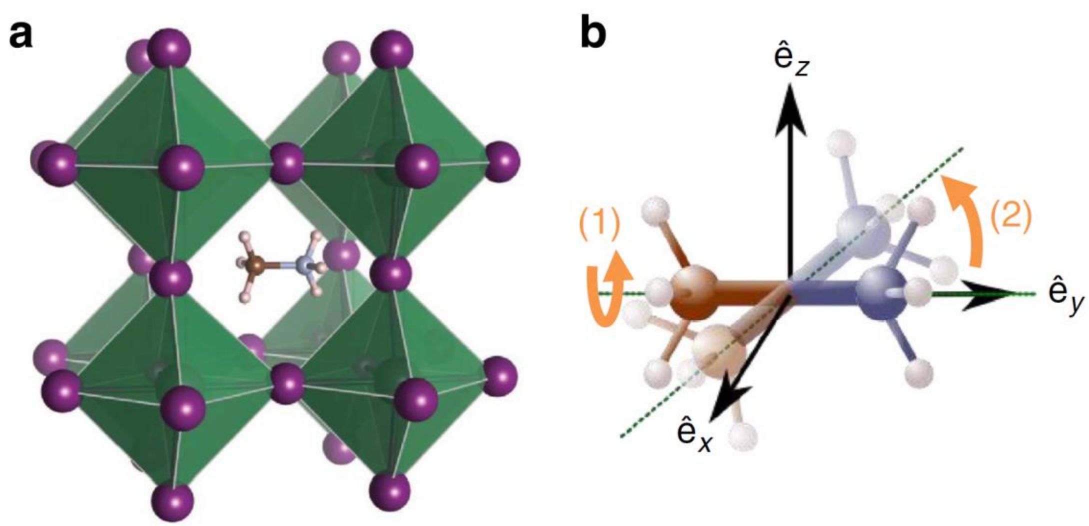
# Neutron Mass: A Lucky Coincidence

$$E = p^2/2m = \hbar^2k^2/2m = 81.81/\lambda^2$$

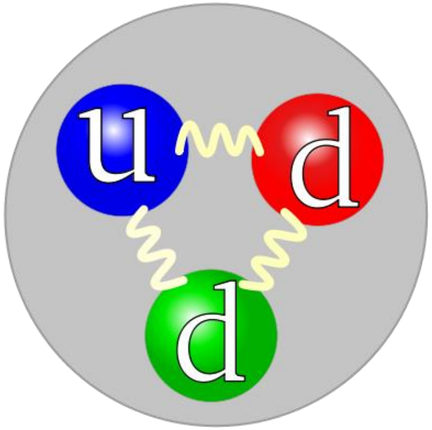
The mass of the neutron is such that thermal neutrons have wavelengths and energies that are well matched to the length and energy scales typically found in most materials.

Thus neutron scattering methods can directly measure the geometry of dynamic processes.

Example: Molecular jump rotations in photovoltaic hybrid perovskites



# The Neutron




$m_n = 1.675 \times 10^{-27}$ kg
Q = 0
S = ½ ħ
$\mu_n = -1.913\ \mu_N$

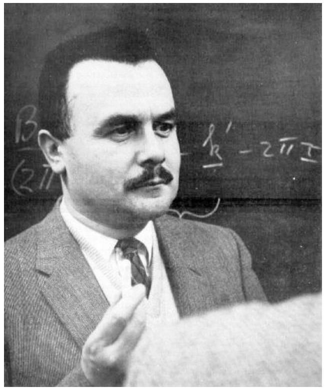
Interactions:
Strong, Electro-weak, Gravity

$\lambda = 1$ Å
$v = 4000$ m/s
E = 82 meV

de Broglie Relation:
$\lambda = h/p = h/m_n v$

$\lambda = 9$ Å
$v = 440$ m/s
E = 1 meV

# The Neutron



"If the neutron did not exist, it would need to be invented."

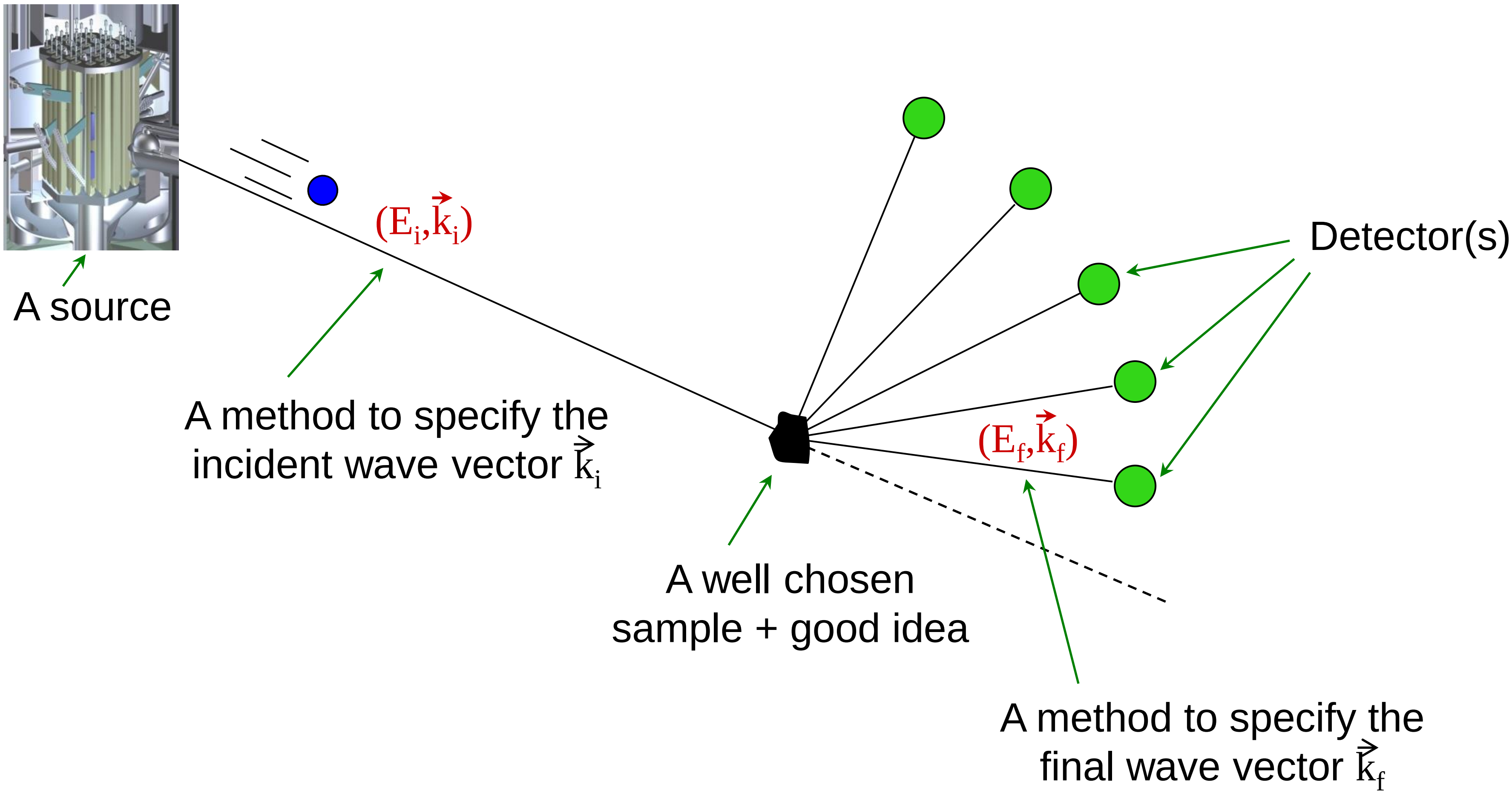
Bertram Brockhouse
1994 Nobel Laureate in Physics

"… for the discovery of the neutron."

Sir James Chadwick
1935 Nobel Laureate in Physics

# Basics of Scattering

## Elements of all scattering experiments



# Basics of Scattering

## Neutron Scattering Kinematics

Neutron scattering experiments measure the flux $F_s$ of neutrons scattered by a sample into a detector as a function of the change in neutron wave vector ($\vec{Q}$) and energy ($\hbar\omega$).

$F_s(Q,\hbar\omega) = \dfrac{\text{neutrons}}{\text{sec–cm}^2}$

**Momentum**

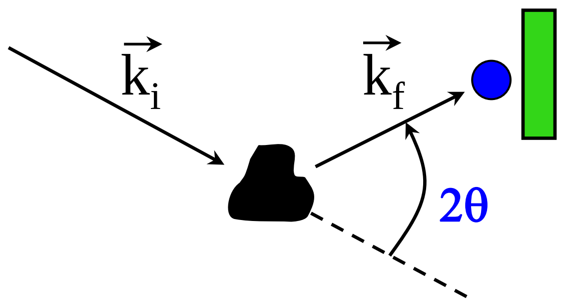
$\hbar k = \hbar(2\pi/\lambda)$

$\hbar\vec{Q} = \hbar\vec{k}_i - \hbar\vec{k}_f$

**Energy**

$\hbar\omega_n = \hbar^2 k_n{}^2/2m$

$\hbar\omega = \hbar\omega_i - \hbar\omega_f$




The expressions for the scattered neutron flux $F_s$ involve the positions and motions of atomic nuclei and unpaired electron spins.

$F_s$ → Contains information about structure and dynamics

# Basics of Scattering

## Scattering Cross Sections

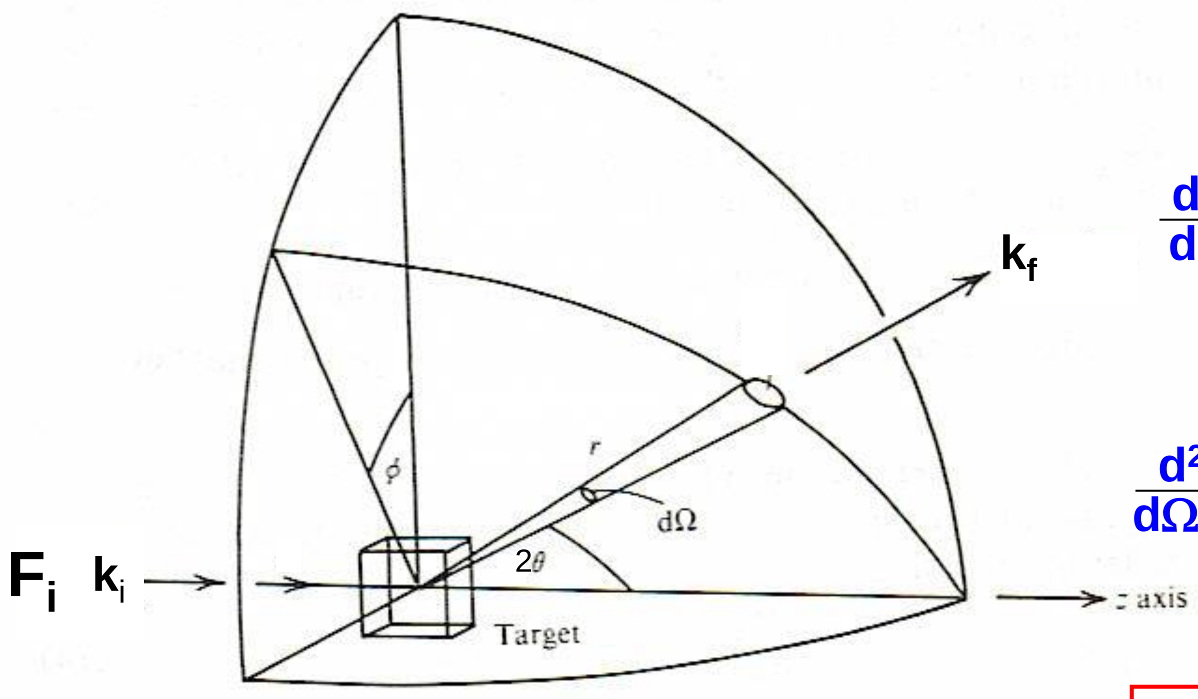
Consider an incident neutron beam with flux $\mathbf{F_i}$ (~$10^6$ to $10^9$ n/sec/cm$^2$) and wave vector $\mathbf{k_i}$ on a non-absorbing sample.

