Quasielastic Neutron Scattering

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June 23, 2014
OUTLINE

• Background – the incoherent scattering cross section of H
• Neutrons and QENS
• Experiment Design
• Connection to Molecular Dynamics Simulations
• The Elastic Incoherent Structure Factor (EISF)
• The Role of Instrumentation
• Restricted Diffusion Example – Tethered Molecules
• References and Summary
Incoherent and Coherent Scattering

• **Origin** – incoherent scattering arises when there is a random variability in the scattering lengths of atoms in your sample – can arise from the presence of different isotopes or from isotopes with non-zero nuclear spin combined with variation in the relative orientation of the neutron spin with the nuclear spin of the scattering center.

• **Coherent scattering** – gives information on spatial correlations and collective motion.
  – Elastic: Where are the atoms? What are the shape of objects?
  – Inelastic: What is the excitation spectrum in crystalline materials – e.g. phonons?

• **Incoherent scattering** – gives information on single-particles.
  – Elastic: Debye-Waller factor, # H-atoms in sample, Elastic Incoherent Structure Factor – geometry of diffusive motion (continuous, jump, rotations)
  – Inelastic: diffusive dynamics, diffusion coefficients.

• **Good basic discussion:**
  – “Methods of x-ray and neutron scattering in polymer science”, R.-J. Roe, Oxford University Press. (available)
Neutron Properties – H is our friend!

- **Isotopic sensitivity of H**
  - H has a large *incoherent* neutron scattering cross-section
  - H and D have opposite signed scattering lengths
  - D has a much smaller cross section

- The signal from samples with H are often dominated by the *incoherent* scattering from H

- The $Q$ and $\omega$ ranges probed in QENS experiments is well-suited to the “self” part of the *dynamic structure factor*
Quasi-elastic Neutron Scattering (Why Should I Care?)

• Applicable to wide range of science areas
  – Biology – water-solvent mediated dynamics
  – Chemistry – complex fluids, ionic liquids, porous media, surface interactions, water at interfaces, clays
  – Materials science – hydrogen storage, fuel cells, polymers, proton conductors

• Probes true “diffusive” motions

• Range of analytic function models
  • Useful for systematic comparisons

• Close ties to theory – particularly Molecular Dynamics simulations

• Complementary
  • Light spectroscopy, NMR, dielectric relaxation

• Unique – Answers Questions you cannot address with other methods

![Bar chart showing the number of publications from 2004 to 2013 involving Neutron AND (QENS OR quasi-elastic OR quasilastic).]
A Neutron Experiment

Measure scattered neutrons as a function of $Q$ and $\omega \rightarrow S(Q, \omega)$.

- $\omega = 0 \rightarrow$ elastic
- $\omega \neq 0 \rightarrow$ inelastic
- $\omega$ near 0 $\rightarrow$ quasielastic

Energy $E = \frac{(\hbar k)^2}{2m_n}$

Energy Transfer $= \hbar \omega = E_i - E_f$

\[
Q \propto \frac{1}{\text{Length}}
\]

\[
\omega \propto \frac{1}{\text{Time}}
\]
Quasi-Elastic Neutron Scattering

- Neutron exchanges small amount of energy with atoms in the sample
- Harmonic motions look like flat background
- Vibrations are often treated as Inelastic Debye-Waller Factor
- Maximum of intensity is always at $\omega = 0$
- Samples the component of motion along $\mathbf{Q}$
- Low-Q – typically less than 5 Å$^{-1}$
Experiment Design

- $\sigma$ is the microscopic cross section (bn/atom) $10^{-24}$ cm$^2$/atom
- $n$ is the number density (atom/cm$^3$)
- $\Sigma$ is the macroscopic cross-section (cm$^{-1}$)

\[
\Sigma = n \sigma
\]

The transmission, $T$, depends on sample thickness, $t$, as:

\[
T = \exp(-\Sigma t)
\]

- Good rule of thumb is $T = 0.9$

**5 – 15 mmole H-atoms for ≈10 cm$^2$ beam (BaSiS, HFBS, CNCS, DCS)**
An Example – Water

\[
n = \frac{1 \text{ gm}}{\text{cm}^3} \times \frac{1 \text{ mole}}{18 \text{ gm}} \times \frac{6.02 \times 10^{23}}{\text{mole}} = \frac{3.34 \times 10^{22}}{\text{cm}^3}
\]

\[
\sigma = 2 \times \left(80 \times 10^{-24} \text{ cm}^2\right)
\]

\[
\Sigma = \sigma n = \frac{5.34}{\text{cm}}
\]

sample thickness = \[ t = \frac{-\ln(0.9)}{5.34} = 0.2 \text{ mm} \]
QENS Spectra

