Basic theory I: elastic neutron scattering

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Overview

- Why neutrons
- Crystal structure
- Diffraction
- Bragg's law
- Mathematical foundation of neutron scattering (elastic)
- Scattering from one fixed nucleus
- Scattering from many fixed nuclei
- Relation to Bragg's law
- Structure factor
- Reciprocal space
- Brillouin zones

….. and tomorrow: inelastic scattering!
Remember what you learned about the properties of neutrons from Ian’s lecture:

Why neutrons?

Neutrons are charged particles. They are:
- neutral in charge
- used as structural probes
- used in non-destructive testing
- used in nuclear fusion
- used in nuclear fission
- can be used to study samples in severe environments
- The wavelengths of neutrons are similar to atomic spacing.
- They can determine the crystal structure and atomic spacing, and other structural information.
- Neutrons have a magnetic moment. They are sensitive to light atoms.

Neutrons have a magnetic moment. They can be used to study:
- NMR spectroscopy, and nuclear magnetic resonance
- Molecular dynamics

Neutrons have spins. They can be used to study:
- Form into polarized neutron beams, and
- used in study of collective motions, structures, and dynamics.

Neutron scattering

Neutron is scattered by matter via:
- interaction with nucleus structural studies, this lecture
- interaction with spin of unpaired electrons, magnetic scattering Dominic Ryan’s Lecture

These interactions can be:
- elastic (diffraction) structural studies, this lecture
- inelastic (spectroscopy) dynamical studies, tomorrow

Analysis of the energy of scattered neutrons provides information on excitations (lattice vibrations and magnetic excitations).

What is a crystal?

A three-dimensional periodic array of atoms.

An ideal crystal = infinite repetition of identical structural units (single atom or many atoms/molecules) in space.

The structure of all crystals can be described in terms of a lattice, with a group of atoms (basis) attached to every lattice point. Repeat of basis in space forms crystal structure.

Crystal Structure
Why study crystal structures?

Solid state physics: crystals and electrons in crystals

Early 1900s: solid state physics began with discovery of x-ray diffraction by crystals and successful predictions of the properties of crystals!

- to describe solids
- be able to compare materials
- to predict physical properties

An example: HTSC

Increasing oxygen content beyond a critical value induces a structural transition and HTSC!

Physical properties are correlated with crystal structure.
Crystal structure is described by a building block called the **unit cell** and atomic coordinates inside the cell. Three dimensional stacking of the unit cell forms the crystal.

**Unit cell**
- a box with 3 sides (a, b and c) and 3 angles (α, β and γ)
- Location of atoms inside the unit cell are given by atomic coordinates: (x, y, z), fractions of a, b and c lattice constants.

Conventional unit cell = 3D repeat unit of a crystal with full symmetry of the structure, not always the smallest possible choice.

Primitive unit cell = minimum-volume cell when stacked completely fills the space, not always displays all symmetries in the crystal.

An example: fcc crystal
- Unit cell = fcc
- Primitive cell = rhombohedral
Periodic arrangement forms planes of atoms. Crystallographic directions = imaginary lines connecting atoms. Crystallographic planes = imaginary planes connecting atoms in different directions. Some directions and planes have a higher density of atoms. 
d-spacing = perpendicular distance between pairs of nearest planes. All planes in one direction are identical.

How to identify/label the planes: Miller indices

Miller indices \((h k l)\) = three lattice points used to identify orientation of a set of parallel planes of atoms within a crystal structure. 

\[
\begin{align*}
\frac{a}{h} & \quad \frac{b}{k} & \quad \frac{c}{l} \\
\end{align*}
\]

where \(h, k,\) and \(l\) are relatively prime integers.

\[
\begin{align*}
\frac{1}{h} & \quad \frac{1}{k} & \quad \frac{1}{l} \\
\end{align*}
\]

fractional intercepts

\[
\begin{align*}
\frac{h}{h} & \quad \frac{k}{k} & \quad \frac{l}{l} \\
\end{align*}
\]

Miller indices of fractional intercepts

We will come back to this.

We will come back to this.

What an index=0 means?

Lattice planes & Miller indices

Examples:

Planes separated by one unit cell or a fraction of a unit cell pass through equivalent atoms throughout the crystal.