We define three cross sections:

$\sigma$ = Total cross section

$\frac{d\sigma}{d\Omega}$ = Differential cross section

$\frac{d^2\sigma}{d\Omega dE_f}$ = Partial differential cross section




These "cross sections" are what we measure experimentally.

# Basics of Scattering

What are the physical meanings of these three cross sections?

$\sigma$ — Total # of neutrons scattered per second / $F_i$.
(Typically of order 1 barn = $10^{-24}$ cm$^2$.)

$\frac{d\sigma}{d\Omega}$ — Total # of neutrons scattered per second into $d\Omega$ / ($d\Omega$ $F_i$).
(Diffraction → structure. Signal is summed over all energies.)

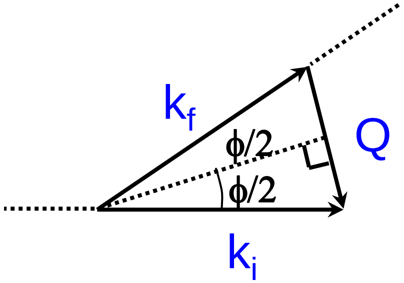
$\frac{d^2\sigma}{d\Omega dE_f}$ — Total # of neutrons scattered per second into $d\Omega$ with a final energy between $E_f$ and $E_f + dE_f$ / ($d\Omega$ $dE_f$ $F_i$).
(Inelastic scattering → dynamics. Small, but contains <u>much</u> info.)

# Basics of Scattering

## Scattering Triangle

$$\frac{d^2\sigma}{d\Omega dE_f}$$

Elastic ($k_i=k_f=k$) $\neq \frac{d\sigma}{d\Omega}$



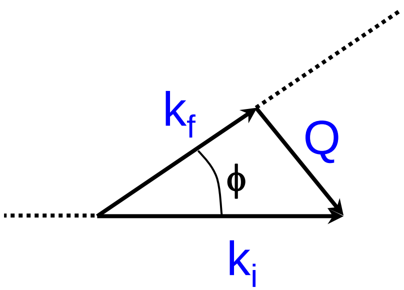

$\sin(\phi/2) = (Q/2)/k$

$Q = 2k\sin(\phi/2) = 4\pi\sin(\phi/2)/\lambda$

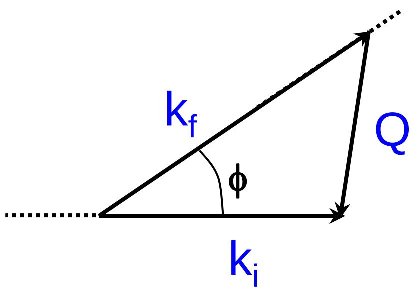
Elastic Scattering:

- Change in neutron energy = 0
- Probes changes in neutron momentum only

Inelastic ($k_i \neq k_f$)




Energy loss ($h\omega>0$)



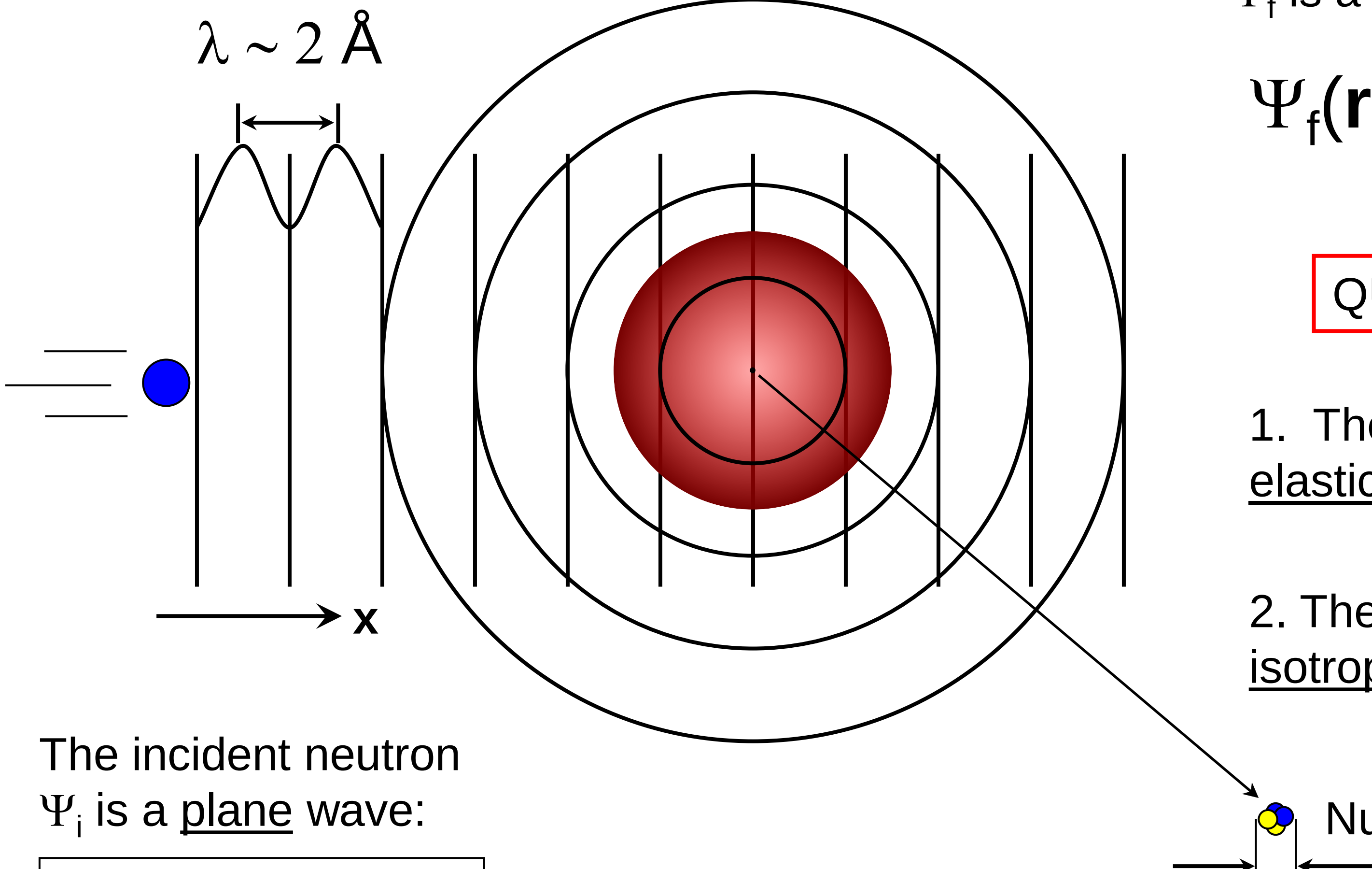

Energy gain ($h\omega<0$)

Inelastic Scattering:

- Change in neutron energy ≠ 0
- Probes changes in both momentum and energy

# Nuclear Scattering

Consider the simplest case:
A fixed, isolated nucleus.




The scattered (final) neutron $\Psi_f$ is a spherical wave:

$$\Psi_f(\mathbf{r}) \sim (-b/r)e^{i\mathbf{kr}-\omega t}$$

QUESTIONS:

1. The scattering is elastic ($k_i = k_f = k$). Why?

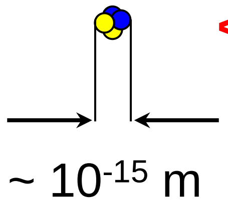
2. The scattering is isotropic. Why?

The incident neutron $\Psi_i$ is a plane wave:

$$\Psi_i(\mathbf{r}) \sim e^{i\mathbf{kx}-\omega t} \quad (k = 2\pi/\lambda)$$

# The Fermi Pseudopotential

The neutron interacts with nuclei via the strong force, which is extremely short-ranged.




<< $\lambda \sim 10^{-10}$ m

The details of V(r) are unimportant!
V(r) can be parametrized by a scalar b that depends only the nucleus and isotope!

$$V(r) = \left(\frac{2\pi h^2}{m_n}\right) \sum_{j=1}^{N} b_j \, \delta(r - r_j)$$

