LECTURE 7: Inelastic Scattering

by

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We Have Seen How Neutron Scattering Can Determine a Variety of Structures

but what happens when the atoms are moving?

Can we determine the directions and time-dependence of atomic motions? Can we tell whether motions are periodic? Etc.

These are the types of questions answered by inelastic neutron scattering
The Neutron Changes Both Energy & Momentum When Inelastically Scattered by Moving Nuclei

(a) Elastic Scattering \((k' = k)\)

\[
\sin \theta = \frac{Q}{2k}
\]

\[
Q = 2k \sin \theta = \frac{4\pi \sin \theta}{\lambda}
\]

(b) Inelastic Scattering \((k' \neq k)\)

Neutron Loses Energy \((k' < k)\)

Neutron Gains Energy \((k' > k)\)

Inelastic scattering

Scattering in which exchange of energy and momentum between the incident neutron and the sample causes both the direction and the magnitude of the neutron's wave vector to change.
The Elastic & Inelastic Scattering Cross Sections Have an Intuitive Similarity

• The intensity of elastic, coherent neutron scattering is proportional to the spatial Fourier Transform of the Pair Correlation Function, $G(r)$ i.e. the probability of finding a particle at position $r$ if there is simultaneously a particle at $r=0$.

• The intensity of inelastic coherent neutron scattering is proportional to the space and time Fourier Transforms of the time-dependent pair correlation function function, $G(r,t) = \text{probability of finding a particle at position } r \text{ at time } t \text{ when there is a particle at } r=0 \text{ and } t=0$.

• For inelastic incoherent scattering, the intensity is proportional to the space and time Fourier Transforms of the self-correlation function function, $G_s(r,t)$ i.e. the probability of finding a particle at position $r$ at time $t$ when the same particle was at $r=0$ at $t=0$. 
Diffraction from a Frozen Wave

Recall that

\[ S(\vec{Q}) = \frac{1}{N} \left| \sum_{k} e^{i\vec{Q}\vec{r}_k} \right|^2 \]

We know that for a linear chain of “atoms” along the x axis \( S(Q_x) \) is just a series of delta function reciprocal lattice planes at \( Q_x = n2\pi/a \), where \( a \) is the separation of atoms.

What happens if we put a "frozen" wave in the chain of atoms so that the atomic positions are \( x_p = pa + u \cos kpa \) where \( p \) is an integer and \( u \) is small?

\[
S(Q) = \left| \sum_{p} e^{iQpa} e^{iQu\cos kpa} \right|^2 \approx \left| \sum_{p} e^{iQpa} (1 + iQu[e^{ikpa} + e^{-ikpa}]) \right|^2 \\
\approx \left| \sum_{p} e^{iQpa} + iQu[e^{i(Q+k)pa} + e^{i(Q-k)pa}] \right|^2 \\
\]

so that in addition to the Bragg peaks we get weak satellites at \( Q = G \pm k \).
What Happens if the Wave Moves?

• If the wave moves through the chain, the scattering still occurs at wavevectors $G + k$ and $G - k$ but now the scattering is inelastic

• For quantized lattice vibrations, called phonons, the energy change of the neutron is $\hbar \omega$ where $\omega$ is the vibration frequency.

• In a crystal, the vibration frequency at a given value of $\mathbf{k}$ (called the phonon wavevector) is determined by interatomic forces. These frequencies map out the so-called phonon dispersion curves.

• Different branches of the dispersion curves correspond to different types of motion

phonon dispersion in $^{36}\text{Ar}$
Atomic Motions for Longitudinal & Transverse Phonons

\[ \vec{Q} = \frac{2\pi}{a}(0.1,0,0) \]

Transverse phonon
\[ \vec{e}_T = (0,0,1,0)a \]

Longitudinal phonon
\[ \vec{e}_L = (0,1,0,0)a \]

\[ \vec{R}_l = \vec{R}_{l0} + \vec{e}_s e^{i(\vec{Q} \cdot \vec{R}_l - \omega t)} \]
Transverse Optic and Acoustic Phonons

Acoustic
\[ \vec{e}_{\text{red}} = (0,0.1,0)a \]
\[ \vec{e}_{\text{blue}} = (0,0.14,0)a \]

Optic
\[ \vec{e}_{\text{red}} = (0,0.1,0)a \]
\[ \vec{e}_{\text{blue}} = (0,-0.14,0)a \]

\[ \vec{R}_{lk} = \vec{R}_{lk}^0 + \vec{e}_s e^{i(\vec{Q}.\vec{R}_l - \omega t)} \]
Phonons – the Classical Use for Inelastic Neutron Scattering

