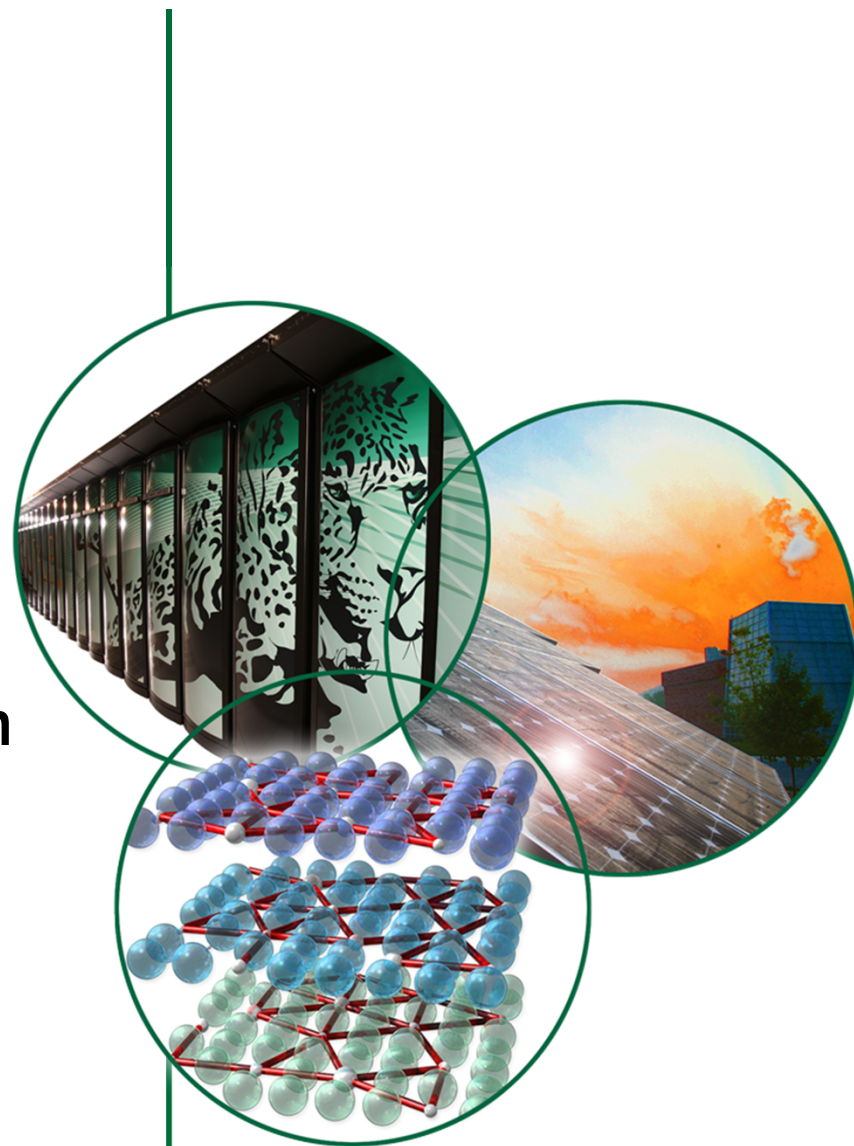# Quasielastic Neutron Scattering

Ken Herwig

Instrument and Source Design Division
**Oak Ridge National Laboratory**

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**

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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

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

- <u>Incoherent scattering</u> – gives information on <u>single-particles</u>.
  - 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)
  - "Theory of Thermal Neutron Scattering", W. Marshall and S. W. Lovesey, Oxford University Press (1971). (out of print)

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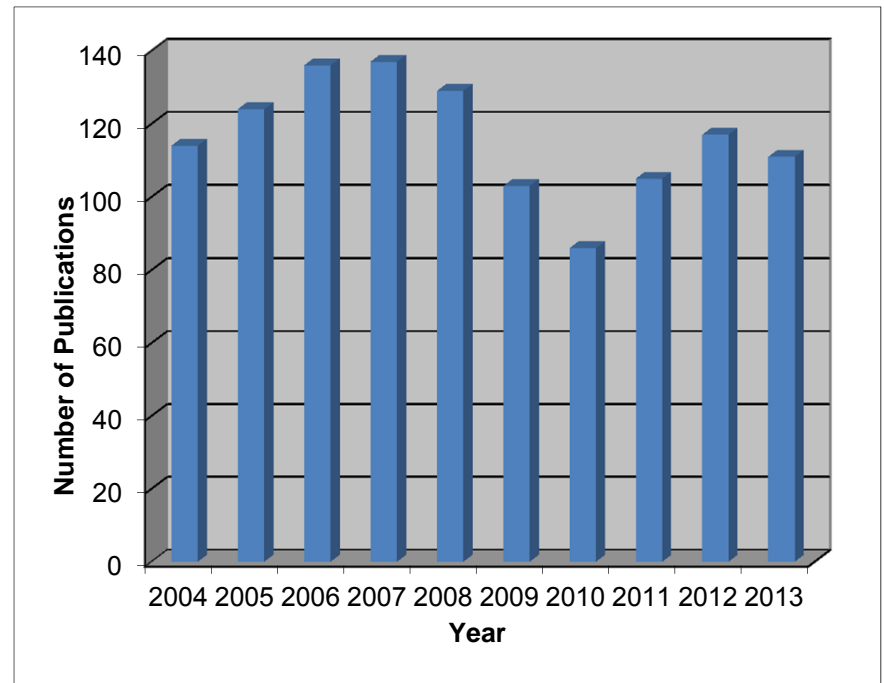
Neutron Properties – H is our friend!
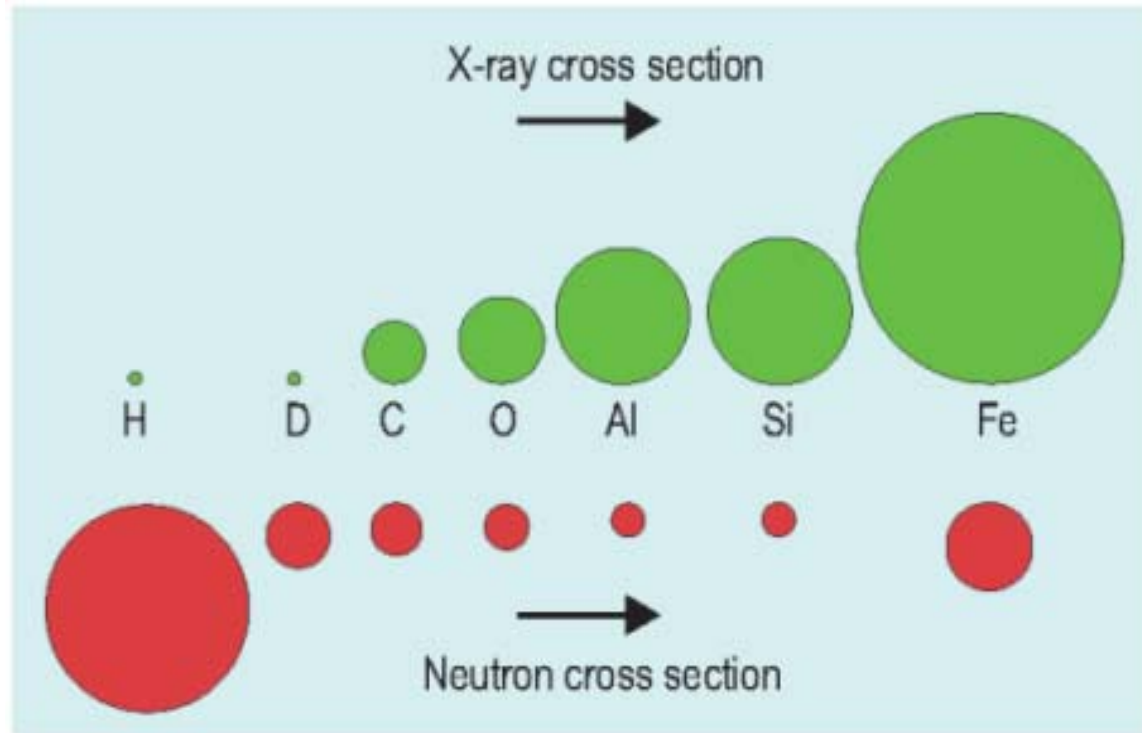
- **Isotopic sensitivity of H**

  – 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**
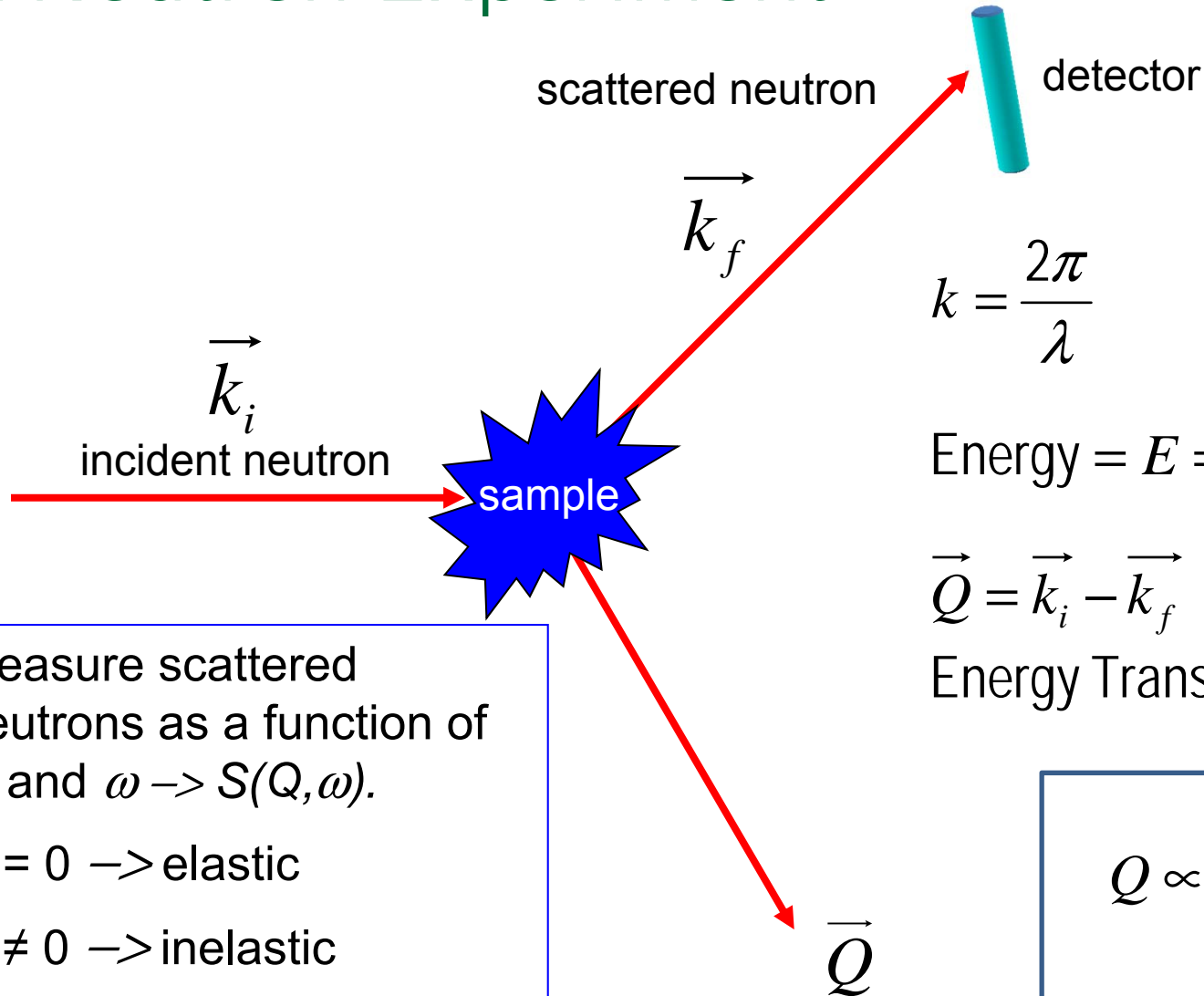
Quasi-elastic Neutron Scattering (Why Should I Care?)