# Nuclear Scattering

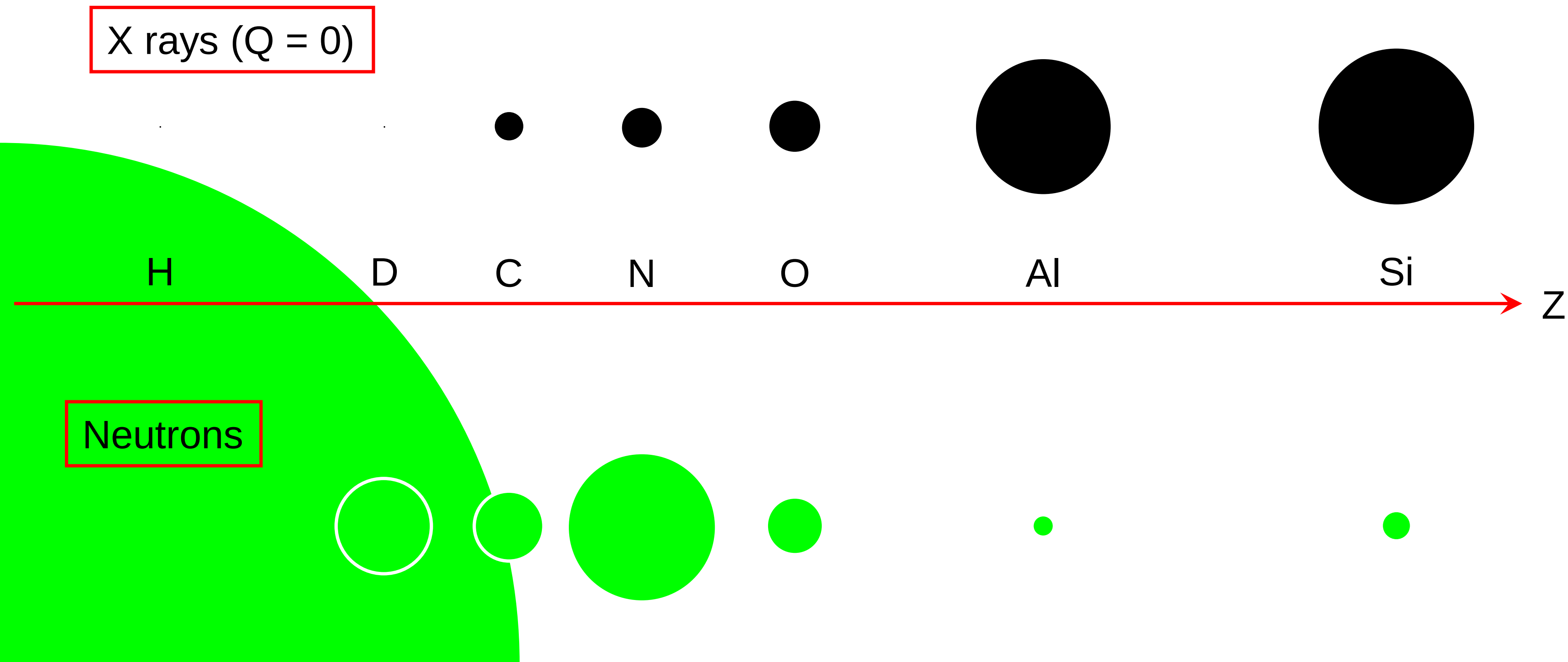
## The Neutron Scattering Length - b

Units of length:
b ~ $10^{-12}$ cm.

Analogous to f(Q), the x-ray form factor.

Varies randomly with Z and isotope
→ Neutrons “see” atoms x rays can’t.

Total Scattering Cross Section: $\sigma = 4\pi b^2$



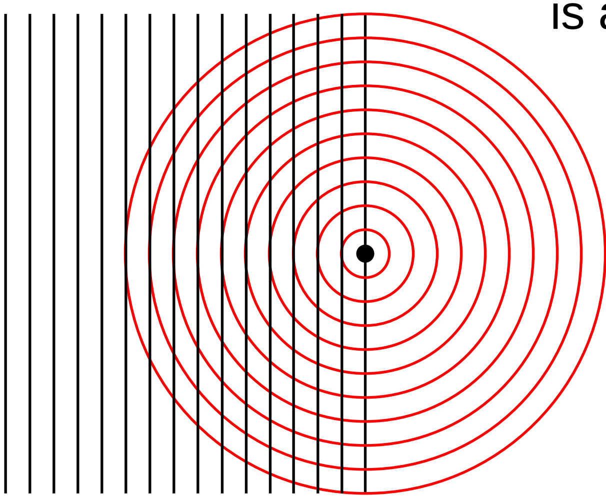
# Nuclear Scattering

What if many atoms are present?

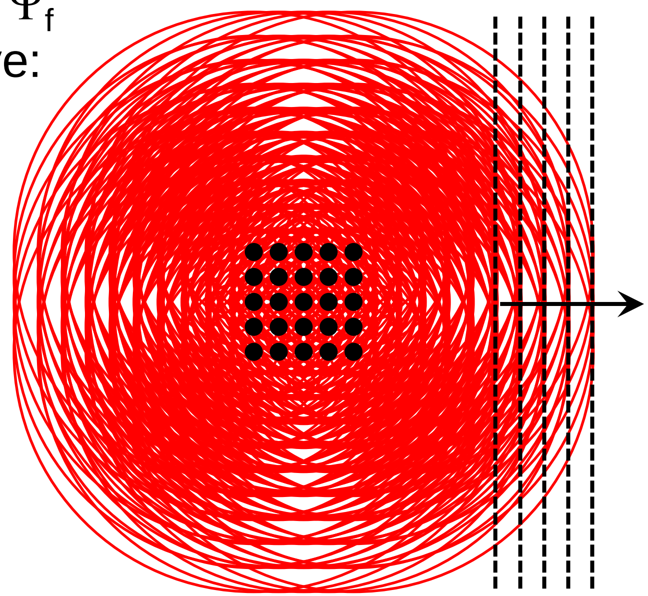
Scattering from one nucleus

Scattering from many nuclei

Scattered neutron $\Psi_f$ is a <u>spherical</u> wave:



The incident neutron $\Psi_i$ is a <u>plane</u> wave:

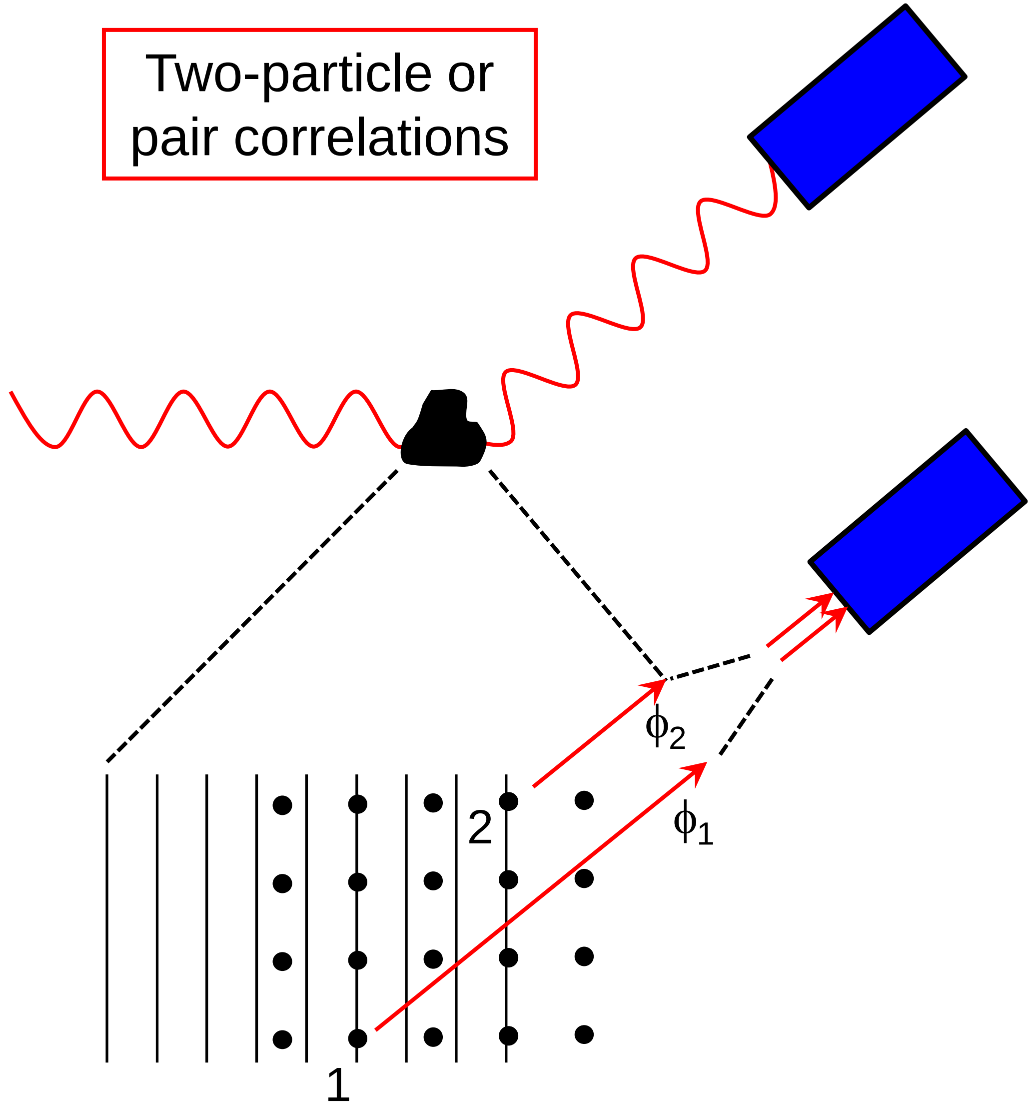


Constructive interference

Get strong scattering in some directions, but not in others.  Angular dependence yields information about how the nuclei are arranged or <u>correlated</u>.

# Correlation Functions

Two-particle or pair correlations




(1) Born Approximation:
Assumes neutrons scatter only once (single scattering event).

(2) Superposition:
Amplitudes of scattered neutrons $\phi_n$ add linearly.

$$\Phi_s = \phi_1 + \phi_2 + \ldots$$

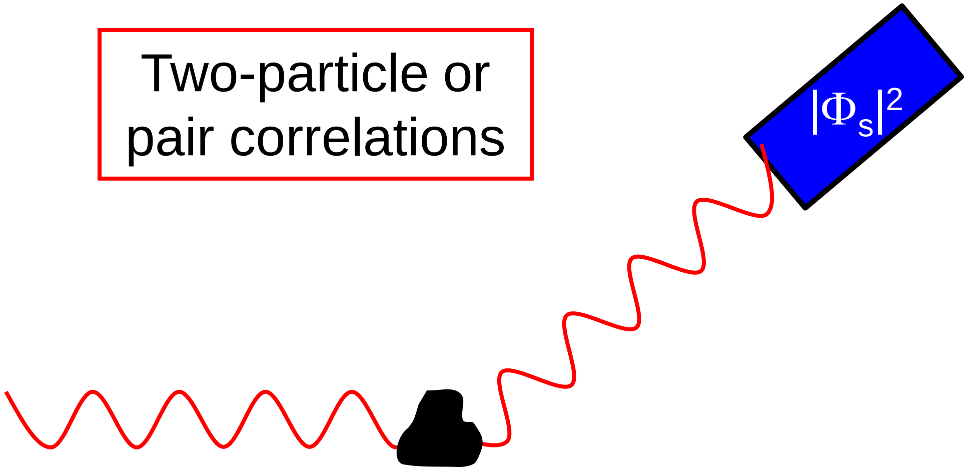
$$\text{Intensity} = |\Phi_s|^2 = |\phi_1 + \phi_2 + \ldots|^2 = |\phi_1|^2 + |\phi_2|^2 + \ldots + \underbrace{\phi_1^*\phi_2 ^* + \phi_2^*\phi_1}_{} + \ldots$$

Depends on relative positions of 1 and 2 → pair correlations!

From Andrew Boothroyd
PSI Summer School 2007

# Correlation Functions

Two-particle or pair correlations




The measured intensity $|\Phi_s|^2$ depends only on time-dependent correlations between the positions of ***pairs*** of atoms.

This is because *neutrons interact only weakly with matter*.

