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 ω 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, 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
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) \( 10^{-24} \text{ cm}^2/\text{atom} \)
- \( n \) 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:

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

- Good rule of thumb is \( T = 0.9 \)

5 – 15 mmole H-atoms for \( \approx 10 \text{ cm}^2 \) 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

Intensity (counts/µeV)

Energy transfer (ω (µeV))

ω<0  0  ω>0

elastic (broadened by instrument resolution)

inelastic

quasielastic
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 meV (fwhm) but higher resolution \( \rightarrow \) 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 Å to 12 Å (5.1 meV to 0.6 meV)

• Why a variety of instruments? (Resolutions vary from 1 \( \mu \text{eV} \) to 100 \( \mu \text{eV} \))
  – 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 λ vs Q
    - large λ → high resolution -> long times/slow motions
    - large λ → limited Q-range, limited length scales
The High-Resolution Neutron Spectrometer Landscape

- Cold Neutron Chopper
- Neutron Spin Echo
- Backscattering
**Restricted Diffusion – Tethered Molecules**

**Samples** – typical 0.7 g

\[ 240 \, \text{K} < T < 340 \, \text{K} \]

**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

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

Onset of diffusive and anharmonic motion

Pore Size Dependence
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

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

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)

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

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

\[ S(Q, \omega) = \left( C_0(Q) + C_1(Q)e^{-Q^2\langle u^2 \rangle/3} \right) \delta(\omega) + C_2e^{-Q^2\langle u^2 \rangle/3} \sum_{i=1}^{15} S_s(Q, \omega, R_i, D_i) \]

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

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

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!
- $R_M$ generally is larger at higher DPP surface coverage
- Small pores and high coverage tend to drive DPP into the pore center where there is more volume available for motion

Partially folded DPP O – terminal H distance 5.9 Å

Extended DPP O – terminal H distance 12 Å

$\beta$-cristobailite

Maximal DPP coverage

$R_M$ (Å)

$\begin{array}{c|c|c|c|c|c|c|c|c} d (\text{nm}) & 1.4 & 1.6 & 1.8 & 2.0 & 2.2 & 2.4 & 2.6 & 2.8 & 3.0 & 3.2 \\
\hline R_M (\text{Å}) & 6.2 & 5.8 & 5.5 & 5.2 & 4.9 & 4.6 & 4.3 & 4.0 & 3.7 & 3.4 \\
\end{array}$

Coverage (DPP/nm$^2$)
$D_M$ – 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

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

\[ E_A = 8.4 \pm 0.9 \text{ kJ/mol} \]

\[ \ln[D_M (10^{-8} \text{ cm}^2/\text{sec})] \]

\[ R_M (\text{Å}) \]

\[ f_m \]

\begin{align*}
\circ & \quad d = 3.0 \text{ nm}; 1.61 \text{ DPP/nm}^2 \\
\bullet & \quad d = 3.0 \text{ nm}; 0.75 \text{ DPP/nm}^2 \\
\square & \quad d = 2.8 \text{ nm}; 0.84 \text{ DPP/nm}^2
\end{align*}
Example 2: Dendrimers – Colloidal Polymer – pH responsive

Dendrimers bind to receptors on HIV virus preventing infection of T cells. Sharpharm 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
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

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

Localized motion modeled as Diffusion in a Sphere

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

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

Localized motion increases as amines are charged!

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