- **Applicable to wide range of science areas**
  - Biology – 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**

Neutron AND (QENS OR quasi-elastic OR quasielastic)

A Neutron Experiment

scattered neutron   detector

$\overrightarrow{k}_f$

incident neutron $\overrightarrow{k}_i$

sample

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

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

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

$$\text{Energy Transfer} = \hbar\omega = E_i - E_f$$

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

$\omega = 0 \rightarrow$ elastic

$\omega \neq 0 \rightarrow$ inelastic

ω near 0 $\rightarrow$ quasielastic

$\overrightarrow{Q}$

$$Q \propto \frac{1}{\text{Length}}$$

$$\omega \propto \frac{1}{\text{Time}}$$

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Quasi-Elastic Neutron Scattering
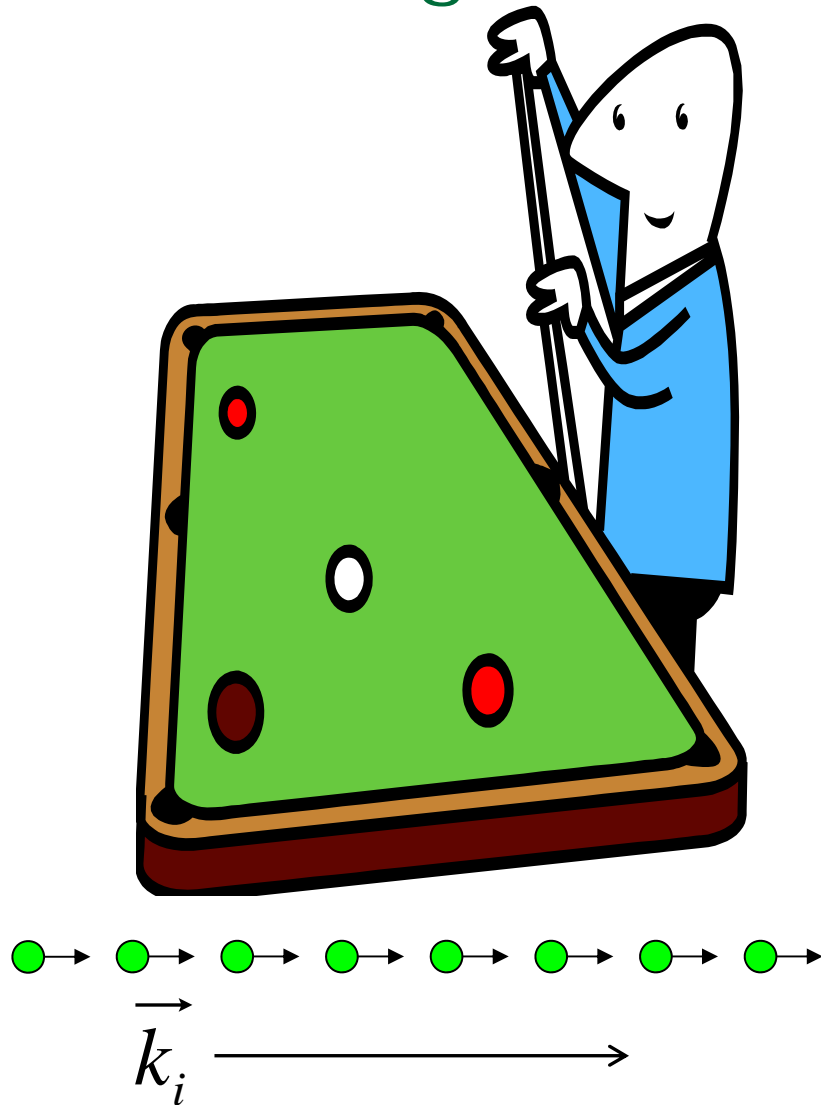
- Neutron exchanges small amount of energy with atoms in the sample

- 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 $\vec{Q}$

- Low-Q – typically less than 5 Å^{-1}

$\vec{k}_f$

$\vec{k}_i$

National x-ray/ne
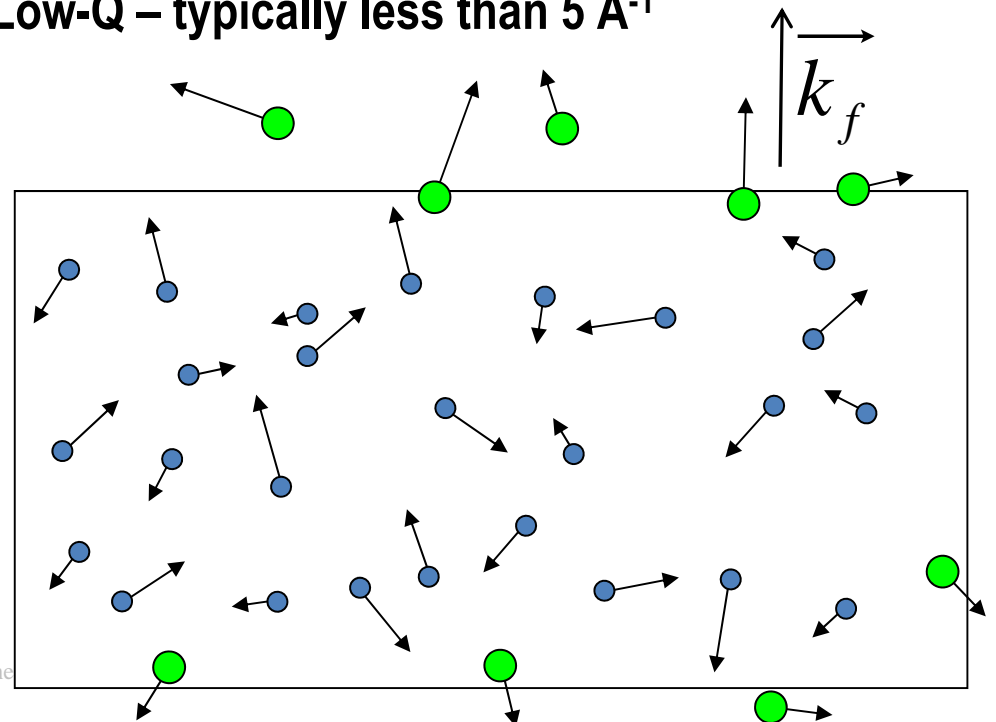
Experiment Design

- σ is the microscopic cross section (bn/atom) 10^{-24} cm^2/atom

- n is the number density (atom/cm^3)

- Σ 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 $T = 0.9$

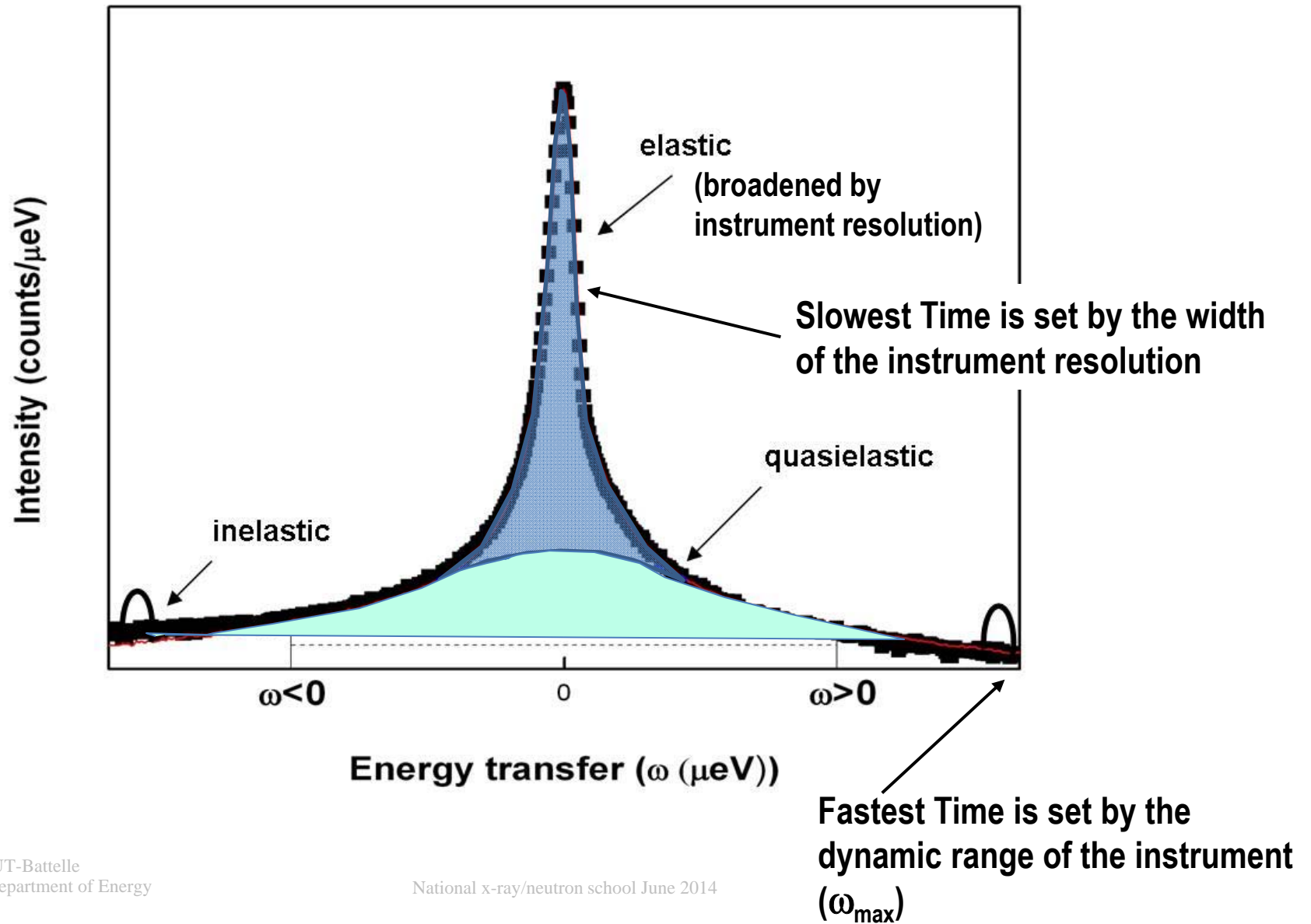### 5 – 15 mmole H-atoms for ≈ 10 cm^2 beam (BaSiS, HFBS, CNCS, DCS)

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An Example – Water

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

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

$$\Sigma = \sigma n = \frac{5.34}{\text{cm}}$$

$$\text{sample thickness} = t = \frac{-\ln(0.9)}{5.34} = 0.2 \text{ mm}$$

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QENS Spectra

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Incoherent Intermediate Scattering Function, *S(Q,ω)*, and Molecular Dynamics Simulations