From Van Hove (1954) …

Differential Cross-Section

$$\frac{d\sigma}{d\Omega} = \sum_{i,j} b_i b_j \, e^{-i(\mathbf{k}_i - \mathbf{k}_j)\cdot(\mathbf{r}_i - \mathbf{r}_j)}$$

Depends only on:
where the atoms are
and
what the atoms are.

# Correlation Functions

From Squires (1996):
Introduction to the theory of thermal neutron scattering

**Partial Differential Cross-Section**

$$\left(\frac{d^2\sigma}{d\Omega dE}\right)_{k_0\rightarrow k_1} = \frac{1}{N}\frac{k_f}{k_i}\left(\frac{m}{2\pi\hbar^2}\right)^2 \sum p_i p_f \sum |<\mathbf{k}_f|V|\mathbf{k}_i>|^2 \delta(E+E_i-E_f)$$

$$\left(\frac{d^2\sigma}{d\Omega dE}\right)_{k_0\rightarrow k_1} = N\frac{k_f}{k_i} b^2 S(\mathbf{Q},\omega)$$

**Neutron Structure Factor**

$$S(\mathbf{Q},\omega) = \frac{1}{2\pi\hbar}\int G(\mathbf{r},t) e^{i(\mathbf{Q}\cdot r - \omega t)} d\mathbf{r} dt$$

**Pair Correlation Function**

Fourier Transform

$$G(\mathbf{r},t) = (\frac{1}{2\pi})^3 \frac{1}{N}\int \sum_{jj'} e^{i\mathbf{Q}\cdot\mathbf{r}} < e^{-i\mathbf{Q}\cdot\mathbf{r}_{j'}(0)} e^{i\mathbf{Q}\cdot\mathbf{r}_j(t)} > d\mathbf{Q}$$

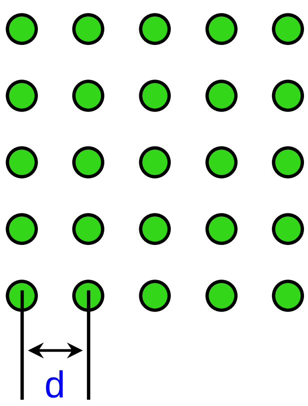
# Correlation Functions

**KEY IDEA** – Neutron interactions are weak → Scattering only probes two-particle correlations in space and time, but does so simultaneously!

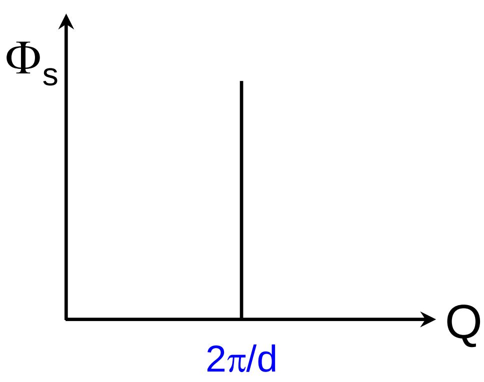
The scattered neutron flux $\Phi_s(\vec{Q},\hbar\omega)$ is proportional to the space ($\vec{r}$) and time (t) Fourier transform of the probability $G(\vec{r},t)$ of finding an atom at ($\vec{r}$,t) given that there is another atom at r = 0 at time t = 0.

$$\Phi_s \propto \frac{\partial^2 \sigma}{\partial\Omega\partial\omega} \propto \iint e^{i(\vec{Q}\cdot\vec{r}-\omega t)} G(\vec{r},t)\, d^3\vec{r}\, dt$$

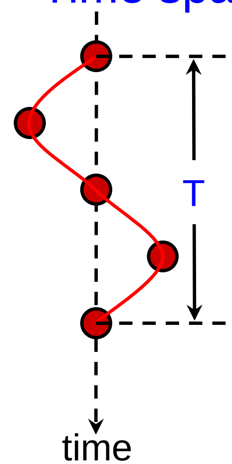
Real space



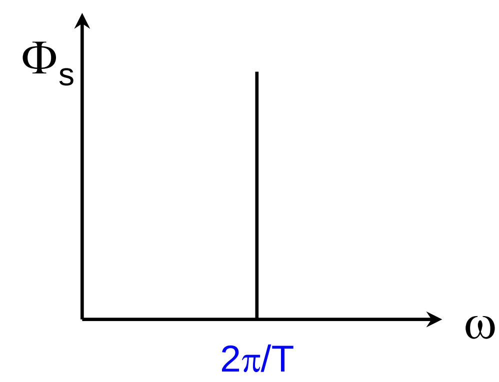

Q-space




Time space




ω-space



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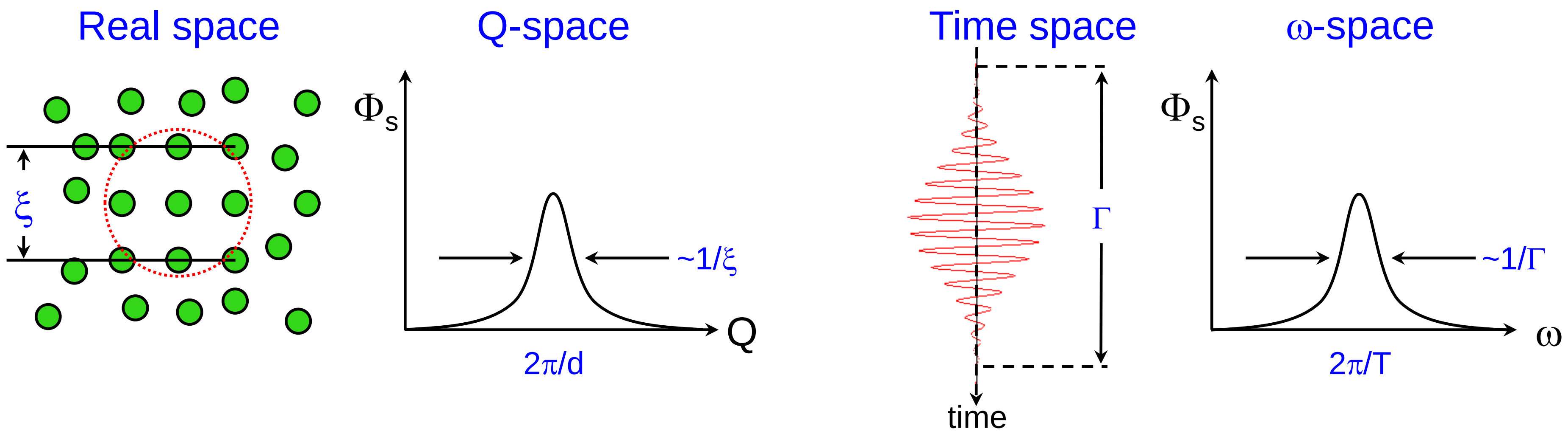
**KEY IDEA** – Neutron interactions are weak → Scattering only probes two-particle correlations in space and time, but does so simultaneously!

The scattered neutron flux $\Phi_s(\vec{Q},\hbar\omega)$ is proportional to the space ($\vec{r}$) and time (t) Fourier transform of the probability $G(\vec{r},t)$ of finding an atom at ($\vec{r}$,t) given that there is another atom at r = 0 at time t = 0.

$$\Phi_s \propto \frac{\partial^2\sigma}{\partial\Omega\partial\omega} \propto \iint e^{i(\vec{Q}\cdot\vec{r}-\omega t)} G(\vec{r},t)\, d^3\vec{r}\, dt$$



# Pop Quiz

Can one measure elastic scattering from a liquid?

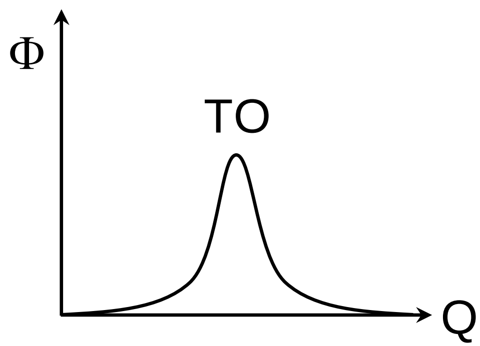
If Yes, explain why?
If No, explain why not?

Hint: What is the correlation of one atom in a liquid with another after a time t?

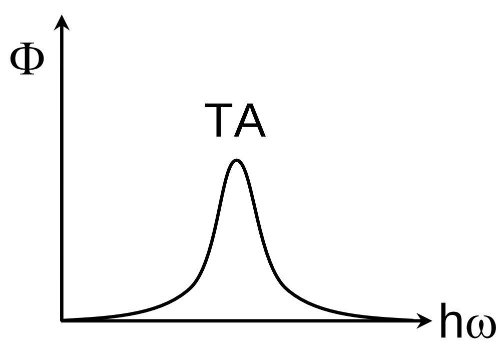
# Correlation Functions

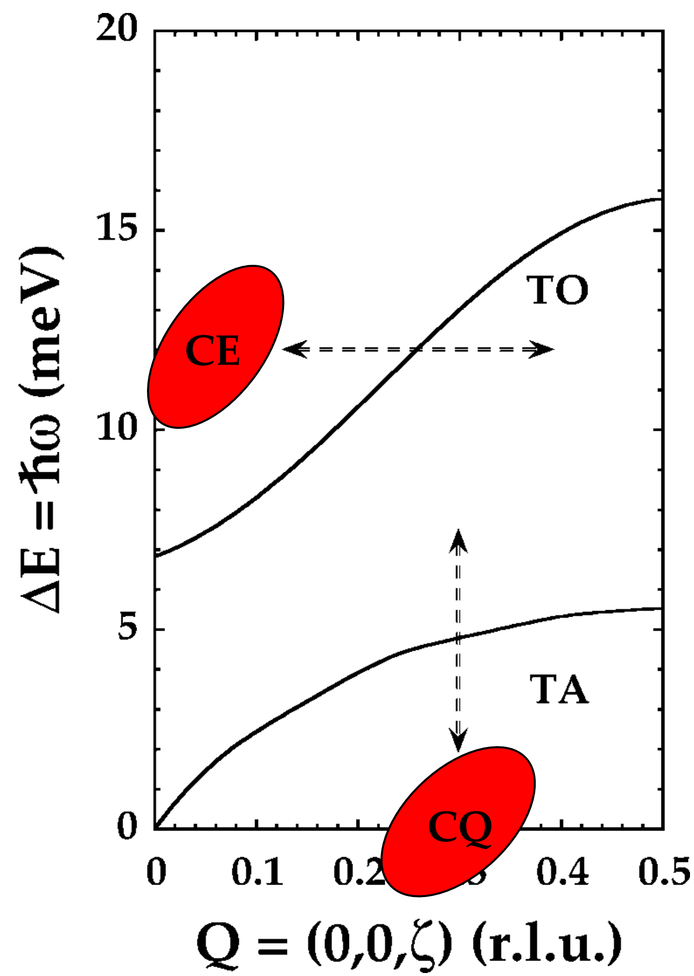
There are two main ways of measuring the neutron scattering cross section S(Q,ω).

Constant-E scans:
vary Q at fixed hω.




