Quasi-Elastic Neutron Scattering

Niina Jalarvo
What is QENS
Quasi Elastic Neutron Scattering (QENS)

- Quasi elastic neutron scattering is a limiting case of inelastic neutron scattering.
- Doppler type of broadening of the elastic line due to a small energy transfer between the neutrons and the atoms in the sample.
Neutron-Material Interaction

- **Cross section** \((\sigma)\) – Area related to the probability that a neutron will interact with a nucleus in a particular way (e.g. scattering or absorption)
- Light element sensitivity in presence of heavy elements
- Systems containing a reasonable proportion of H atoms, scattering from H tends to dominate
- Isotopic sensitivity
  - H-D contrast, H large incoherent cross-section
    - Use of deuteration/selective deuteration to suppress incoherent scattering
- Thermal neutron wavelengths (few Å’s) are comparable to interatomic and intermolecular distances
- Thermal neutron energies (few meV’s) comparable to energies of excitation in materials
  => vibrations, librations, reorientations, diffusion, and relaxational processes can be observed
What is QENS used for

Probes slow dynamics
- Translational diffusion
- Molecular reorientations
- Relaxation processes

Applicable to wide range of scientific topics
- **Materials science**: fuel cells, batteries, hydrogen storage,
- **Soft Matter**: polymer nanocomposites and blends, organic photovoltaics, polymer electrolytes
- **Biology**: hydration water, dynamics of proteins
- **Chemistry**: water interfaces, ionic liquids, clays, porous media, complex fluids, surface interactions

Results are comparable to Molecular Dynamics simulations

Nature Communications 6, 7124 (2015)


Soft Matter, 7, 12, 5745-5755 (2011)
QENS spectra

\[ S(Q, \omega) = p_0 \delta(\omega) + \sum_{i=1}^{n} p_i \frac{\Delta_i(Q)}{\pi \omega^2 + \Lambda_i^2} + B \]

Dynamic scattering function provides information on the sample states

**Elastic intensity** \( p_0 \delta(\omega) \)

**Debye-Waller factor:** Vibrational amplitudes

**Quasielastic intensity** \( \sum_{i=1}^{n} p_i \frac{\Delta_i(Q)}{\pi \omega^2 + \Lambda_i^2} \)

**A_0 = EISF (ratio elastic/total):** Geometry of motion

**Quasielastic broadening** \( B \)

**Width:** Characteristic time scale / diffusion
QENS Instruments

Currently about 20 QENS spectrometers in the world (approximately 4 in the U. S., other locations include Germany, France, Switzerland, Japan and Australia)

Backscattering Spectrometers

- High energy resolution
  - Resolution determined by the instrument (final energy of neutrons fixed)
  - Access to slower dynamics on nanosecond to picosecond time scale
  - Dynamic range limited

Time-of-Flight Spectrometers

- Lower energy resolution
  - Resolution can be varied by changing the energy of incoming neutrons
  - Access to dynamics on picosecond time scale
  - Larger dynamic range accessible
QENS and Neutron Scattering Instruments

• Dynamics in sample measurable
  – Length scales set by Q range (depends on neutron $\lambda$)
    • $Q = \frac{2\pi}{d}$
    • $0.1 \text{ Å}^{-1} < Q < 4 \text{ Å}^{-1} \rightarrow 60 \text{ Å} > d > 1.6 \text{ Å}$
  – Time scales set by the elastic energy resolution
    • higher resolution $\rightarrow$ longer times/slower motion (ns time scales accessible)
    • lower resolution $\rightarrow$ shorter times/faster motion (ps time scales accessible)

• interchange
  – dynamic range / resolution / count rate
  – Neutron $\lambda$ vs Q
    • large $\lambda$ $\rightarrow$ high resolution $\rightarrow$ long times/slow motions
    • large $\lambda$ $\rightarrow$ limited Q-range, limited length scales
The SNS Inelastic Instrument Suite

- Momentum Distributions
- Itinerant Magnets
- Crystal Fields
- Molecular Vibrations
- Lattice and Spin Excitations
- Small Molecule Diffusion
- Large Scale Motions
- Polymers and Biological Systems
- Tunneling Spectroscopy
- Hydrogen Modes
- Molecular Reorientation
- Ultracold Neutrons
- Fundamental Physics
- Slower Motions
- Larger Objects

Instrument Suite:
- ARCS Fermi Chopper
- SEQUOIA Fermi Chopper
- HYSPEC
- Cold Neutron Chopper Spectrometer
- Backscattering
- Neutron Spin Echo

Graph with axes Q (Å⁻¹), d (Å), ω (meV), and t (sec) showing different areas of research coverage.
BASIS backscattering spectrometer at SNS
SNS
BAckscattering SIlicon Spectrometer is a high-energy resolution, wide-dynamic range inverted geometry neutron spectrometer built on BL2 and facing a decoupled supercritical hydrogen, centerline-poisoned moderator