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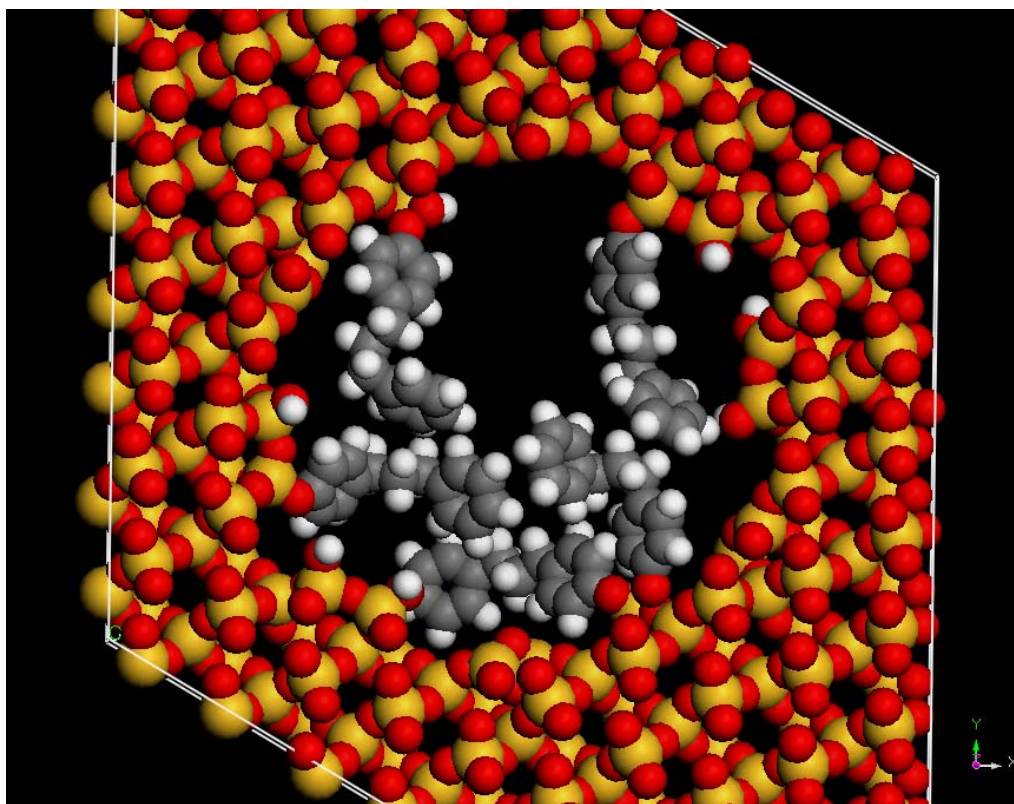 - calculable from atomic coordinates in a Molecular Dynamics Simulation

$$I_{inc}(\mathbf{Q},t) = \frac{1}{N}\sum_i \left\langle \exp\{i\mathbf{Q}\bullet\mathbf{R}_i(t)\}\exp\{-i\mathbf{Q}\bullet\mathbf{R}_i(0)\}\right\rangle$$

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

$$S_{inc}(\mathbf{Q},\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} I_{inc}(\mathbf{Q},t))\exp(-i\omega t)dt$$

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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

12   Managed by UT-Battelle
      for the U.S. Department of Energy
                              National x-ray/neutron school June 2014
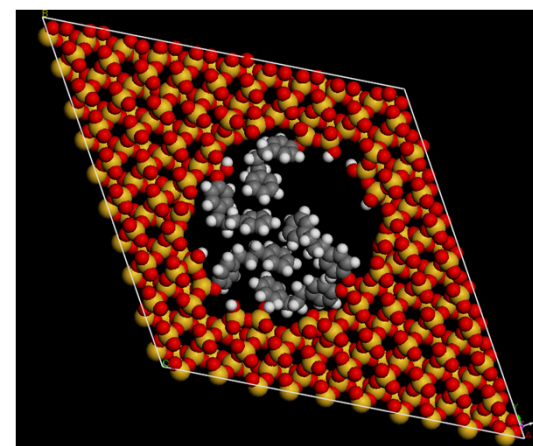
The Elastic Incoherent Structure Factor (EISF)

- 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

$$EISF = \frac{A_E}{A_E + A_Q}$$

$2\pi/Q$

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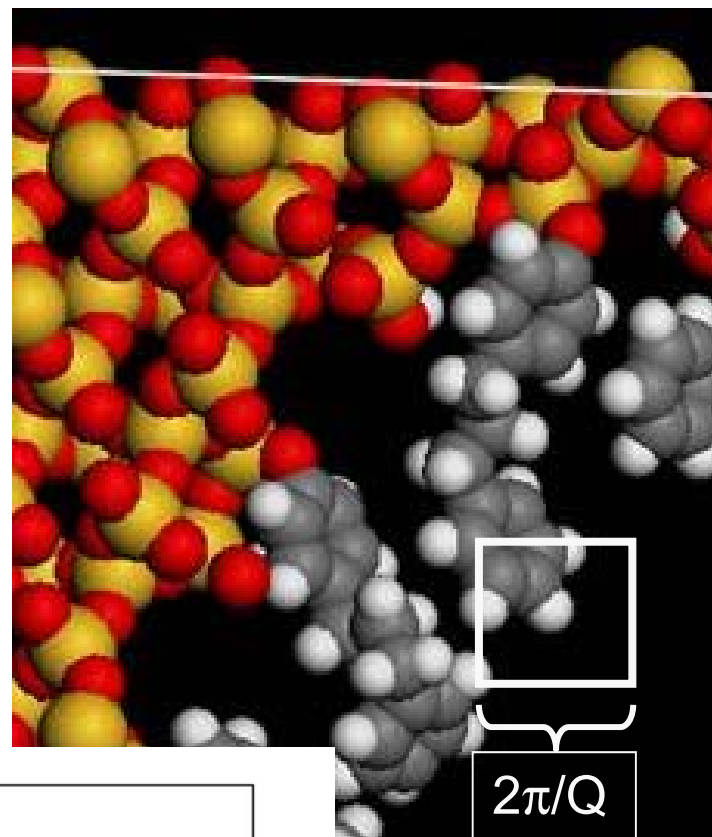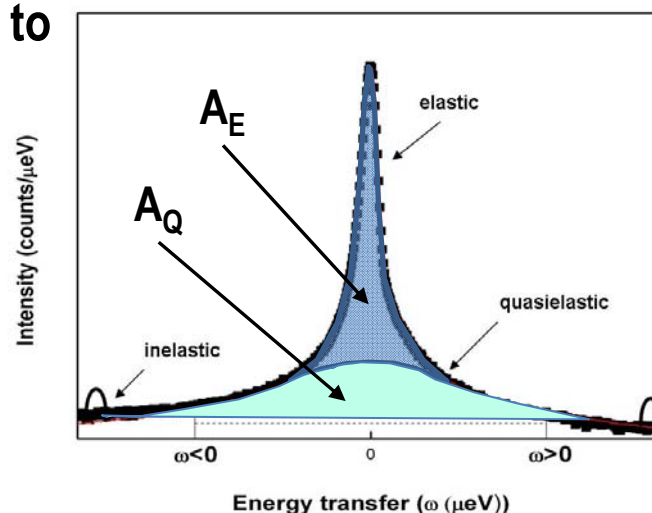
QENS and Neutron Scattering Instruments

- **Probe Diffusive Motions**

  - Length scales set by Q, 0.1 Å^{-1} < Q < 3.7 Å^{-1}, 60 Å > d > 1.7 Å.

  - **Time scales set by the width of instrument energy resolution**, typically at least 0.1 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 λ 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**

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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 – <u>Opportunity is Good- Competition is High</u>**
  - **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**

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The High-Resolution Neutron Spectrometer Landscape
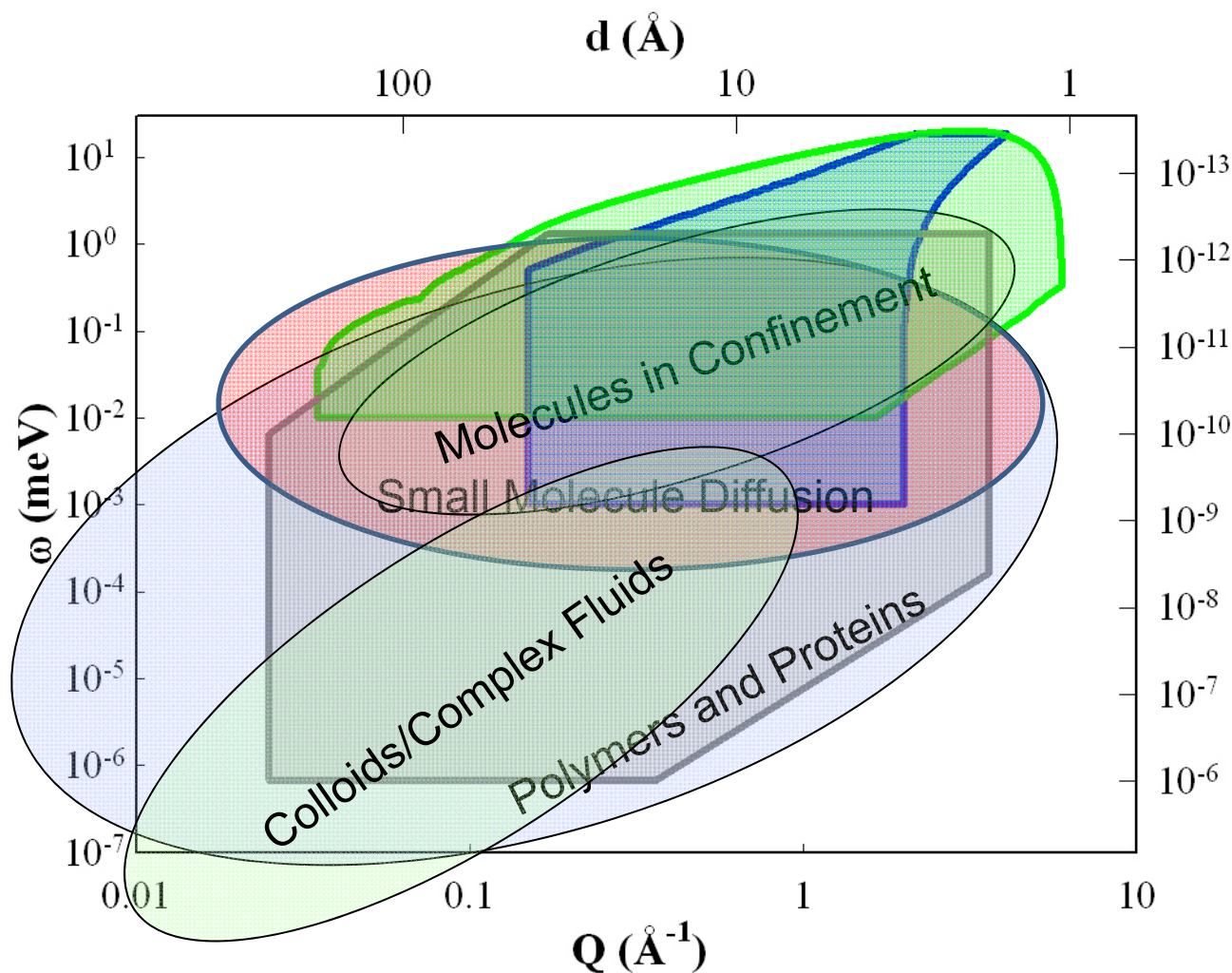
● Backscattering

