Quasi-elastic Scattering: Seeing Atoms Moving Using Neutrons

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BASICALLY TWO TYPES OF INSTRUMENTS

**Diffractometers: 1- 10Å**

Measure structures

neutron : wave

Bragg’s law: $2d \sin \theta = n \lambda$

$E_i = E_f \& k_i = k_f$

**Spectrometers: 1- 80meV**

Measure dynamics

neutron : particle

Newton’s law

$E_i \neq E_f \& k_i \neq k_f$
If there is NO exchange in energy

\[ \frac{\partial \sigma}{\partial \Omega} = \sum_n \frac{\sigma_{\text{inc},n}}{4\pi} + \left\langle \sum_{m,n} b_{\text{coh},m} b_{\text{coh},n} e^{i\mathbf{Q} \cdot (\mathbf{R}_m - \mathbf{R}_n)} \right\rangle \]
For a “thin” sample, the total integrated scattering is:

\[ I_S = \phi N \sigma_s. \]

The measured intensity in a diffraction experiment (on a “thin” sample) is related to the single differential cross section:

\[ I_S(E_i, 2\theta) = \phi N \left( \frac{d\sigma}{d\Omega} \right) \Delta\Omega \]

solid angle

The single differential cross section is related to the “structure factor” \( S(Q) \).

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

\[ \frac{d\sigma}{d\Omega}(E_i, 2\theta) = \frac{\sigma_s}{4\pi} S(Q) \]

ONLY DEPENDS ON THE SAMPLE
If there is an exchange in energy,

\[
\frac{d^2\sigma}{d\Omega \, d\varepsilon_f} = \frac{\sigma_{\text{coh}}}{4\pi\hbar} \frac{k_f}{k_i} S(Q, \omega) + \frac{\sigma_{\text{inc}}}{4\pi\hbar} \frac{k_f}{k_i} S_s(Q, \omega)
\]

collective motion
(phonon)

single particle
(diffusion)
**COHERENT & INCOHERENT SCATTERING**

**coherent scattering**

Scattering in which an incident neutron wave interacts with all the nuclei in a sample in a coordinated fashion; that is, the scattered waves from all the nuclei have definite relative phases and can thus interfere with each other.

**incoherent scattering**

Scattering in which an incident neutron wave interacts independently with each nucleus in the sample; that is, the scattered waves from different nuclei have random, or indeterminate, relative phases and thus cannot interfere with each other.
The measured intensity in a spectroscopy experiment is related to the double differential cross section:

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

The double differential cross section is related to the "scattering function"

\[
S(Q, \omega)
\]

When there is one type of atom,

\[
\frac{d^2\sigma}{d\Omega dE_f}(E_i, 2\theta, E_f) = \frac{\sigma}{4\pi \hbar} \frac{k_f}{k_i} S(Q, \omega),
\]

ONLY DEPENDS ON THE SAMPLE
For most elements the $\sigma_{\text{coh}} > \sigma_{\text{inc}}$.

Hydrogen is a very important exception!

Also vanadium has an $\sigma_{\text{inc}} > \sigma_{\text{coh}}$. 
a simple definition of ‘quasielastic’

“rigid” crystal

‘elastic’ $E=0$

elastic $E=0$

‘inelastic’ $E=\pm dE$

energy transfer

‘quasielastic’: centered at $E=0$

energy transfer

fast moving scatterers, e.g. liquid

vibrations

translation

‘elastic’ $E=0$
What is QENS, and what does it look like?

- QENS is inelastic scattering that is almost elastic, centered at zero energy transfer.
- QENS is associated with relaxation phenomena, such as translational diffusion, molecular reorientations, confined motion within a pore, hopping among sites.
- Accessible time scales range from fractions of ps to 100s of ns.
- Length scales range from Å to 100s of Å.
- Most QENS experiments are designed to study incoherent scattering (single particle motions).
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Overskrift her

Navn på oplægsholder

Navn på KU-enhed

For at ændre "Enhedens navn" og "Sted og dato":

Klik i menulinjen, vælg "Indsæt > Sidehoved / Sidefod".

