An introduction to Quasielastic Neutron Scattering (QENS)

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Outline

• A brief history of neutron scattering
• Scattering fundamentals
• What is QENS, and what does it look like?
• How is QENS measured?
• How is QENS modeled?
• Practicalities
• Examples of QENS
• Further reading
• The bottom line
A brief history of neutron scattering

• Diffraction --- Shull and Wollan (late ’40s)

The original two axis spectrometer at the “Clinton Pile”, Oak Ridge (critical 1943)

C.G. Shull, Rev. Mod. Phys. 67 (4) 753 (1995)
[Nobel lectures in physics 1994]
A brief history of neutron scattering

- Diffraction --- Shull and Wollan (late ’40s)
- Inelastic scattering --- Brockhouse (’50s)
  - Absorbers
  - Triple axis, time-of-flight

American Conference on Neutron Scattering, May 11-15, 2008; QENS Tutorial
A brief history of neutron scattering

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  - Phonons, spin waves, liquids, ...
A brief history of neutron scattering

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  - Phonons, spin waves, liquids, …
- High resolution instruments, high flux reactors ('60s, '70s),…
- USERS: chemists, biologists, etc etc
Scattering fundamentals

Elastic and inelastic scattering

\[ k_f = \frac{\hbar_2}{2\theta} \]

\[ \bar{Q} = \bar{k}_i - \bar{k}_f \]

Coherent and incoherent scattering

\[ \sigma_{coh} = 4\pi \langle b \rangle^2 \]

\[ \sigma_{inc} = 4\pi \left( \langle b^2 \rangle - \langle b \rangle^2 \right) \]

Count rate

\[ I = \Phi N \frac{d^2\sigma}{d\Omega dE_f} \Delta\Omega \Delta E_f \]

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

Correlation functions

\[ I_s(Q,t) = \int S_s(Q,\omega) \exp(i\omega t) d\omega \]

\[ G_s(\vec{r},t) = \frac{1}{(2\pi)^3} \int I_s(Q,t) \exp(-i\vec{Q}\cdot\vec{r}) d\bar{Q} \]

(\text{similar expressions apply to } I \text{ and } S.)

<table>
<thead>
<tr>
<th>\lambda \text{ Å}</th>
<th>E \text{ meV}</th>
<th>v \text{ m/s}</th>
<th>\tau \text{ µs/mm}</th>
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<tbody>
<tr>
<td>1</td>
<td>82</td>
<td>4000</td>
<td>0.25</td>
</tr>
<tr>
<td>2</td>
<td>20.5</td>
<td>2000</td>
<td>0.5</td>
</tr>
<tr>
<td>4</td>
<td>5.1</td>
<td>1000</td>
<td>1</td>
</tr>
<tr>
<td>8</td>
<td>1.3</td>
<td>500</td>
<td>2</td>
</tr>
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</table>

What is QENS, and what does it look like?
What is QENS, and what does it look like?

- QENS is inelastic scattering that is almost elastic, centered at zero energy transfer
- There may or may not be associated elastic scattering
- QENS is associated with relaxation phenomena, such as translational diffusion, molecular reorientations, confined motion within a pore, hopping among sites, etc
- 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)

Examples of $S(Q,\omega)$ data

- W.A. Kamitakahara and N. Wada, PRE 77, 041503(2008)
- A.M. Pivovar (unpublished)
More examples of $S(Q, \omega)$ data

[Graphs and images of data plots]

A.D. Enevoldsen et al., JCP 126, 104704 (2007)


A.P. Sokolov et al., Chem. Phys. 345, 212 (2008)


Typical QENS $S(Q, \omega)$

[Graphs showing long range and restricted diffusion]

American Conference on Neutron Scattering, May 11-15, 2008; QENS Tutorial
Examples of $I(Q,t)$ data

- Z. Bu et al., PNAS 102, 17646 (2005)

Typical $S(Q,\omega)$ and $I(Q,t)$
How is QENS measured?