● Cold Neutron Chopper

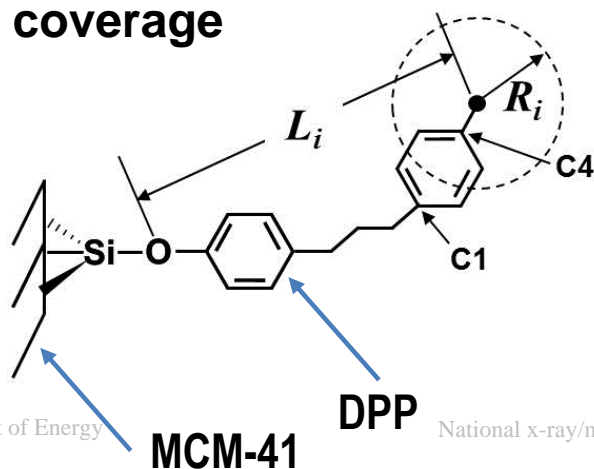● Neutron Spin Echo

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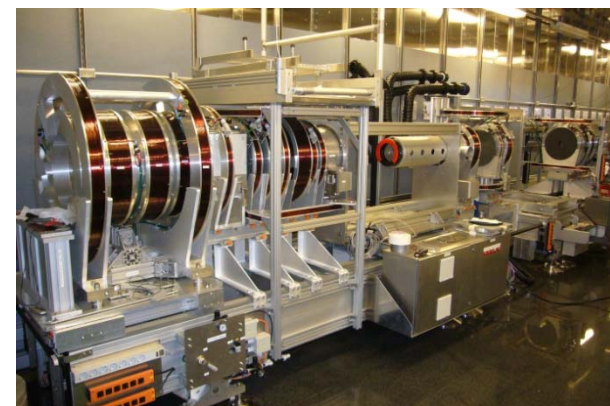
Restricted Diffusion – Tethered Molecules
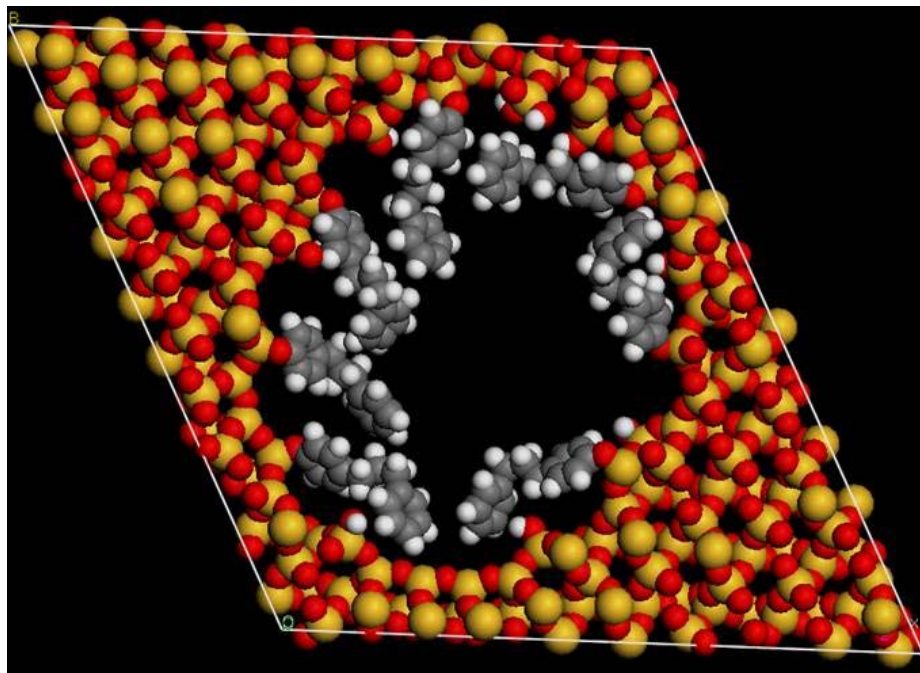
**MCM-41 (2.9 nm pore diameter)
high DPP coverage**

Samples – typical 0.7 g

240 K < T < 340 K

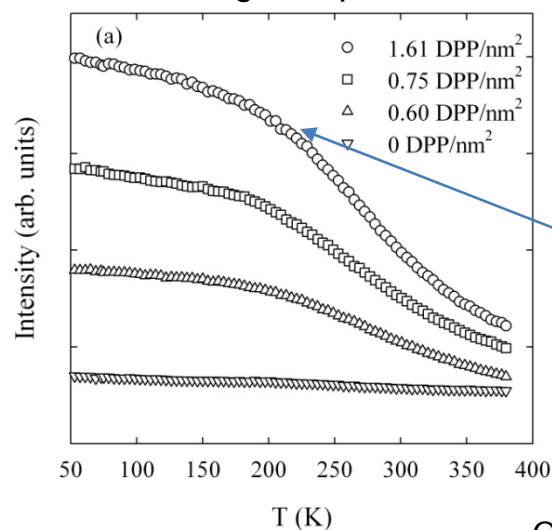Simple Fit – Lorentzian + δ

Pore Diameter (nm)	Coverage (molecules/nm^2)
1.6	0.85 (saturation)
2.1	1.04 (saturation)
3.0	0.60 0.75 1.61 (saturation)
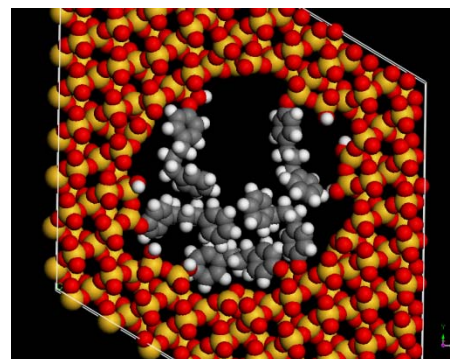
Elastic Scans – Fixed Window Scans
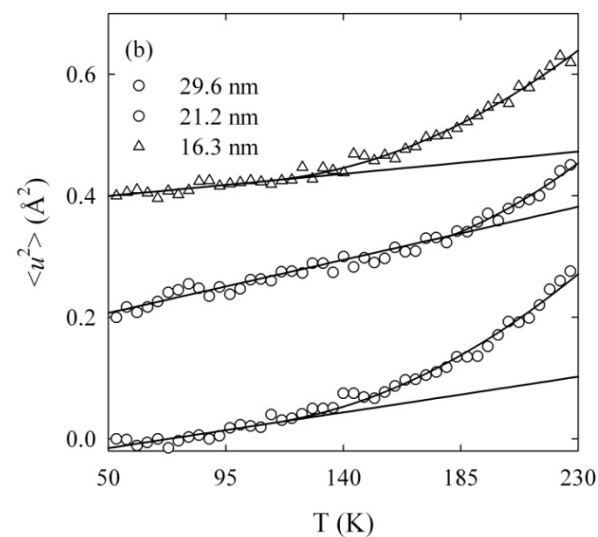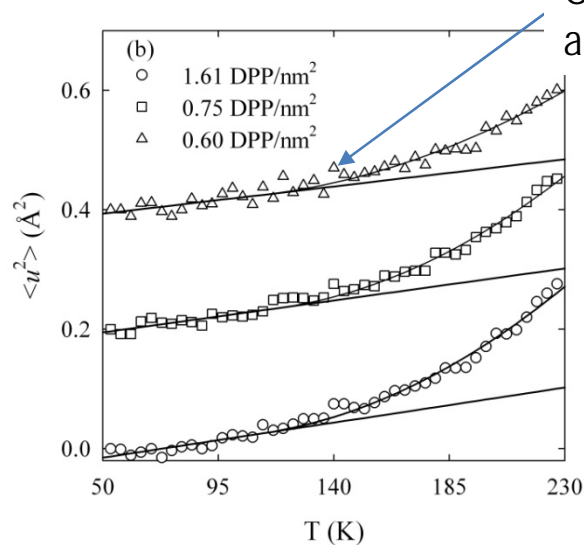
Coverage Dependence

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

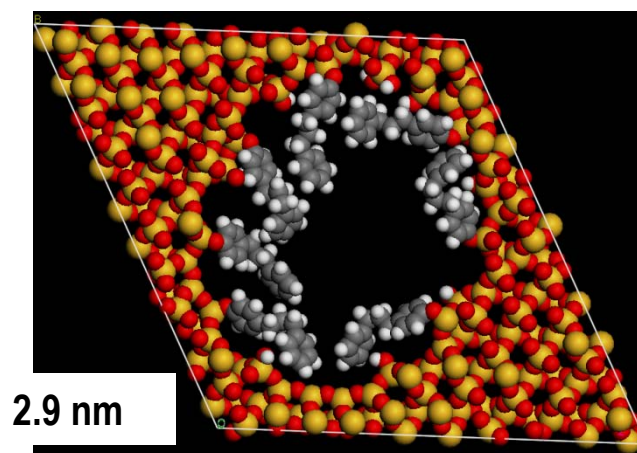$$I(Q) = I(0)\exp\left(-Q^2\langle u^2\rangle/3\right)$$
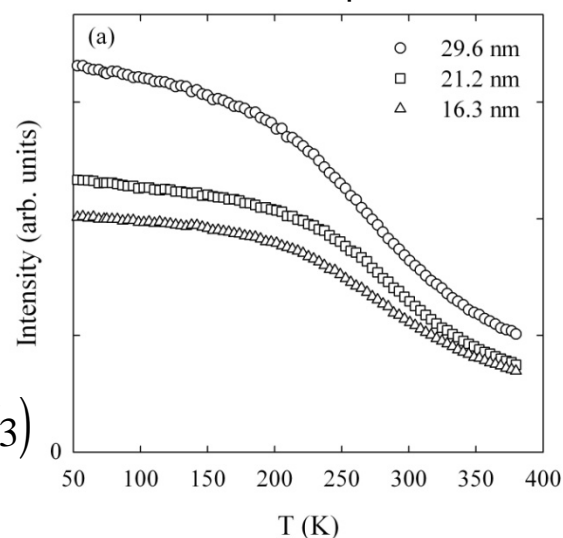
Onset of diffusive and anharmonic motion (T_T)
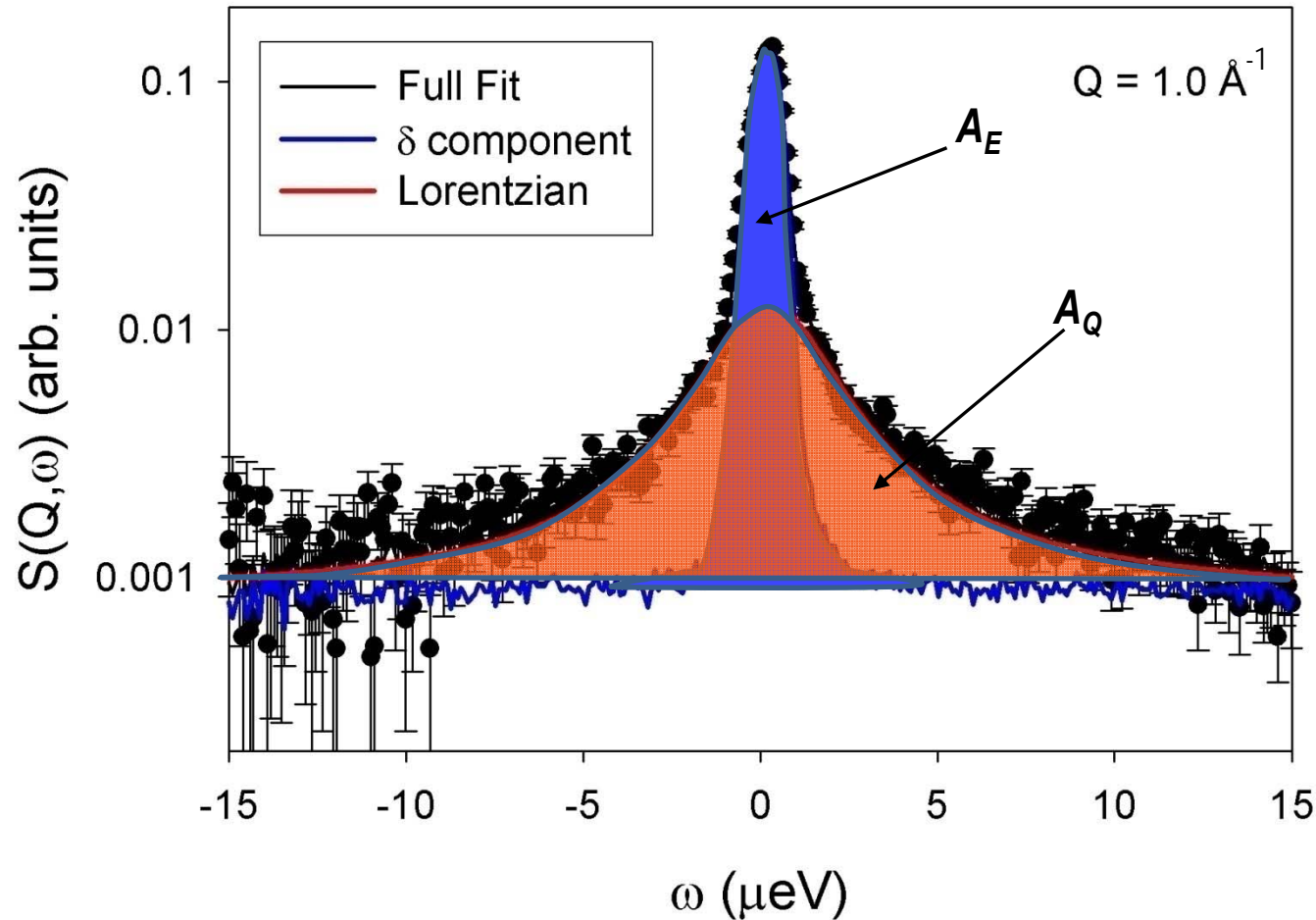
Pore Size Dependence