The QENS spectra is typically divided into three regions:

1. **Elastic** (broadened by instrument resolution)
2. **Quasielastic**
3. **Inelastic**

The slowest time is set by the width of the instrument resolution, while the fastest time is set by the dynamic range of the instrument ($\omega_{\text{max}}$).
Incoherent Intermediate Scattering Function, \( S(Q,\omega) \), and Molecular Dynamics Simulations

- **Intermediate Scattering Function**
  - time dependent correlation function
  - incoherent scattering \( \rightarrow \) no pair correlations, self-correlation function
  - calculable from atomic coordinates in a Molecular Dynamics Simulation

\[
I_{inc}(Q,t) = \frac{1}{N} \sum_i \langle \exp\{iQ \cdot R_i(t)\} \exp\{-iQ \cdot R_i(0)\} \rangle
\]

- \( S_{inc}(Q,\omega) \) – the Fourier transform of \( I_{inc}(Q,t) \)

\[
S_{inc}(Q,\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} I_{inc}(Q,t) \exp(-i\omega t) dt
\]
QENS and Molecular Dynamics Simulations

• Same atomic coordinates used in classical MD are all that is needed to calculate \( I_{inc}(Q,t) \)

1,3 diphenylpropane tethered to the pore surface of MCM-41
The Elastic Incoherent Structure Factor (EISF)

- A particle (H-atom) moves out of volume defined by $2\pi/Q$ in a time shorter than set by the reciprocal of the instrument sensitivity, $d\omega$(meV) – gives rise to quasielastic broadening.

- The EISF is essentially the probability that a particle can be found in the same volume of space at some subsequent time.

- The ratio of the Elastic Intensity to the total Intensity

$$EISF = \frac{A_E}{A_E + A_Q}$$
QENS and Neutron Scattering Instruments

• Probe Diffusive Motions
  – Length scales set by Q, $0.1 \, \text{Å}^{-1} < Q < 3.7 \, \text{Å}^{-1}$, $60 \, \text{Å} > d > 1.7 \, \text{Å}$.
  – Time scales set by the width of instrument energy resolution, typically at least $0.1 \, \text{meV}$ (fwhm) but higher resolution → longer times/slower motion.

• Energy transfers ~ ± 2 meV (or less)
  – High resolution requirements emphasizes use of cold neutrons (but long $\lambda$ limits Q).
  – Incident neutron wavelengths typically 4 Å to 12 Å (5.1 meV to 0.6 meV).

• Why a variety of instruments? (Resolutions vary from 1 μeV to 100 μeV)
  – Terms in the resolution add in quadrature – typically primary spectrometer (before sample), secondary spectrometer (after the sample).
  – Improvement in each resolution term cost linearly in neutron flux (ideally).
  – Optimized instrument has primary and secondary spectrometer contributions approximately equal.
  – Factor of 2 gain in resolution costs at a minimum a factor of 4 in flux.
Role of Instrumentation

• Currently about 25 neutron scattering instruments in the world useful for QNS (6 in the U.S., including NSE)

• U.S. instruments – **Opportunity is Good- Competition is High**
  – NIST Center for Neutron Research
    • Disc Chopper Spectrometer
    • High Flux Backscattering Spectrometer
    • Neutron Spin Echo
  – Spallation Neutron Source
    • BaSiS – near backscattering spectrometer (3 μeV)
    • Cold Neutron Chopper Spectrometer (CNCS) (10 – 100 μeV)
    • Neutron Spin Echo (t to 400 nsec)

• Trade-offs
  – Resolution/count rate
  – Flexibility
  – Dynamic range
  – Neutron $\lambda$ vs Q
    • large $\lambda$ --> high resolution -> long times/slow motions
    • large $\lambda$ --> limited Q-range, limited length scales
The High-Resolution Neutron Spectrometer Landscape

- Cold Neutron Chopper
- Neutron Spin Echo
- Backscattering

- Molecules in Confinement
- Small Molecule Diffusion
- Colloids/Complex Fluids
- Polymers and Proteins