Can you identify \((010), (030), (110), (-110),\) and \((120)\) planes?

Notice larger Miller indices mean closer spacings (reciprocal)!
Planes & d-spacing

Orientation of a plane is defined by direction of its normal vector: \( n_{hkl} = h \mathbf{a}^* + k \mathbf{b}^* + l \mathbf{c}^* \)

\[ \mathbf{a}^* = 2\pi \frac{\mathbf{b} \times \mathbf{c}}{V}, \quad \mathbf{b}^* = 2\pi \frac{\mathbf{c} \times \mathbf{a}}{V}, \quad \mathbf{c}^* = 2\pi \frac{\mathbf{a} \times \mathbf{b}}{V} \]

\( V = \mathbf{a} \cdot (\mathbf{b} \times \mathbf{c}) \) (real space unit cell volume)

\( \mathbf{a}^* \cdot \mathbf{a} = 1, \quad \mathbf{a}^* \cdot \mathbf{b} = 0, \) what about \( \mathbf{a}^* \cdot \mathbf{c} = ? \)

\[ d_{hkl} = \frac{|a|}{h} \cos \phi = \frac{|a|}{h} \cdot \left| \frac{n_{hkl}}{|n_{hkl}|} \right| = \frac{2\pi}{|n_{hkl}|} \]

\[ \frac{4\pi^2}{d_{hkl}^2} = |n_{hkl}|^2 \quad \text{Orthogonal:} \quad \frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \]

What about...?

Diffraction

How to determine crystal structure? **Diffraction** is the main technique!

Reflection of radiation from crystallographic planes modelled by Bragg’s Law.

Considering interatomic distances \( \sim 1 \text{ Å} \), can it be done with visible light?

Diffraction

Can be done with X-rays, electrons and neutrons!

Wave-particle duality

Extension of the idea of wave-particle duality from light to matter: any moving particle or object has an associated wave \( \rightarrow \) particles can be wavelike!

Everything has a wavelength:

\[ E = mc^2 = (mc)c = pc = p \lambda, \quad \lambda = \frac{h}{p} = \frac{h}{mv} \]

What is the velocity of a neutron with \( \lambda = 1 \text{ Å} \)?

\( h = 6.626 \times 10^{-34} \text{ J s} \) and \( m_n = 1.675 \times 10^{-27} \text{ kg} \)

\[ v = \frac{h}{m_n} = 4000 \text{ m s}^{-1} \quad \text{Speed of neutron in vacuum (or free space!)} \]

Maximum speed of a Ferrari: 105.5 ms\(^{-1}\)

Cruising speed of a modern jet airliner: 250 ms\(^{-1}\)

Speed of Apollo 10: 11,082 ms\(^{-1}\)

For a baseball (m=0.15 kg) moving at 30 ms\(^{-1}\):

\[ \lambda = 1.5 \times 10^{-24} \text{ Å} \]
**Diffraction: single nucleus**

**Single nucleus:** analogy with diffraction of light:
- Incident waves = plane waves
- Nucleus = ideal point scatterer
- Nucleus scatters the incident neutron beam uniformly in all directions:
- Scattered waves = spherical isotropic waves.

**Diffraction due to interference between waves scattered elastically from nuclei in the crystal.**

**Wave description**

Intensity of a wave moving with a velocity \( v \) along \( x \)-direction, at any given position is:

\[ I(x,t) = A \cos((kx - \omega t) - \varphi) \]

- **Wave number:** \( k = \frac{2\pi}{\lambda} \)
- **Angular freq.** \( \omega = \frac{2\pi}{\tau} \)
- **Phase velocity:** \( v = \frac{\lambda}{\tau} \)
- **Angular velocity:** \( \omega = \frac{2\pi}{k} \)
- **Wave number:** \( k = \frac{2\pi}{\lambda} \)
- **Frequency:** \( \nu = \frac{\omega}{k} \)

**Diffraction due to interference between waves scattered elastically from nuclei in the crystal.**
Addition of waves

Adding waves with the same wavelength but different initial phase:
- **constructive**: if exactly in phase \((\Delta \phi = 2\pi)\), maximum possible amplitude.
- **destructive**: if exactly out of phase \((\Delta \phi = \pi)\), zero amplitude.
- **anything between**: if partially out of phase \((\Delta \phi)\), anything between amplitude.