Elastic Scans
Fixed Window Scans

- T_T

  – No dependence on DPP surface coverage at 3.0 nm pore diameter (≈ 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

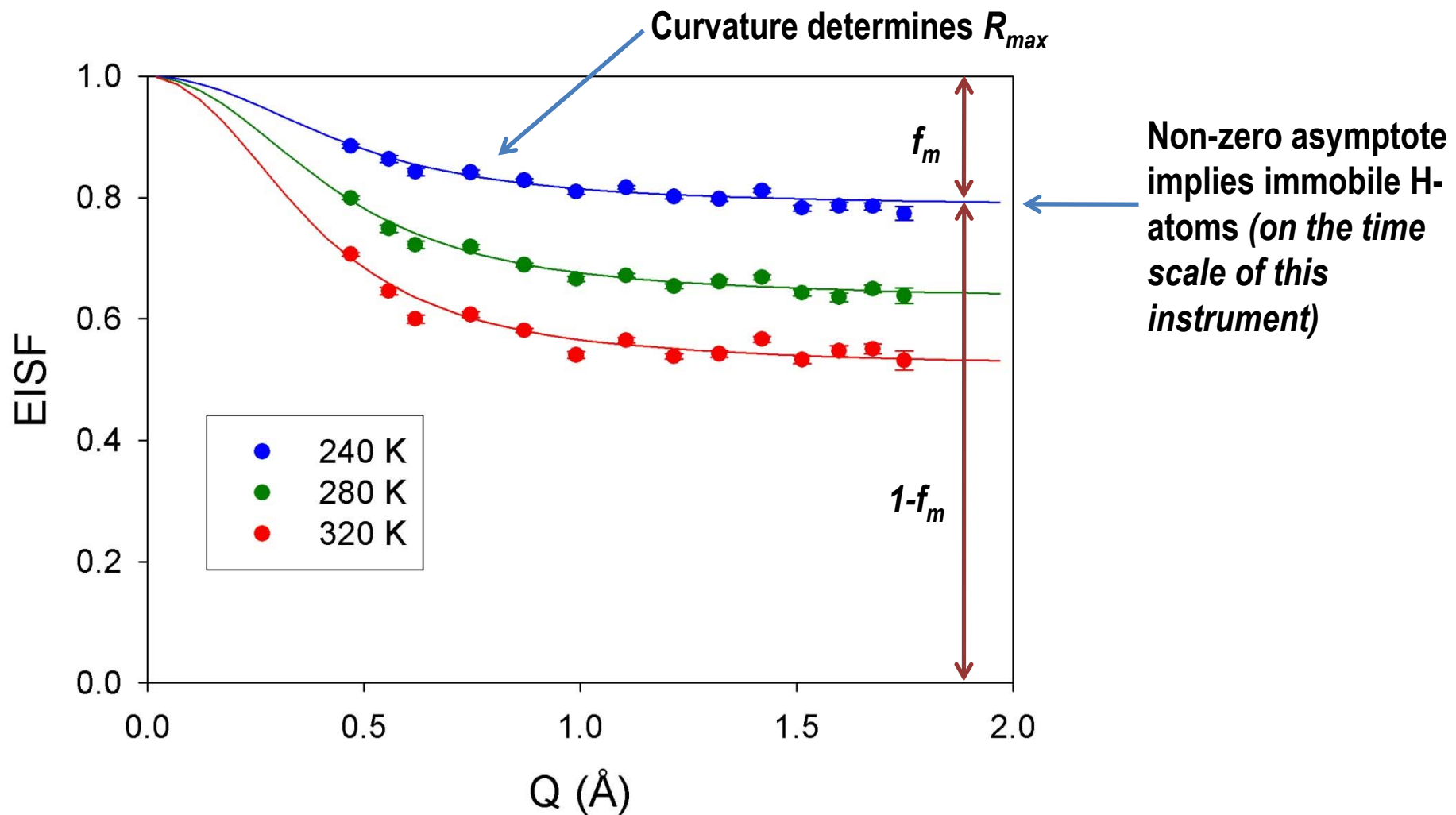- Large pores have enough surface area for DPP to orient near the MCM-41 surface

1.7 nm

2.2 nm

2.9 nm

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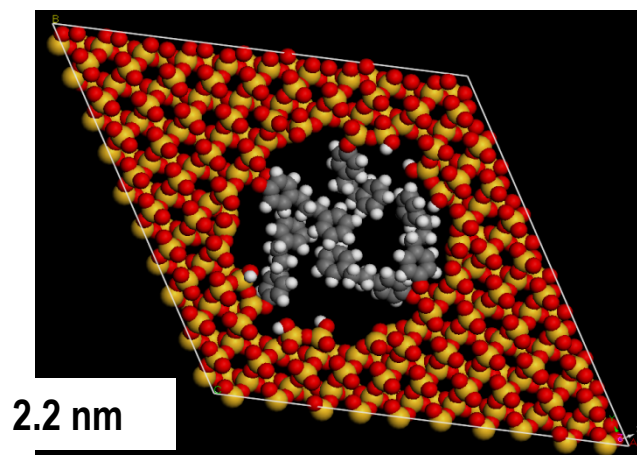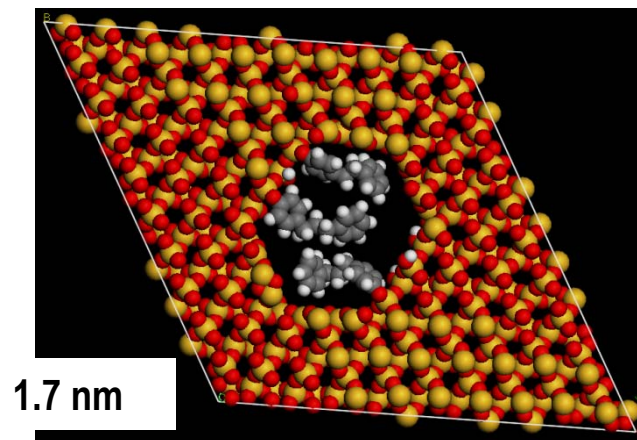
Simple Fit to data (HFBS – NCNR) 30 Å diameter pore, 320 K, Q = 1 Å⁻¹

$$EISF = \frac{A_E}{A_E + A_Q}$$

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EISF – 30 Å DPP sample, saturation

Curvature determines R_{max}

f_m

Non-zero asymptote implies immobile H-atoms *(on the time scale of this instrument)*

$1-f_m$

EISF

Q (Å)

240 K
280 K
320 K

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Lorentzian Γ(Q)

Non-zero intercept
Implies restricted/confined diffusion
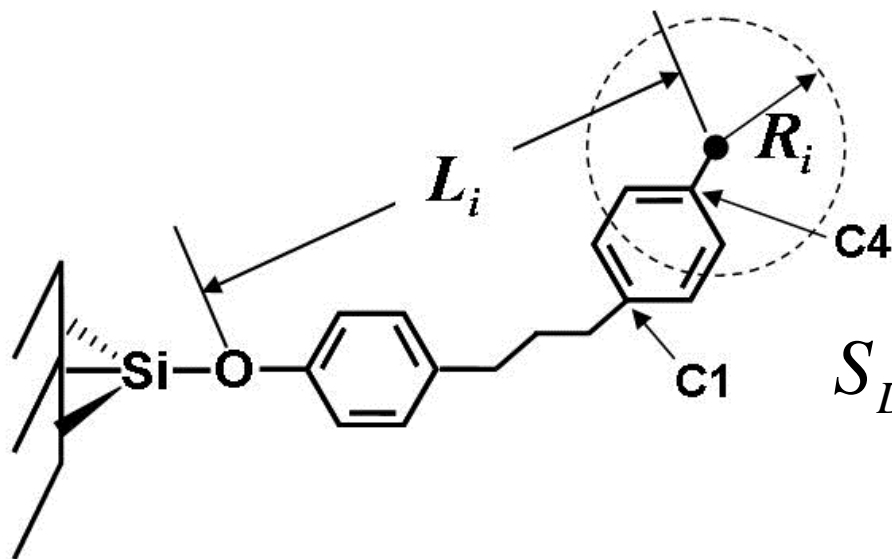
National x-ray/neutron school June 2014
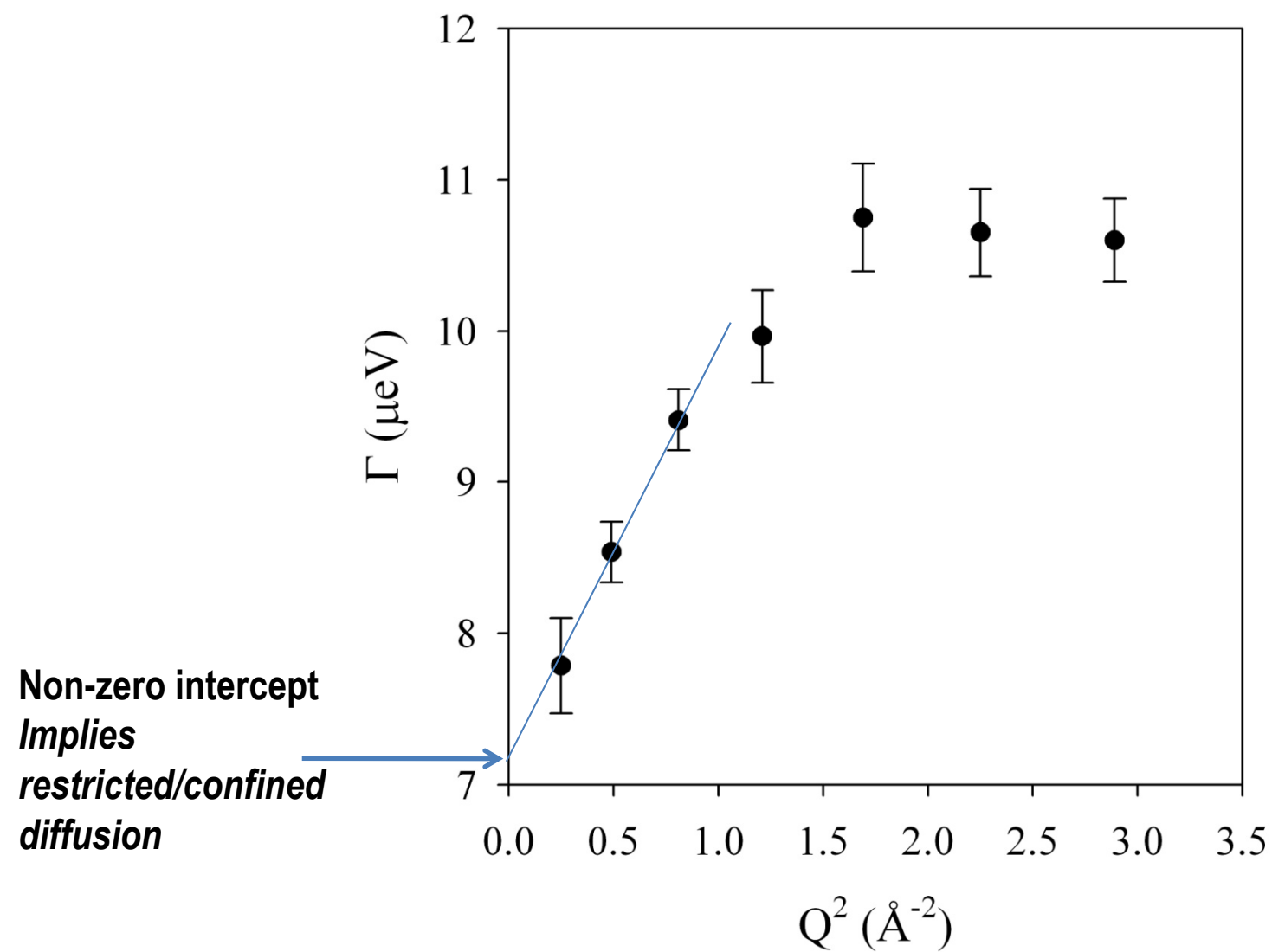
Simple Analytical Model – e.g. Diffusion in a Sphere