- Incident Flight Path - 84 m moderator-sample position
  - Curved Guide: 10 cm wide x 12 cm tall, 1000 m radius of curvature, line-of-sight at 31 m
  - Straight Guide: 10 cm wide x 12 cm tall
  - Converging Funnel: last 7.7 m; exit 3.25 cm x 3.25 cm, stops 27.5 cm from sample
- Chopper System
  - 3 bandwidth/frame overlap choppers at 7, 9.25 and 50 m
  - Operation at 60 (standard), 30, 20, 15, 12, or 10 Hz
  - Bandwidth (full choppers transmission) of about 0.5 Å at 60 Hz
### Instrument Specifications

- **Radial Collimator** – restricts analyzer view of the sample
- **Final Evacuated Flight Path** - 2.5 m sample - analyzer, ~ 2.23 m analyzer – detector
- **Detector Choice** – LPSD \(^3\)He tubes

<table>
<thead>
<tr>
<th></th>
<th>Si111</th>
<th>Si311</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elastic energy</td>
<td>2.08 meV</td>
<td>7.63 meV</td>
</tr>
<tr>
<td>Bandwidth 60 Hz</td>
<td>±100 µeV</td>
<td>±660 µeV</td>
</tr>
<tr>
<td></td>
<td>±200 µeV</td>
<td>±1700 µeV</td>
</tr>
<tr>
<td>Bandwidth 30 Hz</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Elastic resolution (HWHM)</td>
<td>3.6 µeV</td>
<td>15 µeV</td>
</tr>
<tr>
<td>Q range (elastic)</td>
<td>0.2 Å(^-1) &lt; Q &lt; 2.0 Å(^-1)</td>
<td>0.4 Å(^-1) &lt; Q &lt; 3.8 Å(^-1)</td>
</tr>
</tbody>
</table>
• Typical sample holders: annular cylindrical or flat plate
  – Keep sample thin to avoid multiple scattering effects
  – Transmission probability ~ 95 %
Vanadium Standard

- Energy resolution (Q-averaged): 3.6 $\mu$eV (FWHM)
- Signal-to-background ratio (at the elastic line): better than 1000:1
- Dynamic range: variable (affects counting statistics, but not the energy resolution)
Incident spectrum and \((Q, \omega)\) coverage

- Incident band (full chopper opening): \((60/\nu)[0.5 \text{ Å}]\), where \(\nu = 60, 30, 20, 15, 12, 10 \text{ Hz}\)

- Inelastic resolution: \(\delta E \approx 0.001*E_i\) at high energy transfers

1 Hz signal (no frame overlap), \(1/\nu\) efficiency corrections applied
CNCS Cold Neutron Chopper Spectrometer
Instrument Description

• direct-geometry, multi-chopper inelastic / QENS spectrometer designed to provide flexibility in the choice of energy resolution
  • best at low incident energies (2 to 50 meV).
  • typical experiments use energy resolutions between 10 and 500 µeV.
Specifications

Source-sample distance  36.2 m
Sample-detector distance  3.5 m
Angular coverage  Horizontally: −50° – +140°
          Vertically: ±16°
Energy resolution  10 – 500 µeV
Incident energy range  0.5 – 80 meV
Momentum transfer range  0.05 – 10 Å−1
QENS theory
Scattering Kinematics

The collision of two objects (e.g. neutron and sample atom) can be described in terms of **momentum and energy conservation**.

Neutron scattering events are described by means of **energy** and **momentum transfer**.

\[
\hbar \mathbf{Q} = \hbar \mathbf{k}_1 - \hbar \mathbf{k}_0 \\
\hbar \omega = E_1 - E_0
\]

- \( \hbar \omega = 0 \) \rightarrow **ELASTIC** scattering
- \( \hbar \omega \neq 0 \) \rightarrow **INELASTIC** scattering
- \( \hbar \omega \approx 0 \) \rightarrow **QUASIELASTIC** scattering
Incoherent vs Coherent Neutron Scattering

Different atoms and isotopes have different coherent and incoherent scattering cross sections.

If the scattered neutron waves from the different nuclei have definite relative phases, they can interfere => COHERENT SCATTERING

If the scattered neutron waves from the different nuclei have random relative phases (no interference) => INCOHERENT SCATTERING

<table>
<thead>
<tr>
<th>Element</th>
<th>$\sigma_{coh}$ (barns)</th>
<th>$\sigma_{inc}$ (barns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen (H)</td>
<td>1.8</td>
<td>79.9</td>
</tr>
<tr>
<td>Deuterium (D)</td>
<td>5.6</td>
<td>2.0</td>
</tr>
<tr>
<td>Carbon (C)</td>
<td>5.6</td>
<td>0.001</td>
</tr>
<tr>
<td>Oxygen (O)</td>
<td>4.232</td>
<td>0</td>
</tr>
</tbody>
</table>

- **Protonated** sample to observe single particle dynamics (quasielastic) and for the inelastic spectrum to weight hydrogen vibrations.
- **Deuterated** sample to obtain structure and collective excitations.