Constant-Q scans:
vary hω at fixed Q.



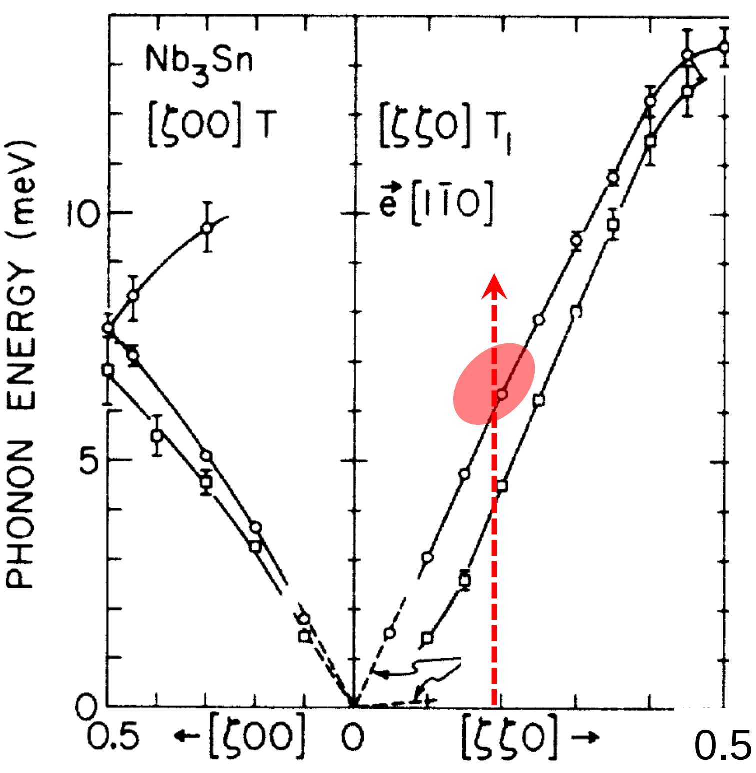
Classic Example

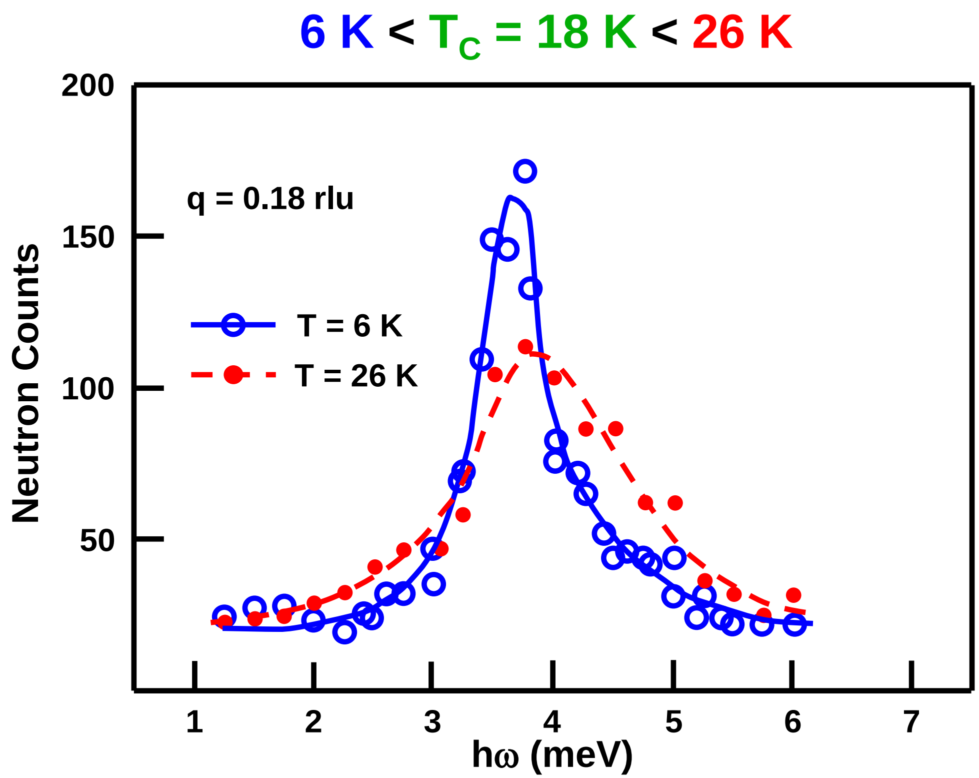
BCS Superconductivity

VOLUME 30, NUMBER 6 PHYSICAL REVIEW LETTERS 5 FEBRUARY 1973

**Influence of the Superconducting Energy Gap on Phonon Linewidths in $Nb_3Sn$†**

J. D. Axe and G. Shirane
*Brookhaven National Laboratory, Upton, New York 11973*
(Received 7 December 1972)



Classic Example

# BCS Superconductivity

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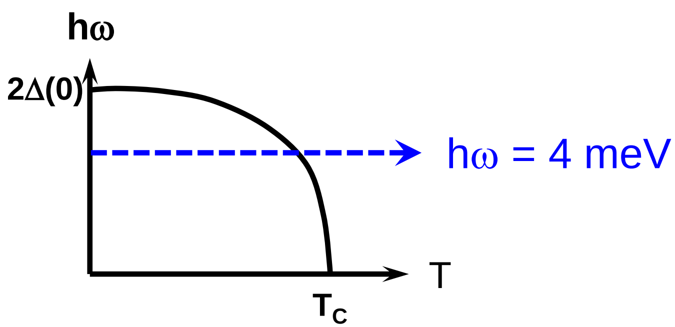
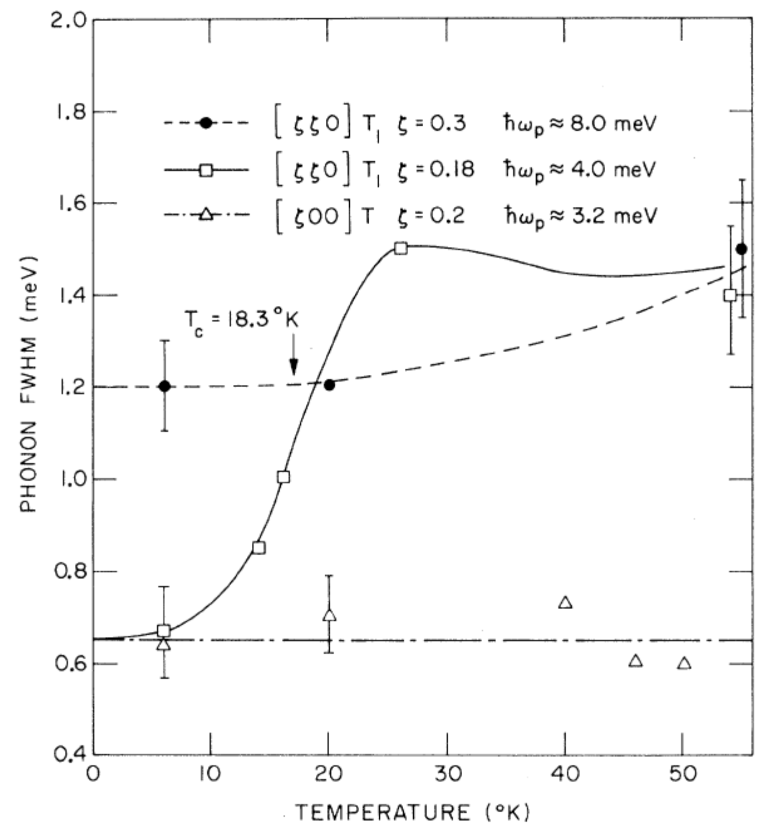


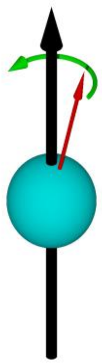

This behavior occurs because phonons with $h\omega < 2\Delta(T)$ cannot decay by creation of excited electron-quasiparticle pairs.

These measurements give an estimate of $2\Delta(0) = (4.4 + 0.6)k_BT$, and reveal a strong anisotropy in the electron-phonon interaction.

# Magnetic Scattering

Neutron Magnetic Dipole Moment

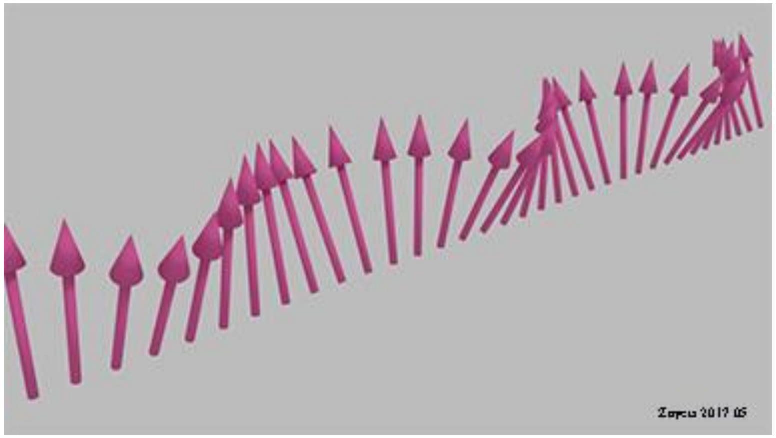
$\vec{\mu}_n$



Neutrons can characterize magnetic structure and magnetic dynamics as well!

$\mu_n = -1.913\ \mu_N$

The size of the neutron magnetic moment is such that the neutron magnetic scattering cross section is comparable in size to the nuclear scattering cross section.



# Magnetic Scattering

## Magnetic vs Nuclear Scattering

<u>Nuclear Potential</u>

$$V_N(\mathbf{r}) = \frac{2\pi h^2}{m_n} b\delta(\mathbf{r})$$

Scalar interaction →
Isotropic scattering

Very short range

Depends on nucleus,
isotope, and nuclear spin

<u>Magnetic Potential</u>

$$V_M(\mathbf{r}) = -\boldsymbol{\mu}_n \bullet \mathbf{B}(\mathbf{r})$$

Vector interaction →
Anisotropic scattering

Longer range

Depends on neutron
spin orientation.

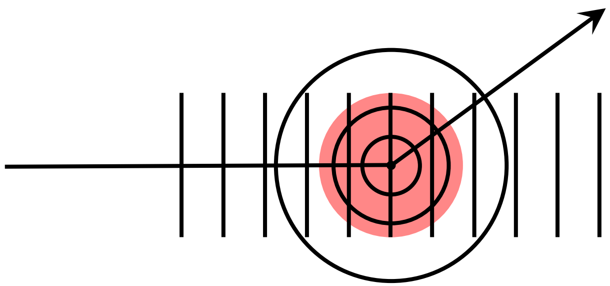
Polarized neutrons can measure the different components of M.