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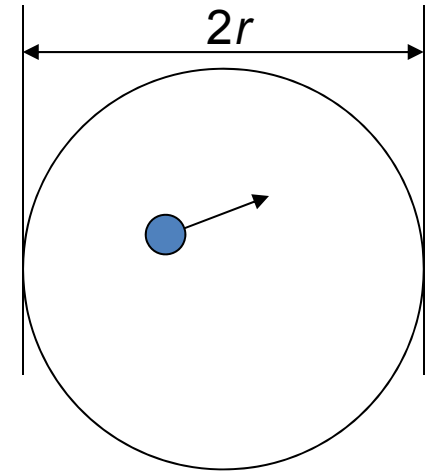
$$S_s(Q, \omega, r, D) = A_0^0(Qr)\delta(\omega) + \frac{1}{\pi} \sum_{(l.n) \neq (0,0)} (2l+1) A_n^l(Qr) \frac{\left(x_n^l\right)^2 D / r^2}{\left[\left(x_n^l\right)^2 D / r^2\right]^2 + \omega^2}$$

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

Volino and Dianoux, Mol. Phys. **41**, 271-279 (1980).

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

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

C4

C1

L_i
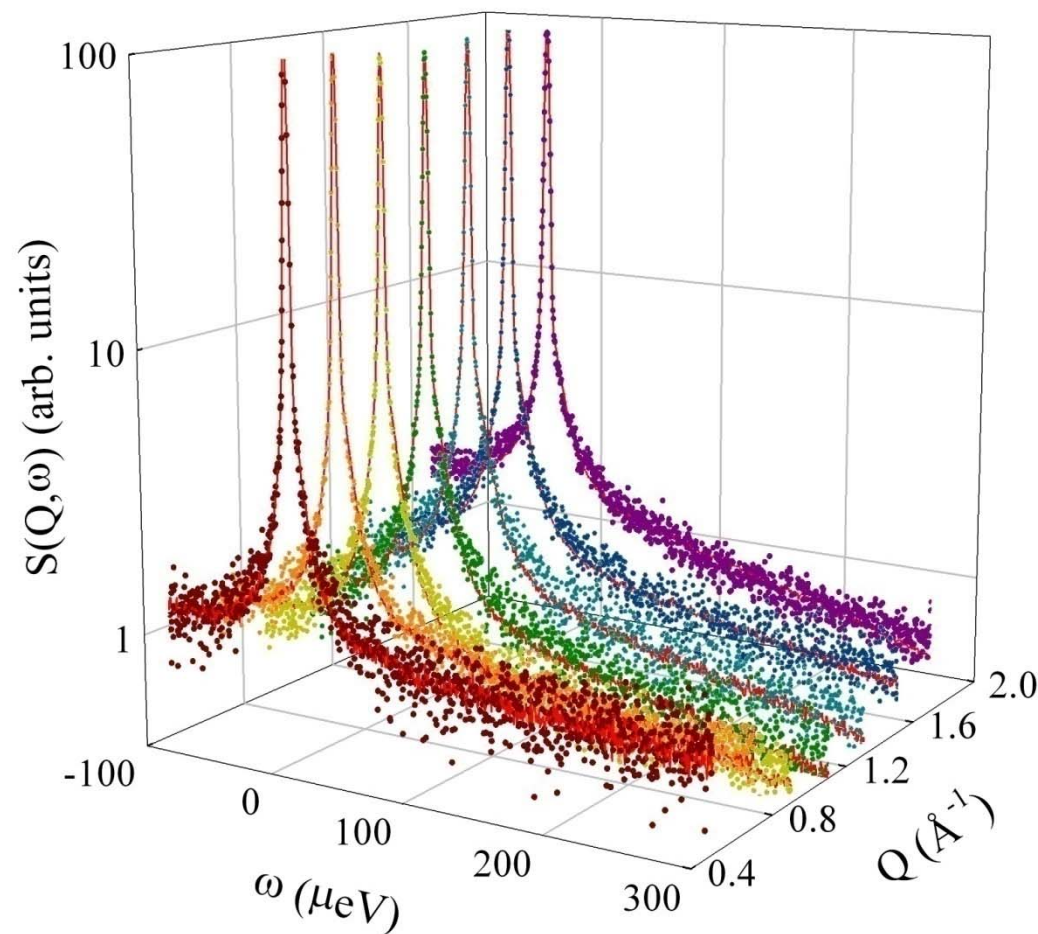
R_i

$$R_i = R_{max} \times \frac{L_i}{L_{natom}}$$

Fits to Data

$$S(Q,\omega) = \left(C_0(Q) + C_1(Q)e^{-Q^2\langle u^2\rangle/3} \right)\delta(\omega) + C_2 e^{-Q^2\langle u^2\rangle/3} \sum_{i=1}^{15} S_S(Q,\omega,R_i,D_i)$$
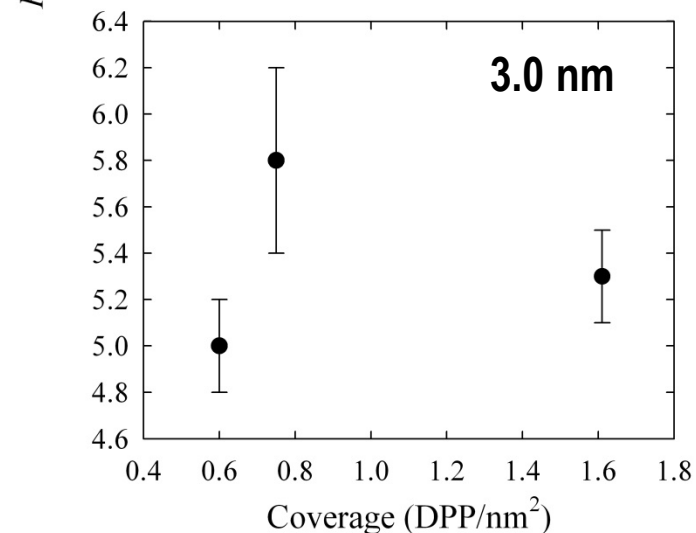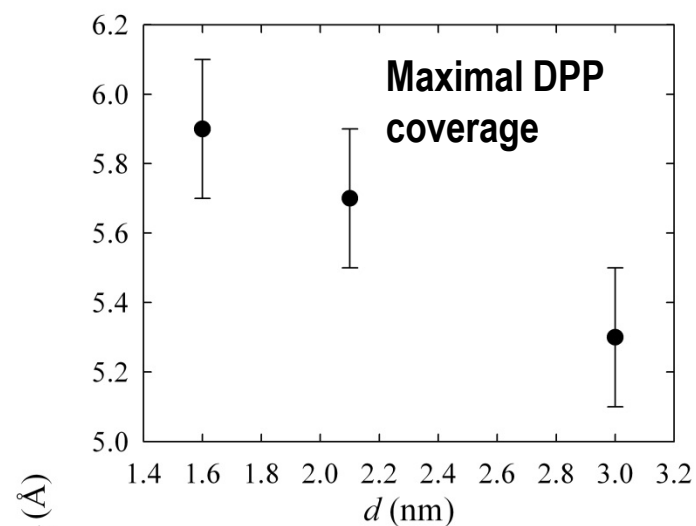
MCM-41

$$f_m = \frac{C_2}{C_1 + C_2}$$

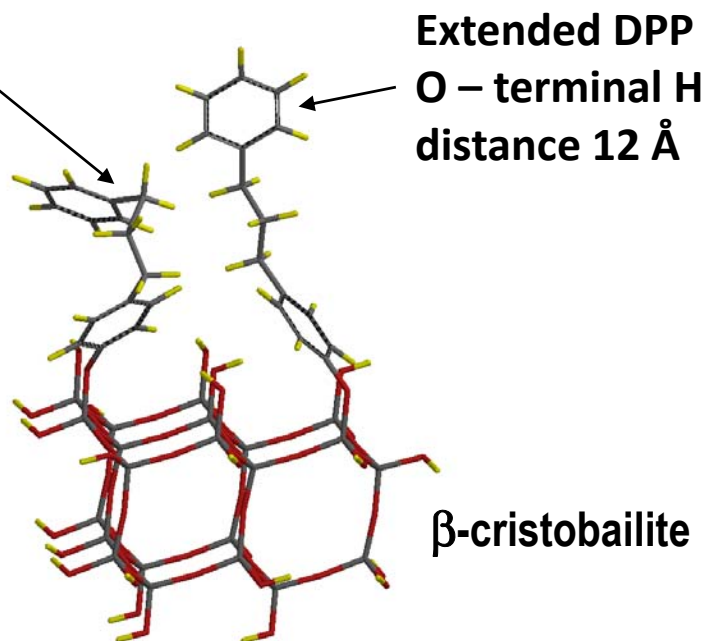**Fraction of DPP H-atoms moving on time scale of instrument**

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

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R_M – How extended is the motion?

