Quasielastic Neutron Scattering

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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

• **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 – dynamic transition in proteins, hydration water
  - Chemistry – complex fluids, ionic liquids, porous media, surface interactions, water at interfaces, clays
  - Materials science – hydrogen storage, fuel cells, polymers

- 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
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

$k = \frac{2\pi}{\lambda}$

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

$\vec{Q} = \vec{k}_i - \vec{k}_f$

Energy Transfer $= \hbar \omega = E_i - E_f$
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 $Q$
- Low-Q – typically less than 5 Å$^{-1}$
Experiment Design

• $\sigma$ is the microscopic cross section (bn/atom) $10^{-24}$ cm$^2$
• $n$ 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:

$$T = \exp\left(-\Sigma t\right)$$

• Good rule of thumb is $T = 0.9$

$5 - 15$ mmole H-atoms for $10$ cm$^2$ beam

$(\text{BaSiS}, \text{HFBS}, \text{CNCS}, \text{DCS})$
An Example – Water

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

\[
\sigma = 2 \times 8.0 \times 10^{-24} \text{ cm}^2
\]

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

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

![QENS Spectra Diagram](image)

- **Intensity (counts/\(\mu\)eV)**
- **Energy transfer (\(\omega (\mu\)eV))**

- **Elastic**
- **Quasielastic**
- **Inelastic**

\(\omega < 0\), \(\omega = 0\), \(\omega > 0\)
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

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

- $S_{inc}(Q, \omega)$ -- 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, \(d\omega(\text{meV})\) – 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
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 $\sim \pm 2 \text{ meV (or less)}$
  – High resolution requirements emphasizes use of cold neutrons (but long $\lambda$ limits Q).
  – Incident neutron wavelengths typically $4 \text{ Å}$ to $12 \text{ Å}$ ($5.1 \text{ meV}$ to $0.6 \text{ meV}$).

• Why a variety of instruments? (Resolutions vary from $1 \text{ μeV}$ to $100 \text{ μeV}$)
  – 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 1-2 μsec)

• 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

- Backscattering
- Cold Neutron Chopper
- Neutron Spin Echo

Managed by UT-Battelle for the U.S. Department of Energy
BaSiS - SNS Near Backscattering Spectrometer
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 0.75 1.61 (saturation)</td>
</tr>
</tbody>
</table>

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

Coverage Dependence

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

Onset of diffusive and anharmonic motion

Pore Size Dependence
What if I don’t have Molecular Dynamics or other Theory?
Simple Analytical Model – e.g. Diffusion in a Sphere

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

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)

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

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

\[
EISF(Q) = (1 - f_m) + f_m \times \frac{1}{15} \sum_{i=1}^{15} \left[ \frac{3j_1(QR_i)}{QR_i} \right]^2
\]

\[
S(Q, \omega) = A(Q)\delta(\omega) + (1 - A(Q)) \times \text{Lorentzian}
\]

\[
EISF(Q) = A(Q)
\]
Fit to data (HFBS – NCNR) 30 Å diameter pore, 320 K, Q = 1 Å\(^{-1}\)
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)
30 Å DPP sample, saturation

![Graph showing the relationship between temperature (T) and Rmax](image-url)
Lorentzian $\Gamma(Q)$

Non-zero intercept

Implies

restricted/confined diffusion
DPP – 29 Å diameter pores – 370 K
(BaSiS - SNS) – Beyond the EISF – Fitting
the Model to the Full Data Set
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

Geometry – nearly identical – determined by intensity measurements

Dynamics
- Similar activation energies
- Different magnitudes

\[
\ln[D_M (10^{-8} \text{ cm}^2 \text{ sec}^{-1})] = E_A = 10.2 \pm 0.9 \text{ kJ/mol}
\]

\[
R_M (\text{Å})
\]

\[
f_m
\]

\[
d = 3.0 \text{ nm}; 1.61 \text{ DPP/nm}^2
\]
\[
d = 2.8 \text{ nm}; 0.84 \text{ DPP/nm}^2
\]
\[
d = 3.0 \text{ nm}; 0.75 \text{ DPP/nm}^2
\]
Example 2: Dendrimers – Colloidal Polymer – pH responsive

Dendrimers bind to receptors on HIV virus preventing infection of T cells. SharpPharm C & 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

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

Localized motion modeled as Diffusion in a Sphere

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

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

Localized motion increases as amines are charged!
Reference Materials

- 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
  – Large range of time scales (sub-picosecond < t < nanosecond (μsec 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)

• Software – DAVE at the NCNR at NIST – available from the NCNR Web site
  – Need much closer coupling to theoretical modeling, especially molecular dynamics simulations – coherent QNS