Magnetic Scattering

# Magnetic Form Factor

## Nuclear Potential

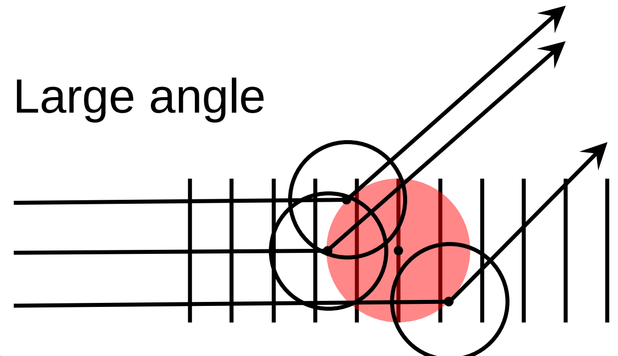
$$V_N(\mathbf{r}) = \frac{2\pi h^2}{m_n} b\delta(\mathbf{r})$$



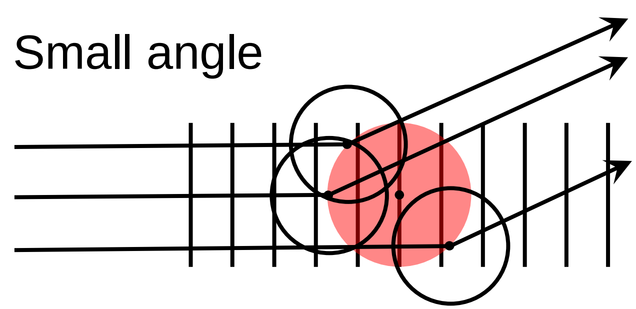
## Magnetic Potential

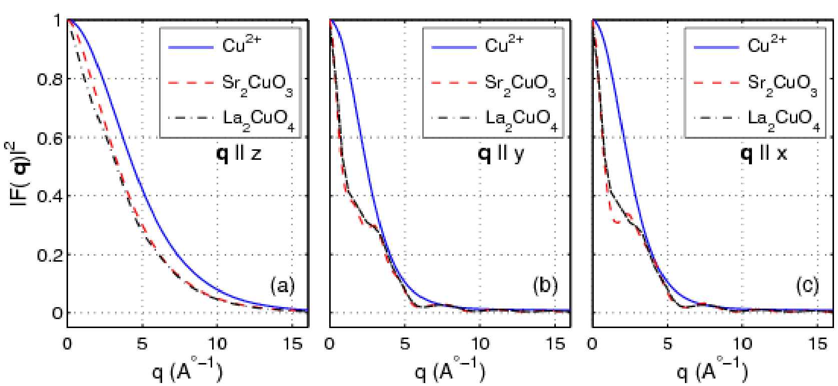
$$V_M(\mathbf{r}) = -\boldsymbol{\mu}_n \bullet \mathbf{B}(\mathbf{r})$$

Large angle



Small angle





# Magnetic Scattering

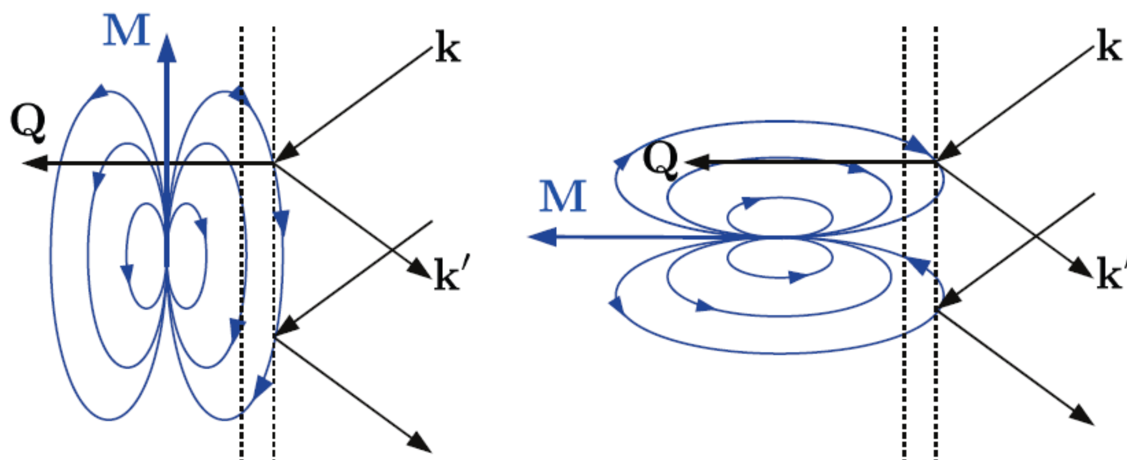
**Neutrons Scatter from M Perpendicular to Q**

Magnetic scattering depends on Fourier transform of interaction potential $V_M(\mathbf{r})$:

$$V_M(\mathbf{Q}) = -\mu_n \bullet \mathbf{B}(\mathbf{Q})$$

$$\nabla \cdot \mathbf{B}(\mathbf{r}) = 0 \quad \xrightarrow{\text{F.T.}} \quad i\mathbf{Q} \cdot \mathbf{B}(\mathbf{Q}) = 0$$

James Clerk Maxwell
(1831 – 1879)

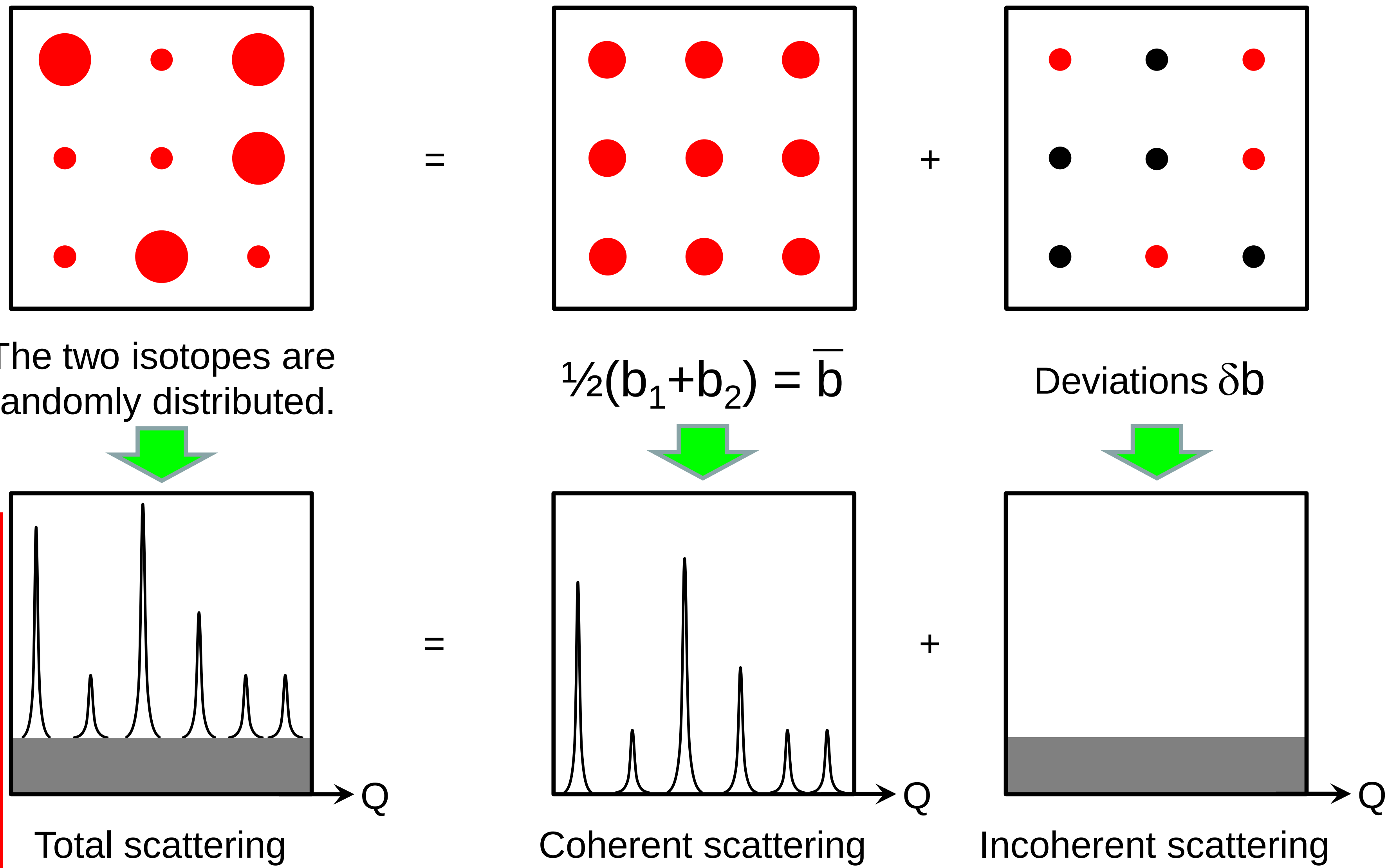



From "Principles of Neutron Scattering from Condensed Matter" by Boothroyd

# Coherent vs Incoherent

Consider a system composed of two different scattering lengths, $b_1$ and $b_2$.

$b_1$ = (small dot)
$b_2$ = (large dot)



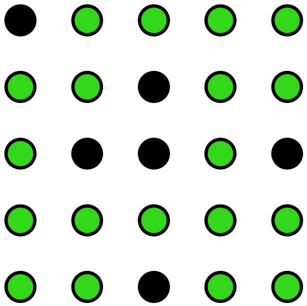

After Andrew Boothroyd PSI Summer School 2007

# Coherent vs Incoherent

This can also happen for a single element material.

This situation could arise for two reasons.

1. Isotopic incoherence
2. Nuclear spin incoherence



Both reasons can occur because the scattering interaction is <u>nuclear</u>.

Recall that $$\left(\frac{d^2\sigma}{d\Omega dE}\right)_{k_0\rightarrow k_1} = N\frac{k_f}{k_i}b^2 S(\mathbf{Q},\omega)$$

Then the above equation must be generalized:

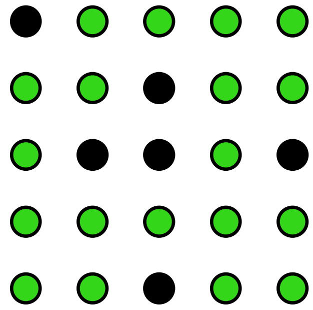
$$\frac{d^2\sigma}{d\Omega dE_f} = \sum_{i,j} \overline{b_i b_j}\, S_{ij}(Q,\omega)$$

$\overline{\phantom{xx}}$ = average

$$\overline{b_i b_j} = (\overline{b})^2, \text{ for } i=j$$

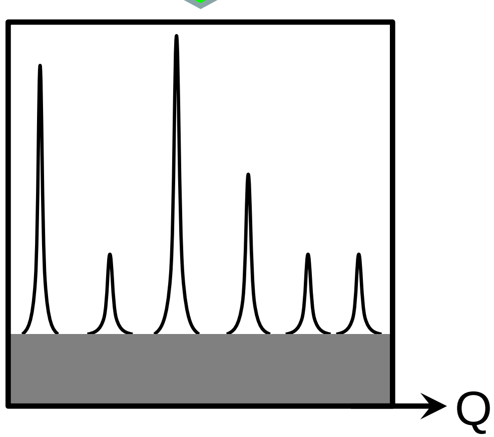
$$\overline{b_i b_j} = \overline{b^2}, \text{ for } i\neq j$$

# Coherent vs Incoherent



Our partial differential cross section can then be recast into the form:

$$\frac{d^2\sigma}{d\Omega dE_f} = \sigma_c S_c(Q,\omega) + \sigma_i S_i(Q,\omega)$$




$$\sigma_c = 4\pi(\bar{b})^2$$ c = coherent

$$\sigma_i = 4\pi\{\overline{b^2} - (\bar{b})^2\}$$ i = incoherent

# Coherent vs Incoherent

What do these expressions mean physically?