Maximal DPP coverage

3.0 nm

Partially folded DPP
O – terminal H distance 5.9 Å

Extended DPP
O – terminal H distance 12 Å

β-cristobailite

- R_M <u>decreases</u> 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
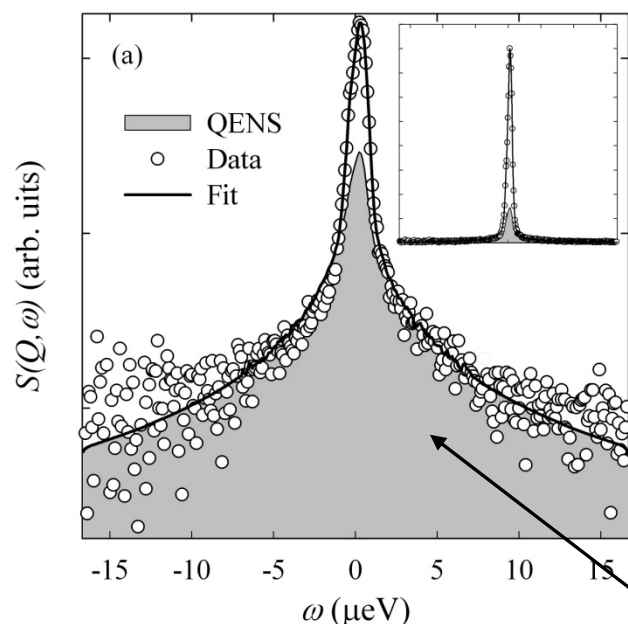
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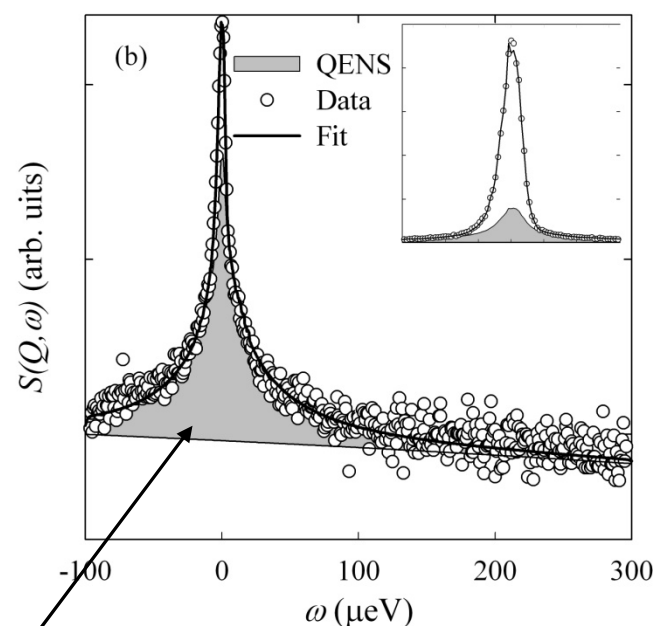
D_M – How fast is the motion?
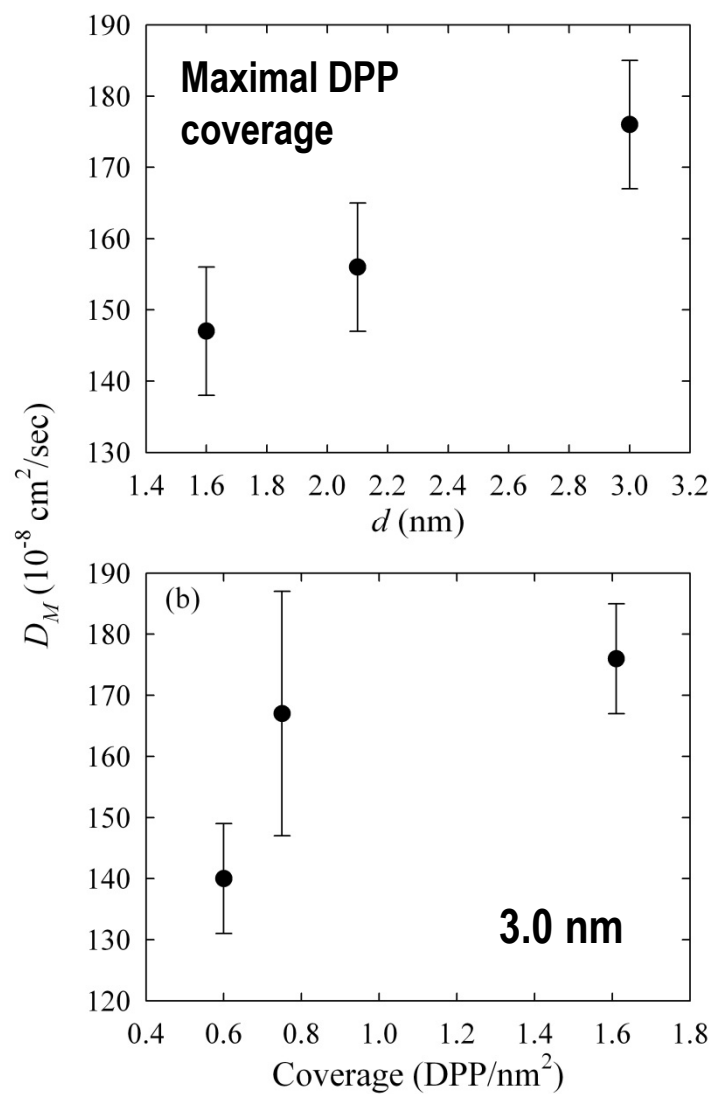
- D_M increases with pore diameter while the radius decreases
  - Diffusion in the pore volume depends on how crowded it is

- 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

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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)

QENS

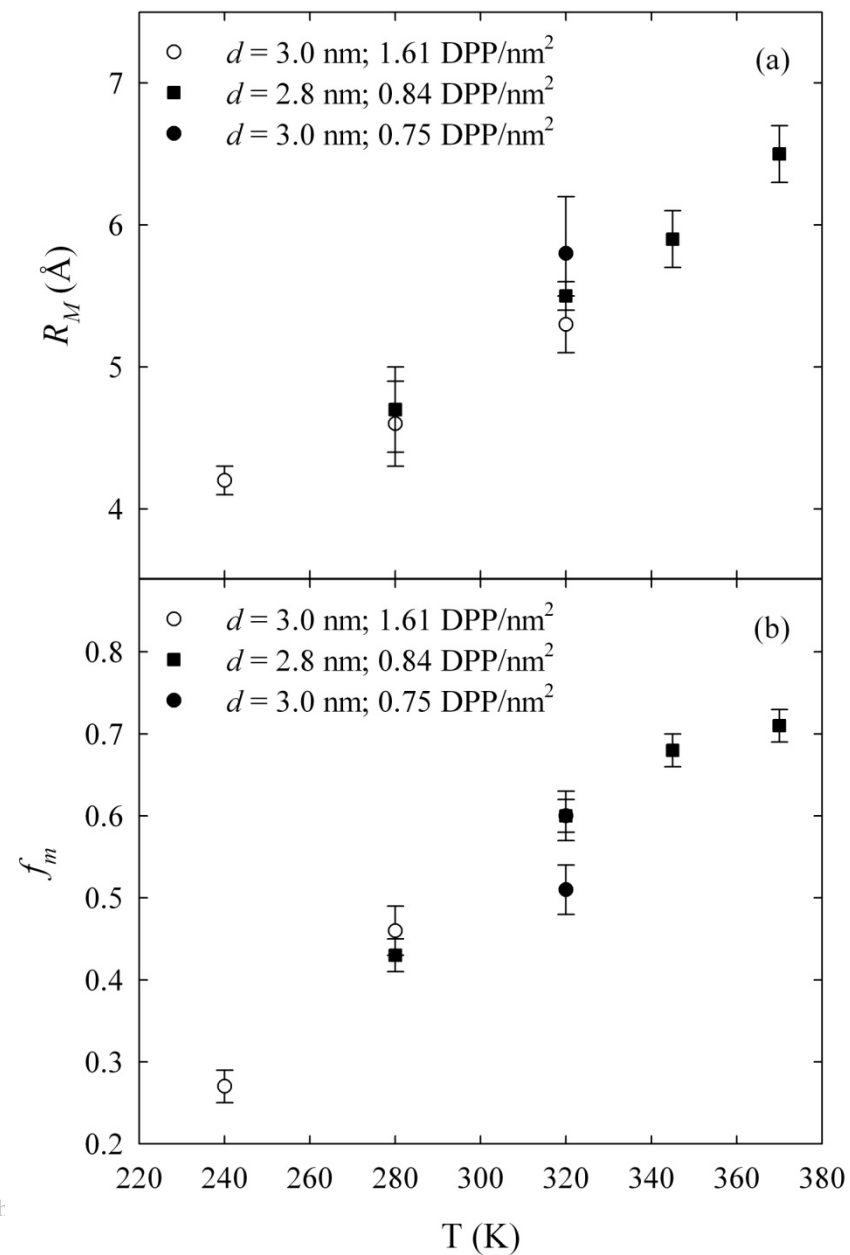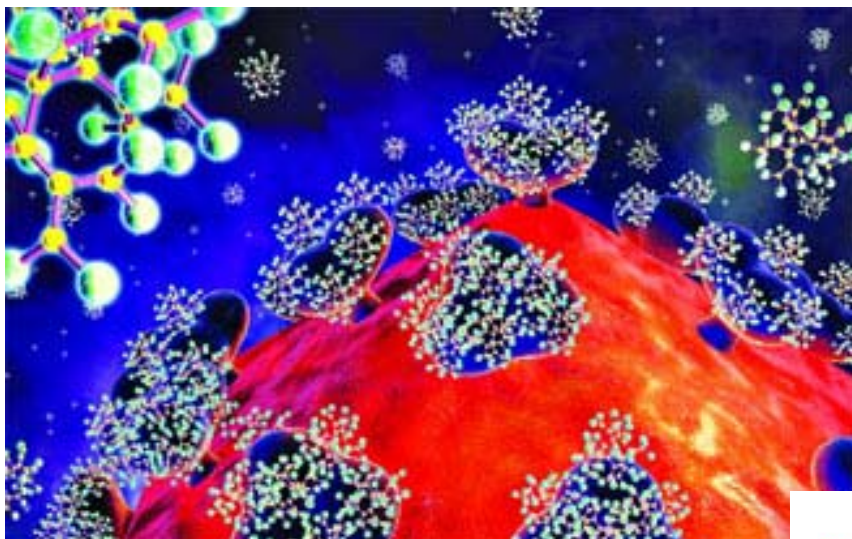E.J. Kintzel, et al., J. Phys. Chem. C **116**, 923-932 (2012).

Two Instruments

Geometry – nearly identical – determined by intensity measurements
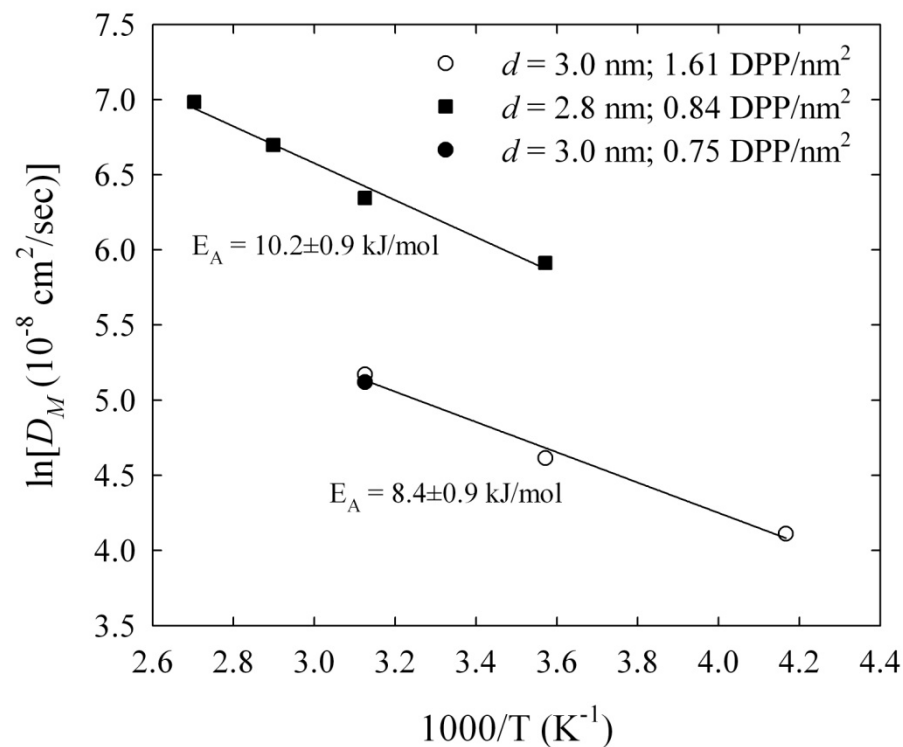
Dynamics
- Similar activation energies
- Different magnitudes
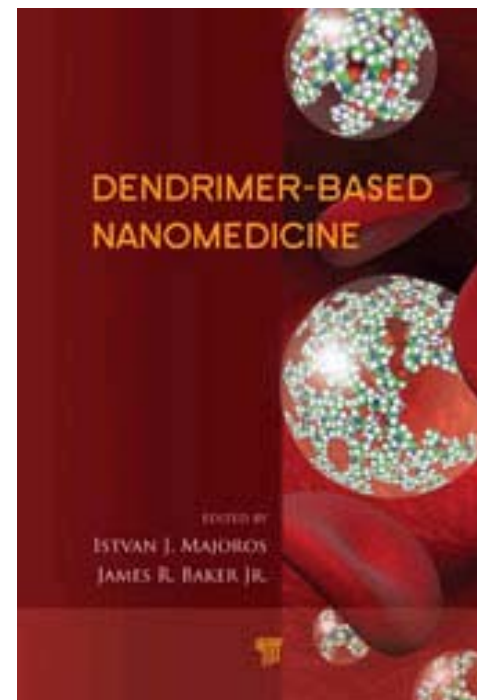
National x-ray/neutron sch

Example 2: Dendrimers – Colloidal Polymer – pH responsive

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

DENDRIMER-BASED NANOMEDICINE

EDITED BY
ISTVAN J. MAJOROS
JAMES R. BAKER JR.