- Triple axis spectrometer (TAS)
- Time-of-flight spectrometer (TOF)
- Backscattering spectrometer (BS)
- Neutron spin echo spectrometer (NSE)

Triple axis spectrometer

The “SPINS” spectrometer at NIST

Incident energy 14 ~ 2 meV (2.4 ~ 6.1 Å)
Flux at sample: $3.9 \times 10^6$ n/cm²/s at 4 Å.
Resolution: from 0.02 to 1.0 meV
**Time-of-flight spectrometer**

![Diagram of Time-of-flight spectrometer with source, sample, choppers, and detector(s)](image1)


**The Disk Chopper Spectrometer (NIST)**

![Graphs showing data from the Disk Chopper Spectrometer](image2)

**Backscattering spectrometer**

![Diagram of Backscattering spectrometer with source, monochromator, sample, detector(s), and analyzer](image3)

\[
\frac{\delta E}{E} = \frac{2}{\delta d} + \frac{1}{4} (\delta \alpha)^2
\]

M. Birr et al, Nucl. Instr. Meth. 95, 435 (1971)

**The HFBS Spectrometer (NIST)**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength</td>
<td>6.271 Å</td>
</tr>
<tr>
<td>Neutron Energy</td>
<td>2.08 meV</td>
</tr>
<tr>
<td>Neutron Flux at Sample</td>
<td>$3 \times 10^9$ n cm$^{-2}$ s$^{-1}$</td>
</tr>
<tr>
<td>Energy range</td>
<td>$\pm 36$ μeV</td>
</tr>
<tr>
<td>Energy resolution at $\pm 36$ μeV</td>
<td>About 1 μeV</td>
</tr>
<tr>
<td>Analyzer Span</td>
<td>165°</td>
</tr>
<tr>
<td>Q range</td>
<td>$0.25$ Å$^{-1} - 1.75$ Å$^{-1}$</td>
</tr>
</tbody>
</table>

Spin echo spectrometer

The spin echo technique uses the precession of a neutron’s magnetic moment (spin) in a magnetic field as a “clock” to measure the neutron’s speed.

The neutron spins undergo many (of order $10^5$) turns in the precession coils.

In effect each spin is “wound up” in the first coil and “unwound” by the same amount in the second coil when the scattering is elastic.

If the scattering is inelastic, the “winding up” and “unwinding” processes do not completely cancel. The polarization of the neutron beam at the echo position is a measure of the inelasticity of the scattering.

\[
\phi = \gamma \frac{J_0}{v_0} \quad (J_t = \int B \, dl) \quad (\omega_x = \gamma B)
\]

\[
[\gamma = 1.83247185(43) \times 10^8 \text{ rad/s/T}]
\]

\[\Delta \phi = \frac{\gamma J_0}{v_0} - \frac{\gamma J_1}{v_1} \approx \gamma \frac{\delta \nu}{v_0} \frac{\delta J}{v_0} \]

At the echo condition $\delta J$ vanishes.

\[h \omega = \frac{1}{2} m \delta \left( v^2 \right) = m v_0 \delta v \quad v_0 = \frac{h}{m \lambda} \]

\[\Delta \phi \approx \gamma \frac{J_0}{v_0} \frac{h \omega}{m v_0} = t_i \omega \quad t_i = \gamma \frac{J_0 h}{m v_0} \]

\[P_x = \left< \cos (\Delta \phi) \right> \quad t_i = \frac{\gamma m^2}{2 \pi \hbar} J_0 \lambda^2 \]

\[= \frac{\int S(Q, \omega) \cos (t_i \omega) \, d\omega}{\int S(Q, \omega) \, d\omega} \frac{I(Q, t_i)}{I(Q, 0)} \]
Comparison of spectrometers

- **Resolution**
  TAS → TOF → BS → NSE
  Good → Very good → Excellent

- **Q and ω coverage**
  TOF has wide coverage in Q and ω,
  BS has wide Q coverage (but poor Q resolution), TAS/NSE are more restricted. BS has restricted ω range.

- **Coherent and incoherent scattering**
  NSE is best suited to measurements of coherent diffusive or dispersionless excitations at long times. Other forms of dynamical behavior (in the same time range) can be studied, but they are less straightforward.

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**How is QENS modeled?**

Separation of motions with different time scales
Vibrations (internal, external), translations
Local motions (local diffusion, reorientations)
Translational diffusion

It is generally assumed that motional time scales differ so much that the coupling between different types of motion can be neglected.