Graph showing the relationship between wave vector (Q) and momentum transfer (ω) for different spectrometers.
Restricted Diffusion – Tethered Molecules

Samples – typical 0.7 g
240 K < T < 340 K

Simple Fit – Lorentzian + $\delta$

<table>
<thead>
<tr>
<th>Pore Diameter (nm)</th>
<th>Coverage (molecules/nm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.6</td>
<td>0.85 (saturation)</td>
</tr>
<tr>
<td>2.1</td>
<td>1.04 (saturation)</td>
</tr>
<tr>
<td>3.0</td>
<td>0.60</td>
</tr>
<tr>
<td></td>
<td>0.75</td>
</tr>
<tr>
<td></td>
<td>1.61 (saturation)</td>
</tr>
</tbody>
</table>

MCM-41 (2.9 nm pore diameter)
high DPP coverage
Elastic Scans – Fixed Window Scans

Coverage Dependence

Pore Size Dependence

Onset of diffusive motion giving rise to QENS signal (typically)

\[ I(Q) = I(0) \exp \left( -\frac{Q^2 \langle u^2 \rangle}{3} \right) \]

Onset of diffusive and anharmonic motion (\(T_T\))
Elastic Scans
Fixed Window Scans

- $T_T$
  - No dependence on DPP surface coverage at 3.0 nm pore diameter ($\approx 130$ K)
  - 196 K for 2.1 nm pore (maximum DPP surface coverage) – Deeper potential

- Simulations indicate that at 2.1 nm (2.2 nm) DPP molecules adopt a conformation that has a more uniform density throughout the pore volume

- Large pores have enough surface area for DPP to orient near the MCM-41 surface
Simple Fit to data (HFBS – NCNR) 30 Å diameter pore, 320 K, Q = 1 Å⁻¹

\[ EISF = \frac{A_E}{A_E + A_Q} \]
EISF – 30 Å DPP sample, saturation

Curvature determines $R_{\text{max}}$

Non-zero asymptote implies immobile H-atoms (on the time scale of this instrument)
Lorentzian $\Gamma(Q)$

Non-zero intercept

*Implies*

*restricted/confined diffusion*
Simple Analytical Model – e.g. Diffusion in a Sphere

\[ S_s(Q, \omega, r, D) = A_0^0(Qr)\delta(\omega) + \frac{1}{\pi} \sum_{(l,n) \neq (0,0)} (2l+1) A_n^l(Qr) \left( \frac{x_n^l}{r} \right)^2 \frac{D}{r^2} + \omega^2 \]

EISF: \[ A_0^0(Q) = \left[ \frac{3j_1(Qr)}{Qr} \right]^2 \]

Extend to a Sum over Spheres of Varying Size (15 H-atoms)

\[ S_{DPP}(Q, \omega) = \sum_{i=1}^{15} S_s(Q, \omega, R_i, D_i) \]

\[ R_i = R_{\text{max}} \times \frac{L_i}{L_{\text{natom}}} \]

\[ S(Q, \omega) = \left( C_0(Q) + C_1(Q) e^{-Q^2 \langle u^2 \rangle/3} \right) \delta(\omega) + C_2 e^{-Q^2 \langle u^2 \rangle/3} \sum_{i=1}^{15} S_s(Q, \omega, R_i, D_i) \]

Fraction of DPP H-atoms moving on time scale of instrument

\[ f_m = \frac{C_2}{C_1 + C_2} \]

Fits to Data

MCM-41
DPP – 29 Å diameter pores – 370 K
(BaSiS - SNS) – Beyond the EISF – Fitting the Model to the Full Data Set
$R_M$ – How extended is the motion?

- $R_M$ decreases with increasing pore diameter! (Molecules can interact with surface)
- $R_M$ generally is larger at higher DPP surface coverage (Molecules are excluded from surface)
- Small pores and high coverage tend to drive DPP into the pore center where there is more volume available for motion
$D_M$ – How fast is the motion?