Wave description

Complex form

What is a complex number? Consider a point (vector), \(Z = (x, y)\), on a 2d Cartesian coordinate system with \(x\)=real component, \(y\)= imaginary one:

\[
Z = x + iy = A \cos(\phi) + i A \sin(\phi)
\]

Can a plane wave be considered as a vector in this system?

Amplitude = magnitude of vector: 
\[
|Z|^2 = ZZ^* = Re\{Z\}^2 + Im\{Z\}^2
\]

Phase= angle of vector & horizontal axis: 
\[
\tan(\phi) = \frac{Im\{Z\}}{Re\{Z\}}
\]

Using complex exponentials one easily can see adding waves of the same wavelength but different initial phase, results in a wave of the same wavelength!

**Complex form**

\[
F(x,t) = F_0 e^{i(kx - \omega t - \phi)}
\]

\[
F = \sum_{n} F_n e^{i(kx_n - \omega t)}
\]

\[
F_n = \frac{1}{2} [F_n + \cdots + F_n e^{i(kx_n - \omega t)}] + \cdots
\]

where \(n\) is the index of the wave, \(k\) is the wave number, and \(\omega\) is the angular frequency.
Crystals diffract radiation of a similar order of wavelength to the inter-atomic spacings. This diffraction is modeled by considering the "reflection" of radiation from equally spaced (d) planes:

\[ 2d \sin \theta = n\lambda \]

Bragg's Law: \( 2d \sin \theta = n\lambda \)

Diffraction from crystals: Bragg's law

Diffraction from a single layer of atoms: Specular reflection.

Similar to reflection of visible light of a smooth surface like a mirror.

Constructive interference of waves scattered from the two successive lattice points A and B in the plane:

\[ AC = DB \]
\[ \theta_i = \theta_f \]

Diffraction: neutrons interact with nuclei → scattered in all directions by every nucleus they encounter. Scattered waves from different nuclei travel different distances → acquire different phase → interfere as they add up!

Constructive interference of waves scattered from two lattice points A and D in adjacent planes:

\[ AB + AC = n\lambda \]

\[ 2d \sin \theta = n\lambda \]

Bragg's Law
More on Bragg’s law

Diffraction peaks observed only when successive planes scatter in phase (it is relative phase that matters): Coherent scattering from a single plane not sufficient.

For a set of lattice planes diffraction occurs only at a particular angle given by Bragg’s law. Larger d-spacing → smaller diffraction angle: inverse relation between d-spacing and q (reciprocal space).

No Bragg’s scattering when λ is larger than 2d_max (largest spacing Bragg planes in a material). This is why visible light cannot be used. What is the incident angle for λ=2d_max?

Planes must pass through same points in all the unit cells in the crystal to diffract in phase. Only if planes cut all the 3 cell edges an integral number of times, unit cells diffract in phase.

Miller indices used to label the planes: \( d_{hkl} = d_{hkl} \sin \theta = \lambda \). Only need to consider the n=1 values, since higher values of n for the (hkl) planes correspond to the n=1 value for the (nh nk nl) planes.

Plane of “reflection” bisects the angle between incident and scattered beams: 2θ is measured in experiment. Either (a) rotate the sample (single crystal) or (b) have lots of crystals at different orientations simultaneously (powder).

Mathematical foundation of neutron scattering

Reminder: neutron can be thought about as a wave! described by a wavefunction, \( \psi \).

Probability of finding a neutron at a given point in space

\[
| \psi |^2 = \psi \times \psi^* 
\]

Neutron wavevector \( k \): a vector pointing along neutron’s trajectory.

Wavevector magnitude: \( k = |k| = \frac{2\pi}{\lambda} = 2\pi m v h \).
The number of scattered neutrons as a function of $Q$ is measured. The result is the scattering function $S(Q)$ depending only on the properties of the sample.