- Coherent scattering measures scattering from single phonons

\[
\frac{d^2\sigma}{d\Omega dE} = \sigma_{coh} \frac{k^\prime}{k} \frac{\pi^2}{MV_0} e^{-2W} \sum_s \sum_G \frac{\left(\vec{Q} \cdot \vec{e}_s\right)^2}{\omega_s} \left(n_s + \frac{1\pm1}{2}\right) \delta(\omega + \omega_s) \delta(\vec{Q} - \vec{q} - \vec{G})
\]

- Note the following features:
  - Energy & momentum delta functions => see single phonons (labeled \(s\))
  - Different thermal factors for phonon creation (\(n_{s+1}\)) & annihilation (\(n_s\))
  - Can see phonons in different Brillouin zones (different recip. lattice vectors, \(G\))
  - Cross section depends on relative orientation of \(Q\) & atomic motions (\(e_s\))
  - Cross section depends on phonon frequency (\(\omega_s\)) and atomic mass (\(M\))
  - In general, scattering by multiple excitations is either insignificant or a small correction (the presence of other phonons appears in the Debye-Waller factor, \(W\))
The Workhorse of Inelastic Scattering Instrumentation at Reactors Is the Three-axis Spectrometer

“scattering triangle”
What Use Have Phonon Measurements Been?

- Quantifying interatomic potentials in metals, rare gas solids, ionic crystals, covalently bonded materials etc.
- Quantifying anharmonicity (i.e. phonon-phonon interactions).
- Measuring soft modes at 2\textsuperscript{nd} order structural phase transitions.
- Electron-phonon interactions including Kohn anomalies.
- Roton dispersion in liquid He.
- Relating phonons to other properties such as superconductivity, anomalous lattice expansion etc.
Brockhouse’s first 3 axis spectrometer at NRU reactor in 1959

The constant-Q method
Roton Minimum in Superfluid $^4$He was Predicted by Landau
SrTiO$_3$ looked like a simple mean-field displacive phase transition described by a soft-mode theory until Riste discovered the Central Peak.
Dr. Taner Yildirim
is the recipient of the
2006 Science Prize
of the Neutron Scattering Society of America with the citation:

“For his innovative coupling of first principles theory with neutron scattering to solve critical problems in materials sciences”
MgB$_2$ Superconducts at 40K. Why?

- Yildirim did first-principles calculation of phonons in MgB$_2$ (particulary anharmonicity & electron-phonon interaction) & compared with neutron scattering

Crystal structure is layered

- Optic & acoustic modes separated
- Red modes frequencies dominated by e-p interaction

Graphics courtesy of Taner Yildirim
Motions Associated with Zone Center Modes

$E_{1u}$

$A_{2u}$

$B_{1g}$

$E_{2g}$

Very anharmonic
The Large Displacements Associated with $E_{2g}$ Cause Large Electron-Phonon Coupling

- Because the effective potential for the $E_{2g}$ mode is shallow and wide, the B atom-motions are large amplitude.
- This causes significant overlap of electron shells and significant effects on the band structure close to $E_F$.
- The strong e-p interaction causes the “high” $T_c$.
The Inelastic Scattering Cross Section

Recall that

\[ \left( \frac{d^2 \sigma}{d \Omega \cdot dE} \right)_{coh} = b^2_{coh} \frac{k'}{k} NS(\tilde{Q}, \omega) \quad \text{and} \quad \left( \frac{d^2 \sigma}{d \Omega \cdot dE} \right)_{inc} = b^2_{inc} \frac{k'}{k} NS_i(\tilde{Q}, \omega) \]

where

\[ S(\tilde{Q}, \omega) = \frac{1}{2\pi \hbar} \int \int G(\vec{r}, t)e^{i(\tilde{Q} \cdot \vec{r} - \omega t)} d\vec{r} dt \quad \text{and} \quad S_i(\tilde{Q}, \omega) = \frac{1}{2\pi \hbar} \int \int G_s(\vec{r}, t)e^{i(\tilde{Q} \cdot \vec{r} - \omega t)} d\vec{r} dt \]

and the correlation functions that are intuitively similar to those for the elastic scattering case:

\[ G(\vec{r}, t) = \frac{1}{N} \int \left\langle \rho_N(\vec{r}, 0) \rho_N(\vec{r} + \vec{R}, t) \right\rangle d\vec{r} \quad \text{and} \quad G_s(\vec{r}, t) = \frac{1}{N} \sum_j \int \left\langle \delta(\vec{r} - \vec{R}_j(0))\delta(\vec{r} + \vec{R} - \vec{R}_j(t)) \right\rangle d\vec{r} \]