For example, consider vibrations and diffusion:

\[
I(Q, t) = I_v(Q, t) \cdot I_0(Q, t)
\]

\[
S(Q, \omega) = S_v(Q, \omega) \otimes S_D(Q, \omega)
\]

In this case the approximation is justified. On the other hand an equivalent approximation, separating translational and rotational diffusive motions, is less satisfactory.
Detailed balance and moment rules

\[ S(Q, -\omega) = e^{-\frac{h\omega}{k_B T}} S(Q, \omega) \]

Most model \(S(Q, \omega)\)'s do not satisfy these rules.

At sufficiently large \(Q\) and \(\omega\) the ideal gas scattering function applies.

\[ S_{ig}(Q, \omega) = \frac{1}{\sqrt{2\pi} \sigma} \exp\left[\frac{-(\omega - \Delta)^2}{2\sigma^2}\right] \]

\[ = \frac{1}{\sqrt{2\pi} \sigma} \exp\left[-\frac{\Delta^2}{2\sigma^2}\right] \exp\left[\frac{-\omega^2}{2\sigma^2}\right] \exp\left[\frac{h\omega}{2k_B T}\right] \]

\[ S_{ig}(Q, \omega) \text{ is Gaussian: unit area, width } \propto Q, \text{ shift } \propto Q^2 \]

### Popular models

**Long range continuous diffusion**

\[ I(Q, t) = \exp\left[-DQ^2 t\right] \]

and \(S(Q, \omega)\) is a Lorentzian:

\[ S(Q, \omega) = \frac{1}{\pi \omega^2 + \left[\Delta\omega(Q)\right]^2} \]

with \(\Delta\omega(Q) = DQ^2\)

**Spatially confined continuous diffusion on a sphere, radius \(r\)**


\[ S(Q, \omega) = j_0^2(Qr) \delta(\omega) + \sum_{\ell=1}^{\infty} j_\ell^2(Qr) \times \]

\[ \times \left(2\ell + 1\right) \frac{1}{\pi} \left[\ell\left(\ell + 1\right)D_R\right]^2 + (\hbar\omega)^2 \]

**Spatially confined jump diffusion**

(2 sites, separation \(d\))

\[ I(Q, t) = A_v(Q) + \left[1 - A_v(Q)\right] \exp\left(-2t/\tau\right) \]

\[ S(Q, \omega) = A_v(Q) \delta(\omega) + \left[1 - A_v(Q)\right] \frac{1}{\pi \omega^2 + \Gamma^2} \]

\[ A_v(Q) = \frac{1}{2} \left[1 + j_0(Qd)\right], \Gamma \text{ independent of } Q \]
The Elastic Incoherent Structure Factor (EISF)

\[ S(Q, \omega) = A_0(Q) \delta(\omega) + S_{\text{inel}}(Q, \omega) \]

\[ \int_{-\infty}^{\infty} S(Q, \omega) d\omega = 1 \]

\[ A_0(Q) = I(Q, \infty) = \frac{1}{2\pi} \int_{-\infty}^{\infty} G(r, \infty) \exp(-iQ \cdot r) dr \]

\[ A_0 = \frac{\text{elastic}}{\text{elastic + inelastic}} \]

\[ A_0(Q) = \frac{1}{N^2} \left| \sum_j \exp(iQ \cdot r_j) \right|^2 \]

- For long-range diffusion \( A_0 = 0 \) (except at \( Q = 0 \))
- For both long-range and restricted diffusion \( A_0 = 1 \) at \( Q = 0 \)
- For a continuous set of sites \( A_0 \to 0 \) at large \( Q \)
- For a discrete set of sites \( A_0 \to >0 \) at large \( Q \), e.g., \( A_0 \to 1/N \) for \( N \) equivalent sites.