Scattering by a fixed single nucleus

Neutrons interact with matter via nuclear force: very short range ~10^{-15} m, size of a nucleus ~100,000 times smaller than distance between centers! Nucleus $\rightarrow$ point scatterer (isotropic scattering)!

Incident plane wave: $e^{i k x}$

Scattered spherical wave: $\frac{b}{r}$

Squared modulus $= \frac{b^2}{r^2}$, neutron is found with same probability at all positions!

The spatial extent of the potential is exaggerated to be able to show it on the same scale!

The detector measures all the neutrons into solid angle $d\Omega$ in the direction of $(\theta, \phi)$.

Differential cross-section:

$$\frac{d\sigma}{d\Omega}$$

number of neutrons scattered per second into $d\Omega$

Total cross-section:

$$\sigma = \int d\Omega \frac{d\sigma}{d\Omega}$$

total number of neutrons scattered per second

$\Phi$ total number of scattered neutrons in all directions (units: barn=10^{-24} cm^2).
Cross-section for a fixed single nucleus

Incident flux: \( \Phi = \int \psi_{\text{incident}} \, d^2 \Phi = v \)

Number of scattered neutrons with a velocity \( v \) passing through area \( dS \):

\[
\frac{d\sigma}{d\Omega} = \frac{\Phi d\Omega}{v^2} \left( \frac{b^2 d\Omega}{v dS} \right) = \frac{b^2 d\Omega}{v dS} \]

\[
\sigma_{\text{total}} = 4\pi b^2
\]

Scattering by many fixed nuclei

Measures scattering intensity is the sum of scattering from each individual nucleus!

Pseudo-potential (Fermi): interaction between a neutron and a nucleus is replaced by a much weaker effective potential.

Perturbation approximation (Born): effective potential is weak enough to use perturbation in calculating scattering!

Scattering law (Van Hove): probability of a neutron wave \( k_i \) being scattered by \( V(r) \) into outgoing wave of \( k_f \) is:

\[
\left\{ \int e^{i\mathbf{k}_f \cdot \mathbf{r}} V(\mathbf{r}) e^{-i\mathbf{k}_i \cdot \mathbf{r}} \, d\mathbf{r} \right\}^2 = \left\{ \int V(\mathbf{r}) e^{i\mathbf{Q} \cdot \mathbf{r}} \, d\mathbf{r} \right\}^2
\]

Integration is over the volume of the sample.

Fermi pseudo-potential for an assembly of nuclei at positions \( \mathbf{r}_j \):

\[
V(\mathbf{r}) = \frac{2\pi\hbar^2}{m} \sum \mathbf{b}_j \delta(\mathbf{r} - \mathbf{R}_j)
\]

\[
\frac{d\sigma}{d\Omega} = \frac{m}{2\pi\hbar^2} \int \left\{ \sum \mathbf{b}_j \delta(\mathbf{r} - \mathbf{R}_j) \right\} \left( \frac{2\pi\hbar^2}{m} \right) \left\{ \sum \mathbf{b}_j \right\} e^{i\mathbf{Q} \cdot \mathbf{r}} \, d\mathbf{r}
\]

\[
= \sum \mathbf{b}_j e^{i\mathbf{Q} \cdot \mathbf{r}} \left\{ \sum \mathbf{b}_j \right\} e^{-i\mathbf{Q} \cdot \mathbf{r}} \left\{ \sum \mathbf{b}_j \right\}
\]

Double sum over all positions of nuclei in the sample.
More on scattering by many fixed nuclei

\[
\frac{d\sigma}{d\Omega} = \sum_{b_1} b_1 e^{-i(b_1 \cdot R_1)} = \sum_{b_1} b_1 \int dr \, \delta(r - (R_1 - R_j)) e^{-i Q \cdot r} dr
\]

For \( b_1 = b_k \):

\[
\frac{d\sigma}{d\Omega} = N b_k^2 \int dr \, G(r) e^{-i Q \cdot r} dr
\]

\[G(r) = \frac{1}{N} \sum_{j,k} \delta(r - (R_j - R_k))\]

Intensity is proportional to Fourier transform of pair correlation function \( G(r) \) (probability of finding two atoms being a certain distance apart). Scattering gives information about correlations between positions of pairs of nuclei.