The evaluation of the correlation functions (in which the \( \rho \)'s and \( \delta \) - functions have to be treated as non - commuting quantum mechanical operators) is mathematically tedious. Details can be found, for example, in the books by Squires or Marshal and Lovesey.
Examples of $S(Q,\omega)$ and $S_s(Q,\omega)$

- Expressions for $S(Q,\omega)$ and $S_s(Q,\omega)$ can be worked out for a number of cases e.g:
  - Single phonons
  - Phonon density of states
  - Various models for atomic motions in liquids and glasses
  - Various models of atomic & molecular translational & rotational diffusion
  - Rotational tunneling of molecules
  - Transitions between crystal field levels
  - Spin waves and other magnetic excitations such as spinons

- Inelastic neutron scattering reveals details of the shapes of interaction potentials in materials
Measured Inelastic Neutron Scattering Signals in Crystalline Solids Show Both Collective & Local Fluctuations*

Spin waves – collective excitations

Crystal Field splittings (HoPd₂Sn) – local excitations

Local Fluctuations – energy does not depend on Q

Collective fluctuations – energy is usually Q-dependent

Local spin resonances (e.g. ZnCr₂O₄)

* The following 5 viewgraphs contain material supplied by Dan Neumann, NIST
Measured Inelastic Neutron Scattering Signals in Liquids Generally Show Diffusive Behavior

Diffusive motion is usually measured using the incoherent neutron scattering cross section and is manifested by a spectral peak centered at $E = 0$ – so-called quasielastic scattering.
Measured Inelastic Neutron Scattering in Molecular Systems Span Large Ranges of Energy

- Vibrational spectroscopy (e.g. C$_{60}$)
- Molecular reorientation (e.g. pyrazine)
- Rotational tunneling (e.g. CH$_3$I)

- Polymers
- Proteins
Quasielastic Neutron Scattering

- For a single diffusing particle, the probability, $p$, of finding it within a sphere around its starting position looks like:

$$ p = e^{-t/\tau} $$

$$ 1/\tau = DQ^2 $$

- $S_{inc}(Q,E)$ is the time Fourier transform of this probability:

$$ S_{inc}(Q,E) = \frac{\hbar}{\pi} \frac{DQ^2}{(\hbar DQ^2)^2 + E^2} $$
Quasielastic Neutron Scattering

• If there is a finite probability that a particle occupies its initial position as $t \to \infty$ the scattering will include an elastic component

• For example, if two sites may be occupied and

\[
\begin{align*}
    p_1 &= \frac{1}{2} + \frac{1}{2} e^{-2t/\tau} \\
    p_2 &= \frac{1}{2} - \frac{1}{2} e^{-2t/\tau}
\end{align*}
\]

we get

\[S(Q,E) = A_0 \delta(E) + A_1 \mathcal{L}\]

$A_0$ is called the Elastic Incoherent Structure Factor (EISF)
Note that the $\delta$-function is always broadened by instrumental effects

Half Width $\sim 1/\tau$
(independent of $Q$)
Spectrometers for Measuring Quasielastic Scattering

Chopper spectrometer with pulsed monochromatic incident neutron beam and time-of-flight energy analysis
$0.01 < \Delta E < 0.1 \text{ meV}$ for cold neutrons
$1 < \Delta E < 10 \text{ meV}$ for thermal neutrons

Backscattering spectrometer with polychromatic incident beam and energy analysis by crystal analyzer
$0.001 < \Delta E < 0.1 \text{ meV}$ for cold neutrons

Note (1) that the value of the energy resolution, $\Delta E$, sets the minimum observed width of spectral line and (2) that the good energy resolution of backscattering is obtained at the expense of poor Q resolution
Another Way to Measure Quasielastic Scattering: Neutron Spin Echo

NSE measures the energy Fourier transform of \( S(Q,E) \)

It is easier to measure coherent Scattering with NSE

\[ 0.00001 < \Delta E < 0.001 \text{ meV} \]
i.e. times between ns and \( \mu \text{s} \)

- NSE works by using the precession of a neutron’s magnetic moment (spin) in a field as a “clock” to measure the neutron’s speed.
- The neutron spins undergo many (~10^5 turns) in the green solenoid magnets above.
- In effect the spins are “wound up” in the first field and “unwound” by the same amount in the second field if the scattering by the sample (between the solenoids) is elastic.
- If the scattering is inelastic, the exact unwinding (or echo) is suppressed and the polarization of the neutron beam at the echo position is a measure of the inelasticity of the scattering.
Much of the Scientific Impact of Neutron Scattering Has Involved the Measurement of Inelastic Scattering

Energy & Wavevector Transfers accessible to Neutron Scattering