Spatially confined jump diffusion

1. **Jumps among 2 sites (site separation \( d \))**

\[ S(Q, \omega) = \frac{1}{2} \left[ 1 + j_0(Qd) \right] \delta(\omega) + \frac{1}{2} \left[ 1 - j_0(Qd) \right] \frac{1}{1 + \omega^2 \tau^2} \]

2. **Jumps among 3 sites on a circle of radius \( r \)**

\[ S(Q, \omega) = \frac{1}{3} \left[ 1 + 2j_0\left( Qr / \sqrt{3} \right) \right] \delta(\omega) + \frac{2}{3} \left[ 1 - 2j_0\left( Qr / \sqrt{3} \right) \right] \frac{1}{1 + \omega^2 \tau^2} \]

3. **Jumps among \( N \) sites on a circle of radius \( r \)**

\[ S(Q_n, \omega) = A_0(Q) \delta(\omega) + \sum_{\ell=1}^{N} A_\ell(Q) \left( \frac{\tau_\ell}{1 + \omega^2 \tau_\ell^2} \right) \]

\[ \tau_\ell^{-1} = 2 \tau^{-1} \sin^2 \left( \frac{\pi \ell}{N} \right) \]

\[ A_\ell(Q) = \frac{1}{N} \sum_{n=1}^{N} j_0(Qr_n) \cos \left( \frac{2\ell \pi n}{N} \right) \]

\[ r_n = 2 \tau \sin \left( \frac{n\pi}{N} \right) \]
Examples of EISFs and widths

Practicalities ("caveat utor")

- Planning an experiment
  - Choice of spectrometer: match instrument/instrument setup (e.g. choice of wavelength) to time scale(s) of interest
  - Choice of sample shape: typically annular for TOF and BS - flat plate for TAS and NSE
    - Both geometries can be challenging, esp. annular powders, since optimum thicknesses are of order tenths of a mm
  - Choice of sample dimensions (consider self-shielding, multiple scattering)
Choice of spectrometer

Matching the instrument to time scale(s) of interest

\[ \text{(slow)} \rightarrow S(Q,\omega) \rightarrow \text{(fast)} \]

<table>
<thead>
<tr>
<th>Resolution</th>
<th>delta-function peak</th>
<th>Narrow peak</th>
<th>Medium width peak</th>
<th>Broad peak</th>
<th>Flat background</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low resn. (broad)</td>
<td>(Elastic)</td>
<td>Elastic</td>
<td>Match</td>
<td>Flat</td>
<td>(Flat)</td>
</tr>
<tr>
<td>Med. resn. (medium)</td>
<td>(Elastic)</td>
<td>Match</td>
<td>Flat</td>
<td>Flat</td>
<td>(Flat)</td>
</tr>
<tr>
<td>High resn. (narrow)</td>
<td>(Elastic)</td>
<td>Match</td>
<td>Flat</td>
<td>Flat</td>
<td>(Flat)</td>
</tr>
</tbody>
</table>

Multiple scattering and self-shielding

- For slab geometry self-shielding (SS) depends strongly on orientation; for annular geometry it is almost isotropic.
- The 90% transmission "rule of thumb":
  - The "rule" is that if T=90%, S1=10% and Sm/S1=10%, and if that is the case multiple scattering (MS) can be neglected.
  - The first part is valid for slab geometry, not necessarily valid for other geometries: for example, consider annular geometry with b=0.1 mm and R=10 mm, i.e. b/R = 0.01; if T=90%, S1=8.5% and Sm/S1 = 18%.
  - If indeed Sm/S1 = 10%, can neglect of MS be justified? What if Sm/S1 = 15%?
- If T is calculated what value should be used for \( \sigma_s \)?
  - In general \( \sigma_s \) depends on \( E_\infty \), T, chemistry, morphology, … See J.R.D. Copley, Neutron News, 18(1), 30 (2007).
### Multiple scattering

**Quotes from early papers**

“The average of distributions obtained at small angles of scattering (Q<1.4) was taken to be the multiple scattering component, …”

“The thickness of the water films ranged from 0.01 inches (~0.08 M.F.P.) to 0.035 inches (~0.3 M.F.P.) depending on the amount of multiple scattering which could be tolerated. … Multiple scattering was estimated roughly [ref.] as shown …”

**Quotes from more recent papers**

“Sample thicknesses were kept around 0.2 mm to achieve transmissions of ≈90% and avoid multiple scattering effects.”

“The sample thickness was chosen to ensure 90% neutron transmission and thus minimize multiple scattering effects.”

“… sample holders chosen to ensure greater than 90% neutron beam transmission through the sample in order to minimize the effects of multiple scattering …”

“The multiple scattering was minimized using a small thickness for the sample, which was also confirmed by a transmission higher than 0.9.”