**Deuteration** can help to suppress dynamics of particular groups.
**QENS - Incoherent and Coherent Scattering**

- Large proportion of QENS experiments focus on dynamics of hydrogenous samples

\[ S(Q, \omega) = S_{inc}(Q, \omega) + S_{coh}(Q, \omega) \]

No information about structure  
Dominated by H dynamics  
Contaminates QENS signal (Bragg peaks)

- Coherent QENS signal observable e.g. oxide ion diffusion  
- Mixed coherent and incoherent QENS signal e.g. lithium or sodium diffusion
Elastic Window Scan

- Elastic intensity scan as a function of temperature is a typical approach to estimate dynamic transitions.
- Resembles a DSC scan, i.e. locate transition temperature at which the dynamics enter the time window of the neutron spectrometer.
- Derive MSD using Gaussian approximation

\[ S_{el}(Q, \omega) = A * e^{-Q^2 \langle r^2 \rangle / 3} \]
QENS diffusion models

- **(TD)** Translational Diffusion following Fick’s law
- **(CE)** Chudley-Elliot -model, jump diffusion on a lattice
- **(SS)** Singwi-Sjölander -model, alternation between oscillatory motion and directed motion
- **(HR)** Hall-Ross –model, jump diffusion within a restricted volume

**Spatially restricted diffusion**
- Jumps between 2, 3, … n sites
- Rotational diffusion on a circle
- Diffusion on a sphere
- Diffusion inside a sphere, cylinder

Angular dependency gives access to fundamental processes
QENS - Science examples
Science Example 1: Molecular Reorientation

- Polyoligosilsesquioxane Ligand Dynamics
- How do ligand dynamics contribute to the functionalities of POSS?

Science Example 1: Molecular Reorientation

Octamethyl POSS @ BASIS

\[ S(Q, \omega) = f \left[ p_0 \delta(\omega) + \sum_{i=1}^{n} p_i \frac{\Lambda_i(Q)}{\pi \omega^2 + \Lambda_i^2} \right] \otimes R(Q, \omega) + B \]
Science Example 1: Molecular Reorientation

\[ EISF = \frac{\text{elastic intensity}}{\text{elastic intensity} + \text{quasielastic intensity}} \]

For a CH\(_3\) group – site site jumps

\[ EISF = \frac{1}{3} [1 + 2j_0(\sqrt{3} Qr)] \]

Science Example 1: Molecular Reorientation

\[ V(\theta) = \frac{V_3}{2} (1 - \cos 3\theta) \]

\[ H\psi_n(\theta) = E_n \psi_n(\theta) \]

\[-\rightarrow V_3 = 74.4 \text{ meV (7.18 kJ/mol)}\]

Science example 2: Elucidate Li⁺ vs H⁺ ion diffusion

H⁺ ions were found to be immobile while Li⁺ ion maintained a desired mobility in the solid electrolyte (Li_{6.25-x}H_xAl_{0.25})La_3Zr_2O_{12}

Science example 2: Elucidate Li$^+$ vs H$^+$ ion diffusion

H$^+$ ions are found to be immobile while Li$^+$ ions maintain mobility in H-LLZO at the operating temperature range of ALBs.

Science Example 3: Water Dynamics in Anion Exchange Membranes Studied by QENS

Ionic conductivity and water transport are key properties for applications

- Depends on water content

Water transport in AEM multiscale problem

- Investigation of transport in multiple time- and length scales for structure – function insight

Science Example 3: Water Dynamics in Anion Exchange Membranes Studied by QENS

TOFTOF: time-of-flight spectrometer

$$S(Q, \omega) = f \left( a_0(Q) \delta + \sum_n \frac{a_n(Q)}{\pi} \left( \frac{\Gamma}{\omega^2 + \Gamma^2} \right) \right) \otimes \text{Res} + \text{Backg}$$

Science Example 3: Water Dynamics in Anion Exchange Membranes Studied by QENS

\[ \Gamma \sim \frac{1}{\tau_d} \left( 1 - e^{-Q^2 D \tau_d} \right) \]

SPHERES: high-resolution backscattering spectrometer

Science Example 3: Water Dynamics in Anion Exchange Membranes Studied by QENS

\[ D / \text{m}^2\text{s}^{-1} \]

\[ \tau / \text{s} \]

\[ \lambda = 5 \]

\[ T = 293 \text{ K} \]

Summary:

- QENS is a unique technique to measure diffusive dynamics providing exclusive information about the geometry of the diffusion
  - accessible through Q-dependence
  - Large range of time scales available depending on the selected QENS instrument (sub-picosecond < t < nanosecond (µsec for NSE)
  - Hydrogen sensitivity

- Instrument selection is a critical decision
  - resolution to match the time scale of the diffusion process
  - Q range to match the diffusion length scale

- Suitable technique to study dynamics in a large variety of materials and science problems.
• Questions?

• Literature:
  – Quasielastic Neutron Scattering, M. Bee (Bristol, Adam Hilger, 1988).