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Evaluating the double sum

One single nucleus:

\[
\frac{d\sigma}{d\Omega} \propto b^2 \Rightarrow \sigma_{\text{true}} = 4\pi b^2
\]

1D periodic arrangement of \( N \) nuclei:

\[
\frac{d\sigma}{d\Omega} = F(Q) \cdot F^*(Q) = b^2 \left( \sum_{j,k} e^{iQ \cdot (R_j - R_k)} \right)^2 = b^2 \frac{\sin^2(\pi aQ)}{\pi aQ}
\]

Non-zero only when \( aQ = 2\pi \), \( m \) integer \( \rightarrow Q = 2\pi m / a \)

For many repeats the peaks become very narrow (Bragg peaks). The width of the peak is a convolution of the instrumental resolution with the correlation length: grain size, magnetic correlation length, etc...

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Relation to the Bragg's law

Orientation of a plane is defined by direction of its normal vector: \( n_{\text{Bragg}} = ha^* + kb^* + lc^* \)

\[a^* = 2\pi \frac{b \times c}{V}, \quad b^* = 2\pi \frac{c \times a}{V}, \quad c^* = 2\pi \frac{a \times b}{V}\]

Does \( n_{\text{Bragg}} \) satisfy the following condition?

\[
a.Q_{\text{Bragg}} = 2\pi m, \quad b.Q_{\text{Bragg}} = 2\pi n, \quad c.Q_{\text{Bragg}} = 2\pi p
\]

Laue condition

\[Q_{\text{Bragg}} \parallel 2k \sin \theta = \frac{4\pi}{\lambda} \sin \theta = n_{\text{Bragg}} \parallel 2\pi \lambda_d = \frac{2\pi}{d_{\text{Bragg}}}
\]

\[2d_{\text{Bragg}} \sin \theta = \lambda\]
Many nuclei: Structure factor

\[
\frac{d\sigma}{d^2} = \sum_{i,j} b_i^* b_j \delta(r_i - r_j) \delta(Q - Q_{ij})
\]

Position of nucleus \(j\) is given by: \(R_j = T + r_j\) where \(T\) is lattice translation vector, \(r_j\) is the position of nucleus relative to the cell origin.

Structure Factor:

\[
F(Q) = \sum_{\text{atoms}} b_i e^{iQ \cdot R_i} = \sum_{\text{atoms}} e^{iQ \cdot \delta R_{\text{cell}}} + \sum_{\text{basis}} b_i e^{iQ \cdot \delta R_{\text{cell}}}
\]

Example: Structure factor for BCC structure:

\(r_1=(0,0,0), r_2=(a/2, a/2, a/2)\):

\[
F_{hkl} = b [1 + \cos(\pi(h+k+l))]
\]

\(F_{hkl} = 2b\) for \(h+k+l\) even, 0 if \(h+k+l\) odd.

Reciprocal Space

Reciprocal features so far:

- Inverse relation between \(d\) and \(\theta\).
- Miller indices: reciprocal (or inverse) of unit cell intercepts.
- Intensity is proportional to Fourier transform of pair correlation function.

Reciprocal lattice:

Reciprocal unit cell vectors:

\(a^* = G_{100}, b^* = G_{010}, c^* = G_{001}\)

\([a^*] = 2\pi d_{100}, [b^*] = 2\pi d_{010}, [c^*] = 2\pi d_{001}\)

Bragg condition in reciprocal space for elastic \(|k_i| = |k_f|\):

\[
Q = k_i - k_f \rightarrow (Q + k_f)^2 = k_i^2
\]

\[
2 Q \cdot k = Q^2
\]

Can you see this is equivalent to Bragg's law?

Geometrical interpretation of Bragg condition: \(k\) must end on a Bragg plane to have a constructive diffraction.

Bragg zones for a 2d square lattice:

Geometrical interpretation of Bragg condition: \(k\) must end on a Bragg plane to have a constructive diffraction.

Bragg zones are widely used in condensed matter physics: theory of electron bands and other types of excitations.

Brillouin zones for a 2d square lattice:

Brillouin zone surfaces exhibits all the wavevectors that can be Bragg-reflected by the crystal.
References and further readings

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