“Total neutron scattering from the samples was ~10%; thus, multiple scattering was negligible, …”

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### Total scattering cross sections

- Total scattering cross sections vary with incident energy, temperature, morphology, and chemical environment (not just chemical composition)
- Total scattering cross sections vary as 1/ν at sufficiently long wavelengths (as do absorption cross sections)

\[
\sigma_S(E_0) = \int \int \frac{d^2\sigma}{d\Omega dE_f} dE_i d\Omega \\
\propto \frac{1}{E_0} \int_{\text{KAR}(E_0)} S(Q,\omega) Q d\omega
\]
Practicalities (contd.)

• Performing the experiment
  – What to run, apart from the sample(s), and how to divide the time?
    • Empty can? Empty cryostat/CCR?
    • Elastic scatterer (for detector efficiencies, normalization, resolution)?
    • Time-independent background (“dark count”)?
  – Choices of wavelength, resolution, dynamic range etc.

• Data treatment (“postparation”)
  – The options available for data treatment depend on how the experiment was planned and performed.
  – Keep in mind:
    • the resolution-limited “elastic” scattering may include elastic scattering from host material in the sample, and other sources, as well as QENS due to motions too slow to be distinguished from truly elastic scattering
    • The flat “background” may include true background as well as QENS from motions too fast to be detected as such
  – When subtracting the empty can, consider the attenuating effect of the sample
Examples of QENS

- Water
- Cubane
- Liquid lead
- C₆₀


Liquid water


Fig. 1. The scattering function $S(Q,ω)$ for water (a) at 25°C and (b) at 75°C for small values of $ω$. The energy resolution functions are shown as dashed curves. The multiple-scattering $Δω$ which was subtracted is also shown.
Cubane, $\text{C}_8\text{H}_8$

Phase transition, from orthorhombic ($\alpha=73^\circ$) to orthorhombic ($\alpha=103^\circ$) at 394K. Melting at 405K.

T. Yildirim et al, PRB 60, 314 (1999)

Liquid lead

B.N. Brockhouse and N.K. Pope, PRL 3, 259 (1959)

S($Q,\omega$)

FIG. 1. A selection of energy distribution of neutrons scattered from liquid lead at 640K, each with its resolution function (appropriate to the incident energy). All patterns have been corrected for background, for container scattering, for instrument sensitivity, and all except (a) or multiple scattering. (Figure 1 (a) is thought to contain - 10% multiple scattering.) The factor $K^2\rho$ of Eq. (2) has also been removed. Figures 1 (a), (d), and (e) show energy distributions obtained under different resolutions of the main diffraction peak. In Fig. 1(b) the resolution function has been normalized at the peak to illustrate the energy broadening. Figures 1(a) and (b) are in agreement that the half-width at half maximum of the distribution is $\sim 3.5 \times 10^{-4}$ ev, compared with the $8 \times 10^{-4}$ ev expected on simple arguments of diffusion broadening by small scattering lengths.
**Liquid lead**

- $I(Q,t) \times t$ (times $t$ in 0.1ps)
- $G(r,t)$

**Ideal gas**

- FIG. 3. A selection of smoothed curves of $G(Q,t)$ vs $Q$, and curves of $I(Q,t)$ vs $Q$ for values of $t$, 0, 1, 2, 6, and $2 \times 10^{-10}$ sec.
- The closed circles in Figs. 2(a) show the experimental points for the integrated intensities $I(Q,t)$ of Series I. The open circles in Fig. 3(a) show values of $G(Q,0)$ calculated following Eq. (a).
- Note that the left-hand scales in Figs. 1(a) and (b) apply to the self-correlation functions.

**Buckminsterfullerene, C$_{60}$**

- An orientational order-disorder phase transition occurs at $\approx 255$K.
- N.B. Jumps among equivalent orientations produce no (coherent) intensity.
- D.A. Neumann et al, JCP 96, 8631 (1992)
Further reading

- Proceedings of QENS conferences (next slide)

Recent QENS Conferences/Proceedings

- **QENS 2000:** Physica B: 301, Issues 1-2, July 2001
- **QENS 2009:** to be held 2/10-13/09 at the Paul Scherrer Institut, Switzerland.