## Coherent Scattering

Measures the Fourier transform of the *pair* correlation function G(r,t) → interference effects.

This cross section reflects collective phenomena such as:

Phonons

Spin Waves

## Incoherent Scattering

Measures the Fourier transform of the *self* correlation function $G_s(r,t)$ → no interference effects.

This cross section reflects single-particle scattering:

Atomic Diffusion

Vibrational Density of States

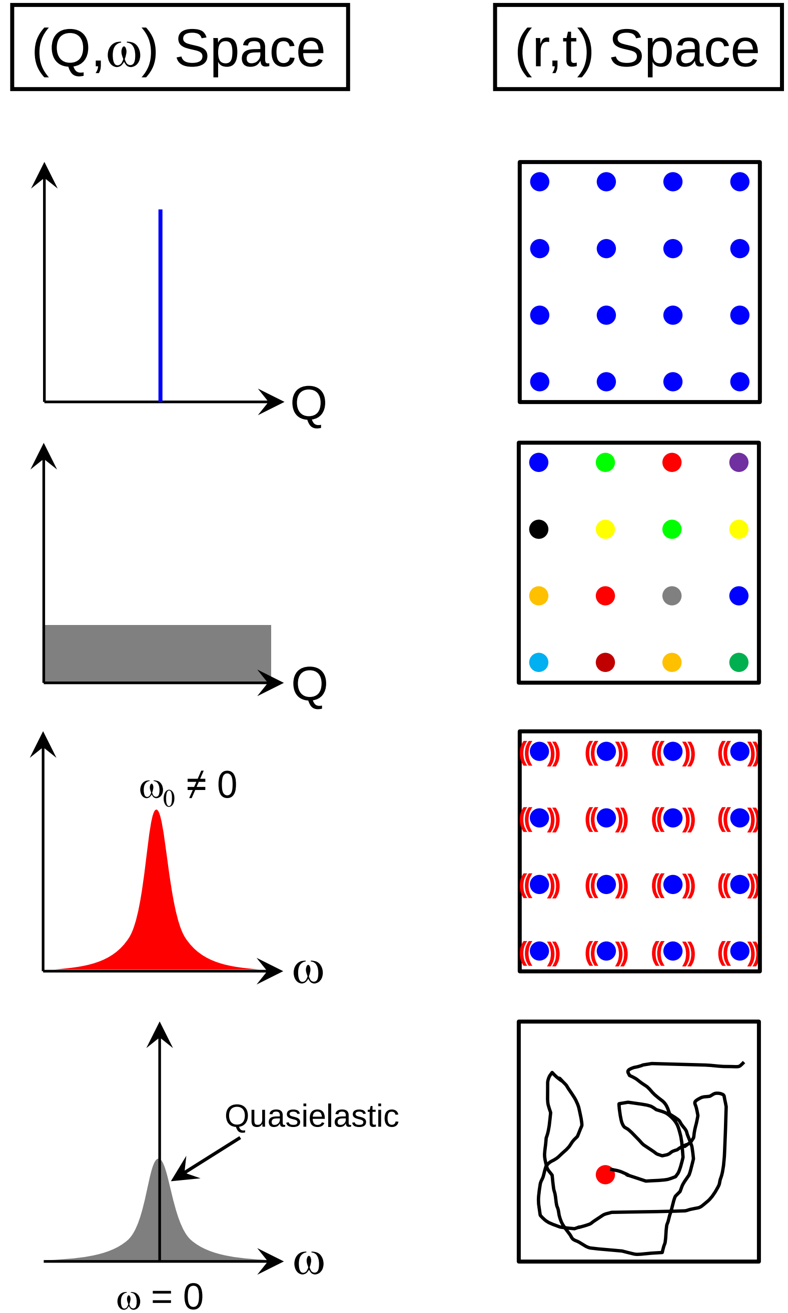
# Brief Summary

$$\left.\frac{d\sigma}{d\Omega}\right|_{coh} = \frac{\sigma_{coh}}{4\pi} S(Q)$$

$$\left.\frac{d\sigma}{d\Omega}\right|_{inc} = \frac{\sigma_{inc}}{4\pi}$$

$$\left.\frac{d^2\sigma}{d\Omega dE_f}\right|_{coh} = \frac{k_f}{k_i}\frac{\sigma_{coh}}{4\pi} S_{coh}(Q,\omega)$$

$$\left.\frac{d^2\sigma}{d\Omega dE_f}\right|_{inc} = \frac{k_f}{k_i}\frac{\sigma_{inc}}{4\pi} S_{inc}(Q,\omega)$$



# Quick Review

Please try to remember these things …

1. Neutrons scattering probes two-particle correlations in both space and time (simultaneously!).

2. The neutron scattering length, b, varies randomly with Z → allows access to atoms that are usually unseen by x-rays.

3. Coherent Scattering

Measures the Fourier transform of the pair correlation function G(r,t) → interference effects.

This cross section reflects collective phenomena.

4. Incoherent Scattering

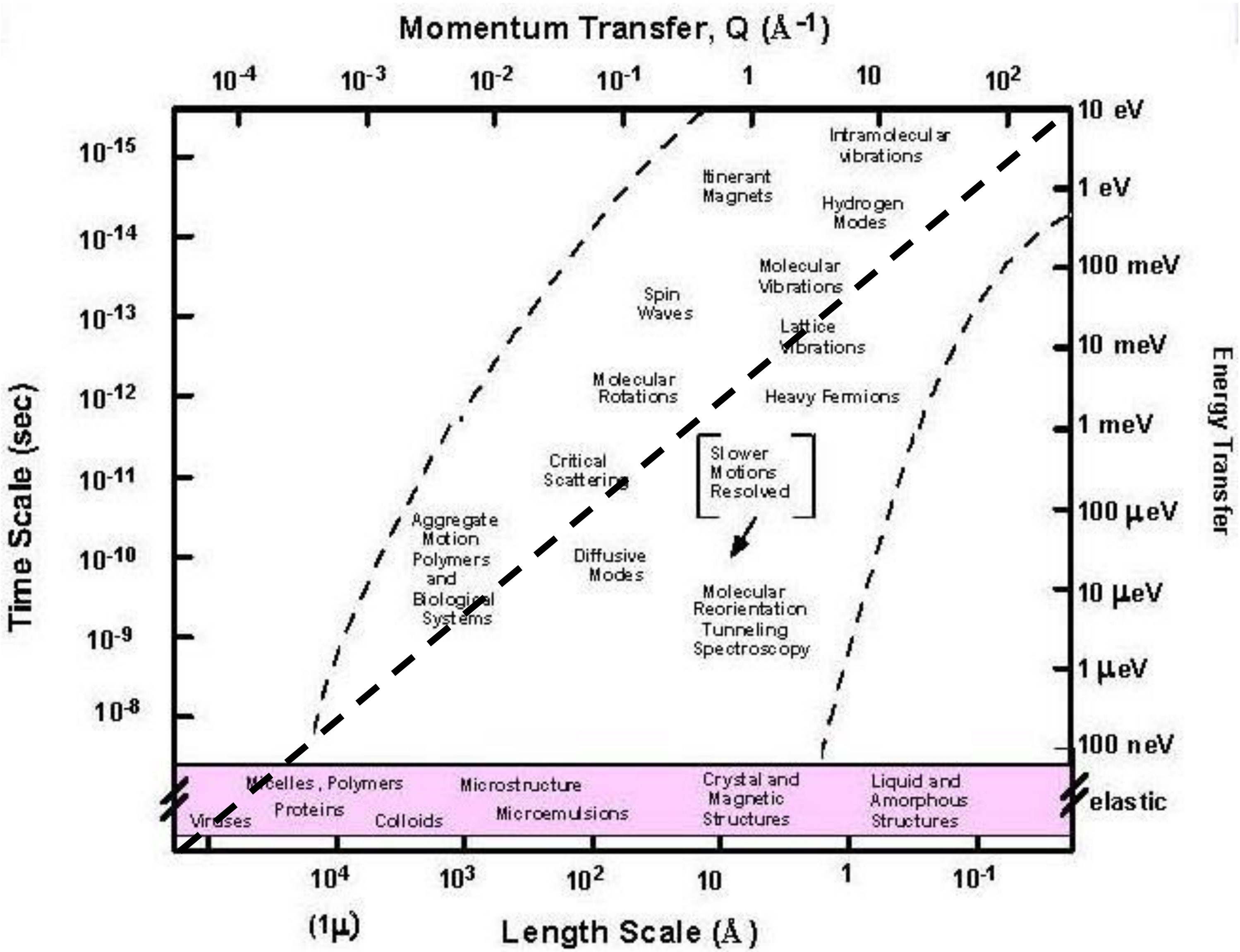
Measures the Fourier transform of the self correlation function $G_s(r,t)$ → no interference effects.

This cross section reflects single-particle scattering.