- $D_M$ increases with pore diameter while the radius decreases
  - Diffusion in the pore volume depends on how crowded it is

- $D_M$ increases with surface coverage in large pores
  - More molecules are forced into the more open volume of the pore and away from the pore surface
Two Instruments – Two Resolutions – Two Dynamic Ranges – 3.0 nm 320 K

HFBS (1 µeV, ±17.5 µeV)  
BaSiS (3 µeV, -100 to 300 µeV)

Two Instruments

Dynamics

• Similar activation energies
• Different magnitudes

Geometry – nearly identical – determined by intensity measurements

\[
E_A = 10.2 \pm 0.9 \text{ kJ/mol}
\]

\[
E_A = 8.4 \pm 0.9 \text{ kJ/mol}
\]
Example 2: Dendrimers – Colloidal Polymer – pH responsive

Dendrimers bind to receptors on HIV virus preventing infection of T cells. SharpharpmC & E News 83, 30 (2005)

“Trojan horse” – folic acid adsorbed by cancer cell delivering the anti-cancer drug as well
James R. Baker Jr., Univ. of Michigan Health Sciences Press Release
SANS Results – Global Size Constant, Redistribution of Mass

Samples: 0.05 gm protonated dendrimer in 1 ml deuterated solvent

Molecular Dynamics Simulations

Basic

Acidic

High pH
Neutral pH
Low pH

pH decreases

Dense Core

Dense Shell
Methodology

• Determine center-of-mass translational motion with pulsed field-gradient spin echo NMR
  – Could have been determined directly from QENS measurement but this tied down parameter set

• Measure (dendrimer + deuterated solvent) – (deuterated solvent) -> dendrimer signal

• Vary pH to charge dendrimer amines \( \alpha = 0 \) (uncharged), \( \alpha = 1 \) (primary amines charged), \( \alpha = 2 \) (fully charged))

\[
S(Q, \omega) = S_{\text{int}}(Q, \omega) \otimes S_{\text{COM}}(Q, \omega)
\]

modeled localized internal motion as

\[
S_{\text{int}}(Q, \omega) = A_0^0(Qr)\delta(\omega) + \frac{1}{\pi} \sum_{(l,n) \neq (0,0)} (2l + 1) A_n^l(Qr) \frac{(x_n^l)^2 D}{r^2} \left[ \frac{(x_n^l)^2 D}{r^2} \right]^2 + \omega^2
\]
Localized Motion of Dendrimer Arms

Localized motion modeled as Diffusion in a Sphere


Localizes motion increases as amines are charged!

\[ R \sim 2.8 \, \text{Å}, \, \alpha \, \text{independent} \]

\[
\begin{align*}
D_{\alpha = 0} &= 1.60 \pm 0.03 \times 10^{-10} \, \text{m}^2/\text{s} \\
D_{\alpha = 1} &= 2.58 \pm 0.03 \times 10^{-10} \, \text{m}^2/\text{s} \\
D_{\alpha = 2} &= 3.11 \pm 0.03 \times 10^{-10} \, \text{m}^2/\text{s}
\end{align*}
\]
Reference Materials - 1

• Reference Books
  – *Quasielastic Neutron Scattering*, M. Bee (Bristol, Adam Hilger, 1988).
Reference Materials - 2

- Classic Papers
  - L. Van Hove
    - Phys. Rev. 95, 249 (1954)
    - Phys. Rev. 95, 1374 (1954)
  - V. F. Sears
    - Canadian J. Phys. 44, 867 (1966)
    - Canadian J. Phys. 44, 1279 (1966)
    - Canadian J. Phys. 44, 1299 (1966)
  - G. H. Vineyard
    - Phys. Rev. 110, 999 (1958)
  - S. Chandrasekhar
    - “Stochastic Problems in Physics and Astronomy”, Rev. Mod. Phys. 15, 1 (1943) (not really QNS but great reference on diffusion models)

- Data Analysis – DAVE – NIST Center for Neutron Research
  http://www.ncnr.nist.gov/dave/
SUMMARY

• QENS is an excellent technique to measure diffusive dynamics
  – Length scales/geometry accessible through Q-dependence
  – Many analytic models form a framework for comparison and parametric studies
  – Large range of time scales (sub-picosecond < t < nanosecond (100’s nsec for NSE)
  – H-atom sensitivity

• Instrument selection is a critical decision – the resolution must match the time scale of the expected motion

• World-class instrumentation is currently available in the U.S.

• Natural connection to theory (Molecular Dynamics Simulations)

• Analysis Software – DAVE at the NCNR at NIST – available from the NCNR Web site