Folic acid (targeting)
Methotrexate (drug)
Fluoresceine (imaging)
G5-dendrimer (platform)

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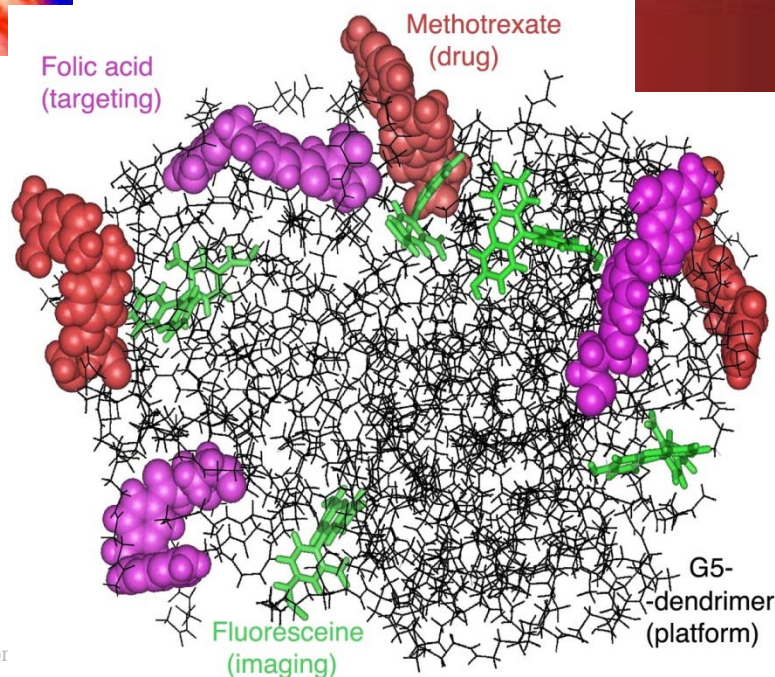
SANS Results – Global Size Constant, Redistribution of Mass

Samples: 0.05 gm protonated dendrimer in 1 ml deuterated solvent
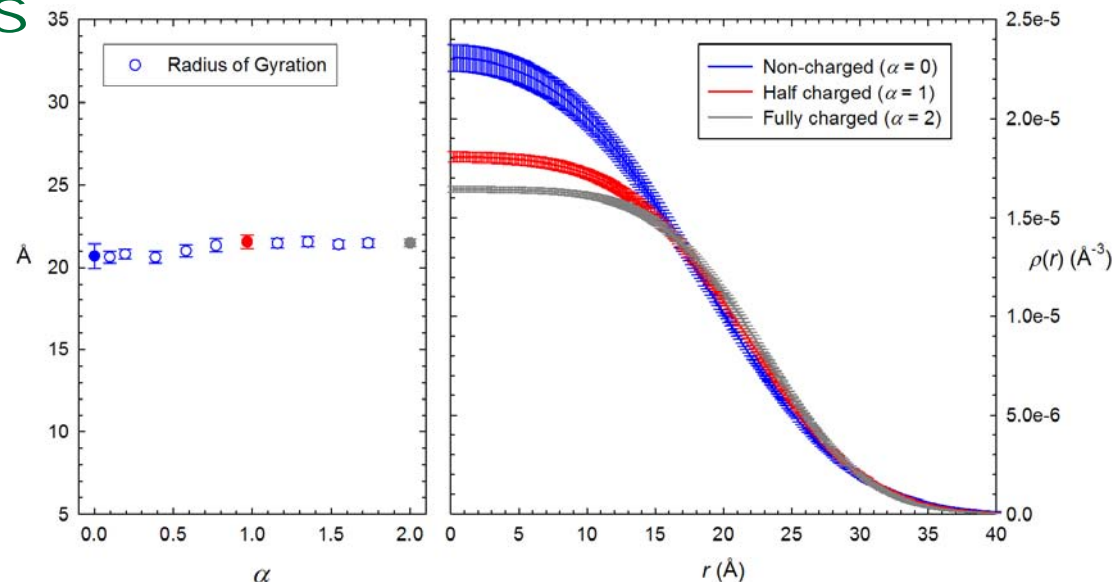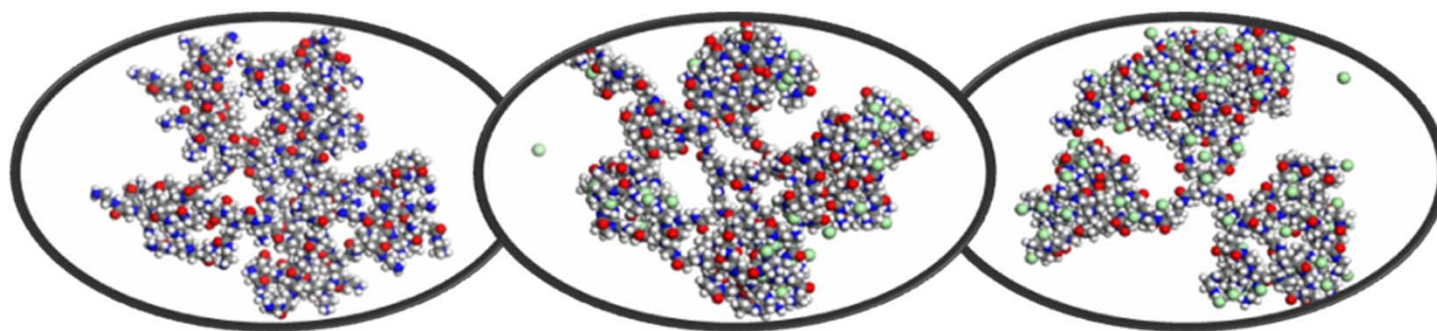

Molecular Dynamics Simulations
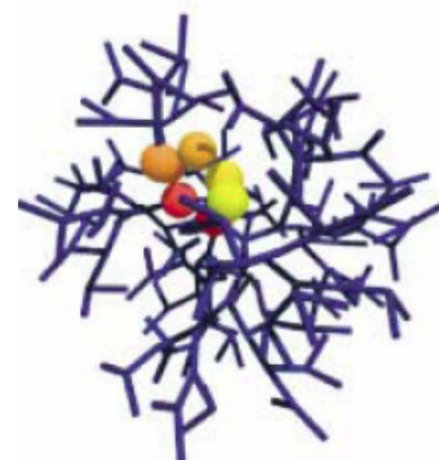
Basic   **Acidic**

High pH   **Neutral pH**   **Low pH**

pH decreases

Dense Core ➔ **Dense Shell**

for the U.S. Department of Energy   National x-ray/neutron school June 2014
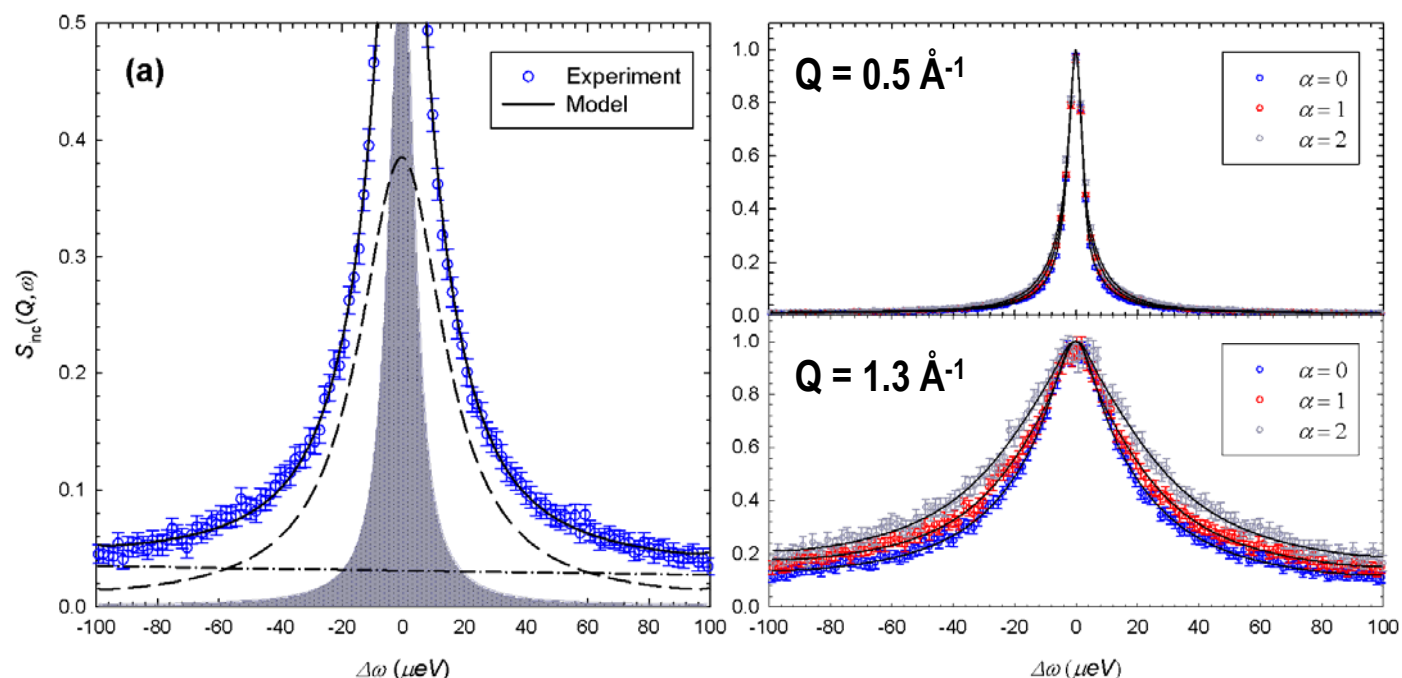
Methodology

- **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 (α = 0 (uncharged), α = 1 (primary amines charged), α = 2 (fully charged))**

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

modeled localized internal motion as

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

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Localized Motion of Dendrimer Arms

(a) Experiment / Model — $S_{nc}(Q,\omega)$ vs $\Delta\omega$ (μeV)

Q = 0.5 Å⁻¹ ($\alpha = 0$, $\alpha = 1$, $\alpha = 2$)

Q = 1.3 Å⁻¹ ($\alpha = 0$, $\alpha = 1$, $\alpha = 2$)

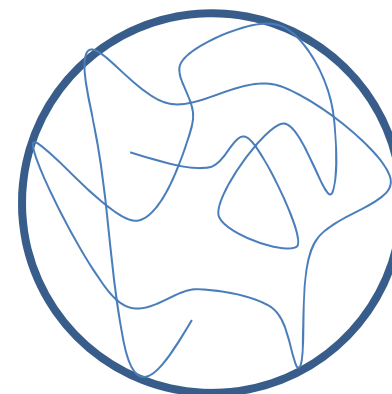**Localized motion modeled as Diffusion in a Sphere**

X. Li, et al, Soft Matter **7**, 618-622 (2011)

R ~ 2.8 Å, α independent

$$D \begin{cases} 1.60 \pm 0.03\ 10^{-10}\ \text{m}^2/\text{s} & \alpha = 0 \\ 2.58 \pm 0.03\ 10^{-10}\ \text{m}^2/\text{s} & \alpha = 1 \\ 3.11 \pm 0.03\ 10^{-10}\ \text{m}^2/\text{s} & \alpha = 2 \end{cases}$$

Localized motion increases as amines are charged!

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Reference Materials - 1

- **Reference Books**

  – **Quasielastic Neutron Scattering**, M. Bee (Bristol, Adam Hilger, 1988).

  – **Methods of X-Ray and Neutron Scattering in Polymer Science**, R. –J. Roe (New York, Oxford University Press, 2000).

  – **Quasielastic Neutron Scattering and Solid State Diffusion**, R. Hempelmann (2000).

  – **Quasielastic Neutron Scattering for the Investigation of Diffusive Motions in Solids and Liquids, Springer Tracts in Modern Physics**, T. Springer (Berlin, Springer 1972).

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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**