# Length and Time Scales

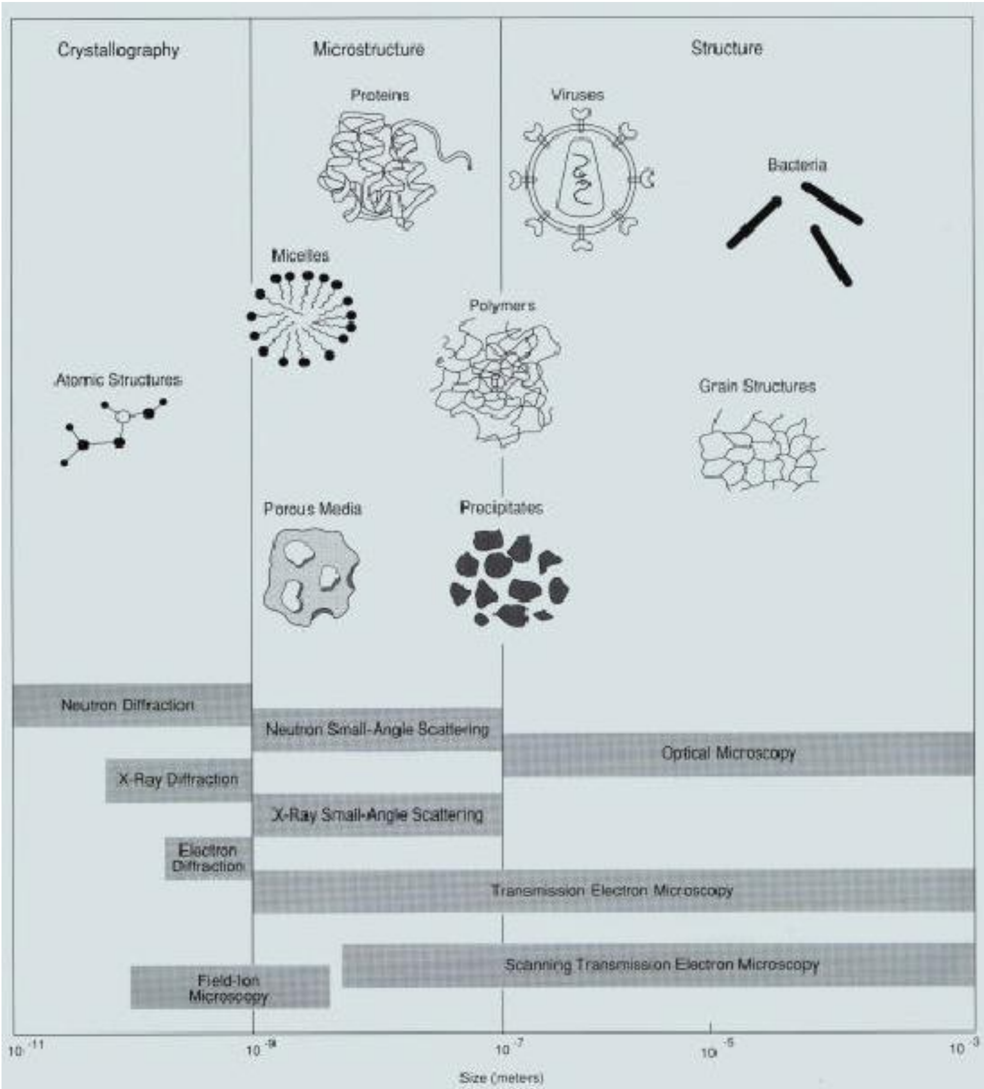
Do you see a pattern here?

Larger "objects" tend to exhibit slower motions.

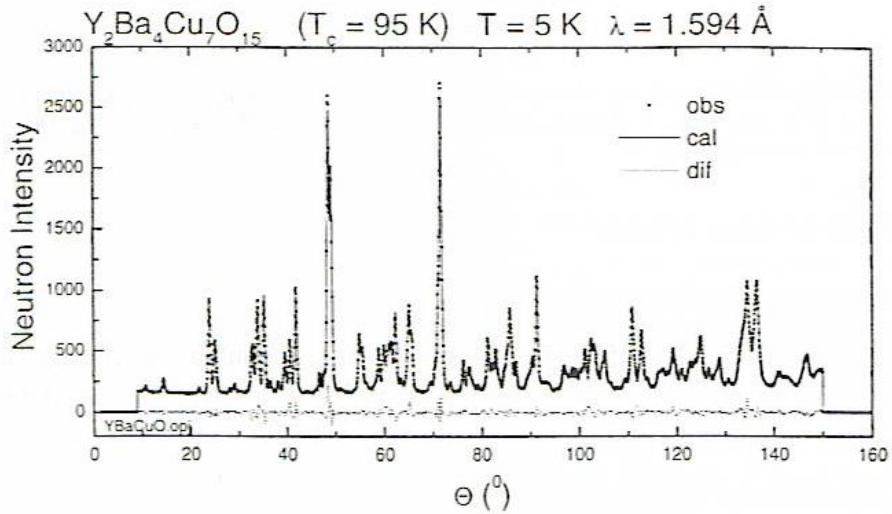


# Elastic Scattering

Neutrons can probe length scales ranging from ~0.1 Å to ~1000 Å




Pynn, *Neutron Scattering: A Primer* (1989)



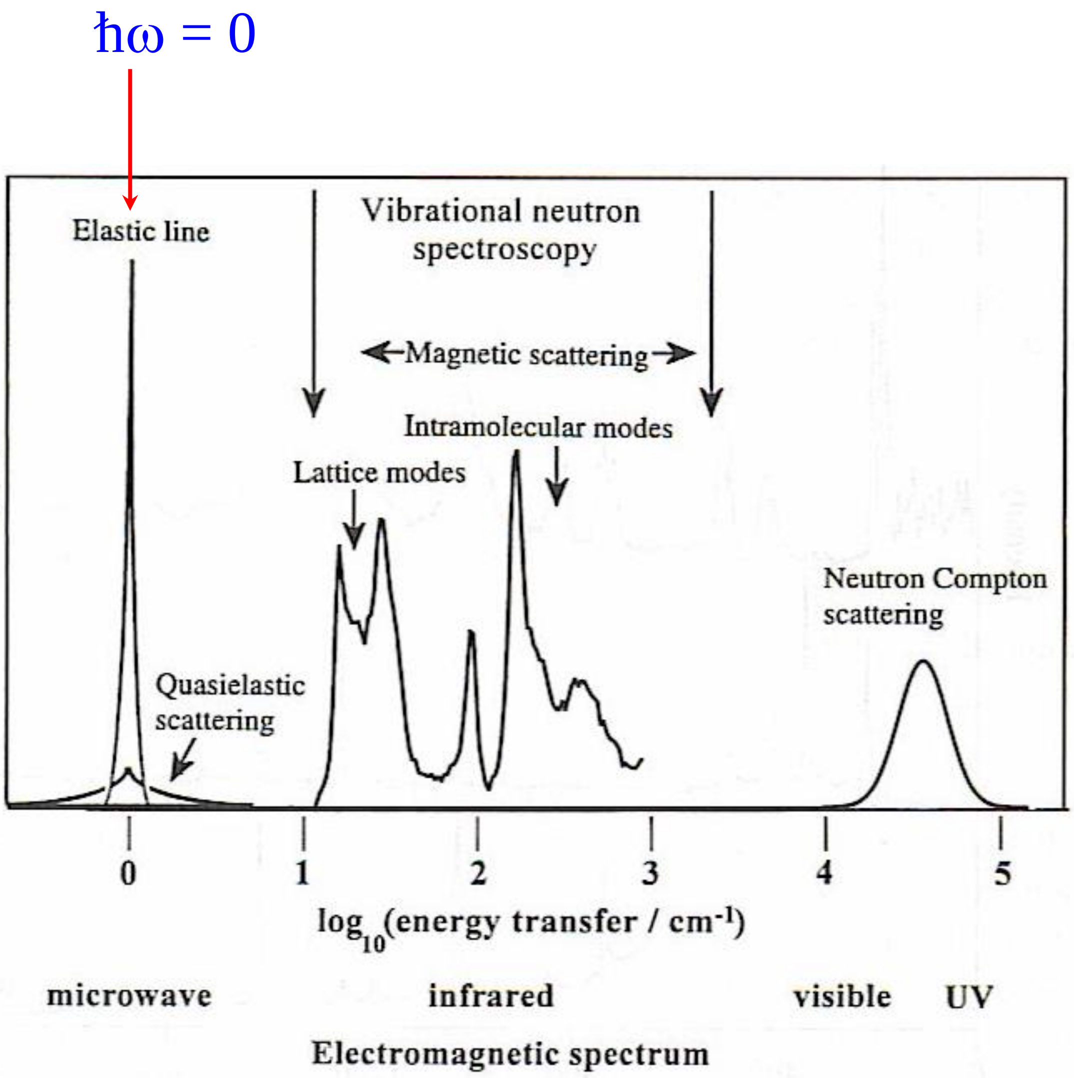

Mitchell et. al, *Vibrational Spectroscopy with Neutrons* (2005)

Neutrons needed to determine structure of 123 high-$T_c$ cuprates because x rays weren't sufficiently sensitive to the oxygen atoms.

# Inelastic Scattering

Neutrons can probe time scales ranging from ~$10^{-14}$ s to ~$10^{-8}$s.

Probes the vibrational, magnetic, and lattice excitations (dynamics) of materials by measuring changes in the neutron momentum and energy simultaneously.




Mitchell et. al, *Vibrational Spectroscopy with Neutrons* (2005)

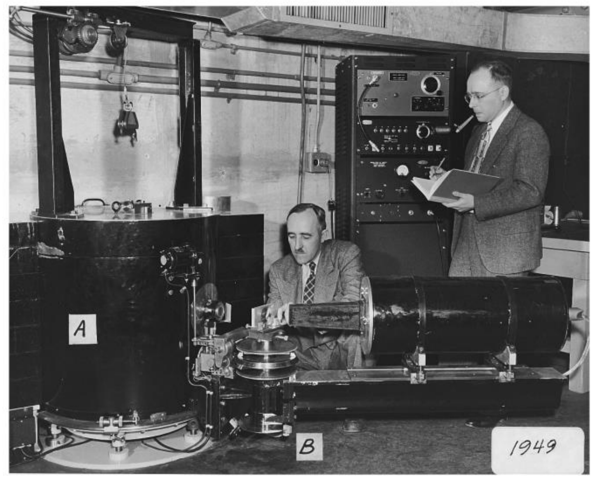
Nobel Prize
in Physics
1994

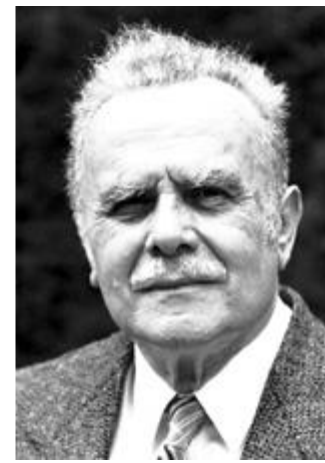
# The Fathers of Neutron Scattering

“For pioneering contributions to the development of neutron scattering techniques for studies of condensed matter"

“For the development of the neutron diffraction technique"

“For the development of neutron spectroscopy"



Clifford G Shull
MIT, USA
(1915 – 2001)

Ernest O Wollan
ORNL, USA
(1910 – 1984)

Bertram N Brockhouse
McMaster University, Canada
(1918 – 2003)

Showed us where the atoms are …

Did first neutron diffraction expts …

Showed us how the atoms move …

# Useful References

- http://www.mrl.ucsb.edu/~pynn/primer.pdf
- "Introduction to the Theory of Thermal Neutron Scattering"
  - G. L. Squires, Cambridge University Press
- "Theory of Neutron Scattering from Condensed Matter"
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  - G. E. Bacon, Clarendon Press, Oxford
- "Structure and Dynamics"
  - M. T. Dove, Oxford University Press
- "Elementary Scattering Theory"
  - D. S. Sivia, Oxford University Press
- "Principles of Neutron Scattering from Condensed Matter"
  - A. T. Boothryod, Oxford University Press