Indføj "Sted og dato" i feltet for dato og "Enhedens navn" i Sidefod.
### Matching Time Scales

<table>
<thead>
<tr>
<th>Resolution</th>
<th>(slow)</th>
<th>S(Q,ω)</th>
<th>(fast)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>delta-function peak</td>
<td>Narrow peak</td>
<td>Medium width peak</td>
</tr>
<tr>
<td>Low resn. (broad)</td>
<td>(Elastic)</td>
<td>Elastic</td>
<td>Elastic</td>
</tr>
<tr>
<td>Med. resn. (medium)</td>
<td>(Elastic)</td>
<td>Elastic</td>
<td>Match</td>
</tr>
<tr>
<td>High resn. (narrow)</td>
<td>(Elastic)</td>
<td>Match</td>
<td>Flat</td>
</tr>
</tbody>
</table>
typical incoherent scattering law

\[ S_{inc}(Q, \omega) = A_0(Q)\delta(\omega) + (1 - A_0(Q))L(Q, \omega) \]

elastic, EISF
stationary part; sign of confined motion

quasi-elastic decaying part

for a given Q: \[ \int_{-\infty}^{\infty} S_{inc}(Q, \omega)d\omega = 1 \]

\[ EISF = \frac{S_{inc}(Q)}{S_{inc}(Q) + S_{inc}(Q)} \]
example for a simple incoherent scattering law

isotropic translational diffusion

no stationary part -> not confined -> no elastic scattering

time space

\[ S_{inc}(Q, t) = \exp(-DQ^2 t) \]

energy space

\[ S_{inc}(Q, \omega) = \frac{1}{\pi} \frac{DQ^2}{\omega^2 + (DQ^2)^2} \]

Lorentzian with energy width

\[ \text{HWHM} = \frac{\Gamma}{2} = \frac{\hbar DQ^2}{2} \]

\( D=\text{self diffusion constant [m}^2/\text{s}] \)

\( D\sim\exp(-E_a/kT) \)

example:

\( D(\text{H}_2\text{O @ RT}) \sim 2 \times 10^{-5} \text{cm}^2/\text{s} \)

FWHM \sim 270 \mu\text{eV @ 1Å}^{-1}; \tau=5\text{ps}

FWHM \sim 2.7 \mu\text{eV @ 0.1Å}^{-1}; \tau=50\text{ps}

\[ \Rightarrow\text{TOF dynamic range} \]
Functional Materials

- To understand functionality we need structural information.
- Beneath the crystal (molecular) structure, there are important motions.
- How the functional groups are arranged in a sequence defines the dynamics of the complex systems.
Functional Materials
Functional Materials

Paracetamol

Phenacetin
Methyl Groups Flexibility

![Chemical structures and graphs showing the flexibility of methyl groups at different temperatures.](image)

- Plot 1: In(HWHM(meV)) vs. 1000/T(K)
- Plot 2: Intensity(0)/Intensity(elastic(2)) vs. T (K)

Graphs illustrating the energy (meV) vs. intensity at various temperatures (20 K to 296 K).
Methyl Groups Flexibility

\[ \Gamma = \Gamma_0 e^{-\frac{E_{\text{act}}}{kT}} \]

\( E_{\text{act}} = 41 \text{ meV} \)

expect libration at 17meV
Time-averaged mean square displacement

\[ S(Q, \omega) = A_0(Q) \delta(\omega) + \sum_{i=1}^{N} A_i(Q)L_i(\omega) \]

\[ A_0(Q) = a_0(Q) \exp\left(-\langle u^2 \rangle Q^2 \right) \]
Time-averaged mean square displacement

\[ S(Q, \omega) = A_0(Q)\delta(\omega) + \sum_{i=1}^{N} A_i(Q)L_i(\omega) \]

\[ A_0(Q) = a_0(Q)\exp(-\langle u^2 \rangle) \]

Inelastic zone \( \lambda \ll \lambda_0 \)
Elastic peak \( \lambda_0 \) or \( \Delta E = 0 \)
Quasi-elastic zone \( \lambda = \lambda_0 \pm \delta \lambda \)
Methyl Groups Flexibility
Phenacetin Dynamics : Conclusion

- Understanding the lattice vibrations is a difficult task, however the application of solid-state density functional theory (DFT) methods can be used as a reliable approach to simulate the vibrational spectra and to reveal the underlying physical nature of the low-energy vibrational motions.

- The correlation times of the methyl group rotation with deviations of the mean square displacements, <u2>.

- Phenacetin can assume different conformations and knowing this can help the understanding of how chemical reactions occur. In the particular case of biochemists and molecular biologists such results can help understating the ways molecules interact with each other in living systems.
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